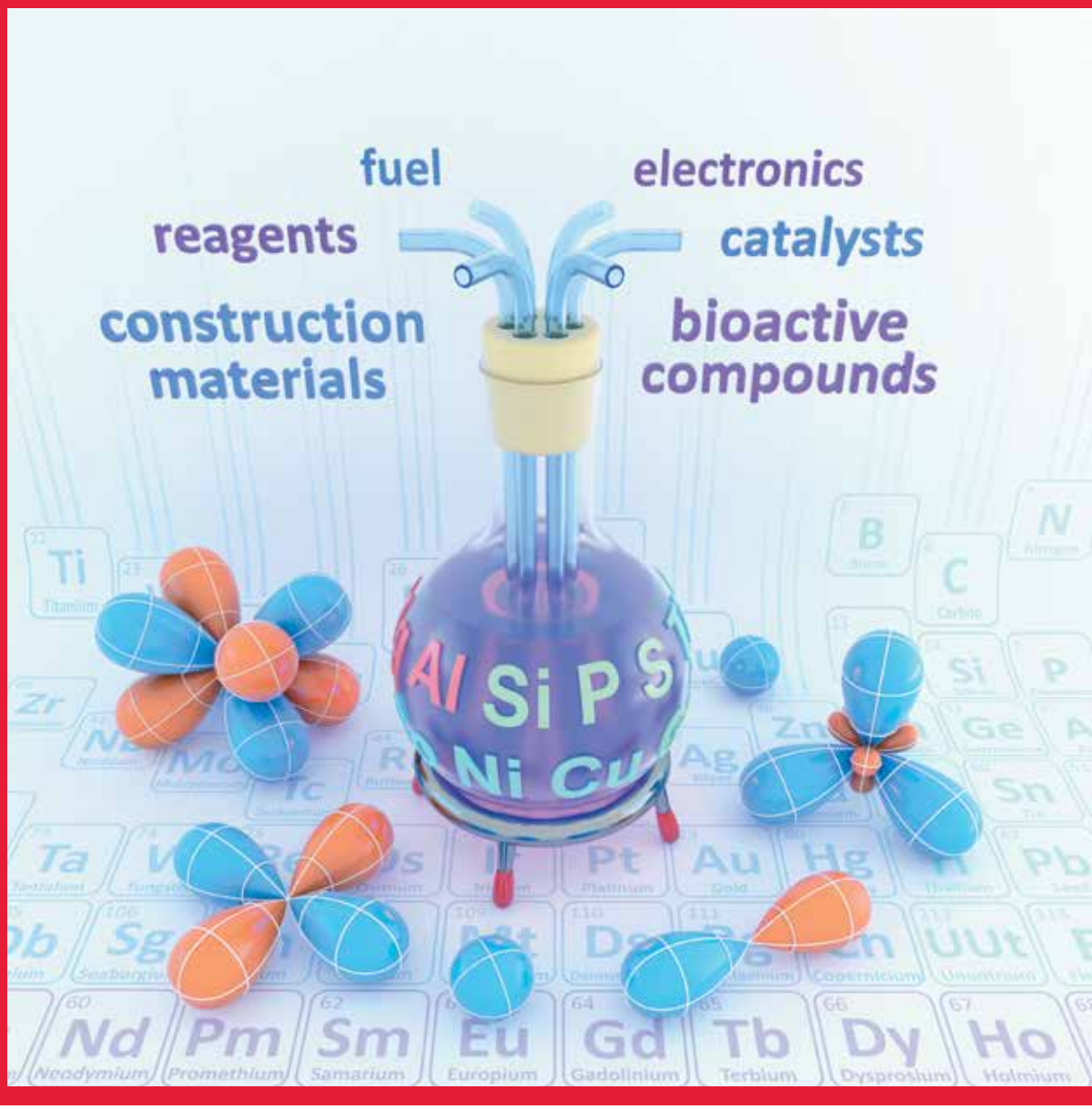
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Organoelement chemistry

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Organoelement chemistry: promising growth areas and challenges

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The chemistry of organoelement compounds is now one of the most rapidly developing fields of research, regarding both fundamental science and solution of applied problems. This review covers a variety of classes of organoelement compounds, ranging from molecules with highly labile carbon – element bonds to compounds with stable bonds that form the basis of novel structural materials and demonstrates their role in scientific research and industrial production. The use of Grignard reagents in modern organic synthesis and application of catalytic cyclomagnesiation and cycloalumination reactions for the preparation of difficult-to-access metallacycles are considered. The electron transfer processes in redox-active derivatives of Group 14 elements and the role of radical ions in these processes are discussed. Considerable attention is paid to organometallic compounds, first of all, as catalysts; the dynamic nature of catalysis with these compounds is noted. Unusual strained metallacycles of high thermal stability, zirconacyclocumulenes, which also exhibit catalytic activity, are described. Complexes with redox-active ligands that substantially affect the reactivity of the metal centre and directly participate in reactions with various substrates as well as organometallic compounds of lanthanides are considered. Modern environmentally benign methods for the synthesis of organosilicon compounds and production of unique materials based on them are discussed. Particular Sections are devoted to organophosphorus compounds, including those exhibiting therapeutic properties and possessing unusual optical characteristics, and organic chalcogen compounds, which find use as ligands and biologically active molecules.
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1. Introduction

Classical organic chemistry stems from the chemistry of natural compounds and living systems. However, organoelement compounds are rarely encountered in nature; therefore, organoelement chemistry should be considered to largely originate from scientific research. Organoelement chemistry combines organic and inorganic chemistry and covers most of elements in the Periodic Table. Owing to great diversity of physicochemical properties of these compounds and multitude of vivid practical applications, organoelement chemistry became one of the key driving forces in the development of chemical science of the 21st century. Modern chemical industry and advanced research and development products cannot be imagined without organoelement compounds.

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Historically, the preparation of organoelement compounds was noted back in the 19th century. For example, $ZnEt_2$, one of the first organometallic products, was synthesized by Frankland in 1848, while in 1859, the first organic compound of aluminium, $Et_3Al_2I_3$, was prepared.[1,2] Tetraethylsilane, the first organosilicon compound, was prepared by Friedel and Crafts in 1863.[3] The Grignard reaction involving organomagnesium compounds, which has found very extensive use in organic synthesis, was described more than 100 years ago, particularly, in 1900.[4] In the 20th century, the number of publications on organoelement compounds and design of new materials based on them rapidly enhanced. A powerful impetus for the development of organoelement chemistry came from systematic studies of organometallic catalysis, which brought organometallic compounds to the class of most important components of modern chemical industrial production, which provide the synthesis of products of any complexity with a nearly atomic precision.[5] Most of elements of the Periodic Table are metals; therefore, organometallic chemistry opens up infinite opportunities for the design of new catalytic systems, especially in view of the fact that catalysts based on polymetallic systems, multinuclear complexes, metal clusters and metal nanoparticles have been developed especially vigorously in recent years.[6]

The structure and chemical reactivity of organoelement compounds are determined, first of all, by the nature and energy of the bond between the element and organic substituent, which are in turn controlled by the electronic structure of the atom of this element (Fig. 1). Group 1 and 2 metals (s-elements) form polar bonds with organic groups, with a substantial charge separation and relatively low energy; therefore, these derivatives are efficient metallating reagents. For example, the $Mg-C^{Bu}$ bond energy in n-butylmagnesium bromide (Bu^nMgBr) is 50.9 kcal mol^{-1} (for comparison, the $H-C^{Bu}$ bond energy is 100.7 kcal mol^{-1}).[7]

The bonds formed by p-elements with carbon vary in the electronic structure and energy. In the case of Group 14 elements (C, Si, Ge, Sn), the X–C bond energy is lower for X = Ge, Sn and Pb, since the increase in the size of atom reduces the size match (and, hence, overlap efficiency) between the p-orbitals of the heteroelement and carbon atoms. For example, in the $(CH_3)_3X-CH_3$ type molecule, the X–C bond energies are 86.9, 94.4, 67.8, 70.5 and 57.0 kcal mol^{-1} for X = C, Si, Ge, Sn and Pb, respectively. Since elements of Period 3 possess vacant d-atomic orbitals (see Fig. 1), some cases of expansion of the coordination sphere of these elements (first of all, silicon) are explained by involvement of the d-orbitals in the formation of additional coordination bonds.

A numerous group of elements is composed of transition metals in which d-atomic orbitals are gradually filled. The chemistry of these elements is rather diverse because of the proximity of the s-, p- and d-levels in transition metal atoms and their ability to act as both electron donors and acceptors. The ability of d-elements to form coordination bonds with electron transfer from the metal atom to the antibonding orbitals of the ligand, resulting in bond activation in the ligand, forms the basis for the catalytic activity of transition metals.

For lanthanide atoms, the f-orbitals are gradually filled on movement along the series, with the s-level being fully occupied; therefore, the properties of these elements are very similar. For example, the $M-C_2$ bond energies in metal carbides are 161.0, 161.0, 155.0, 132.0, 159.0 and 137.0 kcal mol^{-1} for M = Ce, Pr, Nd, Eu, Gd and Er, respectively.[7]

This review is structured according to the chemical properties of elements determined by their electronic struc-

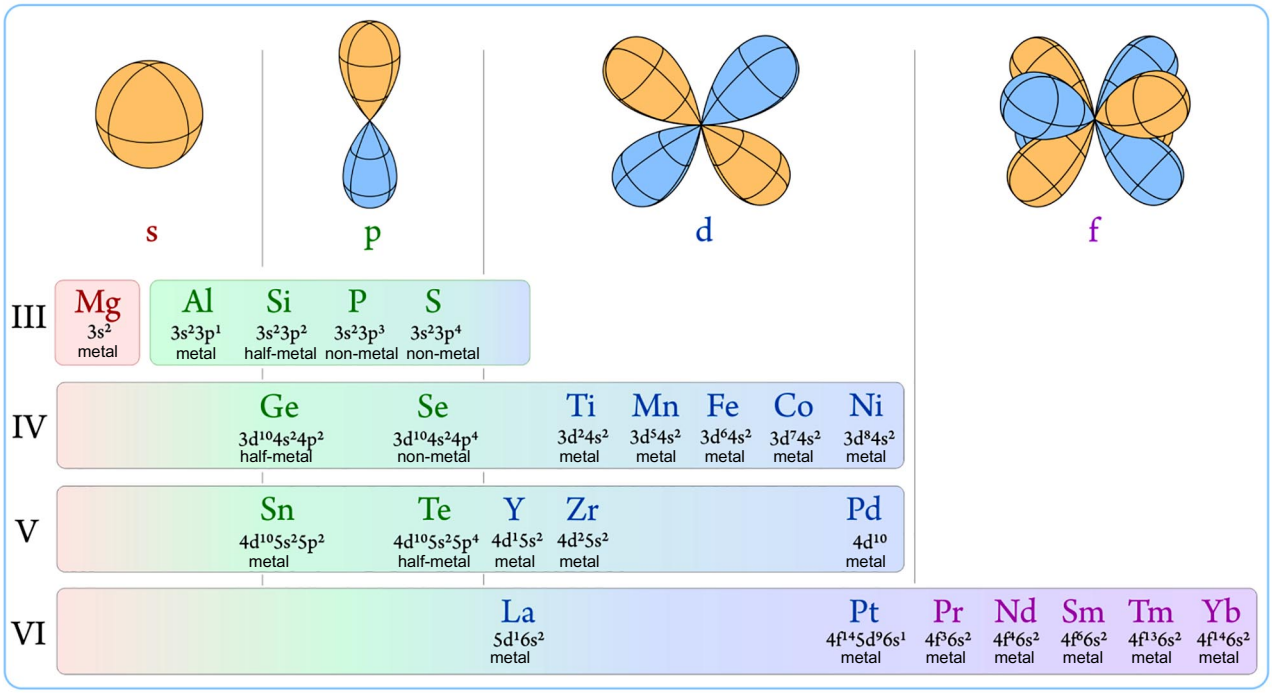


Figure 1. Representative images of s-, p-, d- and f-orbitals and electronic configuration of some elements considered in this review.

ture, with allowance made for the areas of practical use and prospects of chemical application. Among Group 2 s-elements, organomagnesium compounds have influenced organic chemistry most appreciably and have found a very extensive use in organic synthesis (Section 2). The appearance of the p-electrons gives rise to a number of unique properties, which is reflected in the chemistry of aluminium (Section 3); silicon, germanium and tin (Sections 4 – 6); phosphorus (Section 7); sulfur, selenium and tellurium (Section 8).

Transition metals in which d-electron shells are being filled can stabilize highly unstable chemical systems, which is demonstrated in this review in relation to seven-membered zirconacyclocumulene metallacycles (Section 9). They are also able to activate various chemical bonds, which is widely utilized in catalysis. The catalytic applications of transition metal complexes are considered in relation to nickel, palladium and platinum (Section 10). A unique feature of organoelement and organometallic compounds is high sensitivity to the local chemical environment, which allows for fine optimization of their properties by selecting appropriate ligands. A vivid example of such targeted modification of the behaviour of organometallic compounds is the use of redox-active ligands (Section 11). The recent decades have seen ever increasing interest in f-element organometallic compounds, which are considered in Section 12 of the review.

It is noteworthy that detailed description of the whole organoelement chemistry was beyond the scope of this review. The authors concentrated on the most interesting aspects of the chemistry and practical applications and illustrated them by representative examples for some chemical elements. The goal of this review is to define the promising growth areas in the research of organoelement compounds and to stimulate discussions for setting and solving the challenges faced by the modern organoelement chemistry.

The list of abbreviations:

acac — acetylacetonate;
Ad — adamantyl;
AIBN — azobis(isobutyronitrile);
AIM — 'atoms in molecules' calculation method;
BDE — bond dissociation energy;
bipy — bipyridine;
Boc — *tert*-butoxycarbonyl;
cod — cycloocta-1,5-diene;
Cp — cyclopentadienyl;
CV — cyclic voltammetry;
Cy — cyclohexyl;
dba — dibenzylideneacetone;
DCC — *N*,*N*′-dicyclohexylcarbodiimide;
DFT — density functional theory;
DIPEA — diisopropylethylamine;
DMAP — 4-dimethylaminopyridine;
DME — 1,2-dimethoxyethane;
dppb — 1,4-bis(diphenylphosphino)butane;
dppe — 1,2-bis(diphenylphosphino)ethane;
dppf — 1,1′-bis(diphenylphosphino)ferrocene;
dppp — 1,3-bis(diphenylphosphino)propane;
EDS — energy-dispersive X-ray spectroscopy
Fu — furyl;
GLC-MS — gas liquid chromatography – mass spectrometry;
GPC — gel permeation chromatography;
Hex — n-hexyl;
HFC — hyperfine coupling;
HMPA — hexamethylphosphoramide;
HOMO — highest occupied molecular orbital;
HPC — hydrolytic polycondensation;
LUMO — lowest unoccupied molecular orbital
MCC — metal-containing compound;
MOM — methoxymethyl;
MW — microwave radiation;
nano-MOCS — nanometal-oligocarbosilane;
Naph — naphthyl;
NBO — natural bond orbital;
NHC — N-heterocyclic carbene;
OAC — organoaluminium compound;
OCS — oligocarbosilane;
Oct — n-octyl;
OMC — organometallic compound;
OPC — organophosphorus compound;
PBN — α-phenyl-*N*-*tert*-butylnitrone;
PCS — polycarbosilane;
PDMS — polydimethylsilane;
PXRD — powder X-ray diffraction;
rt — room temperature;
SAXS — small-angle X-ray scattering;
SCE — saturated calomel electrode;
SEM — scanning electron microscopy;
SET — single electron transfer;
SOMO — singly occupied molecular orbital;
S-phos — 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl;
SQ — semiquinone;
TBDMS — *tert*-butyldimethylsilyl;
TEM — transmission electron microscopy;
Tf — trifluoromethanesulfonyl;
TGA — thermogravimetric analysis;
Th — thienyl;
THP — tetrahydropyran-2-yl;
TMEDA — tetramethylethylenediamine;
TMP — 2,2,6,6-tetramethylpiperidino;
TON — catalyst turnover number;
Ts — *p*-toluenesulfonyl;
TS — transition state;
Xantphos — 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene;
X-phos — 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl;

2. Organomagnesium compounds: the past and the present

More than a hundred years have passed since the Grignard reagent was discovered, and one can hardly find an organic chemist who has not prepared or used this reagent. It still remains the most important and the best known representative of organometallic compounds. Numerous reactions of nucleophilic substitution and addition to the C=O and C=C double bonds are widely used not only in laboratory, but also in industry for the production of a broad variety of products, including pharmaceuticals, for example, the anticancer drug tamoxifen.[8,9] The number of publications devoted to the Grignard reagent amounts to tens of thousands; back in 1975 it was counted that this reagent is mentioned in some way in 40 000 chemical articles.[10]

A huge body of literature is devoted to the synthesis of the Grignard reagent, the mechanism of this reaction, structure of the compound in the solid state, equilibria

observed in solutions, mechanisms of reactions of the Grignard reagent with various organic compounds and industrial applications (*e.g.*, see Ref. 11). This literature not only reflects the initiation and development of the chemistry of organomagnesium compounds, but is also useful for the understanding of evolution of the organoelement chemistry as a whole. An engrossing and worthwhile occupation is to analyze the past of this important area, essential for the development of the whole organic chemistry. The first comprehensive description of the overall knowledge about the Grignard reagent has been presented in a book.[12] In the mid-1990s, two exhaustive monographs were published.[13,14] Highly important is the fact that the scope of applicability of the Grignard reagent continues to develop and the understanding of the Grignard reaction as an unusual phenomenon becomes more fundamental. Particularly this progress forms the subject of this Section of the review.

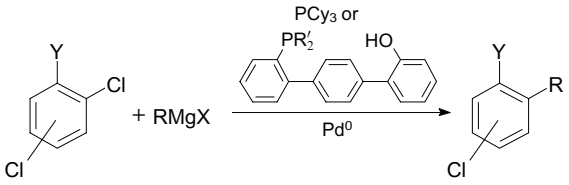
The elaboration of new synthetic methods based on cross-coupling reactions catalyzed by transition metal complexes and giving rise to $C_{sp^2}-C_{sp^2}$ or $C_{sp^2}-C_{sp}$ bonds was among the important achievements of chemistry of the 20th century. These methods are widely used in fine organic synthesis including the preparation of natural compounds and pharmaceuticals. The cross-coupling reactions of organolithium and -magnesium compounds were discovered simultaneously in 1972 by Kumada and Tamao's team [15] in Japan and Corriu's group [16] in France. Both research teams used vinyl halides as electrophilic agents and nickel complexes as catalysts.[17] Later, in 1974, palladium complexes started to be actively used instead of nickel complexes. The stereoselectivity of these reactions was governed by the phosphine ligand. Reactions of less reactive organometallic compounds (Negishi, Stille and Hiyama reactions [18–20]) easily proceeded in the presence of palladium phosphine catalysts without additional activation of the nucleophilic reagent. Reactions involving reactive Grignard reagents often did not require the presence of a ligand, but they were accompanied by formation of homo-coupling products. However, particularly the high reactivity of organomagnesium compounds allowed cross-coupling reactions involving alkyl halides to be accomplished in the 21st century. The difficulty of conducting these reactions is caused by the fact that usual alkyl halides are not prone to oxidative addition, while the organometallic intermediate of the reaction is prone to β-hydride elimination. This problem has been solved not only for the Ni- and Fe-catalyzed reactions, but also for reactions catalyzed by palladium compounds. It was found that the use of electron-donating trialkylphosphine ligands, instead of triphenylphosphine, facilitates the oxidative addition and retards the β-hydride elimination.[21] Nevertheless, there are cases in which products of cross-coupling of alkyl halides can also be obtained in high yields using triarylphosphine ligands.[22]

2.1. Palladium catalysis of the Kumada – Tamao – Corriu reaction

According to the mechanism of the Kumada – Tamao – Corriu (K – T – C) reaction, in which reductive elimination is the rate-limiting step, ligands with a large bite angle should facilitate the reaction and suppress β-hydride elimination. Indeed, it has been found that in the reaction of (1-bromoethyl)benzene with vinylmagnesium bromide, the $Pd(MeCN)_2Cl_2-$Xantphos system (angle of 111°) provides a high product yield (98%) as compared with the 86% yield achieved with the dppf ligand (96°).[23] However, in the reaction of alkyl bromide with magnesium acetylenides $RC{\equiv}CMg$, the best results were found for the $Pd_2(dba)_3-PPh_3$ system (83% yield), whereas in the presence of the dppb ligand, the reaction did not proceed at all.[22] Allylsilanes were prepared from 1,1-dibromoalk-1-enes by reaction with Me_3SiCH_2MgCl in THF catalyzed by palladium acetate with triphenylphosphine followed by protodesilylation.[24] The allylation of 4-bromoisoindoline hydrochloride on treatment with allylmagnesium chloride was catalyzed by bis(*tert*-butyl)neopentylphosphonium tetrafluoroborate and afforded 4-allylisoindoline in a high yield.[25] Salts of 2,5-dibromobenzoic acid react with 1,3-dioxolan-2-ylmethylmagnesium bromide in the presence of the $Pd_2(dba)_3$ catalyst to give the product in 78% yield in the presence of equimolar amounts of sodium *tert*-butoxide and *tert*-butyl alcohol.[26]

Reactions of aryl chlorides were investigated for a number of dichloroarenes $C_6H_3Cl_2Y$, which were reacted with RMgX. Due to the effect of the Y group, the reaction is selective, with only the chlorine atom located in the *ortho*-position to this group being displaced. The reaction is catalyzed by palladium complexes with tricyclohexylphosphine or with an unusual phosphine ligand based on 1,4-diphenylbenzene (Scheme 1).[27]

Scheme 1

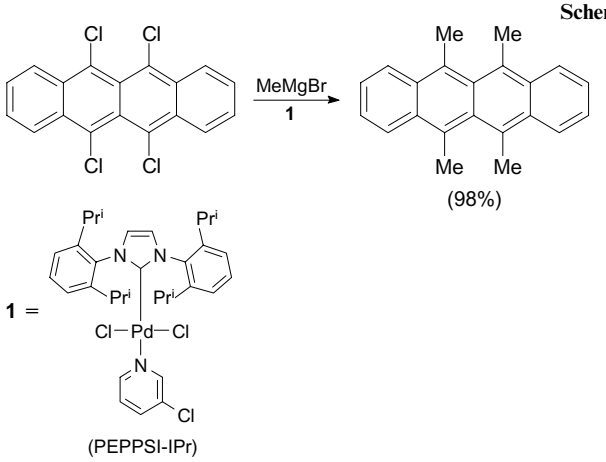


Y = OH, CH_2OH, NH_2, NHAc, NHBoc; R = C_6H_4OMe-4, 2-Th, *etc.*; X = Br, Cl; R′ = Cy, Ph

Polymethylation of polychloroarenes in almost quantitative yields can be achieved by using palladium carbene complexes such as PEPPSI-IPr as catalysts in the reaction with methylmagnesium bromide (Scheme 2). With other ligands, *e.g.*, X-Phos, the product yields are lower.[28]

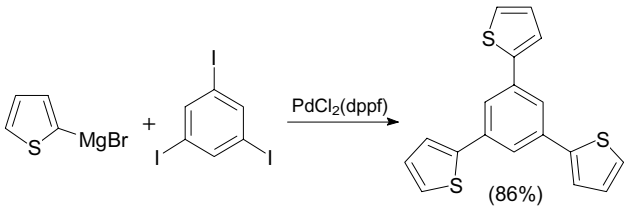
The K – T – C reaction was used to prepare biaryls. For example, the reaction of *m*-$CF_3C_6H_4MgCl$ with *m*-$BrC_6H_4C(O)Pr^i$ catalyzed by a palladium acetate com-

Scheme 2



plex with the S-Phos ligand follows a radical mechanism, with the product yield depending on the reagent that has been used to prepare the initial arylmagnesium chloride.[29] A similar catalytic system, $Pd_2(dba)_3-(1\text{-}Ad)_2P(O)H$, was utilized for the reaction of α-pyridylmagnesium bromide with aryl bromides.[30] Aryl- and hetarylmagnesium bromides react with aryl iodides in the presence of $Pd(dba)_2$ with the Buchwald diphenylphosphine ligands.[31] Thienylbenzenes were obtained by the $PdCl_2$(dppf)-catalyzed reactions of mono-, di- and triiodobenzenes with α-thienylmagnesium bromide (Scheme 3).[32]

Scheme 3

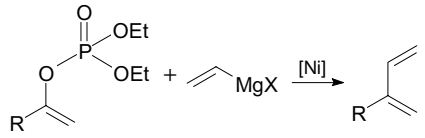


A mixture of disubstituted (46%) and monosubstituted (10%) products was obtained from tribromobenzene at 60 °C. The synthesis of biaryls can be catalyzed by both palladium and nickel complexes.

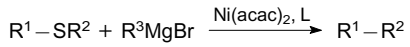
Nitrogen heterocycles are of considerable interest for pharmaceutical industry.[33] In the early stage of research into cross-coupling, Tamao, Kumada and co-workers[34] obtained such compounds in 34% – 76% yields by the reaction of 3-pyridylmagnesium bromide and nitrogen-containing halohetarenes catalyzed by the $Ni(acac)_2$ – dppf system.

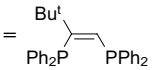
Substrates with leaving groups other than a halogen atom, *e.g.*, a phosphate or sulfide group, have been described (Scheme 4).[35, 36]

Scheme 4



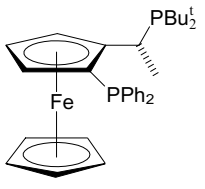
R = Alk, Ar, Het



R^1 = Ar, Het, PhCH=CH, n-C_6H_{13}CH=CH; R^2 = Me, n-$C_{12}H_{25}$;
R^3 = Pr^i, Bu^n, Cy; L = 

The phosphate group was used in the reaction of arylmagnesium halides with vinyl phosphates catalyzed by

Structure 2

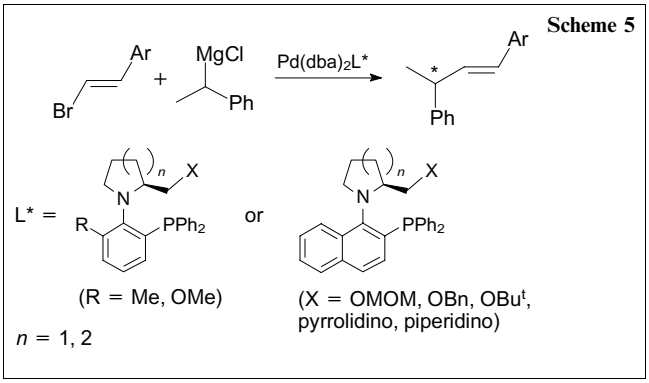


2 (PPF-Bu^t)

palladium chloride without additional organic ligands.[37] Aryl tosylate is known to react with arylmagnesium bromide in the presence of minor amounts of the catalyst (0.1 mol.% – 1.6 mol.%) with the PPF-Bu^t ligand (**2**).[38]

Asymmetric reactions involving alkylmagnesium halides catalyzed by chiral pyrrolidine and piperidine derivatives have been reported (Scheme 5).[39]

Scheme 5

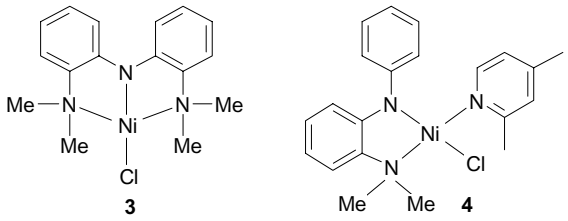


2.2. Nickel catalysis of the Kumada – Tamao – Corriu reaction

Reactions catalyzed by nickel complexes are among the best studied and most demanded K – T – C reactions. It is this type of catalysis that was used by the pioneering researchers in 1972. This catalysis allows one to conduct, without complications, reactions of alkyl halides containing various functional groups with alkyl, aryl and hetaryl Grignard reagents. The nickel amide complex **3** was used, for example, as the precatalyst.[40]

The reactions of alkyl iodides with n-octylmagnesium chloride were carried out with the same type of complexes; complex **3** proved to be inefficient, the best result (74% yield) being attained with the square planar complex **4**.[41]

Structures 3, 4

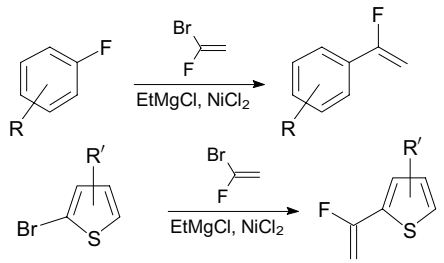


The reactions with alkyl halides are catalyzed by nickel(II) chloride without additional ligands in the presence of buta-1,3-diene.[42]

Cross-coupling involving ate complexes is accompanied by homocoupling; palladium and cobalt complexes proved to be inefficient in these reactions, but in the case of nickel(II) chloride, a high product yield can be attained by appropriate selection of the ligand [30% with $NiCl_2(PPh_3)_2$, 50% with $NiCl_2$(dppe), 93% with $NiCl_2$(dppp)].[15, 43]

The Grignard reagent obtained *in situ* from (het)aryl halides reacts with α-bromofluoroethylene in the presence of nickel(II) chloride as the catalyst, thus providing the introduction of the α-fluoroethenyl group into an arene or hetarene molecule to give, for example, α-fluorostyrene and α-fluorothiophene (Scheme 6).[44]

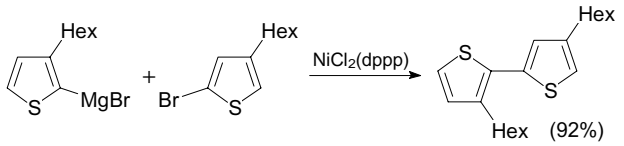
Scheme 6



R = 4-OMe, 4-CO_2Me, *etc.*; R′ = 3-Br, *etc.*

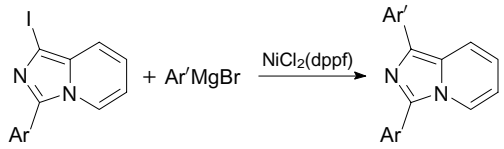
The use of dppe and, especially, Xantphos ligands can minimize the formation of side products in the reaction of 3-bromo- or 3-chloro(trifluoromethyl)benzene with ethylmagnesium bromide.[45] Dimethylation of 1,5-dichloroanthracene was accomplished with $NiCl_2$(dppp) as the catalyst;[46] this complex was also efficient for the synthesis of dihetaryl compounds (Scheme 7).[47]

Scheme 7



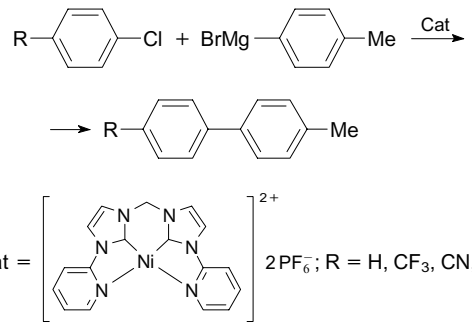
The reaction of 3-aryl-1-iodoimidazo[1,5-*a*]pyridines with arylmagnesium bromides using the same catalyst resulted in the synthesis of 1,3-diarylimidazo[1,5-*a*]pyridines in good yields (Scheme 8).[48]

Scheme 8



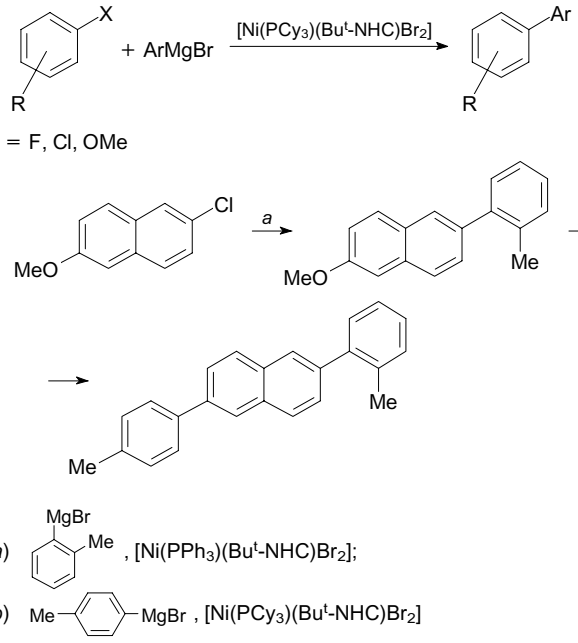
N-Heterocyclic nickel carbene complexes proved to be efficient for the reactions of aryl halides and aryl triflates and also vinyl halides.[49, 50] The hybrid cationic pincer nickel carbene complexes catalyze reactions of unactivated vinyl, aryl and hetaryl chlorides with arylmagnesium bromide (Scheme 9).[51]

Scheme 9



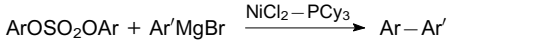
The anisole reaction with RMgX catalyzed by the $Ni(OAc)_2$ complex with carbene ligand has been reported.[52] The reactions of ArCl, ArF and ArOMe with Ar′MgBr, catalyzed by hybrid Ni^{II} complexes with phosphine ligands and carbene with isopropyl and *tert*-butyl substituents, proceed in a similar way.[53] Diaryl derivatives are formed in high yields. When the molecule contains both a chlorine atom and a methoxy group, it is possible to successively and selectively introduce various aromatic substituents (Scheme 10).

Scheme 10



The C–O bonds, including the C_{sp^3}–O bonds, are easily cleaved in nickel-catalyzed reactions.[54] The carbon–sulfur bond in sulfides is also readily broken under Ni-catalysis.[55] The use of diaryl sulfate, a 'green' electrophile, as the arylating reagent has been reported.[56] Tricyclohexylphosphine proved to be an efficient ligand, whereas other mono- and bidentate phosphines were inactive, like also palladium-, iron- and cobalt-based catalytic systems (Scheme 11).

Scheme 11

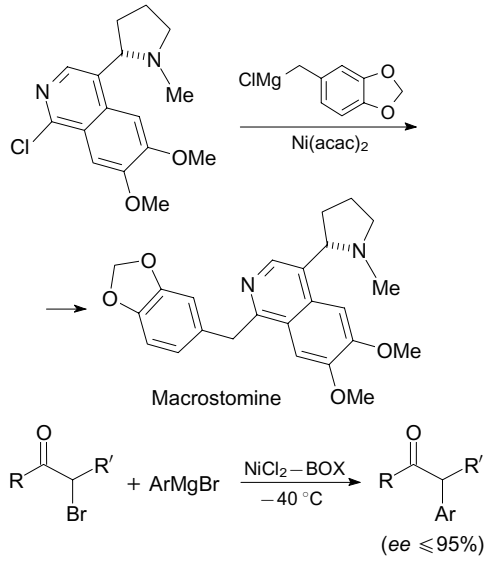


Ar = 4-$MeOC_6H_4$, 2-Naph, *etc.*

The $NiCl_2(PCy_3)_2$-catalyzed methylation of methoxybenzene with methylmagnesium bromide was the first example of replacement of the methoxy group.[57] At high temperature, magnesium naphtholate reacts with PhMgX.[58]

The K–T–C reaction is used to obtain pharmaceutical agents and biologically active compounds, for example, for the synthesis of the alkaloid macrostomine from 1-chloro-6,7-dimethoxyisoquinoline (Scheme 12).[59] 2,2′-Bis(oxazoline) (BOX) ligands proved to be efficient for the reaction of α-bromo ketone, an alkyl electrophile; the reaction was

Scheme 12

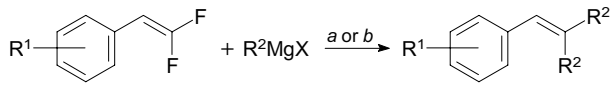


R = Ph: R′ = Me, $Cl(CH_2)_2$, $AcO(CH_2)_2$, *etc.*; R′ = Me: R = 2-FC_6H_4, 3-ClC_6H_4, 3-$MeOC_6H_4$, 2-Th, Et, Pr^i, Br, *etc.*

enantioselective and resulted in 95% enantiomeric excess (*ee*) (see Scheme 12).[60]

Catalysis by nickel complexes can be utilized to carry out Grignard reactions for aryl fluorides[61] and alkenyl fluorides.[62] In some cases, the reactions are catalyzed by not only nickel, but also palladium complexes.[63] Consider examples of such reactions involving *gem*-difluoroalkenes and various Grignard reagents (Scheme 13).[64]

Scheme 13



(*a*) $Pd(PPh_3)_4$ (5 mol.%), Et_2O, argon, Δ; for R^2MgX = MeMgCl, PhMgBr, BnMgCl, 4-MeC_6H_4MgBr, 4-FC_6H_4MgBr;
(*b*) [$NiCl_2$(dppe)] (4 mol.%), Et_2O, argon, rt; for R^2MgX = Bu^{n}MgCl, EtMgCl, Pr^{n}MgBr, n-$C_5H_{11}MgBr$, $PhCH_2CH_2MgCl$;
R^1 = 4-OMe, 4-OBn, 4-SMe, *etc.*

Thus, $Pd(PPh_3)_4$-catalyzed reactions can be carried out for the Grignard reagents containing no β-hydride atom, that is, for methyl and aryl magnesium halides, while Ni-catalyzed reactions are possible for various magnesium alkyl derivatives.

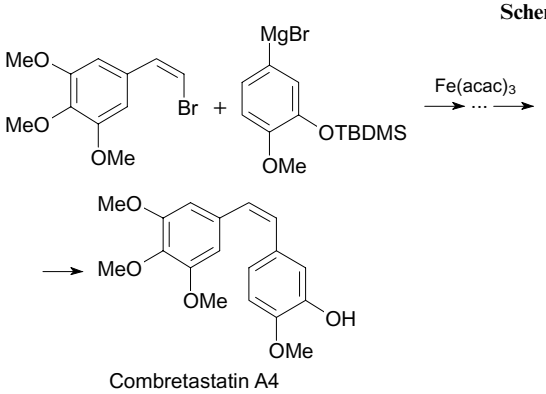
2.3. Iron catalysis of the Kumada – Tamao – Corriu reaction

Catalysis by iron salts and complexes added a new chapter to the chemistry of K – T – C reactions. The use of these catalysts made it possible to construct a wide variety of carbon – carbon bonds ($C_{sp^2} - C_{sp^2}$, $C_{sp^2} - C_{sp}$, $C_{sp^2} - C_{sp^3}$, $C_{sp^3} - C_{sp^3}$) with various combinations of electrophilic (RX) and nucleophilic ($R'MgX'$) reagents. The published data concerning these reactions are surveyed in detail in a review;[65] therefore, we will consider only the most typical cases. Although there are known examples of the Negishi and Suzuki – Miyaura reactions catalyzed by iron complexes, this type of catalysis has been best developed as applied to organomagnesium compounds. It is quite likely that this is caused by the radical nature of the reaction.

The Fe^{III}–catalyzed reaction of PhMgBr with PhBr was first carried out in 1941 by Kharasch and Fields,[66] who obtained biphenyl in 47% yield; this did not rule out partial or complete homo-coupling. The research was interrupted by the Second World War, but in 1971, Tamura and Kochi[67] reported a $FeCl_3$-catalyzed reaction between alkylmagnesium bromide and vinyl bromide, which gave the product in 83% yield. The reaction occurs for both *E*- and *Z*-alkenyl bromides with retention of the geometric configuration.[68] Thus, particularly this publication was the starting point of research into cross-coupling reactions. Subsequently, reaction conditions have been improved and various Grignard reagents (aryl and alkynyl ones) have been tested.[69] Iron acetate $Fe(acac)_3$ started to be used, apart from $FeCl_3$, while triflates and alkynyl bromides were started to be applied apart from alkenyl halides.[70, 71] Not only trivalent iron salts, but also divalent iron compounds such as arylthiolates proved to be suitable as catalyst precursors.[72]

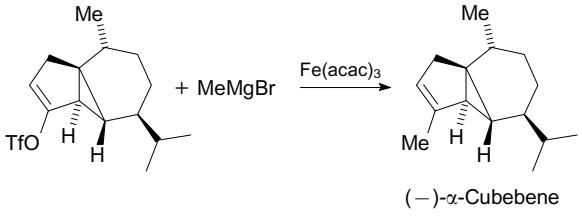
The $Fe(acac)_3$-catalyzed reaction of substituted *cis*-styryl bromide with arylmagnesium bromide resulted in the synthesis of the anticancer drug combretastatin A4 (Scheme 14).[73]

Scheme 14



It was shown that arylmagnesium bromides can be obtained in the reactions of aryl bromides with vinyl bromides *in situ* rather than in advance.[74] The methylation of vinyl triflates with methylmagnesium bromide serves for the synthesis of some natural products. In particular, this reaction is the final step in the total synthesis of the sesquiterpene (−)-α-cubebene (Scheme 15).[75]

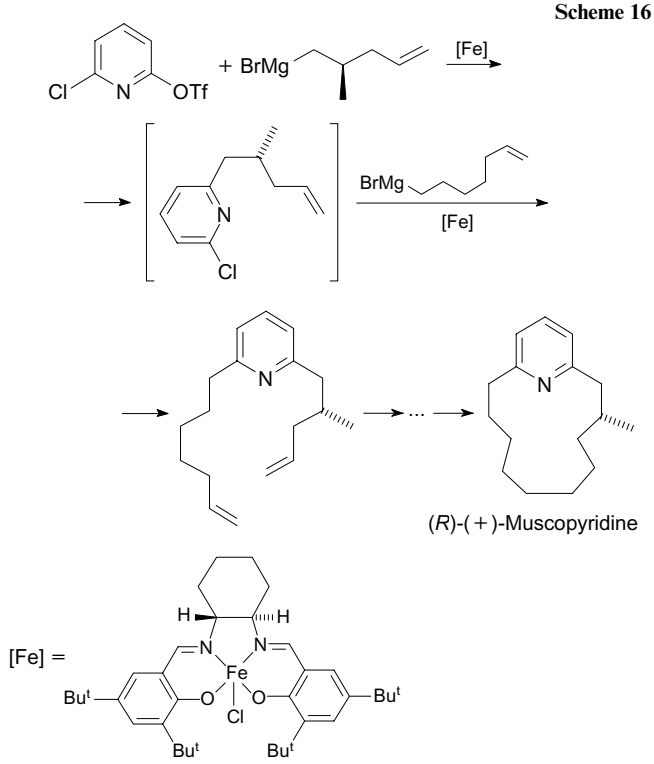
Scheme 15



The $Fe(acac)_3$ complex demonstrated a good behaviour in the synthesis of biaryls.[76] An important factor for the

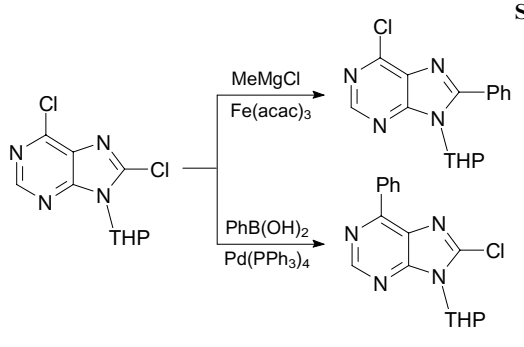
reaction to proceed in THF is the presence of some additives such as *N*-methyl-2-pyrrolidone,[77] 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one[78] or TMEDA.[79] In the presence of TMEDA, the reaction of aryl chloride with alkylmagnesium bromide can be performed at low catalyst concentration (0.1 mol.% – 1 mol.%) to afford high yields of products with various functional groups.[80] For the reactions of substrates comprising the $C_{sp^2}-X$ moiety with various leaving groups (non-activated chlorides, triflates, tosylates, phosphates, pivalates), it was necessary to apply more sophisticated iron complexes, for example, homoleptic tetraalkyl ferrate $(Me_4Fe)(MeLi)[Li(OEt_2)_2]$[81] or complexes with carbene ligands[82] or salen complexes, which were employed to introduce two different alkyl groups into the pyridine molecule in the synthesis of the alkaloid (*R*)-(+)-muscopyridine (Scheme 16).[83]

Scheme 16



It is noteworthy that the substrates ArCl, ArOTf and ArOTs show higher reactivity towards AlkMgBr than ArBr or even ArI,[84] which is completely the opposite to the reactivity series of these substrates in Pd-catalyzed reactions. Note that the regioselectivity of Grignard reactions catalyzed by iron compounds also differs from that of the reaction of $PhB(OH)_2$ catalyzed by the palladium complex,[85] as can be seen in Scheme 17.

Scheme 17

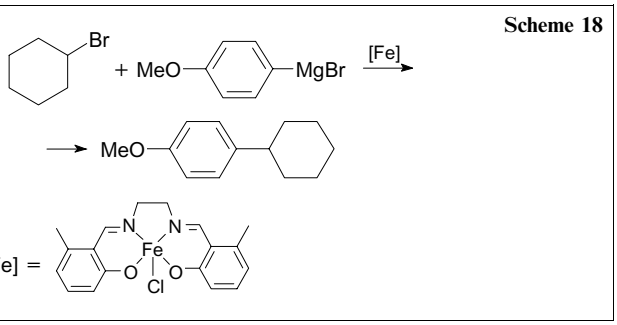


The high reactivity of organomagnesium compounds is known to give rise to homo-coupling products. This reaction can be suppressed by using $CuCN \cdot 2\,LiCl$,[86] which is added to the Grignard reagent obtained by the Knochel method. This reagent poorly reacts with ArOTf and does not react with ArOTs; however, this mild reagent allows one to retain all substrate functional groups (ketone, nitrile, ester, amide and acetal groups). Aryl iodides are reactive under these conditions.

Iron(III) fluoride proved to be an active catalyst in the K – T – C reaction.[87] In this case, aryl chlorides were also more reactive than iodides, bromides or triflates. Iron tribromide was found to be an excellent catalyst for the reactions of arylmagnesium bromides with heterocyclic chlorides or bromides, especially in the presence of isoquinoline, which is used as a ligand.[88]

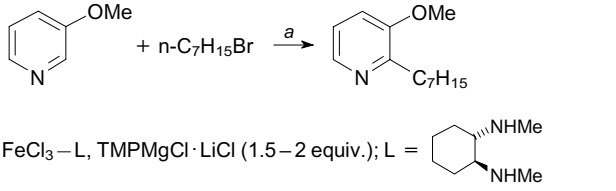
The β-hydride elimination problem, known for Pd catalysis and precluding the use of alkyl halides that have a β-hydrogen atom as electrophilic reagents, does not arise at all when $FeCl_3$ is used as the catalyst, especially in the presence of ligands. Various Grignard reagents react with cyclohexyl bromide under mild conditions to give high product yields (an example is depicted in Scheme 18).[89]

Scheme 18



Electron-deficient arenes can be metallated to give Grignard reagents *in situ*. The latter are then alkylated, as shown in Scheme 19.[90]

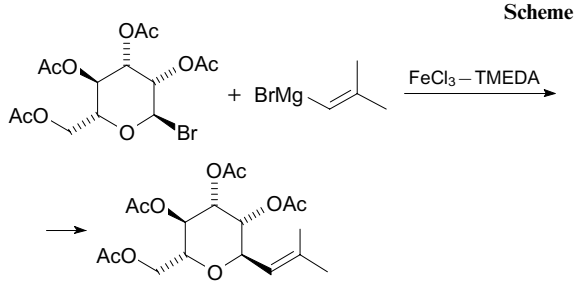
Scheme 19



When used with the 1,2-bis(diethylphosphino)ethane ligand, divalent iron catalyzes the alkylation of even sterically crowded bis(*ortho*-substituted) Grignard reagents.[91] In the presence of TMEDA, $FeCl_3$-catalyzed alkylation of the alkenyl Grignard reagents has been carried out. An example is vinylation of acylated *C*-bromomannopyranoside (Scheme 20).[92]

Catalysts based on $Fe(OAc)_2$ with various ligands were used to form the $C_{sp^3}-C_{sp^3}$ bond, for example, in the synthesis of n-$C_{14}H_{30}$ from Bu^nMgBr and n-$C_{10}H_{21}Br$.[93] The Fe^{II} activity depends substantially on the nature of the ligand, in particular, donor phosphine ligands promote

Scheme 20

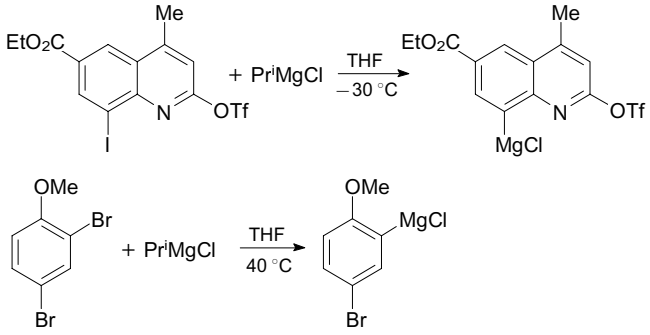


cross-coupling in the reactions of benzyl halides, while acceptor ligands lead to homo-coupling.[94] Consideration of the mechanism, which is apparently radical, is beyond the scope of this review, because different mechanisms are considered in the literature for different types of reactions and different iron catalysts, and determination of the most likely catalytic cycle requires further investigation.

2.4. Knochel reaction for the synthesis of complex organomagnesium compounds

The method based on metal – halogen exchange, developed by Knochel and his team, has been an important stage in the preparation of functionalized organomagnesium compounds. The exchange occurs between (Het)ArX (X = I, Br) and Pr^iMgY (Y = Cl, Br).[95] This exchange, giving rise to (Het)ArMgY, proceeds most readily for aryl halides with electron-withdrawing groups (NO_2, CN, CO_2R, *etc.*) at a reduced temperature, but is also possible at 40 °C for aryl halides with electron-donating groups (Scheme 21).

Scheme 21



The organomagnesium compounds thus formed react with various electrophilic reagents.

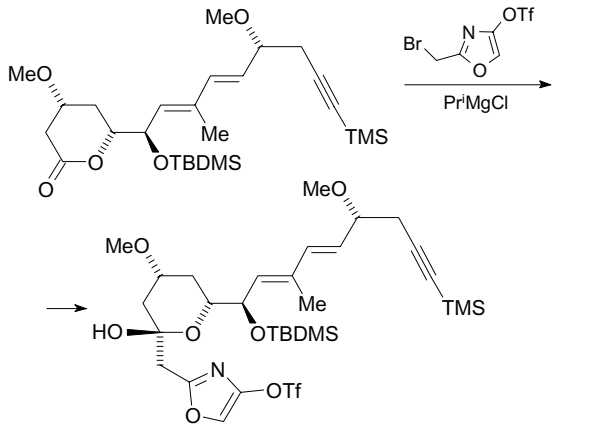
This procedure can serve for the preparation of polyfunctional heterocycles;[96] it is applicable to the synthesis of alkenyl and alkyl organomagnesium compounds.[97] The addition of $CuCN \cdot 2\,LiCl$ or $CuI \cdot 2\,LiCl$ leads to modified compounds (ate complexes), and the reaction can proceed selectively under mild conditions.

The exchange of the bromine atom in bromomethyloxazole with magnesium at −78 °C affords an unstable benzyl type Grignard reagent, which has been used to prepare the building block needed for the total synthesis of phorboxazole (Scheme 22).[98]

2.5. Asymmetric reactions of Grignard reagents

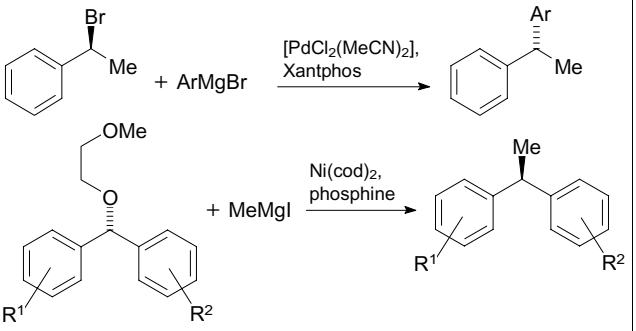
In the K – T – C reaction, chiral phenylethyl bromide is converted almost completely to give 1,1-diarylethanes,

Scheme 22



because the oxidative addition follows the S_N2 mechanism (Scheme 23). The β-hydride elimination can be avoided by using the Xantphos ligand.[23] The reaction of alkyl ethers with the Grignard reagent catalyzed by nickel complexes proceeds in a similar way (see Scheme 23).[99]

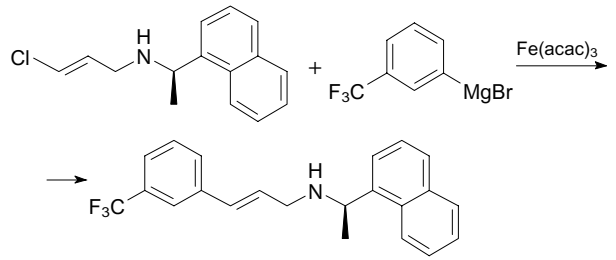
Scheme 23



R^1 = H, 4-Ph, 4-CF_3, *etc.*; R^2 = H, 4-OMe, 4-Ph, 4-CF_3, 3-CF_3, *etc.*

Some chiral compounds have been produced in kilogramme amounts by the K – T – C reaction. The Fe-catalyzed reaction was used as a step in the synthesis of the drug cinacalcet hydrochloride (Scheme 24).[100]

Scheme 24



2.6. Unusual organomagnesium compounds

Metal-containing compounds obtained in thin films have attracted researchers' attention since the 1970s when systematic research in this area was started,[101] although it is fair to mention that N.N.Semenov and A.I.Shal'nikov[102] had carried out reactions in metal-containing films back in

the 1920s. Usually these low-temperature reactions involve metal clusters. Naturally, to obtain the product, it is important that the reaction rate be higher than the rate of metal particle aggregation. The synthesis of magnesium organic derivatives in the films by co-condensation of magnesium and organic halide on a liquid nitrogen-cooled surface was accomplished for the first time in 1972. The fact that the reaction has proceeded was ascertained considering the products of hydrolysis. However, more recent studies demonstrated that at low temperature, the reaction on the surface occurs with the Mg_4 cluster rather than with atomic magnesium and gives the compounds $PhMg_4X$ (X = F, Cl).[103,104] It is the formation of the magnesium cluster that enables the insertion into strong bonds such as C—Cl and C—F. In the case of weaker C—Br and C—I bonds, a mixture of $PhMg_4Hal$ and the conventional Grignard reagent PhMgHal (Hal = Br, I) is formed.

The Mg_4 adducts with aromatic hydrocarbons are formed under similar conditions. The possibility of *trans*-metallation has been demonstrated, with the magnesium cluster being preserved upon the insertion into the strong C—Cl bond [reaction (1)] and being partly destroyed upon the insertion into the weaker C—Br bond [reaction (2)]. In the latter case, phenyl radicals are generated, as indicated by the presence of benzene and biphenyl among the products.

$$PhMg_4F + PhCl \longrightarrow PhMg_4Cl \quad (1)$$

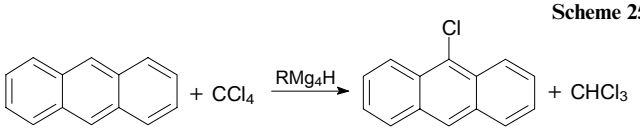
$$C_9H_8Mg_4 + PhBr \longrightarrow PhMg_4Br + PhMgBr\,(+PhH + Ph-Ph) \quad (2)$$

C_9H_8 is indene

The calculated activation energy for the insertion of the Mg_4 cluster into the C—X or C—H bond proved to be lower than the activation energy for the insertion of atomic magnesium into the same bonds. The behaviour of the $PhMg_4F-PhF$ and $PhMg_4Cl-PhCl$ systems differs from the behaviour of analogous $PhMg_4Br-PhBr$ and $PhMg_4I-PhI$ systems, which readily form radicals. The reaction of $PhMg_4Br-PhBr$ with n-propyl bromide occurs as cross-coupling and furnishes propylbenzene. The halogen atom exchange takes place in the reaction of $PhMg_4Cl$ with n-propyl bromide, which gives PhMgBr and Pr^nCl. This reaction can be carried out in a catalytic version. The catalytic isomerization of n-heptyl chloride to isoheptyl chloride also takes place under the action of $PhMg_4F$.

The RMg_4X-catalyzed halogen exchange proceeds not only in the film at low temperature, but also in solution at room temperature.[105] The organomagnesium compounds RMg_4H generated in films from aromatic hydrocarbons can catalyze some reactions with a TON of up to 5000, which far exceeds that observed in the $PhMg_4X$-catalyzed reactions (Scheme 25).[106]

Scheme 25



To summarize, one can state that the role of Grignard reagents in organic synthesis and catalysis does not decline with time and their unusual properties are widely used.

3. Catalytic cyclomagnesiation and cycloalumination of unsaturated compounds — the new in the synthesis of metallacarbocycles

The previous Section of the review considers in detail the classical methods of synthesis and synthetic applications of organomagnesium compounds, including magnesium clusters. Also, the achievements in the use of metal complexes as catalysts in the OMC chemistry are demonstrated. This Section addresses new classes of organometallic reactions — catalytic cyclomagnesiation, cycloalumination and cycloboration; the unique potential of these reactions catalyzed by metal complexes in organic and organometallic synthesis is demonstrated for a large number of cases.

The pioneering studies in organoelement chemistry with metal complex catalysts carried out in the last 10 – 15 years by the authors of this review and their followers resulted in initiation and development of a new field of organometallic chemistry — the chemistry of small, large and giant metallacycles based on main group elements (Mg, Al, B).[107–116] These studies formed a fundamentally new synthetic platform for the development of efficient and adaptable processes for preparation of practically valuable classes of small, medium, large and giant carbocycles and metallacarbocycles; spirocarbocycles; oxygen-, nitrogen-, sulfur- and phosphorus-containing heterocycles; new classes of biologically active terpenoids and steroids; higher *Z*,*Z*-dienoic acids; lembehynes and pheromones with unique stereomeric purity. Studies along this line resulted in the development of a new strategy of one-pot organic and organometallic synthesis *via* the preparation of structurally diverse metallacycles *in situ*.

The presence of two highly reactive metal – carbon bonds in main group metal-based metallacycles, as distinct from analogous rings with transition metals (Ti, Zr, Hf, Ta, Cu, Mo, W, Mn, Re, Fe, Ru, Rh, Co and Ni),[117] in combination with relatively high stability of these compounds under ambient conditions and the possibility to prepare and convert them in one preparative step, make these organometallic derivatives highly promising and valuable for targeted organic and organometallic synthesis aimed at constructing new carbon – carbon, metal – carbon, metal – hydrogen and heteroatom – carbon bonds.

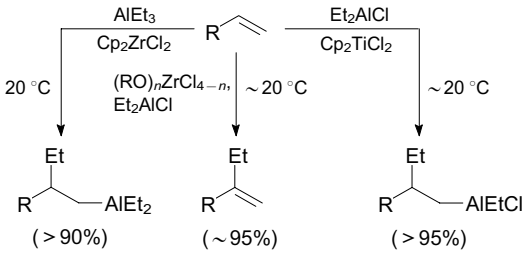
How could it happen that chemists did not previously pay attention to these classes of organometallic compounds, although this held up the development of main group metal-based metallacycle chemistry, in particular, the chemistry of alumina-, magnesa- and boracarbocycles, which obviously possess polyfunctional reactivity and, hence, a broad synthetic potential? In our opinion, the key obstacle in the way of extensive investigations and applications of main group metal-based metallacycles was the lack of efficient preparative methods for their synthesis or theoretical investigations considering the thermodynamic stability and possible existence of small, medium and large metallacycles, for example, alumina- and magnesacyclopropanes, aluminacyclopropenes, boriranes, borirenes, alumina- and magnesacyclopentanes, alumina- and magnesacyclopentenes, aluminacyclopentadienes and other metallacycles based on the above-mentioned main group elements.

It should be noted that the authors' ideas concerning the synthesis and study of previously unknown metallacycles based on main group metals coincided in time with the studies aimed at the development of original catalytic

methods of hydro- and carbometallation of alkenes containing an unactivated double bond with available alkylalanes (Bu^i_2AlH, Bu^i_3Al, $AlEt_3$, Et_2AlCl), Grignard reagents (RMgX) and R_2Mg.[118–122] The initiation and development of this research was greatly affected by the original publications of Negishi and co-workers,[123–125] which are devoted to stereoselective carboalumination of acetylenes with $AlMe_3$ catalyzed by Zr complexes.

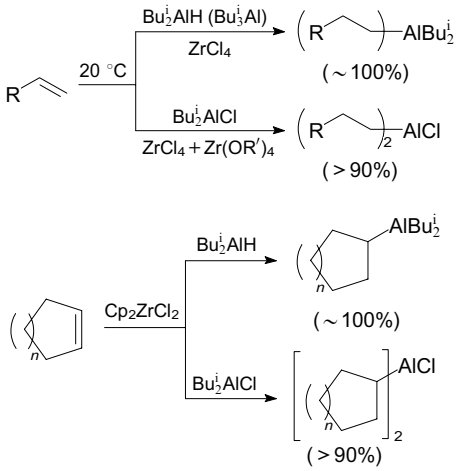
The research along this line carried out by the authors of this Section between the 1980s and 2000s culminated in the development of efficient chemo- and regioselective preparative methods for catalytic hydro- and carboalumination as well as carbomagnesiation and β-alkylation of alkenes with un unactivated double bond on treatment with Bu^i_2AlH, Bu^i_2AlCl, Et_2AlCl or $AlEt_3$ and with the Grignard reagents $RMgR'$ in the presence of Ti and Zr complexes as catalysts (Scheme 26).[109, 112, 113, 126]

Scheme 26



In addition, methods efficient for practical application both in laboratory and in industry have been proposed for catalytic hydroalumination of cyclic and acyclic alkenes on treatment with commercially available OAC, such as Bu^i_2AlH, Bu^i_2AlCl and Bu^i_3Al, (Scheme 27).[112]

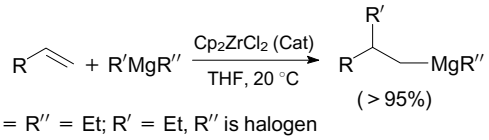
Scheme 27



The obtained experimental results were used to formulate the idea and implement a strictly regioselective catalytic carbomagnesiation of α-alkenes, including functionally substituted and cyclic enol ethers, by means of simple Grignard reagents and Et_2Mg, catalyzed by Cp_2ZrCl_2; this substantially extended the scope of applicability of organomagnesium compounds in organic and organometallic synthesis as compared with the Grignard reagent, the synthesis of which requires the use of halogenated organic compounds.

The developed carbomagnesiation of unactivated alkenes, unlike the above-mentioned hydro- and carboalumination reactions of cyclic and acyclic alkenes, has become popular in synthetic organic and organometallic chemistry and is known as the Dzhemilev reaction (Scheme 28).[127]

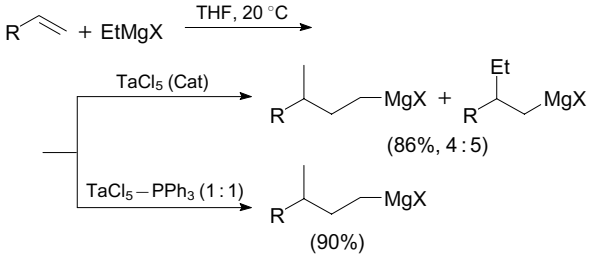
Scheme 28



R′ = R″ = Et; R′ = Et, R″ is halogen

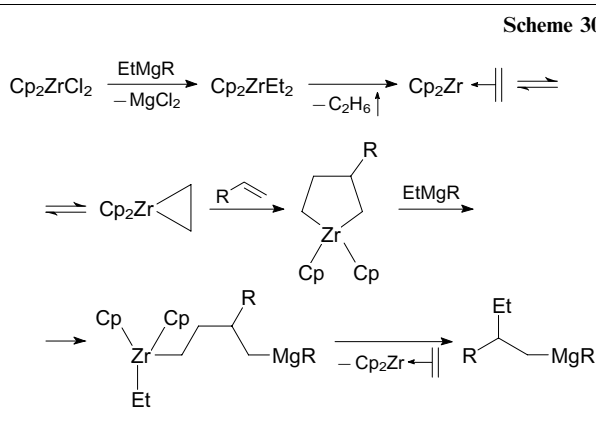
The use of a $TaCl_5$-based catalyst, instead of Cp_2ZrCl_2, changes the route of carbomagnesiation, which then affords a mixture of regioisomers in 4 : 5 ratio (Scheme 29).[128] More recently, the same researchers found that in the presence of triphenylphoshine, the regioselectivity of the reaction reaches 90%.

Scheme 29



Detailed mechanistic study of alkene 1,2-carbomagnesiation with EtMgR catalyzed by Cp_2ZrCl_2 carried out by Professor Whitby and co-workers [129] from the University of Southampton has shown that the reaction intermediates are bis(cyclopentadienyl)zirconacyclopropane and 3-substituted bis(cyclopentadienyl)zirconacyclopentane. The latter undergoes an intramolecular β-hydrogen elimination to give the target 1,2-carbomagnesiation product of the starting α-alkene, with the active catalyst being regenerated (Scheme 30).

Scheme 30



Like the catalytic 1,2-ethylmagnesiation (Dzhemilev reaction), the 1,2-ethylalumination of α-alkenes,[130, 131] which was first accomplished on treatment with Et_2AlCl or $AlEt_3$ in the presence of the $TiCl_4$, $Ti(OR)_4$ and $Cp_2ZrCl_2 – MgEt_2$ catalysts, involves the formation of

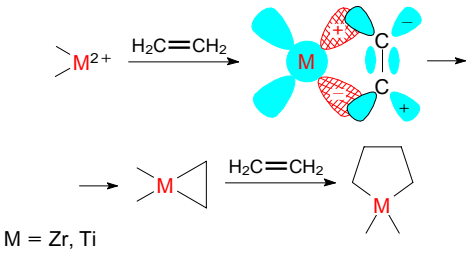
zircona- or titanacarbocycles as key intermediates *via* a similar pathway.

It follows from the above that catalytic 1,2-carbometallation of alkenes with Mg and Al alkyl derivatives catalyzed by Zr and Ti complexes proceeds *via* generation of intermediate transition metal-based metallacycles, which are responsible for the formation of molecules of the target organometallic products.

The formation and the subsequent transformations of zircona- and titanacarbocycles in the 1,2-carbomagnesiation and 1,2-carboalumination occur owing to the unique ability of Zr and Ti alkyl and cycloalkyl complexes to transfer σ- and π-bonded ligands to main group atoms and *vice versa*.[130 – 132]

The above results prompted the idea[111 – 113] that magnesa- and aluminacarbocycles could be prepared by the catalytic cyclometallation of alkenes on treatment with Mg and Al alkyl derivatives in the presence of Zr and Ti complexes as catalysts. The idea was based on the ability of coordinatively unsaturated Zr and Ti complexes to coordinate alkenes to give donor-acceptor complexes according to the Dewar – Chatt – Dunkanson model,[133 – 135] which is expected to activate the alkenes and induce the subsequent intramolecular oxidative cyclization yielding three- and five-membered transition metal-based metallacycles (Scheme 31).

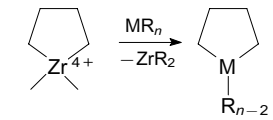
Scheme 31



M = Zr, Ti

It was postulated that the transition metal atoms in the metallacycles may be replaced, either stoichiometrically or catalytically, by main group metal atoms *via* the reaction of the transition metal-based rings with alkyl or alkyl halide main group metal (*e.g.*, Mg, Al and B) derivatives. This reaction resulted in the synthesis of main group metal-based metallacycles (Scheme 32).

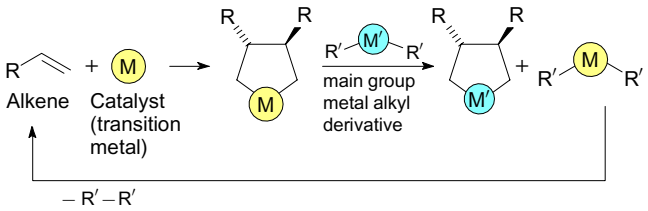
Scheme 32



M = Mg, Al, B

The active research to implement this idea has met with success. As a result, original one-pot catalytic processes were developed for the synthesis of a broad range of previously unknown or difficult-to-access classes of metalla-, carbo-, hetero- and macrocycles of a specified structure. Studies of the mechanisms of this reactions resulted in the discovery of the catalytic replacement of transition metal atoms (Ti, Zr, Ta, Hf, Nb, Co) in metallacycles by main group metal atoms (Zn, Mg, Al, In, Ga, B) with the

Scheme 33



M is catalyst (Ti, Zr, Hf, Nb, Ta, Co);

M′ is main group metal (Mg, Al, Zn, Ga, In)

synthesis of small, medium, large and giant main group metal-based metallacycles (Scheme 33).

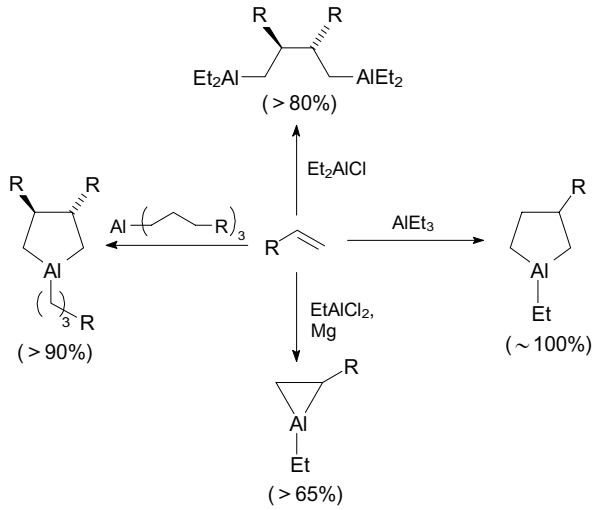
Unfortunately, within the framework of this review, it is impossible to give a complete account of the results obtained on the synthesis, properties and applications of metallacycles based on main group elements (Mg, Al, B); below we present the most interesting and also synthetically and practically valuable data.

3.1. Catalytic cycloalumination of alkenes, acetylenes and 1,2-dienes

The possibility of the preparative synthesis of aluminacyclopentanes by the Cp_2ZrCl_2-catalyzed reaction of α-alkenes with $AlEt_3$ was first indicated in 1989,[107] although the results were obtained back in 1985.[136]

Detailed investigation of the scope of applicability of the discovered reaction,[136] the key kinetic parameters affecting the product yields and selectivity, and the nature and the effects of catalyst components and reactants on the pattern and structural selectivity of formation of five-membered OACs led to the development of preparative routes to previously unknown aluminacyclopropanes, aluminacyclopentanes and 1,4-dialuminium compounds (Scheme 34).

Scheme 34

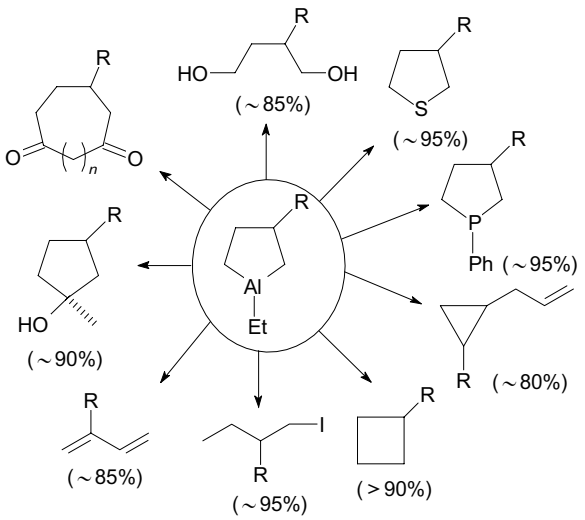


Conditions: Cp_2ZrCl_2 catalyst (~ 5 mol.%), PhMe, 20 °C

Considering the fact that the above-mentioned aluminacarbocycles contain two Al – C bonds, they were studied in the reactions with nucleophilic and electrophilic reagents,

cross-coupling, carbocyclization and demetallation. This resulted in the development of efficient one-pot processes involving *in situ* formation of cyclic and acyclic organoaluminium compounds to convert structurally different α-alkenes to carbo- and heterocyclic and bifunctional derivatives the syntheses of which by other methods include large numbers of steps or require poorly accessible and expensive reagents (Scheme 35).[137–142]

Scheme 35

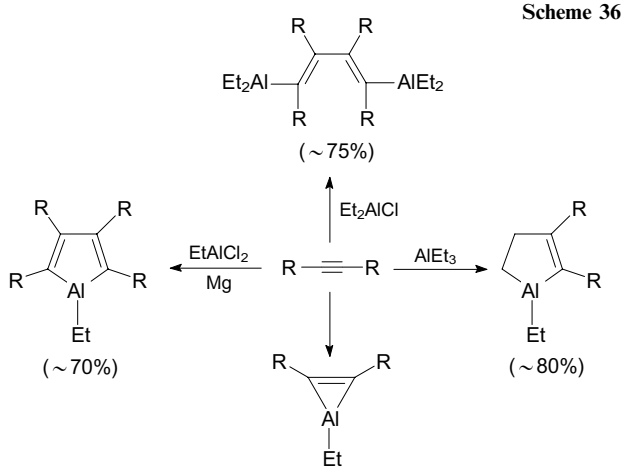


The above-mentioned targeted transformations of aluminacarbocycles indicate that the considered catalytic cycloalumination of alkenes possesses a broad synthetic potential; however, it remained unknown whether this reaction is characteristic only of alkenes or it can be extended to other classes of unsaturated compounds such as alkynes or 1,2-dienes. In this case, one could expect the preparation of previously unknown aluminacarbocycles such as aluminacyclopentenes, aluminacyclopentadienes, (alkylidene)aluminacyclopropanes, (alkylidene)aluminacyclopentanes as well as similar metallacycles derived from other main group metals and their acyclic analogues provided that they are thermodynamically stable.

