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Alkali and transition metal phospholides †

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Major tendencies in modern chemistry of alkali and transition metal phospholides (phosphacyclopentadienides) are systematized, analyzed and generalized. Basic methods of synthesis of these compounds are presented. Their chemical properties are considered with a special focus on their complexing ability. Potential applications of phospholides and their derivatives are discussed.
The bibliography includes 184 references.

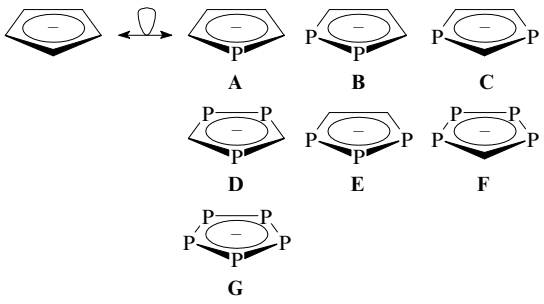
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I. Introduction

The concept of isolobal analogy proposed by R Hoffmann [1] is one of the most popular theories in various fields of chemistry — inorganic, organometallic, coordination and cluster chemistry. Application of this concept to trivalent phosphorus compounds gave a kind of impetus to the synthesis of numerous novel and extraordinary phosphorus compounds, in particular, phosphacyclopentadienide anions (phospholide-anions) **A** – **G** (Scheme 1).

Scheme 1



Being isolobal analogues of cyclopentadienide anions, phospholide anions also form mainly sandwich and half-sandwich complexes with transition metals. However, the presence of the lone pair of electrons (LPE) on the phosphorus atom is responsible for the possibility of realization of different coordination motifs, which enables the design of complex supramolecular assemblies that can be treated as inorganic fullerene analogues.[2,3] Moreover, catalytic systems based on phospholide anion derivatives show high activity in the Suzuki reaction,[4] the Miyaura reaction,[5] alkene polymerization reaction,[6] *etc*. Over the last 10 – 15 years, there has been a qualitative leap in this field of chemistry, so that phospholide anions and their organic derivatives — phospholes — transformed from exotic chemicals to new promising compounds.

Although reactions of phospholide anions have been covered in numerous reviews and monographs published in the last decades,[7 – 16] they have focused only on separate, specific issues and have not given a complete picture of the current trends in this field. Abundant new data have remained out of sight of their authors and, as a result, have not been scrutinized and summarized.

In the present review, we consider new trends in the chemistry of phospholide anions, in particular, the develop-

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Current research interests of the authors: chemistry of the low-coordination phosphorus, organometallic chemistry and chemistry of coordinated compounds.

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† Dedicated to Academician B A Trofimov on the occasion of his 75th birthday.

ment of novel convenient methods of their synthesis and study of their structure and reactivity. Special attention is paid to the complexing properties of transition metal phospholides as 'building blocks' (tectons) for designing complex supramolecular systems.

II. Synthesis of metal phospholides

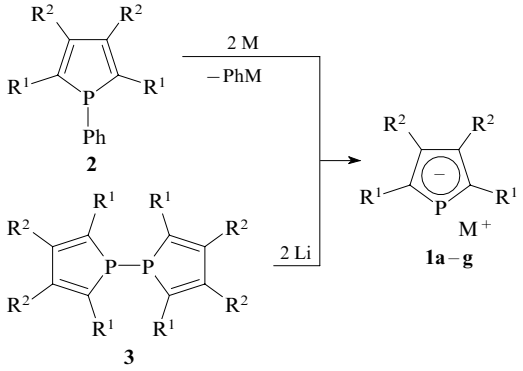
Although the first publication dedicated to the synthesis of monophospholide anion dated back to 1971,[17] simple and convenient methods of synthesis of phospholide anions **A**–**G** (see Scheme 1) characterized by high selectivity and yields of target products have been developed relatively recently, which has provided the impetus to the rapid development of this field of chemistry.

Current approaches to the synthesis of phospholide anions can be divided into two large groups. The first group comprises methods based on modification of cyclic phosphorus compounds — P–C or P–P bond cleavage in phospholes, biphospholes or 1,2-diphosphetes under the action of alkali metals. The second group comprises methods of covalent self-assembly of small synthons (elemental phosphorus, alkali metal polyphosphides, *tert*-butylphosphaalkyne or its trimerization product — 1,3,5-triphosphabenzene) under the action of alkali or transition metals.