The implementation of these ideas led to the first syntheses of aluminacyclopropenes, aluminacyclopentenes, aluminacyclopentadienes and 1,2-dialuminaethylenes; the products were studied for their physicochemical properties; preparative processes for the synthesis of these classes of OACs were developed (Scheme 36).[143, 144]

In the case of allenes, (alkylidene)aluminacyclopropanes, 2-(alkylidene)aluminacyclopentanes and 2,5-(dialkylidene)aluminacyclopentanes were obtained for the

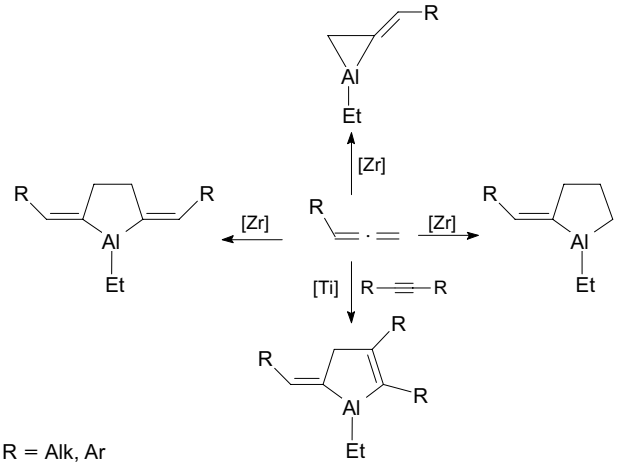
Scheme 36



Catalyst: Cp_2ZrCl_2, Cp_2TiCl_2; R = Et, Pr^n, Bu^n, *etc.*

first time. The simultaneous cycloalumination of disubstituted acetylenes and 1,2-dienes with $AlEt_3$ affords 5-alkylidene-1-aluminacyclopent-2-enes (Scheme 37).[145–147]

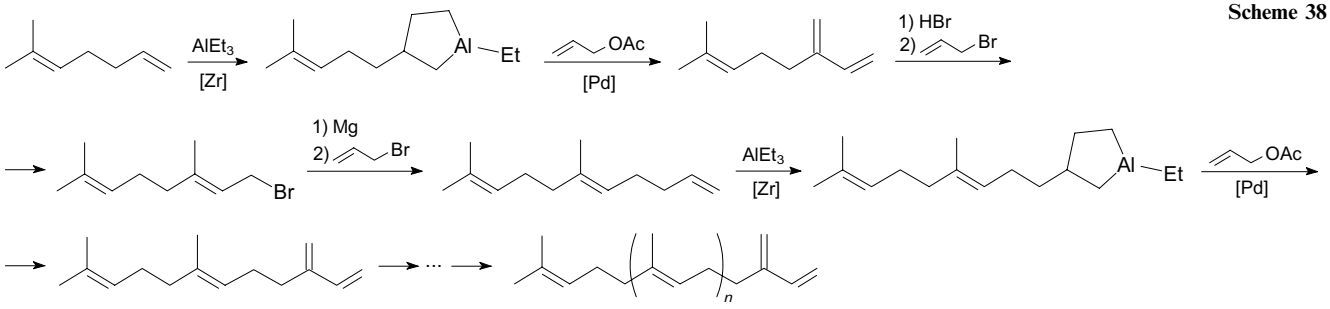
Scheme 37



Scheme 38 shows the results of application of this reaction in the syntheses of regular isoprenoids.

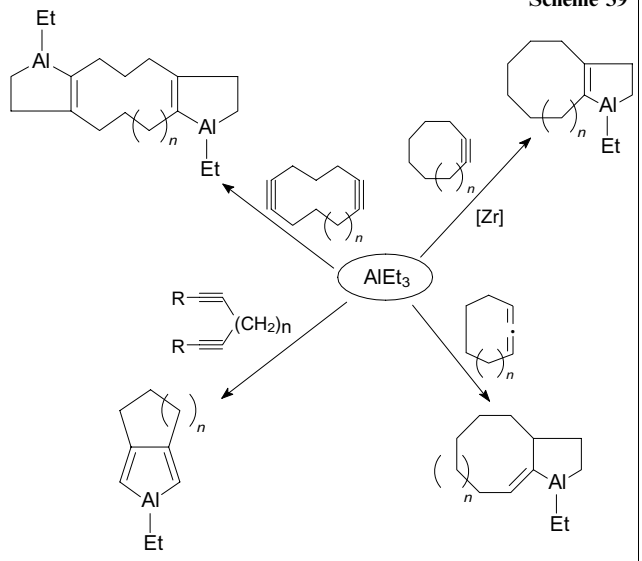
Previously, the above-mentioned cyclic 1,2-dienes and acetylenes and methylenecarbocycles were considered to be inactive in cycloalumination. Recent studies filled this gap and resulted in the development of a number of original one-pot methods for the construction of macrometallacycles, which are readily converted to polyfunctional macrocarbocycles.

Scheme 38



Indeed, cyclic 1,2-dienes and acetylenes react with $AlEt_3$ in the presence of the Cp_2ZrCl_2 catalyst (5 mol.% [Zr], hexane, 6 h) to give previously unknown bi- and tricyclic OAC in 65% – 95% yields (Scheme 39).[148 – 151]

Scheme 39

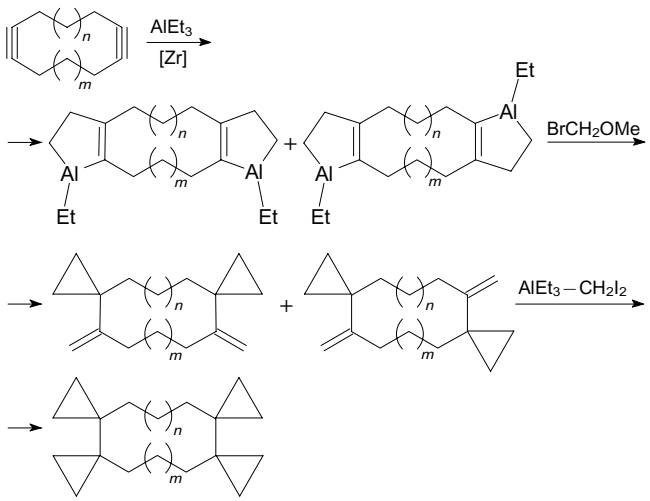


Catalyst: Cp_2ZrCl_2; n = 3 – 6

These original methods for the synthesis of bi- and tricyclic aluminacarbocycles were used to develop new efficient processes for the design of macrocyclic ($C_{20}-C_{28}$) polyketones,[152, 153] based on the use, as the key reaction steps, of Cp_2ZrCl_2-catalyzed intermolecular cyclometallation of cycloalkynes with RMgX and R_nAlCl_{3-n}, cross-coupling and oxidative cleavage of double bonds in the resulting tri- and tetracyclic unsaturated molecules (Scheme 40).[154]

As further development of these works, the catalytic cycloalumination of cyclic diacetylenes was employed to design structurally unique carbon macrocycles containing spirocyclopropane moieties by carbocyclization of tricyclic OACs (Scheme 41).[155, 156]

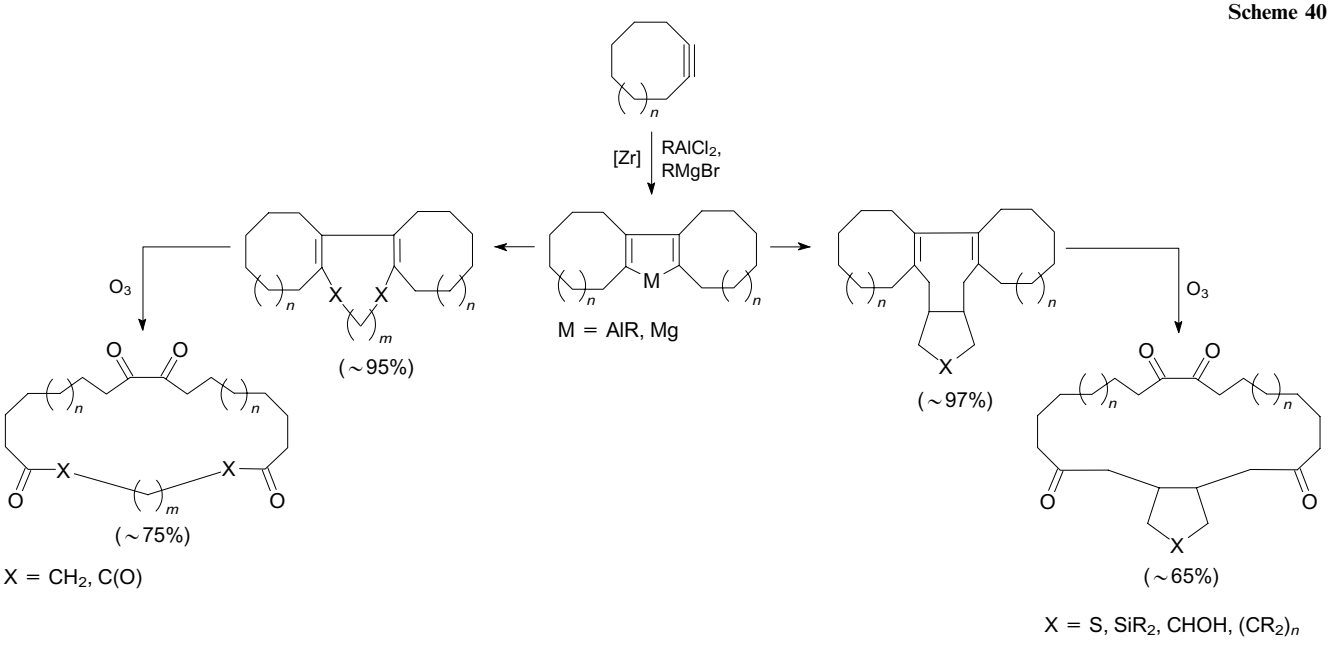
Scheme 41



Zr = Cp_2ZrCl_2; $n = m$ = 2 – 7; n = 2, m = 3; n = 3, m = 4; n = 3, m = 5

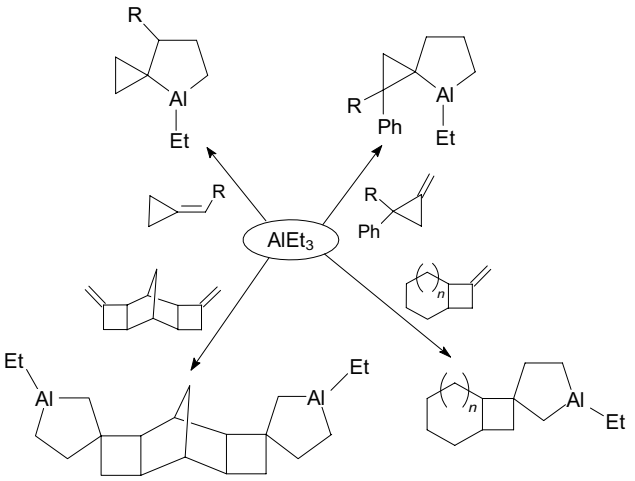
For a long period since the discovery of catalytic cycloalumination of unsaturated compounds, 1,1-disubstituted alkenes were considered to be inactive in these reactions. Therefore, it was assumed that, unlike acyclic alkenes with a relatively inert 1,1-disubstituted double bond, strained cyclic alkenes with an activated double bond will react with $AlEt_3$ in the presence of transition metal complexes as catalysts to give spiro OAC. Studies along this line demonstrated that Cp_2ZrCl_2-catalyzed cycloalumination of methylidene- and alkylidenecyclopropanes on treatment with $AlEt_3$ affords previously unknown spiro OACs, namely, substituted aluminaspiro[2.4]octanes, in high yields

Scheme 40



(~95%).[157] A similar reaction can be carried out for structurally diverse methylenecyclobutanes (Scheme 42).[140, 158]

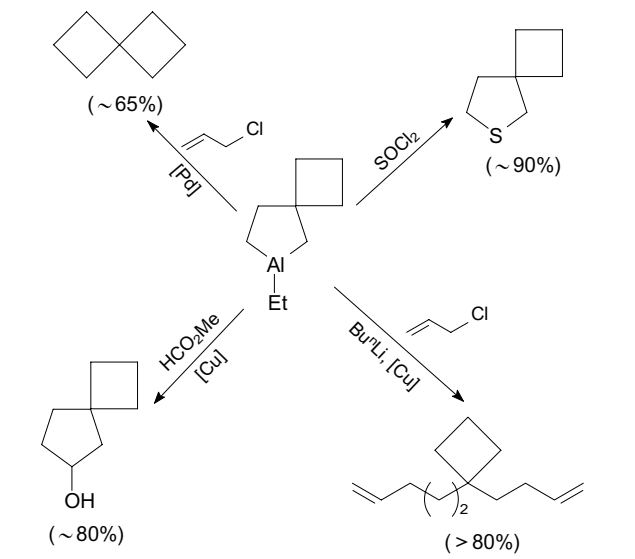
Scheme 42



R = H, Alk, Ar; *n* = 1, 3, 5

The obtained spiro metallacarbocycles can be successfully converted, without isolation, to carbo- and heterocyclic spiro compounds and bifunctional compounds containing a cyclobutane moiety (Scheme 43).[158]

Scheme 43

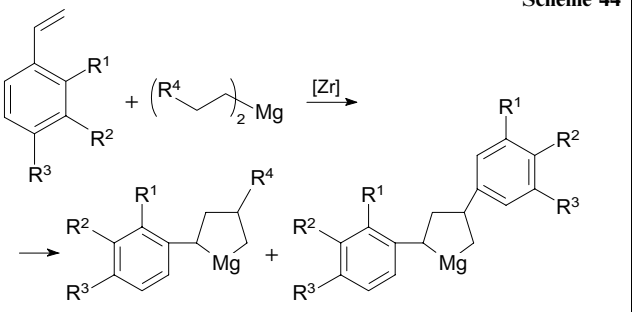


The above results indicate that a new research area, the chemistry of small, medium and large aluminacarbocycles, has appeared in the last 10 – 15 years in the chemistry of organoaluminium compounds; this research is being successfully pursued, including both extending the scope of applicability of the new developed reactions and original reagents and application of these methods in the synthesis of practically valuable compounds and materials.

3.2. Catalytic cyclomagnesiation of alkenes, acetylenes and 1,2-dienes catalyzed by Ti and Zr complexes

The first information about the cyclomagnesiation of alkenes with RMgX or R_2Mg to the corresponding magnesacyclopentanes appeared in 1989.† The authors reported that the Cp_2ZrCl_2-catalyzed conversion of styrene and its substituted derivatives in a Et_2O – THF solution at 20 °C leads to a mixture of magnesacyclopentanes in a total yield of > 80% (Scheme 44).

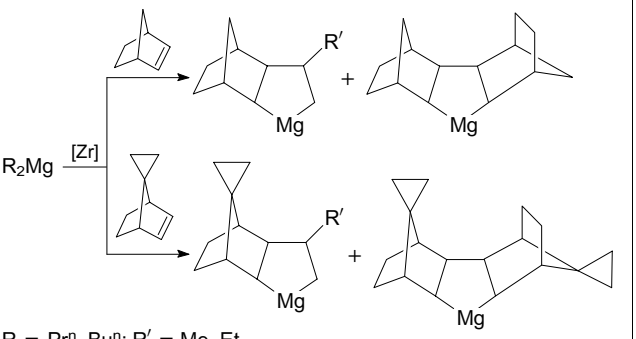
Scheme 44



R1, R2, R3 = H, Me; R4 = Me, Et

The cyclomagnesiation of norbornenes, unlike that of styrenes, carried out by treatment with Pr^n_2Mg or Bu^n_2Mg in the presence of catalytic amounts of Cp_2ZrCl_2 (3 mol.% – 5 mol.%) in a Et_2O – THF solution for 8 h at ~22°C gives rise to diastereomerically pure tri-, tetra-, penta- and hexacyclic magnesacyclopentanes (Scheme 45) (see ‡).[120]

Scheme 45



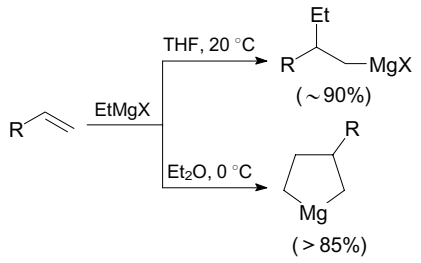
R = Pr^n, Bu^n; R′ = Me, Et

The reagents EtMgX and Et_2Mg, unlike derivatives with larger alkyl groups R_2Mg (R = Pr^n, Bu^n, Hex, Oct), react with α-alkenes in the presence of catalytic amounts of Cp_2ZrCl_2 to afford either 1,2-ethylmagnesiated or cyclomagnesiated products depending on the reaction conditions. The reaction pathway can be rather strictly controlled by varying the nature of solvent, temperature and reactant ratio (Scheme 46).

† See U.M.Dzhemilev, R.M.Sultanov, R.G.Gaimaldinov, R.R.Muslukhov. *Materialy Vsesoyuznoi Koferentsii 'Primenenie Metallokompleksnogo Kataliza v Organicheskom Sinteze' (Tez. Dokl.)*. [Proceedings of All-Union Conference 'Application of Metal Complex Catalysis in Organic Synthesis (Abstracts of Reports). Ufa, 1989] p. 40

‡ See U.M.Dzhemilev, R.M.Sultanov, R.G.Gaimaldinov. *Russ. Chem. Bull.* (*Engl. Transl.*), **42**, 149 (1993)

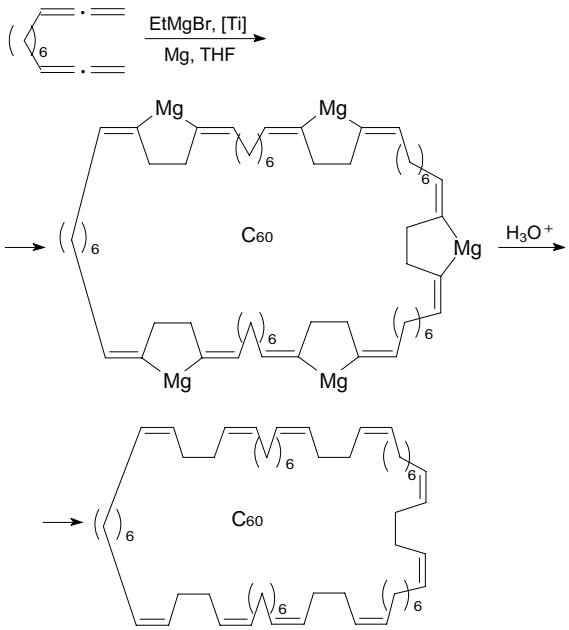
Scheme 46



The mechanism of the Cp_2ZrCl_2-catalyzed ethyl- and cyclomagnesiation of unactivated alkenes was studied almost simultaneously by several research teams.[108, 129, 159, 160] The authors of this review investigated the catalytic cyclomagnesiation of cyclic and acyclic alkenes and 1,2-dienes for a broad range of substrates.[120, 129] The results of the use of this reaction in the syntheses of natural and synthetic biologically active compounds obtained in the last five years are outlined below.

The cyclomagnesiation of dodeca-1,2,10,11-tetraene on treatment with EtMgBr catalyzed by Cp_2ZrCl_2 (~10 mol.%) and chemically activated Mg metal (halide ion acceptor) (THF, ~20 °C, 12 h) was used to synthesize the giant Mg-containing macrometallacarbocycle comprising 60 carbon atoms with strictly alternating *Z*-double bonds and unique stereomeric purity (>99%) (Scheme 47).[161]

Scheme 47

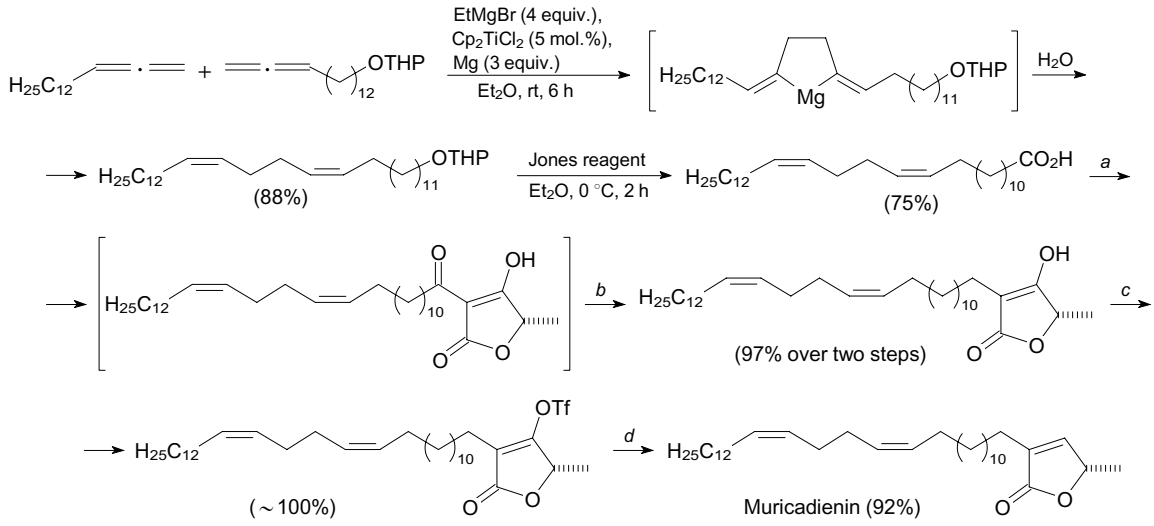


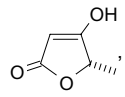
The same approach was used to develop the total synthesis of Muricadienin, which was isolated for the first time from the *Annonacea* plants and exhibits high antitumour, immunosuppressive and antimalarial activities (Scheme 48).[162]

Further application of the catalytic cyclomagnesiation of functionally substituted aliphatic and aromatic 1,2-dienes included the syntheses of practically valuable insect pest pheromones, diene and triene 5*Z*,9*Z*-mono- and -dicarboxylic acid derivatives, hybrid molecules comprising natural antioxidants together with unsaturated acids, widely used anticancer agents and a number of natural acetylenic alcohols possessing neuritogenic activity.[163 – 168] The obtained compounds have a high biomedical potential and can form the basis for the development of advanced low-toxic antitumour agents exhibiting inhibitory activity against human topoisomerases I and II and pharmaceutical drugs for the treatment of neurodegenerative diseases (Scheme 49).[169 – 172]

By analogy with alkylalanes, organomagnesium reagents readily react with disubstituted acetylenes to give magnesacyclopentadienes. In 2007, it was shown for the first time that disubstituted acetylenes react, for example, with Bu^nMgBr in diethyl ether in the presence of Cp_2ZrCl_2

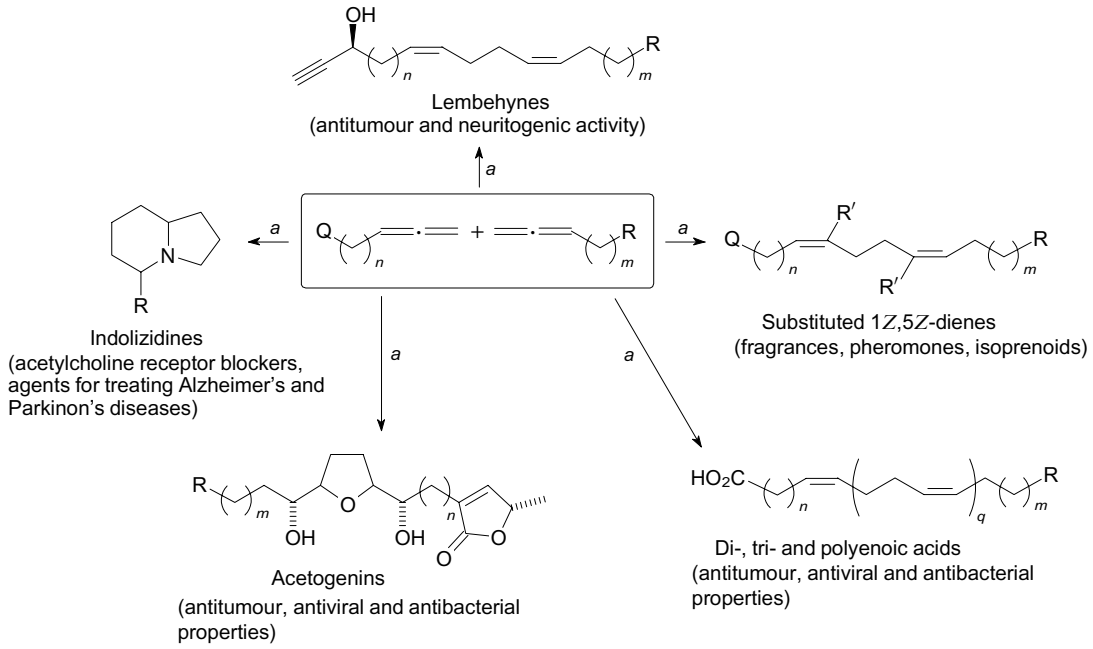
Scheme 48



(*a*) , DCC (1.2 equiv.), DMAP (0.3 equiv.), DIPEA (1.1 equiv.), CH_2Cl_2, 0 °C – rt, 12 h; (*b*) $NaBH_3CN$ (2 equiv.), AcOH, 10 °C – rt, 12 h;

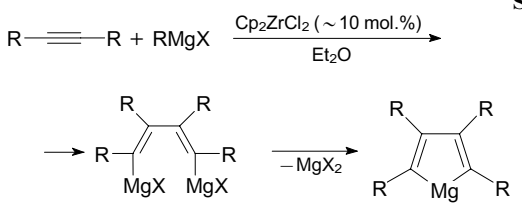
(*c*) Tf_2O (1.2 equiv.), DIPEA (1.5 equiv.), CH_2Cl_2, −78 °C, 2 h; (*d*) $Pd_2(dba)_3$ (1.5 mol.%), PPh_3 (15 mol.%), Bu^n_3SnH (3 equiv.), THF, rt – 50 °C, 5 h

Scheme 49



(*a*) EtMgBr, [Ti], Mg; R = Alk, Ar, cycloalkyl; Q = OR'', NR''_2, SiR''_3

Scheme 50

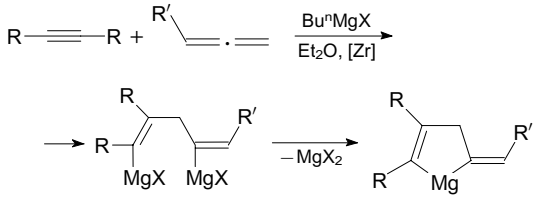


X = Cl, Br; R = Et, Bu^n

(~20 °C, 2 h) to give tetrasubstituted magnesacyclopentadienes in ~50% yields (Scheme 50).[173]

Under the chosen conditions, catalytic cyclomagnesiation can be simultaneously carried out for disubstituted acetylenes and aliphatic 1,2-dienes taken in 1 : 1 ratio; this gives 5-ethylidenemagnesacyclopent-2-enes in < 15% yield. Apart from the target magnesacyclopentenes, these reactions give minor amounts of tetrasubstituted magnesacyclopentadienes and 2,5-bis(ethylidene)magnesacyclopentanes (Scheme 51).[173]

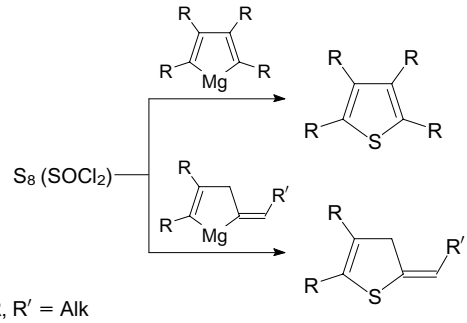
Scheme 51



R′ = n-C_5H_{11}: R = Et, Pr^n; R = Pr^n, R′ = Ph; X = Cl, Br

The magnesacyclopentadienes and magnesacyclopentenes synthesized in this way readily react *in situ* with

Scheme 52



elemental sulfur (S_8) or $SOCl_2$, being converted to thiophenes or dihydrothiophenes in satisfactory yields (> 60%) (Scheme 52).[139]

The high reactivity of the Mg–C bonds in magnesacyclopentadienes and magnesacyclopentenes makes the metallacycles of this class very promising for the synthesis of a broad range of practically important and difficult-to-obtain cyclic, acyclic and heterocyclic compounds.

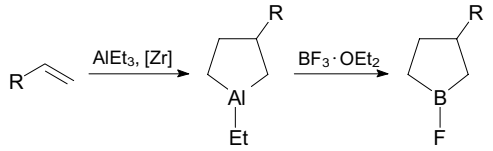
3.3. Catalytic cycloboration of alkenes and acetylenes catalyzed by Ti and Zr complexes

In order to extend the scope of applicability of catalytic cyclometallation of unsaturated compounds with alkyl derivatives of main group metals (Mg, Al, Zn, In, Ga), an attempt was made to carry out this reaction for alkyl and alkyl(aryl) halide boron derivatives (BEt_3, $RBCl_2$) with the goal to develop a one-pot synthesis of three- and five-membered boracarbocycles. The interest in this class of boracarbocycles was due to their practical significance as donor-acceptor nonlinear optical materials[174] and promising precursors for the development of modern antiviral and antifungal agents.[175, 176]

It is noteworthy that all efforts to carry out direct cycloboration of α-alkenes with BEt_3 in the presence of the

most active and selective catalyst, Cp_2ZrCl_2, which is widely used in reactions of this type, were unsuccessful. It was assumed that substituted aluminacyclopentanes, resulting from Cp_2ZrCl_2-catalyzed cycloalumination of alkenes with $AlEt_3$, can react *in situ* with $BF_3 \cdot OEt_2$ to give 3-alkyl-1-fluoroborolanes (Scheme 53).[177]

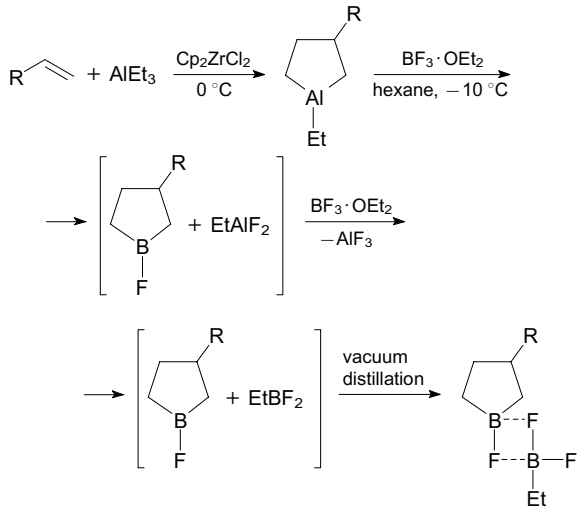
Scheme 53



This idea relied, first of all, on the publications[178–182] reporting synthetic routes to cyclic organoboron compounds involving the reaction of stoichiometric amounts of cyclic or α,ω-bis-organometallic compounds of both transition and main group elements (Li, Mg, Sn, Hg, Zr, Ti) with boron halides. Before our studies, no data on the preparation of boracycles using OACs were available from the literature.

The research carried out by the authors of this review revealed that 3-substituted aluminacyclopentanes, synthesized *in situ* by cycloalumination of aliphatic α-alkenes with $AlEt_3$ in the presence of Cp_2ZrCl_2 (5 mol.%), react with excess $BF_3 \cdot OEt_2$ (hexane, −10 °C) to afford 1-fluoro-3-substituted borolanes as molecular complexes with $EtBF_2$ in > 50% yields. The structures of the borolanes were reliably proved by advanced spectroscopic and chemical methods (Scheme 54).[177]

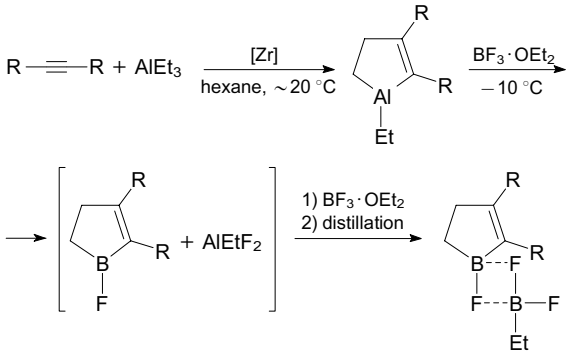
Scheme 54



This reaction is general and has been applied to a large number of aluminacyclopentanes.

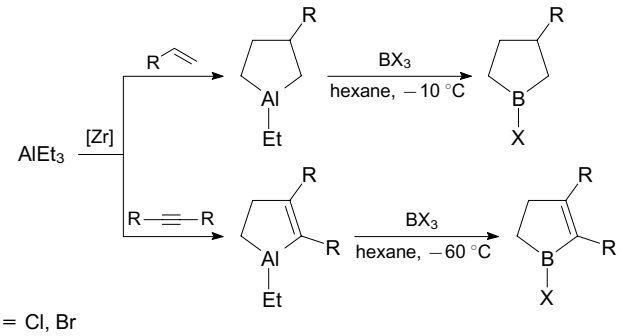
2,3-Disubstituted aluminacyclopentenes obtained *in situ* by Cp_2ZrCl_2-catalyzed cycloalumination of disubstituted acetylenes with $AlEt_3$ react with $BF_3 \cdot Et_2O$ under the same conditions (hexane, −10 °C, 0.5 h); this gives 4,5-dialkyl-1-fluoro-2,3-dihydro-1*N*-boroles, which were isolated and identified as molecular complexes with $EtBF_2$ (Scheme 55).[183]

Scheme 55



Unlike $BF_3 \cdot OEt_2$, boron halides such as BCl_3 or BBr_3 react with substituted aluminacyclopentanes or aluminacyclopentenes taken in 2 : 1 ratio (B : Al = 2 : 1) under the above-indicated conditions to afford 1-chloro(bromo)-3-substituted borolanes or 4,5-disubstituted 1-chloro(bromo)-2,3-dihydro-1*N*-boroles, which were isolated in a pure state (Scheme 56).[184]

Scheme 56

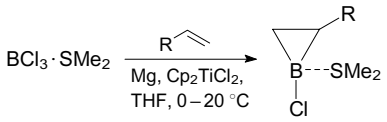


X = Cl, Br

Thus, the developed one-pot method for the *in situ* conversion of aluminacycles to the corresponding five-membered boracycles by treatment with $BF_3 \cdot OEt_2$, BCl_3 and BBr_3 opens up a facile and efficient route to 1-haloborolanes and 1-halo-2,3-dihydro-1*H*-boroles, which were previously difficult to access.

The replacement of the Cp_2ZrCl_2 catalyst in the above syntheses of aluminacarbocycles by Ti complexes enables direct catalytic cycloboration of structurally diverse α-alkenes by treatment with $BCl_3 \cdot SMe_2$ or $BF_3 \cdot THF$ in the presence of Mg as the halide ion acceptor to give three-membered boriranes, which are fairly difficult to prepare by another method (Scheme 57).[185, 186]

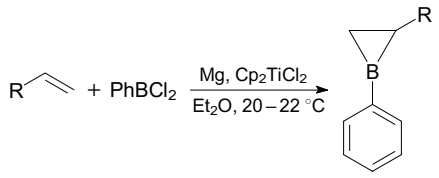
Scheme 57



R = Alk, Ph, $PhOCH_2$, Bn

The generation of borinanes from α-alkenes catalyzed by Cp_2TiCl_2 is practicable if $PhBCl_2$ is used as the organoboron reagent. Unlike the use of $BCl_3 \cdot SMe_2$ (or

Scheme 58



R = Bu^n, Oct, Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4

$BF_3 \cdot THF$), the application of $PhBCl_2$ in these reactions leads to the synthesis of 2-alkyl(aryl)-1-phenylborinanes in an individual state (Scheme 58).[187]

The results integrated in this Section demonstrate that the most significant achievements in the field of organoaluminium, -magnesium and -boron synthesis of the last 10 – 15 years are related to the discovery and advancement of catalytic cycloalumination, cyclomagnesiation and cycloboration reactions of alkenes, acetylenes and 1,2-dienes with Mg, Al and B alkyl and haloalkyl derivatives catalyzed by Ti and Zr complexes.

The Mg-, Al- and B-based metallacarbocycles obtained from accessible monomers and reagents can be readily converted *in situ*, without isolation, to practically important cyclopropanes, cyclobutanes, macrocarbocycles, heterocycles, regular isoprenoids, highly stereomerically pure unsaturated acids and other important natural and synthetic biologically active compounds. Undoubtedly, catalytic cyclometallation of unsaturated compounds described in this Section would be further developed and would provide the basis for modern chemical engineering processes.

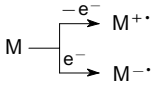
4. Radical ions of organic compounds of Group 14 elements

The electronic structure of atoms of Group 14 elements is determined by both the state of the outer p-electron shell and possible involvement of vacant d-orbitals. The combination of these factors gives rise to a high diversity of processes, including stabilization of unusual radical ion intermediates.

While comparing elements of this Group, one can state that the organic chemistry of silicon, germanium, tin and lead resembles classical organic chemistry. This is due to the fact that these elements are carbon analogues and, together with carbon, they form the 'carbon family', *i.e.*, Group 14 of the Periodic Table. However, more complex electron shells compared to that of carbon, longer bonds, diffuse orbitals and hypercoordination make the chemistry of these elements markedly more diverse, which is clearly seen even for silicon — the closest carbon analogue.[188] The most pronounced difference is the formation of hypercoordinate compounds, in particular, metallatranes, metallocanes and so on.[189] Notably, the proneness of Group 14 elements to hypercoordination is manifested in the fact that many reactions of their four-coordinate derivatives are accompanied by expansion of the coordination sphere involving nucleophilic co-reactants. Of considerable interest are structure and reactivity details of low-coordinate compounds of Group 14 elements — heavy analogues of carbocations,[190] carbanions,[191] organic free radicals,[192] carbenes,[193 – 195] alkenes, allenes, alkynes and arenes.[196, 197]

Electron transfer reactions are very significant for chemistry ranging from laboratory practice to the development of organic electronics and also in a broader sense, since the electron transfer in living nature is associated with energy exchange and accumulation, respiration, photosynthesis and other processes. The key role in the mechanism of redox reactions is played by the formation and reactions of primary products of electron transfer involving an organic molecule, *viz.*, the corresponding radical cations and radical anions (Scheme 59), which are considered in a number of reviews.[198 – 200]

Scheme 59



In this context, it is surprising that virtually no attempts to integrate the variety of interesting data concerning the formation and reactivity of the radical ions derived from organic compounds of Group 14 elements can be found in the literature. This is the subject of the present Section of the review.

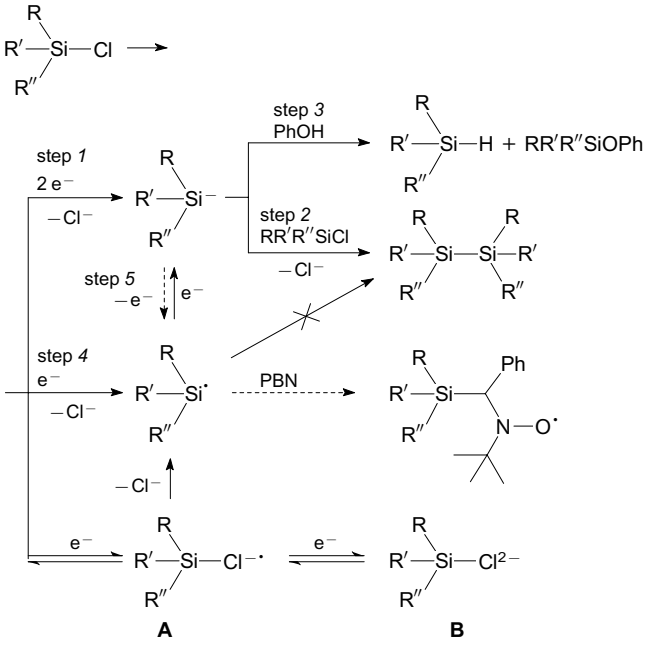
4.1. Radical ions of four-coordinate compounds of Group 14 elements

The attachment of an additional electron to the molecule giving a radical anion or elimination of an electron giving a radical cation (see Scheme 59) are often accompanied by bond cleavage; therefore, the experimental detection of the primary radical ion species by standard EPR procedures is often a difficult task. This problem can be successfully solved by using quantum beat spectroscopy[201, 202] and optically detected EPR spectroscopy for spin-correlated radical ion pairs[203] in combination with quantum chemical calculations.[204] These methods have been used to study the radical anions of the silicon and germanium analogues of 1,2,3,4-tetraphenylcyclopenta-1,3-diene — siloles and germoles.[203] It is noteworthy that electron transfer is common in organic chemistry and is the subject of quite a few papers, whereas for Group 14 element-based organoelement analogues, there are much less such papers. Meanwhile, the available publications indicate that bond cleavage reactions initiated by electron transfer are also typical of compounds of four-coordinate Group 14 elements and can occur both by a dissociative mechanism and *via* the formation of radical ions.[205]

4.1.1. Cleavage of the Si – Hal bond in radical anions

The reduction of Group 14 element organic halides ends, most often, in the formation of compounds with $M-(M)_n$ bonds ($n \geqslant 1$),[205 – 207] resulting from two-electron reduction and M – Hal bond cleavage followed by nucleophilic displacement of the halide ion in the initial molecule (Scheme 60, steps *1*, *2*). The M-centred radicals are usually reduced to the corresponding anions at the formation potential and do not participate directly in the process, as shown by experiments in the presence of proton donors (steps *1*, *3*);[208] however, they can be obtained upon single electron oxidation of these anions using reversed electrochemstry (steps *4*, *5*).[209]

Scheme 60

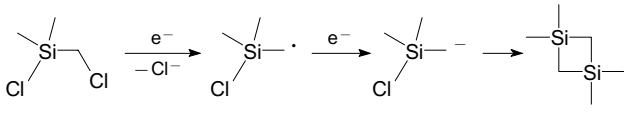


If the chlorosilane molecule contains at least one aromatic substituent (Ph, 4-$CF_3C_6H_4$),[205,210,211] the interaction between its π* system and the σ*(Si–Cl) orbital gives rise to radical anion **A** in the reaction coordinate; this species can be substantially stabilized at low temperature (−41 °C)[210] or *via* coordination with hard supporting cations (Me_4N^+ or Li^+), for example, $[ArR_2SiCl\cdots Li]^{-\bullet}$ (Ref. 205). Elimination of Cl^- from the radical anion $[4\text{-}CF_3C_6H_4SiMe_2Cl]^{-\bullet}$ ($Bu^n_4NBF_4$ supporting electrolyte, $k = 0.8 \times 10^2\ s^{-1}$) is terminated when CF_3SO_3Li is the supporting electrolyte at the sweep rate $v > 0.5\ V\ s^{-1}$ (20 °C). The subsequent single-electron reduction of the $[Ph_2SiCl_2]^{-\bullet}$ radical anion leads to dianion **B**, which rapidly loses Cl^- ($k = 172\ s^{-1}$, 20 °C).[210] The reduction of other halo derivatives, for example, Ph_3SnCl, is also reversible and gives the $[Ph_3SnCl]^{-\bullet}$ radical anion.[212]

It is noteworthy that, whereas alkoxy and acetoxy silicon derivatives cannot be reduced,[213] diacetyl(di-n-butyl)lead (as $Bu^n_2Pb^{2+}$) reversibly adds an electron to give a radical cation, which is reduced to afford dibutylplumbylene Bu^n_2Pb: and then the polymer $(Bu^n_2Pb)_n$.[214]

The competition of halide anion elimination reactions from radical anions for substrates containing both Si–Cl and C–Cl bonds has been investigated.[215] The electrochemical reduction of $ClCH_2Me_2SiCl$ in MeCN (Scheme 61) is accompanied by elimination of the chloride anion from the carbon atom yielding α-silyl carbanion, which undergoes intermolecular cyclization to give tetramethyl-1,3-disilacyclobutane.

Scheme 61



A well studied reaction is the reduction of cyclic permethylated oligosilanes $[(Me_2Si)_n,\ n = 4-7]$ giving the radical anions $(Me_2Si)^{-\bullet}_n$, which were obtained both chemically (with a Na/K alloy) and electrochemically.[216,217] The radical anions of *syn*-tetrasilane can be generated by pulse radiolysis (in THF); the UV spectra of these species exhibit two transitions involving orbitals located at the tetrasilane chain: SOMO → LUMO-1 and SOMO → LUMO.[218]

The radical anions derived from heavy cyclopropane analogues with a sterically hindered reaction centre can be obtained and identified by EPR spectroelectrochemistry. Indeed, the reduction of hexa(*tert*-butyl)cyclotrisilane in THF – 0.1 M $Bu^n_4NClO_4$ yielded a radical anion ($g = 2.0039$), in which the unpaired electron was located on three equivalent Si atoms [$a(^{29}Si) = 6.9$ G, a is the HFC constant].[219] The lifetime of this species at room temperature was ~1 min.

4.1.2. Oxidative cleavage of the M–C bonds (M = Si, Sn)

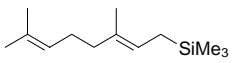
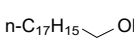
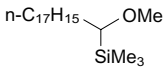
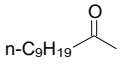
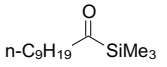
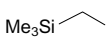
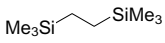
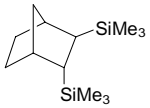
The σ orbitals of C–Si and C–Sn bonds are higher in energy and noticeably more bulky than the C–H or C–C σ orbitals. Therefore, they can interact with the neighbouring π-systems, nonbonding orbitals of heteroatoms (in the series N ≈ O > S > Se) and other σ-systems. These interactions increase the HOMO level, which facilitates ionization and oxidation of the compound. The changes in the oxidation potentials of the compounds caused by introduction of the trimethylsilyl group are presented in Table 1.[220]

This effect was used to implement various types of redox reactions of organosilicon (and -tin) compounds. In all cases, the Me_3Si^+ cation is eliminated from the radical cation formed primarily upon oxidation. This allows, for example, selective oxidation of one double bond of geranyltrimethylsilane, the other bond remaining unaffected (Scheme 62).

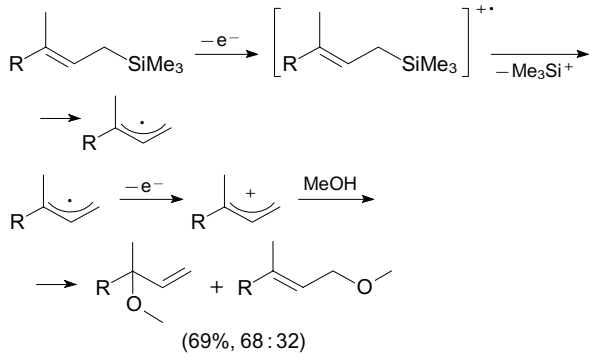
Unlike direct single-electron electrochemical oxidation of benzyltrimethylsilanes resulting in fragmentation of the radical cation at the C–Si bond [205,213] and replacement of the Me_3Si^+ 'super-proton' by an external nucleophile, the peroxidase-catalyzed oxidation of 4-methoxybenzyltrimethylsilane with H_2O_2 is accompanied by C_α–H deprotonation and affords 4-methoxybenzaldehyde.[221]

The same concept also underlies the application of 2-(2-pyridyl)ethylsilyl electroauxiliary[220] (Scheme 63), which has been successfully used in various compounds. In this

Table 1. Effect of introduction of the $SiMe_3$ group on the oxidation potentials of some compounds at a platinum electrode *versus* Ag/AgCl in $MeCN/LiClO_4$.[220]

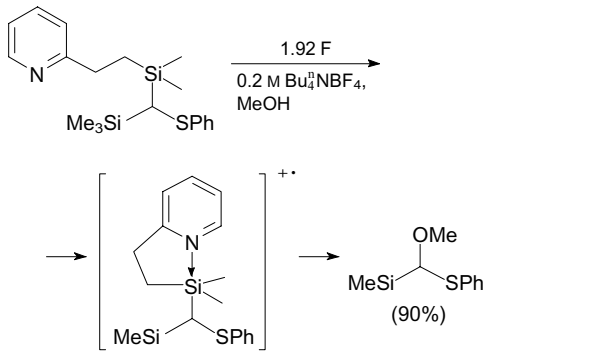
Compound	E/V	Compound	E/V
	1.85		1.30
	> 2.5		1.72
	> 2.0		1.23
	2.19		1.74
	> 2.5		1.65

Scheme 62



R = $Me_2C{=}CHCH_2CH_2$

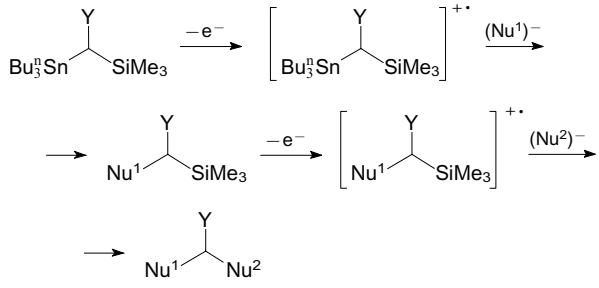
Scheme 63



case, the oxidative cleavage of the Si – C bond is facilitated by hypercoordination of the silicon atom (see below).

If two electroauxiliaries, $SiMe_3$ and $SnBu^n_3$, are present at one carbon atom, the C – Sn bond is the first to be cleaved (Scheme 64), which was confirmed by preparative electrolysis and quantum chemical calculations.[220] Further oxidation may be accompanied by cleavage of the C – Si bond in the secondary radical cation; this makes it possible to selectively introduce different nucleophiles to the same carbon atom in the molecule.

Scheme 64



Y = OR, SR

In addition, catalytic amounts of $RSnBu^n_3$ can be used to promote cyclic redox transformations, as was shown in relation to reactions of benzyltributylstannanes with *N*-acyliminium cations as electrophiles.[220]

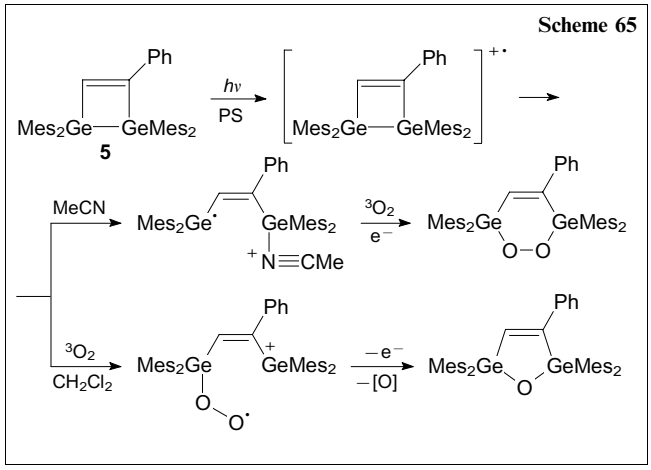
4.1.3. Oxidative cleavage of the E – E bonds

The single-electron oxidation of dimetallanes $R_3EE'R'_3$ (where E and E′ = Si, Ge, Sn) is accompanied by cleavage of the E – E′ bond in the primarily generated radical cations to give metal-centred radicals ($R_3E^{\bullet}$) and cations (R_3E^+), which is the subject of several publications.[222 – 225] The time-resolved magnetic field effect arising in recombination fluorescence was used to characterize the $R_4E^{+\bullet}$ and $(R_3EER_3)^{+\bullet}$ (E = Si, Ge, Sn; R = Me, Et)[226] and also $(Me_3CSiMe_3)^{+\bullet}$ and $(Me_3CGeMe_3)^{+\bullet}$ radical cations,[227] which are generated upon γ-radiolysis in solutions in alkanes and rapidly decompose with cleavage of the central bond. The $Me_4E^{+\bullet}$ (E = Ge, Sn, Pb) radical cations obtained by ^{60}Co-γ-radiolysis in an inert matrix at 77 K have different structures: in the trigonal-bipyramidal $Me_4Ge^{+\bullet}$, the spin is located on the Ge_{sp^2} orbital in the equatorial plane,[228] whereas in C_{3v}-symmetric $Me_4Sn^{+\bullet}$ and $Me_4Pb^{+\bullet}$, it is located on one of the C – E σ-bonds.[229] Similarly, the unpaired electron in $(Me_3EEMe_3)^{+\bullet}$ (E = Ge, Sn) resides on the E – E σ-bonding orbital having p character between the two virtually planar Me_3E groups.[229, 230]

The radical cations derived from 1,2-diaryl-1,1,2,2-tetramethyldisilanes were obtained by nanosecond laser photolysis in $(CF_3)_2CHOH$. The nucleophilic participation of the donor solvent (MeCN) decreases the lifetime of these species to < 100 ns. When MeOH is present, it rapidly reacts with these species, with the Si – Si bond being cleaved [$k_{293} = (0.63 – 2.1) \times 10^8$ litre mol^{-1} s^{-1}].[225]

The electron abstraction from 1,2-digermacyclobutene with bulky substituents [1,1,2,2-tetramesityl-3-phenyl-1,2-digermacyclobutene (**5**), E_{ox} = 1.34 V *versus* SCE] during photochemical oxidation in the presence of a number of photosensitizers (PS) generates radical cations (stabilized by steric effects and by intermolecular coordination to a nucleophilic solvent), which react with molecular oxygen to give cyclic oxadigermane and dioxadigermane (Scheme 65).[222]

Scheme 65



The pulse radiolysis of *syn*-tetrasilane in CH_2Cl_2 can be used to generate radical cations. The UV spectra of these intermediates show two characteristic transitions: HOMO-1 → SOMO and HOMO → SOMO. The electron delocalization in *anti*-tetrasilane is similar to that in silyl pentamers and germyl hexamers.[218]

Similarly to how the $R_3Si^{\bullet}$ radicals cannot be detected during the electrochemical reduction of chlorosilanes, as they are rapidly further reduced to the R_3Si^- anions, the

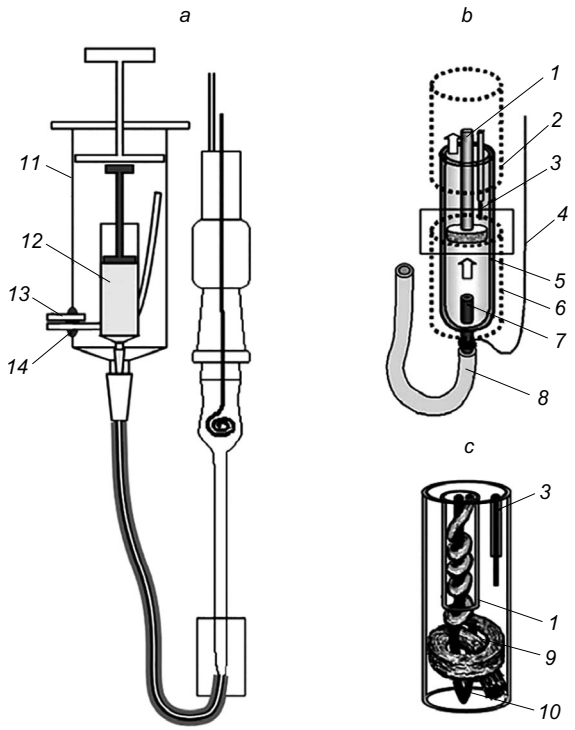
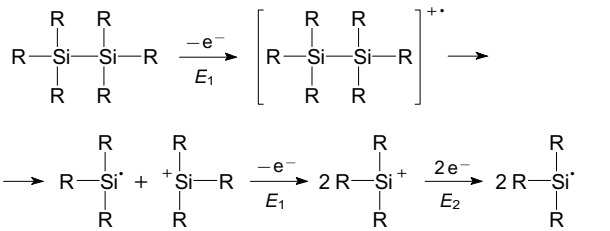


Figure 2. Four-electrode flow-through EPR spectroelectrochemical cell and a solution supply system: whole cell assembly (*a*), electrode area (*b*, marked by a frame in Fig. *a*), enlarged working electrode area (*c*, marked by a frame in Fig. *b*).[209]
(*1*) Pyrex capillary isolating the Pt working electrode; (*2*) upper aluminium foil shield; (*3*) capillary-sealed quasi-reference electrode; (*4*) contact wire for lower counter electrode; (*5*) Pyrex EPR cell; (*6*) lower aluminium shield; (*7*) tubular Pt counter electrode; (*8*) Teflon solution inlet tube; (*9*) glassy carbon fibre working electrode; (*10*) Pt wire contact for working electrode; (*11*) casing syringe; (*12*) solution in the internal syringe; (*13*) argon inlet/outlet; (*14*) silicone sealing.

$R_3Si^{\bullet}$ radical formed upon the Si–Si bond cleavage is rapidly oxidized to the R_3Si^+ silicenium cation in a two-electron process.[231] However, the silyl radicals proved to be detectable and characterizable by EPR both directly and in the presence of spin traps by using a four-electrode flow-through cell (Fig. 2), in which disilane undergoes a successive two-electron oxidation to two cationic fragments (at the potential E_1) followed by their reduction to radicals at a lower potential (E_2) (Scheme 66).[209]

Scheme 66



The design of the cell is rather simple and has been successfully employed in the reversed electrochemistry mode to generate highly reactive and sensitive silicon-centred radicals inaccessible by direct electrochemical methods.

4.2. Radical ions of low-coordinate compounds of Group 14 elements

Along with radicals, ions and radical ions, other important intermediates of organic chemistry are carbenes and their analogues. The advances made in the carbene chemistry undoubtedly stimulated development of the chemistry of carbene analogues — silylenes, germylenes and stannylenes.[193, 232] The development of the chemistry of low-coordinate silicon, germanium and tin and the synthesis of stable carbene analogues (R_2M) and dimetallanes ($R_2M{=}MR_2$) brought to the forefront the problem of generation of low-valent radical ions from these molecules. Indeed, owing to low ionization potentials and rather high electron affinities known for some carbene analogues, these species are able to participate in reactions involving electron transfer with various reagents. Finally, the radical ions of carbene analogues possess a unique electronic structure, in which both nucleophilic (electrophilic) and radical centres are located on the same atom (the radical centre may be of either σ or π type).

4.2.1. Radical anions of metallenes

High reactivity and low stability are the major problems associated with the synthesis, isolation and identification of radical anions of carbene analogues. In early studies related to this new trend of the chemistry of Group 14 elements, the generated highly reactive species were only detected by EPR and cyclic voltammetry (CV).

The $H_2Si^{-\bullet}$ silylene radical anion was generated in a low-pressure discharge source from silane (SiH_4), and its photoelectron spectrum was recorded (three resolved lines: 1.41 eV, a satellite at 1.56 eV and a broadened line at ~0.8 eV).[233] The experimentally determined electron affinity of silylene SiH_2 is 1.124 eV, and analysis of the spectrum indicates that its radical anion is a π radical (Fig. 3).

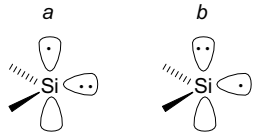
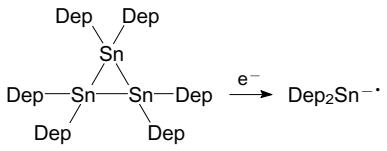


Figure 3. Structure of silylene π- (*a*) and σ-radical anions (*b*).

The stannylene radical anion was obtained by the reduction of hexa(2,6-diethylphenyl)cyclotristannane with 0.5% sodium amalgam (1 equiv.) in the presence of cryptand (THF, 20 °C, Scheme 67).[234]

The Sn–Sn bond cleavage in the primary radical anion affords the bis(2,6-diethylphenyl)stannylene radical anion,

Scheme 67



Dep = 2,6-$Et_2C_6H_3$

which has been detected by EPR spectroscopy;[235] the spectrum of the obtained red solution is a singlet (g = 2.024) with two satellites of the ^{117,119}Sn nuclei. The intensity ratio of the major signal and satellites unambiguously attests to a mononuclear paramagnetic species.

The relatively stable radical anions $[(Me_3Si)_2CH]_2Ge^{-\bullet}$ [g = 2.0125, $a(^{73}Ge)$ = 12.5 G] and $[(Me_3Si)_2CH]_2Sn^{-\bullet}$ [g = 2.0177, $a(^{117,119}Sn)$ = 116 G] were prepared by the reduction of stable metallenes $[(Me_3Si)_2CH]_2M$ (M = Ge, Sn) with sodium mirror (Scheme 68).[236] Low HFC constants [a(Ge) and a(Sn)] of M-centred radical anions attest to only minor spin localization on the s-orbital, which accounts for the π-nature of the radical anions formed.

Scheme 68

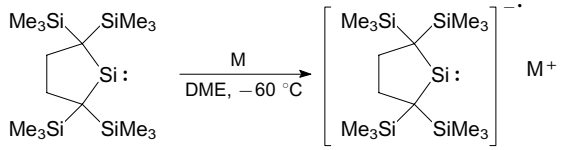
$$[(Me_3Si)_2CH]_2M + Na \xrightarrow{THF} [(Me_3Si)_2CH]_2M^{-\bullet}\ Na^+$$

M = Ge, Sn

The redox properties of the simplest dihalogermylenes, dihalostannylenes and their complexes with Lewis bases (B) have been studied by electrochemical methods.[237, 238] The voltammograms of these compounds show one single-electron oxidation peak and one single-electron reduction peak; for most MX_2 and $MX_2 \cdot B$, the processes proved to be irreversible, which is indicative of low stability of the corresponding radical ions. A quasi-reversible reduction was found for the $GeCl_2 \cdot$dioxane complex and for GeI_2. The lifetimes of $[GeCl_2 \cdot \text{dioxane}]^{-\bullet}$ and $[GeI_2]^{-\bullet}$ at 20 °C are estimated to be 4 and 2.5 s, respectively.[237, 238]

The single-electron reduction of 2,2,5,5-tetrakis(trimethylsilyl)silylene with, for example, potassium mirror (Scheme 69) in DME gives rise to an intense EPR signal (g = 2.0077) of a radical anion stable at temperatures below −60 °C.[239] At 25 °C, its half-life ($t1/2$) is ∼20 min.

Scheme 69



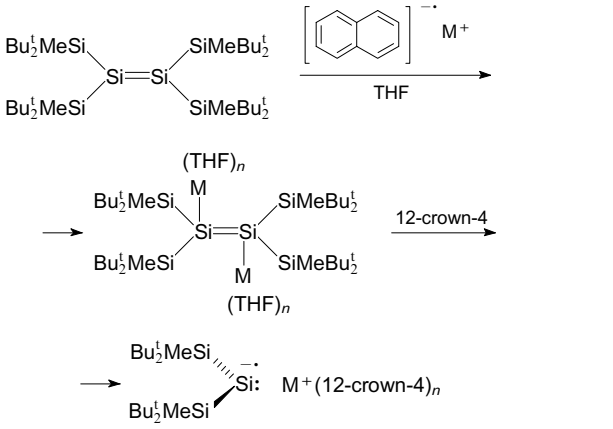
M = Cs, Rb, K, Na, Li/4,4′-bis(*tert*-butyl)biphenylide

The first silylene radical anion stable in solution and in the solid phase was obtained in 2007 by Sekiguchi's research team.[240] The reduction of tetrakis(di-*tert*-butylmethylsilyl)-disilene with lithium or sodium naphthalenide in THF leads to the formation of the 1,2-dianion, which dissociates into two species, on treatment with crown ether, namely, into the radical anion and the metal cation complex with the crown ether (Scheme 70).

X-Ray diffraction study of the radical anions thus formed demonstrated that the distance between the metal and silicon atoms is much longer than the sum of their van der Waals radii. This evidences that radical anions are free in the solid phase.[240]

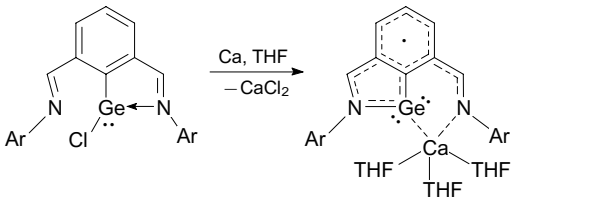
The germylene diradical anion in the form of the $[LGe]^{2-\bullet} \cdot Ca(THF)_3^{2+}$ complex (Scheme 71) is stable under inert atmosphere at room temperature and is highly sensitive to oxygen and water traces. Data of EPR spectroscopy attest to spin density delocalization in this species (g = 2.004).[241]

Scheme 70



M = Li, Na

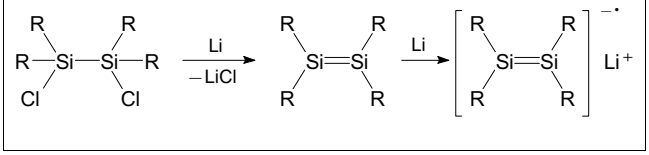
Scheme 71



4.2.2. Radical anions of dimetallenes

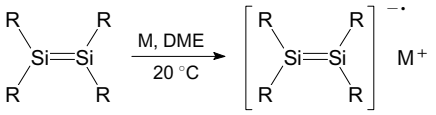
The first radical anions of disilenes that have been described by EPR [a(Si) = 33.6 G] were obtained by reduction of 1,2-dihalo-1,1,2,2-tetraorganyldisilanes (R = Pr^i, Bu^t) with lithium metal (Scheme 72).[242]

Scheme 72



The reduction of a series of kinetically stable persilyldisilenes (R = Pr^i_2MeSi, Bu^t_2MeSi, Pr^i_3Si) in DME also gave their radical anions (Scheme 73).[243] When potassium metal was replaced by lithium, stable dilithium derivatives were formed, which were isolated as white powders.[243] The HFC constants for the unpaired electron and the silicon nucleus of persilyldisilene radical anions are in the range of 24.5 – 31.8 G [approximately half of a(Si) = 65 G in $(Me_3Si)_3Si^{\bullet}$], which was attributed to the virtually planar structure of these species, unlike the averaging observed

Scheme 73



when the radical centre is exchanged between the planar and pyramidal Si atoms (for comparison, see Refs 240 and 244).

There is a radical anion of this type [g = 2.0061, a(Si) = 24.5 G], stable in the solid state, in which the fast exchange (at 298 K) between two Si atoms stops at 120 K.[245] Similar radical anions were generated by the reduction of persilyl-substituted digermenes[246] and distannenes.[247] Recently, stable radical anions of phosphasilenes, phosphagermenes[248] and disilacarbenes[249] have been obtained.

The radical anion generated by the reduction of tris(cyclopentasilano)hexasilabenzvalene with potassium naphthalenide forms a solvent-separated ion pair, in which the distance from [>Si=–Si<]$^{-\bullet}$ to the [2.2.2]cryptand-coordinated K^+ cation is ~10 Å.[250] A specific feature of this radical anion [g = 2.0065, four groups of ^{29}Si satellites with a(Si) = 48.3, 10.9, 8.9 and 4.1 G], as distinct from the [$(Bu^t_2MeSi)_2Si{=}Si(SiMeBu^t_2)_2]^{-\bullet}$ radical anion,[245] is a pronounced pyramidalization of the Si atoms of the oxidized disilene moiety, an increase in the *trans*-angles they form and a decrease in the *twist*-angle.

The single-electron reduction of the bicyclic tetrasilylated digermene[244] in DME – 0.1 M $Bu^n_4N[B(C_6F_5)_4]$ affords a relatively stable Ge-centred radical anion (decomposition rate $k_{298} = 1.2 \times 10^{-3}$ s^{-1}). The EPR spectrum at g = 2.0272 (Fig. 4) with ^{73}Ge [a(Ge) = 22.09 G] and ^{29}Si [a(Si) = 7.8 G] satellites is indicative of exchange between the spin- and charge-bearing Ge atoms of the central Ge=Ge bond (one of the atoms is virtually planar, whereas the other one has a nearly pyramidal geometry); this resembles the situation in the $[(Bu^t_2MeSi)_2Si{=}Si(MeBu^t_2Si)_2]^{-\bullet}$ radical anion derived from acyclic disilene.[245] EPR spectroelectrochemistry confirms that further single-electron reduction of this radical anion to the dianion (the peak potential E_p = –2.166 V) is reversible, similarly to the two successive reversible steps observed for 1-thiatetrasilacyclopent-3-ene with an endocyclic Si=Si bond.[251]

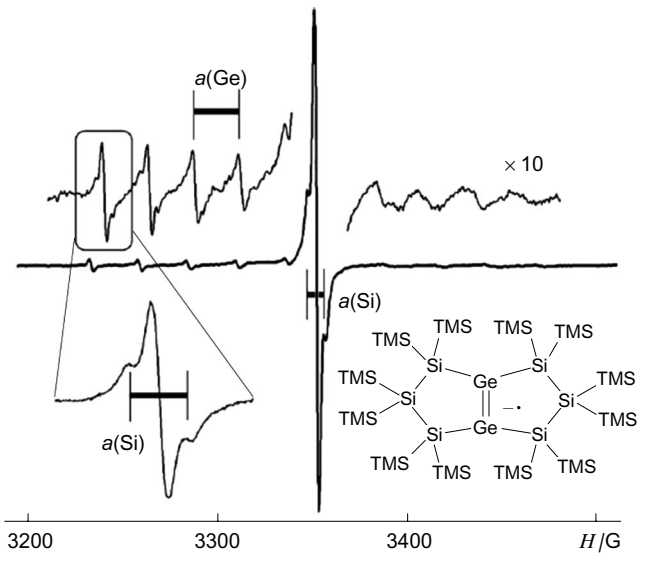


Figure 4. EPR spectrum of electrogenerated radical anion of bicyclic tetrasilylated digermene showing the spin – orbit coupling with two ^{73}Ge atoms and four ^{29}Si atoms.[244] TMS = $SiMe_3$.

The distannyne radical anion $[ArSnSnAr]^{-\bullet}$ [Ar = C_6H_3(2,4,6-$Pr^i_3C_6H_2$)$_2$-2,6], which was characterized by EPR [g = 2.0069 with moderate HFC constants of tin: $a(^{117}Sn)$ = 8.3 G and $a(^{119}Sn)$ = 8.5 G] and X-ray diffraction, has a *trans*-bent structure, in which the lone pairs are located on the Sn atoms, while the unpaired electron is on the π-orbital formed *via* the overlap of the Sn(p) orbitals.[252]

Photolysis of Bu^tOOBu^t in the presence of the silanol $(Me_3Si)_3CSiH(R)OH$ in Bu^tOH/Bu^tOK yielded the silanol radical anions $(Me_3Si)_3CSi(R){=}O^{-\bullet}$ (R = Me, Et, Bu^n, Ph). According to EPR data, the silicon atom in these unusual species is pyramidal.[253]

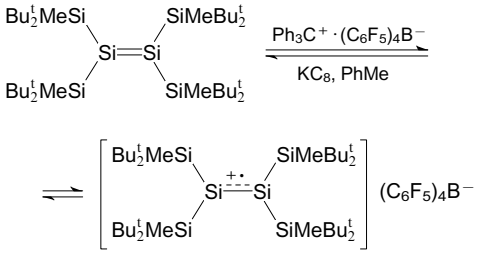
4.2.3. Radical cations

Analysis of the EPR spectra of the $^{28}SiH_2^{+\bullet}$ and $^{29}SiH_2^{+\bullet}$ radical cations recorded upon phtoionization (16 eV) of silane SiH_4 in a neon matrix at 4 K demonstrated that the spin density (~0.87) in $SiH_2^{+\bullet}$ is mainly concentrated in the silicon $3p_z/s$ hybrid orbital with hybridization ratio of 3.94, which indicates that these species are π type silylene radical cations.[254]

Voltammetry of the simplest dihalogermylenes, dihalostannylens and their complexes with Lewis bases revealed one single-electron oxidation peak corresponding to the formation of radical cations.[237, 238]

A stable radical cation derived from disilene [g = 2.0049, a(Si) = 23 G] was prepared (in 65% yield) by single-electron oxidation of tetrakis(di-*tert*-butylmethylsilyl)disilene in toluene at room temperature (Scheme 74).[255]

Scheme 74



The X-ray diffraction study of the borate salt attests to the absence of interaction between the central silicon – silicon bond and the borate anion (the distance l > 5.9 Å). Unlike the radical anion of this disilene with the Si_{sp^3}-anionic and Si_{sp^2}-radical centres,[245] this salt exists in the twist form with a planar angle of 64.9° (Fig. 5), resulting from the Si–Si σ–π interaction. The reduction of the radical cation with the potassium graphite rapidly regenerates the initial disilene (see Scheme 74).[255]

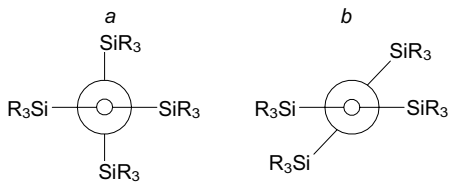


Figure 5. Perpendicular (*a*) and twist forms (*b*) of the disilene radical cation.

The electrochemical single-electron oxidation of similar tetrakis(di-*tert*-butylmethylsilyl)digermene at a Pt-electrode also gives its radical cation.[246]

The primary Ge-centred radical cation ($g = 2.0238$, $t_{1/2} \approx 10$ s at 245 K) generated by single-electron oxidation of the bicyclic tetrasilylated digermene at a platinum anode at $E_p = 0.3$ V in DME – 0.1 M $Bu^n_4N[B(C_6F_5)_4]$ undergoes intramolecular hydride shift to give a secondary Ge-centred radical [$g = 2.0258$, $a(H) = 19.98$ G with three groups of ^{29}Si satellites: $a(Si^{\alpha}) = 7.95$, $a(Si^{\beta\text{-ax}}) = 13.01$ and $a(Si^{\beta\text{-eq}}) = 5.37$ G] with the cleaved Ge – Ge bond and two $Si(SiMe_2)$ branches at the planar Ge atom.[244] Two silicon atoms [with $a(Si^{\alpha}) = 7.95$ G] are located in the central plane of the spin-bearing $Ge(p_z)$ orbital and interact with this orbital, mainly, as a result of spin polarization.

The formation of the radical cation from cyclic disilene [$g = 2.011$, $a(Si) = 24.37$ G] and its reversible single-electron oxidation ($E_p = 1.1$ V *versus* SCE) to the diamagnetic dication without $[Si{-}{-}Si]^{+\bullet}$ bond cleavage was demonstrated by reversed EPR spectroelectrochemistry (Fig. 6).[209]

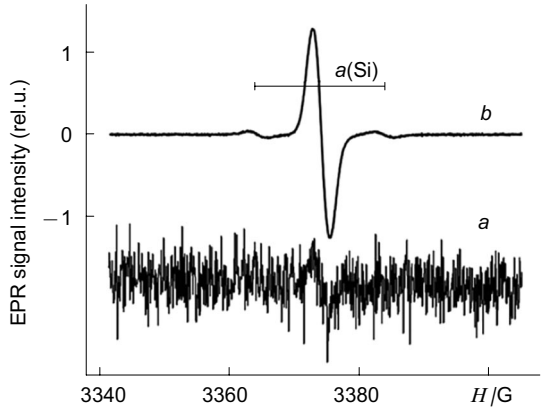


Figure 6. EPR spectra of the radical cation derived from cyclic disilene, 2,2,3,4,5,5-hexakis(2,4,6-triisopropylphenyl)-1-thia-2,3,4,5-tetrasilacyclopent-3-ene, obtained by a $-2e^-/+e^-$ process.[209] Working electrode potential $E = 1.2$ (*a*), 0.7 V (*b*).

4.3. Radical ions of hypercoordinate compounds of Group 14 elements

The proneness of heavy Group 14 elements to extracoordination, which distinguishes the chemistry of these elements from the chemistry of carbon is related to their Lewis acidity (Sn > Ge > Si), which can be controlled by the electronegativity and polarizability of the substituent and by the Lewis basicity of the expernal ligand. As a result, the coordination sphere of the element can be extended from 4 to 5 or 6 and even more. On the one hand, this accounts for numerous nucleophilic reactions of these compounds; however, on the other hand, this hampers electron transfer to such centres. Meanwhile, the additional coordinated group, which partially loses electron density, thus becomes more prone to add an electron. In view of the fact that Group 14 elements in hypercoordinate compounds do not form systems with occupied orbitals tend to lose electrons, it is not surprising that their redox reactions involve, most often, oxidation of the ligands.

4.3.1. Radical anions

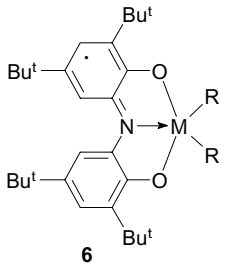
Electrochemical reduction of trialkylchlorosilanes $R^1R^2R^3SiCl$ ($R^1 = R^2 = R^3 = Me$, Et; $R^1 = R^2 = Me$, $R^3 = Bu^t$) in DMF is facilitated by formation of a complex in which the silicon atom is five-coordinate and the solvent acts as the silicophilic agent.[256] When the solvent used for reduction does not possess this feature (DME or THF), the rate of electron transfer from the mediator to triphenylhalogermanes Ph_3GeX (X = Cl, Br) is considerably lower,[257] despite their stronger electrophilic properties.

Halostannatranes such as $N(CH_2CMe_2O)_3SnX$ (X = Cl, Br, I) are reduced at a glassy carbon electrode [$E_p(Cl) = -1.94$ and $E_p(Br) = -2.04$ B *versus* SCE][258, 259] with Sn – X bond dissociation (LUMO of these molecules). The process at transition metal (Pt, Pd, Hg) electrodes includes preliminary formation of the oxidative addition product $Sn-M^{II}-X$, as in the case of chlorosilatrane.[260] This intermediate is subsequently reduced by a single-electron mechanism at 500 – 1000 mV less negative potentials to give stannatranyl radical, which can be detected by EPR as a stable spin adduct with α-phenyl-*N*-*tert*-butylnitrone [for chloro derivative: $g = 2.0083$, $a(N) = 14.596$ G, $a(H) = 3.357$ G].[259] Both direct and transition metal-catalyzed reduction give rise to distannatrane — a new 4c – 6e system [$\delta(^{119}Sn)$ are -243.00 and -639.72 ppm for chlorostannatrane and distannatrane, respectively].

The single-electron reduction of tetraarylporphyrin (Por) complexes $(Por)SiX_2$ (X = F, Cl, CF_3SO_3),[261] $(Por)GeF_2$,[262] $(Por)SnX_2$ (X = F, Cl, Br, ClO_4, OH)[263] and (Por)SnCh (Ch = S, Se)[264] affords stable radical anions, with the ease of reduction changing in the order Sn > Ge > Si and F > Cl > CF_3SO_3. The EPR spectroscopy data for the $[(Por)GeF_2]^{-\bullet}$ radical anion indicate that the reduction involves the porphyrin ring (a ~8 G wide singlet indicating the absence of interaction with germanium).

Paramagnetic complexes **6** with the formula LMR_2 (M = Si, Sn, Pb; R = Me, Et, Bu^n, Bu^t, Ph) with the redox-active 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine ligand were studied by EPR spectroscopy and cyclic voltammetry.[265] The complexes with the doubly reduced ligand have nitrogen HFC constants $a(N) = 5.63 – 7.06$ G, changing in the order Si < Sn < Pb, and different isotopic constants for the Group 14 element [$a(Si) = 7.06$ G, $a(Sn) = 45.8 – 64.6$ G, $a(Pb) = 35.70$ and 42.99 G]. The redox potentials of tin complexes are moderately negative: for example, for R = Et and Ph, the half-wave potentials ($E_{1/2}$) are -0.44 and -0.3 V *versus* Ag/AgCl/KCl(sat.), respectively.

Structures 6

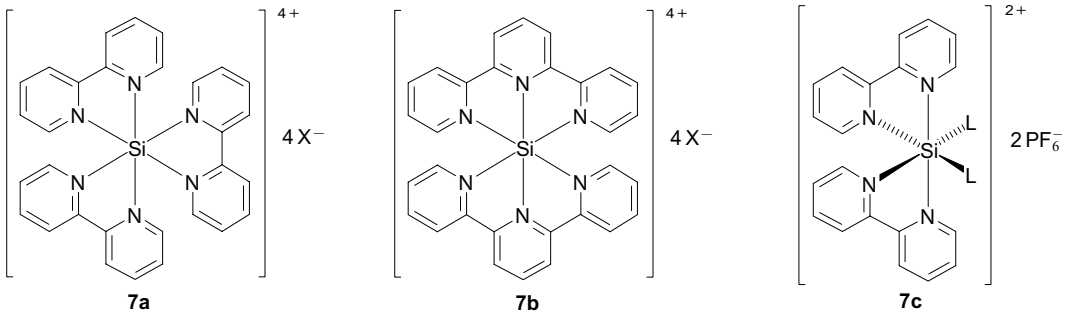


6

M = Si, Sn, Pb;
R = Me, Et, Bu^n, Bu^t, Ph

The complexes of SiI_4 with 2,2′-bipyridine (bipy) and 2,2′,6′,2″-terpyridine (terpy), namely, $Si(bipy)_3^{4+}$ and

Structures 7



7a **7b** **7c**

X = PF_6, NO_3; L = OMe, OPh; L – L = OCH_2CH_2O, catechol and *o*-biphenol dianions

$Si(terpy)_2^{4+}$ (with PF_6^- as the counter-ion) (structures **7a – c**) undergo a number of successive single-electron reduction steps involving the ligand [6 steps for the tris(bipyridine) complex $Si(bipy)_3(PF_6)_4$ (**7a**)].[266] The first step of reduction occurs at about 0 V *versus* SCE, which is attributable to high electron deficiency of the ligand resulting from coordination to the silicon atom. Analogous bis(bipyridine) complexes with oxo ligands $Si(bipy)_2L_2$ (**7c**) undergo three successive reversible reduction steps, with the first step proceeding at a more negative potential than that in the analogues considered above (~ -0.61 to -0.75 *versus* SCE), which is still much less negative than the reduction potential of the ligand itself.[267]

MacDiarmid and co-workers[268] observed a strong EPR signal of a frozen solution of $Si(bipy)_2Cl_2$ (width of 5 G at $g = 2.002$; $T = 113$ K) with two lateral resonance signals ($g_{x,y} = 2.003$ and $g_z = 2.001$ with the spectral width $\Delta = 172$ G), which was assigned to a weakly interacting triplet radical pair. Although the authors tend to consider Si^{IV} coordination to bipy, in the absence of an external reducing agent, this may correspond to electron transfer from dichlorosilylene Cl_2Si: to bipy, because the former is a potent reducing agent.[237, 238] Thus, the species that occur in equilibrium can be characterized as six-coordinate nonclassical siliconium cations (Scheme 75).[268]

Scheme 75

$$[Cl_2Si^{2+}(bipy^{2-})(bipy) \leftrightarrow Cl_2Si^{2+}(bipy)(bipy^{2-})] \rightleftharpoons$$

Diamagnetic

$$\rightleftharpoons Cl_2Si^{2+}(bipy^{-})(bipy^{-})$$

Paramagnetic

The weak 1 : 1 and 1 : 2 complexes that are formed in solutions of halosilanes, for example Et_3SiCl,[256, 269] and halogermanes R_nGeCl_{4-n} ($n = 0-3$) with soft nitrogen-containing ligands such as bipy, imidazole, pyrimidine and 2,6-dichloropyridine[270] can be stabilized in their ligand-localized radical anion forms (*via* the single-electron reduction, which occurs approximately 1 V more easily than reduction of the ligand), which have been investigated by CV and EPR spectroscopy. The two nitrogen atoms in the bipy radical anion complex are non-equivalent, one being in axial [a(N) = 2.507 G] and the other being in equatorial [a(N) = 1.787 G] position. Elimination of chloride ion from this radical anion ($k_{293} = 2.7\ s^{-1}$) affords a reversible bipy-coordinated radical anion pair [E_0(bipy · $Ph_3Ge^{\bullet}$/bipy · Ph_3Ge^-) ≈ -1.4 V *versus* SCE]; the bipy → Ph_3Ge stabilization energy can be estimated as ~ 18 kcal mol^{-1}. The bipy-coordinating radical loses an electron to give the system (bipy · $Ph_3Ge)^+$/(bipy · $Ph_3Ge)^{\bullet}$, which was identified in the anodic part of the curve. The loss of bipy from (bipy · $Ph_3Ge)^{\bullet}$ leads to release of the $Ph_3Ge^{\bullet}$ free radicals, which can be detected using the PBN radical trap as stable spin adducts [$g = 2.0069$, a(N) = 14.73 G, a(H) = 5.84 G]. In all of these species, the redox processes affect the ligand shell, while the germanium atom retains the 10-electron configuration.

4.3.2. Radical cations

The nature of radical cations obtained to date for many metallatranes (M = Si, Ge, Sn) is determined by position of their HOMO. The inversion of this orbital [located either on the silatrane cage ('true metallatranes')[271–273] or on the Si-substituent] depends on the Si – N distance and can give rise to radical cations with different spin localizations.[273, 274] The considerable shifts of the oxidation peak potentials of metallatranes compared with that of triethanolamine $N(CH_2CH_2OH)_3$ reflect strong intramolecular N → M donor-acceptor interaction (changing in the order Si < Ge < Sn),[258, 271, 273, 275–278] which reduces the accessibility of the nitrogen lone pair for electron elimination.

Square-wave pulse cyclic voltammetry at a Pt electrode (in MeCN/0.1 M $Bu_4^nNPF_6$) revealed reversible single-electron oxidation of vinyl, tolyl and *tert*-butyl silatrane derivatives, although the relatively slow electron transfer becomes rate-limiting for scan rates $> 1-2$ V s^{-1} (Ref. 273). The 'stretch isomerism' of the N → Si donor–acceptor bond was revealed for silatrane radical cations as two minima on the potential energy surface. In these isomers, the spin density is located either on the substituent in the *endo*-form (with five-coordinate silicon and short Si···N coordination contact, $d_{Si-N} < 2.13$ Å) or on the silatrane nitrogen atom in the *exo*-form (with four-coordinate silicon and long Si···N contact, $d_{Si-N} > 3.0$ Å). Unlike the *endo*-radical cations, the silatrane radical cations existing in the *exo*-form (in which the nitrogen atom is accessible for external interactions) are coordinated to ferrocene to give reversible redox pairs with considerably less positive (by 0.5 – 0.8 V) standard potentials than those of ferrocene.[273]

The oxidation potentials E_p determined experimentally and the standard potentials E° calculated by the MP2//B3PW91 (C-PCM) method for 18 silatranes are well correlated ($R = 0.99$ for the mean absolute error of 0.03). These values are closely connected with the geometric, energetic, electronic and orbital parameters and with the

N→Si interaction intensity. As a result, the oxidation susceptibility of silatranes is well correlated with the N···Si distance (d_{Si-N}), the Mulliken (P_{SiN}) and Wiberg (W_{SiN}) populations of the N→Si contact, the interaction energy between the nitrogen lone pair (n_N) and the σ*(Si−X) antibonding orbital, the AIM energy of the N → Si contact (E_{SiN}) and the degree of delocalization of the electron density of the nitrogen lone pair ($\Delta N[n_N]$) towards the $XSiO_3$ acceptor group.[273] Chloro- and bromosilatranes in which the N→Si bonds are the strongest in the reaction series are markedly more difficult to oxidize than other silatranes (E_p = 2.05 and 2.10 V *versus* SCE).

The single-electron oxidation of phenylsilatrane in MeCN/0.1 M $Bu^n_4NPF_6$ affects the atrane cage of the 3c–4e system and gives a radical cation in which the nitrogen atom bears most of the spin density. The 164 G wide EPR spectrum of the radical cation contains 184 lines in 9 groups (the intensity ratio is 1 : 1 : 4 : 3 : 6 : 3 : 4 : 1 : 1) with the isotropic *g*-factor corresponding to an N-centred radical (g = 2.0037).[276, 279] The singly occupied N(p_z)-orbital of the nearly planar N atom [a(N) = 18.41 G] shows strong spin–orbit coupling with three axially arranged C−H bonds of the CH_2 groups adjoining nitrogen [a(α-H) = 37.93 G], whereas the three equatorially arranged C−H protons have a much lower HFC constant [a(α-H′) = 0.23 G]; six C−H protons of the β-CH_2 groups are combined with a(β-H) = 1.8 G. The UV spectrum of the phenylsilatrane radical cation shows the ($n^1-\pi^*$) electron transition from SOMO to LUMO (ψ^*_{as}Ph) at λ_{max} = 294 nm.

The oxidation peak potentials E_p of 20 germatranes are well correlated with their ionization potentials (IP) (determined as $-\varepsilon_{HOMO}$ by B3LYP/Lanl2DZ calculations) with the slope $\Delta E_p/\Delta IP = 0.52 \pm 0.02$.[271] The EPR spectra of the electrogenerated radical cations of *o*-bromo- and *o*-fluorophenylgermatranes[271, 278] resemble the spectra of the radical cations derived from phenylsilatranes: they have 165 and 160 G widths, respectively, are centred on the planar nitrogen atom [$g \sim 2.0045$, a(N) = 18.62 and 18.48 G) and have large HFC constants for the axial α-C−H protons [a(α-H) = 37.09 G, a(α-H′) = 0.88 G, a(β-H) = 1.185 G (Ref. 278) and a(α-H) = 37.67 G, a(β-H) = 1.96 G (Ref. 271), respectively]. The benzylgermatrane radical cation observable at T = 223 K is less stable and corresponds to an organic radical (g = 2.0035) with the HFC constant determined by the $CH_2C_6H_5$ moiety [a(*p*-H) = 8.426 G, a(*o*-H) = 2.907 G, a(*m*-H) = 0.972 G and $a(CH_2)$ = 0.31 G] with only a minor involvement of the nitrogen atom [a(N) = 4.337 G].

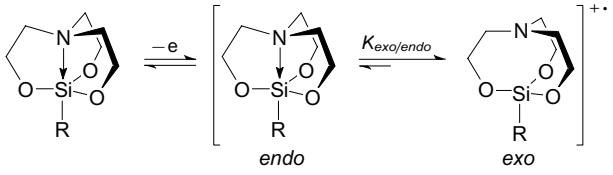
It is worth noting that spin density in metallatrane radical cations has never been observed on the metal atom.[271, 276, 278, 280] Due to the orthogonal arrangement of the π-orbitals of aromatic and unsaturated (vinyl, ethynyl) substituents with respect to the axial 3c–4e HOMO of metallatranes, spin interaction with these groups does not occur either, which makes them similar to alkyl groups.[260, 271, 276]

The radical cations of phenylsilatrane are deprotonated at the α-CH_2 group (k_{293} = 0.33 s^{-1});[276] deprotonation of benzylgermatrane is much faster ($k_{295} = 3.98 \times 10^3$ s^{-1}).[277] This reaction has been used for anodic α-cyanation of vinylsilatrane and *m*-bromobenzylgermatrane.[277]

The silatrane cage can be covalently grafted to a conducting carbon substrate *via* a $(CH_2)_3$ linker; the resulting surface was found to exhibit spin commutation properties, with switching between the neutral (diamagnetic) and oxidized (paramagnetic) forms of the grafted silatrane occurring at the potentials E(spin-on) = 1.25 V and E(spin-off) = 0.75 V.[260]

The quasi-reversible oxidation of oligosilanyl-substituted silatranes in MeCN/0.1 M $Bu^n_4NPF_6$ requires[272] a considerable reorganization energy related to conversion of the primary *endo*-radical cation (kinetic product) to the thermodynamically stable *exo*-product; both products were detected by square-wave CV (Scheme 76). The difference between the *exo*- and *endo*-radical cations is 0.134 eV for the model tris(trimethylsilyl)silylsilatrane (which corresponds to $K_{exo/endo} = 1.8 \times 10^2$) with the inversion barrier of 0.38 eV (~10 kcal mol^{-1}). For this radical cation, the N−Si distance is 0.4 Å shorter in the *endo*-form and 0.8 Å longer in the *exo*-form than in the neutral molecule.

Scheme 76

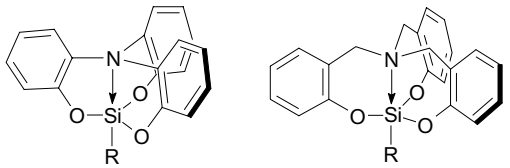


R = $Si(SiMe_3)_3$, $Si(SiMe_3)_2(SiMe_2)_2Si(SiMe_3)_3$, $Si(SiMe_3)_2(SiMe_2)_2Si(SiMe_3)_2Si(OCH_2CH_2)_3N$

The virtually equal oxidation peak potentials observed for compounds with one and two silatranyl moieties (1.332 and 1.335 V *versus* SCE, respectively) attest to the absence of electronic interaction through the oligosilanyl substituent. The standard potential of the *exo*-form (E° = 0.67 V) is close to the oxidation potential of triethanolamine, which implies the absence of the donor-acceptor N → Si interaction in this form[272] and is in line with the disappearance of the binding character of the 3c–4e system of silatrane [bond critical points (*bcp*) are (3, −1) in the N···Si region] upon its transformation into the 3c–3e system after electron detachment, as shown by NBO and AIM analysis [the radical cation is devoid of the N···Si *bcp* (3, −1)].[273]

o-Phenylene-containing silatranes **8** with five-membered side groups (all-five, R is vinyl, Ph) lose one electron to be converted to *endo*-radical cations, which rapidly rearrange to the *exo*-form. In the case of the vinyl derivative, the latter form is 12.19 kcal mol^{-1} more stable than the *endo*-form.[280] Phenylsilatranes **9** with six-membered side moieties (all-six) obtained from 2,2′,2″-nitrilotris(methylene)triphenol show analogous, although less distinct, properties for the *endo*- and *exo*-radical cations. The poorly resolved EPR spectra of the all-five and all-six radical cations consist mainly of a nitrogen triplet [a(N) = 11.5 and 11.73 G,

Structures 8, 9



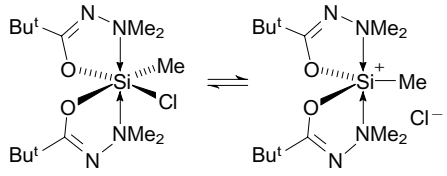
8 **9**

respectively] without any noticeable spin–orbit coupling with protons of the aromatic rings, the planes of which are attached to the silatrane ring in such a way that the interaction with the spin-bearing N(p_z) orbital is precluded.[280]

In the $CH_2Cl_2/Bu^n_4NPF_6$ system, 1-R-substituted stannatranes $N(CH_2CMe_2O)_3SnR$ (R = 4-$Bu^tC_6H_4O$, E_p = −1.33 V and 4-MeC_6H_4S, E_p = −1.40 V) undergo reversible oxidation to give radical cations in which the spin density is located on the substituent. The EPR spectrum of the former contains a triplet of triplets (1 : 2 : 1) typical of the phenoxyl radical [g = 2.0036, a(*o*-H) = 6.27, a(*o*-H′) = 6.03 G, a(*m*-H) = 1.85 G] with a Sn coupling constant [$a(^{119}Sn)$ = 6.7 G and $a(^{117}Sn)$ = 7.4 G], but without a noticeable coupling with the atrane nitrogen.[258] If the N−Sn distance changes slightly or does not change at all upon removal of an electron, the stannatrane cage is rotated with respect to the Bu^t-phenoxy group in such a way that the C−C−O−Sn dihedral angle changes from 93.63° in neutral stannatrane to 3.81° in the radical cation. A considerable structural reorganization upon electron detachment is caused by interaction of the O(p_z)-orbital with the π-system of the aryl substituent, which destabilizes neutral stannatrane, but stabilizes its radical cation. It is of interest that halostannatranes also undergo oxidation, which affects their 3c–4e system, although at rather high positive potentials [E_p(Cl, I) ~ 2.2–2.3 V].

The six-coordinate chlorosilicon dichelate with the $Me_2NNC(Bu^t)O$ ligands (existing in equilibrium in 15 : 85 ratio with the dissociated non-oxidizable five-coordinate form, Scheme 77) undergoes single-electron oxidation in $CH_2Cl_2/Bu^n_4NBPh_4$ (E_p = 1.5 V) involving the hydrazine ligand; this affords the diazenium cation ($t_{1/2} \approx 67$ s at 20 °C), which can subsequently be reduced at −1.9 V.[260]

Scheme 77



Conversely, the LUMO of five- and six-coordinate forms of dichelates is not sufficiently low to enable their own reduction.

The tetraarylporphyrin complexes (Por)MX_2 (M = Si, Ge, Sn; X = Hal, CF_3SO_3, OH) undergo reversible oxidation involving the porphyrin ring,[261–263] giving rise to stable radical cations; the Ge-containing complex was characterized by EPR spectroscopy.

Thus, even a brief consideration of the progress in the chemistry of radical ions formed by compounds of Group 14 elements clearly demonstrates the good prospects of using redox processes for performing $M^+ \rightleftharpoons M^{\bullet} \rightleftharpoons M^-$ interconversions by single-electron reactions. The appearance of paramagnetism in compounds of Group 14 elements, which can be commuted electrochemically and virtually instantaneously, and the change in the structural (and, hence, macromechanical) characteristics of the radical ion species open up prospects for their application in modern molecular and nanotechnologies.

Yet another promising line of research related to the redox chemistry of hypercoordinate compounds of Group 14 elements is the development of the concept of the multicentre multielectron hyperbonds; this issue can be directly related to possible applications in organic microelectronics.

Selective generation of triplet and singlet radicals in single-electron reactions of metallylenes can open up the way to magnetochemical control over the reactivity of these species. The unusual stability of low-coordinate compounds of Group 14 elements with the central M−M bond to population of their vacant (antibonding) orbitals often allows the formation of stable radical anions (which in some cases can even be isolated). It is even more remarkable that transfer of not only one, but even two electrons (that is, the maximum filling of the LUMO in these systems), often does not induce cleavage of the M−M bond and is reversible. In this context, markedly lower stability of the corresponding radical cations appears somewhat strange and is at variance with the chemistry of carbon, because oxidation is associated with only a partial decrease in the population of HOMO, which remains a binding orbital. Evidently, low stability of these species in comparison with radical anions is generally due to the increase in the electrophilicity of the cationic sites of Group 14 elements upon electron detachment and formation of full positive charge on these sites and, as a consequence, higher proneness to the interaction with Lewis basic sites.

Various positions of the unpaired electron in the radical ions derived from dimetallenes and, as yet, few dimetallynes, including stable localization on one atom of the M−M bond and geometry differentiation; fast exchange between the atoms; or delocalization on the diatomic M−M group (for radical cations, also there is a possibility of stabilizaion in the *twist*-form), gives rise to an array of reaction centres for subsequent transformations, in particular, for the activation of small molecules.

The proneness of Group 14 elements to extracoordination is also manifested in the electron transfer reactions of four-coordinate derivatives. The dynamic expansion of the coordination sphere upon the reaction with an external silicophilic co-reagent promotes electron transfer to the initially four-coordinate form and fast nucleophilic substitution in chlorosilanes. Meanwhile, the oxidative cleavage of the M−C and M−M bonds in radical cations is also nucleophile-assisted.

The redox transformations draw together the low-coordinate (metallylenes) and hypercoordinate compounds (with the Jutzi silicocene, the redox chemistry of which is still to be studied, being intermediate between them) and reveal an interesting analogy, which connects these two formally opposite classes of compounds, namely, access to the atomic element stabilized by means of coordination. The first publications along this line have already appeared, but analysis of these studies is beyond the scope of this review.

5. Problems and prospects of development of chlorine-free methods for the formation of the silicon – element bond

The previous Section of the review considers some aspects of reaction mechanisms involving Group 14 elements and a number of fundamental trends of their reactivity. Organosilicon compounds and materials based on them are highly valuable for possible practical applications, which deserves special attention.

Indeed, silicon is the base for the whole inorganic nature, its content in the Earth's crust is estimated to be up to 29 mass %. Therefore, silicon is almost inexhaustible feedstock for the production of any silicate or silicone materials. Since the second half of the 20th century, polyorganosiloxanes have been at the cutting edge of important fields of science, technology, construction engineering and medicine. High reactivity of the Si – Cl bond accounts for the key role of chlorinated derivatives in the conversion of natural silicates to polymeric products. This process is well developed and all process stages are optimized. However, the proper nature of these processes is associated with unavoidable risk. The current state of science allows for the planning of a chlorine-free, more environmentally benign (green) process for the production of polymeric products[281] using alkoxysilane monomers. Active studies along this line are in progress and considerable advances have already been made.

This Section of the review addresses methods for generation of Si – O – R (where R is a C- or Si-containing substituent) and Si – N bonds and three possible types of Si – C bonds differing in hybridization of the carbon atom. The Si – C_{sp^3} bond is present in the most abundant type of organosilicon products with methyl or ethyl substituents at the silicon atom; these derivatives account for 80% – 85% of the silicone market. The Si – C_{sp^2} bond is mainly encountered in vinyl- and phenylsilyl groups; these products are manufactured on a much smaller scale than the previous group, but they are highly important for the production of silicones with specific properties. For example, thermally and radiation stable silicones contain phenyl substituents, and vinylsilyl groups are indispensable modules for modification of organosilicon products, first of all, for rubber and composite vulcanization. The Si – C_{sp} bond is present in acetylenic organosilicon derivatives, which are least abundant, but very important for organic synthesis and for the preparation of conjugated linear and cyclic organosilicon structures. For the development of green silicone chemistry, a key issue is to devise chlorine-free methods for the synthesis of organosilicon derivatives of the above-mentioned types.

5.1. Preparation of compounds with the Si – O bond

5.1.1. Compounds with the Si – O – Si group

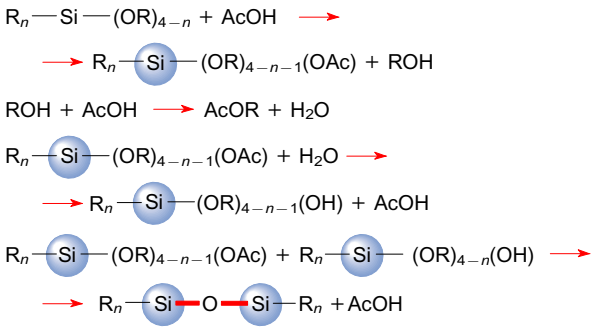
Compounds with the Si – O – Si group form the basis of all organosilicon polymers. A traditional method for the generation of the siloxane bond is hydrolytic polycondensation (HPC) of organochlorosilanes;[282] however, the modern trend towards green chemistry dictates new rules that require replacing halogenated compounds by their environmentally benign analogues. The main routes to the formation of the Si – O – Si bond without participation of chlorine-containing compounds are considered below.

5.1.1.1. Hydrolytic polycondensation of organoalkoxysilanes

The hydrolytic polycondensation of alkoxysilanes is used most often to prepare siloxane derivatives by a chlorine-free method; commonly, this reaction is carried out using sol – gel technique. This process is very important and is described in detail in some review articles.[283 – 285] By varying conditions of hydrolysis, the nature of monomers (both the organic substituent[286] and alkoxy groups[287]), type of the catalyst[288] and reactant ratio,[289] it is possible to synthesize hybrid organic-inorganic materials,[290 – 293] silicates and nanomaterials of various structures,[292, 294 – 296] aerogels,[297 – 307] xerogels[308, 309] and cage metallasiloxanes.[310, 311] The chemistry of this process is well investigated, but its consideration is beyond the scope of this review.

In recent years, one more chlorine-free approach to the preparation of organosiloxane products has been developed; this approach is based on the HPC of organoalkoxysilanes with an excess of anhydrous acetic acid. In the general form, this reaction has been known for long;[312] however, only the detailed mechanistic study reported by Egorova *et al.*[313] demonstrated that this process consists of a number of interrelated steps (Scheme 78). The first one is acetylation of alkoxysilane with acetic acid to release the alcohol, which reacts with acetic acid to give water, and water hydrolyzes the reactive acetoxysilyl groups *in situ*. The final step is condensation to give the siloxane bond.

Scheme 78



The major benefits of this method include its versatility, complete conversion of alkoxy groups, irrespective of their nature, homogeneity of the reaction (which ensures the compositional uniformity of all products), the possibility of selective preparation of either linear or cyclic polyorganosiloxanes by changing the reaction conditions.[314 – 318] These benefits make the method suitable for the preparation of the whole assortment of organosilicon products.

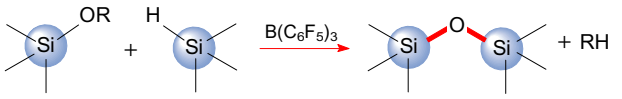
One more protocol for the preparation of linear or cyclic siloxane derivatives is the HPC of alkoxysilanes in supercritical CO_2.[319] Carbonic acid formed in this reaction catalyzes hydrolysis and condensation of dimethyldiethoxysilane. As in the case of HPC in acetic acid, by varying the conditions of synthesis, it is possible to change the selectivity towards either cyclic or linear products, with ethoxy group conversion being complete in all cases. A comparison of HPC of trialkoxymethylsilane at elevated pressure in the presence and in the absence of CO_2 has been reported.[320] The condensation in carbonic acid affords polycyclic methyl silsesquioxane, while condensation in water at elevated pressure gives branched products.

Thus, it follows from the above that HPC of organoalkoxysilanes is suitable for the synthesis of both complex nanostructured systems and the major commercial polymers. This fact makes organoalkoxysilanes the most promising monomers for the preparation of organosilicon polymers according to the green chemistry concept.

5.1.1.2. Non-hydrolytic methods for Si – O – Si bond formation

Today, there are several main non-hydrolytic methods for siloxane bond formation.[321] The most important one is the Piers – Rubinsztajn reaction,[322, 323] which comprises the catalytic condensation involving the alkoxy group and hydro-

Scheme 79



gen atoms at silicon giving off the hydrocarbon (Scheme 79).

The reaction is normally carried out using methoxy- and ethoxysilanes at room temperature; it has a short induction period and is highly exothermic. Study of the reaction mechanism has shown that the $B(C_6F_5)_3$ catalyst is complexed with the hydrosilane; the complex reacts with alkoxysilane to generate the oxonium zwitter ion.[324] The reaction proceeds in the presence of alkenyl- and haloalkylsilanes.[325] However, the reaction does not tolerate epoxy or thiol groups.[326] A more detailed description of the mechanism and details of the Piers – Rubinsztajn reaction have been reported by Chen *et al.*[327] The key benefit of this method for siloxane bond formation is the possibility to prepare a number of products of various architecture, ranging from classical linear oligomers and polymers,[328] linear polymers with terminal and side functional groups[325, 327] to highly and hyperbranched polymers,[323, 328] dendrones and dendrimers.[329 – 331]

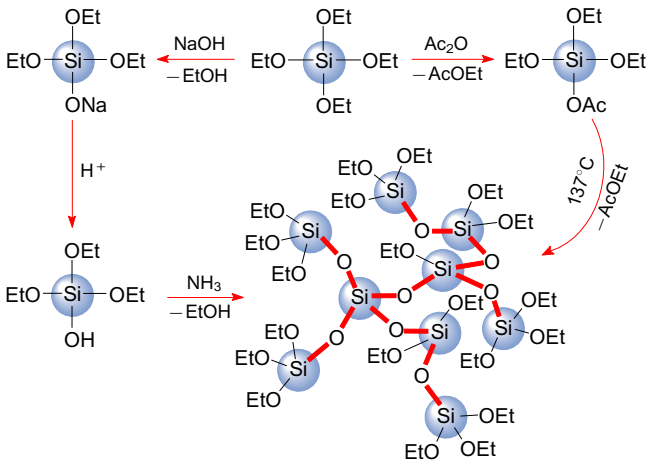
Yet another application of the Piers – Rubinsztajn reaction is vulcanization of siloxane rubbers; the release of gaseous alkane during the reaction provides the formation of polysiloxane elastomer foams of various density.[332, 333] Khalimon *et al.*[334] were able to obtain a sulfonium salt, which decomposed on exposure to UV radiation to give off $B(C_6F_5)_3$; this approach can be rather promising for photocuring of siloxane thin films. Matsumoto *et al.*[335] used the $B(C_6F_5)_3$ catalyst in combination with the organometallic catalyst $[\{Ir(coe)_2Cl\}_2]$ (coe is cyclooctene) to prepare organosiloxanes of various lengths with a specified structure. The authors succeeded in preparing pentasiloxane with five different siloxane units and a hydrogen atom at the central Si atom.

One more non-hydrolytic method for siloxane bond formation is the condensation involving the alkoxy group and acetoxy or hydroxy group. It has been shown[336, 337] that these reactions can serve to prepare hyperbranched polyethoxysiloxanes. These processes in a general form are depicted in Scheme 80. In both cases, the synthesis of the initial monomer is required: in the former case, this is triethoxysilanol, which is formed *in situ* upon neutralization of sodium triethoxysilanolate,[338, 339] while in the latter case, this is acetoxytrialkoxysilane. Sodium alkoxysilanolates and organoalkoxysilanolates, called Rebrov salts,[338, 339] are versatile synthons for the synthesis of not only hyperbranched polysiloxanes,[338 – 343] but a series of other organosilicon products such as siloxane dendrones and dendrimers,[344] polysiloxane brushes[345] and functional organodisiloxanes.[346]

There are also more odd ways of formation of the Si – O – Si group, *e.g.*, a coupling reaction involving the silanol and unsaturated groups.[347 – 349] The reaction can be catalyzed by $Sc(OTf)_3$ or $Ru(Cl)(CO)(PPh_3)_2$.

Thus, there are quite a few methods for siloxane bond formation free from the use of environmentally hazardous chlorine compounds. They include, first of all, hydrolytic methods, which can provide the whole diversity of siloxane

Scheme 80

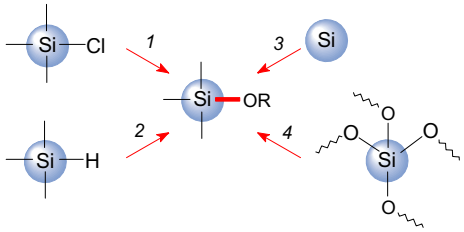


nanomaterials, aero- and xerogels and hybrid materials. The HPC in acetic acid is applicable for the synthesis of the major commercial linear, cyclic or branched organosiloxanes. The development of non-hydrolytic condensation methods allows the preparation of more sophisticated architectures such as dendrones and dendrimers, highly and hyperbranched polysiloxanes, linear polymers with a definite microstructure and so on. All this indicates the relevance of switching from organochlorosilanes to their ether analogues. The major obstacle to this switching is the lack of industrially feasible, cheap and environmentally benign methods for direct synthesis of organoalkoxysilanes; therefore, investigation of these processes is the key and the most crucial issue for switching to environmentally safe production of silicones.

5.1.2. Compounds with the Si – O – C group

As noted above, the environmentally safe production of the whole range of organosilicon products is based on replacement of chlorine-containing monomers, *i.e.*, chlorosilanes, by the corresponding alkoxysilanes. These compounds may be prepared by one of the routes shown in Scheme 81.

Scheme 81

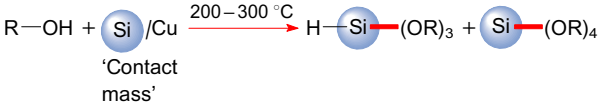


The first route (*1* in Scheme 81) is traditional and is based on etherification of chlorosilanes.[350, 351] An alcohol is used most often as the etherifying agent. Since hydrogen chloride is formed, an HCl acceptor is required. The second route (*2* in Scheme 81) is catalytic dihydrocoupling of various alcohols with hydride-containing silanes. Advantages of this method include mild reaction conditions and the formation of hydrogen as the only by-product; the reaction is catalyzed by various metal complexes, which are comprehensively surveyed in a review.[352] The drawback

of the method is the use of mainly non-functionalized hydrosilanes, which is of interest only for organic synthesis.

The most relevant route is direct synthesis of alkoxysilanes from silicon or SiO_2 (*3*, *4* in Scheme 81). Studies along this line have been carried out for long, and the most considerable achievements were made in the synthesis of tri- and tetraalkoxysilanes. The process, which was discovered back in the 1940s,[353–355] occurs as the reaction of metallic silicon with an alcohol (usually methanol or ethanol) at temperatures of 200 – 300 °C (Scheme 82):

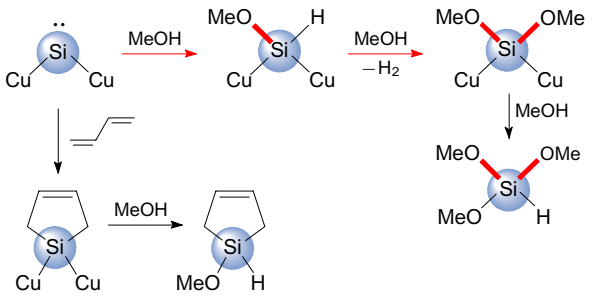
Scheme 82



The catalyst used most often is copper(I) chloride (0.5% – 20%). The reaction affords trialkoxysilane, which then reacts with alcohol to give tetraalkoxysilane. According to a publication,[356] the last step is catalyzed by Cu^0 formed in the reaction. The addition of substances that poison Cu^0, most often, alkyl chlorides, makes it possible to avoid the formation of tetraalkoxysilane and to selectively obtain trialkoxysilane.

The current view on the mechanism of this reaction is based on experiments carried out by Okamoto's team and described in detail in a review.[357] It was shown that the active sites on the silicon copper, so-called 'contact mass', have a silylene nature (Scheme 83).

Scheme 83



Analogous studies have also been carried out for chlorosilane synthesis.[358] However, the product yields were moderate and the selectivity to organoalkoxysilanes varied from 3% to 33%. The difficulty of studying the actual mechanism is caused by a large number of factors that affect the reaction: selection and pretreatment of the reactants and reactant ratio,[359–362] pretreatment and activation of the contact mass,[359, 363, 364] the use of co-catalysts [356, 361] and the process mode.[365]

The tangled pattern of the direct synthesis of alkoxysilanes is illustrated most vividly when the possible process mode is considered. The relevant literature clearly demarcates the gas-phase and liquid-phase processes. Out of the seven publications that appeared in peer-reviewed journals over the last ten years (Refs 356, 359 – 363 and 366), only two papers [363, 366] describe the liquid-phase process. Meanwhile, patents demonstrate the opposite trend. Out of the nine patents we found,[367–375] eight patents describe the liquid-phase process, and two of them [371, 372] present process flow diagrams, indicating that the method has approached the industrial implementation. A comparison of these two process modes, all other factors being the same, was carried out.[365] The results provide the conclusion that the gas-phase process is preferable for direct synthesis, because the production rate is higher and the process design is simpler in this case. The selectivity of this process can be controlled by adding a small amount of methyl chloride, which allows selective synthesis of either tri- or tetraalkoxysilanes. This seemingly indicates that the liquid-phase process is more industrially feasible. However, the results of studies in which the authors prefer the gas-phase method are by no means inferior and even superior to the data for the liquid-phase process. The process conducted without a solvent is obviously considerably simplified. This means that investigation and optimization of direct synthesis of tri- and tetraalkoxysilanes are still relevant.

Tetraalkoxysilane can be prepared directly from SiO_2 (*4* in Scheme 81). In the early studies dealing with this method,[376, 377] high-temperature reaction of silica gel with dimethyl carbonate catalyzed by a strong base was carried out. The authors have shown that at 230 – 350 °C in the presence of 5 mass % – 10 mass % KOH, the conversion of SiO_2 is complete and tetramethoxysilane is the major product. In all probability, the requirements to silica gel characteristics for this reaction are fairly high, which accounts for the difficulty of its preparation [378] and, hence, makes it cost-ineffective for this process. Lewis *et al.*[379] performed screening for natural diatomite minerals that would be more economical. It was shown that the key factors affecting the yield of tetramethoxysilane are the degree of crystallinity and the specific surface area of the sample. Using commercially available Celite Snow Floss, the authors attained 60% yield of tetramethoxysilane. Laine *et al.*[380–382] were able to prepare tetraethoxysilane from rice hulls, which contain 92% – 97% of SiO_2 and are formed as a large-scale waste of rice processing plants. The highest yield of tetraalkoxysilane was 60%.

Despite the fact that we do not consider the use of halogenated silanes, one such example still deserves mention. Silicon tetrafluoride (SiF_4) is formed as a large-scale by-product of the production of phosphorus fertilizers and needs to be utilized. Huang *et al.*[383] considered the reaction of silicon tetrafluoride with methanol in the presence of an equivalent amount of aluminium and a catalytic amount of iodine for activation, resulting in the formation of tetramethoxysilane.

Thus, tetraalkoxysilanes can be prepared by rather efficient and industrially feasible methods from waste products, *e.g.*, SiF_4 or rice hulls. The direct synthesis of trialkoxysilane from metallic silicon and alcohol is most efficient. Considerable progress has been attained along this line, but it is yet difficult to draw an unambiguous conclusion about the preferable mode for conducting this process. Nevertheless, direct synthesis of organoalkoxysilanes is the key issue needed for switching from organochlorosilanes to organoalkoxysilanes. As shown below, this is still a challenge.

5.2. Preparation of compounds with the Si – C bond

5.2.1. Direct synthesis

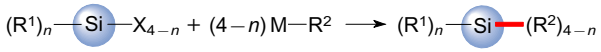
A key process in the synthesis of organosilicon substrates that is widely used in practice is the direct synthesis developed by Rokhov. This approach is based on the reaction of organic halides with the contact mass, a silicon–copper alloy, which furnishes a complex mixture of Si-containing compounds comprising more than 50 products with Si – C, Si – Cl and Si – H bonds. Although the method is applicable to various organic halides, it has been successfully commercialized only for the synthesis of methyl- and phenylchlorosilanes. In the case of long-chain aliphatic halides, unsaturated substrates such as vinyl and allyl chlorides or polychlorinated hydrocarbons, organosilanes are formed in low yields and as hardly separable product mixtures.[384]

In recent years, vigorous research has been carried out to develop synthetic routes to organoalkoxysilanes using the general concept of direct synthesis.[356, 359, 360, 363] The key challenge is to switch to chlorine-free syntheses of organosilicon monomers, that is, to replace the starting organic halides by the corresponding alcohols or ethers and to use elemental Si or SiO_2 as the source of silicon; this would give organoalkoxysilanes, which are preferable over organochlorosilanes for the subsequent use. However, the problem of forming the Si – C bond is still open, as opposed to the Si – O bond (the developed processes are suitable for preparing tetraethoxysilane and triethoxysilane).

5.2.2. Reactions involving Si – X bonds (X = Cl, OR). Synthesis of organosilanes using organometallic reagents

One more general approach to the synthesis of organosilanes is based on reactions of Grignard reagent and other organometallic reagents with chloro- or alkoxysilanes (Scheme 84).[315, 384 – 388]

Scheme 84



X = Cl, OMe, OEt; M = MgY, Li, Ag, AlY_2, ZnY (Y = Hal, Alk, Ar, OAlk);
R^1, R^2 = Alk, All, Alkenyl, Ar, Alkynyl

This approach is actively used to introduce both saturated and unsaturated hydrocarbon substituents. If chlorosilanes are used as the substrates, the control over the degree of replacement of chlorine atoms in the initial chlorosilane by organic groups is a non-trivial problem, and usually a mixture of organochlorosilanes with various degrees of substitution is formed. When organometallic reagents with bulky groups, such as the *tert*-butyl group, are used, the reaction is more selective and organosilanes of specified composition can be obtained. In some cases, this reaction is conducted in the presence of copper salts as catalysts, which substantially increases the selectivity.[384]

Alkoxysilanes are relatively less reactive than chlorosilanes, which allows for better control over the degree of substitution of alkoxy groups in the substrate.

However, reactions involving the Grignard reagent are used in industry only in exclusive cases to obtain especially valuable organosilicon products, because these reactions require large amounts of anhydrous fire- and explosion hazardous ether solvents; furthermore, various by-products are usually formed.

The employment of more reactive organolithium compounds instead of the Grignard reagent is less favourable because of their low selectivity and less convenient handling — they are readily ignited and hydrolyzed in the presence of oxygen and water traces. The application of organolithium substrates is of interest only for the introduction of sterically hindered organic groups in laboratory syntheses. Organozinc, -silver and -aluminium compounds are also used for alkylation, but not often.

Thus, although Mg and Li organic reagents are actiely employed in the synthesis of organosilicon compounds, they have considerable drawbacks: these reagents are incompatible with many functional groups (carbonyl, carboxyl, nitro, hydroxy, *etc.*), and large amounts of metal salts are formed as by-products; this substantially restricts the potential of these reactions for the preparation of new functionalized organosilicon products.

5.2.3. Reaction involving the Si – H bond. Hydrosilylation — addition of hydrosilanes to unsaturated compounds

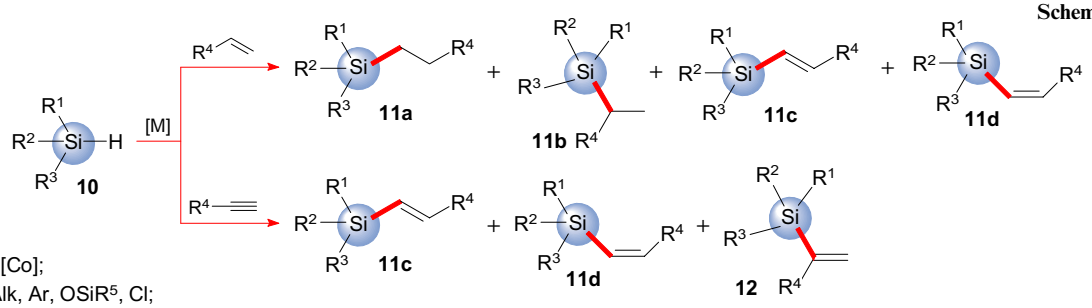
One more fundamental and practically valuable approach to Si – C bond formation is hydrosilylation of unsaturated hydrocarbons in the presence of transition metal complexes (Scheme 85).[384, 389 – 392]

The first studies addressing hydrosilylation of alkenes and alkynes appeared back in the second half of the 20th century, but this method became practically applicable for the synthesis of organosilicon products only after the appearance of Pt-containing Speier's catalysts and later Karstedt's catalysts. This reaction is used for the preparation of both alkyl- and vinylsilanes.

Although this approach is important and highly demanded, the Pt-catalyzed hydrosilylation still suffers from a number of drawbacks and limitations:

— hydrosilylation of alkenes gives mainly the anti-Markovnikov addition product **11a** (in up to 99% yield), but other by-products can also be present: Markovnikov addition product **11b**, dehydrogenative silylation (dehydrosilylation) products **11c**,**d**, isomerization products (this is especially relevant for internal alkenes) and so on;

Scheme 85



[M] = [Pt], [Ni], [Fe], [Co];
R^1, R^2, R^3 = Alk, OAlk, Ar, $OSiR^5$, Cl;
R^4 = Alk, Ar, SiR^6_3, C(O)X

— hydrosilylation of alkynes is a relatively less selective reaction, giving rise to not only vinylsilanes [two anti-Markovnikov products with *E*- (**11c**) and *Z*-configurations (**11d**) of the double bond and Markovnikov product **12**], but also products of subsequent hydrosilylation of vinylsilanes **11c**,**d** and **12**;

— when hydridosilanes **10** are reacted with alkenes and alkynes containing heteroatoms (nitrogen, oxygen and so on), the substrate conversion may drop to 0%, and in the case of unsaturated hydrocarbons containing carbonyl, carboxyl and some other groups, hydrosilylation primarily involves these groups.

Thus, the above-listed drawbacks of the Pt-catalyzed hydrosilylation of unsaturated hydrocarbons in combination with high cost of platinum imply that new catalytic systems are needed. A number of recent studies consider Fe-, Co- and Ni-containing catalysts for hydrosilane addition to multiple bonds.[389 – 392]

Despite the advances made in the Fe-, Co- and Ni-catalyzed hydrosilylation, including high yields of products (up to 99%), regio- and stereoselectivity, selective hydrosilylation of internal and sterically crowded alkenes and alkynes, tolerance of the catalysts to some functional groups (carbonyl, carboxyl, hydroxyl, thienyl, dialkylamine, *etc.*) present in the starting unsaturated hydrocarbons and mild reaction conditions (usually 25 °C), these catalyst still cannot seriously compete with Pt-containing catalysts in the practical application, in particular, because of their relatively low stability in the presence of water and oxygen traces.

The addition of hydrosilanes to compounds with multiple bonds can also be accomplished in the presence of various catalysts/initiators by radical and ionic mechanisms. However, these methods are of little utility and are mainly of interest for pure research; in some cases, they are used for laboratory synthesis.

Chain radical mechanism. This approach is based on the formation of the silyl radical, which is generated under the action of radical initiators (acyl peroxides, AIBN, *etc.*), UV radiation or heating and then reacts with the vinyl-containing substrate.[384] Due to low selectivity, the radical hydrosilylation is used only in the radical polymerization, cross-linking of silicone rubbers and other related processes.

Ionic mechanism is accomplished *via* electrophilic activation of the Si – H bond and is mainly catalyzed by B-, Al-, P- and Zn-containing Lewis acids.[393, 394] Tris(pentafluorophenyl)borane is used most often as the catalyst.

In most cases, ionic hydrosilylation is applicable to carbonyl and carboxyl compounds and their analogues as a selective method for reduction (ionic hydrogenation) of the functional groups. As a method for forming a Si – C bond, ionic hydrosilylation is rather of interest for pure research.

The electrophilic activation of the Si – H bond can also be accomplished using Rh, Ru and Ir complexes *via* the formation of metal silylene complexes or hypercoordinate silicon intermediates.[393] Nevertheless, this approach has not yet found practical use because of restrictions with respect to various substrates.

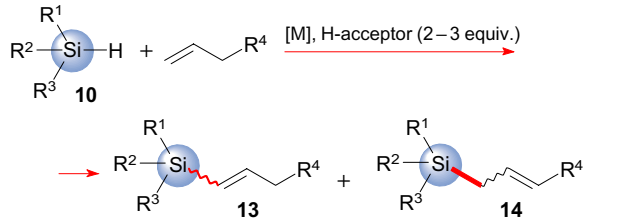
Transfer hydrosilylation is a relatively new approach to hydrosilylation of unsaturated compounds, which may be accomplished as both a radical [di(*tert*-butyl)peroxide- or AIBN-initiated] and an ionic [usually catalyzed by tris(pentafluorophenyl)borane] reaction.[395] The driving force for this reaction is aromatization of the starting Si-containing cyclohexa-1,4-diene by a homolytic or heterolytic mechanism to give a Si-centred radical or cation, respectively, which then reacts with the unsaturated substrate.

These methods are not versatile and are applied in special cases for laboratory synthesis; however, in the future, they would be able to compete with metal-catalyzed hydrosilylation.

5.2.4. Dehydrogenative silylation: synthesis of vinyl- and allylsilanes

This reaction has been mentioned above (see Scheme 85) as a side reaction involved in the hydrosilylation of alkenes. The dehydrogenative silylation gives rise to a new Si – C bond, with the unsaturated nature of the starting alkene being retained. This is a rather appealing method for the synthesis of vinyl- (**13**) and allylsilanes (**14**) (double bond migration product), which are important organosilicon monomers (Scheme 86).

Scheme 86



[M] = [Ir], [Ru], [Ni], [Fe], [Co]; R^1, R^2, R^3 = Alk, OAlk, Ar, $OSiR^5$; R^4 = Alk, Ar, SiR^6_3, C(O)X, NR^7_2, OH, OR^8

In recent years, an ever increasing number of publications have been devoted to Ir-,[396, 397] Ru-,[398] Fe-, Co- and Ni-catalyzed[389 – 392] dehydrogenative silylation reactions, which afford silanes **13** and **14** with various functional groups in the organic substituent in up to 98% yields. The hydrogen released in the reaction is usually trapped by acceptors such as internal and sterically crowded alkenes (cyclohexene, cycloocta-1,5-diene and its analogues) or, in some cases, by the starting alkene, which is taken in excess with respect to hydrosilane **10**.

However, despite certain advances made in this area in recent years, this reaction is not used as a general approach to the synthesis of vinyl- and allylsilanes. This is attributable to high cost of catalytic systems, low stability of the catalysts in the presence of water and oxygen traces and the need to use an excess of hydrogen acceptor.

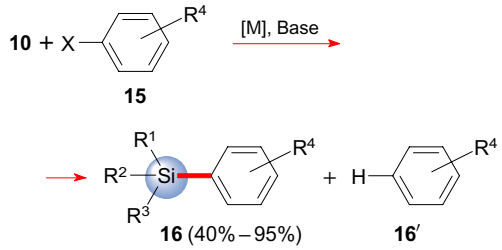
5.2.5. Cross-coupling of hydrosilanes and aryl halides

The first studies dealing with the synthesis of arylsilanes by the reaction of hydrosilanes with aromatic compounds appeared back in the second half of the 20th century.[384] However, drastic conditions ($T > 500$ °C) and low selectivity precluded practical application of these reactions for the synthesis of arylsilanes.

Nevertheless, the benefits of this approach, the simplicity and commercial availability of the reactants used, in combination with the subsequent development of cross-coupling reactions and metal complex catalysis, provided the possibility to arrange unique catalytic systems that lead to selective formation of arylsilanes under substantially milder conditions.

The first approach to Si – Aryl bond formation to be considered here is metal-catalyzed cross-coupling of hydrosilanes with aryl halides (Scheme 87).[399 – 403]

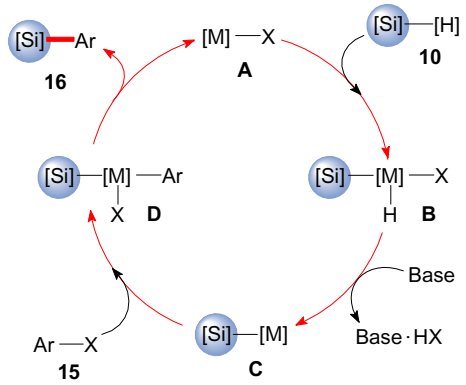
Scheme 87



[M] = [Pd], [Rh]; Base = Et_3N, K_3PO_4, AcONa, Cs_2CO_3; R^1, R^2, R^3 = Alk, OAlk, Ar, $OSiR^5$; R^4 = Alk, Ar, C(O)X, CN, NR^6_2, OH, OR^7; X = Br, I

The general mechanism is shown in Scheme 88. The oxidative addition of hydrosilane **10** to metal complex **A** affords intermediate **B**, which then reacts with hydrogen halide acceptor to give intermediate **C**. The subsequent oxidative addition of aryl halide **15** to intermediate **C** affords intermediate **D**. This is followed by reductive elimination to give arylsilane **16** as the reaction product and metal complex **A**, which closes the catalytic cycle. Arene **16′**, resulting from reduction of aryl halide **15**, is the major reaction product without a hydrogen halide acceptor.

Scheme 88



Despite the advances made in this field, this method is of limited utility for the synthesis of functionalized alkoxy- and, the more so, chloroarylsilanes, which are used most actively for the production of silicone materials. This is attributable, first of all, to the necessity to employ strong bases, which induce hydrolysis of alkoxy- and chlorosilanes.

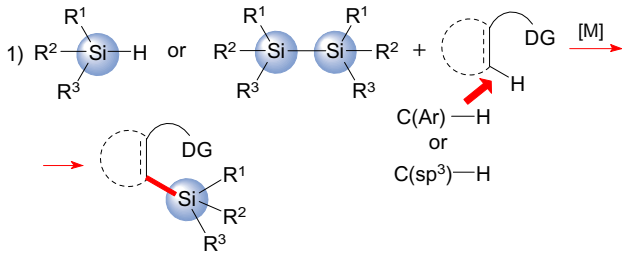
5.2.6. Catalytic silylation of a non-activated C – H bond

The C – H bond is the most abundant bond in organic chemistry, and it is also one of the most chemically inert. The catalytic functionalization of C – H bonds has revolutionized the synthetic strategies used to prepare pharmaceuticals and natural products and to discover new synthetic routes to unique materials and polymers.

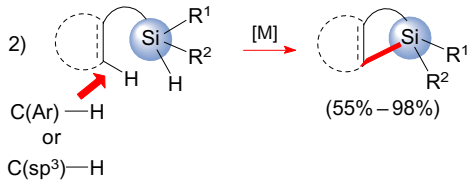
Direct regioselective transformation of C – H bonds to C – C or C – E bonds is a challenge for classical catalytic cross-coupling reactions involving organic halides (RBr, RI, *etc.*) and organometallic reagents (RM, M = Li, MgX, ZnX, BR_2, SnR_3, SiR_3, *etc.*).

The possibility of selective functionalization of molecules with a minimum preactivation may facilitate the synthesis and extend the opportunities for studying the practical significance of complex molecules in various fields, ranging from the pharmaceutical industry to materials science. Lately, vigorous research has been carried out in the C – H bond functionalization to form the Si – C bond. John F.Hartwig and co-workers are among the leaders in the research of Si-arylation through C – H functionalization. Hydrosilanes and (much more rarely used) disilanes are the most promising and convenient sources of the silyl group for Si – C bond formation (Scheme 89).[404]

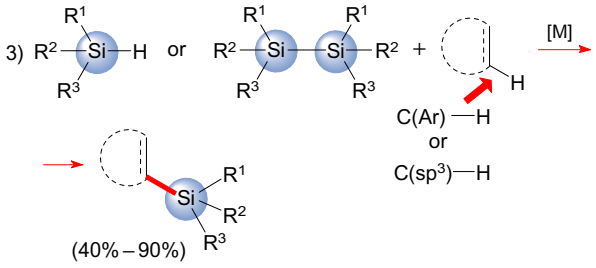
Scheme 89



R^1, R^2, R^3 = Alk, Ph, OTMS; [M] = [Ru], [Rh], [Ir], [Pd]



R^1, R^2 = Alk; [M] = [Rh], [Ir], [Pt]

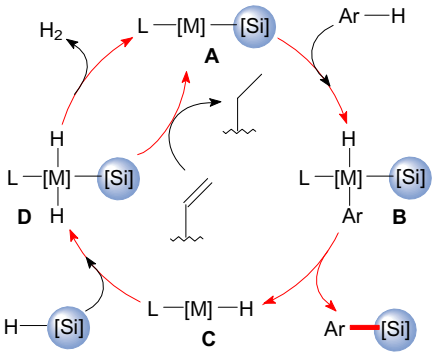


R^1, R^2, R^3 = Alk, Ph, OTMS, F; [M] = [Rh], [Ir], [Pt], [Ni], [Ru], [Fe]

Thus, Si-arylation through C(Ar) – H functionalization of arenes or hetarenes can be accomplished by means of three major approaches: 1) intermolecular Si-arylation with a directing group (DG), 2) intramolecular Si-arylation with a directing group [the reacting and directing group is R^1R^2SiH, see Scheme 89, reaction (2)] and 3) direct intermolecular Si-arylation without directing groups. The last-mentioned approach is evidently most attractive for the synthesis of arylsilanes as the final products, unlike the first and second approaches, which are usually associated with the application of rather expensive directing groups; moreover, the number of synthetic steps is greater, because at least two additional steps are needed to introduce and to eliminate the directing group.

The general mechanism is depicted in Scheme 90 in relation to the C(Ar) – H functionalization. The oxidative addition of arene (Ar – H) to intermediate **A**, accompanied by C(Ar) – H bond activation, yields intermediate **B**. The subsequent reductive elimination affords Si-arylation product (Ar – [Si]) and monohydride intermediate **C**. This is followed by the oxidative addition of hydrosilane to form

Scheme 90



dihydride intermediate **D**, which gives off a hydrogen molecule to produce the initial intermediate **A**, thus closing the catalytic cycle. The hydrogen molecule is either eliminated from the metal coordination sphere of intermediate **D** or is transferred to a hydrogen acceptor. Usual hydrogen acceptors are cyclic alkenes — cyclohexene, norbornene, cycloocta-1,5-diene, *etc.*

A similar approach can be implemented for $C_{sp^3}-N$ functionalization to form the $Si-C_{sp^3}$ bond; however, it has been much less developed, as the $C_{sp^3}-H$ bond is less prone to functionalization than the $C_{sp^2}-H$ bond (see Scheme 89).[404–407]

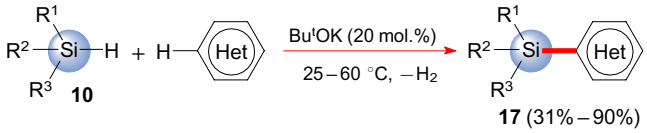
However, in this case, too, the possibility of preparing the most valuable organosilicon monomers, organoalkoxy- and organochlorosilanes, for their subsequent use in the manufacturing of new materials remains limited.

It is noteworthy that in some studies, Si-arylation was carried out without transition metal complexes using acid[408,409] or base catalysis[410–412] for arene C–H functionalization. In the acid-catalyzed Si-arylation, Lewis acids and, more rarely, Brønsted acids serve as catalysts.[408,409]

The Si-arylation *via* aromatic electrophilic substitution (S_EAr) is applicable only to aromatic heterocycles and arenes with electron-donating functional groups, and suitable hydrosilanes include only alkyl- and phenylsilanes. Thus, this reaction can proceed for a relatively small range of substrates.

A major achievement related to Si-arylation is the base-catalyzed C(Ar)–H functionalization of aromatic heterocycles reported by R.H.Grubbs and co-workers in 2015 (Scheme 91).[410–412] The reaction proceeds under relatively mild conditions (25–60 °C, atmospheric pressure) in the presence of catalytic amounts of potassium *tert*-butoxide and can be scaled up to 100 g of product **17**. However, the reaction can be carried out only for alkyl- and phenylhydrosilanes **10** and N-, O- and S-containing heteroaromatic compounds.

Scheme 91



R^1, R^2, R^3 = H, Me, Et, Ph

5.2.7. Reactions involving the Si–M bond (M = BR_2, ZnR, SiR_3)

Reactions using the compounds R_3Si-M (M = BR_2, ZnR, SiR_3) as the sources of the silyl group to form the Si–C bond [Si–C(Ar) and $Si-C_{sp^3}$] have also been reported.[413–415] Currently, these reactions are of no practical interest. As a rule, they are not versatile; however, they are undoubtedly important from the pure research standpoint and can be useful for studies aimed at the development of novel approaches to Si–C bond generation.

5.3. Formation of compounds with the Si–N bond

Compounds containing an Si–N bond, silylamines and silazanes, are practically valuable products. They are widely used as silylating agents, ligands in the coordination chemistry, bases and protecting groups in organic synthesis and polymeric precursors for the production of silicon nitride-based ceramics. Until recently, silylamines and silazanes have been mainly prepared by the reaction of halosilanes with amines, in which two equivalents of amine are consumed, one being used to accept the released hydrogen halide.[416] The major drawbacks of this method include the presence of toxic chlorosilanes sensitive to air moisture and the necessity to dispose the HCl, which is formed as a by-product. Currently, this method gradually loses its significance because of the development of new modern catalytic approaches using both metal-containing catalysts and Lewis acids.

5.3.1. Substitution of metal amines for alkoxy groups

Considering the general views on the reactivity of organosilicon compounds, it can be stated that direct substitution of amines for the alkoxy groups in alkoxysilanes does not take place, as it is at variance with general thermodynamic laws (Scheme 92). Although several examples of direct substitution are known, they are rather exceptions. Heating of 3-aminopropyltrialkoxysilanes in the presence of ammonium chloride affords cyclic aminoalkoxysilanes.[417,418]

Scheme 92



A way for displacing an alkoxy group from alkoxysilane to give the Si–N bond is to use metal amides as nucleophiles; an example of such reaction is shown in Scheme 93. This procedure provides selective formation of silylamines or mixed aminoalkoxysilanes in high yields.[419–423]

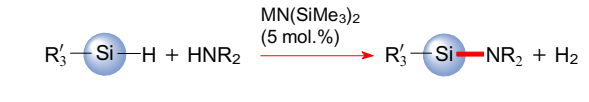
Scheme 93



5.3.2. Dehydrosilylation of amines (SiH + HN)

Cross-coupling involving Si–H and H–N groups with hydrogen evolution (cross-dehydrogenative coupling) is now a promising, convenient and efficient method for the preparation of silylamines.[424–427] The Si–N coupling is catalyzed by both metal complexes and Lewis acids. Group 1 metal bis(trimethylsilyl)amides [$MN(SiMe_3)_2$] are efficient catalysts for this reaction. Anga *et al.*[428] reported that lithium, sodium and potassium bis(trimethylsilyl)amides efficiently catalyze the coupling of hydrosilanes with amines to a high conversion (>90%) and with high chemoselectivity (Scheme 94). The catalytic activity increases with increasing size, polarizability and electropositivity of the metal in the series Li < Na < K.

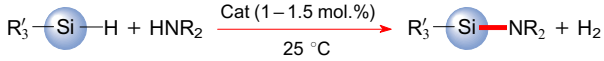
Scheme 94



Complexes of other metals can also act as efficient precatalysts in the dehydrosilylation of amines. For example, there are catalysts based on Group 2 metals: Mg,[429, 430] Ca,[430, 431] Ba,[432 – 435] Sr;[430] Group 3 metals: Al;[436] d metals: Fe,[437] Cu,[438] Zn,[439] Y,[440] Ru,[441, 442] Rh,[443] Pd,[444] Ir;[445] and lanthanides: Sm,[446, 447] Yb.[447, 448] Palladium[449] and gold [450, 451] nanoparticles can also catalyze this reaction.

The dehydrosilylation of amines is efficiently catalyzed by Lewis acids such as $B(C_6F_5)_3$ (Ref. 452) or $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (Scheme 95).[453]

Scheme 95

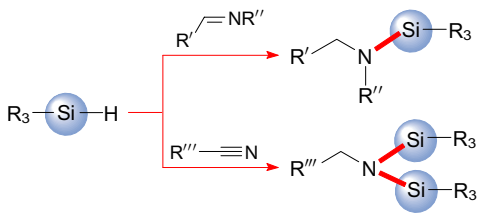


Cat = $B(C_6F_5)_3$ or $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$

5.3.3. Hydrosilylation of imines and nitriles (SiH + CH═N, C≡N)

One more approach to the Si – N bond formation is the widely used hydrosilylation of imines and nitriles (Scheme 96). This reaction has been known for rather long time; it is catalyzed by various metal complexes. For example, hydrosilylation of imines giving the Si – N bond takes place in the presence of catalysts based on Sm,[446] Rh,[454, 455] Ir,[456, 457] Fe,[458] Ru,[459, 460] Pd [461, 462] and La;[463, 464] Karstedt's, Speier's and Wilkinson's catalysts;[465] and Lewis acids.[466 – 472] The addition of hydrosilanes to the C═N bond without a catalyst has been reported, but this is rather a special case.[473] Like imines, nitriles can also react with hydrosilanes to give the Si – N bond. This reaction is catalyzed by Fe,[474] Zn,[475, 476] Ru,[460, 477] Rh,[455, 478, 479] Mo [480 – 486] and W [487] compounds and by Lewis acids, *e.g.*, $B(C_6F_5)_3$.[472, 488, 489]

Scheme 96



Among other, less popular methods for the preparation of compounds with the Si – N bond, mention should be made of the reduction of azides [490] and amides [491, 492] with hydrosilanes to give silylamines; N-silylation of amines with vinylsilanes with the release of alkene;[493] and silylation of amines with disilanes.[494]

Thus, this Section of the review addressed both the main commercially important methods for the formation of the Si – E bond (E = O, C, N) and achievements in this fields made in the last decade and also development of modern approaches to functional organosilanes.

The processes related to the synthesis of organosilicon monomers described in publications of the last decade make it possible to synthesize a variety of alkyl-, aryl-, vinyl- and alkynyl-containing silanes. On the one hand, unique opportunities and prospects are appearing for the application of organosilicon substrates in the cross-coupling, oxidation and other reactions for generation of new C – C and C – E bonds; however, on the other hand, the progress in the synthesis of amino-, alkoxy- and chloro-organosilanes with various functional groups in organic substituents (carbonyl, carboxyl, hydroxyl, amino, nitro group and so on) is still modest.

Although the achievements in the formation of Si – E bonds are somewhat moderate, the existing approaches have formed a solid foundation for further research aimed at the preparation of most demanded organosilicon monomers: amino-, alkoxy- and chloro-organosilanes with various functional groups in organic substituents, which are needed for the development of new silicone and hybrid materials with a set of unique physicochemical properties: heat and frost resistance, biocompatibility, amphiphilicity, electrical conductivity, mechanical strength, *etc.*

6. Organoelement compounds of silicon and aluminium and their derivatives as the basis for manufacture of unique materials

While continuing to consider the synthesis and properties of organosilicon compounds, it is necessary to pay attention to the design of materials with special properties based on these compounds. Of particular note are both silicon derivatives as such and composite materials comprising two or more components (for example, $Y_2O_3/Al_2O_3/SiO_2$).

It is noteworthy that traditional materials, including engineering ceramics, which are usually manufactured by sintering oxide, carbide, nitride and silicide powders, today do not satisfy the increasing demands of advanced technology and do not comply with the technical requirements that are imposed in the design of various articles operating under harsh conditions. Therefore, a priority task is to design new highly functional materials possessing a set of properties markedly superior to the physicomechanical characteristics of existing materials.[495]

Organoelement poly(oligo)mers represent a new class of unsurpassed precursors for the production of high-temperature, oxidation-resistant, high-strength nanostructured ceramic composites: ceramic fibres, matrices, protective coatings, *etc.* They allow one to use a fundamentally different 'polymeric technology' for the manufacture of ceramics by pyrolysis of ceramic-forming organoelement poly(oligo)mers.[496]

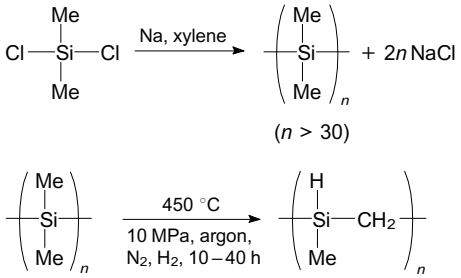
The benefits of precursors based on ceramic-forming oligomers (polymers) include the absence of uncontrolled impurities, attainment of high component compatibility, the possibility of modelling the ceramic micro- and macrostructure during the synthesis of ceramic-forming oligomers (polymers) and the possibility to prepare nanoceramic articles of intricate geometry without the use of extremely high temperatures and pressures.