1. Methods based on phosphorus–carbon bond cleavage in phospholes and phosphetes

Monophospholide anion (**1**)‡ was identified for the first time in the reaction of phenylphosphole (**2**) with lithium (Scheme 2).[17] However, the presence of phenyllithium in the system prevented the detailed study of chemical properties of anion **1**. To synthesize pure compound **1**, it was suggested to use the reduction of 1-halogen-substituted monophospholes or biphospholes (**3**) by alkali metals (see Scheme 2).[18] Later, this method has been successfully used for synthesizing new functionalized monophospholides **1** containing halide (**1c**),[19] trimethylsilyl (**1d**),[20] thienyl (Th, **1e**),[21] menthyl (Ment, **1f**)[22] and binaphthyl (Binaph, **1g**)[23] substituents in the 2- and 5-positions of the phospholide ring. It is worth noting that Rb and Cs are also capable of breaking the P–C bond to form corresponding metal monophospholides.[24]

Scheme 2

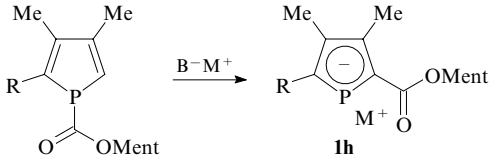


R^1 = Ar (**a**), Alk (**b**), Br (**c**), $SiMe_3$ (**d**), Th (**e**), Ment (**f**), Binaph (**g**);
R^2 = H, Ph; M = Li, Na, K, Rb, Cs

‡ For simplicity, we assign the same number to the phospholide anion and to its salts with different cations.

Phosphorus–carbon bond cleavage occurs much smoother in phospholes containing an electron-withdrawing substituent at the phosphorus atom. In this case, potassium *tert*-butoxide or lithium diisopropylamide can be used as reducing agents rather than alkali metals. This method has afforded, for the first time, 2-menthyloxycarbonyl- (**1h**) (Scheme 3)[25,26] and 2-(2′methoxynaphthyl)phospholide anions.[27]

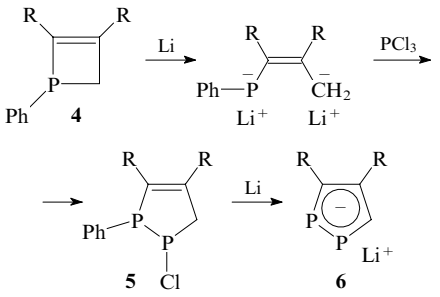
Scheme 3



R = H, Ph; $B^-M^+ = Pr^i_2NLi$ or Bu^tOK

The above approach is basic for synthesis of monophosphacyclopentadienide anions in quantitative yield; however, it cannot be applied to the synthesis of polyphosphacyclopentadienide anions containing more than one phosphorus atom. To synthesize the latter, special methods based on phosphorus–carbon bond cleavage in phosphetes under the action of alkali metals were developed in the 1990s. In particular, phosphorus–carbon bond cleavage in 1,2-dihydrophosphete **4** under the action of lithium metal, then the reaction with PCl_3 and further reduction of chlorodihydro-1,2-diphosphole **5** with lithium metal yielded, for the first time, lithium 1,2-diphosphacyclopentadienide **6** (Scheme 4).[28] Compound **6** was not isolated from the reaction mixture and was characterized only by ^{31}P NMR and mass spectrometry.

Scheme 4



R = Et, Ph

In addition, the method has been successfully applied to the synthesis of pure potassium 4,5-diphenyl-1,2,3-triphosphacyclopentadienide (**7a**) from 1,2-dihydro-1,2-diphosphete.[29] Nowadays, these methods are more of historical rather than of practical significance.

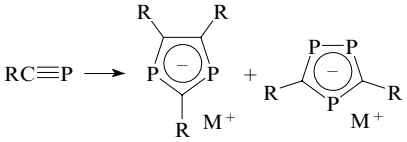
Thus, the above method based on phosphorus–carbon bond cleavage in phospholes and phosphetes under the action of alkali metals is a convenient and universal technique for producing metal monophosphacyclopentadienides. However, for synthesis of 1,2-diphosphacyclopentadienide anion (**6**) and 1,2,4- (**8**) and 1,2,3-triphosphacyclopentadienide anions (**7**), corresponding phosphetes are required, and their synthesis is a challenging experimental task and is characterized by low yields. Therefore, another method has been proposed for synthesis of alkali metal triphosphacyclopentadienides. This method is based on the reaction of

tert-butylphosphaalkyne ($Bu^tC{\equiv}P$) and its derivatives with alkali metals.

2. Covalent self-assembly of phospholide anions from small synthons

Alkali metal polyphospholides were obtained for the first time by the reaction of $LiP(SiMe_3)_2$ or sodium amalgam [30] with *tert*-butylphosphaalkyne and later by the reaction of alkali metal alkoxides with trimethylsilylphosphaalkyne ($Me_3SiC{\equiv}P$) (Scheme 5).[31] In both cases, mixtures of alkali metal 1,3-di- (**9**) and 1,2,4-triphospholides (**8**) are formed. The products are difficult to separate, which significantly decreases the yield of target compounds and is the major disadvantage of this method.