6.1. Ceramic-forming polycarbosilanes

Ceramics used primarily in science-intensive technologies are C/SiC and SiC/SiC oxygen-free ceramic composites. The

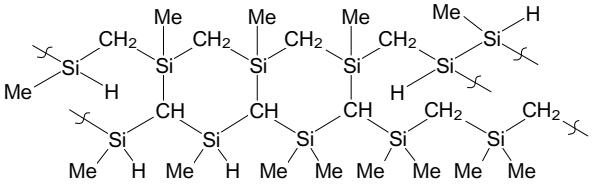
active research aimed at the development and investigation of ceramic-forming poly(oligo)carbosilanes (PCS) is in progress in many countries.[495 – 500] Pioneering studies of polycarbosilanes were reported by Professor Yajima *et al.*,[501, 502] who obtained polydimethylsilane (PDMS) from dichlorodimethylsilane and metallic sodium (lithium) in xylene and carried out thermal rearrangement at high pressure (Scheme 97).

Scheme 97



A structural model of PCS as ring – chain molecules with a relatively low molecular weight (from 800 to 2000 amu) was proposed for the first time (structure **18**).[502]

Structure 18



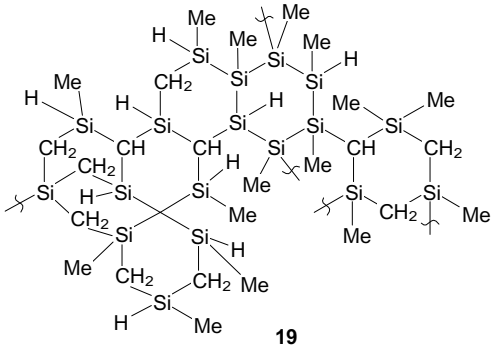
18

At the end of the 20th century, a method for PCS preparation with milder parameters was developed.[503] Polycarbosilanes were prepared at the laboratory setup from available staring compounds and with standard chemical equipment (Scheme 98).

The standard identification of PCS composition and structure, including elemental analysis and IR and NMR (^{1}H, ^{29}Si, ^{13}C) spectroscopy, was supplemented by GPC, dilute solution viscometry and small-angle X-ray scattering. Analysis of the results, in particular, low intrinsic viscosity of PCS samples in various solvents in combination with relatively high molecular weights (from 3500 to 30 000 amu) found from light-scattering data leads to the conclusion that molecular entities of PCS exist as globules. This conclusion is in good agreement with the results of SAXS of dilute solutions of PCS; the equal values of hydrodynamic radius and radius of gyration attest to a nearly spherical shape of the molecular globules with a rigid polycyclic structure.[504]

Considering the obtained results, a structural fragment of the ceramic-forming carbosilane can be represented by structure **19**.

Structure 19



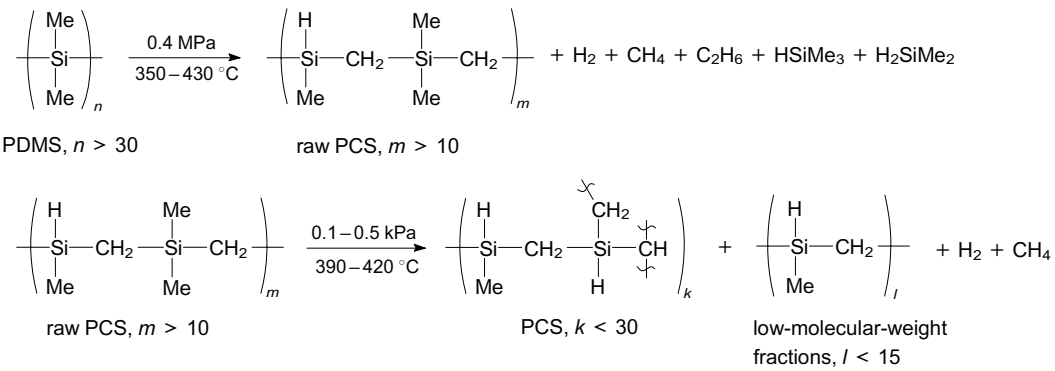
19

The high-strength ceramics obtained from ceramic-forming PCS has a nano-sized polycrystalline structure with an initial crystallite size of 5 – 10 nm. However, after being kept for tens of hours at 1200 – 1300 °C, they grow to 15 – 20 nm, while at 1400 °C, their size increases to 40 – 100 nm and more. In addition, PCS-based ceramics very often contain oxygen and free carbon (each up to 10 mass %), which start to react with each other at > 1200 °C. This disrupts the homogeneity and density of pseudo-amorphous ceramic structure and leads to the loss of material strength. This working temperature restricts the applicability of these materials.[495]

In order to develop PCS meant for high-temperature composite materials, it has been proposed to modify the polycarbosilane matrix by introducing various metals. Processes for PCS modification by elemental metals and by organometallic compounds have been developed. There are quite a few suitable metals ranging from aluminium to refractory metals.[505 – 519]

Since the late-1990s, studies have been carried out with the goal to obtain oxygen-free organosilicon oligomer ceramic precursors containing nanoparticles of refractory metal compounds, so-called nanometal-oligocarbosilanes (nano-MOCS).[520] The key step of the synthesis of these

Scheme 98



compounds is co-condensation of low-molecular-weight oligocarbosilane (OCS) and oxygen-free metal-containing compound (MCC). During the thermal and chemical decomposition of MCC, the metal is detached from the ligand and the resulting metal nanoparticles are homogeneously distributed in the final oligomer and then in the ceramic matrix, thus forming carbide, silicide or nitride nanoparticles. Without disrupting the single-phase nature of ceramics, these particles stabilize the high-strength ultrafine structure; the stabilization mechanism is associated with the ability of nanoparticles to retard the growth of crystallites and to absorb oxygen at elevated temperature.

According to early studies [521, 522] addressing the synthesis of organic nanopolymers, metal-containing nanoparticles are located in the microvoids of the substructure of polymer molecules. Later studies [523 – 525] revealed rather active chemical interaction between the matrix, initial MCC and nanoparticles of the metal being detached from the ligand. Metal-containing compounds such as zirconium and titanium dicyclopentadienyl dichlorides (Cp_2ZrCl_2, Cp_2TiCl_2) and tetrabenzylzirconium and tetrabenzyltitanium ($TiBn_4$, $ZrBn_4$) were employed as modifying additives for fibre-forming oligocarbosilanes; in this case, zirconium- and titanium-containing MOCS were obtained.[523] However, titanium and zirconium benzyl derivatives actively cross-link OCS, which gives rise to insoluble products. In the case of metallocene derivatives, the resulting polymers retain 33 mass % to 85 mass % of the initial chlorine content; this is an undesirable impurity precluding the formation of ceramic materials of an acceptable quality upon further processing of MOCS precursors.[524]

The performed studies have demonstrated [495, 496, 526 – 529] that alkylamine compounds of refractory metals, Zr, Hf and Ta, which are free from oxygen and chlorine impurities, detrimental for SiC ceramics, are most efficient modifying agents for carbosilanes. Using these agents, it is possible to modify raw polycarbosilane, which is the major product of thermal rearrangement of polydimethylsilane — the first stage of preparation of polycarbosilane (see Scheme 98). Raw polycarbosilane is always isolated and purified before the second stage. The addition of alkylamide modifying agents in this stage allows for efficient synthesis of nanometal carbosilanes in the second stage. It is also important that, owing to decreasing reaction time and increasing polymer and ceramic yields, the synthesis of nanometal carbosilanes is not inferior (or in some cases even superior) in efficiency to the synthesis of polycarbosilanes. The preparation process of nanometal oligocarbosilanes using Zr, Hf and Ta alkylamide derivatives has been recognized to be the optimal and has been recommended for industrial implementation.[495] The co-condensation is depicted in the general form in Scheme 99.[495, 529]

The proposed approach to the synthesis of nanometal carbosilanes affords fusible and soluble modified organosilicon oligomers with a homogeneous distribution of nanosized (5 – 20 nm) metal-containing particles in the oligomer matrix. These oligomers have a high capacity for fibre and film formation from melts or solutions; they are cured by thermochemical treatment; and give a high yield of the ceramic residue upon pyrolysis (up to 80 mass %).[526, 527]

Ceramic samples obtained by pyrolysis of nano-MOCS at 1100 °C in argon have been studied by TEM, SEM coupled with EDS and powder X-ray diffraction.[527 – 529] Elemental composition mapping with element superimposition on one map has demonstrated that elements present in ceramic samples after the pyrolysis of nano-MOCS (M = Zr, Hf) are homogeneously distributed.[528, 529]

According to powder X-ray diffraction analysis of ceramic samples prepared from nano-MOCS, they represented nanocrystalline silicon carbide ceramics [β- SiC was the major phase (> 99%); crystallite size $D \approx 2$ nm] with an ultra-fine homogeneous structure.[529]

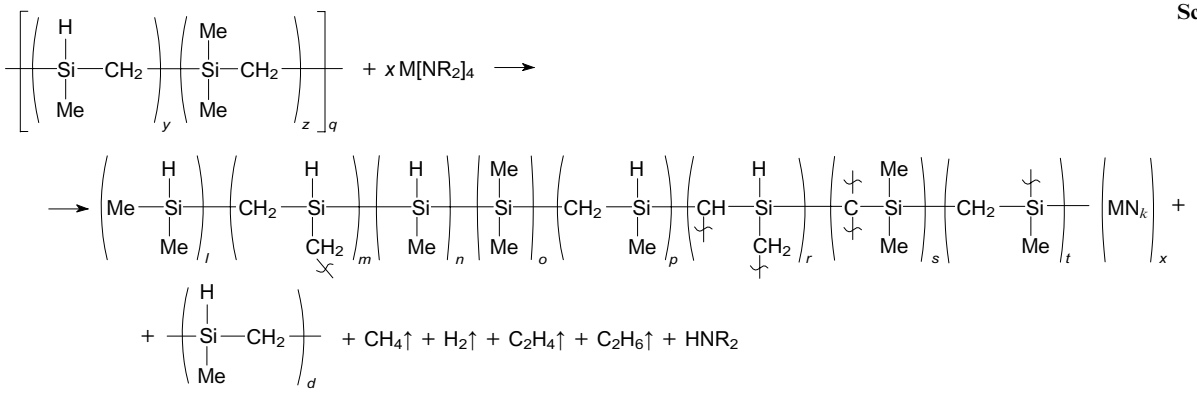
In the ceramic samples formed after pyrolysis of nano-MOCS at 1100 °C, no known crystalline phases of refractory metal compounds were detected. This means that they are embedded into the crystal lattice of the major phase. Considering the small crystallite size of the major phase, this assumption is quite reasonable, since the presence of the metal (Zr, Hf, Ta) is confirmed by the SEM and PXRD data.[528]

Pyrolysis of nano-ZrOCS in a nitrogen atmosphere (heating for 20 h to 1000 °C and then for 8 h to 1600 °C) results, according to PXRD, in the formation of silicon carbide (β-SiC) and zirconium carbonitride (Zr_2NC) as the major phases and SiC and zirconium silicide polytypes as the minor phases.[527]

All of the synthesized nanometal carbosilanes possessed fibre-forming behaviour. They were processed to polymer fibres, which were cured (in an oxidative atmosphere) and pyrolyzed to give silicon carbide fibres modified by refractory metal compounds.[495]

Thus, ceramic-forming nanometal-carbosilanes are the most promising precursors for the formation of components (reinforcing fibres, coatings of fibres, matrices, powders,

Scheme 99



M = Zr, Hf, Ta; R = Me, Et; $x = 0-1$; $y, z, d = 1-8$; $q = 3-6$; $l, m, n, p, s, t = 0-5$; $r = 2-20$; $k = 0-4$

etc.) for novel nanostructured ceramic composite materials, which in turn would boost the design of ceramic composites with high durability at temperatures > 2000 °C in oxidative and other corrosive environments.[495, 496, 524, 529]

6.2. Ceramic-forming organoelementoxanes

Good prospects for the development of advanced oxide ceramics are determined by the huge investments made by developed countries to the design of new highly thermally stable and chemically inert ceramics based on aluminium oxide.[530, 531]

Mullite ($3\,Al_2O_3 \cdot 2\,SiO_2$) is well known for high thermal stability. Mullite ceramics have a bending strength of 150 MPa at 1400 °C, they possess a creep resistance and low thermal expansion coefficients, and also exhibit high chemical stability in acid media.[532, 533]

Aluminium oxide-based composites containing 3 mol.% of yttrium oxide stabilized by tetragonal zirconium oxide show excellent mechanical properties.[534] Yttrium aluminates with the garnet structure $3\,Y_2O_3 \cdot 5\,Al_2O_3$ serve for production of high-strength ceramic and piezoelectric materials, luminophores and semiconductors, and active materials for optical and quantum generators.[534] The major phases crystallizing in the $Y_2O_3 - Al_2O_3 - SiO_2$ system possess high melting points and low linear thermal expansion coefficients close to those of silicon carbide; therefore, this system is promising as an antioxidant protective coating for C/C – SiC composites.[535]

The binary ceramics made of aluminium magnesium spinel ($MgAl_2O_4$) are widely used for the manufacture of heat-resistant, catalytically active, optically transparent, chemically stable and corrosion and radiation resistant electrical goods; they are considered as promising materials for nuclear power engineering owing to the high melting point of the $MgAl_2O_4$ spinel (2135 °C), low dielectric constant, high mechanical strength at high temperature, chemical stability, good thermal shock resistance, and also owing to their good optical characteristics.[536, 537] The transparent aluminium magnesium spinel is used to manufacture infrared domes and windows for missiles, transparent armour for air and ground vehicles, optical lenses, windows for lasers, optical heat exchangers, windows for radio frequency powder injectors and plasma diagnostic devices, sight glasses for high pressure vessels and glasses for high pressure arc lamps and chromatographs.[538, 539]

The authors of the present review took part in the synthesis of ceramic-forming organoelementoxane oligomers, which represent a new class of precursors for components (binders, coatings, fibres, *etc.*) of corundum (α-Al_2O_3), aluminosilicate ($x\,Al_2O_3 \cdot y\,SiO_2$), yttrium aluminium ($x\,Y_2O_3 \cdot y\,Al_2O_3$), yttrium aluminosilicate ($x\,Y_2O_3 \cdot y\,Al_2O_3 \cdot z\,SiO_2$) and aluminium magnesium ($x\,MgO \cdot y\,Al_2O_3$) composites for the manufacture of high-strength, heat resistant and oxidation resistant ceramic composites.[496]

Unstable chemically reactive aluminium organic compounds were used to develop [540] a method for the synthesis of hydrolytically and air stable ceramic-forming organoalumoxane oligomers (chelated alkoxyalumoxanes) by successive hydrolysis and alcoholysis of organoaluminium compounds stabilized by compounds with keto–enol tautomerism (Scheme 100).

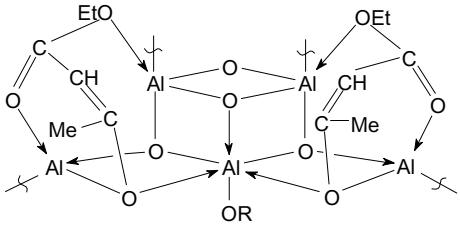
Scheme 100

$$x\,AlR_3 + y\,H_2O + z\,R'OH + m\,R''OH \longrightarrow$$
$$\longrightarrow [Al_x(OR')_z(OR'')_m(OH)_kO_y] + 3x\,RH\uparrow$$

$x = 3-10$, $y = 0-9$, $z = 1-10$, $k = 0-3$, $m = 1-5$;
$R = C_nH_{2n+1}$, $C_nH_{2n+1}O$, $(C_nH_{2n+1})_2Al-O-[(C_nH_{2n+1})Al-O]_t$;
$n = 2-4$, $t = 3-10$; $R' = Et$, Pr^i, Bu^n;
$R'' = MeC(O)CH{=}CMe$, $EtOC(O)CH{=}CMe$

For the chelated alkoxyalumoxanes, comprehensive physicochemical investigations were performed and thermochemical destruction was studied; as a result, a probable structure was proposed for their molecular moieties (Structure **20**).[540]

Structure 20



20

The thermochemical treatment of these compounds was found to give corundum ceramics based on α-Al_2O_3 (Scheme 101).[540 – 542]

Scheme 101

$$\{Al_x(OC_nH_{2n+1})_y[OC(Me){=}CHC(O)OEt]_z(OH)_kO_q\} \xrightarrow[-y\,C_nH_{2n}]{80-250\ ^\circ C}$$
$$\longrightarrow [Al_x[OC(Me){=}CHC(O)OEt]_z(OH)_{k-y}O_q] \xrightarrow[-z\,(CO_2,\ C_2H_4,\ MeC{\equiv}CH)]{300-420\ ^\circ C}$$
$$\longrightarrow [Al_x(OH)_{k-y-z}O_q] \xrightarrow[H_2O]{450-550\ ^\circ C}$$
$$\longrightarrow \underset{\text{Boehmite}}{[Al(O)(OH)]_n} \xrightarrow[H_2O]{650-700\ ^\circ C} \underset{\text{Amorphous}}{Al_2O_3} \xrightarrow{700-900\ ^\circ C}$$
$$\longrightarrow Al_2O_3(\gamma, \delta, \theta, \eta, \varepsilon) \xrightarrow{1200\ ^\circ C} \alpha\text{-}Al_2O_3$$

According to X-ray diffraction data, the sample obtained after successive pyrolysis of ethyl acetoacetate-alkoxy-hydroxyalumoxane at various temperatures remains X-ray amorphous up to 500 °C. At the annealing temperatures of 700 and 800 °C, the X-ray diffraction patterns exhibit broad peaks corresponding to the intermediate (metastable) aluminium oxide phase ε-Al_2O_3. At 900 °C, ε-Al_2O_3 starts to transform into the thermodynamically stable corundum phase, the transformation being almost completed at 1000 °C. Powder X-ray diffraction analysis confirms that the sample is a single phase — corundum α-Al_2O_3 (Fig. 7).[542]

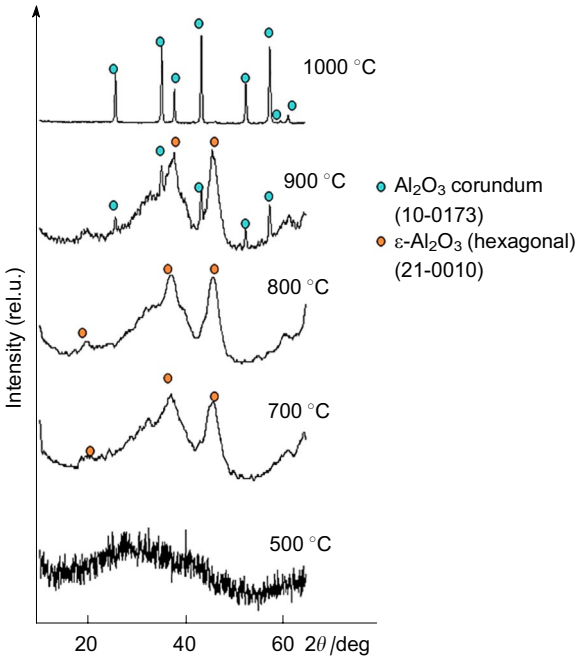


Figure 7. X-Ray diffraction patterns of the sample obtained after successive pyrolysis of ethyl acetoacetate-alkoxy-hydroxyalumoxane at different temperatures.[542]

On the basis of ceramic-forming organoalumoxanes, a manufacturing process for finished high-purity nanostructured silica-free organoalumoxane-based corundum α-Al_2O_3 binder, having no analogues in the world, was developed and patented.[541 – 544]

It was found that ceramic-forming organoalumoxanes easily react with metal alkoxides and acetylacetonates and can incorporate a broad range of elements and metals in various combinations and ratios, being distributed homogeneously (at the molecular level) in the oligomer matrix. This provides a perfect nanostructure and enhanced physicomechanical and performance characteristics of ceramic composites obtained from ceramic-forming organoelementoxanes. Organometallic synthesis provides high purity of the initial oligomers. This allows one to obtain high-purity oxides of a specified composition and manufacture materials at considerably lower temperature than in the case of using commercial oxides.

Ceramic-forming organoalumoxanesiloxane oligomers were prepared by the reaction of chelated alkoxyalumoxanes with tetraethoxysilane or ethyl silicates (Scheme 102).[545]

Scheme 102

$$[Al(OR')]_k(OR'')_x(OH)_zO_y]_n + m\,(EtO)_4Si \longrightarrow$$
$$\longrightarrow [Al(OR')_k(OR'')_x(OH)_zO_y]_n\cdot[Si(OEt)_2O]_m + EtOH$$

$R' = Et, Pr^i, Bu^n$; $R'' = C(Me){=}CHCO_2Et$;
$n = 3-12$; $m = 3-12$; $k + x + 2y + z = 3$

Pyrolysis of ceramic-forming organoalumoxanesiloxanes affords homogeneous high-purity aluminosilicates with a specified Al : Si molar ratio, in particular, mullite ceramics ($3\,Al_2O_3\cdot 2\,SiO_2$) (Scheme 103).

Scheme 103

$$[Al(OC_nH_{2n+1})_k(OC(Me){=}CHCO_2Et)_x(OH)_zO_y]_n\cdot[Si(OEt)_2O]_m \xrightarrow{a}$$
$$\longrightarrow [Al(OC(Me){=}CHCO_2Et]_x(OH)_{z+k}O_y]_n\cdot[Si(OEt)_2O]_m \xrightarrow{b}$$
$$\longrightarrow [Al(OH)_{k+x+z}O_y]_n\cdot[Si(OEt)_2O]_m \xrightarrow{450-550\ ^\circ C}$$
$$\longrightarrow [[Al(O)(OH)]_n\cdot[Si(OEt)_2O]_m \xrightarrow[H_2O]{650-700\ ^\circ C}$$
$$\longrightarrow n\,Al_2O_3\cdot m\,SiO_2 \xrightarrow{800-1000\ ^\circ C}$$
Amorphous
$$\longrightarrow n\,Al_2O_3(\gamma, \delta, \theta, \eta, \varepsilon)\cdot m\,SiO_2 \xrightarrow{1200-1300\ ^\circ C} 3\,Al_2O_3\cdot 2\,SiO_2$$
Mullite

(*a*) 80 – 300 °C, $-k\,C_nH_{2n}$; (*b*) 320 – 420 °C, $-(CO_2, C_2H_4, MeC{\equiv}CH)$

The purity of aluminosilicates prepared from chelated organoalumoxanesiloxanes, in relation to the main trace impurities, is 10 – 100 higher than the purity of the oxide system based on aluminium and silicon oxides;[545] hence, they can be employed to produce nanostructured aluminosilicate ceramics, in particular, chemically stable and heat resistant mullite ceramics.[496]

Co-condensation of chelated organoalumoxane oligomers and yttrium acetylacetonate resulted in the synthesis of ceramic-forming organoyttrium oxane alumoxanes, hydrolytically stable in air and soluble in organic solvents, which possess fibre-forming properties at certain Al : Y molar ratios (Scheme 104).[546, 547]

Scheme 104

$$[Al(OR)_k(OR'')_x(OH)_zO_y]_n + m\,(R'O)_3Y\cdot 2.5\,H_2O \longrightarrow$$
$$\longrightarrow [(R'O)_sY(OH)_tO_r]_m\cdot[Al(OR)_{k-p}(OR'')_x(OH)_zO_y]_n + p\,ROH$$

$R = Et, Bu^n$; $R' = CMe{=}CHC(O)Me$; $R'' = C(Me){=}CHCO_2Et$;
$m, n = 3-12$; $s + t + 2r = 3$; $(k-p) + x + 2y + z = 3$

Spectral characteristics of the organoyttrium oxane alumoxanes (NMR and IR spectra) and SEM/EDS data, elemental analysis, TGA data up to 1100 °C and PXRD data for ceramic samples obtained after pyrolysis at 1600 °C of organoyttrium oxane alumoxanes with different Al : Y molar ratios have been reported by Shcherbakova *et al.*[546] Powder X-ray diffraction study of the yttrium aluminium oxide powders prepared by pyrolysis of organoyttrium oxane alumoxanes demonstrated that, depending on the Al : Y molar ratio, the obtained yttrium aluminium garnet ceramics consist of yttrium aluminate $Y_3Al_5O_{12}$ (yttrium aluminium garnet $3\,Y_2O_3\cdot 5\,Al_2O_3$, YAG) or of yttrium aluminum garnet and corundum (α-Al_2O_3).[546]

The processes that accompany the thermal destruction of organoyttrium oxane alumoxanes are shown in Scheme 105.

The surface morphology and elemental composition of a ceramic sample based on organoyttrium oxane alumoxane according to SEM/EDS data are presented in Fig. 8.

Organoyttrium oxane alumoxanes can be used to design new-generation heat-resistant, highly strong and chemically inert yttrium aluminium ceramics.[496, 546, 547]

Melt molding of fibre-forming organoyttrium oxane alumoxanes afforded polymer fibres (Fig. 9), which were

Scheme 105

$$[Y(OC(Me)=CHC(O)Me)_s(OH)_tO_r]_m\cdot[Al(OC_nH_{2n+1})_k(OC(Me)=CHCO_2Et)_x(OH)_zO_y]_n \xrightarrow[-C_nH_{2n}]{80-300\ ^\circ C}$$

$$\longrightarrow [Y(OC(Me)=CHC(O)Me)_s(OH)_tO_r]_m\cdot[Al(OC(Me)=CHCO_2Et)_x(OH)_{z+k}O_y]_n \xrightarrow[-(CO_2,\ C_2H_4,\ MeC\equiv CH)]{320-420\ ^\circ C}$$

$$\longrightarrow [Y(OH)_{t+s}O_r]_m\cdot[Al(OH)_{k+x+z}O_y]_n \xrightarrow[-H_2O]{450-550\ ^\circ C} \underset{\text{Amorphous}}{m\,Y_2O_3\cdot n\,Al_2O_3} \xrightarrow{800-1000\ ^\circ C} m\,Y_2O_3\cdot n\,Al_2O_3(\gamma,\ \delta,\ \theta,\ \eta,\ \varepsilon) \xrightarrow{1300-1500\ ^\circ C}$$

$$\longrightarrow Y_3Al_5O_{12}\cdot\alpha\text{-}Al_2O_3$$

cured and pyrolyzed to give yttrium oxide-modified aluminium oxide fibres (Fig. 10).[548]

The X-ray diffraction pattern of yttrium aluminium ceramic fibres shows that the sample is crystalline (Fig. 11). The X-ray diffraction pattern exhibits peaks that can be assigned to the corundum (α-Al_2O_3) and yttrium aluminium garnet ($Y_3Al_5O_{12}$) phases.[548]

These fibres are valuable for the use as matrix and reinforcing phases in the design of heat-shielding, heat-insulating or composite ceramic materials able to withstand high temperature in an oxidative environment.

The reaction of chelated alkoxyalumoxanes with magnesium acetylacetonate resulted in the synthesis of ceramic-forming organomagnesium oxane alumoxanes, hydrolytically stable in air and soluble in organic solvents, which exhibited fibre-forming properties at Al : Mg molar ratios of 2 : 1 and 1 : 1 (Scheme 106).[549]

Unlike alkylmagnesium oxane alumoxanes synthesized more than 30 years ago and meant for application as

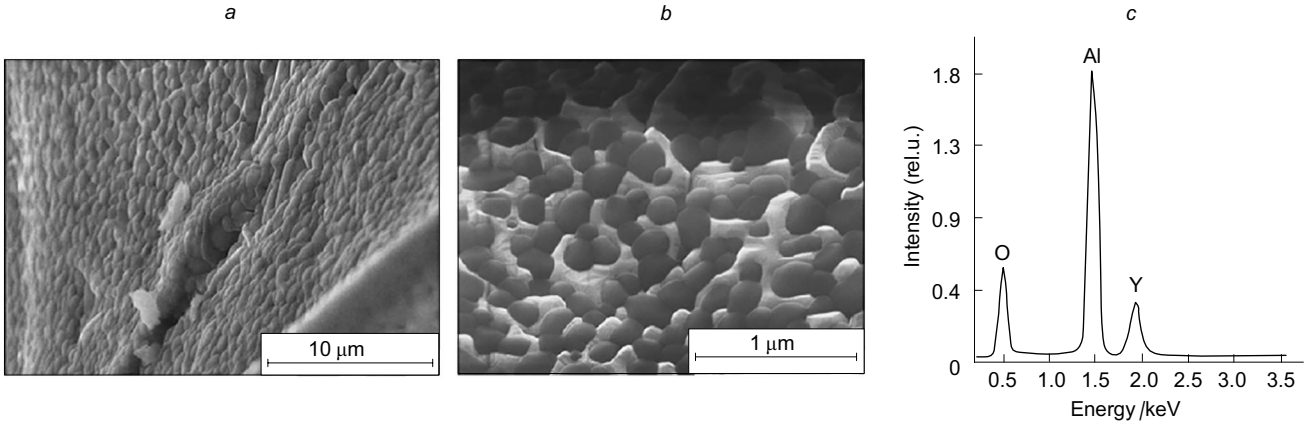


Figure 8. SEM images of the surface (*a*, *b*) and elemental composition of the yttrium aluminium ceramic powder according to energy-dispersive X-ray spectroscopy (*c*).[546]

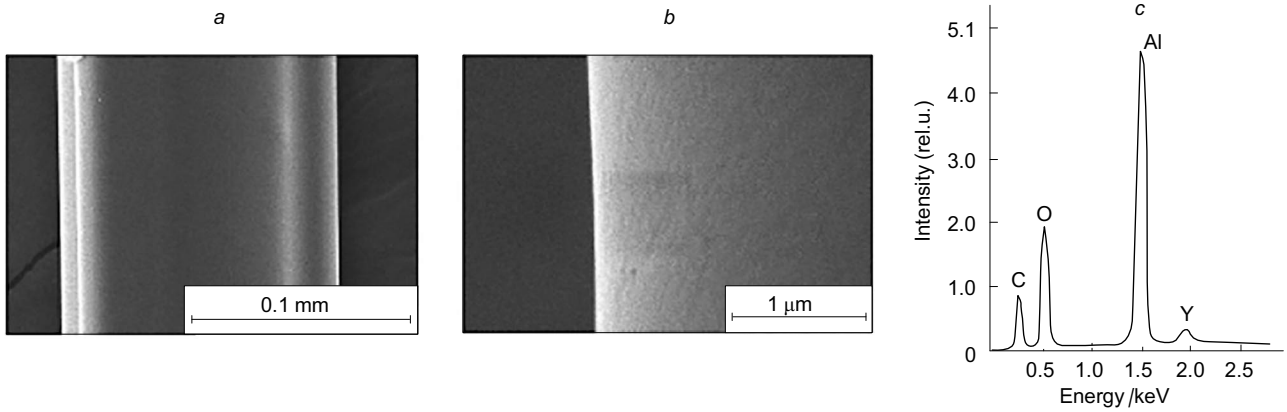


Figure 9. SEM images of the surface (*a*, *b*) and elemental composition of polymer fibres according to energy-dispersive X-ray spectroscopy (*c*).[547]

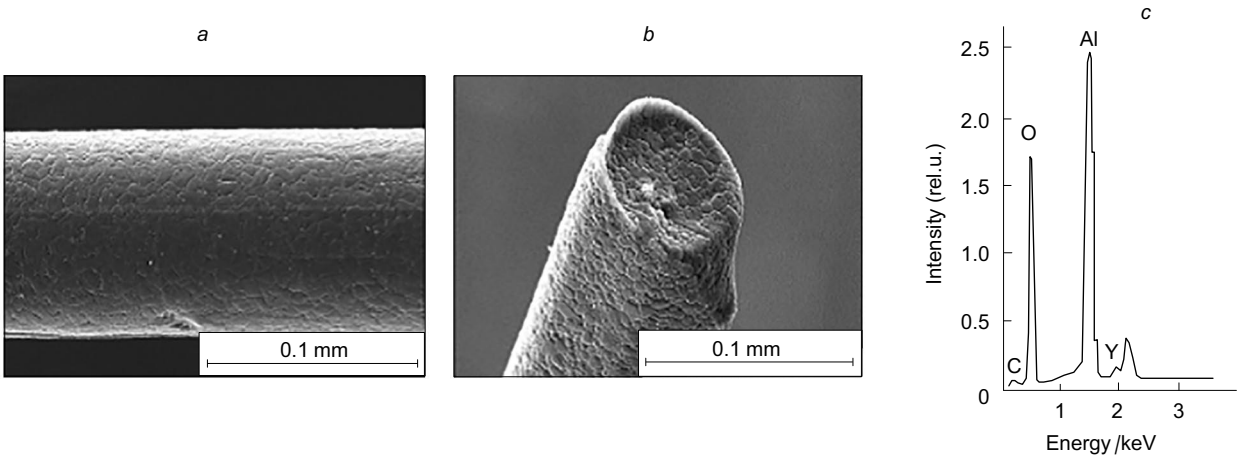


Figure 10. SEM images of the surface (*a*, *b*) and elemental composition of ceramic fibres according to energy-dispersive X-ray spectroscopy (*c*).[547]

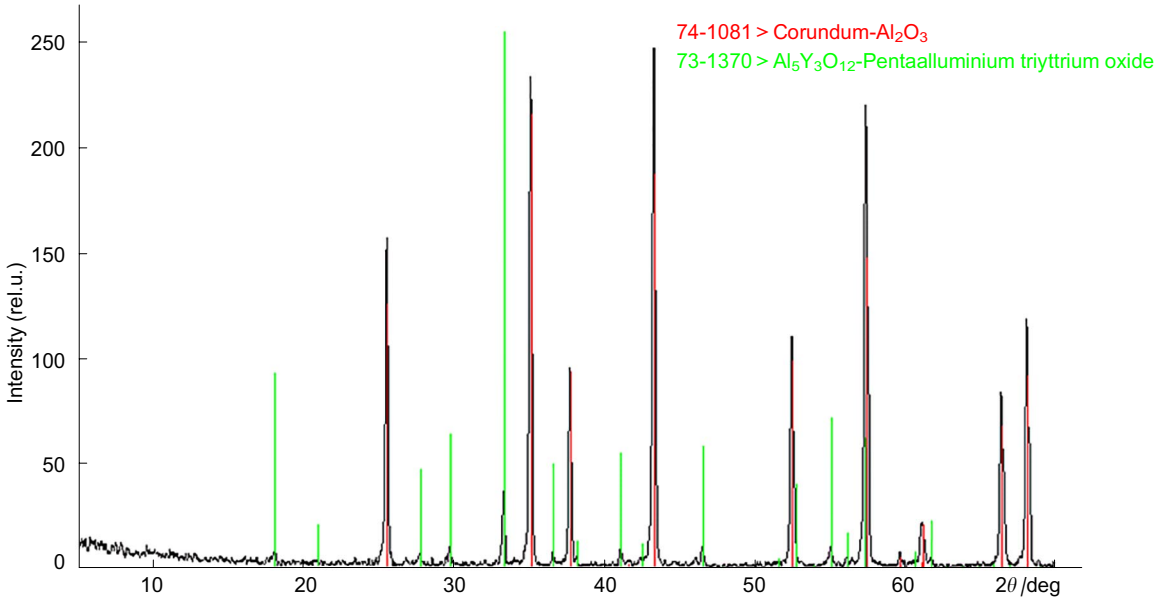


Figure 11. X-Ray diffraction pattern of a ceramic yttrium aluminium fibre sample from organoyttrium oxane alumoxane.[548]

components of ethylene and propylene polymerization catalysts, these organomagnesium oxane alumoxanes are ceramic-forming oligomers, which can serve as precursors for components of high-purity ceramics based on aluminium and magnesium oxides, in particular, magnesium aluminate spinel ($MgAl_2O_4$).[549]

Scheme 106

$$[Al(OR)_s(OR')_x(OH)_pO_q]_m + k\,(R''O)_2Mg \longrightarrow$$

$$\longrightarrow [(R''O)MgO]_k \cdot [Al(OR)_l(R''O)_g(OR')_x(OH)_zO_y]_m + (s-l)\,ROH$$

$R = C_nH_{2n+1}$; $R' = C(Me){=}CHCO_2Et$; $R'' = C(Me){=}CHC(O)Me$; $k = 0.1-12$; $m = 3-12$; $s+x+2q+p = 3$; $k/m+l+g+x+2y+z = 3$; $n = 2-4$

The reactions involved in the thermal destruction of organomagnesium oxane alumoxanes with Al : Mg molar ratio of 2 : 1 are depicted in Scheme 107.

The reaction of chelated organoalumoxanes with ethyl silicates and yttrium acetylacetonate resulted in the synthesis of ceramic-forming organoyttrium oxane alumoxane siloxanes soluble in organic solvents (Scheme 108).[550]

Pyrolysis of organoyttrium oxane alumoxane siloxanes at 1500 °C affords transparent or enamel glass ceramic samples. Mapping of the ceramic sample showed a homogeneous distribution of elements and the $Y_2O_3-Al_2O_3-SiO_2$ composition corresponding to theoretical models for this type of glass (Fig. 12).[550]

The thermal destruction of organoyttrium oxane alumoxane siloxanes can be represented by Scheme 109.

The X-ray diffraction pattern of the ceramic sample obtained by pyrolysis of organoyttrium oxane alumoxane

Scheme 107

$$[Mg(OC(Me)=CHC(O)Me)O]_k \cdot [Al(OEt)_l(OC(Me)=CHC(O)Me)_g(OC(Me)=CHCO_2Et)_x(OH)_zO_y]_{2k} \xrightarrow[-l\,C_2H_4]{80-250\ ^\circ C}$$

$$\longrightarrow [Mg(OC(Me)=CHC(O)Me)O]_k \cdot [Al(OC(Me=CHC(O)Me)_g(OC(Me)=CHCO_2Et)_x(OH)_{z+1}O_y]_{2k} \xrightarrow[-(CO_2,\ C_2H_4,\ MeC\equiv CH)]{320-420\ ^\circ C}$$

$$\longrightarrow [Mg(OH)_{z+1}O_r]_k \cdot [Al(OH)_{t+x+z}O_y]_{2k} \xrightarrow[-H_2O]{450-550\ ^\circ C} \underset{\text{Amorphous}}{MgO \cdot Al_2O_3} \xrightarrow{800-1100\ ^\circ C} \underset{\text{Spinel}}{MgAl_2O_4}$$

Scheme 108

$$[Al(OR)_k(OR'')_x(OH)_zO_y]_n + l\,(EtO)_4Si + m\,(R'O)_3Y \cdot 2.5\,H_2O \longrightarrow [(R'O)_sY(OH)_tO_r]_m \cdot [Al(OR)_k(OR'')_x(OH)_zO_y]_n \cdot [Si(OEt)_2O]_l$$

R = Et, Pr^i, Bu^n; R′ = C(Me)=CHC(O)Me; R″ = C(Me)=CHCO$_2$Et; l, m, n = 3 – 12; $s + t + 2r = 3$; $k + x + 2y + z = 3$

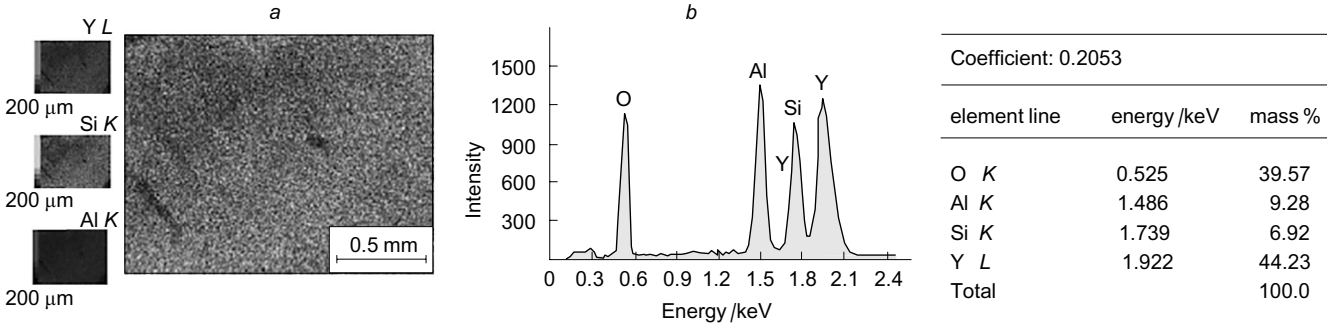
siloxanes at 1500 °C shows the presence of the $Y_2Si_2O_7$, silicon oxide (cristobalite), YAG, $Al_2Y_4O_9$ and $Y_{4.67}(SiO_4)_3O$ phases.[550]

The main phases that crystallize in the $Y_2O_3-Al_2O_3-SiO_2$ system have high melting points and low linear thermal expansion coefficients similar to that of silicon carbide; therefore, this system is promising as an antioxidant protective coating for C/C – SiC composites.[551–554]

Organoyttrium oxane alumoxane siloxanes were used to manufacture binder and film-forming composites that served for the fabrication of high-temperature $Y_2O_3-Al_2O_3-SiO_2$ antioxidant protective coatings for carbon and silicon carbide fibres.[553] Using binders based on organoyttrium oxane alumoxane siloxanes, ceramic suspensions were prepared and applied onto carbon fibre bundles (Fig. 13 *a*,*b*). Pyrolysis at 1600 °C in an oxidative atmosphere afforded carbon fibres coated by a $Y_2O_3-Al_2O_3-SiO_2$ protective layer (Fig. 14 *a*–*d*).[553]

It is noteworthy that carbon fibres with unprotected surface can operate in an oxidizing atmosphere at temperatures up to 500 °C.[551, 552] The application of a protective oxide coating based on organoyttrium oxane alumoxane siloxanes extends the range of thermal stability of carbon fibres in oxidizing atmosphere up to 1500 °C.[496, 553]

Film-forming composites based on organoyttrium oxane alumoxane siloxanes were employed to prepare antioxidant glass ceramic protective coatings on both coreless and cored silicon carbide fibres with the $Y_2O_3-Al_2O_3-SiO_2$ coating (Fig. 15).[553]



Coefficient: 0.2053

element line	energy /keV	mass %
O *K*	0.525	39.57
Al *K*	1.486	9.28
Si *K*	1.739	6.92
Y *L*	1.922	44.23
Total		100.0

Figure 12. SEM element distribution map (*a*) and chemical composition of ceramics after pyrolysis of organoyttrium oxane alumoxane siloxane (*b*).[550]

Scheme 109

$$[Y(OC(Me)=CHC(O)Me)_s(OH)_tO_r]_m \cdot [Al(OC_nH_{2n+1})_k(OC(Me)=CHCO_2Et)_x(OH)_zO_y]_n \cdot [Si(OEt)_2O]_p \xrightarrow[-C_nH_{2n}]{}$$

$$\longrightarrow [Y(OC(Me)=CHC(O)Me)_s(OH)_tO_r]_m \cdot [Al(OC(Me)=CHCO_2Et)_x(OH)_{z+k}O_y]_n \cdot [Si(OEt)_2O]_p \xrightarrow[-(CO_2,\ C_2H_4,\ MeC\equiv CH)]{500-650\ ^\circ C}$$

$$\longrightarrow [Y(OH)_{t+s}O_r]_m \cdot [Al(OH)_{k+x+z}O_y]_n \cdot [Si(OH)_2O]_p \xrightarrow[-H_2O]{750-850\ ^\circ C} \underset{\text{Amorphous}}{m\,Y_2O_3 \cdot n\,Al_2O_3 \cdot p\,SiO_2} \xrightarrow{900-1100\ ^\circ C}$$

$$\longrightarrow m\,Y_2O_3 \cdot n\,Al_2O_3 \cdot p\,SiO_2 \xrightarrow{1300-1500\ ^\circ C} \underset{\text{Keiviite}}{(Y_2Si_2O_7)} \cdot \underset{\text{Mullite}}{(3\,Al_2O_3 \cdot 2\,SiO_2)}$$

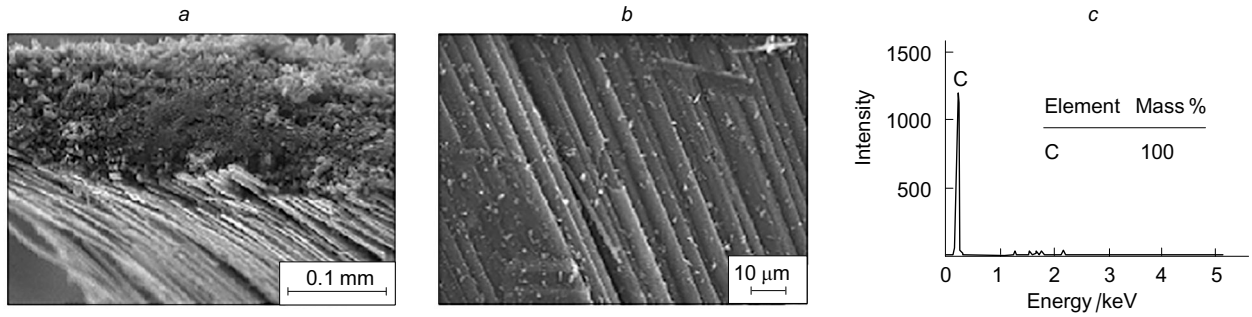


Figure 13. Surface micrographs (*a*, *b*) and elemental composition (*c*) of a carbon fibre bundle.[553]

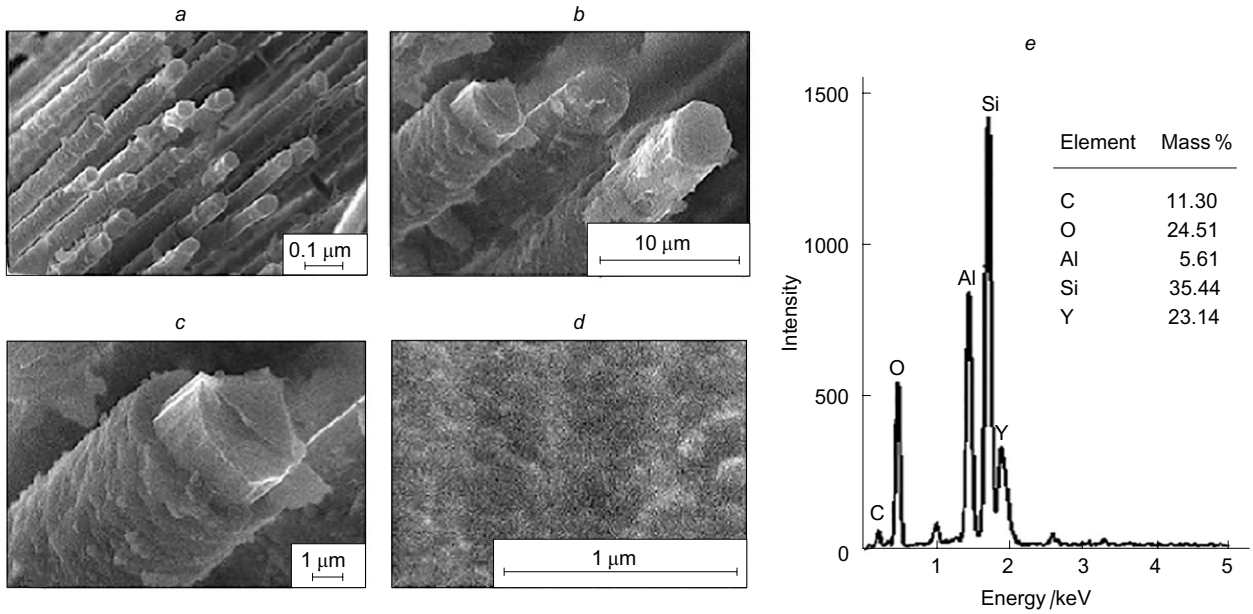


Figure 14. Surface micrographs (*a* – *d*) and elemental composition (*e*) of a carbon fibre bundle with the $Y_2O_3 - Al_2O_3 - SiO_2$ coating.[553]

Figure 16 presents data for SiC fibres with the $x\,Y_2O_3 - y\,Al_2O_3 - z\,SiO_2$ glass ceramic coating obtained by heat treatment at 1500 °C in an oxidizing atmosphere for 30 min.

The thermooxidative stability of the pristine and glass ceramic-coated SiC fibres has been tested at 1600 °C in an oxidizing atmosphere for 60 min. It was found that after heat treatment of uncoated SiC fibres, a surface SiO_2 layer is formed and is gradually cracked and peels off the SiC fibre surface, thus destroying the fibre. Meanwhile, after testing of coated fibres at 1600 °C, no destruction is observed, the coatings do not peel off and do not crack (Fig. 17).[554]

During high-temperature oxidation, glass ceramic protective coatings based on organoyttrium oxane alumoxane siloxanes reduce the oxygen diffusion into SiC fibre more than 2 – 3-fold and prevent the fibre destruction, which confirms the necessity of the antioxidant protective coating on the silicon carbide fibres for increasing their thermooxidative stability.[554]

Thus, it has been shown that organoelement poly(oligo)meric ceramic-forming precursors with a specified chemical composition can be used for the design of high-purity materials with unique physicochemical properties that could not be attained previously. In addition, these precursors with deliberately varied composition can serve for the development of components of ceramic composite materials (fibres, coatings and matrices) with specified construction properties. A particular benefit of poly(oligo)meric organoelement ceramic-forming precursors is the possibility to control the composition and structure of ceramic compositions at any level (microcrystalline, nanostructure or amorphous), which cannot be accomplished in full measure by any other known method.

7. Recent achievements in the synthesis of organoelement compounds with the phosphorus – carbon bond

As has already been noted in relation to silicon (see Section 5), development of a chlorine-free strategy for the synthesis of organoelement compounds is now a challenge. This Section of the review addresses the methods of chlorine-free synthesis of organophosphorus compounds (OPCs) and some of their most interesting chemical reactions.

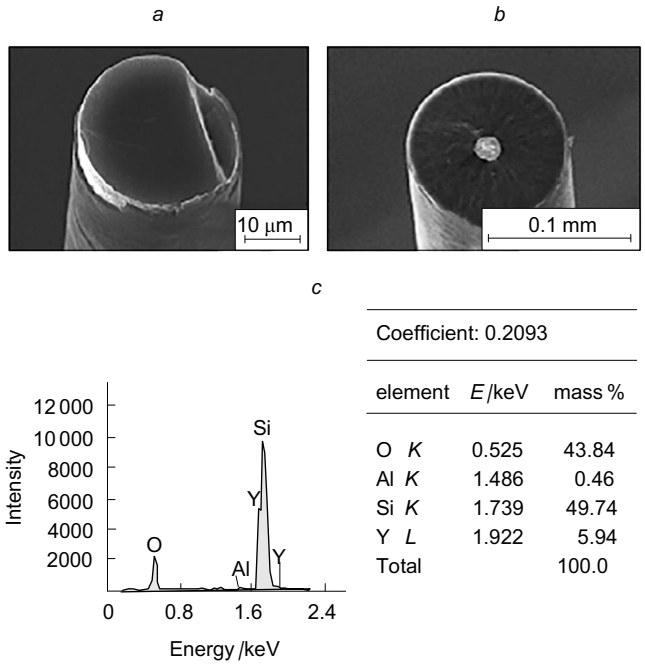


Figure 15. Surface micrographs (*a*, *b*) and elemental composition (*c*) of coreless (*a*) and cored (*b*) SiC fibres with the $Y_2O_3-Al_2O_3-SiO_2$ coating.[553]

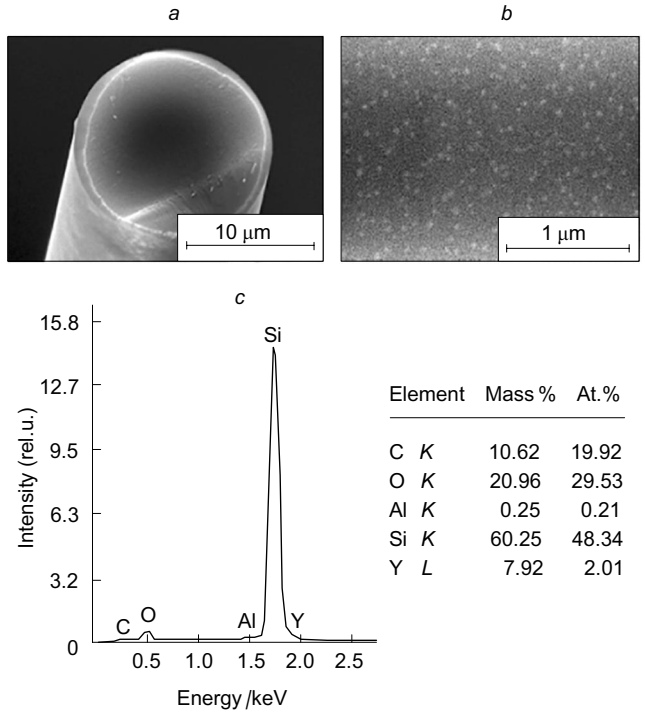


Figure 16. SiC fibre with the $x\,Y_2O_3-y\,Al_2O_3-z\,SiO_2$ glass ceramic coating.[554]
(*a*, *b*) SEM images of the end-face and lateral face, (*c*) X-ray elemental microanalysis data for the lateral face.

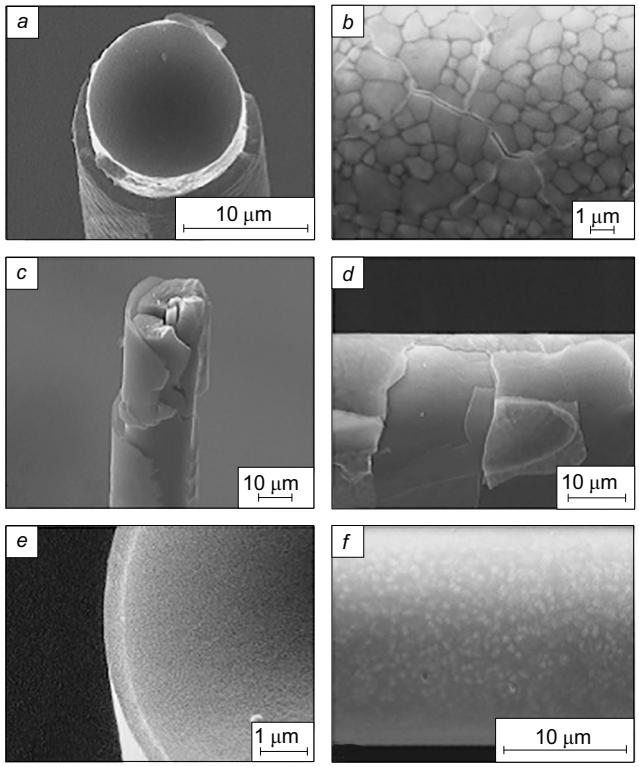


Figure 17. SEM images of the end-face and lateral face of SiC fibres.[554]
(*a*, *b*) Pristine fibres after heat treatment at 1500 °C in oxidizing atmosphere for 30 min; (*c*, *d*) pristine fibres after heat treatment at 1600 °C in oxidizing atmosphere for 60 min; (*e*, *f*) fibres with the $x\,Y_2O_3-y\,Al_2O_3-z\,SiO_2$ coating after heat treatment at 1600 °C in oxidizing atmosphere for 60 min.

The significance of OPCs with a phosphorus – carbon bond is related to their extensive use in medicinal chemistry, biochemistry and catalysis and in the design of materials with special properties.[555, 556] Compounds with the P – C bond exhibit anticancer, antibacterial and antiviral, including anti-HIV, activities, which has led to the synthesis of drug candidates based on them. The presence of the phosphoryl group substantially improves the hydrophilicity and bioavailability of organic molecules. Therefore, development of new efficient and atom-economical, first of all, catalytic methods for the formation of carbon – phosphorus bond is of considerable interest for modern synthetic organoelement chemistry. In recent years, phosphorylation strategies have been formed with the use of 1) superbasic media, 2) metal complex catalysis, 3) electrocatalysis, 4) radical initiators. The widely used phosphorylating agents include not only traditional phosphorus acid chlorides and esters and organic phosphines, but also elemental phosphorus and polyphosphides, which can be utilized for the development of production processes for OPCs with P – C bonds complying with green chemistry principles. Electrochemical and electromagnetic activation are commonly used for the transformations of elemental phosphorus.

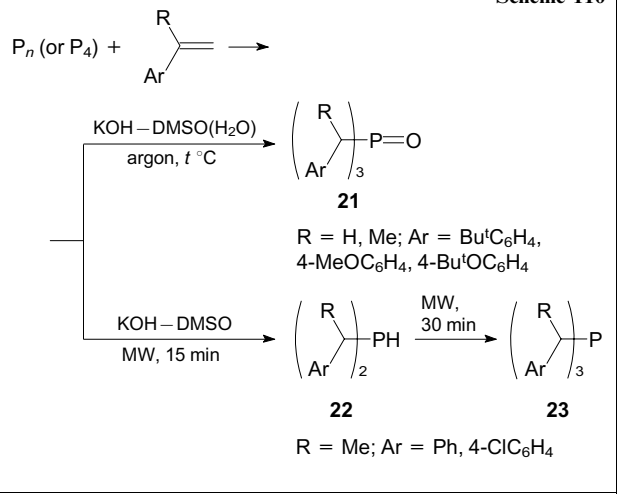
7.1. Chlorine-free strategy for the synthesis of compounds with the P – C bond

7.1.1. Phosphorylation of electrophilic compounds with elemental phosphorus in superbasic media

An important method for the formation of P – C bonds is based on reactions of elemental phosphorus (white P_4 or red P_n) with electrophilic alkenes, acetylenes and (het)aryl halides in superbasic media, which underlies a new chlorine-free process of OPC synthesis.[557] The activation of elemental phosphorus by superbasic systems such as alkali metal hydroxide – dimethyl sulfoxide[557] was used to develop convenient methods for direct phosphorylation of alkenes, acetylenes and aryl halides to afford previously unknown or previously hard-to-prepare OPCs such as organic phosphines, phosphine oxides and phosphinic acids.

In the KOH – DMSO superbasic system, elemental phosphorus rather easily phosphorylates weakly electrophilic alkenes such as styrene, 4-*tert*-butyl- and 4-alkoxystyrenes, 2-vinylnaphthalene and vinylpyridines giving tertiary phosphine oxides **21** (R = H, 30% – 77% yields) (Scheme 110).[557]

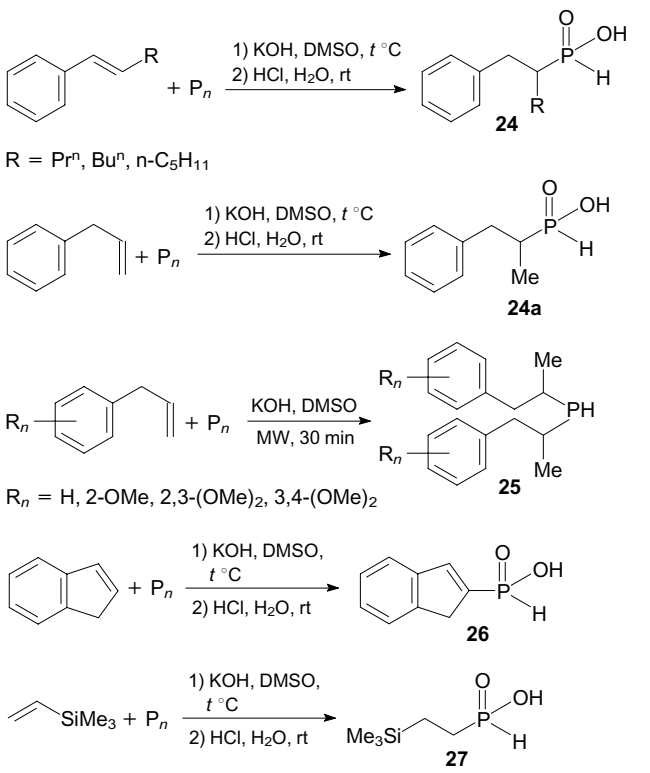
Scheme 110



The phosphorylation of α-alkylstyrenes with P_n in superbasic medium is regioselective and gives tris(2-phenylpropyl)phosphine oxides **21** (R = Alk) in 72% – 78% yields (see Scheme 110).[558] The course of this reaction changes fundamentally under additional microwave activation of the reactants (200 W) when the reaction gives predominantly either bis(2-arylpropyl)phosphines **22** (46% – 54% yields) (irradiation for 15 min) or tris(2-arylpropyl)phosphines **23** (69% – 77% yields) (irradiation for 30 min) (see Scheme 110).[558]

The phosphorylation of β-alkylstyrenes with red phosphorus in a superbasic medium follows a different route, giving rise to 1-alkyl-2-phenylethylphosphinic acids **24** in 34% – 40% yields (Scheme 111).[559] When allylbenzene is reacted with P_n in the KOH – DMSO system, 1-methyl-2-phenylethylphosphinic acid (**24a**) can be isolated as the major product (32% yield).[560] It is evident that the reaction is preceded by the prototropic isomerization of allylbenzene to β-methylstyrene. The microwave-assisted phosphorylation of allylbenzene[560] and methoxyallylbenzenes[561] in a P_n – KOH – DMSO suspension occurs with the participation of polyphosphide anions, which is confirmed by the formation of bis(2-aryl-1-methylethyl)phosphines **25** in up to 48% yield (see Scheme 111).

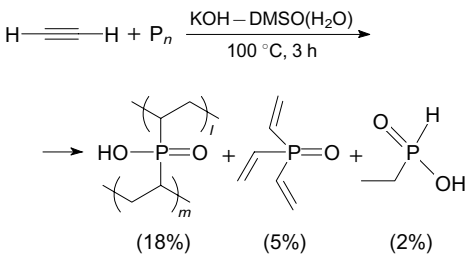
Scheme 111



1*N*-Indene[562] and vinyltrimethylsilane[563] react with P_n on heating in KOH – DMSO(H$_2$O) to afford the corresponding phosphinic acids **26** and **27** (see Scheme 111).

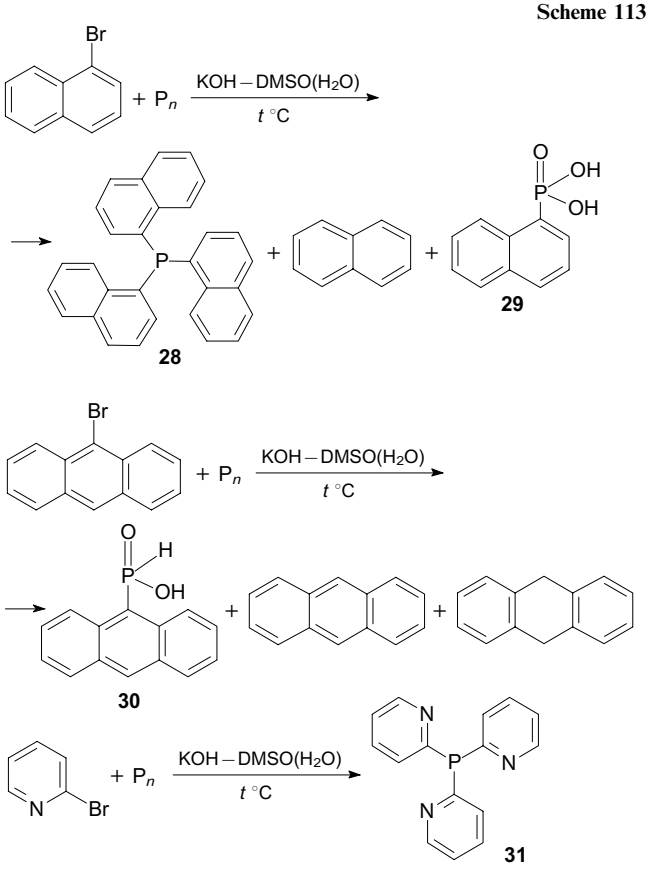
Elemental phosphorus in the KOH – HMPA(H$_2$O) superbasic system can generate polyphosphide anions, which add chemo-, regio- and stereoselectively to phenylacetylene to give tris[(*Z*)-styryl]phosphine (55% yield).[557] Unsubstituted acetylene is phosphorylated in a more complex manner. In the KOH – DMSO(H$_2$O) system, acetylene is phosphorylated by red phosphorus on heating at an elevated pressure; this reaction gives divinylphosphinic acid oligomers as well as ethylphosphinic acid and trivinylphosphine oxide (Scheme 112).[564]

Scheme 112



In the KOH – DMSO system, elemental phosphorus can phosphorylate aryl or hetaryl halides that are not prone to nucleophilic substitution reactions. In this system, P_n reacts with 1-bromonaphthalene, giving rise to tris(1-naphthyl)phosphine (**28**) and 1-naphthylphosphinic acid (**29**) in 10% and 4% yields, respectively (Scheme 113).[565] Microwave

Scheme 113



activation increases chemoselectivity of the reaction and, as a result, phosphine **28** can be obtained in 25% yield.[565]

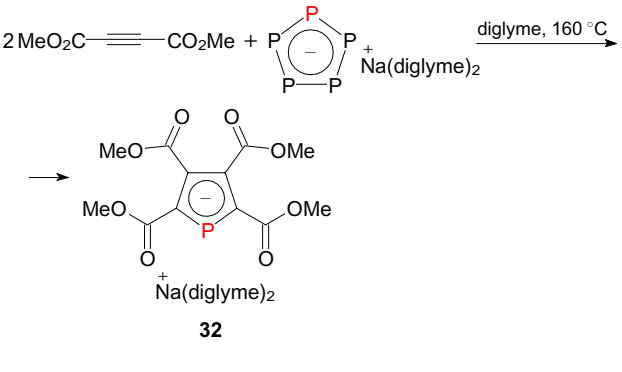
Phosphorylation of 9-bromoanthracene with P_n in a superbasic medium stops after the formation of 9-anthracenylphosphinic acid (**30**) in a yield of not more than 10% (see Scheme 113).[566] Meanwhile, considerable amounts of anthracene and 9,10-dihydroanthracene, resulting from anthracene reduction, can be isolated from the reaction mixture. These results contribute to the understanding of the mechanism of phosphorylation of weakly electrophilic aromatic halides with elemental phosphorus in highly basic multiphase systems.

As further development of these studies, phosphorylation of 2-bromopyridine with elemental phosphorus was carried out for the first time in a superbasic multiphase system. This afforded tris(2-pyridyl)phosphine (**31**) in a yield of up to 62% (see Scheme 113).[567] This and other above-described tertiary phosphines are considered as unique ligands for new-generation complex catalysts[568] or as building blocks in organic synthesis.[569]

7.1.2. Polyphosphides in the synthesis of metal phospholides and their derivatives

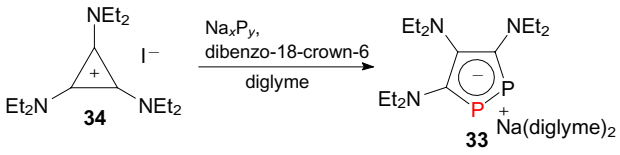
It has already been noted that activation and transformations of elemental phosphorus are accompanied by generation of various polyphosphides, which are also involved in phosphorylation. Alkali metal polyphosphides (*e.g.*, NaP_5 and Na_3P_7) are known to react with small molecules such as cyclopropenyl halides or acetylenes giving rise to phosphacyclopentadienyl (phospholide) anions — 1,2-di-[570] or 1,2,3-triphospholides,[571] respectively. The reactions of the same polyphosphides with half-sandwich nickel complexes, such as $[(\eta^3\text{-}C_3Ph_3)NiBr(PMe_2Ph)]$, proceed in a similar way.[572] Meanwhile, when sodium polyphosphides react with dimethyl acetylenedicarboxylate containing electron-withdrawing groups at the carbon – carbon triple bond, the reaction pathway changes, resulting in the formation of only sodium 2,3,4,5-tetra(methoxycarbonyl)monophospholide (**32**) (Scheme 114).[573]

Scheme 114



A new representative of 1,2-diphosphacyclopentadienide anions — 3,4,5-tris(diethylamino)-1,2-diphosphacyclopentadienide (**33**) containing electron-donating diethylamino groups at carbon atoms — was prepared for the first time in 73% yield by phosphorylation of 1,2,3-tris(diethylamino)cyclopropenyl iodide (**34**) with sodium polyphosphides (Scheme 115).[570]

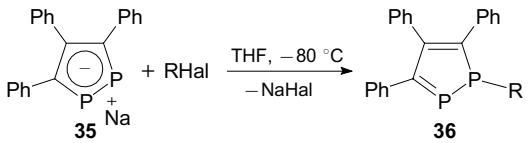
Scheme 115



Phospholide anions and their derivatives present considerable interest for the development of new compounds and materials with valuable properties, which can be useful as homogeneous catalysts or components of organic solar batteries and light emitting diodes.[574] For example, 1-alkyl-1,2-diphospholes are thermally stable and highly reactive towards cycloaddition reactions,[575] which allows for the design of various cage molecules based on them. In this connection, approaches have been developed to the synthesis of new 1-substituted 1,2-diphospholes by the reactions of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**35**) with alkyl halides.

It was found that sodium 1,2-diphosphacyclopentadienide **35** reacts with primary alkyl bromides to give 1-alkyl-1,2-diphosphacyclopenta-2,4-dienes **36** in 50% – 60% yields (Scheme 116).[575]

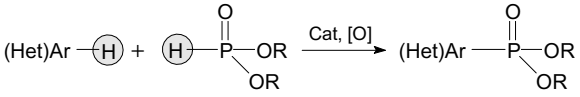
Scheme 116



7.2. Catalytic phosphorylation of arenes, alkenes and alkynes

In recent years, considerable interest has been aroused by phosphorylation of aromatic compounds (*N*,*N*-dialkylbenzamides and nitrobenzene, substituted furans, thiophenes, thiazoles, pyrroles, pyridines and their derivatives and other arenes) [576 – 578] with dialkyl phosphites and diarylphosphine oxides with radical initiation or with metal complexes as catalysts (Scheme 117).

Scheme 117



Cat are Ag, Cu, Mg, Pd and other compounds.

Among the synthetic approaches to bisphosphorylated products, considerable progress is associated with the participation of phosphorus-centred radicals in the reactions.[579 – 581] Several cascade reactions initiated by the addition of P-centred radicals to alkenes [582] and alkynes [583] have been reported.

The most recent advances in the phosphorylation of acetylene are related to reasonable selection of versatile catalysts that provide regio- and stereoselective addition of hydrophosphoryl compounds to various alkynes, resulting in phosphorylated alkenes.[584 – 586] The relative catalytic activity of metal complexes in these reactions depends on the metal nature and decreases in the series Ni > Pd > Rh > Pt. It was established that the reactivity of hydrophosphoryl compounds depends on the nature of substituents at the phosphorus atom and decreases in the series $PR_2 > P(O)R_2 > P(O)(OR)_2$. The mechanisms for alkyne phosphorylation catalyzed by transition metal complexes have been proposed.[587]

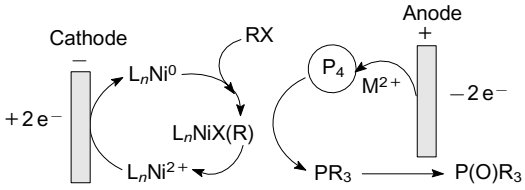
7.3. Electrocatalytic phosphorylation

Extensive opportunities for the synthesis of organophosphorus compounds are opened up by the use of unconventional methods, first of all, electrochemical ones, which combine the benefits of usual homogeneous chemistry in solution and electrochemistry, where reactants are generated at the electrodes directly in the reaction system. The interest in the organic electrosynthesis is caused by several factors, including mild conditions (room temperature, atmospheric pressure), the possibility of conducting reactions in a closed system with a low concentration of the catalyst, which is readily regenerated.[588 – 592]

For example, electrosynthesis of OPCs directly from white phosphorus and alkyl, perfluoroalkyl (Alk^F) or aryl halides has been performed in the presence of electrochemically generated nickel complexes in low oxidation states.[589 – 594] The co-electrolysis of organic halides and a white phosphorus emulsion in DMF in the presence of the $NiBr_2$(2,2′-bipy) complex proceeds to a high conversion of P_4 and gives the target tertiary phosphines and phosphine oxides (Scheme 118).

Another approach to the synthesis of these compounds is based on phosphorylation reactions of aryl, hetaryl or perfluoroalkyl halides with organic chlorophosphines catalyzed by electrochemically generated nickel(0) complexes (Scheme 119).[590 – 594]

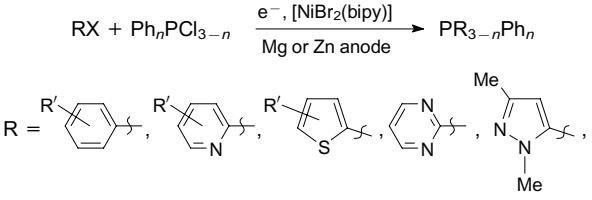
Scheme 118



Cathode: $L_nNi^{2+} \xrightarrow[-L]{2e^-} L_{n-1}Ni^0$ Anode: $M \xrightarrow{-ne^-} M^{n+}$

L = 2,2′-bipy; R = Ar, Alk^F M = Mg, Zn, Al; *n* = 2, 3

Scheme 119

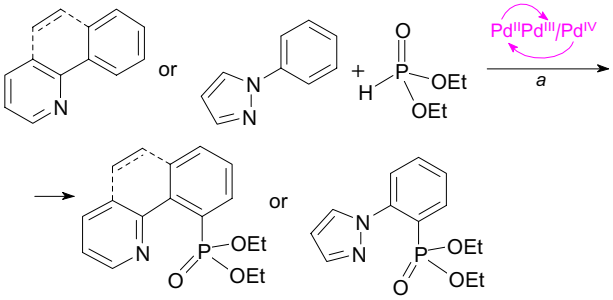


$(CF_2)_5CF_2H$, $(CF_2)_5CF_3$ (R′ = Me, OMe, NMe_2, CN, CO_2Et, Ac); *n* = 0, 1

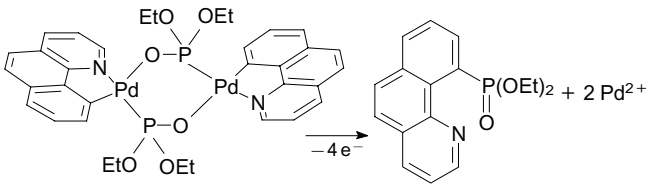
High selectivity and mild conditions of the reaction lead to high conversion of phosphorylating agents even in the absence of supporting electrolytes.

Recently, an electrochemical method has been proposed for oxidative phosphorylation of some aromatic and N-aromatic compounds with dialkyl phosphites in the presence of palladium and other metal (nickel, cobalt, manganese) salts.[595 – 605] An example is successful ligand-directed oxidative phosphonation of N-aromatic compounds [2-phenylpyridine (phpy), benzo[*h*]quinoline (bhq), 2-phenylpyrazole (phpz)], which acted as both the substrates and the ligands directing the process towards the *ortho*-position *via* com-

Scheme 120



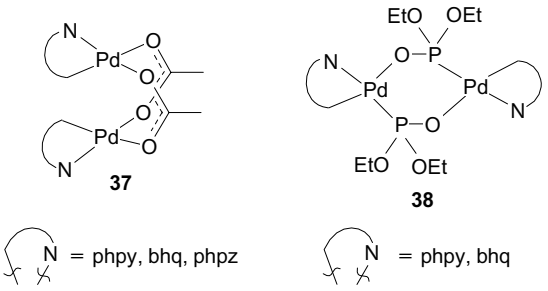
(*a*) $Pd(OR)_2$ (10 mol.%), −2e⁻, +1.3 V (relative to Ag/Ag^+), MeCN; R = Ac, $CF_3C(O)$



plexation of the catalyst metal atom to nitrogen (Scheme 120).[595 – 599]

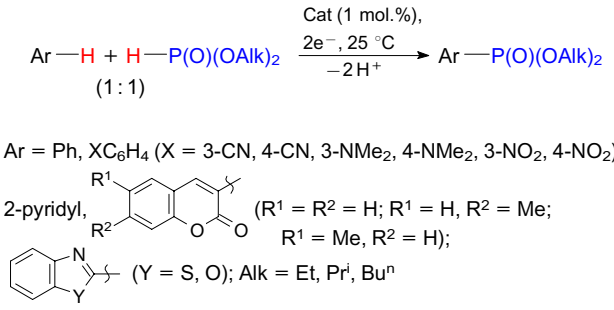
It was shown that both acetate-bridged dimeric palladium complexes **37** and phosphite-bridged binuclear metallocyclic compounds **38** can arise as intermediates of the C – H phosphorylation.[595, 596, 598] It is noteworthy that the geometry of binuclear palladium complexes depends on the nature of the bridging ligand, which affects their reactivity. Preparative oxidation of isolated phosphite-bridged binuclear complexes has shown that the Pd^{II}/Pd^{IV} pair is likely to operate in the catalytic cycle,[596, 597, 599] which provides complete conversion of these metallacycles to the desired phosphorylated N-arene.

Structures 37, 38



A new approach has been proposed for phosphorylation of C – H bond of arenes with both electron-withdrawing and electron-donating substituents in the ring as well as coumarin,[600 – 604] azole[605] and pyridine[606] derivatives on treatment with hydrogen phosphoryl compounds (Scheme 121). For example, co-oxidation of arene and dialkyl phosphite (1 : 1) under mild electrochemical conditions (room temperature, atmospheric pressure) catalyzed by a new Mn^{II}/Ni^{II} system results in the formation of dialkyl arylphosphonates in high yields (up to 70%) and complete conversion of the phosphorylating agent.[600 – 604]

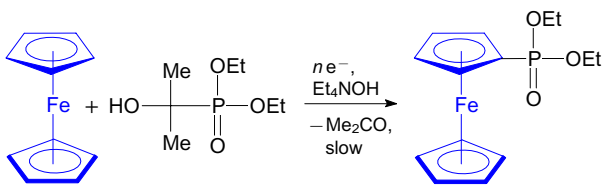
Scheme 121



The CH/PH functionalization of arylphosphine oxides with alkynes catalyzed by silver acetate allows one to directly prepare benzo[*b*]phosphole oxides in high yields.[607]

A new approach has been developed for the synthesis of phosphorus-containing ferrocenes based on electrochemical reduction of a mixture of ferrocene and α-hydroxyethylphosphonate at –50 °C.[608] This process affords the target diethyl ferrocenylphosphonate in one step in a high yield (87% – 89%) with complete conversion of the phosphorylating reagent.

Scheme 122



It has been shown experimentally that the reaction involves the intermediate formation of the radical anion on the ferrocene ligand (Fig. 18).

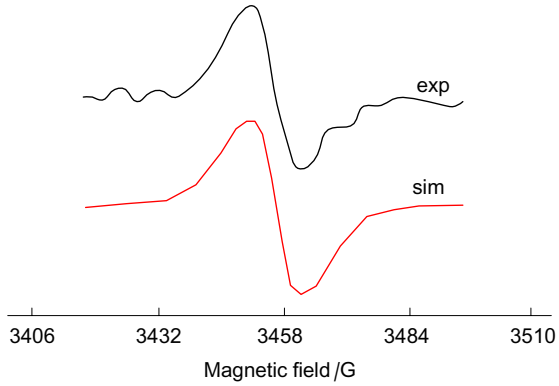


Figure 18. Experimental (exp) and simulated (sim) EPR spectra of ferrocene radical anion in DMF at –3.3 V and –50 °C.[608]

7.4. Polycyclic and cage organophosphorus compounds

Quite a number of publications are devoted to the development of methods of synthesis and investigation of the properties of polycyclic and cage phosphorus compounds, which are formed with participation of various types of endocyclic P – X bonds (X = N, C, O, S). Therefore, development of synthetic routes to such compounds containing P – C bonds is a subject of continuous attention of researchers. Of particular importance is the search for new phosphorylating reagents that provide regio- and stereoselective formation of these polycyclic and cage structures.

7.4.1. Dioxaphospholes: new phosphorylating reagents in the synthesis of hetero- and polycyclic organophosphorus compounds

In recent years, attention of researchers has been drawn to phosphorus-containing analogues of naturally abundant coumarin and α-chromene heterocyclic systems, namely, areno[*e*]-1,2-oxaphosphorins (phosphacoumarins) containing an endocyclic P – C bond. Their synthesis is based on the reaction of *P*,*P*,*P*-trihalobenzo[*d*]-1,3,2-dioxaphospholes **39** with aryl- and alkylacetylenes discovered in the 1990s.[609] The process includes the *ipso*-substitution reaction, in which oxygen in the heterocycle is replaced by carbon and C – C, P – C and P=O bonds are simultaneously formed and which is accompanied by regioselective halogenation of the aromatic ring into the *para*-position relative to the oxaphosphorin oxygen; this can be used to synthesize substituted phosphacoumarins in high yields. The *ipso*-substitution and halogenation are determined by the nature of the substituent in the benzene ring of the

initial 1,3,2-dioxaphosphole: the presence of a halogen atom or the electron-donating methyl or *tert*-butyl group in the *para*-position relative to the oxygen atom directs the *ipso*-substitution to displace this oxygen atom and directs halogenation to the *para*-position to the endocyclic oxygen atom.[609] The reaction can proceed only for chloro- and bromobenzophospholes (X = Cl, Br), which can react with not only arylacetylenes, but also with alkylacetylenes.[610] In the latter case, benzoxaphosphorins **40** – **42** are formed in > 80% yield (for product **40**) (Scheme 123).

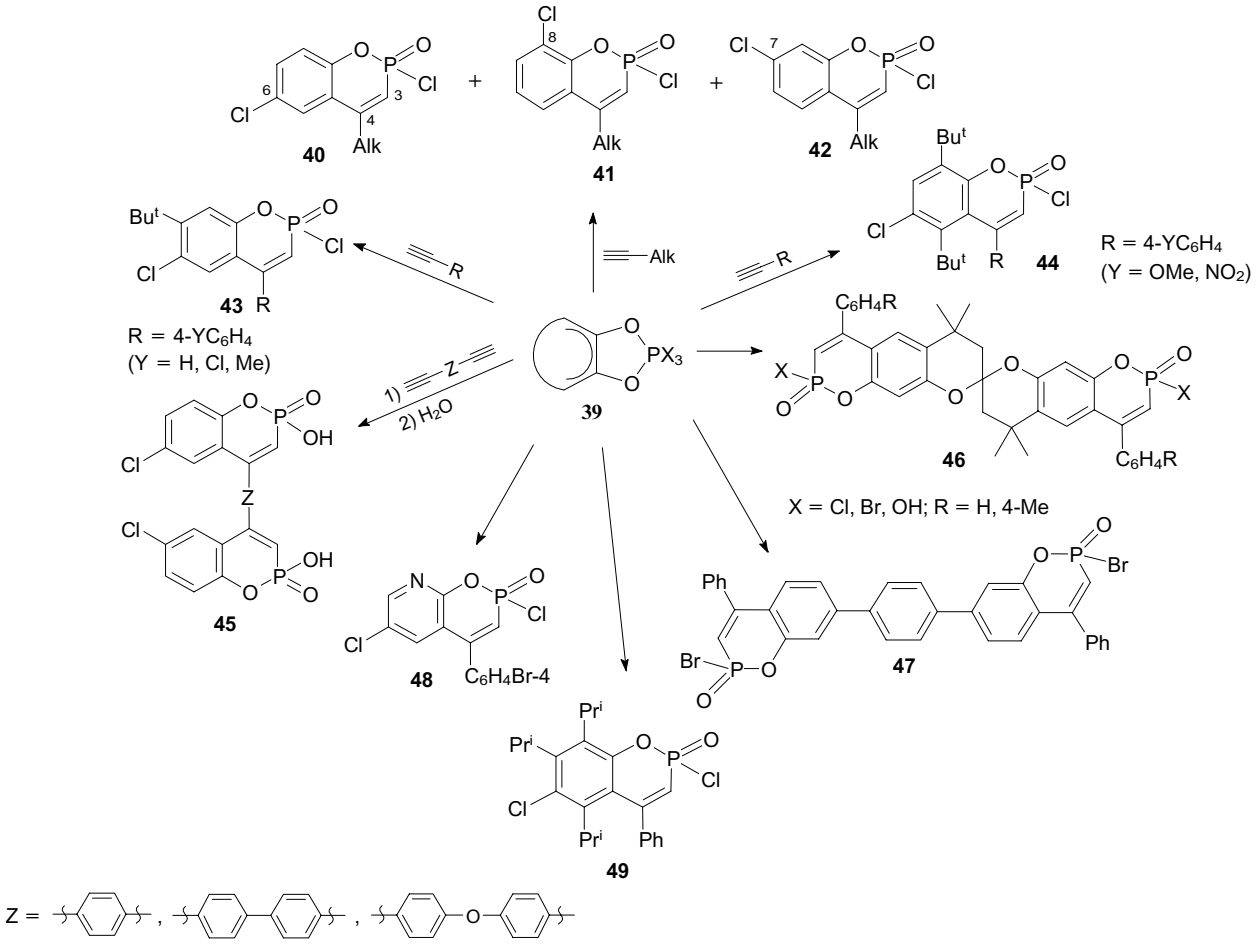
The reactions of 5-*tert*-butyl-2,2,2-trihalobenzo-1,3,2-dioxaphospholes containing a bulky substituent in the *para*-position relative to one dioxaphosphole oxygen with aryl- and alkylacetylenes have been studied.[611] The reactions give predominantly 4-aryl-7-*tert*-butyl-2,6-dichloro-2-oxobenzo[*e*]-1,2-oxaphosphorins **43** (70% – 73% yields). The introduction of a nitro group or a methoxy group into arylacetylene molecule does not hamper the formation of phosphacoumarins **44**.[612] 4-Arylbenzo-1,2-oxaphosphorin derivatives were obtained by the reactions of 2,2,2-trichlorobenzo-1,3,2-dioxaphosphole with 2(3,4)-methoxy-, 3,4-dimethoxy- and 2,3,4-trimethoxyphenylacetylenes.[613]

Dioxaphospholes **39** react with aromatic diacetylenes at 20 °C (CH_2Cl_2), with the subsequent hydrolysis leading to bis-phosphonic acids **45** — bis(benzo-1,2-oxaphosphorin 2-oxide) derivatives spacered by a *p*-phenylene, 4,4′-biphenyl or 4,4′-oxydiphenyl bridge in position 4.[614] The method has also been extended to more complex dioxaphospholes comprising a polyphenol system, which react with arylacetylenes to give bis(phosphorin) derivatives **46**[615] and **47**.[616] Phosphorin **48** containing a pyridine moiety instead of the benzene moiety[617] and compound **49** with three isopropyl substituents in the benzene ring[618] were also prepared.

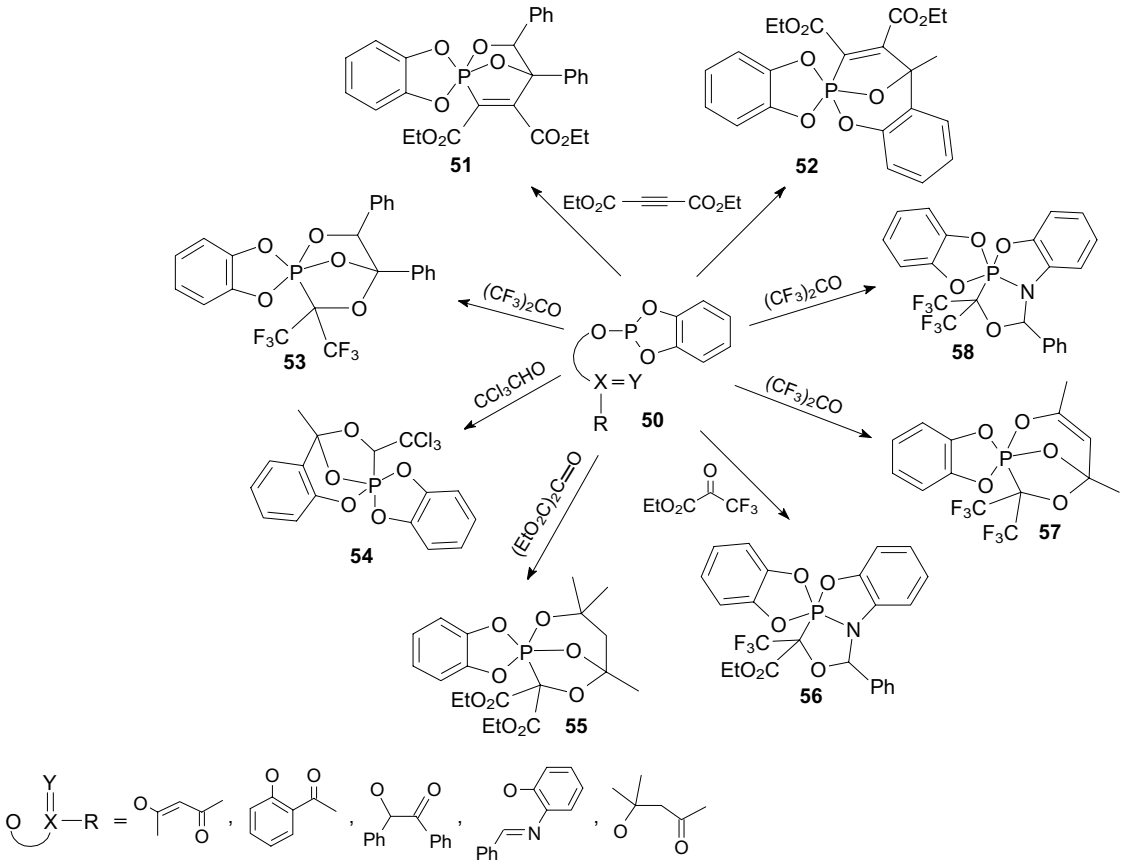
A new approach is being actively developed to the synthesis of polycyclic (cage) compounds of five-coordinate phosphorus with the P – C bond containing several chiral centres.[619] The approach is based on the reaction of benzo-1,3,2-dioxaphospholanes **50**, cyclic esters of three-coordinate phosphorus acids containing groups with a carbonyl or imino function in the γ- or δ-position to phosphorus as the exocyclic substituent, with compounds containing activated double bonds (carbonyl compounds, alkynes) (Scheme 124). The success of the approach being developed was demonstrated in relation to chloral, hexafluoroacetone, ethyl esters of trifluoropyruvic acid and other acids.[620, 621]

Benzodioxaphosphole derivatives **50** were converted, with high regio- and stereoselectivity, to cage phosphoranes **51** – **58** containing the P – C bond and several chiral centres. These reactions can be considered as versions of [4 + 2]- and [5 + 2]-cycloaddition followed by the P – C (or P – N) bond formation. Reactions of this type are possible not only for derivatives **50**, but also for substituted 1,3,2-dioxaphospholanes with a more nucleophilic phosphorus atom in the molecule.[622] The reaction of 4,5-dimethyl- and 4,4,5,5-tetramethyl-2-(2-oxo-1,2-diphenyl)ethoxy-1,3,2-dioxaphospholanes containing a carbonyl group in the γ-position relative to the

Scheme 123



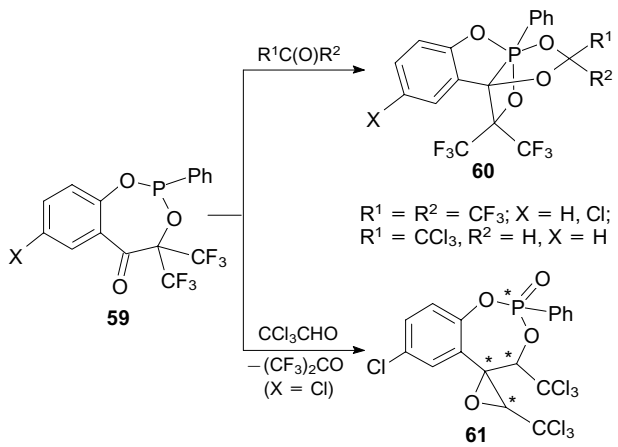
Scheme 124



phosphorus atom with hexafluoroacetone affords cage phosphoranes with P – C and P – O bonds with high stereoselectivity.[622 – 624]

In the presence of an endocyclic carbonyl group in the γ-position relative to P^{III}, the reactions of dioxaphosphepine **59** with chloral and hexafluoroacetone result in the formation of carbaphosphatranes **60** with five-coordinate phosphorus — stable intermediates of the Wittig reaction in which the P – C bond belongs to two five-membered ring and one four-membered ring (Scheme 125).[625, 626]

Scheme 125



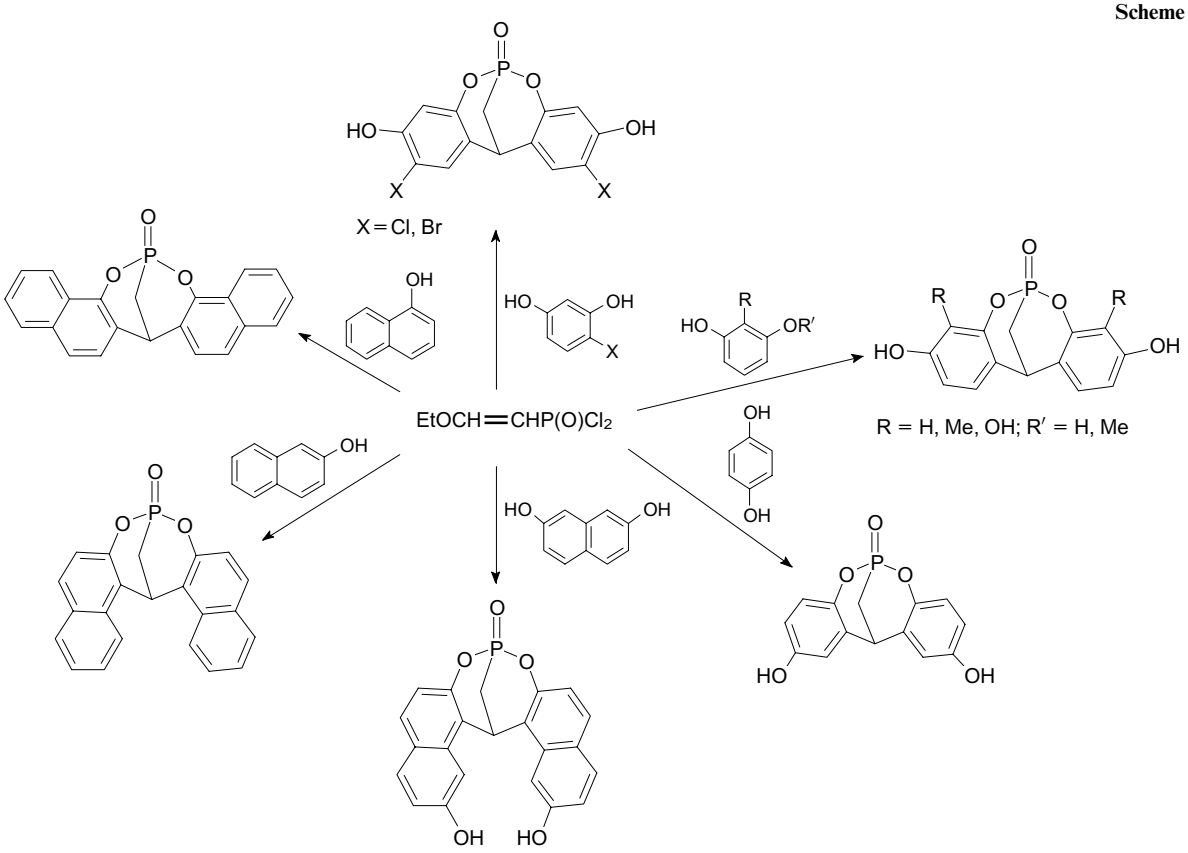
The pathway of the reaction between substrate **59** and chloral depends on the presence of chlorine in the benzene moiety; when X = Cl, the propeller structure **60** is formed as the minor product, while phosphepine **61** containing a spiro moiety is produced as the major product (70%) with high stereoselectivity.[627]

7.4.2. 2-Ethoxyvinylphosphonic dichloride as a versatile phosphorylating reagent in the synthesis of bicyclophosphonates

Published data on the synthesis of phosphorus-containing cage compounds formed by two endocyclic P – O bonds and one P – C bond are almost missing. The authors of this Section developed an original one-pot method for the preparation of this type of structures consisting in condensation of 2-ethoxyvinylphosphonic dichloride with various phenols in 1 : 2 ratio [pristine phenol, hydroquinone, α- and β-naphthols, resorcinol, 2-methylresorcinol, pyrogallol, 2,7-dihydroxynaphthalene, 4-bromo(chloro)resorcinol] and their monoethers (Scheme 126).[628 – 632]

This unexpected outcome is a result of previously unknown cascade reactions comprising intramolecular heterocyclization and electrophilic substitution in the intermediate compound with the phosphoryl group attached to an activated carbon – carbon double bond. The presence of terminal hydroxyl groups in the obtained bicyclophosphonates makes them promising platforms for the design of new structures — analogues of known antitumour agents (RAPTA-C, RAPTA-H, RAPTA-T). In addition, these compounds can serve as the starting reactants for the synthesis of other OPCs.

Scheme 126



7.5. Covalent self-assembly: a route to macrocyclic organophosphorus compounds

Development of methods for the synthesis of macrocyclic OPCs is a relevant task of organoelement chemistry, in view of the prospects of using these molecules as ligands in coordination chemistry and related fields: homogeneous catalysis and extraction of heavy metals. These compounds are considered as promising building blocks for supramolecular assembly. Usually, macrocyclic compounds are designed *via* conventional substitution, addition, condensation and metathesis reactions. In the case of synthesis of macrocyclic OPCs, the difficulty of isolation is related to the high phosphorus inversion barrier, resulting in the formation of stereoisomer mixtures if the ring contains two or more phosphorus atoms. All macrocyclic OPCs known by the end of the first decade of the 21st century and their main characteristics are surveyed in a monograph.[633]

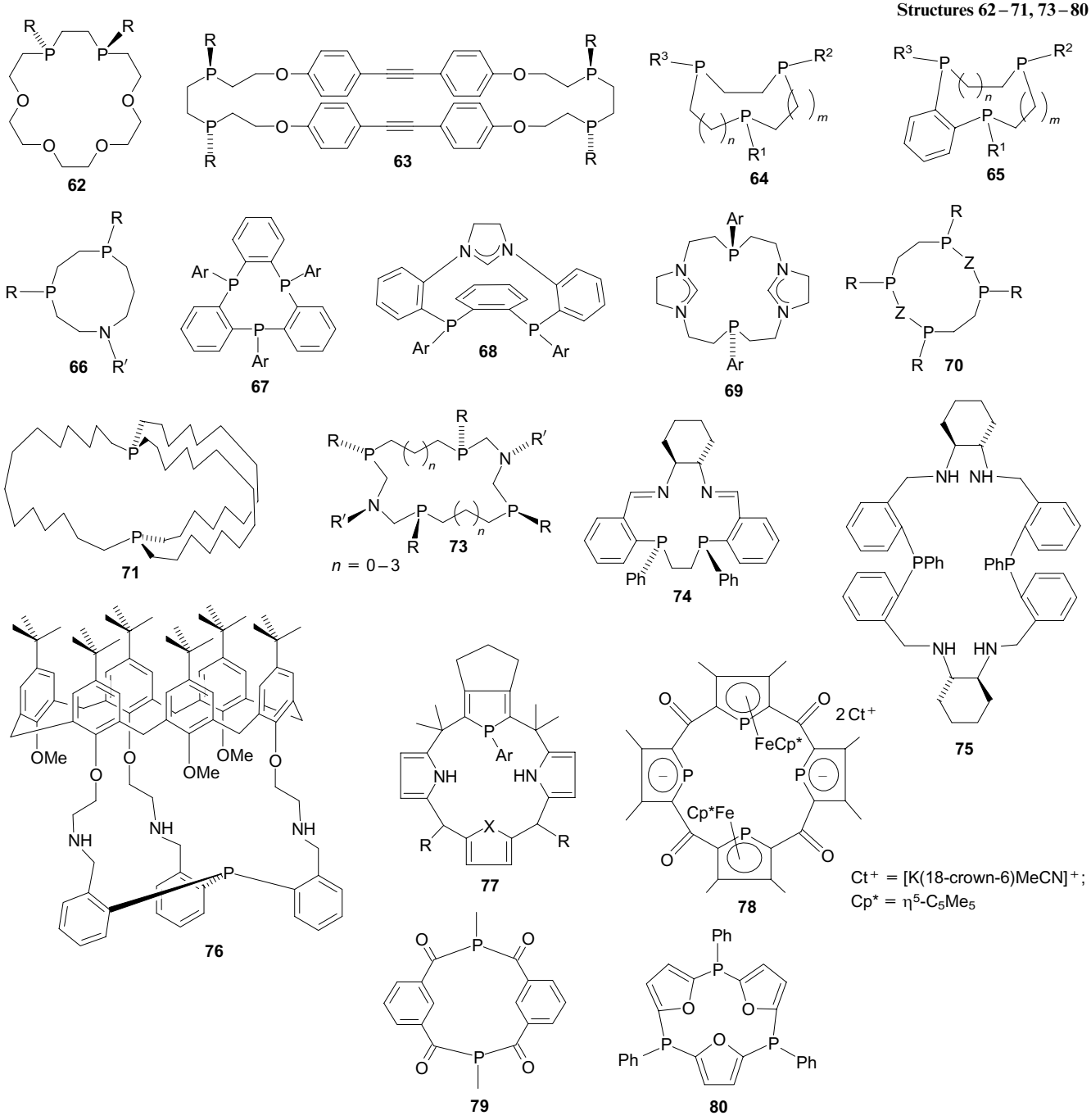
The synthesis of discrete macrocyclic OPCs requires special methods including the use of high dilution, reactant templating on a matrix containing metal ions or creation of conditions for the covalent self-assembly of macrocycles. These approaches have been utilized to prepare a number of macrocyclic OPCs, *e.g.*, bis- (**62**) and tetrakis-phosphines (**63**), cyclic trisphosphaalkanes **64** and their benzo derivatives **65**, **67**, P,N-containing macrocycles **66**, **68** and **69**, macrocyclic tetraphosphines **70** and bicyclic diphosphines **71**.[633]

The concept of covalent self-assembly was formulated recently and implies spontaneous formation of macrocyclic phosphines based on slow reversible reactions, for example, condensation. The reversibility of the process ensures the system self-correction and equilibrium shift towards the most stable or most easily removable macrocyclic product. The covalent self-assembly has extensive synthetic prospects in view of its high efficiency and easy implementation.

The self-assembly concept was proposed for the first time to interpret the efficiency of condensation reaction of primary phosphines with formaldehyde or primary aromatic diamines with spatially separated amino groups, which leads to various types of P,N-containing cage cyclophanes **72** with two 1,5-diaza-3,7-diphosphacyclooctane moieties incorporated into the macrocyclic structure (Scheme 127).[634 – 637] A similar reaction involving secondary bis(arylphosphino)alkanes ends in the isolation of a single stereoisomer of macrocyclic tetrakisphosphine **73**, with the type of diastereomer being determined by the even/odd number of methylene groups between the phosphorus atoms.[634, 638 – 641] It was shown that these types of macrocycles tend to have labile bonds in the $P-CH_2-N$ moiety, resulting in reversible interconversions of isomers[639, 642] and splitting into small rings.[640, 642]

The condensation of phosphinoaldehydes with chiral diamines resulted in P,N-containing macrocycles **74** (Refs 643 and 644) and **75**,[645] the transition metal complexes of which are enantioselective catalysts of ketone reduction.[646] Cryptands **76** were fabricated in a similar way from calix-6-arene bearing three amino groups in the upper-rim substituents.[647] The condensation of phosphatripyrans and 2,5-bis(hydroxymethyl)heterols resulted in the synthesis of several new P-containing porphyrin analogues **77**.[648] Structurally similar tri- and tetraphosphaporphyrinogens **78** were prepared using one-pot procedures.[649] A distinctive feature of this approach is the application of fluorodesilylation, resulting in ring expansion *via* migration

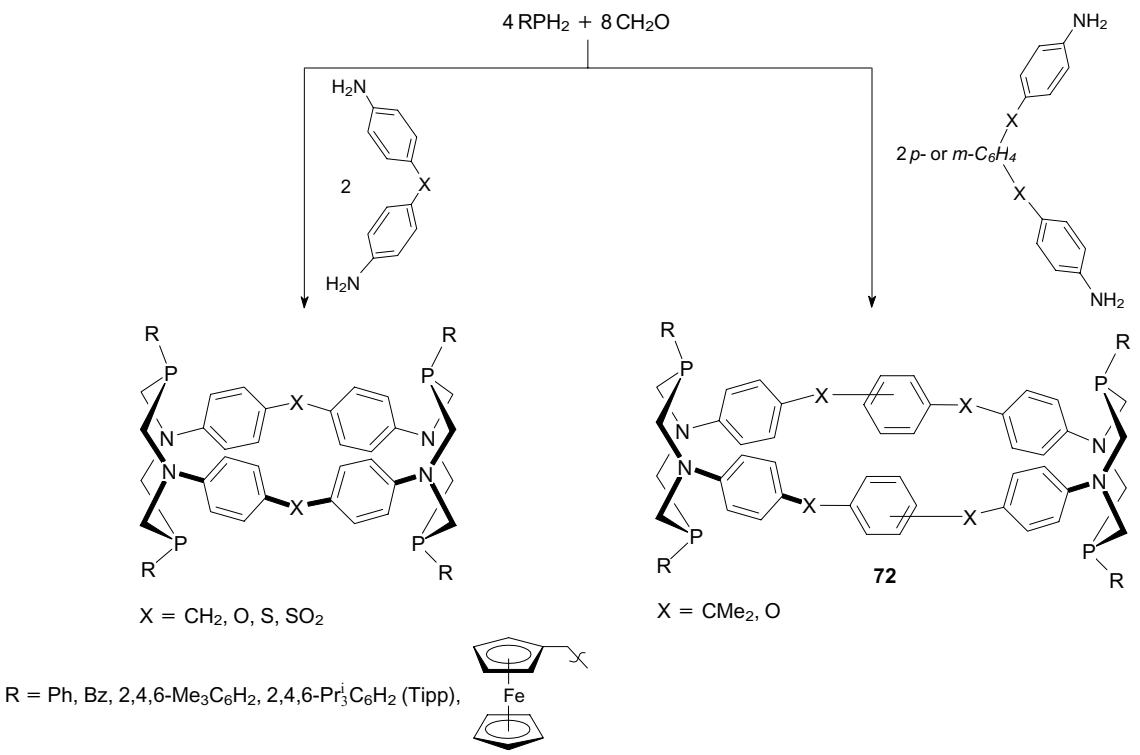
Structures 62 – 71, 73 – 80



of the intracyclic acyl group from phosphorus to carbon. Cyclophanes **79** (Ref. 650) and **80** (Ref. 651) with two and three phosphorus atoms in the macrocycle were prepared in a similar way. The successful conduction of these reactions as a one-pot procedure without using high dilution attests to covalent self-assembly of the listed macrocyclic OPCs.

Thus, the extensive interest in compounds with the P – C bond is largely associated with their practical applications. While looking for new methods of OPC synthesis, it is most advantageous to adhere to green chemistry principles, atom-economical and environmentally benign approaches, first of all, catalytic and chlorine-free processes which ensure the absence of wastes. Using these strategies, one can implement efficient routes to new types of OPCs, which serve as sources of practically valuable products for real economy and social sphere. Broad prospects for synthesis of heterocyclic, cage and macrocyclic OPCs are opened by both the application of new phosphorylating reagents and unusual synthetic concepts, in particular, covalent self-assembly. Integrated solution of these and other problems would boost further progress in this field of organoelement chemistry.

Scheme 127



8. Modern trends in the chemistry of organic sulfur, selenium and tellurium compounds

The details of p-element chemistry considered in the previous Section for phosphorus are also revealed in full measure in the reactivity of Group 16 elements. Among the up-to-date trends in the chemistry of organochalcogen compounds, especially obvious is the revived interest in the addition reactions of hydrogen chalcogenides to double and triple carbon – carbon bonds.[652 – 656] The reason is that these reactions can, as a rule, be accomplished quantitatively by a radical or nucleophilic mechanism,[657] without the need for transition metal-based catalysts, which complies with green chemistry principles. Indeed, hydrochalcogenation of unsaturated compounds proceeds at high rates under rather mild conditions in the presence of available radical initiators or on exposure to UV light. It is important that these processes are tolerant to the functional environment of the double and triple bonds. These studies are stimulated by special attention to the chemical processes that comply with the PASE (pot, atom and step economy) paradigm.[658, 659]

There is steady interest in the use of sulfoxides and sulfones as synthons and ancillary reagents in organic chemistry, in particular, in the total synthesis of natural compounds.[660] The use of sulfones for fabrication of various structures in enantiomerically pure configurations is considered in a number of reviews,[661, 662] which systematically arrange the key trends of using these sulfur compounds in organocatalytic reactions.

The electrophilic reactions (addition and aromatic substitution) of chalcogen halides with various alkenes, acetylenes and aromatic (heteroaromatic) compounds form another rapidly developing trend of the organochalcogen chemistry.[663 – 665] The results concerning selenium and tellurium analogues fundamentally supplemented the existing views on the reactivity of thiiranium and thiirenium cations — intermediates of electrophilic addition of sulfur chlorides to unsaturated hydrocarbons. A breakthrough along this line is associated with systematic use of selenium dihalides as reagents in organic synthesis.[664, 665]

This Section, which does not claim to exhaustively address all important trends of modern organochalcogen chemistry, presents the key results (mainly obtained in the last 10 years) related to the indicated research areas.

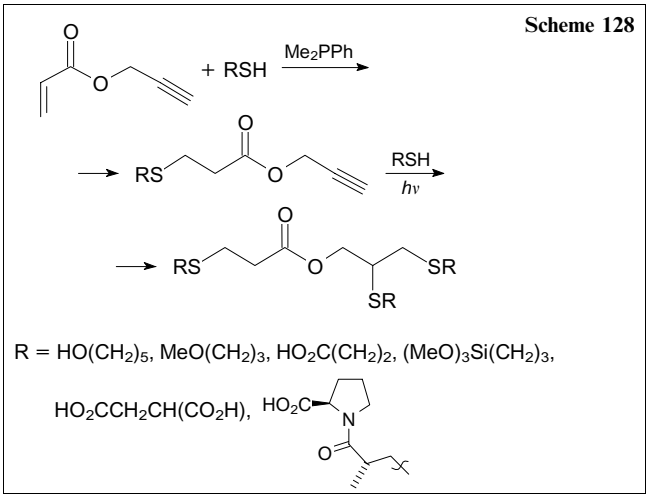
8.1. Hydrochalcogenation of unsaturated compounds

The atom-economical addition of thiols to double and triple bonds is actively used in practical organic synthesis, for example, to obtain polymeric materials with valuable properties.[654] These reactions usually proceed without metal catalysts. In most cases, the addition is quantitative and is distinguished by high anti-Markovnikov regioselectivity. By analogy with the cycloaddition of azides to acetylenes, these reactions are termed as thiol-ene click chemistry.[652 – 657] The popularity of this classical reaction has increased so rapidly that several reviews and monographs considering various aspects and prospects of this subject of chemistry appeared just in recent years.[652 – 656]

Radical-initiated thiol-ene reactions proved to be especially convenient for functionalization of polymers containing unsaturated moieties.[653 – 656] They are also used for the preparation of linear macromonomers.[655, 656] Using this approach, a general strategy of stabilization of polymer coatings has been developed.[654, 656] Electron-deficient alkenes (vinyl sulfones, methacrylates, fumarates, maleimides) easily add thiols under nucleophilic conditions; this reaction is catalyzed by tertiary amines and, in some cases, phosphines.[657] The products of these reactions are considered as promising materials for medicine, in particular, in dentistry.[666] For example, a facile synthesis of complex polyfunctional molecules was accomplished by successive nucleophilic and radical addition of substituted thiols

(including enantiomerically pure ones of natural origin) to double and triple bonds of propargyl methacrylate (Scheme 128).[657]

Scheme 128



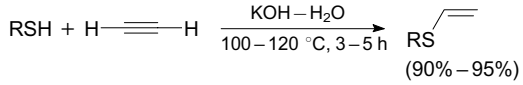
The thiol – ene coupling reactions are also successfully used in the fullerene chemistry.[654]

Development and improvement of rational approaches to the synthesis of vinyl chalcogenides is in progress; among them, mention should be made of new convenient and environmentally benign procedures for atom-economical vinylation of thiols, selenols and elemental chalcogens with acetylenes.[667 – 672]

The addition of thiols to acetylenes proceeds in most cases in the presence of bases[667] or, more rarely, it is catalyzed by metal complexes.[670] Particular attention is given to the search for conditions that would comply with modern green chemistry requirements. In particular, several latest publications emphasize the necessity to eliminate toxic organic media from the processes.[671] In this respect, a promising trend is the use of glycerol as a non-toxic recyclable solvent of natural origin.[669]

The modern environmental standards are met by the recently proposed highly efficient base-catalyzed vinylation of aliphatic and aromatic thiols with acetylene in water (KOH, 100 – 120 °C); vinyl sulfides are formed in 90% – 95% yields (Scheme 129).[671]

Scheme 129



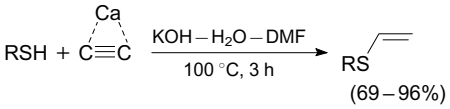
R = Alk, Ph

By analogy with the addition of thiols to alkenes,[652 – 656] the virtually quantitative vinylation of thiols with acetylene in water can be termed as the thiol-yne click coupling.

Recently, potassium thiolates have been vinylated with acetylene generated from calcium carbide and water in DMF.[672] The reaction proceeded on heating (100 °C) of reactants (CaC_2, RSH, KOH, H_2O at a molar ratio of 2 : 1 : 1.5 : 3) in DMF and gave the expected vinyl sulfides in high or good yields (Scheme 130).[672]

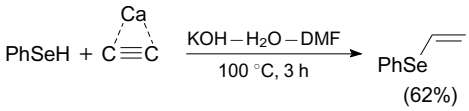
Phenyl vinyl selenide was prepared under similar conditions from benzeneselenol and calcium carbide (Scheme 131).[672]

Scheme 130

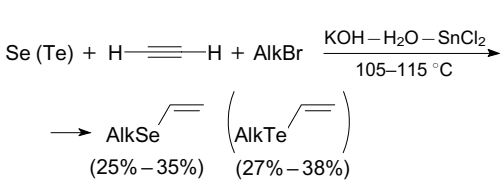


R = Alk, Ph

Scheme 131



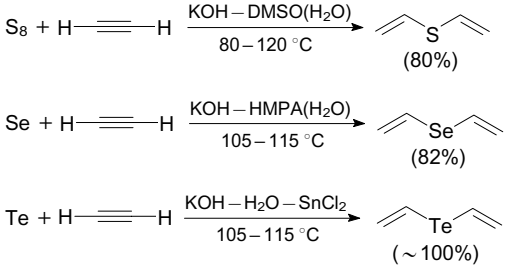
Scheme 132



The three-component reaction of chalcogens with acetylene and alkyl bromides in the KOH – H_2O – $SnCl_2$ system is still the most direct and simple approach to the synthesis of alkyl vinyl selenides and alkyl vinyl tellurides (Scheme 132).[668]

Similarly, chalcogens are vinylated with acetylene in the KOH – DMSO (or HMPA) superbasic system containing minor amounts of water to give the corresponding divinyl chalcogenides in high yield (Scheme 133).[668] Surprisingly, elemental tellurium quantitatively reacts with acetylene even in water under the action of highly basic reducing KOH – $SnCl_2$ system (see Scheme 133).[668]

Scheme 133



In these reactions (see Schemes 132, 133), superbases act as not only catalysts, but also reagents, being involved in the redox disproportionation of the element.[668]

Vinyl and divinyl chalcogenides,[668, 671, 672] which have become accessible, are now widely used as building blocks in organic synthesis, for example, for the preparation of phosphorus-containing organochalcogen compounds, in particular, by hydrophosphorylation.

8.2. Vinyl chalcogenides in hydrophosphorylation reactions

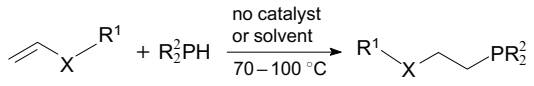
The atom-economical reactions of addition of H-phosphines and their chalcogenides to vinyl chalcogenides form the basis of a convenient one-pot strategy for the synthesis of promising semilabile ligands (containing both chalcogen and phosphorus atoms) for the design of metal complex catalysts,[673] drug precursors[674] and intermediates for the manufacture of nano-sized semiconductor materials.[675]

Traditionally, hydrophosphorylation of vinyl chalcogenides is carried out with radical initiators in organic solvents.[676] It has also been reported that vinyl phenyl sulfide reacts with diphenylphosphine in the Bu^{t}OK – DMSO system to give the anti-Markovnikov adduct in good yield.[677]

In recent years, a lot of attention has been concentrated on the development of non-catalyzed hydrophosphorylation reactions of vinyl chalcogenides without the use of organic solvents, especially those complying with modern PASE requirements.[658, 659]

It turned out that secondary phosphines easily react with vinyl phenyl sulfide[678] and alkyl vinyl selenides[679] only on heating (70 – 100 °C, N_2 or argon) without a catalyst and a solvent to form anti-Markovnikov adducts in high yields (Scheme 134).

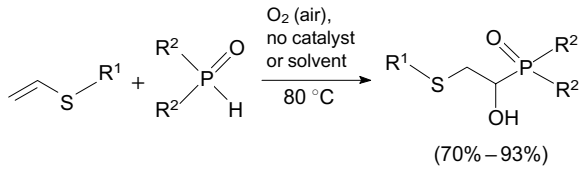
Scheme 134



R^1 = Alk, Ph; R^2 = $(CH_2)_2$Ph, Ph; X = S, Se

Under similar conditions (80 °C, argon, no catalyst or solvent), secondary phosphine oxides virtually do not react with vinyl chalcogenides.[680, 681] However, heating of vinyl sulfides with secondary phosphine oxides in air proceeds as oxidative rearrangement, resulting in unusual hydrophosphorylated products — 1-hydroxy-2-alkyl(aryl)sulfanylethyl(diorganyl)phosphine oxides (Scheme 135).[682]

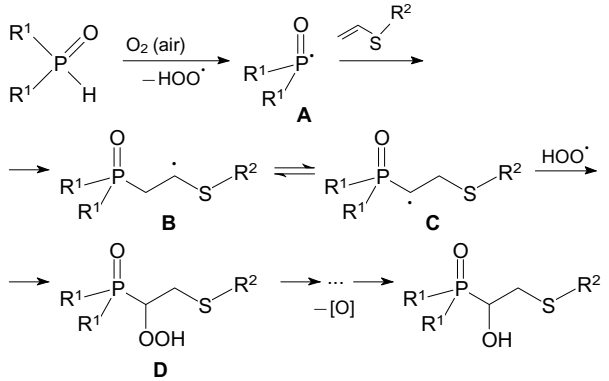
Scheme 135



R^1 = Alk, Ph; R^2 = $(CH_2)_2$Ar, $(CH_2)_2$Het, Ph

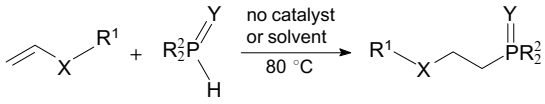
Probably, secondary phosphine oxides are oxidized with air oxygen to give phosphinoyl (**A**) and hydroperoxyl (HOO$^\bullet$) radicals. Phosphinoyl intermediates **A** attack the double bond to give radicals **B**, which are converted to radicals **C** upon proton transfer. Recombination of **C** with hydroperoxyl radicals generates adducts **D**, which are then converted to final products (Scheme 136).[682]

Scheme 136



Interestingly, vinyl sulfides and vinyl selenides react with secondary phosphine sulfides and phosphine selenides without a catalyst or solvent according to the anti-Markovnikov reaction pathway. The reaction readily occurs at 80 °C both in an inert atmosphere and in air (Scheme 137).[680, 681, 683]

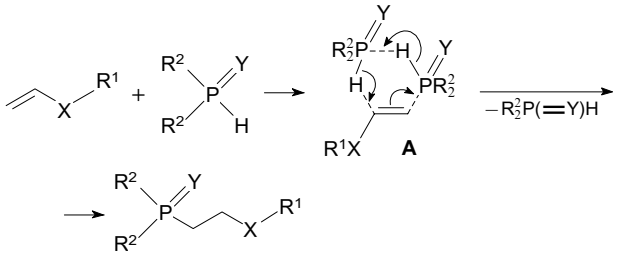
Scheme 137



R^1 = Alk, Ph; R^2 = $(CH_2)_2$Ar, $(CH_2)_2$Het; X = S, Se; Y = S, Se

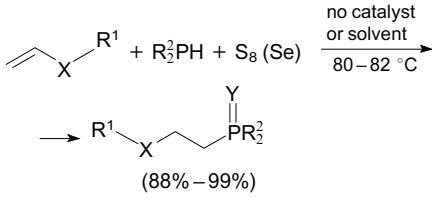
Apparently, these reactions proceed *via* six-membered transition state (**A**) (Scheme 138) with concerted electron transfer without preliminary formation of ions or radicals (the addition is equally smooth in the dark and in the presence of standard radical inhibitors).[681]

Scheme 138



The chalcogen- and phosphoryl-substituted sulfides and selenides obtained according to Scheme 137 were also synthesized in high yields by the three-component non-catalytic reaction between vinyl chalcogenides, secondary phosphines and elemental sulfur or selenium in the absence of a solvent at 80 – 82 °C (Scheme 139).[684]

Scheme 139

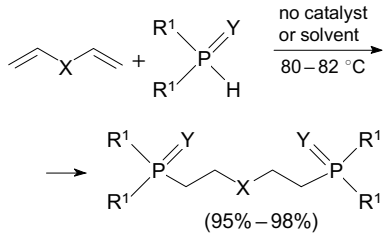


R^1 = Alk, Ph; R^2 = $(CH_2)_2$Ph, Ph, X = S, Se; Y = S, Se

Under similar conditions, divinyl sulfide and divinyl selenide react with secondary phosphine chalcogenides almost quantitatively to give the corresponding diadducts (Scheme 140).[685]

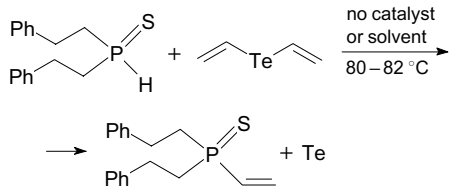
From the synthetic standpoint, it is important that divinyl telluride does not form hydrophosphorylated products under these conditions, but functions as a vinylating agent. When it reacts with bis(2-phenylethyl)phosphine

Scheme 140



$R^1 = (CH_2)_2Ph$, Ph; X = S, Se; Y = S, Se

Scheme 141

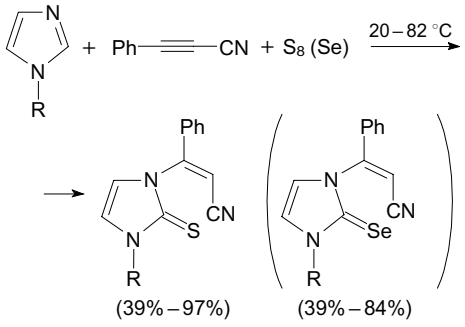


sulfide (80 – 82 °C, no catalyst or solvent), bis(2-phenylethyl)vinylphosphine sulfide is formed in 72% yield, instead of the expected bis-adduct, and tellurium metal is isolated (Scheme 141).[685]

8.3. Chalcogen – acetylene systems in three-component imidazole chalcogenation – vinylation reactions

The recently discovered stereoselective non-catalytic three-component reaction between chalcogens (sulfur or selenium), 1-substituted imidazoles and cyanophenylacetylene[686] serves for the preparation of 3-[(*Z*)-2-cyano-1-phenylethenyl]imidazole-2-thiones or -selenones, promising precursors of pharmaceuticals and drug candidates, in up to 97% yields.[687] In the case of elemental sulfur, the reaction easily proceeds even at room temperature without a solvent, whereas the reaction with elemental selenium requires refluxing in acetonitrile (Scheme 142).[686]

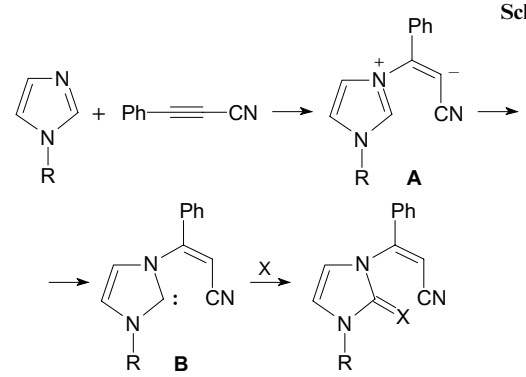
Scheme 142



R = Alk, Bn, All, $Bu^nS(CH_2)_2$

The reaction mechanism includes the formation of the zwitter-ionic imidazole adduct with cyanophenylacetylene (**A**), which is converted to carbene **B** upon proton transfer. The latter reacts with chalcogen to give 3-[(*Z*)-2-cyano-1-phenylethenyl]imidazole-2-thiones or -selenones (Scheme 143).[686]

Scheme 143



X = S, Se

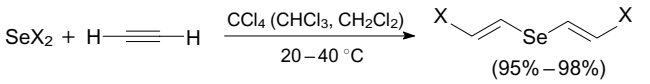
8.4. Electrophilic reactions of chalcogen halides

The regio- and stereoselective synthesis of organochalcogen compounds by the reactions of electrophilic reagents such as RSHal, S_2Cl_2, SCl_2, RSeHal, $RSeHal_3$, $SeHal_4$, $RTeCl_3$ or $TeCl_4$ has long been a highly important and efficient area of organochalcogen chemistry.

A noteworthy trend of the last decade is the use of new electrophilic reagents, selenium dihalides, in the synthesis of organoselenium compounds. These reagents were first introduced into organic synthesis at the A.E.Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the RAS, and showed high efficiency and selectivity for the preparation of new classes of organoselenium compounds.[665, 688] The first synthesis of organoselenium compounds based on selenium dihalides is the preparation of 1,4-selenasilafulvenes by the reaction with dimethyldiethynylsilane.[688] The efficiency of this approach was demonstrated in relation to many reactions that made it possible to prepare and study previously unknown classes of organoselenium compounds.[665, 688 – 695] Later, syntheses of new organoselenium compounds with the use of selenium dihalides have been developed in the USA and in Europe.[665, 696 – 699] For example, the first polyselenophene possessing high conductivity was prepared from 3,4-(ethylenedioxy)selenophene synthesized using selenium dichloride.[696]

The reaction of selenium dihalides with acetylene and its derivatives, including divinyl chalcogenides, have been systematically studied. An important result is the development of an efficient stereoselective method for the synthesis of (*E*,*E*)-bis(2-halovinyl) selenides — new promising intermediates for organic synthesis — based on addition of selenium dihalides to acetylene (Scheme 144).[689]

Scheme 144

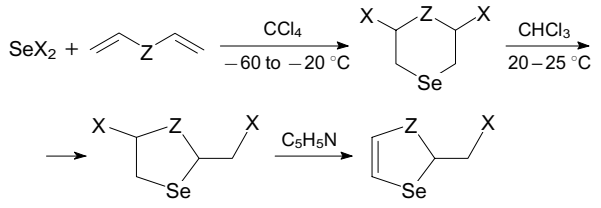


X = Cl, Br

The reactions of selenium dihalides with divinyl sulfide or divinyl selenide in carbon tetrachloride result in the formation of six-membered heterocycles — 2,6-dihalo-1,4-thiaselenanes or -diselenanes — in high yields (Scheme 145).[665] When dissolved in chloroform, these compounds spontaneously rearrange to five-membered 5-halo-2-halomethyl-1,3-thiaselenolanes or -diselenolanes. Under

the action of pyridine, these products are readily converted to 2-halomethyl-1,3-thiaselenoles or -diselenoles in 90% – 95% yields (see Scheme 145).[665] A one-pot method has been developed for the synthesis of 2-bromomethyl-1,3-thiaselenole in 95% yield from selenium dibromide and divinyl sulfide at room temperature.[690]

Scheme 145



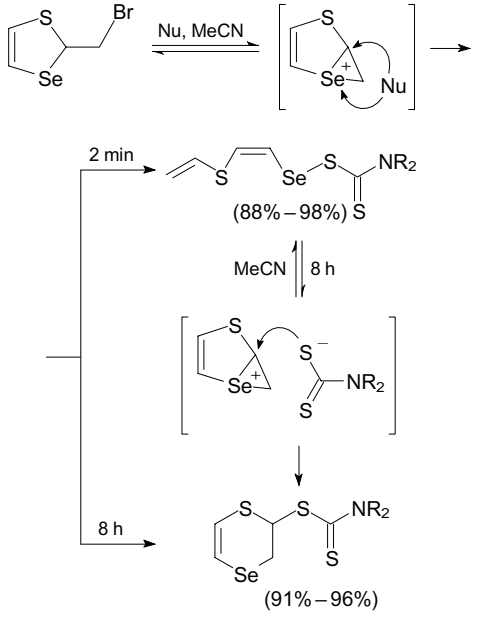
X = Cl, Br; Z = S, Se

The reactions of selenium dihalides with divinyl telluride do not lead to heterocycles under similar conditions; instead, halogenation of the tellurium atom takes place to give dihalodivinyltellanes in a quantitative yield. Thus, the nature of the chalcogen atom in divinyl chalcogenide dictates the pathway of the reaction with selenium dihalides.

2-Bromomethyl-1,3-thiaselenole is a basic reagent demonstrating unusual reactivity in nucleophilic substitution reactions as a result of anchimeric assistance of selenium and intermediate formation of the seleniranium cation conjugated with the endocyclic sulfanylethenyl group.[665, 690]

A regio- and stereoselective reaction of 2-bromomethyl-1,3-thiaselenole with sodium *N*,*N*-dialkyldithiocarbamate was found; the reaction proceeds in acetonitrile at room temperature in 2 min to give (*Z*)-2-{[(dialkylamino)carbothioyl]sulfanylselanyl}ethenyl vinyl sulfides in up to 98% yield. The reaction carried out for 8 h under similar conditions gives a high yield of 2,3-dihydro-1,4-thiaselenin-2-yl-*N*,*N*-dialkylcarbamodithioates, which are formed

Scheme 146



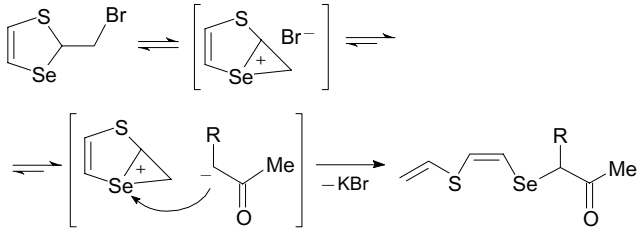
Nu = $Me_2NC(=S)S^-$, $Et_2NC(=S)S^-$; R = Me, Et

via rearrangement of kinetically controlled products (Scheme 146).[690]

According to quantum chemical calculations, the reaction proceeds *via* the seleniranium intermediate. The products were shown to result from the nucleophilic attack of the dithiocarbamate anion on the selenium atom of the intermediate seleniranium cation, affording the kinetic product, which is converted with time into the thermodynamic product. This is the first example of nucleophilic attack on the selenium atom of the seleniranium intermediate (see Scheme 146).[690]

An unexpected regio- and stereoselective reaction has been found between 2-bromomethyl-1,3-thiaselenole and C – H acids — acetone and ethyl methyl ketone.[691] The reaction proceeds at room temperature in an excess of these reagents in the presence of KOH and minor amount of water to give 1-[(*Z*)-2-(vinylsulfanyl)ethenylselanyl]alkan-2-ones within 1 min. The reaction occurs *via* the seleniranium intermediate with nucleophilic substitution at the selenium atom accompanied by ring opening and formation of the vinylsulfanyl group (Scheme 147).[691]

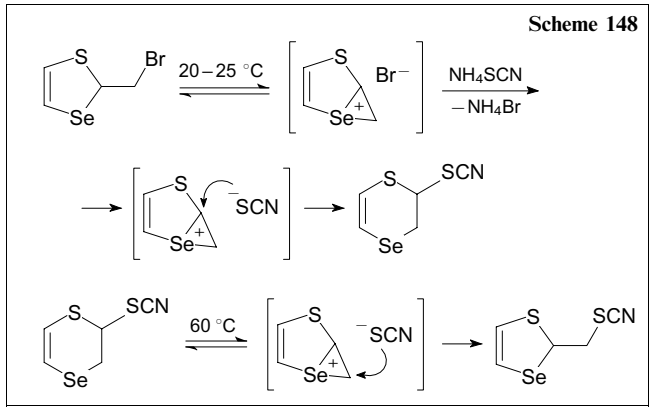
Scheme 147



R = H (82% yield), Me (76%)

The reaction of 2-bromomethyl-1,3-thiaselenole with ammonium thiocyanate in acetonitrile at room temperature results unexpectedly in a six-membered heterocycle, 2,3-dihydro-1,4-thiaselenin-2-yl thiocyanate, in 95% yield (Scheme 148).[665]

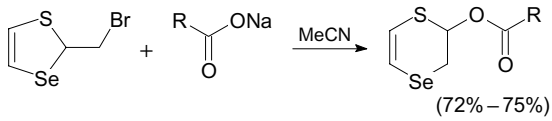
Scheme 148



However, under similar conditions at 60 °C, a five-membered heterocycle, 1,3-thiaselenol-2-ylmethyl thiocyanate, is formed. Monitoring the reaction has shown that 2,3-dihydro-1,4-thiaselenin-2-yl thiocyanate is the kinetic product, which rearranges at 60 °C with ring contraction being converted to the thermodynamic product, 1,3-thiaselenol-2-ylmethyl thiocyanate, with a five-membered ring (see Scheme 148).

Salts of carboxylic acids are known to be weak nucleophiles; esters are obtained, most often, by reactions of acids with alcohols rather than by the alkylation of salts. However, salts of carboxylic acids are readily alkylated with 2-bromomethyl-1,3-thiaselenole.[665] The reaction is accompanied by the rearrangement with ring expansion to give 2,3-dihydro-1,4-thiaselenine esters (Scheme 149).

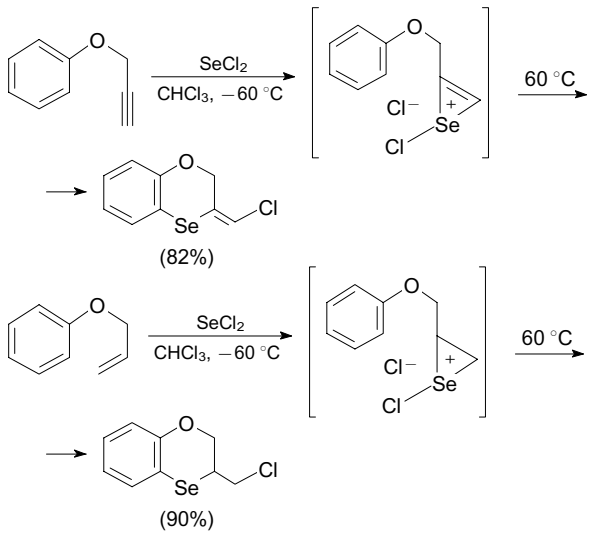
Scheme 149



R = Me, $H_2C{=}C(Me)$, 2-Fu, 2-Th

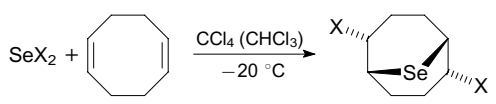
Chemo-, regio- and stereoselective methods have been developed for the synthesis of (*E*)-3-chloromethylidene- and 3-chloromethyl-2,3-dihydro-1,4-benzoxaselenines in high yields by reactions of selenium dichloride with propargyl and allyl phenyl ethers (Scheme 150).[692] These are the first cases of annulation of 3-chloromethylidene- and 3-chloromethyl-2,3-dihydro-1,4-oxaselenines to a benzene ring. The $SeCl_2$ addition to a double or triple bond occurs at −60 °C and the subsequent electrophilic aromatic substitution requires heating to reflux in chloroform. Presumably, the reaction proceeds *via* selenirenium and seleniranium intermediates.

Scheme 150



The transannular addition of selenium dihalides to *cis*,*cis*-cycloocta-1,5-diene proceeds chemo- and regioselectively to give 2,6-dihalo-9-selenabicyclo[3.3.1]nonanes in high yields (Scheme 151).[693, 694]

Scheme 151



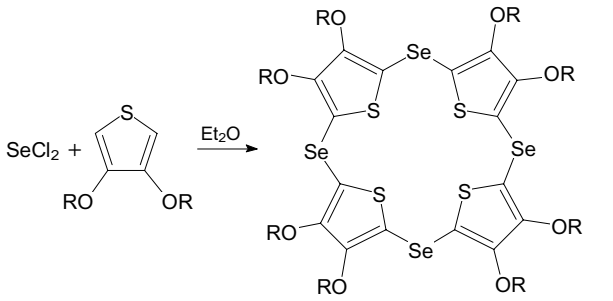
X = Cl, Br

The nucleophilic substitution of the halogen atom in the products of addition of selenium dihalide to alkenes was found to proceed very easily due to the anchimeric assistance effect. A quantitative estimation of the anchimeric assistance of selenium was carried out for the first time by measuring the rates of nucleophilic displacement of chlorine in 2,6-dichloro-9-selenabicyclo[3.3.1]nonane. The rate of nucleophilic substitution was more than an order of magnitude higher than that for similar compounds with sulfur or nitrogen atom instead of selenium.[693] Thus, the anchimeric effect of selenium atom markedly exceeds those of sulfur or nitrogen.

Numerous complexes with organic selenide ligands are known, in which the selenium atom gives off electrons to form a coordination bond.[663, 664] However selenium dichloride and dibromide are able to form complexes of a new type with organic ligands, in which selenium acts as the electron acceptor and the complex-forming atom. Selenium dichloride and dibromide complexes with organic selenides as ligands have been prepared for the first time and studied by X-ray diffraction analysis.[694] These are the first complexes the central moiety of which is composed of three selenium atoms.

Aromatic electrophilic substitution with selenium dichloride has been reported.[695] The ability of selenium dihalides to participate in such reactions opens up new prospects for the synthesis of heterocyclic compounds. Indeed, macrocyclic compounds comprising several thiophene rings have been prepared by reactions of selenium dichloride with 3,4-dialkoxythiophenes (Scheme 152).[697]

Scheme 152



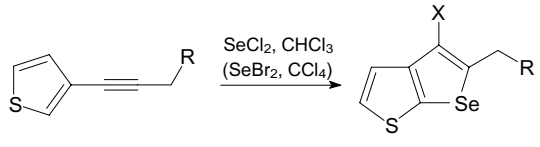
R = Me (83% yield), Hex (44%)

Efficient methods for annulation of the selenophene ring to the benzene or thiophene ring have been developed on the basis of selenium dihalides.[665, 698] For example, reactions of selenium dichloride with 2- and 3-ethynylthiophenes have been utilized in the methods of synthesis of selenopheno[3,2-*b*]thiophenes and selenopheno[2,3-*b*]thiophenes with potential biological activity (Scheme 153).[698]

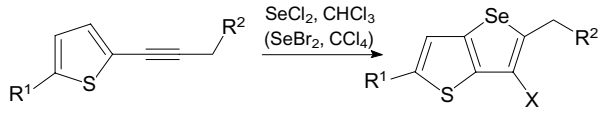
Recently, synthetic routes to linear and angular polycyclic heteroacenes based on chalcogen halides, in particular, selenium dichloride, have been developed.[699]

The reactions of tellurium tetrachloride and tetrabromide with acetylene have been carried out for the first time and comprehensively studied (Scheme 154).[665, 700] Conditions have been found for selective synthesis of either bisadducts, (*E*,*E*)-bis(2-haloethenyl)dihalotellanes, or monoadducts, (*E*)-(2-haloethenyl)trihalotellanes. Efficient methods for the synthesis of (*E*,*E*)-bis(2-haloethenyl)tel-

Scheme 153

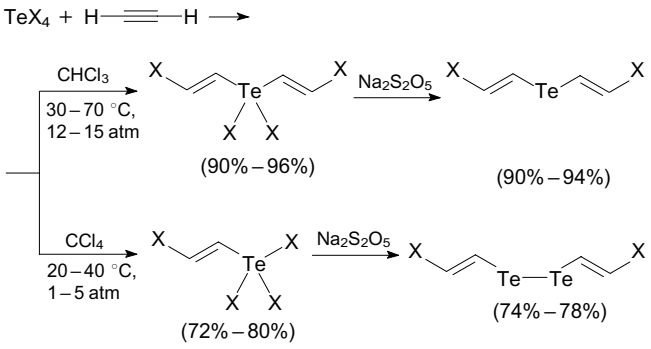


R = N(CH$_2$CH$_2$)$_2$O: X = Cl (99% yield), Br (91%)



R^1 = H, R^2 = N(CH$_2$CH$_2$)$_2$O: X = Cl, Br (99% yield);
R^2 = N(CH$_2$CH$_2$OMe)$_2$, X = Br: R^1 = Ac (71%), C(O)NH$_2$ (77%), SO$_2$NH$_2$ (84%)

Scheme 154



X = Cl, Br

lanes and -ditellanes by the reduction of these adducts were developed.

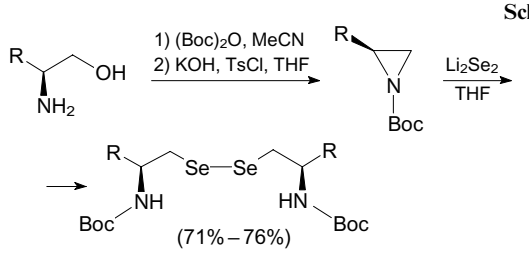
Unlike the reactions of $TeCl_4$ with substituted alkynes, which usually occur as *syn*-addition, the reactions with acetylene occur as *anti*-addition to give products as *E*-isomers, presumably, *via* the tellurirenium intermediate. These reactions are the first examples of *anti*-addition of tellurium tetrahalides to the triple bond of acetylenic hydrocarbons.[700]

The use of sulfur monochloride in organic synthesis has been described in detail in a review.[701]

8.5. Chiral organoselenium ligands in asymmetric synthesis

The application of chiral organoselenium compounds as ligands in asymmetric synthesis has been markedly extended in the last decade.[702 – 705] The benefits of using chiral organoselenium compounds as ligands are high enantioselectivity and accessibility. For example, chiral diorganyl

Scheme 155

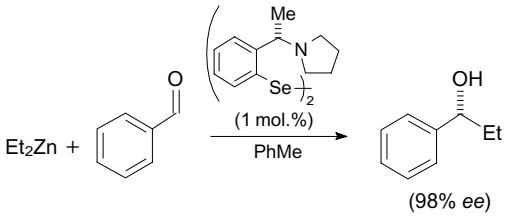


R = Bn, Pr^i, Bu^i, Bu^s

diselenides can be synthesized from accessible chiral amino alcohols (Scheme 155).[702 – 704] A similar reaction was used to prepare chiral diorganyl disulfides.[702]

The first synthesis of chiral alcohols by the addition of diethylzinc to aldehydes in the presence of chiral diorganyl diselenides was reported by Wirth and co-workers[703, 704] (Scheme 156). Lately, enantioselective reactions have been the subjects of keen attention of researchers.[702 – 705]

Scheme 156



It is noteworthy that reactions of diethylzinc with aldehydes can provide a high enantiomeric excess (up to 99%) for chiral alcohols with catalytic amounts (usually 0.5 mol.% – 1 mol.%) of chiral diorganyl diselenide.

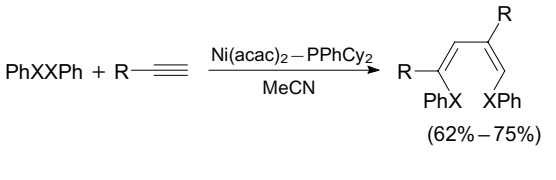
Chiral disulfides are also efficient as ligands for the enantioselective addition of diethylzinc to aldehydes yielding the corresponding chiral alcohols with enantiomeric excess of up to 99%.[702]

It was shown that chiral organoselenium compounds are applicable as ligands in enantioselective Heck reaction, hydrosilylation of ketones, asymmetric allylic alkylation and many other reactions.[703 – 705]

8.6. Reactions of organochalcogen compounds catalyzed by transition metal complexes

The interest in metal complex-catalyzed reactions giving carbon – carbon and carbon – chalcogen bonds has considerably increased in recent years.[703 – 707] A pronounced contribution to the development of regio- and stereoselective approaches to various classes of organochalcogen compounds based on catalysis by metal complexes was made by Beletskaya and Ananikov.[706, 707] Transition metal-catalyzed cross-coupling reactions and addition of chalcogen reagents to give carbon – chalcogen bonds have been described in detail in a review.[706] As an example, consider an elegant regio- and stereoselective synthesis of unsymmetrical 1,4-diphenylchalcogenyl-1,3-dienes by the nickel-catalyzed reaction of diphenyl dichalcogenides with alkynes (Scheme 157).[707]

Scheme 157

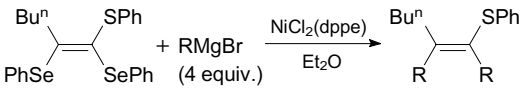


X = S, Se; R = Bu^n, n-C$_5$H$_{11}$, (CH$_2$)$_2$OH, CH$_2$NMe$_2$, C(OH)Me$_2$

The Suzuki, Sonogashira, Negishi, Heck and other cross-coupling reactions with organochalcogen compounds giving target products in high yields have been accom-

plished and studied.[703 – 707] The cross-coupling reactions of vinyl selenides and -tellurides are also efficient; they proceed with retention of the stereoconfiguration of the initial vinyl chalcogenide and give the corresponding vinyl derivatives of organic compounds.[663, 704] It is noteworthy that organylselanyl and especially organyltellanyl groups are, as a rule, more easily displaced in the cross-coupling reactions than analogous sulfur-containing groups. The Ni-catalyzed reaction of alkene containing two phenylselanyl and one phenylsulfanyl groups with a fourfold excess of the Grignard reagent leads to substitution of organic groups for two phenylselanyl groups, while the phenylsulfanyl group does not react (Scheme 158).[708]

Scheme 158



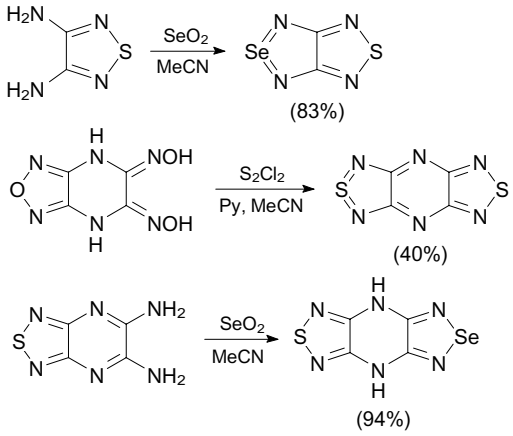
R = Bu^n (75% yield), n-C_8H_{17} (65%)

The hydrochalcogenation of alkynes with thiols and selenols and dichalcogenation of alkynes with diorganyl dichalcogenides catalyzed by transition metal complexes are, most often, regio- and stereoselective and give Markovnikov vinyl chalcogenides and (*Z*)-1,2-bis(organylchalcogenyl)ethenes, respectively.[704 – 706]

8.7. Other current trends in the chemistry of organochalcogen compounds

An important trend in the chemistry of organochalcogen compounds is the synthesis of heterocycles and charge transfer complexes and radical ion salts based on them, which are promising for the design of new conducting materials. In the last decade, a considerable contribution to the development of efficient methods for the synthesis of heterocyclic compounds containing chalcogen and nitrogen atoms was made by Rakitin's and Zibarev's research teams.[709 – 711] Some efficient approaches to the synthesis of diverse fused 1,2,5-thia- and -selenadiazoles are shown in Scheme 159.[709 – 711]

Scheme 159



Py is pyridine

A traditional and important trend of the chemistry of organochalcogen compounds is the development of syntheses of biologically active compounds, including those with glutathione peroxidase-like activity. A number of books and reviews[663, 664, 674, 687, 704] address the latest achievements in this field. Mention should be made of the stable trend of organochalcogen chemistry aimed at the design of environmentally benign and atom-economical synthetic routes either without solvents or with green solvents: water, glycerol, poly(ethylene glycol) or ionic liquids.[652 – 659, 663 – 672, 703 – 706]

Thus, this Section considers the modern trends of the chemistry of organic compounds of chalcogens, outlines the most promising synthetic approaches to practically valuable organochalcogen compounds, including those possessing biological activity. An important subject is still the regio- and stereoselective synthesis of organochalcogen compounds based on addition or substitution, heterocyclization and annulation reactions of hydrogen chalcogenides and selenium dihalides with unsaturated and aromatic or heteroaromatic substrates. The use of chiral organoselenium ligands in asymmetric synthesis; preparation of charge transfer complexes or radical ion salts based on chalcogen-containing heterocycles; and reactions catalyzed by transition metal complexes should certainly be mentioned among the modern, vigorously developing trends of the organic chemistry of chalcogens.

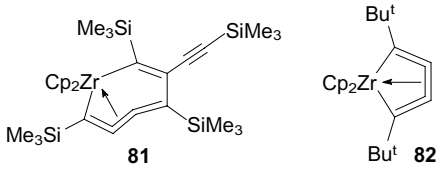
9. Seven-membered zirconacyclocumulenes: strained metallacycles distinguished by high thermal stability. Synthesis, structure and reactivity

The previous parts of the review (see Sections 2 – 8) consider organic compounds of s- and p-elements. Going to metals with the partially occupied d-electron shell gives rise to a set of new properties, in particular, the ability to stabilize unstable chemical systems *via* complexation. This remarkable feature of d-metal compounds is illustrated in the present Section in relation to zirconium; labile organometallic compounds will be considered below for nickel, palladium and platinum (see Section 10).

The chemistry of strained metallacycles containing an acetylenic bond or cumulated C=C bonds in the ring has appeared and is being intensively developed in the last decades. The great interest in these metallacycles is caused by their remarkably high thermal stability compared with their purely organic analogues. The first strained metallacycle of this type, synthesized by Buchwald and co-workers in 1993,[712] was a seven-membered zirconacyclocumulene complex of zirconocene — $Cp_2Zr[\eta^4$-$Me_3SiC{=}C{=}C{=}C(SiMe_3){-}C(C{\equiv}CSiMe_3){=}CSiMe_3]$ (**81**) containing a [3]cumulene group in the ring. In a little while, an even more strained zirconacycle $Cp_2Zr(\eta^4$-$Bu^tC{=}C{=}C{=}CBu^t)$ (**82**), containing the [3]cumulene moiety in the five-membered ring, was obtained.[713]

It is noteworthy that, unlike cyclohepta-1,2,3-triene and cyclopenta-1,2,3-triene, which are either short-lived intermediates or do not exist at all under ambient conditions,[714] metallacycles **81** and **82** are quite stable compounds remaining unchanged at room temperature for indefinite periods of time. Subsequently, numerous analogues of compounds **81** and **82** [713, 715 – 720] as well as various strained metallacycloallenes [387, 721 – 727] and metallacycloalkynes [728 – 733] have been prepared and fully characterized.

Structures 81, 82



Below we consider the available published data on the synthesis, structure and reactivity of seven-membered zirconacyclocumulene complexes.

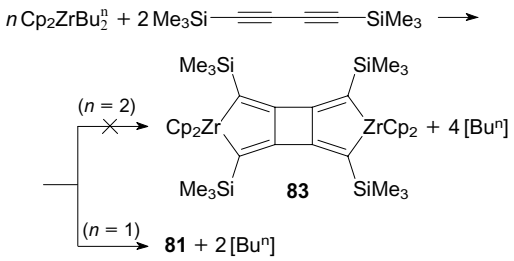
9.1. Methods of synthesis

Several methods for the preparation of seven-membered zirconacyclocumulene complexes containing three cumulated C=C bonds in the ring are now known; although these methods have not been developed thoroughly enough and have a limited practical applicability, they have already served for the preparation of a rather broad range of zirconacycles of this type.

9.1.1. Reactions of the Negishi reagent with conjugated diacetylenes

As noted above, the first seven-membered zirconacyclocumulene complex was described in 1993 by Buchwald and coworkers.[712] The authors studied the interaction of the Negishi reagent $Cp_2ZrBu^n_2$ with bis(trimethylsilyl)butadiyne $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ in n-hexane, hoping to synthesize tricyclic organozirconium [4]radialene **83** (Scheme 160). However, it turned out that no radialene is formed in this reaction. Instead, seven-membered zirconacyclocumulene metallacycle **81** was obtained.

Scheme 160

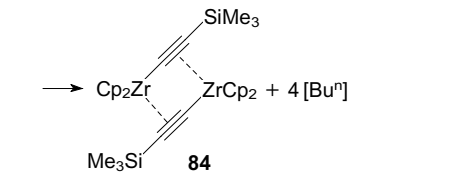


The complex was isolated from the mixture in 66% yield and proved to be quite stable at room temperature even in air; its structure was established by X-ray diffraction analysis. It was also assumed that the central C=C bond of the cumulene moiety of the metallacycle is coordinated to zirconium; however, no evidence supporting this assumption was presented in the paper.

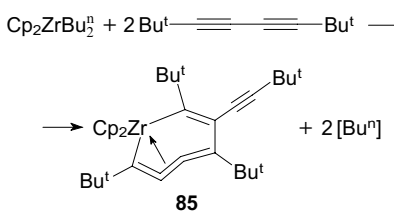
Apart from the seven-membered zirconacyclocumulene **81**, the reaction gives also a small amount of dimeric zirconocene trimethylsilylacetylenide (**84**) (Scheme 161).

The interaction of the Negishi reagent with bis(*tert*-butyl)butadiyne $Bu^tC{\equiv}C-C{\equiv}CBu^t$ gives a complex mixture of products, of which four compounds were isolated and identified, in particular, seven-membered zirconacyclocumulene **85** (Scheme 162).[734, 735] However, according to NMR data, the content of this product in the mixture did not exceed 19%.

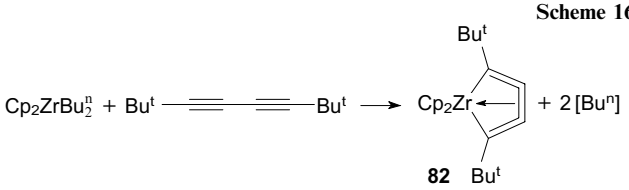
Scheme 161



Scheme 162



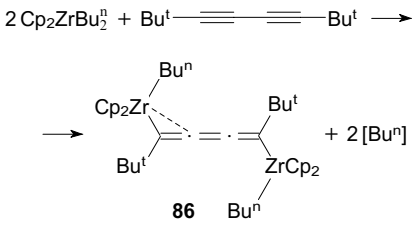
Scheme 163



The five-membered zirconacyclocumulene complex **82** noted above was the major reaction product (72% content in the mixture) (Scheme 163).

The reaction also gave a minor amount (2.4%) of the unusual binuclear butatrienyl zirconocene complex $Cp_2(Bu^n)Zr(Bu^tC_4Bu^t)Zr(Bu^n)Cp_2$ (**86**) with a coordination bond between one of the β-carbon atoms of the butatrienyl moiety and the zirconium atom (Scheme 164).

Scheme 164

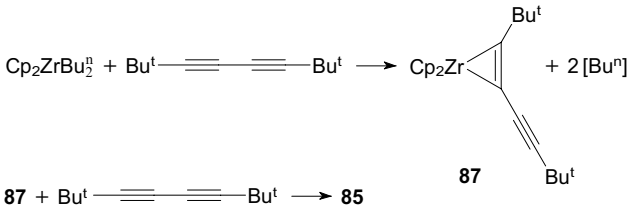


Finally, one more compound that formed in the above-mentioned reaction in a very low amount (0.9%) was the dimeric zirconocene acetylenide complex $[Cp_2ZrC{\equiv}CBu^t]_2$, resembling compound **84** in the structure.

Presumably,[735] the mechanism of the formation of seven-membered zirconacyclocumulene **85** in the reaction of $Cp_2ZrBu^n_2$ with $Bu^tC{\equiv}C-C{\equiv}CBu^t$ includes two key steps, the first one being the formation of the intermediate acetylene complex $Cp_2Zr(Bu^tC{\equiv}CC_2Bu^t)$ (**87**) (with the metallacyclopropene structure), which then reacts with a second butadiyne molecule to give the final metallacycle **85** (Scheme 165).

The formation of seven-membered zirconacyclocumulene **81** in the reaction of $Cp_2ZrBu^n_2$ with

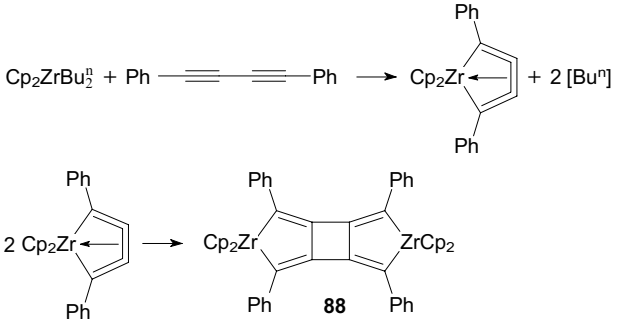
Scheme 165



$Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ probably follows a similar mechanism. The ability of zirconocene acetylene complexes to form metallacyclocumulenes of this type in the interaction with conjugated diacetylenes is evidenced by the data presented in the next Section.

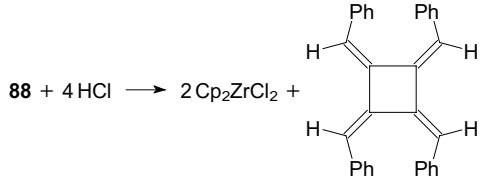
It is of interest that if diphenylbutadiyne $PhC{\equiv}C-C{\equiv}CPh$ reacts with the Negishi reagent in n-hexane, no expected seven-membered zirconacyclocumulene $Cp_2Zr[\eta^4\text{-}PhC_4(Ph)-C(C_2Ph){=}CPh]$ is formed, but the reaction gives tricyclic organozirconium [4]radialene **88** (in 25% yield),[736] analogous to that which Buchwald and co-workers attempted to synthesize (see Scheme 160). Apparently, the five-membered zirconacyclocumulene complex $Cp_2Zr(\eta^4\text{-}PhC_4Ph)$ is formed as an intermediate in this reaction and then undergoes cyclodimerization to give the final radialene (Scheme 166).

Scheme 166



The structure of compound **88** was established by analytical and spectral methods and by conversion of **88** to a mixture of Cp_2ZrCl_2 and the previously described organic [4]radialene[720] in 2 : 1 ratio by treatment with HCl in diethyl ether at 20 °C (Scheme 167).

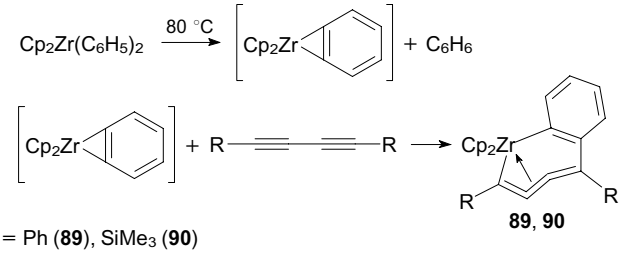
Scheme 167



9.1.2. Reactions of acetylene complexes of zirconocene with diacetylenes

Bredeau *et al.*[737,738] reported the synthesis of seven-membered zirconacyclocumulene metallacycles **89** and **90** by the reaction of $PhC{\equiv}C-C{\equiv}CPh$ and $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ with the benzyne complex of zirconocene $Cp_2Zr(C_6H_4)$ formed as an intermediate of $Cp_2Zr(C_6H_5)_2$ thermal decomposition in toluene at 80 °C. During the reaction, the diacetylene molecule is inserted into the Zr–C σ-bond of the benzene complex, thus yielding the final cumulene (Scheme 168).

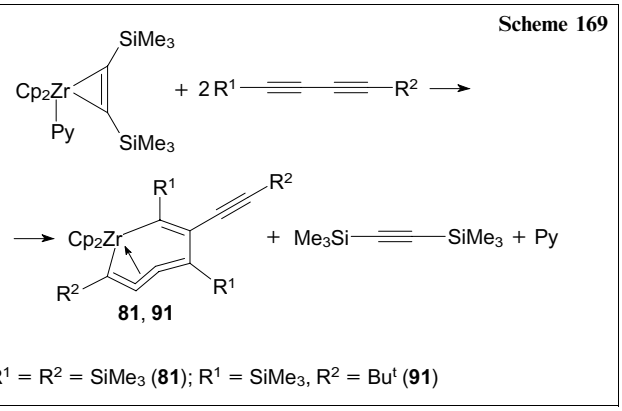
Scheme 168



R = Ph (**89**), $SiMe_3$ (**90**)

In earlier works, diacetylenes $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ and $Me_3SiC{\equiv}C-C{\equiv}CBu^t$ were reacted with the bis(trimethylsilyl)acetylene zirconocene complex $Cp_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)(Py)$ in n-hexane at 20 °C, thus giving seven-membered zirconacyclocumulenes **81** and **91** in 51% and 38% yields, respectively (Scheme 169).[713,739]

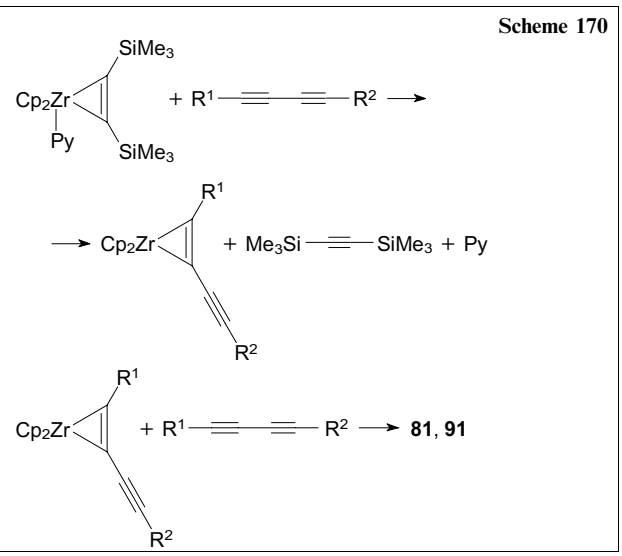
Scheme 169



$R^1 = R^2 = SiMe_3$ (**81**); $R^1 = SiMe_3$, $R^2 = Bu^t$ (**91**)

Presumably, during these reactions, the bis(trimethylsilyl)acetylene and pyridine ligands are displaced from the zirconium coordination sphere by the diyne molecule, giv-

Scheme 170

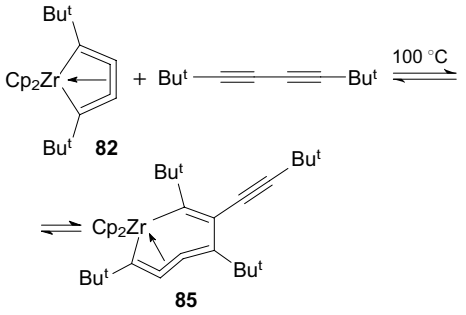


ing rise to the acetylene complex $Cp_2Zr(R^1C{\equiv}CC_2R^2)$, similar to compound **87** (see Scheme 165) with zirconacyclopropene structure. The subsequent insertion of a second diyne molecule into the $Zr-C(C_2R^2)$ σ-bond of this complex yields the final seven-membered zirconacyclocumulene (Scheme 170).

9.1.3. Reactions of five-membered zirconacyclocumulene $Cp_2Zr(\eta^4\text{-}Bu^tC_4Bu^t)$ with monoacetylenes and conjugated diacetylenes

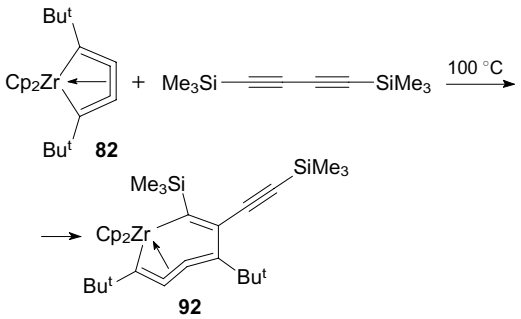
It has recently been shown that heating of five-membered zirconacyclocumulene **82** with conjugated diacetylenes $PhC{\equiv}C-C{\equiv}CPh$ and $Bu^tC{\equiv}C-C{\equiv}CBu^t$ in toluene at 100 °C also results in the formation of seven-membered zirconacyclocumulene complexes.[740] When bis(*tert*-butyl)butadiyne $Bu^tC{\equiv}C-C{\equiv}CBu^t$ is used in this reaction, seven-membered zirconacyclocumulene **85** is formed (Scheme 171), but the reaction is reversible, with equilibrium being established in 24 h with the **82** : **85** ratio of 3 : 1. Increasing the reaction time to 11 days does not result in a noticeable change in this ratio despite the presence of free diyne in the reaction mixture.

Scheme 171



A similar seven-membered zirconacyclocumulene complex **92** is formed as the major product (together with minor amounts of complex **81** and other compounds) in the reaction of zirconacycle **82** with bis(trimethylsilyl)butadiyne $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ in toluene for 11 days at 100 °C (Scheme 172).[740] In this case, however, the reaction is irreversible, as indicated by the inability of the isolated complex **92** to be converted back to the mixture of zirconacycle **82** and $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ even when kept in toluene at 100 °C for a long period of time.

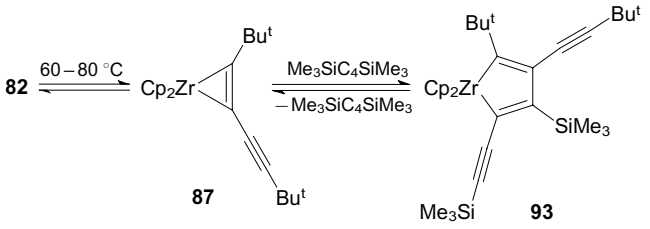
Scheme 172



The obtained data on the synthesis of seven-membered zirconacyclocumulenes in reactions carried out at 100 °C attest to their high thermal stability.

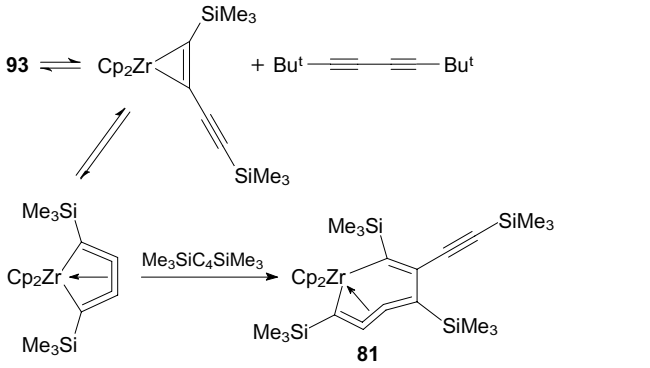
It is worth noting that if compound **82** reacts with $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ at 60 – 80 °C, instead of 100 °C, the reaction gives no seven-membered zirconacyclocumulenes, but five-membered zirconacyclopentadiene complex **93** is formed as the major product (Scheme 173). Apparently, at 60 – 80 °C, the starting complex **82** is in equilibrium with acetylene complex **87**, which reacts with acetylene giving the final zirconacyclopentadiene.

Scheme 173



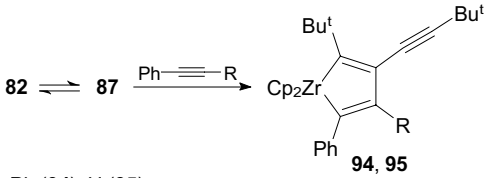
Interestingly, at 100 °C in toluene, zirconacyclopentadiene **93** is gradually converted to zirconacyclocumulene **92** and a minor amount of compound **81**, which means that the formation of zirconacyclopentadiene **93** from compound **82** and $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ is reversible. The presence of complex **81**, apart from cumulene **92**, among the reaction products is attributable to the possible alternative pathway of the thermal decomposition of zirconacycle **93** (Scheme 174).

Scheme 174



Unlike the reactions with conjugated diacetylenes, reactions of complex **82** with tolane or phenylacetylene do not give seven-membered zirconacyclocumulenes even on long-term keeping of the reaction mixture at 100 °C.[740] In this case, zirconacyclopentadiene metallacycles are the major reaction products, namely, compound **94** for tolane and compound **95** for phenylacetylene (Scheme 175). These metallacycles are probably formed *via* acetylene insertion

Scheme 175



R = Ph (**94**), H (**95**)

into the Zr – C(C_2Bu^t) σ-bond of acetylene complex **87**, which probably is in equilibrium with zirconacycle **82**.

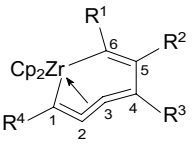
The reactions of seven-membered zirconacyclocumulene **81** with acetylenes at 100 °C resulting in the formation of new seven-membered zirconacyclocumulene complexes are considered below.

9.2. Structure of seven-membered zirconacyclocumulenes

The unusually high thermal stability of the seven-membered zirconacyclocumulene ring containing three cumulated C=C bonds is due to some details of its electronic structure. According to X-ray diffraction data, in all currently known and structurally characterized compounds of this type, the seven-membered zirconacycle is planar and the butatrienyl moiety considerably deviates from linearity, thus acquiring the transoid configuration. The central C(2)=C(3) bond of the cumulene group is markedly elongated [1.298(6) – 1.327(5) Å; average, 1.31 Å] compared with the central C=C bond (1.241 – 1.276 Å; average, 1.26 Å) in usual purely organic butatrienes,[741 – 745] which implies that this C(2)=C(3) bond is involved in the interaction with zirconium (Table 2). The fact that the Zr···C(2) (~2.41 – 2.44 Å; average, 2.43 Å) and Zr···C(3) (~2.36 – 2.49 Å; average 2.42 Å) distances are comparable with the Zr – C(1) (~2.35 – 2.45 Å; average, 2.43 Å) and Zr – C(6) (~2.39 – 2.50 Å; average, 2.42 Å) bond lengths in seven-membered zirconacyclocumulenes is in line with the drawn conclusion. Note also that the supposed coordination of the C(2)=C(3) bond of the cumulene group to zirconium is favoured by the location of one of the p-orbital pairs of the sp-hybridized carbon atoms of this bond in the metallacycle plane, which coincides with the bisecting plane of the dihedral angle between the Cp rings.

One more important detail of the electronic structure of seven-membered zirconacyclocumulenes contributing to their stability follows from comparison of the lengths of the terminal C(1) – C(2) and C(3) – C(4) bonds of the butatrienyl moiety. As can be seen in Table 2, whereas the length of the terminal C(3) – C(4) bond of this moiety is ~1.33 – 1.35 Å in all eight cyclocumulenes, which corresponds to the length of the usual C=C double bond (average, 1.331 Å), the other terminal C – C bond, namely, C(1) – C(2), is essentially shorter (~1.27 – 1.29 Å) and, hence, it is intermediate between the double and triple bonds (average, 1.19 Å). This means that the zirconacyclopentadiene resonance form containing a zirconium-coordinated C≡C triple bond in the α-position makes a substantial contribution to the electronic structure of seven-membered zirconacyclocumulenes (Scheme 176).[735, 740, 746]

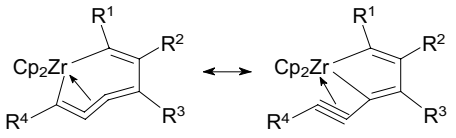
Table 2. C – C (Å) bond lengths in the butatrienyl moiety of the seven-membered zirconacyclocumulene complexes (X-ray diffraction data).



Complex [a]	C – C bond lengths			Ref.
	C(1) – C(2)	C(2) – C(3)	C(3) – C(4)	
81	1.279(6)	1.298(6)	1.337(6)	712
85	1.2697(17)	1.3219(17)	1.3317(17)	735
89	1.293(3)	1.300(3)	1.343(3)	737
90	1.275(5)	1.327(5)	1.338(5)	738
92	1.287(2)	1.317(2)	1.336(2)	740
96	1.287(8)	1.315(8)	1.349(9)	746
100	1.280(3)	1.310(3)	1.338(3)	746
102	1.281(3)	1.318(3)	1.338(3)	746

[a] For complexes **96**, **100** and **102**, see the next Section.

Scheme 176



The data on protolysis of one of the seven-membered zirconacyclocumulenes, namely, compound **96** (see below), are consistent with this assumption.

9.3. Reactivity

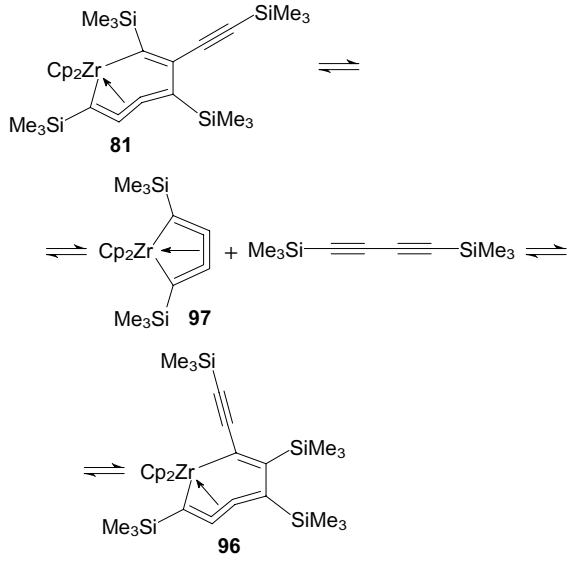
Most of the reactivity data for seven-membered zirconacyclocumulenes known to date were obtained in the studies of chemical properties of zirconacyclocumulene complex **81** as the most available one. For this metallacycle, unusual reactions with various acetylenes, nitriles, *N*-benzylideneaniline and S_2Cl_2 as well as its thermal isomerization giving a new seven-membered zirconacyclocumulene have been described. It is noteworthy that almost all of the mentioned reactions proceed as a rule, at very low rates even at 100 °C, although the product yields are often rather good. This fact vividly illustrates once again the abnormally high thermal stability of the seven-membered zirconacyclocumulene ring, despite its high strain.

9.3.1. Thermal isomerization of seven-membered zirconacyclocumulene 81

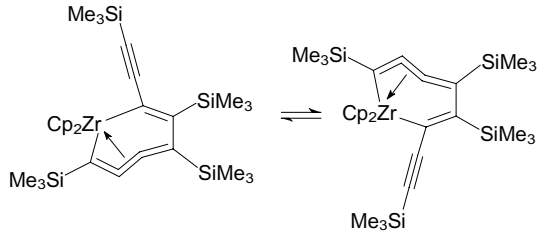
It has been shown[746] that heating of seven-membered zirconacyclocumulene **81** in toluene at 110 °C for three weeks results in isomerization to a different seven-membered zirconacyclocumulene complex **96**, in which the $Me_3SiC{\equiv}C$ group is in the α-position and the $SiMe_3$ substituent is in the β-position with respect to zirconium. The complex was isolated from the solution in a pure state in 43% yield and its structure was established by X-ray diffraction analysis. Presumably, isomerization of **81** to **96** proceeds *via* the reversible formation of the intermediate five-membered zirconacyclocumulene $Cp_2Zr(\eta^4\text{-}Me_3SiC_4SiMe_3)$ (**97**) and free diyne $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ (Scheme 177).

A remarkable feature of complex **96** is its ability to undergo a degenerate rearrangement in a toluene solution at high rate even at −20 °C; as a result, the ^{1}H NMR spectrum of this complex exhibits, under these conditions, only two rather than four singlets for the Me_3Si group protons (Scheme 178). Only at −70 to −80 °C, the rearrangement rate decreases to such an extent that the ^{1}H NMR spectrum of the complex assumes a normal pattern.

Scheme 177



Scheme 178

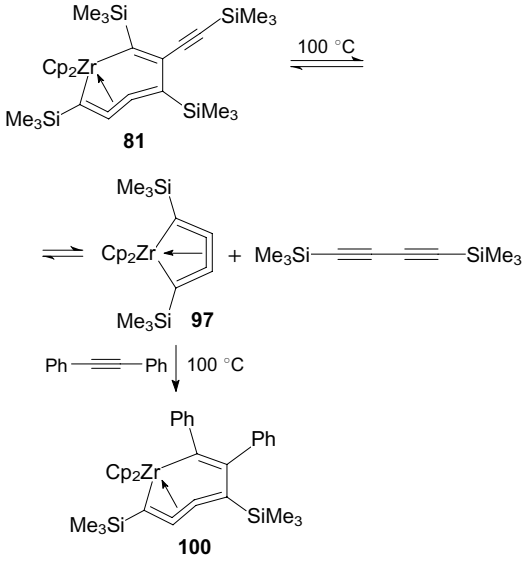


Probably, the driving force of the detected degenerate rearrangement is a considerable contribution of the zirconacyclopentadiene resonance form **96′** to the electronic structure of complex **96**. In accordance with this assumption, protolysis of complex **96** with a solution of HCl in dioxane at 22 °C gives Cp_2ZrCl_2 and 1,3-diene **98**, apart from [3]cumulene **99** (Scheme 179). According to NMR data, the **98** : **99** ratio is 3 : 1.

9.3.2. Reactions with acetylenes

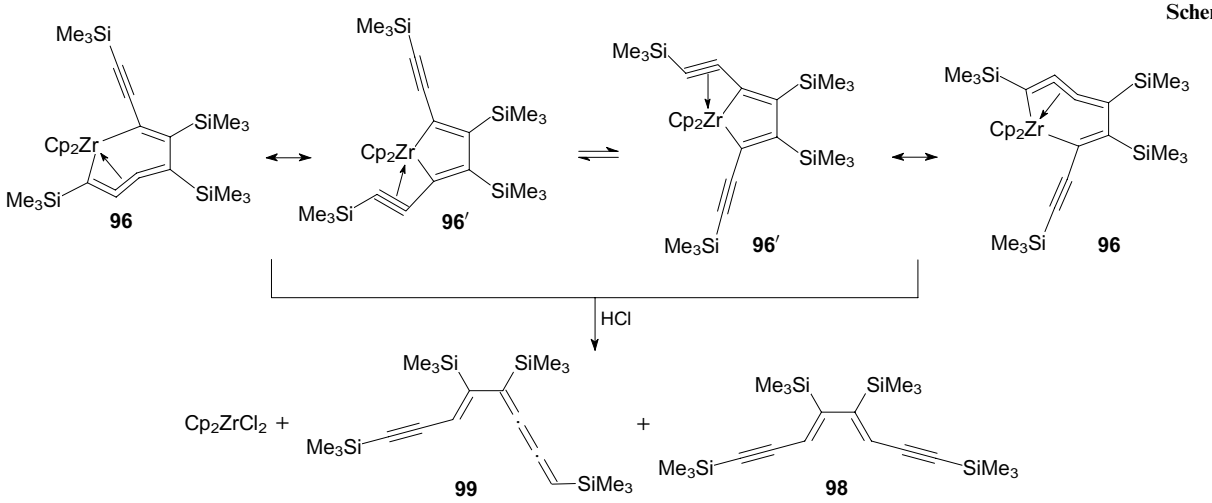
Seven-membered zirconacyclocumulene **81** proved to be reactive towards various monoacetylenes and conjugated diacetylenes, being converted to new zirconacycles of the type that presents interest from the preparative standpoint. Thus, it has been shown that the reaction of compound **81** with tolane in toluene at 100 °C for 16 days gives seven-membered zirconacyclocumulene **100** containing phenyl substituents in the α- and β-positions of the metallacycle, instead of the trimethylsilyl and trimethylsilylacetylenide groups.[746] Complex **100** was isolated from the mixture in 47% yield and fully characterized. Presumably, this reaction, like the thermal isomerization of compound **81** considered above, proceeds *via* the reversible conversion of the starting complex **81** to intermediate five-membered zirconacyclocumulene complex **97** and free $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$. The subsequent insertion of tolane into the Zr–C bond of intermediate zirconacyclocumulene **97** gives rise to final complex **100** (Scheme 180).

Scheme 180

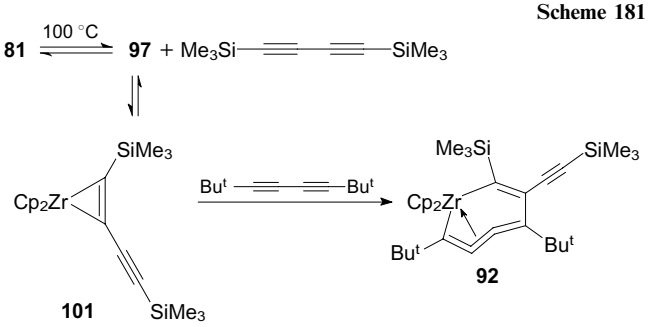


The reaction of complex **81** with bis(*tert*-butyl)butadiyne $Bu^tC{\equiv}C-C{\equiv}CBu^t$ in toluene at 100 °C follows a different pathway.[746] In this case, the butatrienyl moiety $Me_3SiC_4SiMe_3$ in molecule **81** is replaced by $Bu^tC_4Bu^t$, and this gives seven-membered zirconacyclocumulene metallacycle **92** (Scheme 181), which was first synthesized, as

Scheme 179



Scheme 181

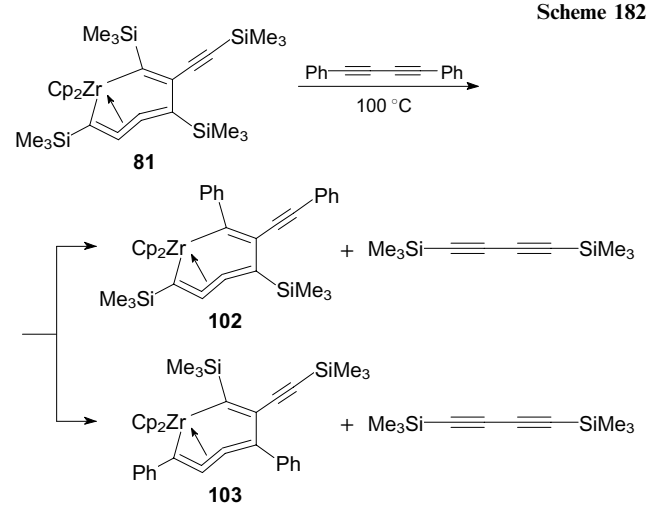


has already been noted, by the reaction of $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ with zirconacumulene **82**.

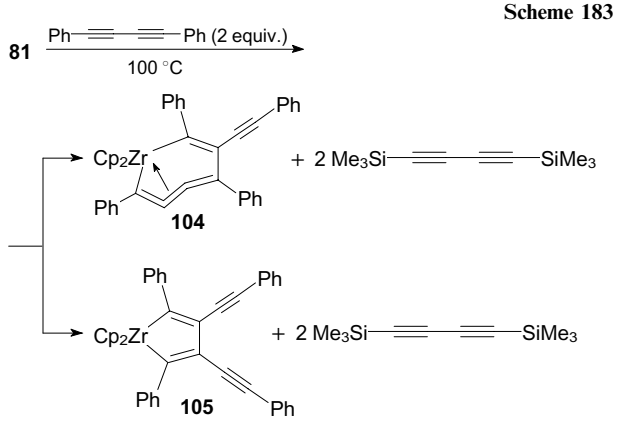
It can be assumed that in a toluene solution at 100 °C, the initial metallacycle **81** is in equilibrium with not only five-membered zirconacycle **97** and $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$, but also with the acetylene complex $Cp_2Zr(Me_3SiC{\equiv}CC_2SiMe_3)$ (**101**), which has a zirconacyclopropene structure. The insertion of $Bu^tC{\equiv}C-C{\equiv}CBu^t$ into the $Zr-C(C_2SiMe_3)$ bond of this zirconacyclopropene gives rise to final product **92**.

The reaction of compound **81** with 1,4-diphenylbutadiyne in toluene at 100 °C generates a complex mixture of products, from which four complexes were isolated and identified.[746] Two of them are isomeric seven-membered zirconacyclocumulenes **102** and **103** (Scheme 182). Complex

Scheme 182



Scheme 183



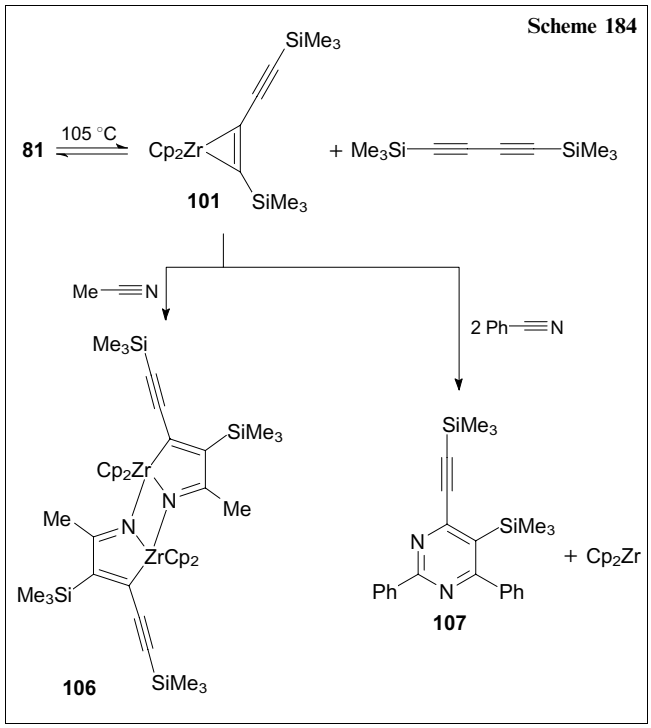
102 is formed by the same mechanism as zirconacycle **100** *via* the reaction of zirconacycle **81** with tolane (see Scheme 180). The mechanism of formation of complex **103** is similar to that proposed for the reaction of compound **81** with $Bu^tC{\equiv}C-C{\equiv}CBu^t$ (see Scheme 181).

The other two products of this reaction are isomeric seven-membered zirconacyclocumulene **104** and symmetric zirconacyclopentadiene **105** containing each four phenyl groups in the molecule (Scheme 183). The formation of these complexes is accompanied by complete replacement of both $Me_3SiC_4SiMe_3$ moieties in metallacycle **81** with two PhC_4Ph moieties.

9.3.3. Reactions with nitriles

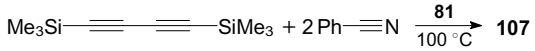
The reactions of zirconacyclocumulene **81** with nitriles occur in different ways depending on the nature of the nitrile. For example, complex **81** reacts with an equimolar amount of acetonitrile in toluene at 105 °C over a period of 26 h to afford $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ and dimeric zirconaazacyclopentadiene metallacycle **106**, which was isolated from the mixture in 67% yield (Scheme 184).[747] The mechanism of this reaction is probably similar to the mechanism of the above-described reaction of compound **81** with $Bu^tC{\equiv}C-C{\equiv}CBu^t$, resulting in the formation of cyclocumulene **92** (see Scheme 181), with the only difference that the last step is insertion of the acetonitrile molecule into the $Zr-C(SiMe_3)$ bond of the intermediate acetylene complex **101**, which occurs in equilibrium with metallacycle **81**, rather than into the $Zr-C(C_2SiMe_3)$ bond, as in the case of $Bu^tC{\equiv}C-C{\equiv}CBu^t$. The structure of complex **106** was determined by X-ray diffraction.

Scheme 184



The reaction of complex **81** with benzonitrile in toluene at 105 °C proceeds in a different way (see Scheme 184). Under these conditions, tetrasubstituted pyrimidine **107** was formed in 64% yield as a result of co-cyclization of two $PhC{\equiv}N$ molecules with the acetylene ligand in the intermediate zirconocene complex **101** mentioned above.[747] In

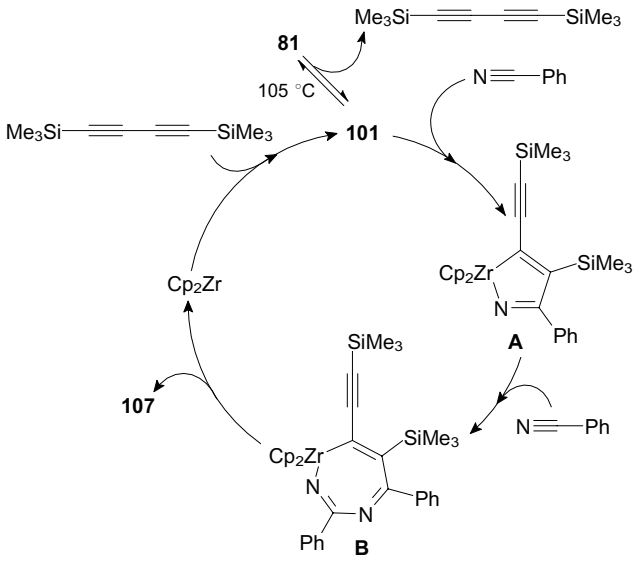
Scheme 185



the presence of excess benzonitrile and diacetylene $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$, the cyclization becomes a catalytic reaction (Scheme 185).

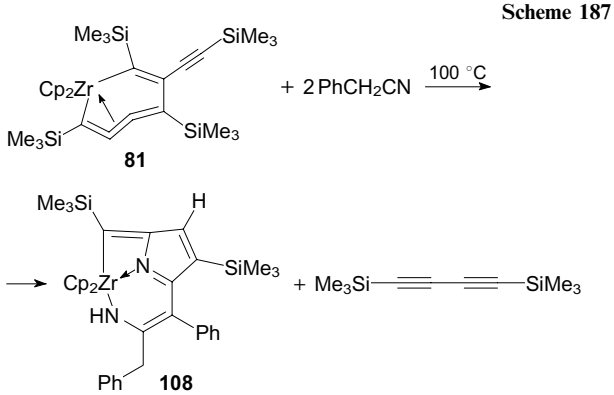
Scheme 186 shows the presumptive mechanism of the catalytic synthesis of pyrimidine **107**. The mechanism includes the insertion of benzonitrile into the Zr–C bond of zirconacyclopropene **101**, which is in equilibrium with complex **81**, to give five-membered zirconazacyclopentadiene metallacycle **A**. The insertion of a second benzonitrile molecule is directed towards the Zr–N bond of this metallacycle giving the intermediate seven-membered diazazirconacycloheptatriene derivative **B**. The subsequent reductive elimination leads to the final pyrimidine **107** and zirconocene Cp_2Zr, which can further react with the next diacetylene molecule, thus recovering the zirconacyclopropene complex **101** and starting a new catalytic cycle.

Scheme 186



Unlike acetonitrile and benzonitrile, phenylacetonitrile $PhCH_2CN$ reacts with compound **81** in toluene at 100 °C, with the formation of unusual tricyclic zirconocene complex **108** containing four-, five- and six-membered rings and the Zr–N coordination bond (Scheme 187).[748] Complex **108** was isolated from solution in 24% yield and its structure was determined by X-ray diffraction analysis; the mechanism of its formation is yet unclear.

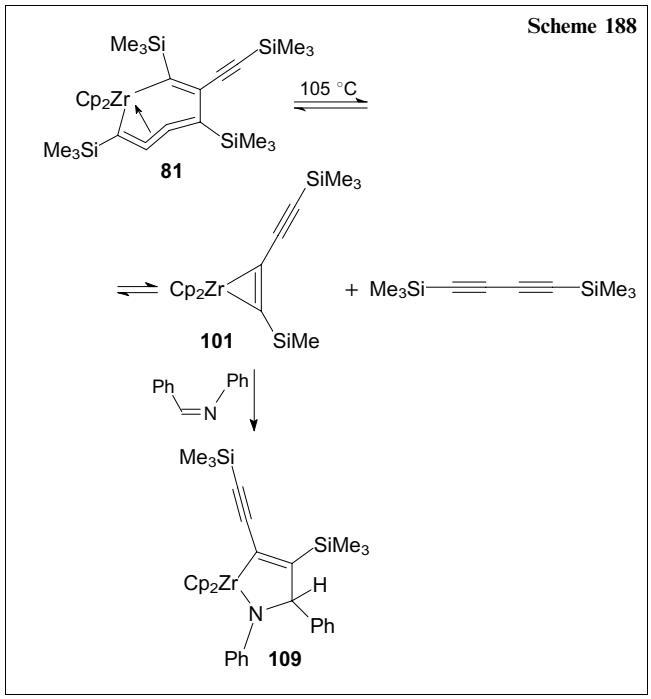
Scheme 187



9.4. Reaction of seven-membered zirconacyclocumulene 81 with *N*-benzylideneaniline

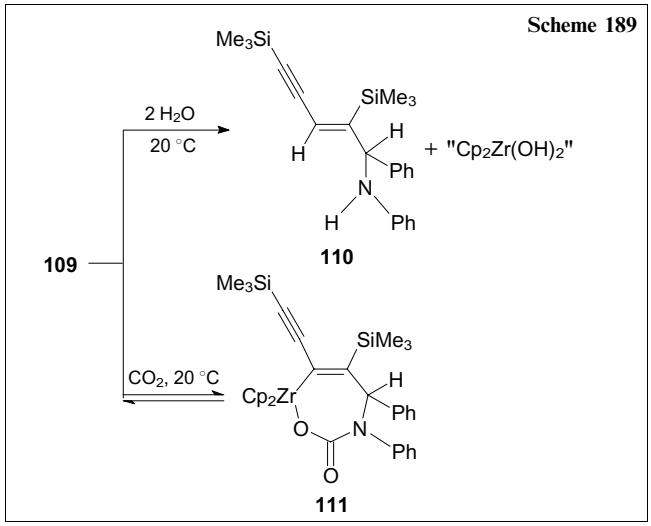
Burlakov *et al.*[747] have shown that heating zirconacycle **81** with *N*-benzylideneaniline in toluene for 3 days at 105 °C produces five-membered zirconaazacyclopentene complex **109** in 61% yield and $Me_3SiC{\equiv}C-C{\equiv}CSiMe_3$ (Scheme 188). According to X-ray diffraction data, the five-membered metallacycle in structure **109** is nearly planar.

Scheme 188



It was also shown that hydrolysis of complex **109** with water leads to N-substituted aniline **110** containing a enyne group,[749] while the reaction of zirconaazacyclopentene **109** with carbon dioxide at room temperature and atmospheric

Scheme 189

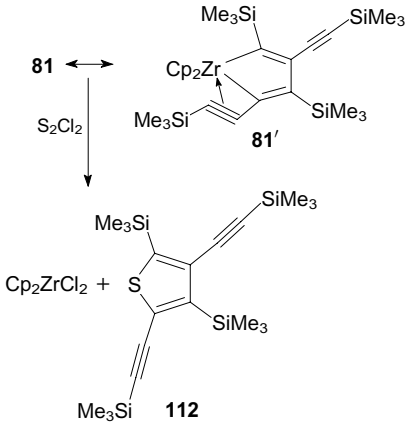


pressure results in CO_2 insertion into the Zr – N bond, giving rise to zirconaoxazepinone **111**, which was isolated from the mixture in 64% yield (Scheme 189).[747] It is noteworthy that the reaction of compound **109** with CO_2 is reversible and heating complex **111** in toluene at 60 – 80 °C leads to CO_2 release and the formation of the starting compound **109**.

9.5. Reaction of seven-membered zirconacyclocumulene 81 with S_2Cl_2

According to Burlakov *et al.*,[750] the reaction of complex **81** with S_2Cl_2 in THF carried out for 1 h at 55 °C affords tetrasubstituted thiophene derivative **112** in 20.4% yield. This result is understandable under the assumption that compound **81** reacts with S_2Cl_2 as the zirconacyclopentadiene resonance structure **81′** (Scheme 190).

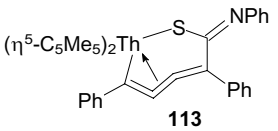
Scheme 190

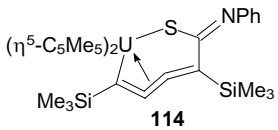


The structure of thiophene **112** was established by ^1H and ^{13}C NMR and IR spectroscopy and GLC/MS.

Thus, in recent years, considerable advances have been made in the studies addressing the chemistry of seven-membered zirconacyclocumulene complexes of zirconocene. New synthetic routes to these unusual compounds have been found; valuable data on their electronic structure and reactivity have been gained. Further progress in this important research of strained rings is held up, however, by the narrow range of currently known seven-membered metallacyclocumulenes of this type, which is due to problems arising from their synthesis. Thus, in contrast to five-membered metallacyclocumulenes $Cp_2M(\eta^4\text{-}Bu^tC_4Bu^t)$ of Group 4 elements, for which both zirconium[713] and the corresponding titanium[715] and hafnium[719,720] analogues have been described, in the case of seven-membered metallacyclocumulene complexes, only the zirconacyclocumulenes considered above have been synthesized, whereas similar titana- and hafnacycles are yet unknown, despite numerous attempts to prepare them. Recently, the synthesis and structures of the first thorium (**113**) and uranium (**114**)

Structures 113, 114





seven-membered metallacyclocumulenes have been reported.[751,752] The central C=C bond of the butatrienyl moiety of these complexes is also coordinated to the metal.

One can hope that further research in this interesting area would bring about the synthesis of a broad range of various seven-membered metallacyclocumulenes and their successful application in organic synthesis and catalysis.

10. Nickel, palladium and platinum complexes in catalytic systems for organic synthesis

Labile organometallic compounds are important, most of all, as catalysts. After a brief introduction devoted to the development of research into catalytic transformations, this Section surveys the fundamental trends concerning the catalysis by nickel, palladium and platinum complexes and is illustrated by some representative examples.

It is difficult to overestimate the role of catalytic processes for fine organic synthesis in the modern world.[5,753] Many compounds that are now actively used have quite recently been very difficult to obtain. The phenomenon of catalysis is the very key that has opened new doors for organic synthesis and made activation of various types of bonds (carbon – carbon, carbon – hydrogen, carbon – heteroatom bonds) an available tool to be used by chemists.[754,755] Transition metal catalysis has revolutionized the chemical science and changed the mode of thinking of synthetic chemists. Of course, palladium-catalyzed reactions, which are widely known, have played a crucial role in the development of catalytic strategies.

By the beginning of the 21st century, quite a number of new reactions catalyzed by transition metal complexes have already been discovered. For example, noteworthy is the Suzuki – Miyaura reaction for organoboron derivatives,[756] the Negishi reaction for organozinc compounds,[757] the Hiyama reaction for organosilicon derivatives,[758] the Kumada – Tamao – Corriu reaction for organomagnesium compounds,[15] the Mizoroki – Heck reaction for alkenes,[759] the Buchwald – Hartwig reaction for amines[760,761] and many other.[762 – 765] The diverse reactivity and a substantial economic benefit caused by low transition metal amounts used resulted in vigorous development of transition metal[766] and nano-sized[767] catalysis.

Study of the reaction mechanism is an important step towards the optimal catalyst, as the elucidation of characteristic features of any process at the molecular level can be used to increase its efficiency. Whereas earlier, the phenomenon of catalysis was interpreted as a relatively simple sequence of interconversions, the subsequent more detailed research brought about the paradigm of 'dynamic nature of catalytic systems'.[768]

The nature of the M – C bond (M is metal) is of key significance for the understanding of catalytic transformations. This issue is considered in a lot of excellent papers; we will only present a comparison of the main types of M – C bonds most often encountered in catalysis and some recent achievements in transition metal catalysis.

Any chemical reaction is a path from reactants to products with a complex energy profile along the path. To traverse this path, it is necessary to overcome an activation barrier associated with cleavage and formation of bonds, in particular, carbon – carbon bonds (Fig. 19).[766] However, the activation barriers for some reactions are too high, the reaction is plainly impossible under acceptable conditions,

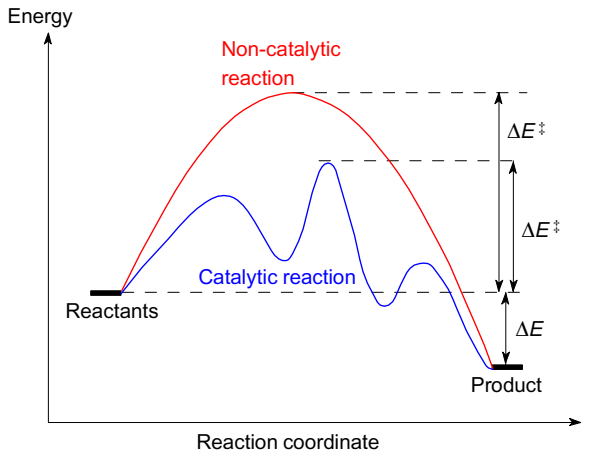


Figure 19. General view of reaction coordinate for non-catalytic and catalytic reactions.[766]

and in this case, transition metal catalysis can be a help. The activation and formation of new bonds force the reaction to follow a different path, thus splitting one step with a high energy barrier into several successive transformations with low activation barriers (see Fig. 19). The rearrangements organic substituents, undergoing in the coordination sphere of a metal with M – C bond making/bond breaking, are markedly less energetically demanding. It is the main cause for the activation energy minimization in a catalytic process.

10.1. Comparison of various metal – carbon bonds

Herein, we will consider in more detail the M – C bonds for Group 10 metals. The bond dissociation energy (BDE) is a convenient feature for evaluating the reactivity. The bond strength for the methyl group depends considerably on the environment: for example, for nickel, the BDE values vary from 38.0 to 51.1 kcal mol^{-1} (Fig. 20). The bond between a palladium atom and a methyl group is noticeably stronger (48.3 – 55.2 kcal mol^{-1}), and the highest bond energy is inherent in platinum, 60.8 to 66.5 kcal mol^{-1} (Refs 769 and 770). Note for comparison that the C – C bond energy, for example, in the ethane molecule is 90.1 kcal mol^{-1} (Ref. 771). These data only confirm the fact that the higher reactivity of transition metal complexes is caused by lower strength of the M – C bond as compared with the C – C bond.

Apart from the methyl group, some other types of substituents at the metal atom should also be considered, namely, vinyl (Vin), phenyl and alkynyl groups. These hydrocarbon groups are important from both the fundamental standpoint for the understanding of structural features of the complexes and the applied standpoint to

	H_3C-CH_3 >	L_2**Pt**$-CH_3$ >	L_2**Pd**$-CH_3$ >	L_2**Ni**$-CH_3$
BDE /kcal mol^{-1}	90.1	60.8 – 66.5	48.3 – 55.2	38.0 – 51.1

Figure 20. Bond dissociation energies of the carbon – carbon bond in ethane and the metal – carbon bonds in the Group 10 metal methyl complexes.[769 – 771]

study particular catalytic systems. The dissociation energies of the M – Vin and M – Ph bonds are in the same ranges as those for the methyl group. If a stronger field ligand, such as phosphine, is introduced into the metal coordination sphere, it is possible to reduce the bond strength by, on average, 5 kcal mol^{-1}. Meanwhile, the M – C≡CH bond is much stronger. In the $M(PH_3)_2(C{\equiv}CH)_2$ complexes of nickel, palladium and platinum, the M – C bond dissociation energies are 76.3, 73.5 and 82.1 kcal mol^{-1}, respectively, which attests to markedly lower reactivity of alkynyl derivatives of transition metals.[770, 772, 773]

Since the bond dissociation energy decreases in the order Pt – C > Pd – C > Ni – C, organic compounds of nickel should be especially reactive. Indeed, among platinum group metals, a higher reactivity is expected of nickel compounds. On the one hand, this considerable advantage can be used to develop highly active catalysts, but, on the other hand, this often makes the system poorly controllable and brings about numerous side reactions. In addition, compounds with the Ni – C bond are highly sensitive during isolation and, hence, their purification is a challenge. Higher strength of the Pd – C bond largely accounts for more extensive application of palladium in catalysis. Palladium-based systems are markedly more predictable, they often allow isolation of reaction intermediates in the crystalline state, the required catalyst amounts are lower, but the temperature conditions are considerably more drastic compared with those for Ni-based systems. A special position in this series is occupied by compounds with the Pt – C bond. This substantially stronger bond accounts for rather rare platinum-based homogenous catalytic systems. However, platinum compounds are used for comparison in the studies of fundamental trends of catalytic reactions involving platinum group metals, because the similar electronic configurations of the metals make it possible to draw analogies basing on the structures of Pt complexes.

The unique properties of platinum group metals as catalysts are caused by their ability to interact with π-systems of unsaturated compounds, in particular, alkenes and alkynes. In this case, the situation changes fundamentally (Fig. 21): the interaction of nickel with multiple bonds is stronger (34.3 kcal mol^{-1} for ethylene and 41.6 kcal mol^{-1} for acetylene) than those for palladium or platinum, which are comparable and energetically less favourable (16.1 – 23.7 kcal mol^{-1}).[770, 773 – 776]

In terms of the molecular orbital theory, the interaction with multiple bonds involves electron density transfer from the π-system to the metal atom and the back donation from the metal atom. This electron density redistribution is manifested as a change in the geometry and spectral characteristics of the ethylene and acetylene moieties. These changes bring about a new reactivity of the molecules in the metal coordination sphere. The coordination to nickel has the most pronounced effect on unsaturated molecules, which accounts for broad applicability of Ni systems in dimerization, cyclotrimerization or polymerization reactions. Since the interactions between the metal and multiple bond π-system are much more labile than interactions with σ-bonds, variation of structures of complexes and ligand environments may have a considerable effect on both the binding strength and the reactivity of unsaturated bonds.

One more important process that accompanies the formation of a new C – C, C – N or C – O bond in the catalytic

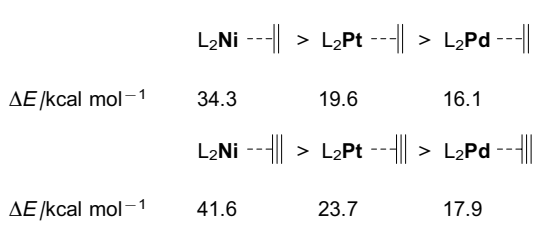


Figure 21. Ethylene and acetylene binding energy to Group 10 metal atoms.[776]

cycle is the reductive elimination step, which is the reverse of the oxidative addition of the initial C – C, C – N or C – O bond to the metal atom. The lowest activation barrier for reductive elimination is inherent in nickel (16.8 kcal mol^{-1} for the C – C bond), with the reaction itself being slightly exothermic (Fig. 22). Considering the same step for palladium reveals a somewhat higher activation barrier compared with that of nickel, namely, 24.9 kcal mol^{-1} (for C – C); however, a distinctive feature of Pd systems is more favourable formation of the reaction product (−19.0 kcal mol^{-1} for C – C). As for platinum, the reductive elimination step requires overcoming a barrier of 45.8 kcal mol^{-1} (for C – C), although the reaction is slightly exothermic.[769, 770, 773]

This picture demonstrates quite vividly the trends involved in transformations catalyzed by Group 10 metal compounds. Palladium complexes are perfectly suited for the formation of C – C, C – N or C – O bonds, as the reverse oxidative addition has very high activation barriers and is endothermic. In the case of nickel, the dual role is again manifested, as both the reductive elimination and oxidative addition are possible and, hence, nickel complexes are expected to be the most active. Meanwhile, platinum complexes are so stable that their reactivity is very low. All the foregoing is well correlated with the frequency of mention of homogeneous catalytic systems based on a particular metal.

Similar trends are revealed in the studies of various catalytic systems irrespective of the organic substrates, ligand effect, electronic state of the metal or solvent effect.

A special role is now played by reactions involving the homolytic M – C bond cleavage. The reactivity of platinum metals in such reactions decreases from nickel to platinum. Since the homolytic bond cleavage is the most preferable for nickel compounds, one can expect that the contribution of radical species is more significant in this case than for palladium or, even more so, for platinum. In addition, nickel is known to be prone to single-electron transfer, unlike palladium or platinum.[769, 770, 772, 773]

In the transition metal catalysis, nickel, palladium and platinum undergo, most often, two-electron transitions: M^0/M^{II} or M^{II}/M^{IV}. These catalytic cycles have been studied most comprehensively, but whereas Pd and Pt occur very rarely in some other oxidation states, in the case of nickel, the M^I or M^{III} states are more often encountered. As a result, unusual catalytic reactions involving the Ni^I/Ni^{III} pair or even the $Ni^I/Ni^{II}/Ni^{III}$ group of three can be found.

Catalytic systems with ligands occupy a primary position, with phosphine ligands being used very extensively in catalysis. The strength of ligand binding to the metal is an important factor for the design of catalytic systems. Since phosphorus is an electron density donor, then, apart from weakening of the M – C bond, it has a considerable influence on the stability of complexes as a whole. In the complexes of $M^{II}L_2X_2$ type, the strength of metal binding to phosphorus decreases in the series from platinum to nickel and is in the range of 40.3 to 24.5 kcal mol^{-1}. A unique feature of the $M^0L_2X_2$ complexes is a stronger M – P bond compared with that in a M^{II} analogues, and a series looks in a different way: Pt^0 – P (45.5) > Ni^0 – P (39.7) > Pd^0 – P (33.6 kcal mol^{-1}).[777] As a result, whereas for palladium and platinum, the stabilization energy of the complexes depends little on the oxidation state (though zerovalent complexes are still stabilized by phosphines to a higher extent), in the case of nickel, this difference is 15.2 kcal mol^{-1}, which implies a higher accessibility of the coordination sphere of particularly nickel(II).

Thus, the fundamental views on the M – C bonds with allowance made for the nature of the metal – ligand bond in the active site environment can be used for the design and tuning the activity of catalytic systems. Nickel is very well suited for reactions in which the key step is either reductive

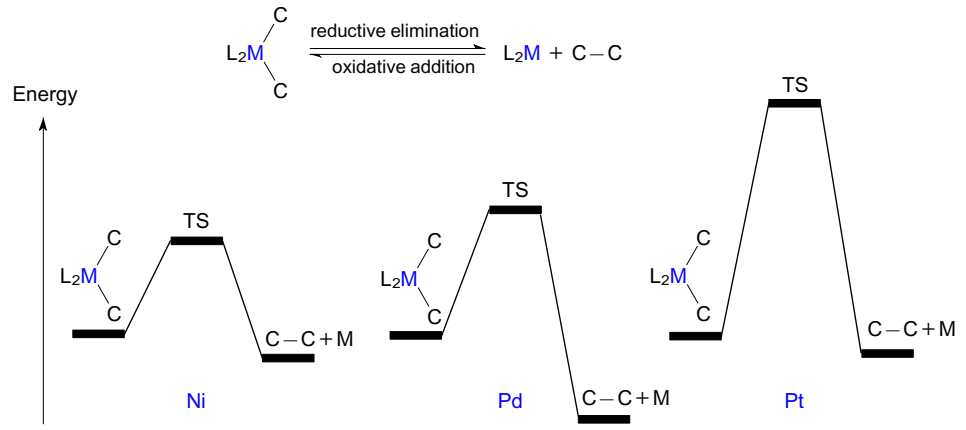


Figure 22. Activation barriers for the reductive elimination and oxidative addition of Group 10 metals.[766]

elimination or oxidative addition, while β-hydride elimination takes place much more rarely. Unlike nickel, palladium is more prone to β-hydride elimination, but the reductive elimination step is more controllable and more exothermic in this case. Furthermore, Pd systems can efficiently operate in many reactions even without stabilizing ligands (this is especially vivid when considering the dynamic nature of the catalyst in the case of a 'cocktail' of active species formation [768]), whereas nickel is highly demanding regarding the choice of appropriate ligands. A special position in this group is occupied by platinum compounds: because of high stability, platinum compounds are less active in the homogeneous form; however, in the case of formation of nanoparticles, platinum can also exhibit unique activity in the carbon – carbon and carbon – heteroatom bond formation reactions.

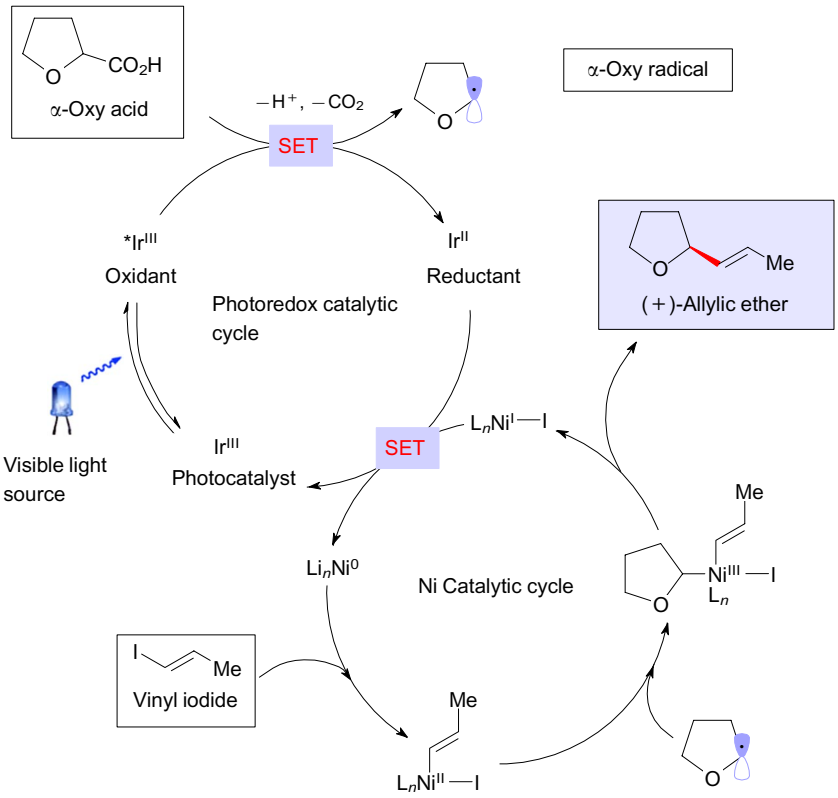
10.2. Examples of catalytic reactions

A number of representative studies addressing the catalysis by complexes of platinum group metals will be considered in somewhat more detail, beginning with nickel. In recent years, nickel has been used more and more often, which favours the discovery of new types of reactions and provides better understanding of reaction mechanisms.[778 – 783] Although nickel complexes are inactive in photochemical transformations, tandem catalysis by nickel complexes together with a photoredox co-catalysts has been vigorously developed in recent years.[784]

MacMillan and co-workers [785] have proposed a unique decarboxylative cross-coupling of α-oxycarboxylic acids with organic iodides. A peculiar feature of this synthetic strategy is replacement of specific substrates for transmetallation by easily accessible organic substrates. An iridium photocatalyst was selected as the photoredox component in the design of a catalytic system (Scheme 191). The photoexcited state of the Ir complex provides acid decarboxylation accompanied by single-electron transfer. This gives the α-oxy radical, and the reduced form of iridium reduces the Ni^{I} complex to zerovalent state (Ni^{0}). This nickel complex easily undergoes oxidative addition (Ni^{II}) followed by interception of α-oxy radical (Ni^{III}). The subsequent reductive elimination affords the target product and regenerates the initial nickel catalyst (Ni^{I}).[785] Thus, this catalytic system is not only an excellent participant for the preparation of a broad range of products, but is also a unique example of reaction recruiting four different oxidation states of nickel — $Ni^{I}/Ni^{0}/Ni^{II}/Ni^{III}$.

As has already been noted, nickel can act as an efficient acceptor for multiple bonds.[786 – 793] One of the most well-known reactions that involve nickel and alkynes is cyclotrimerization discovered long ago by Reppe *et al.*[794 – 796] A key feature of this reaction is the difficulty to control the selectivity. Uyeda and co-workers [797 – 799] were able to develop a bimetallic nickel complex that ensured highly selective synthesis of 1,4,5-substituted benzenes.[797] In the first stage, one alkyne molecule is coordinated between two nickel atoms; the coordination of the next alkyne molecule is followed by oxidative addition to give five-membered metallacycle (Fig. 23). The third molecule is coordinated to the second nickel atom, after which the most favourable pathway is the migratory insertion into the M – C bond giving an eight-membered ring with two nickel atoms. In this stage, the complex is converted from the triplet to singlet state, which reduces the reaction energy, and the reductive elimination releases the target benzene. This cooperative action of two nickel atoms located next to each other in one complex is responsible for the high selectivity of this reaction.[800]

Scheme 191



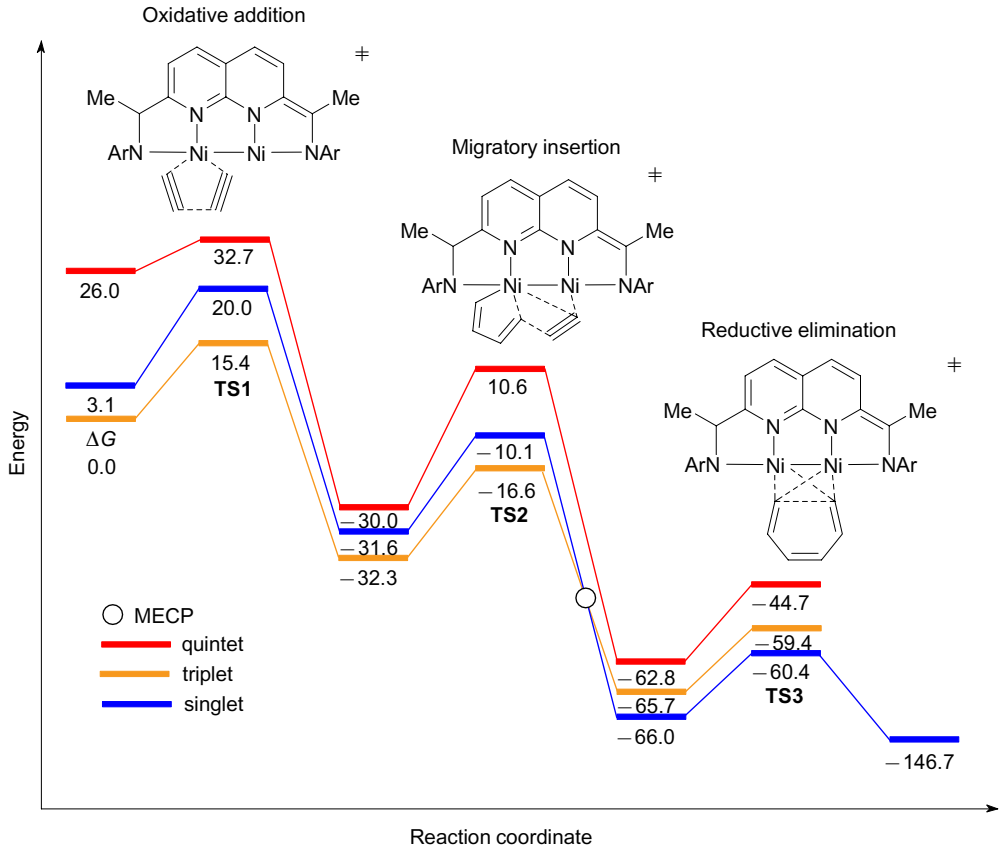
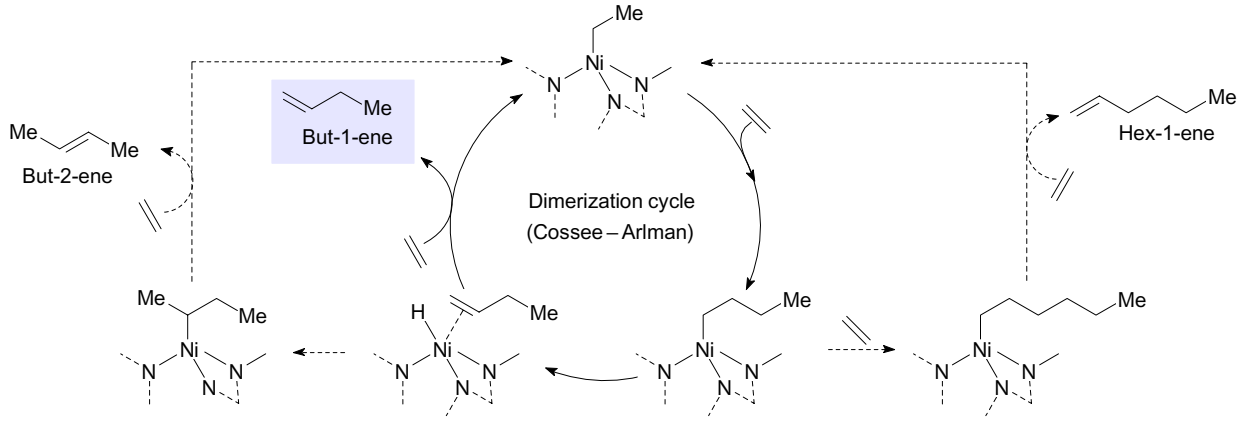


Figure 23. Reaction coordinate profiles for the singlet, triplet and quintet states of the dinickel complex in cyclotrimerization.[800] MECP is the minimum energy crossing point.

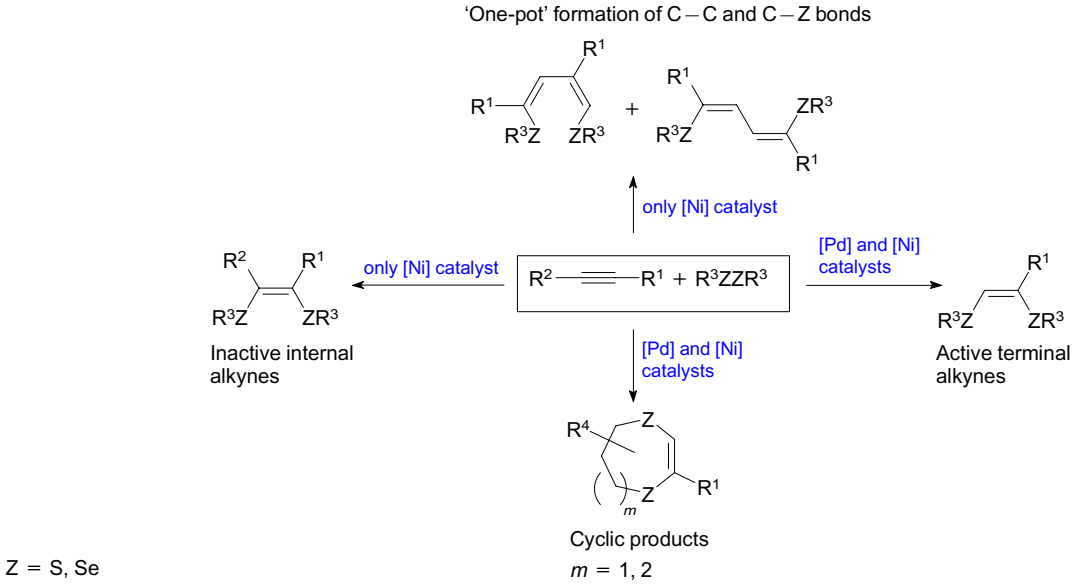
Ethylene dimerization is also a unique case of multiple bond activation. The production of but-1-ene is a large-scale industrial process with output of hundreds of thousands of tons per year, but enhancement of the efficiency of this reaction is still an issue. Brozek and Dincă[801] proposed a convenient approach for replacement of atoms of a metal (most often, zinc) within metal-organic frameworks (coordination polymers) by other metal atoms. Upon modification of the MFU-4l framework[802] by nickel, with the nickel content varying from 1% to 10%, this reaction was carried out with high selectivity (but-1-ene was formed in >92% yield). The first ethylene molecule is coordinated to nickel with oxidative addition (Scheme 192), after which the second molecule is coordinated and inserted into the Ni–C bond. With an optimized environment of the nickel atom, it is possible to avoid the addition of the third ethylene molecule, which would result in hexene. This is followed by reductive elimination and release of but-1-ene, which is more readily replaced by a new ethylene molecule, owing to the ligand environment, than adds once again to the nickel atom, which could have resulted in the formation of but-2-ene (see Scheme 192).[803]

A prospective aim of pharmaceutics and materials science is the formation of the C–S and C–Se

Scheme 192

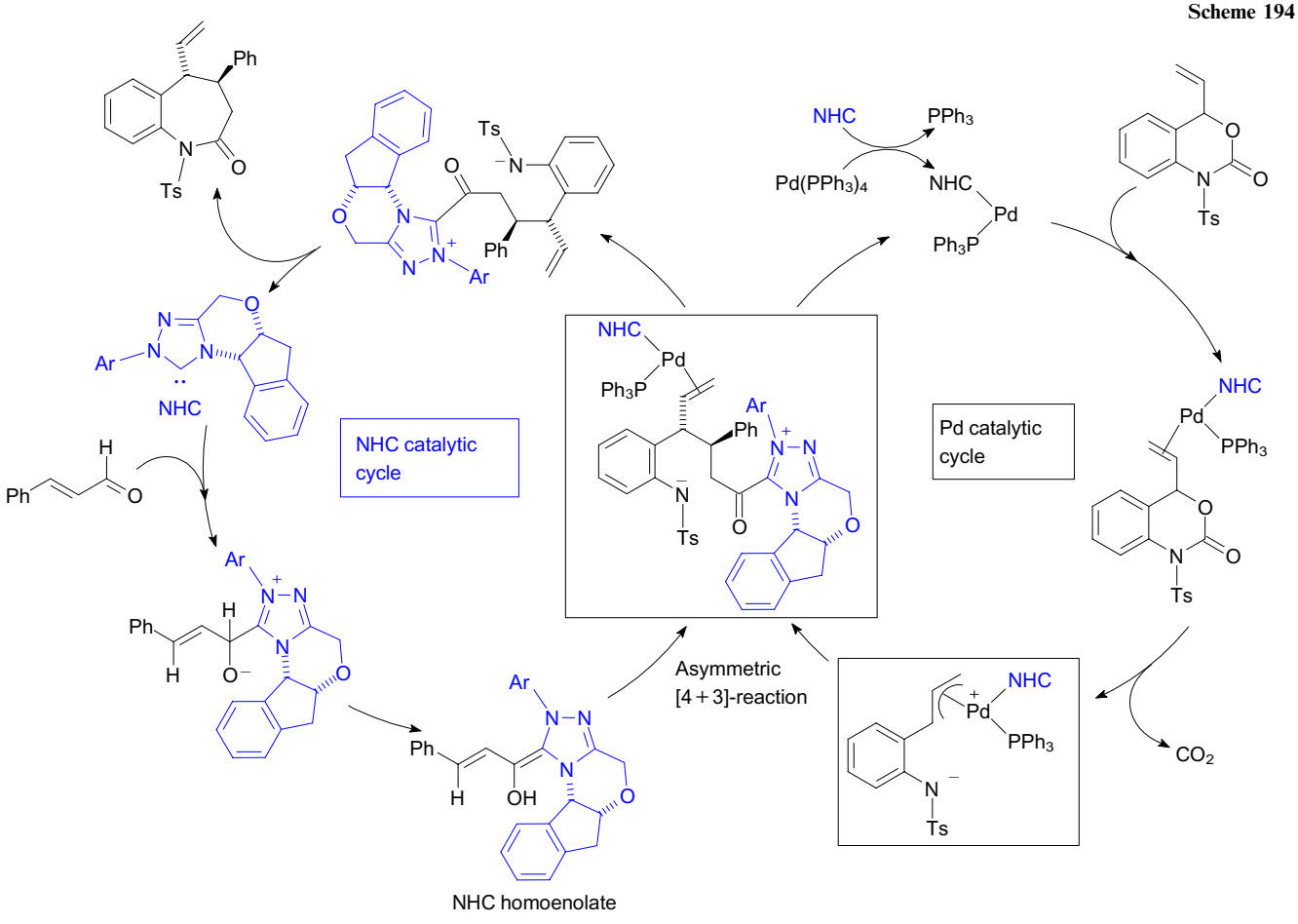


Scheme 193



bonds.[585, 706, 804] Depending on the precatalyst used (Ni or Pd), various products can be generated in the reactions of disulfides or diselenides with alkynes. The atom-economical addition of dichalcogenides to terminal alkynes with the use of either of the two metals delivers a linear or cyclic product (Scheme 193).[766, 805 – 808] Less active internal alkynes undergo the addition reaction only when the nickel precatalyst is used.[809] Owing to optimization of conditions and fine tuning of the catalytic system, apart from the common addition products, 1,3-dienes can be obtained from internal alkynes and disulfides.[707, 810] These examples clearly demonstrate the potential of nickel catalysis towards carbon – carbon and carbon – heteroatom bond formation reactions using starting reactants with similar properties.

Scheme 194



Nickel is followed in the Group by palladium, which has won the hearts and laboratories of chemists all over the world just after the discovery of cross-coupling and Heck reactions. Currently, the use of palladium complexes not only reveals new reactivity, but also maximizes the efficiency of existing reactions *via* optimization.[811 – 817]

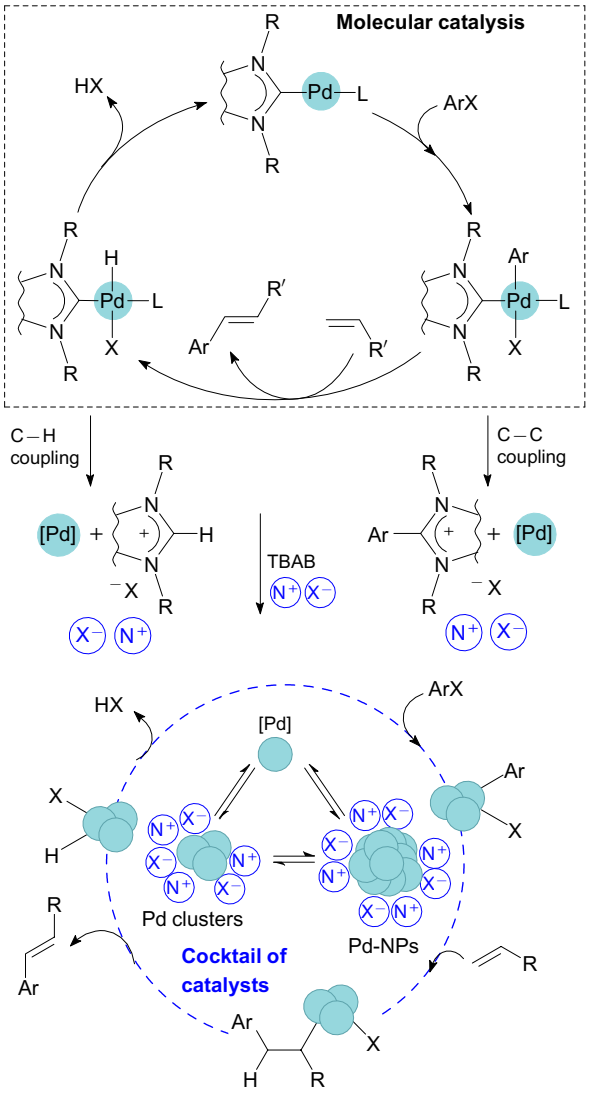
Glorius and co-workers[818] proposed a new type of mixed-ligand palladium complexes. The coordination sphere of one metal atom accommodates simultaneously triphenylphosphine, sterically crowded triazolium N-heterocyclic carbene and an allyl anionic ligand, while tetrafluoroborate is the counter-ion for this cationic complex. In the presence of free phosphine and carbene ligand, this complex catalyzed the stereoselective [4 + 3]-cyclization of vinyl tetrahydrobenzoxazinones and α,β-unsaturated aldehydes with product yields of up to 86% and enantiomeric excess of up to 99%. The presumptive reaction mechanism starts with the coordination of tetrahydrobenzoxazinone to the palladium atom *via* the double bond and subsequent decarboxylation giving a π-allyl complex (Scheme 194), which is attacked by the product of addition of chiral carbene to the carbonyl atom of α,β-unsaturated aldehyde, thus inducing the reductive elimination of palladium followed by release of the zerovalent complex, while intramolecular N-acyl cyclization affords the target product.[818]

However, not in all cases, the N-heterocyclic carbenes remain strongly bound to the palladium atom throughout the reaction. For example, in the Mizoroki – Heck reaction between butyl acrylate and iodobenzene, decomposition of the initial carbene-pyridine palladium complexes has been observed.[819] As a result, palladium forms a 'cocktail' of molecular complexes, clusters and nanoparticles, which all catalyze the target reaction. The ligand is either released in the free form or undergoes reductive elimination reaction with phenyl, thus being converted to azolium salt (Scheme 195). In all probability, these azolium cations stabilize the active species of the catalyst.[819]

Despite the accepted view of much higher stability of palladium compounds in the Pd^0, Pd^{II} and Pd^{IV} oxidation states, increasing attention is given to rare oxidation states such as Pd^I. Schoenebeck, Colacot and co-workers,[820] while investigating the reduction step, have found an alternative mechanism involving the formation of a dimeric complex of monovalent palladium with tris(*tert*-butyl)phosphine ligands. This complex has shown remarkable efficiency in the Buchwald – Hartwig reaction between sterically crowded amines and chlorobenzenes. Further investigation of these complexes resulted in the development of a highly selective procedure for alkylation of aryl bromides. The reaction proceeds at room temperature in an open flask (in air) in 5 min, with neither chlorine, nor triflate, nor carboxyl substituents in the aromatic ring being affected (Scheme 196). The alkylation can be accomplished by either primary or secondary Grignard reagents in the presence of zinc chloride. The wide applicability of this procedure was demonstrated for a variety of substituted benzenes, heterocycles and sterically hindered aryl bromides.[821]

Yet another field of the modern transition metal catalysis using unusual oxidation states of metals is the tandem photoredox catalysis. Although nickel compounds are employed most widely in this field, new reactivity can also arise for palladium complexes. Iwasawa and co-workers[822] developed a carboxylation method for aryl halides with CO_2. The reaction mechanism implies the reduction of

Scheme 195

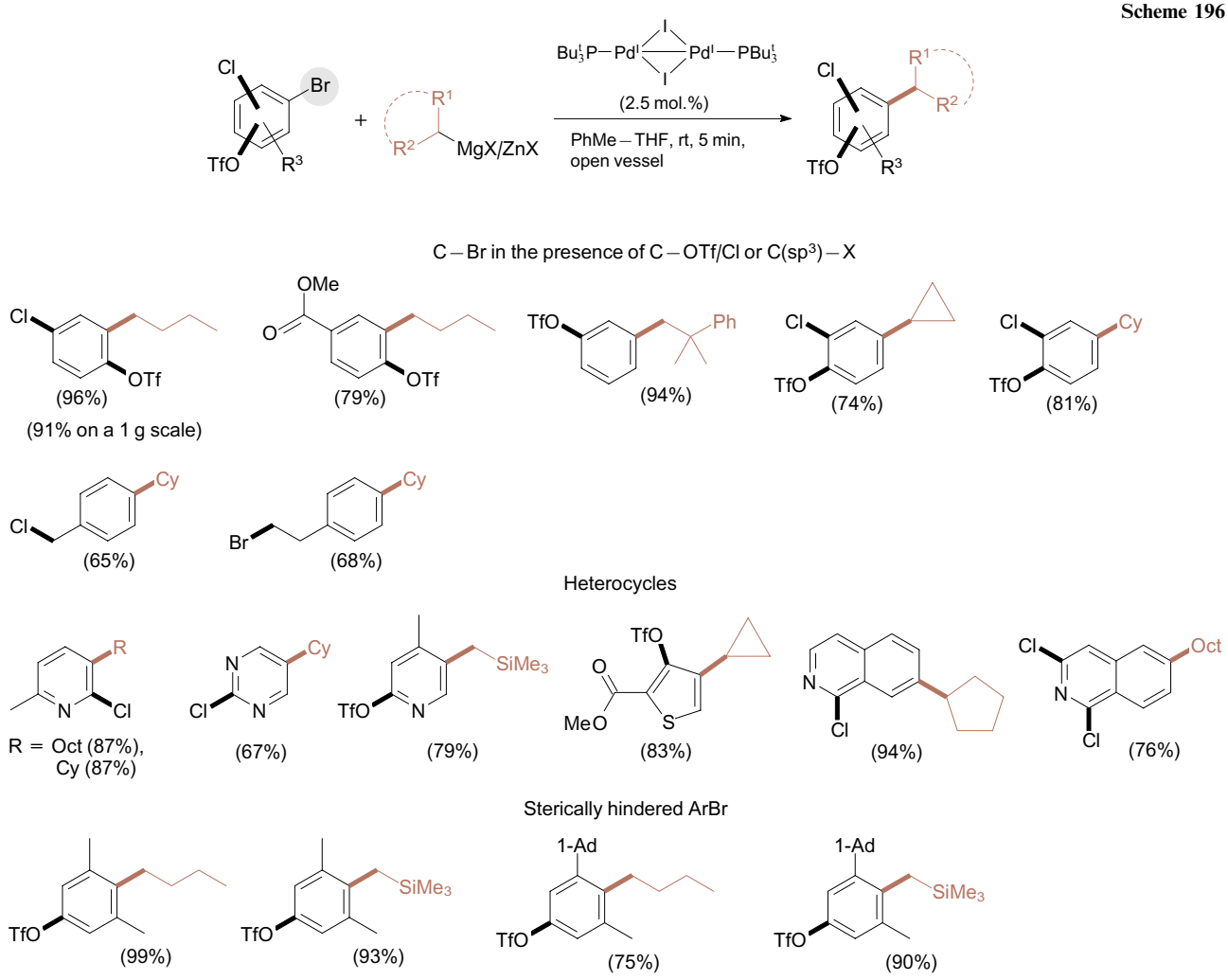


TBAB = Bu^n_4NBr; NPs are nanoparticles

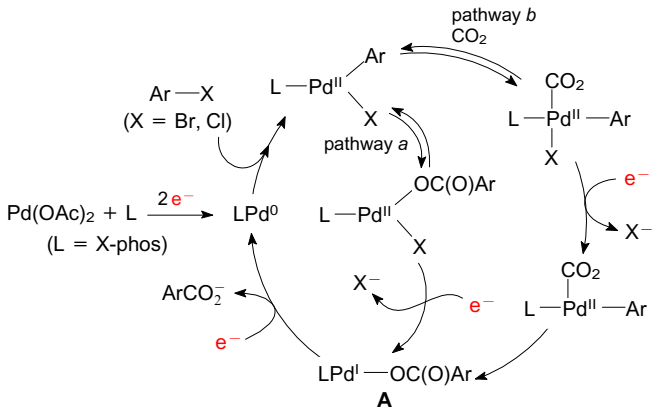
palladium acetate with X-phos followed by the oxidative addition of aryl halide (Scheme 197). The subsequent addition of CO_2 may proceed along two possible pathways. The first one (pathway *a*) involves insertion into the Pd – C bond followed by single-electron reduction (by means of iridium-based photoactive catalyst). The same intermediate **A** can be formed stepwise (second pathway, pathway *b*) *via* coordination of CO_2, which is followed by single-electron reduction and insertion into the Pd – C bond. The intermediate undergoes one more single-electron reduction, resulting in regeneration of zerovalent palladium and release of the carboxylation product. Thus, three palladium oxidation states, $Pd^0/Pd^{II}/Pd^I$, participate in the reaction, which opens up new prospects for palladium catalysis.[822]

Group 10 ends with platinum. The nature of the Pt – C bond and the environment determine the lower reactivity of platinum complexes; however, the similarity in energy of the oxidative addition and reductive elimination steps promotes the development of new platinum-based catalytic systems.[823 – 827]

Scheme 196



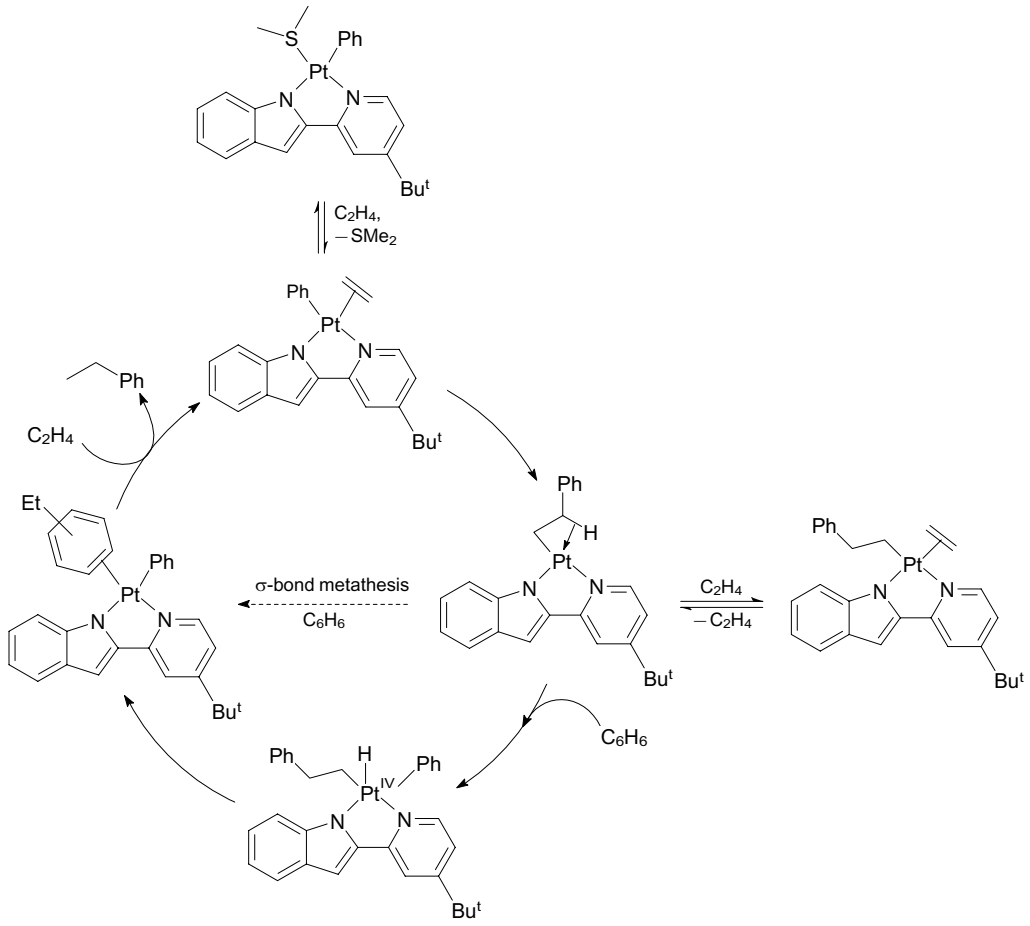
Scheme 197



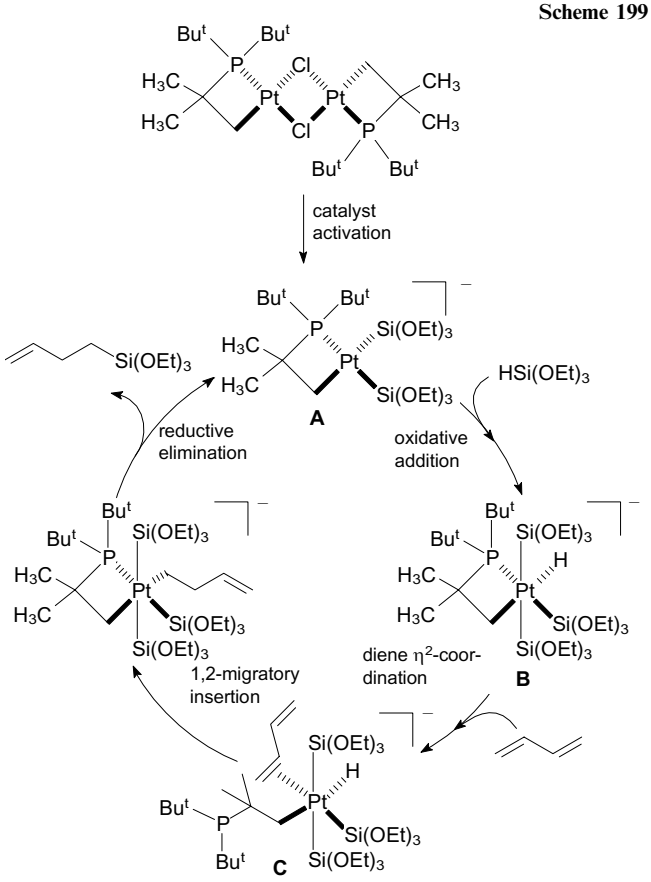
Apart from other metals, platinum is widely used for C – H activation.[828] Don Tilley and co-workers[829] developed an efficient method for the hydroarylation of alkenes using the pyridyl-indolate platinum complex. Detailed investigation of the mechanism identified participation of the Pt^{II}/Pt^{IV} pair. First, alkene is coordinated to the platinum atom and then it is inserted into the Pt – Ph bond; the phenyl group is a significant initial ligand, which helps to avoid additional oxidative addition/reductive elimination steps for metal activation (Scheme 198). This is followed by oxidative addition of a benzene C – H group to give a tetravalent platinum complex. The cycle is completed by reductive elimination of the product, which dissociates from the platinum coordination sphere to generate a coordination site for a new alkene molecule.[829]

Hydrosilylation of multiple bonds is one more application of platinum.[830] Ritter and co-workers[831] proposed a selective method for 1,2-hydrosilylation of conjugated dienes by the Pt^{II}/Pt^{IV} mechanism. The Si – H bond oxidatively adds to the cyclic platinum(II) P,C-complex **A**, thus

Scheme 198



Scheme 199

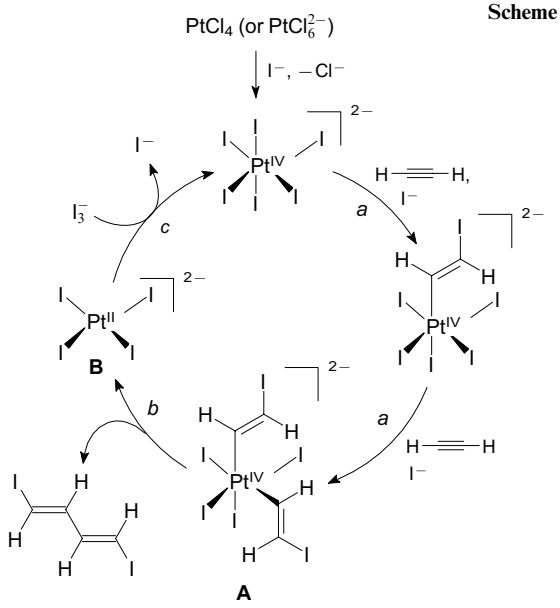


forming the anionic platinum(IV) hydride complex **B**, to which the 1,3-conjugated diene is coordinated (Scheme 199). In the platinum coordination sphere (intermediate **C**), 1,2- migratory insertion of the diene into the Pt – H bond takes place, and the subsequent reductive elimination regenerates the platinum complex **A** and furnishes the product. Silicon derivatives of this type are unique synthons for organic and organoelement chemistry.[831]

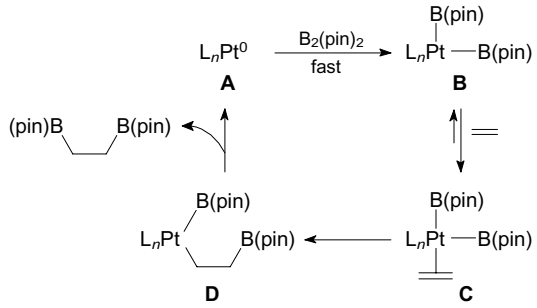
One more vivid case of application of the Pt^{II}/Pt^{IV} pair is the selective preparation of (*E*,*E*)-diodobutadiene.[832] The mechanism of acetylene dimerization giving diiodobutadiene has been studied in detail by the density functional theory.[833] Acetylene is successively inserted two times into the Pt – I bond of anionic hexaiodoplatinate (Scheme 200 *a*). The divinyl complex **A** thus formed undergoes reductive elimination (*b*), which is highly selective. The released tetraiodoplatinate (**B**) is readily oxidized with iodine (*c*) and closes the cycle.

Diboration is a convenient method for multiple bond functionalization;[834] Morken and co-workers[835] developed a method for enantioselective diboration of alkenes catalyzed by the zerovalent platinum complex with dibenzylideneacetone. Platinum is activated by chiral 3,5-diisopropylphenyl-taddol(phenyl)phosphine, and after this, pinacol diborane oxidatively adds to the metal (Scheme 201, **B**). Platinum(II) coordinates the alkene, which is inserted into the Pt – B bond (**C**, **D**). This Pt – C bond formation step determines the product stereochemistry. The subsequent reductive elimination releases the Pt^0 phosphine complex (**A**) and the diboration product. The

Scheme 200



Scheme 201



boron derivatives thus formed can be easily hydrolyzed by alkali with hydrogen peroxide, giving rise to chiral diols.[835]

Thus, catalysis by Group 10 transition metal complexes occupies a special position in synthetic chemistry. From the mechanistic standpoint, the nature of the M–C bond largely accounts for the activity of the compounds used. The M–C bond dissociation energy is much lower than the energy of the usual C–C bond, which accounts for high activity of metal complexes. Apart from the M–C σ-bonds, π-bonds also play a role by promoting activation and functionalization of multiple bonds.

Nickel complexes exhibit high activity; however, optimization and control of Ni-based systems are complicated more than the other ones by the necessity to minimize the side reactions. Nevertheless, the scope of Ni catalysis is rather broad and, moreover, its potential has not been fully disclosed. The broad range of stable oxidation states ($Ni^0/Ni^I/Ni^{II}/Ni^{III}/Ni^{IV}$) and the ability to undergo both single- and double-electron transfers ensure that new applications of nickel complexes would appear in the near future.

Palladium has been much better explored and is more widely used both in the cross-coupling or Heck reaction and in C–H bond activation. Although palladium compounds generally show moderate activity and have been much better investigated, detailed study of relevant reaction mechanisms opens up new horizons. First of all, one should expect the development of single-electron transfer chemistry and more extensive application of unusual oxidation states such as Pd^I.

Platinum complexes are most stable. Therefore, they are still good models for studying the mechanisms of catalytic processes. Furthermore, optimization of the platinum coordination sphere in the presence of highly active C-ligands may not only give rise to new catalytic systems, but also provide the development of highly stable homogeneous catalysts that could be easily separated from the reaction mixture and reused many times.

Obviously, transition metal catalysis is expected to make a new quantum leap in the next decade. Study of the dynamic nature of catalytic systems would be helpful for understanding the details of intricate reactions involving not only substrates, but also the metal. The economic problems of the modern society would stimulate the development of more efficient systems that would require lower amounts of active catalysts, while discovery of new classes of reactions would provide for their extensive application in various fields of pharmaceutics, materials chemistry and many other.

11. Modification of properties of organometallic compounds with redox-active ligands

The previous Section dealing with the catalytic transformations clearly demonstrates the key role of ligands for tuning the reactivity and catalytic properties of organometallic compounds. The conventional properties of various ligand systems are adequately addressed in the literature; however, redox-active ligands, which show unique behaviour not inherent in other types of ligands, deserve special attention.

Redox-active ligands are organic compounds that can change their redox state within complexes they form with metals, without being detached from the central metal atom. In the free uncoordinated state, organic compounds suitable as redox-active ligands can also participate in a variety of chemical transformations known in organic chemistry. However, as in classical coordination chemistry, the coordination of a redox-active ligand to a metal atom enables chemical reactions impossible for the same compound in the uncoordinated state. The use of redox-active ligands in coordination chemistry resulted in the discovery of a number of fundamental phenomena, for example, redox isomerism — reversible intramolecular electron transfer between a redox-active metal and a redox-active ligand induced by an external stimulus.[836] Paramagnetic redox-active ligands can be used as reporter ligands, a sort of spin labels.[837] Classical redox-active *o*-semiquinones and diimines possess unique properties: formation of stable metal chelates; conformational rigidity of the planar metallacycle; and virtually complete localization of the molecular orbital involved in the redox transformations on the ligand. Hence, *o*-semiquinone and diimine radical anions can be used in EPR studies of the composition, structure and dynamics of the coordination sphere for metal complexes in solutions. This approach is most useful when applied to metal compounds containing magnetic isotopes both in the redox-active ligands and in the spectator ligands. Owing to the spin density transfer to the molecular orbitals of spectator ligands, hyperfine structure characterizing the composition and structure of the metal complex appears in

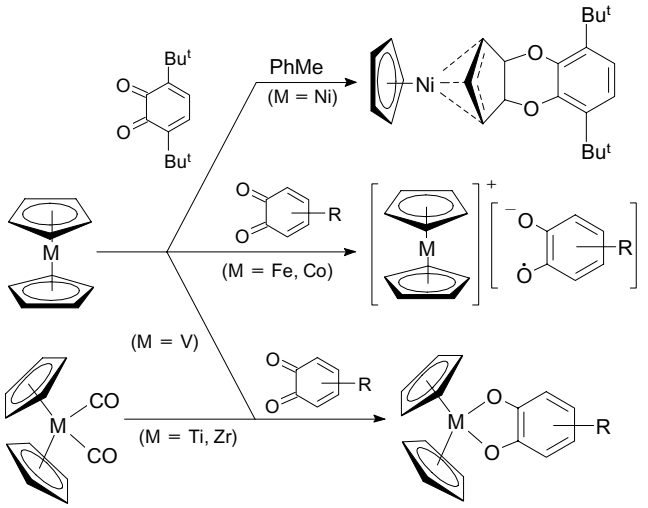
the isotropic EPR spectra. An interesting trend in the modern redox-active ligand chemistry is the preparation of redox-active complexes of redox-inactive metals, including many s-, p- and f-elements. The present Section is aimed at describing the influence of redox-active ligands on the properties of organometallic compounds. This influence is most clear-cut for metal complexes with *o*-quinones and diimines, which form the subject of this part of the review. Examples of reactions between OMCs and organic compounds able to act as redox-active ligands are given. The preparation of redox-active OMCs is considered and the OMCs with the metal – carbon bond reactivity being suppressed by a redox-active ligand are presented. Examples are given for metal and redox-active ligand cooperation in the reactions with organic substrates and for catalysis of organic reactions, including carbon – carbon bond formation reactions, by organometallic compounds with redox-active ligands.

11.1. Redox-active *o*-quinone and *o*-iminoquinone ligands

11.1.1. Transition metal compounds

The interest in transition metal OMCs with quinone type ligands is associated with active development of metallocene chemistry. Cobaltocene and quinones form ionic complexes comprising a cobaltocenium cation and a semiquinone radical anion.[838 – 840] Ferrocene forms either dative π-complexes with most of quinones or does not react at all.[838] A ferrocenium salt is formed only with electron-withdrawing dichlorodicyano-*p*-benzoquinone.[839] Nickelocene reacts with quinones with the loss of cyclopentadienyl ligands.[838, 841] An exception is the reaction of nickelocene with 3,6-bis(*tert*-butyl)-*o*-benzoquinone,[841] which follows the Diels – Alder pathway. Vanadocene as well as titano- and zirconocene dicarbonyls undergo oxidative addition reactions with various *o*-benzoquinones[842 – 845] to give the corresponding catecholate derivatives (Scheme 202).

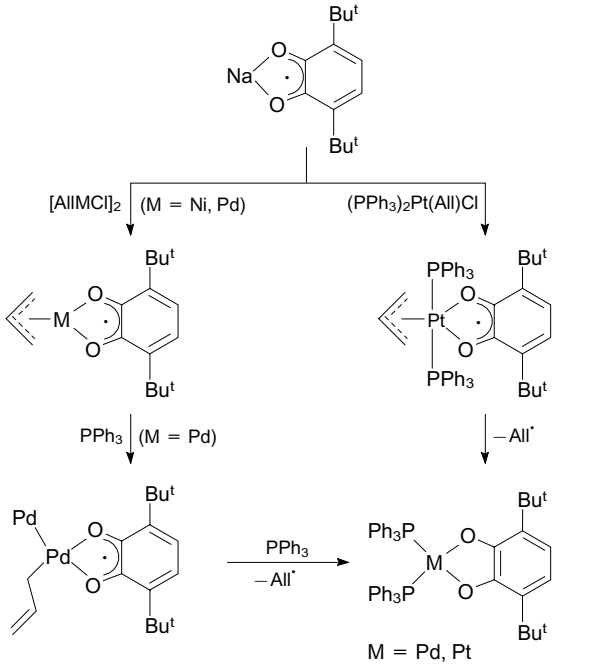
Scheme 202



Molybdenum group metal cyclopentadienyl carbonyl complexes containing various benzoquinone ligands have been studied by spectral methods. They were detected for the first time in the reaction between bis(π-cyclopentadienyltricarbonylmolybdenum)mercury with 3,5-di(*tert*-butyl)-*o*-benzoquinone.[846] The reactions of *o*-benzoquinones with $[(C_5H_5)(CO)_3Mo]_2$, $[(C_5H_5)(CO)_3W]_2$ and $[(C_5H_5)(CO)_2Fe]_2$ occur as successive replacement of carbonyl groups to give catecholate derivatives.[847, 848]

The *o*-semiquinone allyl complexes of nickel, palladium and platinum were synthesized in the mid-1970s (Scheme 203).[849 – 853] Nickel compounds are thermodynamically stable. Meanwhile, the platinum compound undergoes intramolecular electron transfer from the platinum – allyl bond to the *o*-semiquinone ligand with simultaneous elimination of the allyl radical to give platinum(II) catecholate. A similar transformation of the palladium compound is induced by coordination of phosphine ligands; in this case, it is possible to detect the $\eta^3 \rightarrow \eta^1$-rearrangement of the allyl substituent.

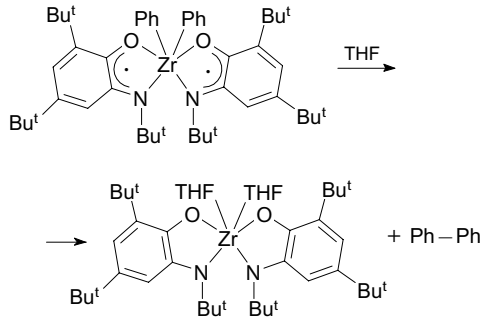
Scheme 203



The replacement of the *o*-quinone ligand by the phenoxazinone ligand with less pronounced acceptor properties results in the formation of paramagnetic platinum and palladium derivatives stable against the loss of the allyl radical.[854] A series of *o*-semiquinone (*o*-iminosemiquinone) compounds formed by nickel group metals with σ-bonded arylazoaryl, cycloalkenyl, tolyl and pincer aryl substituents, stable to metal – carbon bond homolysis, have been synthesized later.[855 – 859] In some cases, conversely, the redox-active ligand is able to stabilize the metal – carbon bond. Currently, only one compound containing the $Cu^{II}-CF_3$ bond has been reliably characterized, namely, the trifluoromethyl copper derivative stabilized by two non-reduced *o*-iminoquinone ligands.[860]

The capability of OMCs with redox-active ligands for reductive elimination of the hydrocarbon radical is due to the ability of the redox-active ligand to change its oxidation state, in particular, to be converted from the radical anion to the dianion. This opens up prospects for application of these compounds in various coupling reactions useful from the practical standpoint. For example, zirconium bis-*o*-amidophenolate derivative containing two phenyl ligands eliminates biphenyl, which is accompanied by conversion of the

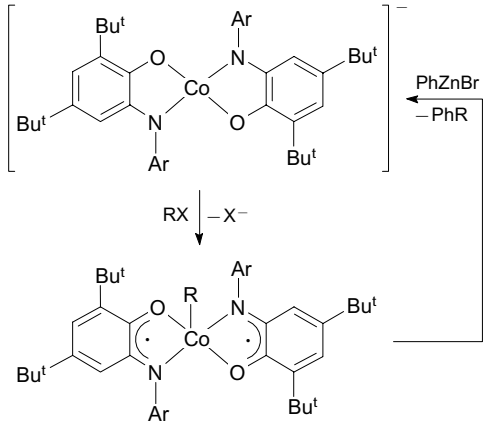
Scheme 204



redox-active ligands from radical anions to dianions (Scheme 204).[861]

The oxidation of the anionic cobalt(III) bis-*o*-amidophenolate complex with alkyl halides is accompanied by the formation of an organometallic biradical derivative. Treatment of this product with phenylzinc bromide induces Negishi type cross-coupling (Scheme 205).[862]

Scheme 205

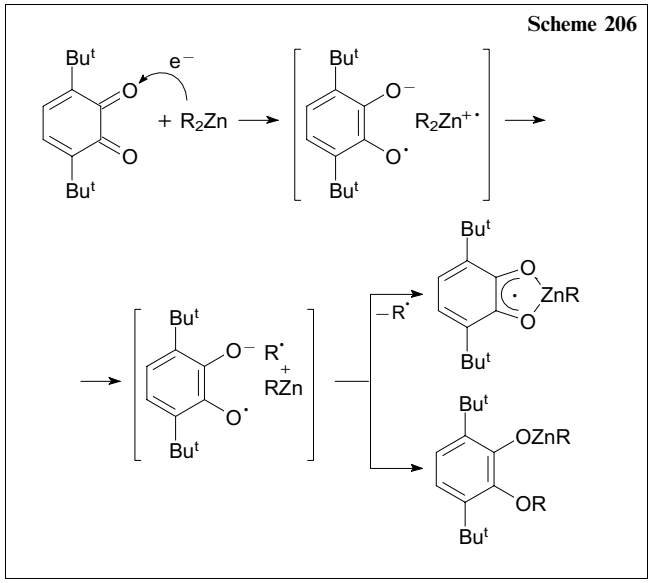


It is noteworthy that reactions of analogous bis-*o*-amidophenolate anionic gallium[863] and indium[864] complexes and neutral tin complexes[865, 866] with alkyl halides do not result in the corresponding OMCs, but are accompanied by insertion of the alkyl group into the ring of the redox-active ligand. One more example of activation of OMCs containing a redox-active ligand is the interaction of molecular hydrogen with the iridium(III) cyclopentadienyl complex with the redox-active *o*-amidophenolate ligand. The ligand oxidation to *o*-iminosemiquinone increases the Lewis acidity of the central metal, which promotes coordination and subsequent oxidation of molecular hydrogen.[867]

11.1.2. Main Group metal compounds

The first studies of reactions of Main Group metal OMCs with quinones were performed 50 years ago for Group 12 elements. These reactions may follow two pathways. The first one is nucleophilic addition of an organometallic compound to the quinone carbonyl group; the second one includes single-electron oxidation of the OMC with a quinone molecule to give radical and ion recombination products inside and outside the solvent cage. Upon the reactions of organic zinc and cadmium compounds with *o*-quinones, various catechol monoalkyl ethers were isolated, apart from the classical nucleophilic addition products.[868] Presumably, the ethers are formed *via* the single-electron oxidation of the OMC with a quinone molecule.[869] This mechanism was confirmed by recording EPR spectra corresponding to the *o*-semiquinone alkylzinc (cadmium) derivatives.[870] Thus, electron transfer from the OMC molecule to the *o*-quinone molecule gives the quinone radical anion and the radical cation derived from the organometallic compound within the solvent cage. The radical cation is stabilized by expelling the organic radical with the formation of a cation. This is followed by either recombination of ions and radicals in the solvent cage or escape of the organic radical from the cage with subsequent transformations (Scheme 206).

Scheme 206



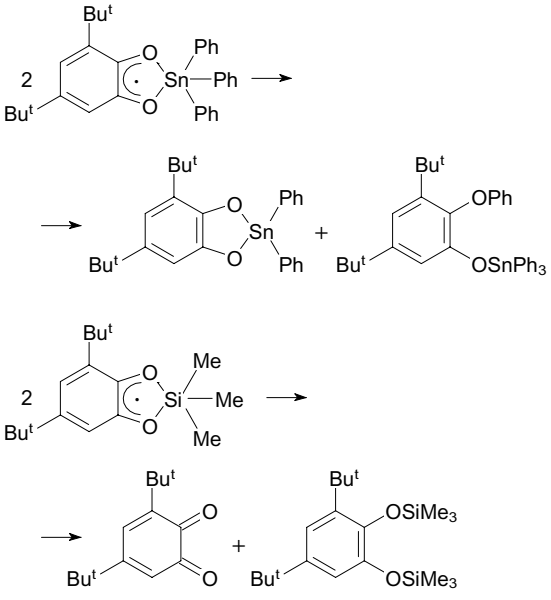
It was shown that in the case of Me_2M (M = Zn, Cd), nucleophilic addition takes place, while for Et_2M and Ph_2M (M = Zn, Cd), only single-electron oxidation products are formed.[871] In the case of other ligands present in the OMC, the ratio of the products formed according to two mechanisms changes depending on temperature and the nature of the hydrocarbon moiety. As the temperature increases and the ionization potential of the OMC decreases, nucleophilic addition predominates. Unstable organomercury semiquinolates are formed in photochemical reactions between R_2Hg and various *o*-benzoquinones and in the reactions of RHgCl with alkali metal semiquinolates.[854, 870] Stable paramagnetic mercury OMCs have been synthesized later using radical anions of the sterically hindered *o*-iminoquinone.[872, 873]

Organometallic compounds of Group 13 elements also easily react with quinones. The reactions of Et_3M with *o*-quinones[874] afford the paramagnetic *o*-semiquinolates $(SQ)MEt_2$ (M is a Group 13 metal), which were characterized by EPR spectroscopy. The stability period of these species in solution increases from 20 min for aluminium and indium to 48 h for gallium and thallium. Diethyl- and dimethylthallium semiquinone complexes have also been prepared by exchange reactions between the monosodium salts of various quinones and R_2TlCl (R = Me, Et) or by displacing a quinone with weaker acceptor properties from $(SQ)TlR_2$ by a more electron-withdrawing quinone.[840, 841, 875] In a later publication, the isolation of stable

dimethylthallium semiquinone derivatives in a pure state is reported.[876, 877] Stable biradical gallium and indium monoalkyl derivatives have been synthesized using radical anions of sterically hindered *o*-iminoquinones.[878 – 880] It should be noted that, whereas the introduction of quinone type redox-active ligands in the radical anion state into Group 13 metal compouds destabilizes, most often, the metal – carbon bond and results in bond lability, *o*-iminoquinone dianions have, conversely, stabilizing effect. Indeed, it has been shown that the reactions of (amidophenolato)alkylgallium[878, 881] and -indium[879] with various oxidants, including air oxygen or molecular iodine, do not affect the M – C bond, but result in oxidation of the redox-active ligand. The alkyl group bound to indium is favourable for stabilization of the iminoquinone dianion within the metal coordination sphere.[882] Without an alkyl group, the redox-active ligand is oxidized by the central metal.[883]

The organosilicon, -germanium and -tin semiquinolate derivatives are unstable. In solution, they rapidly decay. The free valence can be lost by two pathways: *via* disproportionation of the *o*-semiquinone complex and elimination of the hydrocarbon radical from the metal atom. The ratio of these two pathways depends on the natures of the metal, quinone ligand and hydrocarbon group.[884] Organotin compounds tend to give off the hydrocarbon radical. The reaction follows second-order kinetics and gives no products of reactions of free organic radicals R$^{\bullet}$. Thus, the homolytic cleavage of the Sn – C bond occurs only under the action of a free radical scavenger, and this function can be performed by a second metal semiquinolate molecule (Scheme 207).

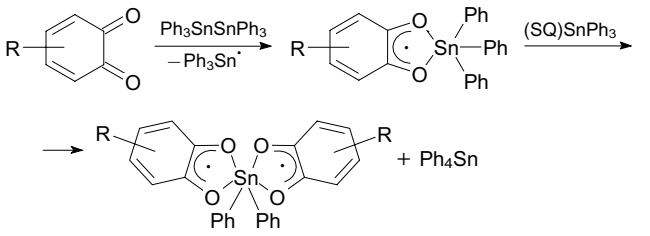
Scheme 207



Brown *et al.*[885] reported the isolation of Ph_4Sn upon the reactions of some *o*-quinones with hexaphenyldistannane. Apparently, triphenyltin semiquinolate is symmetrized in solution to give Ph_4Sn and bis(*o*-semiquinolato)diphenyltin (Scheme 208).

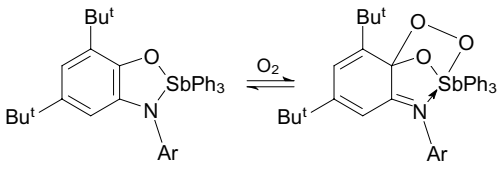
The proposed scheme of (SQ)$SnPh_3$ transformations was proved by isolation and X-ray diffraction characterization of the phenanthrenequinone-based biradical derivative.[886] In more recent studies, another stable biradical compound of the same type has been obtained.[887] Among stable monoradical *o*-semiquinone tin derivatives, mention should be made of the triorganometallic compounds containing the M – Sn – M metal chain (M = Fe, Mo, W).[888] The organotin derivatives containing *o*-iminoquinone radical anions are more stable. Both stable and unstable mono- and biradical alkyl and aryl tin derivatives based on bidentate sterically hindered *o*-iminoquinone have been reported.[889 – 893] The stability of the formed compounds was shown to depend not only on the Sn – C bond energy, but also on the steric crowding of the central metal.[890] The paramagnetic bis-alkyl and bis-aryl organotin and -silicon compounds based on the tridentate redox-active ONO ligand in the dianion diradical form possesses rather high stability,[265, 894 – 897] whereas trialkyl complexes with the monoanion of the same ligand are unstable and undergo intramolecular migration of one hydrocarbon group from the metal atom to the nitrogen atom.[898, 899] In relation to (diphenylcatecholato)tin(IV), metal catecholate derivatives were found to react with both stable and short-lived, including carbon-centred, radicals to generate *o*-semiquinone tin derivatives.[900] This not only indicates the appearance of a new type of radical scavengers, but, in combination with the ability of tin *o*-semiquinolates to eliminate the hydrocarbon radical in the presence of an appropriate scavenger, makes tin catecholates and *o*-iminosemiquinolates applicable for chain propagation control in the radical polymerization of vinyl monomers [901, 902] and as iniferters.[903]

Scheme 208



Regarding the OMCs of Group 15 metals containing redox-active ligands, of obvious interest is the ability of catecholate and *o*-amidophenolate triorganylantimony complexes to reversibly add molecular oxygen (Scheme 209).[904, 905]

Scheme 209



Ar = 2,6-$Pr^i_2C_6H_3$

Depending on the acceptor properties of the redox-active ligand, an antimony compound can either reversibly add molecular oxygen to give endoperoxides or be inert towards oxygen. The effects of the nature of substituents in the *o*-quinone moiety and substituents at the antimony

atom have been described in detail in a series of publications,[904 – 909] including the theoretical aspects of the reaction.[910, 911]

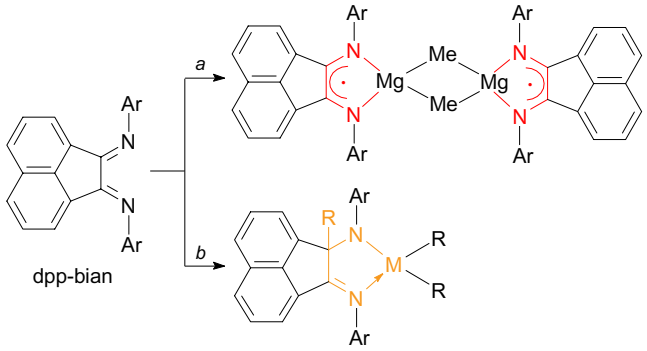
In conclusion, it is necessary to mention the thermo/photomechanical effect, which was first discovered in dicarbonyl rhodium 3,6-di(*tert*-butyl)-*o*-semiquinolate.[912, 913] On exposure to visible or near-IR light, the thread-like crystals of this complex reversibly bend, with the bending angle exceeding in some cases 90°. The maximum sensitivity of the bending crystals is observed on irradiation at 1400 nm, which corresponds to the low-energy metal to ligand charge transfer. The nature of this unusual phenomenon is in the formation of parallel one-dimensional stacks in the crystal consisting of planar organometallic compound molecules and containing short Rh···Rh contacts. The change in the molecular geometry and the state of the metal atom upon light-induced metal to ligand charge transfer changes the Rh···Rh distance in the stacks and, hence, results in crystal deformation along the stacks.

11.2. Redox-active diimine ligands: Main Group and rare earth metal compounds

A substantial difference of diimine (1,4-diazabutadiene) ligands from *o*-quinone is that the nitrogen atoms in diimines, unlike the oxygen atoms in quinones, can bear substituents. The variation of substituents makes it possible not only to affect the acceptor properties of the lowest unoccupied molecular orbital of the diimine, but also to control the structure of metal complexes *via* steric factors. Whereas the coordination chemistry of metal complexes with diazabutadiene ligands has developed during the last 50 years, organometallic compounds with diimine ligands in various redox states have been actively studied only for about 20 years. The first OMCs with diimine ligands [*e.g.*, (dad)Mo(CO)$_4$ and (dad)Ni(CO)$_2$, dad = ArN=C(Me)C(Me)=NAr] were obtained in the mid-1960s by reactions of metal carbonyls with some diimines.[914] In the beginning of the 1970s, Clopath and Zelewsky[915, 916] reported the synthesis of the first metal compounds with the 1,4-di(*tert*-butyl)-1,4-diazabuta-1,3-diene radical anion. In the 1970s, the reactions of diazabutadienes with organometallic compounds were studied by van Koten and Vrieze.[917] In the beginning of the 21st century, Trifonov's team[918] demonstrated that ytterbocenes reduce 1,4-diazabuta-1,3-dienes in toluene to give ytterbium complexes with the radical anion diimine ligand. In tetrahydrofuran, back electron transfer takes place from the diazabutadiene ligand to the ytterbium atom, along with decomposition of the complex to the initial ytterbocene and diimine.

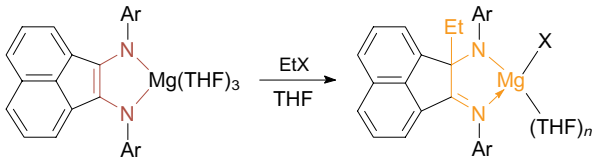
Since the beginning of the 21st century, 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) has been actively used as a ligand in the coordination chemistry.[919] It is distinguished by the conformational rigidity of the diimine moiety caused by its annulation to the acenaphthene system and the presence of bulky substituents at the nitrogen atoms. Similarly to ytterbocene, europium and samarium dicyclopentadienides form complexes with diimines of the bian family. Depending on the acceptor properties of diimine and the redox potential of the metal, complexes with both neutral and reduced bian ligands can be formed.[920] The reactions of OMCs with dpp-bian may proceed with either its reduction with the carbanion to the radical anion[921] or as OMC addition to the C=N bond[922, 923] to give amido-imine complexes (Scheme 210). The amido-imine complexes are also formed in the reactions of ethyl halides with (dpp-bian)Mg(THF)$_3$ (Scheme 211).[923]

Scheme 210



(*a*) $MgMe_2$, PhMeM, −[Me$^•$]; (*b*) MR_3, PhMe; M = Al, Ga, In

Scheme 211

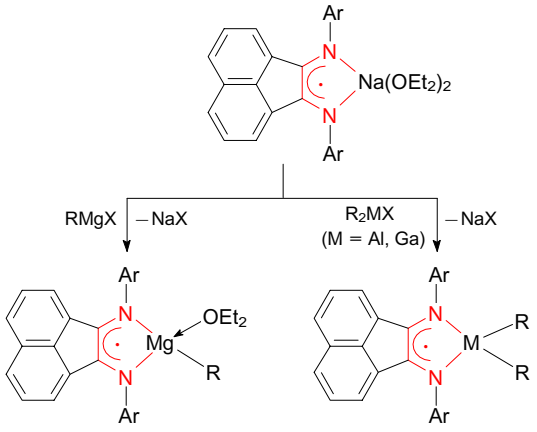


X = Cl, *n* = 0; X = Br, *n* = 2; X = I, *n* = 1

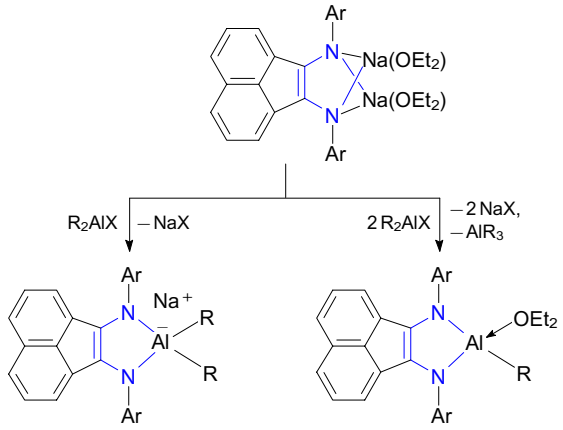
According to EPR spectroscopy, the latter reaction gives a dpp-bian radical anion, which recombines with the ethyl radical to yield the final product. The compound (dpp-bian)Mg(THF)$_3$,[924] containing the dpp-bian dianion, is readily formed upon the reduction of dpp-bian with magnesium. This was the first synthesized metal derivative containing dpp-bian in the reduced state.

A versatile method for the preparation of organometallic compounds containing the dpp-bian ligand in one of the two redox states (radical anion or dianion) is the exchange reaction of the appropriate alkali metal salt with the organometallic halide (Schemes 212, 213).[925 – 928] The starting sodium salts of the dpp-bian diimine are formed upon reduction with an equivalent amount of the alkali metal. The unique character of the dpp-bian ligand is in the fact

Scheme 212



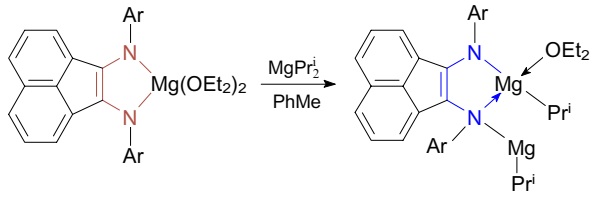
Scheme 213



that it can be reduced by alkali metals to the tri- and even tetraanion.[929]

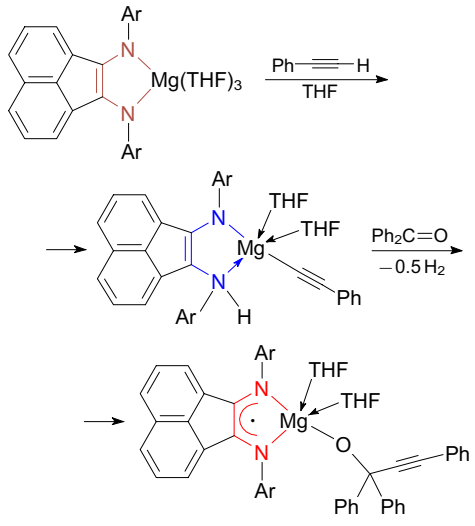
An original method for the synthesis of organomagnesium compounds containing the dpp-bian dianion is the disproportionation reaction between R_2Mg and the complex (dpp-bian)$Mg(OEt_2)_2$ (Scheme 214).[930] This reaction gives rise to two organometallic centres (Mg – C bonds) differing in the ligand environment.

Scheme 214



The basicity of nitrogen atoms in the complex (dpp-bian)$Mg(THF)_3$ is so high that the compound readily reacts with terminal alkynes to give alkynyl magnesium derivatives. Unlike the reactions of Hauser amides (R_2NMgX),[931] the reaction of (dpp-bian)$Mg(THF)_3$ with PhC≡CH cannot be accompanied by elimination of the

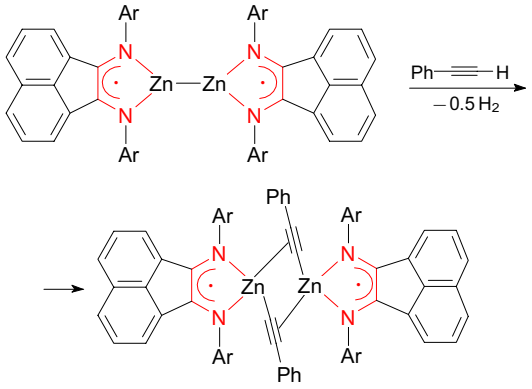
Scheme 215



amine, and actually its addition to the complex *via* σ-bond metathesis takes place (Scheme 215).[932]

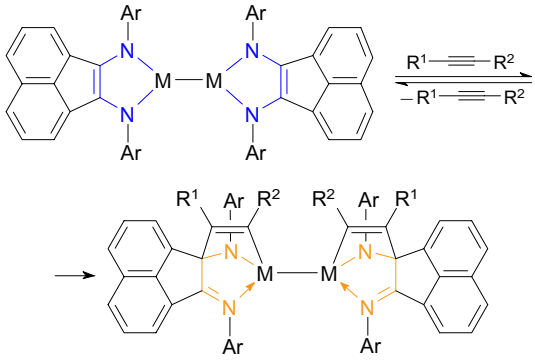
In recent years, molecules combining closely located Lewis base and acid sites linked by an inert bridge have become very popular and have been termed as frustrated Lewis pairs. These systems can be used to activate not only polar bonds, for example, C – H, but also multiple carbon – carbon bonds.[933, 934] The product of phenylacetylene addition to the complex (dpp-bian)$Mg(THF)_3$ reacts with diphenyl ketone with insertion of the carbonyl compound into the Mg – C bond accompanied by hydrogen atom abstraction from the nitrogen ligand, resulting in the paramagnetic alcoholate (see Scheme 215).[932] Paramagnetic zinc acetylenide is formed upon the reduction of phenylacetylene hydrogen with the dizinc derivative (Scheme 216).[935]

Scheme 216



Dialane and digallane containing the dpp-bian dianion possess unique reactivity towards alkynes. Reactions with alkynes occur as cycloaddition and give alkenyl-amino-imine derivatives (Scheme 217).[936 – 938]

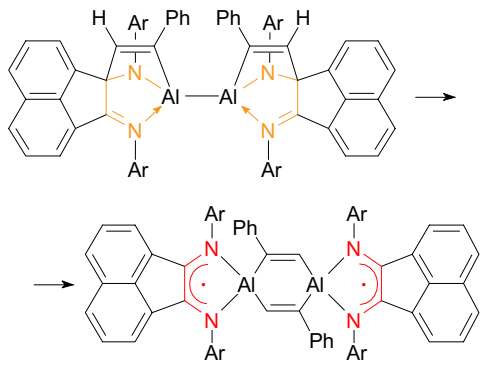
Scheme 217



M = Al, Ga; R^2 = H: R^1 = H, Ph; R^1 = Me: R^2 = CO_2Me, CO_2Et, Ph

Surprisingly, these reactions are reversible: complete elimination of alkynes from cycloaadducts takes place on heating of their solutions to ~100 °C. Thus, the addition of alkynes to Al and Ga derivatives of the dpp-bian ligand resembles, in some respects, the coordination of unsaturated hydrocarbons to transition metal compounds. In a pure state, this coordination to a main group metal atom is rather weak because of the absence of additional ligand – metal binding through the metal to ligand donation of

Scheme 218



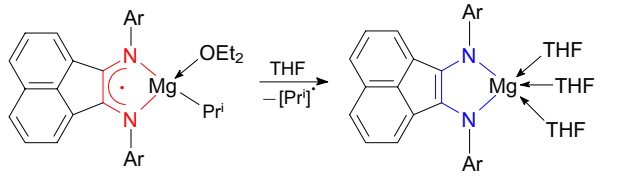
d-electrons. The product of PhC≡CH cycloaddition to dialane rearranges within several hours to thermally stable paramagnetic 1,4-dialacyclohexa-2,5-diene (Scheme 218).[938]

The digallane (dpp-bian)Ga – Ga(dpp-bian) demonstrates high catalytic activity towards the hydroamination of phenylacetylene and carbodiimide with anilines[939,940] and towards phenylacetylene hydroarylation with phenols.[939]

In relation to the complex (dpp-bian)AlEt(OEt$_2$) containing the dpp-bian dianion, the redox-active ligand was demonstrated to have deactivating action on the Al – C bond. Indeed, neither diphenylacetylene nor diphenyl ketone are inserted into the aluminium – ethyl bond: the former compound reacts according to the cycloaddition reaction route,[940] while the latter one displaces the diethyl ether and is coordinated to aluminium (Scheme 219).[941] The reaction of (dpp-bian)AlEt(OEt$_2$) with methyl vinyl ketone (MVK) also occurs as cycloaddition.[940] Acidic substrates such as diphenylamine, phenol or water do not protonate the Al – C(ethyl) bond, but add at the Al – N bond, with water being doubly deprotonated (see Scheme 219).[942]

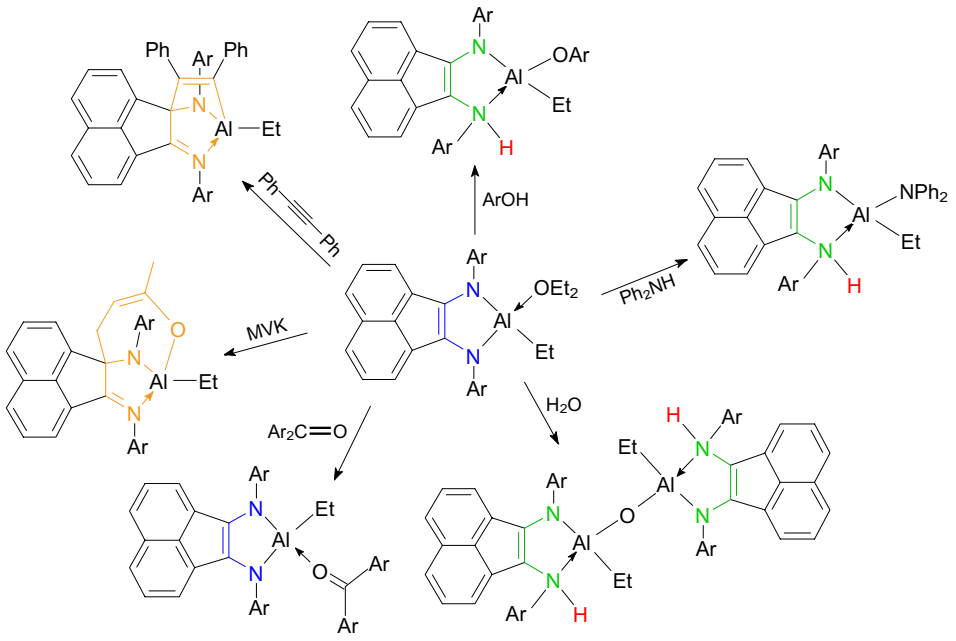
A promising application of main group metal complexes with redox-active ligands is catalysis of organic reactions. A key role in homogeneous transition metal catalysis of the C – C bond formation reactions is played by oxidative addition and reductive elimination taking place at the central metal. About ten years ago, it was proposed to implement these reactions using redox-active ligands incorporated in main group metal compounds.[943] The solvent-induced reductive elimination of the alkyl group is observed for the magnesium acenaphthene-1,2-diimine derivative (Scheme 220).[930]

Scheme 220

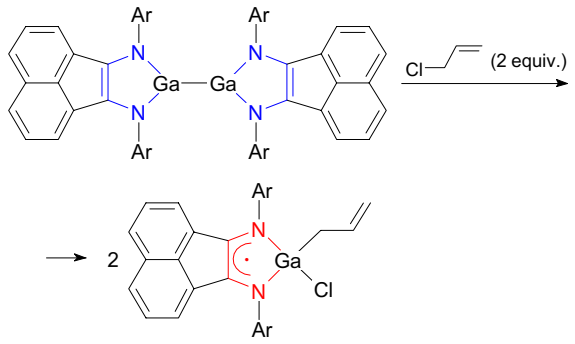


The organomagnesium compound (dpp-bian)MgPr^i(OEt$_2$) can be prepared by the exchange reaction of (dpp-bian)Na(OEt$_2$) with Pr^{i}MgCl in hexane. This compound is stable in solutions in hexane and even in diethyl ether, but in THF it rapidly eliminates the isopropyl radical, being converted to (dpp-bian)Mg(THF)$_3$ (see Scheme 220).[930] Note that the crucial factor for this process is the size of the organic substituent at the magnesium atom. The methyl, ethyl and trimethylsilylmethyl magnesium derivatives (dpp-bian)MgR(OEt$_2$) (R = Me, Et, Me$_3$SiCH$_2$) are stable,[925] whereas 2-methylallyl and *tert*-butyl derivatives decompose. The two-electron reductive elimination has not yet been implemented for main group metal compounds with redox-active ligands. This was accomplished for an iron complex and will be demonstrated below. The two-electron (per one central metal atom) oxidative addition is observed for (dpp-bian)Ga – Ga(dpp-bian). Digallane reacts with allyl chloride with oxidation of both dianionic ligands and the metal – metal bond to give the radical anion derivative having the gallium – carbon bond (Scheme 221).[944]

Scheme 219

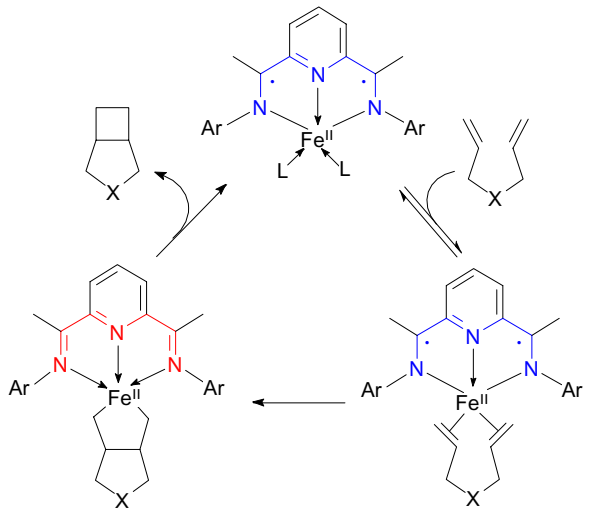


Scheme 221



An interesting example of a catalytic reaction generating the carbon – carbon bond in which a redox-active ligand plays a key role is cyclization of dienes with isolated double bonds in the presence of an iron complex with the redox-active bis(iminopyridinate) ligand (Scheme 222).[945] It should be emphasized that the iron atom does not change its oxidation state in the catalytic cycle, but the redox state of the iminopyridinate ligand changes.

Scheme 222

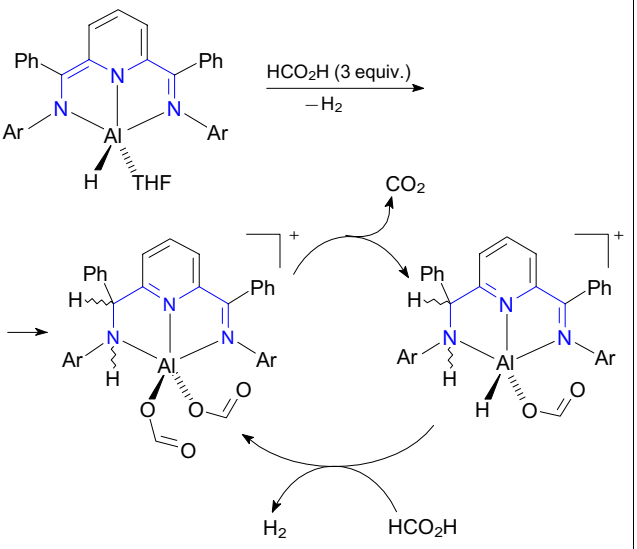


X = CH_2, NAlk, $C(CO_2Et)_2$

In recent years, this ligand has also been employed in the main group metal chemistry. The aluminium complex of this ligand catalyzes (TON > 2200) decomposition of formic acid to hydrogen and carbon dioxide (Scheme 223).[946] It is noteworthy, however, that the redox state of the ligand does not change throughout the catalytic cycle.

Thus, it is demonstrated in this Section how strongly the redox-active ligands affect the chemical properties of organometallic compounds. Redox-active ligands not only markedly influence the reactivity of the central metal atom, but are also involved by themselves in reactions with various substrates. Redox-active ligands can be divided into two groups in terms of the type of chemical transformations in which they participate. Ligands of the first group act as donors or acceptors of the electrons that are transferred from the ligand to the substrate or from the substrate to the ligand. A specific case is the intramolecular

Scheme 223



metal to ligand electron transfer. If this process is not accompanied by a change in the metal complex composition, this implies the redox isomerism phenomenon, which, in turn, defines a unique physicochemical phenomenon, namely, the photo/thermomechanical effect. Ligands of the second group are not only involved in the electron transfer, but also directly form new chemical bonds with the substrates. The metal and the redox-active ligand often act cooperatively, each forming a new chemical bond during the reaction. Apparently, together with development of the chemistry of organometallic compounds with redox-active ligands, the related coordination chemistry will also vigorously develop.

12. Organic compounds of rare earth metals

Due to the specific electronic structure of Group 3 metals, the chemical behaviour of their organic compounds considerably differs, as a rule, from that of derivatives of other metals, which has always attracted considerable attention of researchers. In this Section, this issue is addressed considering complexes of 'uncommon' divalent lanthanides (Nd, Dy, Tm) and alkyl derivatives of all lanthanides. The features inherent in both classes of compounds include poor accessibility, low stability and very high reactivity.

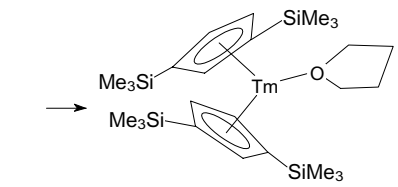
12.1. Complexes of divalent lanthanides

Group 3 metals from Sc to Lu are known to predominantly exist in the oxidation state +3. Only six elements — Nd, Sm, Eu, Dy, Tm and Yb — can have the oxidation state +2; the kinetic stability of Ln^{2+} derivatives substantially decreases in the series Eu > Yb > Sm > Tm > Dy > Nd. The chemistry of organic compounds of divalent lanthanides has long been limited to stable Sm, Eu and Yb complexes, the properties of which are described in detail in hundreds of monographs, reviews and original papers. Derivatives of Tm^{2+}, Dy^{2+} and Nd^{2+} have remained unexplored due to the absence of available methods for their synthesis. However in the late 1990s, the authors of this Section[947–950] discovered convenient methods for the preparation of diioides LnI_2 and synthesized the first molecular complexes of these metals $LnI_2(DME)_3$,

$LnI_2(THF)_5$ and $LnI_2(Pr^iNH_2)_4$; most of these complexes were structurally characterized in cooperation with Evans (University of California, Irvine) and Schumann (Technical University, Berlin). These studies gave impetus to the development of the chemistry of uncommon divalent lanthanides in many research centres and resulted in the publication of numerous papers and reviews.[951–955] The brief survey given below is devoted to molecular compounds of Tm^{II}, Dy^{II} and Nd^{II} and compounds of other lanthanides, except for Sm, Eu and Yb, able to exist in the formal oxidation state +2. The framework of the Section allowed us to include only a minor portion of the existing data; therefore, only the most important, in our opinion, recent results and achievements are considered.

The synthesis of molecular diiodides opened up the opportunity for the preparation of organometallic divalent lanthanide complexes LnI_2L_x. The efforts were concentrated, first of all, on compounds of thulium as the most stable element of the new triad. The attempts to use methods and ligands that are applied for the synthesis of Sm^{II}, Eu^{II} and Yb^{II} complexes were unsuccessful because of fast oxidation of Tm^{II} to Tm^{III}. This problem was solved by using cyclopentadienyl ligands with bulky trimethylsilyl substituents. The first complex of this type — $[(Me_3Si)_2C_5H_3]_2Tm(THF)$ — was obtained by Evans *et al.*[956] in 2001, which marked a breakthrough towards organic complexes of uncommon divalent lanthanides (Scheme 224).

Scheme 224



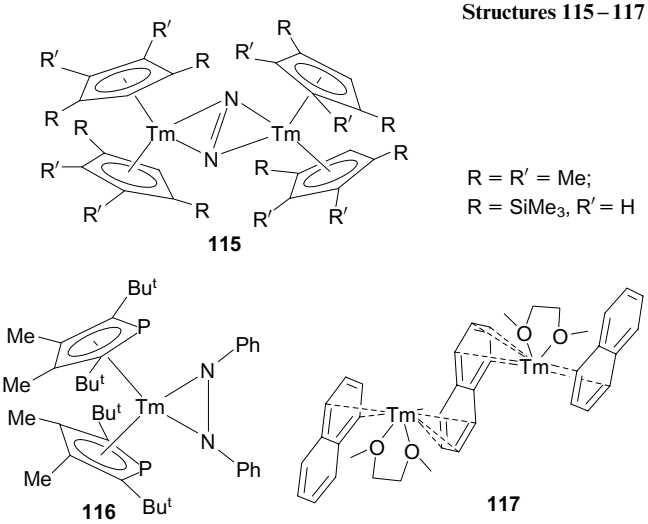
Subsequently, this method has been used to prepare more than 20 Tm^{II} compounds with cyclopentadienyl and related ligands: $(Me_3Si)_3C_5H_2$, $Bu^t_3C_5H_2$, $Me_2(Me_3Si)_2C_4P$, $Me_2Bu^t_2C_4P$, $Me_2(Me_3Si)_2C_4As$, *etc.*[957, 958] Takats and coworkers[959] synthesized the first heteroligand complexes $(L)Tm[N(SiMe_3)_2]$, including the alkyl derivative $(L)Tm[CH(SiMe_3)_2]$ [L is tris(3-*tert*-butyl-5-methylpyrazolyl)borate]. Apart from metathesis reactions, the reduction of trivalent precursors like L_2TmI with potassium graphite (KC_8) has been applied to prepare some Tm^{II} complexes with bulky ligands.[960] All of the novel compounds showed a sufficient stability at room temperature and high reactivity. For Nd and Dy, no organic complexes of the LnR_2 type have been synthesized as yet.

Apparently, the most vivid example of high reactivity of subvalent thulium compounds is the addition of molecular nitrogen, which takes place under ambient conditions and results in the formation of binuclear diazenides similar to complex **115**.[956, 961]

It is noteworthy that the addition of a nitrogen molecule is possible only during the reduction of trivalent derivatives in a nitrogen atmosphere. The pre-synthesized TmL_2 complexes do not react with nitrogen, except for the alkyl complex $(L)Tm[CH(SiMe_3)_2]$, which adds nitrogen in the presence of dibutylaniline without a reducing agent.[959] Similar diazenides have been obtained for the whole series of lanthanides, except for Eu, Pm and Yb.[955] Interestingly, the $(N_2)^{2-}$ dianion present in the complexes cannot be converted to nitrogen compounds in reactions with various substrates, only neutral N_2 being formed in all cases, whereas the nitrogen-fixing systems such as Cp_2Yb/sodium naphthalenide obtained previously are hydrolyzed to give ammonia and hydrazine.[962]

The chemical properties of divalent Tm, Dy and Nd have been mainly studied in relation to the diiodides LnI_2. For organic complexes, only single examples are known. Azobenzene reacts with the phospholyl complex $(Me_2Bu^t_2C_4P)_2Tm$ to give the single-electron reduction product **116**.[963] As distinct from this, reactions with diiodides involve the two-electron reduction of azobenzene to give the binuclear $[LnI(THF)_2]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}trans\text{-}N_2Ph_2)_2$ complexes.[964] Aromatic compounds with reduction potentials greater than −2.0 V (cyclooctatetraene, anthracene, acenaphthylene) are readily reduced with thulium diiodide to mono- and dianions: $(arene)_2TmI(THF)$ and $(arene)TmI(THF)_2$.[965] Arene complex **117** of a different structure is formed in the reaction between TmI_2 and lithium naphthalenide.[966] It is worth noting that diiodides YbI_2 and EuI_2 are converted in this case to mononuclear products $(C_{10}H_8)Ln(THF)_x$, which are distinguished by high reactivity.[967]

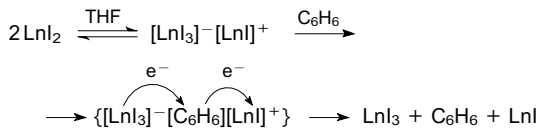
Structures 115 – 117



As noted above, the stability of divalent lanthanide compounds decreases on going from Eu to Nd. Their chemical reactivity as single-electron reducing agents increases in the same series, which corresponds to increasing electrode potential $E^\circ(Ln^{3+}/Ln^{2+})$: −0.35 (Eu), −1.15 (Yb), −1.55 (Sm), −2.3 (Tm), −2.5 (Dy), −2.6 V (Nd). It is noteworthy that the difference between the Eu, Yb, Sm, Tm, Dy and Nd potentials (0.8, 0.4, 0.75, 0.2, 0.1 V) is not correlated with variation of the stability and reactivity of LnR_2: in the case of Eu, Yb and Sm, the differences are 0.8 and 0.4 V, but all compounds are quite stable, whereas on going to Tm [ΔE°(Sm, Tm) 0.75 V], the stability of organic complexes sharply decreases; on going from Tm to Dy and Nd [ΔE°(Tm, Dy) and (Tm, Nd) do not exceed 0.2 V], the stability drop is even more pronounced; and compounds of

the end of the series possess specific properties. In particular, in the presence of traces of aromatic compounds, DyI_2 and NdI_2 rapidly react with THF and DME even at −30 °C. Furthermore, not only C−O bonds, but also relatively inert C−C and C−H bonds are attacked in this reaction, which is not observed in reactions with even the most potent reducing agents including Na and K.[968] Presumably, the exceptionally high reducing ability of DyI_2 and NdI_2, which does not correspond to their electrode potentials, is caused by the intermediate formation of highly reactive monovalent iodides LnI in these reactions (Scheme 225).

Scheme 225



It is noteworthy that the possibility of existence of monovalent molecular compounds of rare earth elements was established in relation to scandium complexes considered below. The unusual scheme of reductive transformations is supported by the fact that this approach accounts for the specific reactivity of NdI_2 and DyI_2 in solutions, which complicates their investigation, and for the differences between the Tm, Dy and Nd diiodides observed in many reactions. In particular, consider the reactivity difference between NdI_2 and DyI_2 towards phenol in THF: at 0 °C, both iodides give the expected phenolates $PhOLnI_2(THF)_x$ in high yields, whereas at a temperature of −90 °C, dysprosium iodide also forms the complex $PhODyI_2(THF)_4$, whereas neodymium diiodide gives a product mixture containing monoiodides: $PhONdI_2(THF)_4$, $(PhO)_2LnI(THF)_5$, $NdI_3(THF)_3$ and [NdI(H)R(THF)].[968] These results indicate that neodymium compounds are more prone to the reactions shown in the scheme. Analogous transformations account for the formation of monoiodides $Et_2LnI(DME)_2$, together with ethyl diiodides $EtLnI_2(DME)_2$, in the reactions of LnI_2 with Et_2Zn and Et_2Cd[969] and also for the formation of a new tridentate bis(imino)amine ligand and isolation of cationic complexes **118** with the triiodide counter-ion upon the reactions of acetonitrile with NdI_2, DyI_2 and TmI_2.[970, 971]

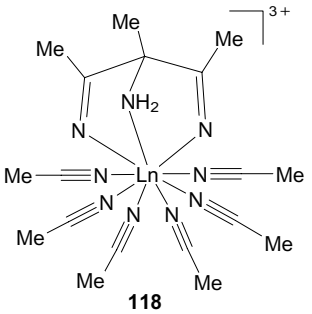
The formation of unusual complexes **119** containing trivalent thulium or dysprosium, apart from the triiodides $LnI_3(THF)_x$, in the reaction of bis(imino)acenaphthenedigallane with TmI_2 and DyI_2 is also well explained in terms of the presented scheme.[972] The disproportionation of LnI_2 and the subsequent electron transfer promoted by the aromatic acenaphthene groups afford the monoiodide LnI, which reduces the THF molecule to give the $^-OCH_2CH_2CH_2CH_2^-$ dianion linked to the lanthanide cation *via* the oxygen atom and to gallium *via* the terminal carbon atom. In the absence of stabilizing Ga substrate, more extensive THF reduction takes place, as noted above, with the C−C and C−H bond cleavage.

Among the few successful syntheses involving neodymium and dysprosium diiodides, note the recent reaction of NdI_2 with the carbodiimide Cy−N=C=N−Cy and potassium cyclopentadienide KCp'' [$Cp'' = \eta^5$-1,3-$(SiMe_3)_2C_5H_3$], which gives the C−C bond and the binuclear complex $Cp''_2Nd(CyN)_2C-C(NCy)_2NdCp''$ (Ref. 973).

The high reducing ability and thermal stability of NdI_2 and DyI_2, as well as the discovered nitrogen-fixing properties of the organic derivatives of these metals served as the grounds for investigation of the reactivity of diiodides towards molecular nitrogen without solvents. It was shown that these reactions do not occur under ambient conditions; however, at 300 – 550 °C, iodide nitrides $(LnI_2)_3N$ are formed in high yields.[974] Their reactions with sulfur, which were carried out in the search for new materials possessing optoelectronic properties, gave rise to complexes (for example, **120**) with no analogues among main group and d- and f-transition metal derivatives in the molecular structure, composition and chemical properties.[975] The structure of these products (identical for Nd and Dy) does not allow them to be unambiguously assignd to inorganic, organic or coordination compounds. The relatively high stability of the unusual trinuclear iodide nitride sulfide molecular cage is probably attributable to the existence of some conjugation in the polycyclic system involving N, S and Ln atoms, which, however, requires experimental and theoretical evidence.

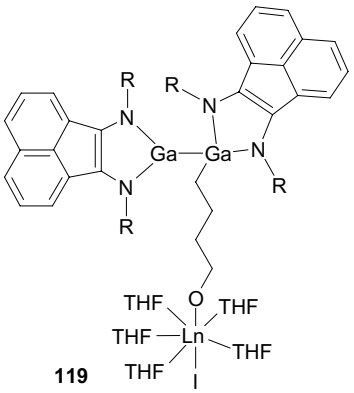
The exceptionally high reducing ability of the diiodides NdI_2 and DyI_2 noted above markedly complicates the studies of their catalytic properties. Nevertheless, some reactions catalyzed by these compounds have been found. In the presence of 2,2′-bipyridine and 1-bromo-1-phenylethane, neodymium diiodide catalyzes polymerization of styrene and methyl methacrylate under mild conditions to

Structures 118 – 120



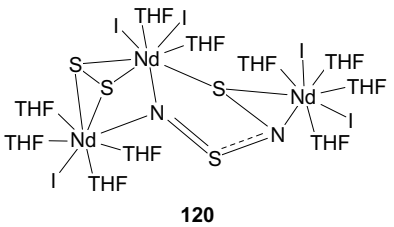
118

Ln = Nd, Dy, Tm



119

Ln = Tm, Dy; R = 2,6-$Pr^i_2C_6H_3$

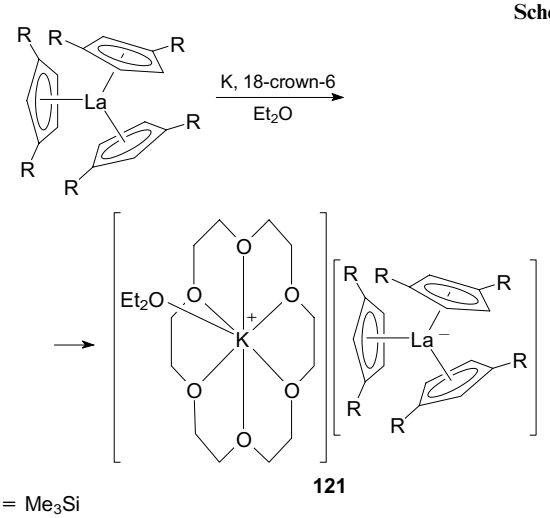


120

give polymers with a narrow molecular-mass distribution;[976] dysprosium diiodide catalyzes cyclotrimerization of alkynes and MMA polymerization.[977]

It has been believed for a long period that rare earth metals, except for Eu, Sm, Yb, Tm, Dy and Nd, cannot exist in the oxidation state +2. In the LnX_2 halides, the third electron of the Ln^{3+} ion is shared to form the conduction band, which is confirmed by physical and chemical properties of compounds. However, at the end of the 1990s, Lappert and co-workers[978] succeeded in preparing the subvalent lanthanum complex $[(Cp^{tt})_4La_2(\mu\text{-}C_6H_6)][K(18\text{-crown-}6)(C_6H_6)_2]$ ($Cp^{tt} = \eta^5\text{-}1,3\text{-}Bu^t_2C_5H_3$) by the reduction of trivalent cyclopentadienides with potassium in benzene. Subsequently, the same researchers[979] obtained analogous lanthanum complexes $[K(18\text{-crown-}6)(Et_2O)][LaCp''_3]$ (**121**) (Scheme 226) and $[K(2.2.2\text{-crypt})(Et_2O)][LaCp''_3]$ (2.2.2-crypt is 2.2.2-cryptand) free from benzene molecules. The presence of lanthanum(II) cations was reliably proved by X-ray diffraction data, magnetic measurements and DFT calculations. Cerium analogues were obtained by the same method, but were less strictly characterized.

Scheme 226



121

R = Me_3Si

Using the reduction of trivalent lanthanide complexes with sterically hindered ligands by potassium or potassium graphite in the presence of crown ether or 2.2.2-cryptand, Evans and co-workers[980–982] synthesized compounds similar to complex **121** for Y, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu. The divalent state of the rare earth metal in the products was confirmed by the molecular structure, magnetic measurements, EPR and electronic spectroscopy and by low stability in solutions noted earlier for DyI_2 and NdI_2. These results demonstrated that all lanthanides surrounded by organic ligands can occur in the oxidation state +2. However, systematic X-ray diffraction study has shown that these compounds and derivatives of 'true' divalent elements (Sm, Eu, Tm, Yb) have considerable differences: in the Sm, Eu, Tm and Yb complexes, the Ln–centroid distances increase by 0.12–0.15 Å on going from $Cp^{\#}{}_3Ln$ to $Cp^{\#}{}_2Ln$ ($Cp^{\#}$ is the cyclopentadienyl ligand with bulky substituents), which corresponds to the change in the ionic radius in the $4f^n$–$4f^{n+1}$ pair, whereas in the 'trivalent' lanthanide series, the transition from $Cp^{\#}{}_3Ln$ to $[Cp^{\#}{}_3Ln]^-$ is accompanied by an increase in this distance by not more than 0.027–0.031 Å.[981–983] The electronic absorption spectra of bimetallic complexes of Pr, Gd, Tb, Ho and Er and also Y and Lu contain one broad band with a maximum at 350–550 nm, unlike the spectra of Ln^{3+} cyclopentadienides containing characteristic narrow bands of the corresponding f–f transitions. These differences were interpreted by Furche, Evans and co-workers,[981,982] who carried out quantum chemical calculations of the electronic states of Ln^{2+} ions and relevant absorption spectra. According to calculations, upon the reduction of cyclopentadienides of the listed trivalent metals with potassium or KC_8, the electron that comes from the reducing agent occupies the vacant, energetically accessible $5d_{z^2}$ orbital, and not the lanthanide 4f orbital. As a result, the reduced ion has the $4f^n5d^1$ rather than $4f^{n+1}$ configuration, that is, actually it has the configuration of d-transition metals, which are characterized by a slight increase in the ionic radius upon reduction and by broadened poorly resolved bands in the absorption spectra.

As noted above, Nd and Dy belong to the group of 'true' divalent lanthanides, *i.e.*, their doubly charged cations have $4f^4$ and $4f^{10}$ configurations, respectively, which is confirmed by structural and spectral characteristics and by chemical properties of the molecular diiodides $LnI_2(THF)_5$, $LnI_2(DME)_3$ and $LnI_2(Pr^iNH_2)_4$.[970] However, recently Furche, Evans and co-workers[983] have found that regarding the molecular structure (minor differences between the Ln–centroid distances in neutral $Cp^{\#}{}_3Ln$ molecules and $[Cp^{\#}{}_3Ln]^-$ anions) and the absorption spectra (broadened single bands), the bimetallic cyclopentadienyl complexes of these metals such as complex **121** are similar to Pr group derivatives and sharply differ from compounds of common divalent lanthanides. These data, together with DFT calculations, demonstrate that the Nd^{2+} and Dy^{2+} cations in the $[Cp^{\#}{}_3Ln]^-$ cyclopentadienyl anions, unlike the diiodides LnI_2, have the $4f^n5d^1$ configuration, which is due to proximity of the 4f and 5d levels, resulting in their partial mixing. In the authors' opinion, the electronic configurations of the Nd^{2+} and Dy^{2+} ions are determined by their ligand environment.[983] However, this assumption is apparently valid only if the potassium cations, coordinated to the crown ether or cryptand and located in the outer sphere of the complex, are ascribed to the coordination environment of lanthanide ions. Otherwise, it should be admitted that configurations of the Nd^{2+} and Dy^{2+} ions depend on the number and size of substituents in the cyclopentadienyl ligand, because the reduction of Cp_3Ln gives 'normal' $4f^{n+1}$ ions, while the reduction of complexes with the substituted $Cp^{\#}$ ligands yields $4f^n5d^1$ ions. It cannot be ruled out that the dual natures of neodymium and dysprosium are responsible for the above-noted exceptionally high reducing ability of NdI_2 and DyI_2.

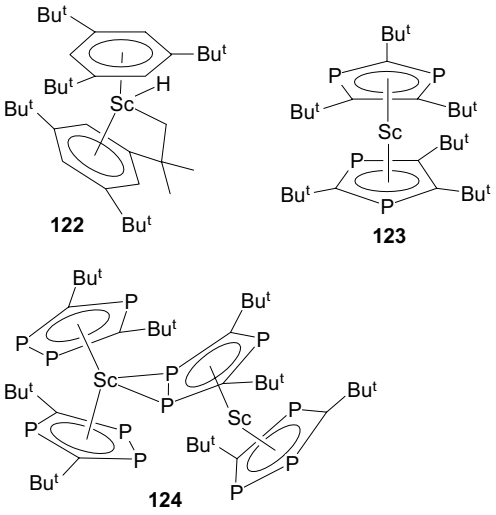
The reactivity of bimetallic lanthanide(II) complexes such as **121** is poorly known, except for their ability to add molecular nitrogen under ambient conditions, which has been studied in detail. They are somewhat more stable in THF solutions than neodymium and dysprosium diiodides, but less stable than thulium diiodide. Magnetic measurements for the bimetallic complexes confirmed the $4f^n5d^1$ configuration of the doubly charged La, Ce, Pr, Gd, Tb, Ho and Er ions and the transient nature of the Nd^{2+} and Dy^{2+} ions.[984] Dysprosium and holmium complexes showed effective magnetic moments of 11.35 and 11.41 μ_B, respectively (μ_B is the Bohr magneton), which are record values for

mononuclear single molecule magnets; this is attributable to addition of the moments of 4f and 5d electrons.

Among the organic compounds of low-valence rare earth metals, a special place is occupied by scandium derivatives, among which Sc^0, Sc^{1+} and Sc^{2+} arene complexes have been obtained. These compounds were synthesized by Cloke and co-workers [985, 986] in the late 1990s using cryosynthesis (co-condensation of metal and ligand vapours on a cooled surface). Divalent scandium derivative **122** is formed upon intramolecular oxidation of Sc^0 in the bis(arene) complex $(1,3,5\text{-}Bu^t_3C_6H_3)_2Sc$ obtained by co-condensation of scandium vapour with substituted benzene vapour. The second scandium(II) complex **123**, resembling metallocenes in the nature and properties, was isolated from the scandium and phosphaalkyne $Bu^tC{\equiv}P$ co-condensation products.[987] Its molecular structure was not exactly determined; the divalent state of the metal was confirmed, along with the fragment composition, by magnetic measurements and EPR spectroscopy.

It is of interest that reduction of the trivalent scandium complex $[Sc(\eta^5\text{-}P_3C_2Bu^t_2)_2(\eta^2\text{-}P_3C_2Bu^t_2)]$ with potassium graphite (KC_8), unlike the reduction of the above-described lanthanide derivatives, does not give the scandium(II) product, but affords mixed-ligand (Sc^{III}/Sc^{I}) binuclear compound **124**.[988]

Structures 122 – 124



As the conclusion of this brief account, it can be stated that since the discovery of molecular complexes of divalent rare earth metals, considerable advances have been made in this vigorously developing research area. A large body of information has been gained on the methods of synthesis and molecular and electronic structures of compounds. The synthesis of complexes containing doubly charged lanthanide ions with the $4f^n5d^1$ configuration marked the discovery of actually a new group of elements, fd metals, possessing unique properties. The key achievements of this area of lanthanide chemistry are related to the synthesis. The information accumulated to date is sufficient for switching to detailed investigation of the chemical and physical properties of new compounds, which would obviously bring about new prominent achievements and discoveries.

12.2. Alkyl derivatives of rare earth metals: stabilization problem, selective activation of C – H bonds

Over the last three decades, rare earth metal derivatives with the M – C σ-bond [989 – 994] have been the focus of attention due to the unique set of properties they possess, first of all, exceptionally high reactivity, which may promote a number of reactions that are difficult to accomplish, such as C – H bond activation [995 – 998] and functionalization of alkanes.[999] Furthermore, they have demonstrated high catalytic potential in a large number of practically valuable reactions of unsaturated substrates such as polymerization,[1000 – 1005] hydrogenation,[1006, 1007] hydrosilylation,[1008] hydroamination,[1009 – 1012] hydrophosphination [1013] and hydroboration.[1014, 1015] However, the development of chemistry of alkyl derivatives of rare earth metals has been held up for long by the thermal instability of these compounds and difficulty of their synthesis and isolation in a pure state. Rare earth metals are characterized by large ionic radii;[1016, 1017] in combination with the Lewis acidity and the presence of unfilled 5d and 6s (for Ln^{3+} ions) orbitals, this gives rise to a pronounced tendency of their compounds to form complexes with large coordination numbers. Rare earth metals are electropositive,[1018] the metal – ligand bonding in their organic derivatives are mainly ionic; that is why ligands capable of forming stable organic anions (*e.g.*, cyclopentadienyl anions) have been traditionally used in this field of chemistry.[1019] The stability and reactivity of organic derivatives of rare earth metals are largely determined by the degree of coordination and steric saturation of the metal ion; therefore, a number of requirements are imposed on the ligands used in the rare earth metal chemistry. First of all, ligands should be sufficiently bulky and provide steric saturation of the metal coordination sphere, resulting in the kinetic stabilization of the metal complex. The ligands should preferably be polydentate, which, in some cases, suppresses the ligand redistribution reactions, which are characteristic of heteroligand rare earth metal derivatives due to the essentially ionic metal – ligand bonds. Therefore, the rational design of the coordination sphere of the metal ion may be one of the most efficient ways to achieve stabilization of the alkyl derivatives of rare earth metals; this brings to the forefront the issue of selection and development of new stabilizing ligand systems that would meet all of the above requirements.

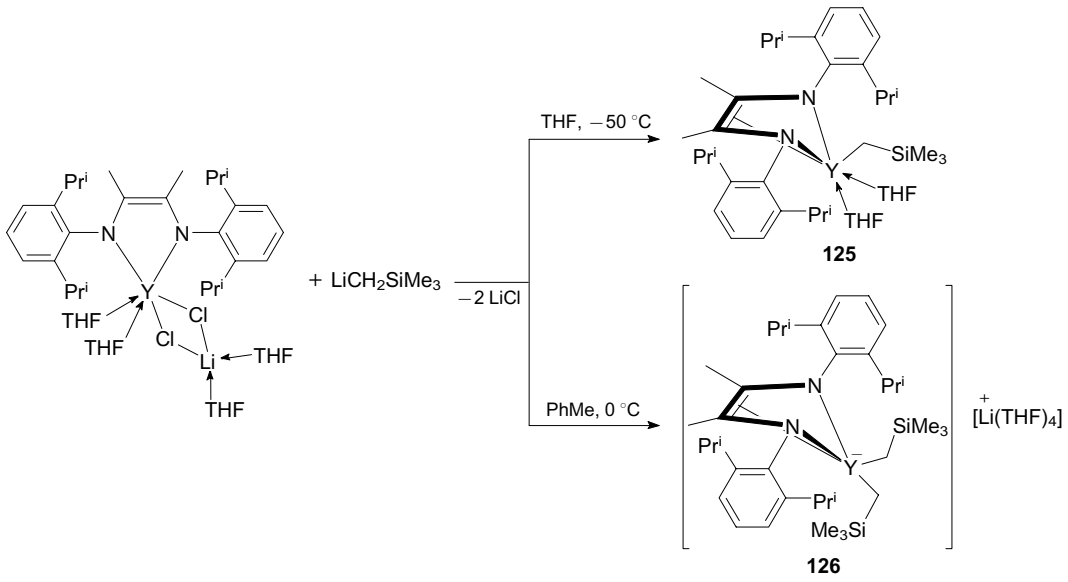
This part of the review addresses the synthesis, structure and reactivity issues of mono- and bis-alkyl complexes of rare earth metals stabilized by various polydentate N,N-ligands and selective intra- and intermolecular activation reactions of the sp^3- and sp^2-hybridized C – H bonds involving them.

12.2.1. Monoalkyl derivatives of rare earth metals

The most popular synthetic approaches to the alkyl complexes of rare earth metals are reactions of their tris(alkyl) derivatives with the stabilizing ligand proto-form or alkylation of the halides $(L)LnX_n$ (L is the stabilizing ligand; X = Cl, Br, I; n = 1, 2) with alkali metal or, more rarely, alkaline earth alkyl derivatives.[989 – 995]

Neutral and anionic metallacyclic yttrium alkyl complexes containing dianionic enediamide ligands $\{[2,6\text{-}Pr^i_2C_6H_3NC(Me){=}C(Me)NC_6H_3Pr^i_2\text{-}2,6)] = L\}$, $[(L)Y(CH_2SiMe_3)(THF)_2]$ (**125**), $[(L)Y(CH_2SiMe_3)_2]^-[Li(THF)_4]^+$ (**126**) and $[(L)Y(OEt_2)(\mu\text{-}Me)_2Li(TMEDA)]$, were synthesized by alkylation of the appropriate chloro derivative

Scheme 227

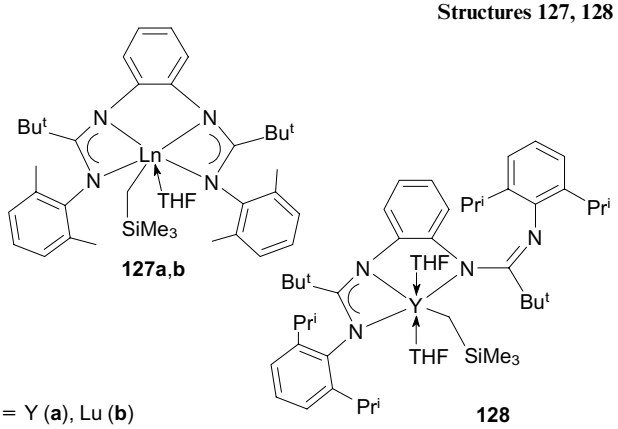


[(L)Y(THF)$_2$(μ-Cl)$_2$Li(THF)$_2$] and were isolated in 70%, 85% and 72% yields, respectively (Scheme 227). The outcome of the reaction was found to be determined by the nature of the solvent. When the reaction was carried out in THF at −50 °C, neutral alkyl complex **125** was obtained, whereas in toluene, anionic complex **126** was formed. An interesting structural feature of complexes **125** and **126** is η^2-coordination of the C=C bond of the enediamide moiety to the Y cation. The DFT calculations confirmed the electron density donation from the C=C double bond to the vacant orbitals of the yttrium ion.[1020]

The reactions of *ansa*-bis(amidines) with the conformationally rigid *o*-phenylene linker, C$_6$H$_4$-1,2-{NC(Bu^t)N(2,6-R$_2$C$_6$H$_3$)H}$_2$ (R = Me, Pr^i) and Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$, were used to prepare the bisamidinate-monoalkyl complexes [C$_6$H$_4$-1,2-{NC(Bu^t)N(2,6-R$_2$C$_6$H$_3$)}$_2$]Ln(CH$_2$SiMe$_3$)(THF)$_n$ [R = Me, *n* = 1: Ln = Y (**127a**), Lu (**127b**); Ln = Y, R = Pr^i, *n* = 2 (**128**)]. According to thermal stability studies for compounds **127** and **128**, lutetium complex **127b** was the most stable, starting to noticeably decompose only at 60 °C with the half-life at 20 °C being 830 h. The yttrium analogue was somewhat less stable (290 h), while yttrium complex **128** with a bulky ligand showed the least thermal stability (210 h). The activation energy for decomposition of complex **128** was 67.0 ± 1.3 kJ mol^{-1} (Ref. 1021).

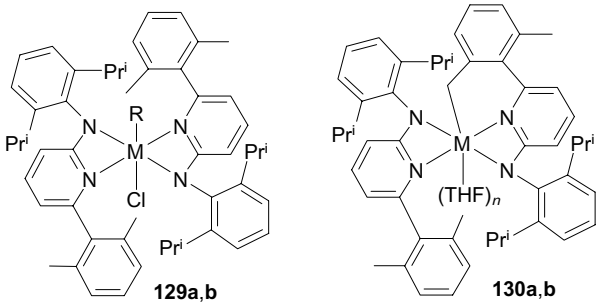
The alkylation of bis(amido-amidinate) chloride complexes of scandium (Ap′)$_2$ScCl(THF) and lutetium (Ap′)$_2$LuCl(THF)] {Ap′ is (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]amide} having the smallest ionic radii with equimolar amounts of LiCH$_2$SiMe$_3$ in hexane resulted in the synthesis of the corresponding monoalkyl derivatives (Ap′)$_2$ScCH$_2$SiMe$_3$(THF) (**129a**) and (Ap′)$_2$LuCH$_2$SiMe$_3$(THF) (**129b**). Meanwhile, in the case of metals with larger ionic radii (La, Nd), this reaction is accompanied by activation of the sp^3-hybridized C–H bonds and gives rise to benzyl derivatives Ap′(Ap′$_{-H}$)La(THF)$_2$ (**130a**) and Ap′(Ap′$_{-H}$)Nd(THF) (**130b**).[1022]

Structures 127, 128



Ln = Y (**a**), Lu (**b**)

Structures 129, 130

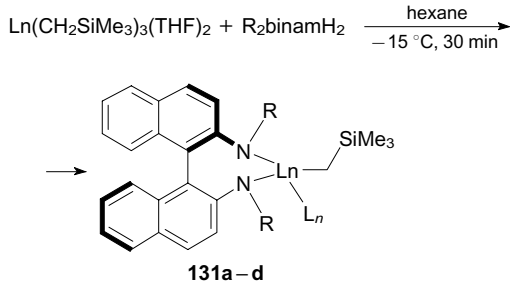


R = CH$_2$SiMe$_3$; M = Sc (**a**), Lu (**b**)

M = La, *n* = 2 (**a**);
M = Nd, *n* = 1 (**b**)

The chiral bis(binaphthylamido) core with bulky cyclopentyl and trimethylsilyl groups at the nitrogen atoms (R$_2$binam) proved to be an appropriate coordination environment of the central metal for the synthesis of neutral monoalkyl Y and Yb derivatives. Monoalkyl derivatives **131a**–**d** were obtained by treatment of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Y, Yb) with (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl[1023] and (*R*)-(+)-

Scheme 228



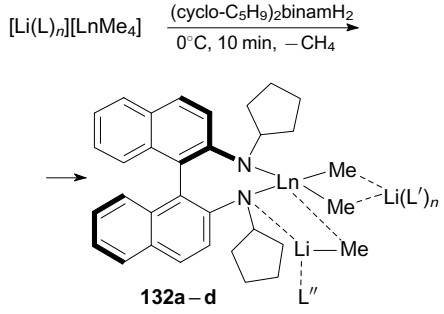
R = cylo-C_5H_9: Ln = Y, L = THF, n = 2 (**a**); L = DME, n = 1 (**b**); Ln = Yb, L = THF, n = 2 (**c**); R = $SiMe_3$, Ln = Y, L = THF, n = 1 (**d**)

2,2′-bis(trimethylsilyl)-1,1′-binaphthyl[1024] (1 : 1 molar ratio, hexane, −15 °C) (Scheme 228).

Yttrium complexes **131a**,**b** slowly decompose at room temperature in C_6D_6 to give $SiMe_4$; the degrees of decomposition after two weeks were 7% and 12%, respectively. Complex **131d** containing a ligand with the $SiMe_3$ substituent proved to be much less stable and completely decomposed within 24 h under the same conditions.

Using a similar synthetic approach consisting in the alkane elimination reaction, the authors of this part of the review prepared a series of ionic methyl derivatives containing a chiral binaphthyldiamido ligand. An important benefit of this method is the possibility to stabilize the usually highly unstable alkyl derivatives of the early lanthanides with large ionic radii (La, Sm). The reactions of $[Li(L)_n][LnMe_4]$ (L = THF, TMEDA, Et_2O) with (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl [(cyclo-$C_5H_9)_2$binamH_2] in THF or Et_2O–TMEDA (0 °C) afforded complexes **132a**–**d** in 58%, 62%, 64% and 62% yields, respectively (Scheme 229).[1023]

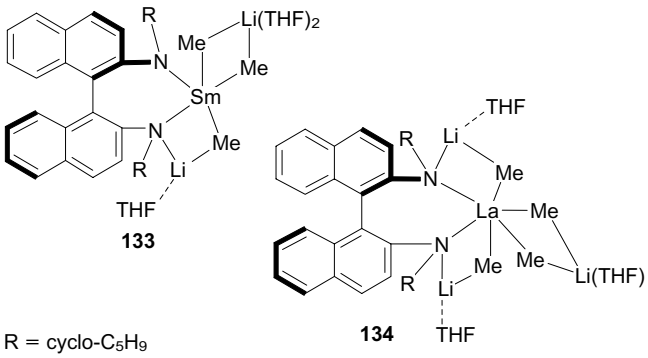
Scheme 229



L′ = L″ = THF, n = 2: Ln = Y (**a**), Yb (**c**); L′ = TMEDA, L″ = Et_2O, n = 1: Ln = Y (**b**), Yb (**d**)

In the case of metals with greater ionic radii, the hexamethyl ate-complexes $[Li(THF)_n]_3[LnMe_6]$ (Ln = La, Sm) served as the starting compounds. It is noteworthy that in the case of samarium, the reaction generates the trinuclear heterometallic complex {(*R*)-(cyclo-$C_5H_9)_2$binam}Sm{(μ-Me)$_2$Li(THF)$_2$(μ-Me)Li(THF)} (**133**), whereas in the case of lanthanum, the reaction gives the tetranuclear derivative {(*R*)-(cyclo-$C_5H_9)_2$binam}La.{(μ-Me)$_2$Li(THF)[(μ-Me)Li(THF)]$_2$} (**134**).[1025]

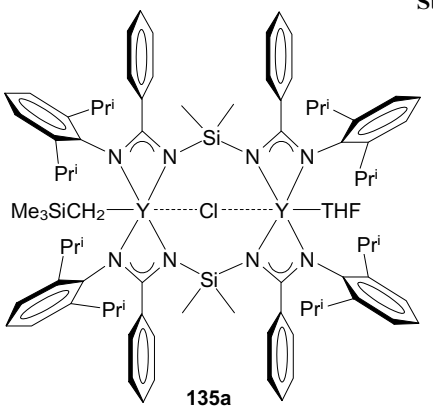
Structures 133, 134

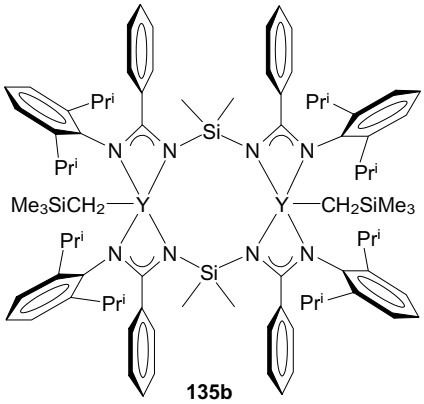


R = cyclo-C_5H_9

Unusual binuclear alkyl and chloroalkyl yttrium complexes **135a**,**b** were obtained using *ansa*-bis-amidinate ligands with a short $SiMe_2$ bridge. The binuclear structure is formed as a result of bridging coordination of the amidinate moieties with various metal ions.[1026]

Structures 135

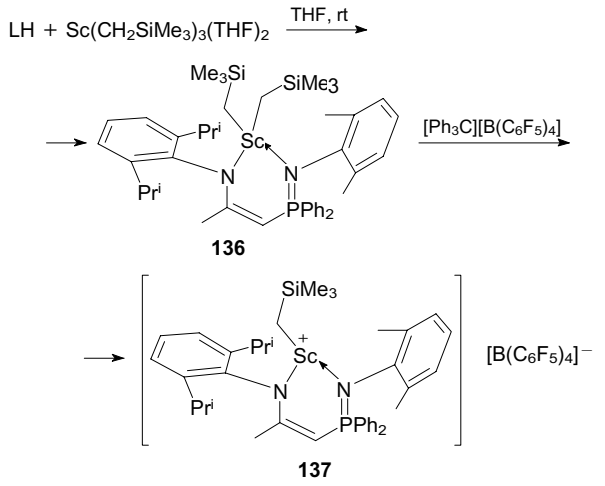




12.2.2. Bis(alkyl) derivatives of rare earth metals

The sterically hindered phosphinimino-amide ligand L [LH = (2,6-$Pr^i_2C_6H_3$)NHC(Me)CHP(Ph_2)=N(2,6-$Me_2C_6H_3$)] was used to synthesize the bis(alkyl) scandium complex (L)Sc($CH_2SiMe_3)_2$ (**136**) devoid of a THF molecule in the coordination sphere (Scheme 230).[1027] Treatment of this complex with [Ph_3C][$B(C_6F_5)_4$] afforded the cationic alkyl complex [(L)Sc(CH_2SiMe_3)][$B(C_6F_5)_4$] (**137**).

Scheme 230

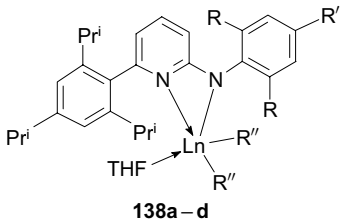


The alkylation of the dichlorides Ap*$LnCl_2(THF)_n$ {Ln = Sc, Yb; Ap* is (2,6-diisopropylphenyl)[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amide} and the derivative {[$Ap^{9Me}Y(THF)$](μ^2-Cl)$_3$Li$(THF)_2$}$_2$ {Ap^{9Me} is mesityl-[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amide} on treatment with $LiCH_2SiMe_3$ resulted in the synthesis of the bis(alkyl) complexes (L)Ln$(CH_2SiMe_3)_2(THF)$ {L = Ap*: Ln = Sc (**138a**), Yb (**138b**); L = Ap^{9Me}, Ln = Y (**138c**)}. The molecular structures of bis(alkyl) complexes **138a**,**b** in the crystalline state ware determined by X-ray diffraction analysis.

Owing to the bulky amidopyridinate ligand Ap^{9Me}, it was possible to synthesize and characterize the complex $Ap^{9Me}YBu^t_2(THF)$ (**138d**), a rare example of di-*tert*-butyl derivatives of rare earth metals, which usually decompose according to the β-hydride mechanism. According to NMR spectroscopy data, the complex $Ap^{9Me}YBu^t_2(THF)$ was unstable in a C_6D_6 solution and decomposed within 72 h to give isobutane and isobutylene in 2 : 1 molar ratio.[1028]

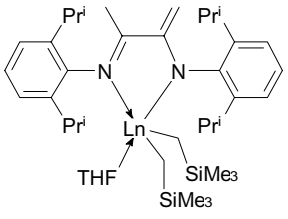
The monoanionic amidoimine ligand $[(2,6\text{-}Pr^i_2C_6H_3)N{=}C(Me)C(=CH_2)N(C_6H_3Pr^i_2\text{-}2,6)]^-$ has been successfully used to prepare the bis(alkyl) complexes $[(2,6\text{-}Pr^i_2C_6H_3)N{=}C(Me)C(=CH_2)N(C_6H_3Pr^i_2\text{-}2,6)]$.$Ln(CH_2SiMe_3)_2(THF)$ [Ln = Y (**139a**), Lu (**139b**)].[1029]

Structures 138, 139



138a – d

R = Pr^i, R′ = H, R″ = CH_2SiMe_3:
Ln = Sc (**a**), Yb (**b**);
R = R′ = Me, Ln = Y:
R″ = CH_2SiMe_3 (**c**), Bu^t (**d**)

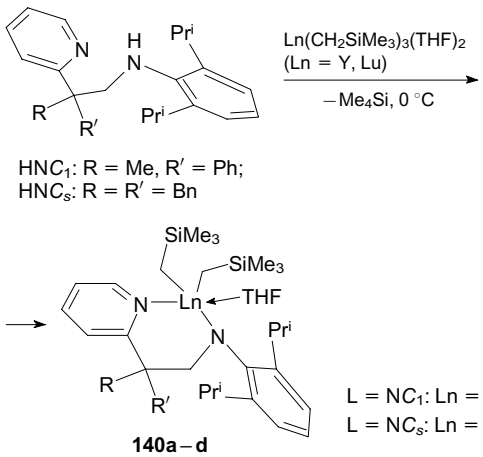


139a,**b**

Ln = Y (**a**), Lu (**b**)

The yttrium and lutetium complexes containing bidendate C_1- and C_s-symmetric 2-pyridylethylanilide ligands (NC_1 and NC_s) have been prepared by the reactions of $Ln(CH_2SiMe_3)_3(THF)_2$ with HNC_1 and HNC_s (Scheme 231).[1030] Note that the resulting bis(alkyl) derivatives with a six-membered metallacycle were fairly thermally stable; they did not noticeably decompose at room temperature for two weeks.

Scheme 231

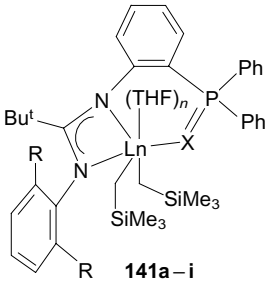


The bulky amidinate ligands containing various side-chain donor groups (P=O, P=NR) linked to one of the amidinate nitrogens *via* the rigid *o*-phenylene bridge were used to prepare bis(alkyl) derivatives **141a – i** with tridentate amidinate ligands.[1031, 1032] Note that in the case of amidine with the P=S group, the attempted preparation of bis(alkyl) derivatives failed. The steric features of the amidinate core and the additional donor group allow variation of the coordination number (C.N.) of the central metal. For the P=O ligands with the 2,6-$Me_2C_6H_3$ substituent, complexes with a coordinated THF molecule are formed (C.N. = 6), while by using ligands with either 2,6-$Pr^i_2C_6H_3$ or P=NR groups, it is possible to prepare five-coordinate complexes containing no THF. Lutetium complex **141c** showed exceptionally high stability: its half-life at 20 °C in C_6D_6 was 1153 h; the half-life of yttrium analogue **141a** was 63 h.

Six-coordinate bis(alkyl) derivatives of yttrium and lutetium with tridentate amidinate ligands the containing quinoline [NC_9H_6-8-$NC(Bu^t)N(2,6\text{-}Pr^i_2\text{-}C_6H_3)$] (**142**)[1033] or anisole [2-$MeOC_6H_4NC(Bu^t)N(2,6\text{-}R_2C_6H_3)$] (R = Me, Pr^i) (**143a – d**) moiety[1034] in the side chain have also been obtained and structurally characterized. Complex **142** was thermally stable and did not show signs of decomposition when stored in C_6D_6 at room temperature for a week. Treatment of complex **143b** with DME led to replacement of the THF molecule and the methoxy group in the metal coordination sphere and formation of the six-coordinate adduct with DME [2-$MeOC_6H_4NC(Bu^t)N(2,6\text{-}Me_2C_6H_3)$].$Lu(CH_2SiMe_3)_2(DME)$ (**144**). The ^1H and ^{13}C NMR studies of compounds **142 – 144** over a broad temperature range (from −80 to 60 °C) did not reveal a dynamic behaviour of these complexes, thus confirming the retention of tridentate coordination of amidinate ligands in solution.

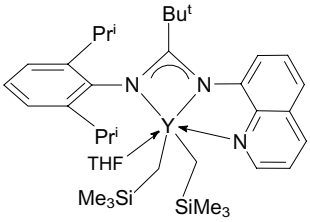
The amidine-amidopyridinate ligand system, which has four nitrogen atoms potentially accessible for coordination to metals, proved to be an interesting object for studying the coordination chemistry involving rare earth metal ions.

Structures 141 – 143

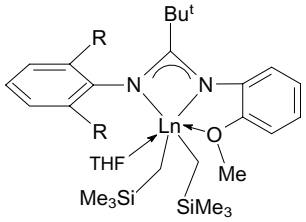


141a – i

X = O, R = Me: Ln = Y, *n* = 1 (**a**), Ln = Er, *n* = 1 (**b**), Ln = Lu, *n* = 0 (**c**); X = O, R = Pr^i, *n* = 0: Ln = Y (**d**), Er (**e**), Lu (**f**); X = NPh, R = Me, *n* = 0: Ln = Y (**g**), Lu (**h**); X = N(C$_6$H$_3$Me$_2$-2,6), R = Me, *n* = 0, Ln = Lu (**i**)



142

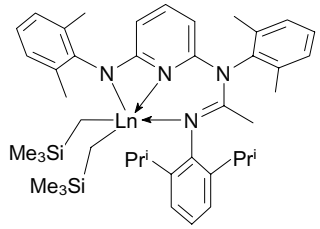


143a – d

R = Me: Ln = Y (**a**), Lu (**b**); R = Pr^i: Ln = Y (**c**), Lu (**d**)

Furthermore, with rational selection of substituents in the amidinate moiety, this system can serve to prepare bis(alkyl) complexes with thermal stability unusually high for this class of compounds. The bis(alkyl) complexes (L)Ln(CH$_2$SiMe$_3$)$_2$ of scandium (**145a**), yttrium (**145b**)[1035] and lutetium (**145c**)[1036] were prepared by the reaction of *N′*-(2,6-diisopropylphenyl)-*N*-(2,6-dimethylphenyl)-*N*-{6-[(2,6-dimethylphenyl)amino]pyridin-2-yl}acetimideamide [(2,6-Me$_2$C$_6$H$_3$)NH(2,6-C$_6$H$_3$N)N(2,6-Me$_2$C$_6$H$_3$)C(Me)=N(2,6-Pr$^i_2$C$_6$H$_3$), LH] with equimolar amounts of Ln(CH$_2$SiMe$_3$)$_3$.(THF)$_2$. Complex **145c** exhibited an exceptional stability without signs of C – H activation or other types of decomposition in a C$_6$D$_6$ solution even when kept for long at 60 °C.

Structures 145

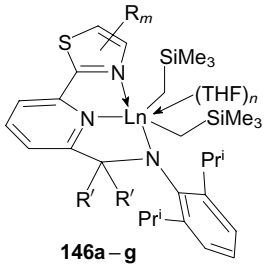


145a – c Ln = Sc (**a**), Y (**b**), Lu (**c**)

Neutral bis(alkyl) complexes (L)Ln(CH$_2$SiMe$_3$)$_2$ **146a – g** with monoanionic {N,N,N}-amidopyridinate ligands containing the 5-methylthiazole or benzothiazole substituent in position 6 of the pyridine ring have been reported.[1037, 1038]

As expected, only the hard N-donor site is coordinated to the metal, whereas the soft S-donor site is not involved in the metal – ligand interaction. It was found that the nature of the bridge between the amide and pyridinate moieties (CMe$_2$ or CH$_2$) affects the composition of the yttrium complex. In the case of the CH$_2$ linker, the complex contains a coordinated THF molecule, whereas the CMe$_2$ bridge provides the formation of the complex without a coordinated solvent molecule.

Structures 146

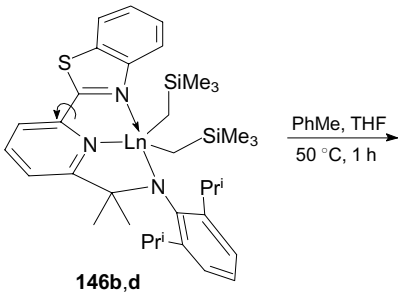


146a – g

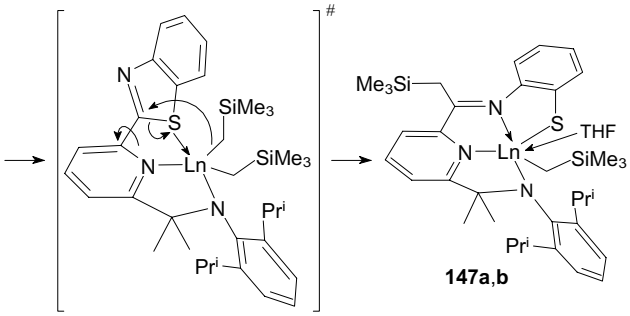
R′ = Me, *n* = 0, R$_m$ = 5-Me: Ln = Y (**a**), Lu (**c**), Er (**e**), Yb (**f**); R$_m$ is benzo[*d*], R′ = Me, *n* = 0: Ln = Y (**b**), Lu (**d**); R$_m$ = 5-Me, R′ = H, *n* = 1, Ln = Y (**g**)

An unusual rearrangement was found for yttrium and lutetium complexes with a benzothiazole-substituted ligand; the rearrangement is promoted by addition of THF or heating and consists in migration of one alkyl group to the *ipso*-carbon atom of the thiazole ring, C – S bond cleavage and Ln – S bond formation (Scheme 232). As a result, complexes **147a**,**b** with a new dianionic tetradentate {N,N,N,S}$^{2-}$ ligand were obtained and characterized. In the case of derivatives **146a**,**c**,**e – g** with the 5-methylthiazole ligand, this rearrangement is not observed.

Scheme 232



146b,**d**

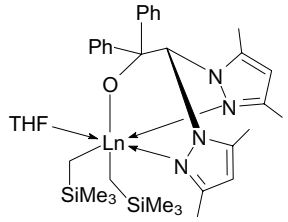


147a,**b**

146: Ln = Y (**b**), Lu (**d**); **147**: Ln = Y (**a**), Lu (**b**)

By reactions of equimolar amounts of 2,2-bis(3,5-dimethylpyrazol-1-yl)-1,1-diphenylethanol (LH) and Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu), a series of alkoxybis(alkyl) complexes (L)Ln(CH$_2$SiMe$_3$)$_3$(THF) have been obtained [Ln = Sc (**148a**), Y (**148b**), Lu (**148c**)].[1039] According to X-ray diffraction data, the so-called heteroscorpionate ligand is coordinated to the lanthanide ion in the *fac*-κ^3 fashion *via* the oxygen atom and two pyrazole nitrogen atoms.

Structures 148



148a – c Ln = Sc (**a**), Y (**b**), Lu (**c**)

12.2.3. Heteroalkyl derivatives of rare earth metals. Selective inter- and intramolecular activation of sp^2- and sp^3-C – N bonds as a synthetic approach to rare earth metal complexes with various M – C bonds

The selective intermolecular activation of sp^3-hybridized C – H bonds possible for alkyl derivatives of rare earth metals has been used to prepare heteroalkyl derivatives containing two different hydrocarbon groups.[1040] Using reactions of bis(pyrazolyl)methane $CH_2(C_3HN_2Me_2\text{-}3,5)_2$ with bis(alkyl) yttrium derivatives $(L)Y(CH_2SiMe_3)_2(THF)_n$ [L is amidopyridinate (Ap′), amidinate (Amd) or tridentate amidinate with the 2-methoxyphenyl group in the side chain (Amd^{OMe}), C_5Me_5; $n = 0, 1$], the heteroalkyl derivatives $(L)Y(CH_2SiMe_3)\{CH(C_3HN_2Me_2\text{-}3,5)_2\}(THF)_n$ (**149** – **152**) have been successfully obtained in high yields.

It should be noted that the reaction is highly selective, resulting exclusively in the product of monosubstitution. The attempts to replace also the second CH_2SiMe_3 group were unsuccessful. Complexes **149** – **151** proved to be rather stable: in C_6D_6 at room temperature, no signs of decomposition were observed for a month. Complex **152** was substantially less stable; under the same conditions, it completely decomposed within 3 days.

The selective intramolecular activation of the sp^3- and sp^2-hybridized bonds has been observed in attempted synthesis of bis(alkyl) yttrium derivatives by reactions of $Y(CH_2SiMe_3)_3(THF)_2$ with aminopyridines containing a phenyl or xylyl moiety in position 6 of the pyridine ring. In both cases, the reaction involved C – H bond activation and resulted in the formation of $SiMe_4$ and alkyl-aryl (**153**) and alkyl-benzyl (**154**) yttrium complexes.[1041]

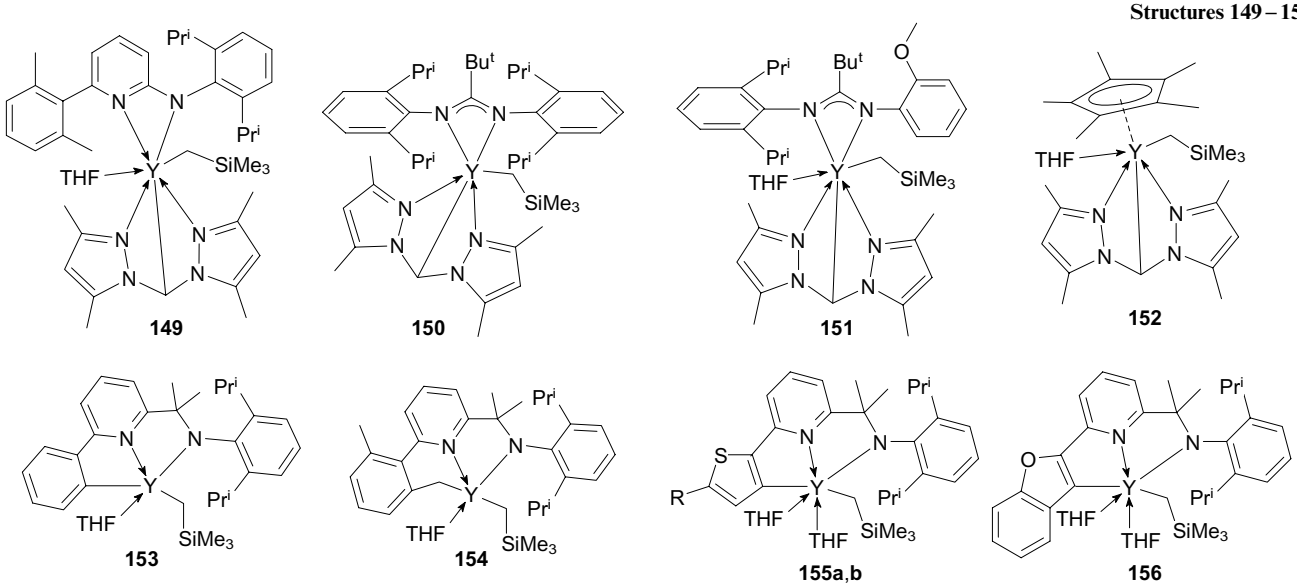
In order to suppress the C – H activation *via* metal coordination of an additional Lewis base, heterocyclic moieties (thiophene, α-ethylthiophene, benzofuran) have been introduced into pyridine position 6 of the aminopyridine core. However, in the case of thienyl- and even (despite the oxophilic nature of rare earth metal ions) benzofuryl-substituted aminopyridines, the reactions with $Y(CH_2SiMe_3)_3(THF)_2$ were accompanied by C – H bond activation in the β-position of the heterocycle, giving rise to alkyl-hetaryl yttrium derivatives **155a**,**b**, **156**.

Study of the chemical properties of the obtained heteroalkyl complexes has shown that the reactivities of the chemically different Y – C bonds in them are dramatically different. Indeed, σ-bond metathesis on treatment with $PhSiH_3$ occurs only for the $Y-CH_2SiMe_3$ bond, whereas the Y – C(aryl, benzyl, hetaryl) bonds do not react even under more stringent conditions. This reaction has allowed the synthesis of a number of unusual metallacyclic aryl, benzyl and hetaryl hydride yttrium complexes. It should be noted that even with a rather strong EH acid such as 2,6-diisopropylaniline, the reaction is selective and involves only the $Y-CH_2SiMe_3$ bond.[1041 – 1043]

The selective intramolecular activation of the $C_{sp^3}-H$ bonds was also observed in reactions of $Y(CH_2SiMe_3)_3(THF)_2$ with amidine-amidopyridine **157** (Scheme 233). Unlike the more bulky analogue, *N*′-(2,6-diisopropylphenyl)-*N*-(2,6-dimethylphenyl)-*N*-{6-[(2,6-dimethylphenyl)amino]pyridin-2-yl}acetimideamide, which made it possible to prepare stable bis(alkyl) derivatives, compound **157** reacted with activation of the $C_{sp^3}-H$ bonds of the xylyl substituent in the amidinate moiety (see Scheme 233).

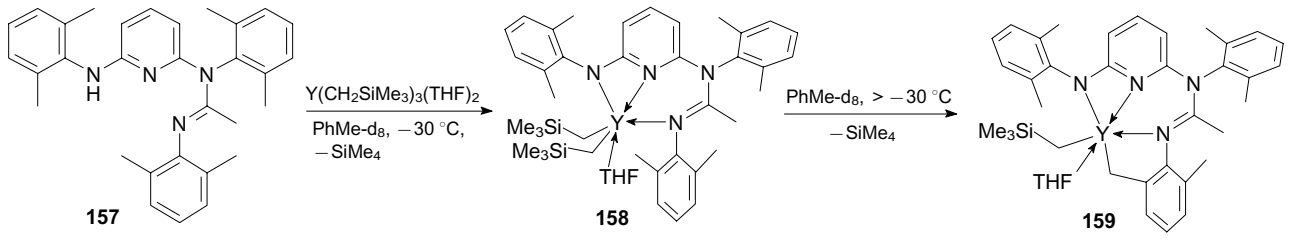
As in the case of the above-described complexes **155** and **156**, in compound **159**, the $Y-CH_2SiMe_3$ and Y – C(benzyl) bonds show different reactivities. On treatment of complex **159** with $B(C_6F_5)_3$, the Y – C(benzyl) bond is cleaved, whereas protonolysis with the Brønsted acid $[Et_3NH][BPh_4]$ affects the $Y-CH_2SiMe_3$ bond.[1035, 1044] Both reactions give cationic alkyl complexes **160** and **161**,

Structures 149 – 156

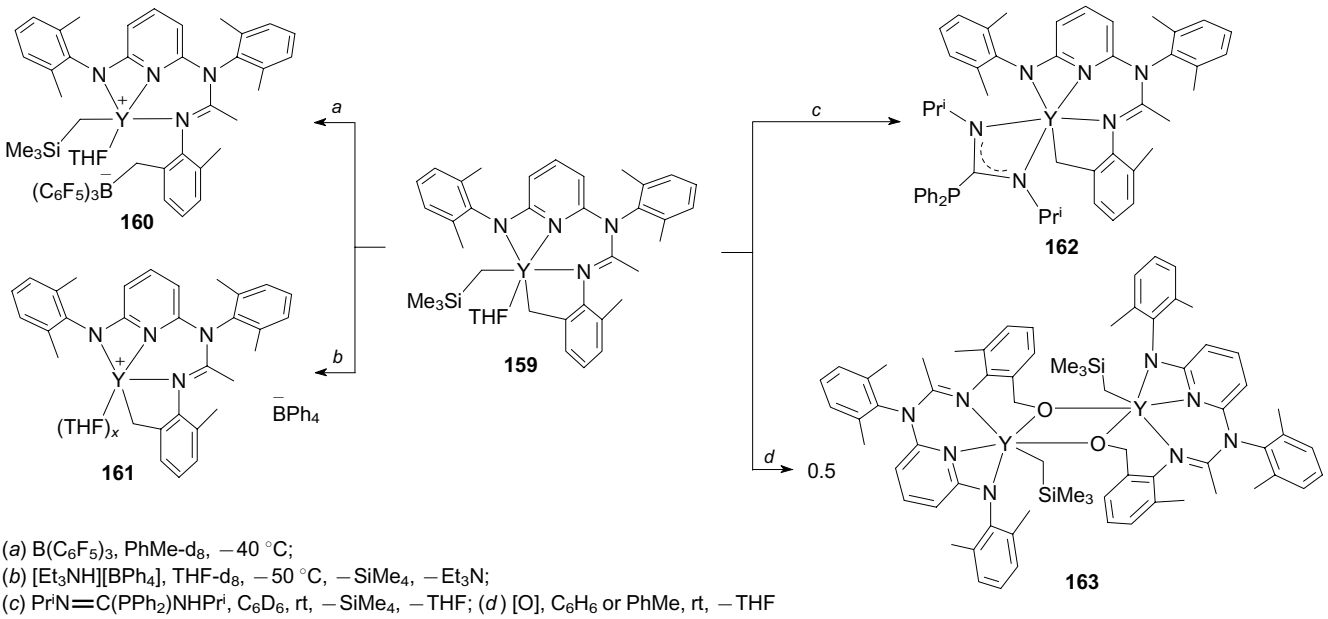


R = H (**a**), Et (**b**)

Scheme 233

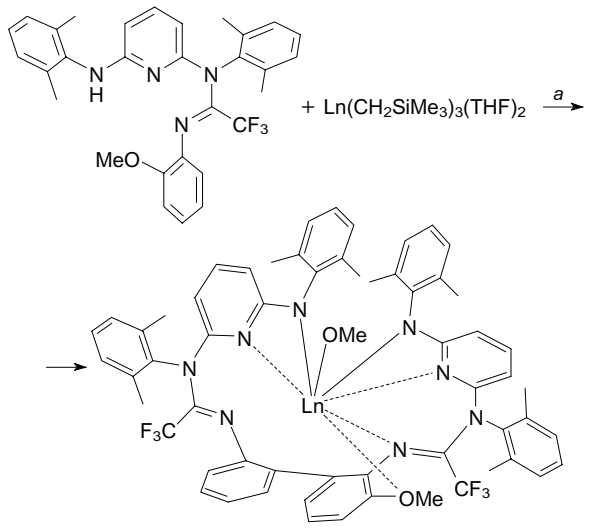


Scheme 234



(*a*) $B(C_6F_5)_3$, PhMe-d_8, −40 °C;
(*b*) $[Et_3NH][BPh_4]$, THF-d_8, −50 °C, $-SiMe_4$, $-Et_3N$;
(*c*) $Pr^iN{=}C(PPh_2)NHPr^i$, C_6D_6, rt, $-SiMe_4$, −THF; (*d*) [O], C_6H_6 or PhMe, rt, −THF

Scheme 235



(*a*) PhMe or THF, −3 Me_3SiH; Ln = Y, Sc

respectively (Scheme 234). Carbodiimide is inserted into the $Y-CH_2SiMe_3$ bond to afford product **162**, while the oxidation with dry oxygen under mild conditions involves selectively the Y−C(benzyl) bond, giving rise to binuclear complex **163** (see Scheme 234).[1044]

A unique selective intramolecular tandem reaction comprising the $C_{sp^2}-OMe$ bond cleavage and the $C_{sp^2}-C_{sp^2}$ bond formation took place on treatment of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y) with amidine–aminopyridine containing an anisole substituent at the amidinate nitrogen atom (Scheme 235).[1045]

Thus, we demonstrated that the design of new ligand systems provides the possibility of considerable variation of the stability of alkyl rare earth metal derivatives and, in some cases, obtaining complexes possessing high stability with respect to both thermal decomposition and disproportionation reactions, but retaining high reactivity inherent in the Ln−C bond. Of particular interest are selective inter- and intramolecular C−H bond activation reactions, which proved to form a convenient synthetic approach to heteroalkyl complexes of rare earth metals. It is beyond doubt that this ability of alkyl rare earth metal complexes may provide the basis for the development of new catalytic methods of C−C and C–heteroatom bond formation.

13. Conclusion

The chemistry of organoelement compounds is now one of the vigorously developing and interesting fields both for fundamental research and for solution of applied problems. This is due, on the one hand, to increasing accessibility and advancement of the modern methods for studying chemical phenomena. New NMR techniques, mass spectrometry,

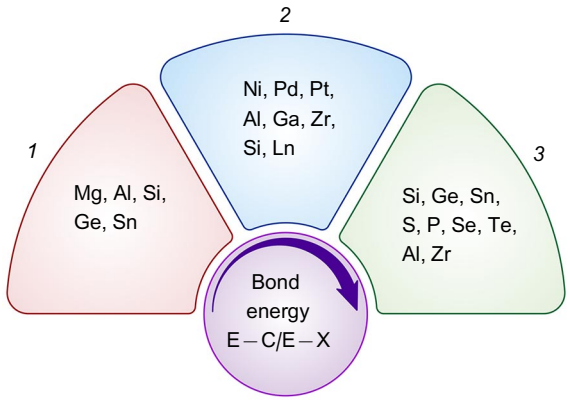


Figure 24. Applications of organoelement compounds depending on the element – carbon, element – heteroarom bond energy. (*1*) Short-lived intermediates and highly reactive compounds; (*2*) catalysts, reagents for organic synthesis and catalysis; (*3*) materials, end products and reagents for organic synthesis.

electron microscopy, efficient molecular modelling combined with high performance and accessible computing systems are gradually becoming routine methods used to study complex chemical phenomena and structures of single molecules, supramolecular complexes and materials. On the other hand, the chemistry of organoelement compounds offers a very broad spectrum of compounds and materials with unique properties: active reagents and catalytic systems, which allow conducting reactions with nearly atomic precision, biocompatible materials and materials with enhanced chemical, thermal and radiation stability.

The unique role of the chemistry of organoelement compounds for the whole chemical science consists in the involvement of all chemical elements and diversity of types and mechanisms of chemical reactions including interactions of s-, p-, d- and f-elements. Details of the chemistry and applications of organic derivatives of each element depend on the element – carbon or element – heteroatom bond energy (Fig. 24).

Compounds with highly labile element – carbon bonds are widely used as active reagents in fine organic synthesis. Such compounds are, first of all, organometallic derivatives of Group 1 and 2 elements, in particular, organomagnesium compounds, well known among which is the Grignard reagent (see Section 2). Organomagnesium compounds have served for decades as indispensable tools of fine organic synthesis, being utilized for the preparation of complex organic molecules of a variety of types. Catalytic cyclomagnesiation (see Section 3), a reaction of a new type involving organomagnesium compounds, opens up the synthetic routes to three- and five-membered, macrocyclic and giant metallacarbocycles difficult to obtain by other methods.

Electron transfer processes involving organic silicon derivatives active in redox reactions are significant for the design of new promising materials based on organosilicon compounds for molecular electronics, photovoltaics and signal and energy transfer-related fields (see Section 4).

Organometallic compounds with moderately labile metal – carbon bonds form the basis for transition metal catalysis, which is a cornerstone of fine organic synthesis both in laboratory practice and industry. Complexes of nickel, palladium, platinum and other transition metals are used most often in catalytic processes. Owing to the ability to form complexes with a variety of ligands, on the one hand, and formation of labile bonds with carbon atoms, on the other hand, these metals form the basis for really universal 'molecular meccanos' for the design of catalytic systems active in a broad range of chemical processes. Detailed investigation of the mechanisms of catalytic reactions carried out in recent years revealed the dynamic nature of catalysts, *i.e.*, coexistence in the reaction mixture of numerous types of catalytically active species (sites) involved in the reaction, a 'cocktail' of catalysts (see Section 10). Other metal complexes important for catalysis are magnesium, aluminium and gallium complexes containing redox active ligands, which can not only considerably affect the reactivity of the metal site, but also actively participate by themselves in the reactions with various substrates (see Section 11). Interesting representatives of catalytic systems are complexes in which the metal atom stabilizes the ligand that is unstable in the free state. An example is provided by zirconacyclocumulenes, which are exceptionally stable, but exhibit catalytic activity in some reactions of fine organic synthesis (see Section 9). Unique chemical, catalytic and physical properties are inherent in organic compounds of lanthanides, which are already used in optoelectronics, energy engineering, biomedicine and other fields (see Section 12).

Organoelement compounds with highly strong element – carbon and element – heteroatom bonds are valuable products for a variety of applications and the base for the manufacture of new construction materials with extraordinary performance. For example organophosphorus compounds synthesized recently exhibit unusual therapeutic properties (especially anticancer, antibacterial, antiviral), optical and electronic characteristics (see Section 7). In recent years, new organic chalcogen compounds have been obtained, some of them are being utilized as ligands in asymmetric synthesis (see Section 8). Various alkyl-, aryl-, vinyl-, allyl- and alkynylsilanes are valuable substrates for cross-coupling and oxidation reactions and monomers for the development of novel silicone hybrid materials (see Section 5). Organoelement ceramic-forming poly(oligo)mers are necessary for elaboration of new critical processes for the manufacture of high-strength, heat resistant and oxidation resistant components for nanostructured ceramic composites for the use in state-of-the-art and prospective equipment (see Section 6).

The possibility of varying the element – carbon or element – heteroatom bond strengths over wide limits and changing the physicochemical properties of obtained compounds are unique features of organoelement chemistry (see Fig. 24). Thus, the chemistry of organoelement compounds is an essential source of new materials, biologically active products, catalysts, reagents and systems for studying the mechanisms of chemical reactions and molecular structures. This field of chemistry brings about the unique possibility for the appearance of new growth areas for breakthrough investigations, generation of fundamental knowledge and development of industrial processes.

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