Scheme 5

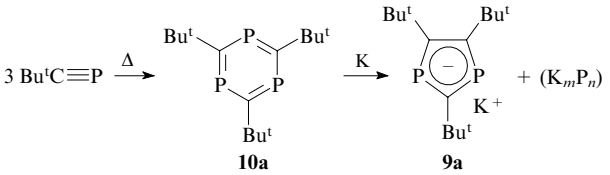


9a,**b** **8a**,**b**

R = Bu^t (**a**), $SiMe_3$ (**b**); M = Li, Na, K

For targeted synthesis of potassium 1,3-diphospholides **9**, it has been suggested to use the reaction of 1,3,5-triphosphabenzene **10a** with potassium mirror (Scheme 6).[32] The yield of compound **9a** in this reaction is as high as 40%.

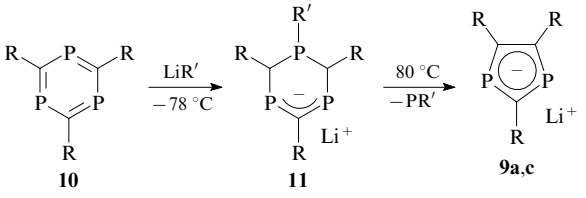
Scheme 6



10a **9a**

The formation of compounds **9** from 1,3,5-triphosphabenzenes **10** occurs under the action of lithium alkyls or amides. In this reaction, lithium 1,3,5-triphosphacyclohexadienides **11** are isolated as intermediates; when heated, the latter release phosphinidene species to give lithium 1,3-diphospholides **9a**,**c** (Scheme 7).[33]

Scheme 7



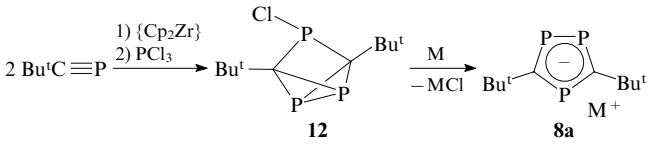
10 **11** **9a**,**c**

R = Bu^t (**9a**), CMe_2Et (**9c**); R′ = Bu^n, Me

This process is driven by the formation of aromatic anion **9**, which is supported by quantum chemical calculations.[34]

A method of selective synthesis of 1,2,4-triphospholide anion **8** has been developed rather recently. In particular, it has been shown that triphosphatricyclopentane **12**, which readily forms upon dimerization of *tert*-butylphosphaalkyne in the zirconium coordination sphere and subsequent treatment with PCl_3,[35] reacts with alkali metals to give salt **8a** in nearly quantitative yield (Scheme 8).[36] The reduction of compound **12** under the action of magnesium, europium or samarium metal occurs by the same scheme.[37]

Scheme 8

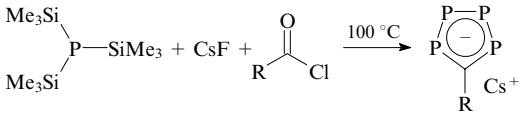


12 **8a**

M = Na, Li, $\frac{1}{2}$Mg, $\frac{1}{3}$Eu, $\frac{1}{3}$Sm; Cp = η^5-C_5H_5

(Trimethylsilyl)phosphine has also been successfully used as a substrate for synthesis of phospholide anions. In particular, prolonged heating of the three-component system $P(SiMe_3)_3-CsF-RC(O)Cl$ leads to tetraphosphacyclopentadienide anions **13a**,**b** (Scheme 9). The reaction mixture also contains alkali metal phosphides, phosphaalkenes and phosphaalkynes, 1,3,5-triphosphabenzenes and 1,2,4-triphosphacyclopentadienide anion **8**; however, prolonged heating (for ~10 days) shifts the equilibrium toward thermodynamically more stable products **13** in a yield of 44%–48%.[38, 39]

Scheme 9

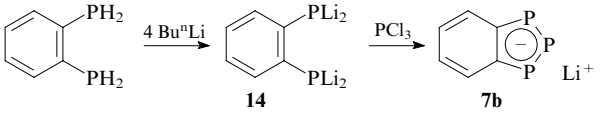


13a,**b**

R = 2,4,6-$Bu^t_3C_6H_2$ (**a**), $Bu^tCH{=}CBu^t$ (**b**)

Fused 1,2,3-triphospholide anion derivative **7b** is synthesized by the reaction of the lithium derivative of 1,2-diphosphinobenzene (**14**) and phosphorus(III) chloride (Scheme 10).[40] The reaction occurs under mild conditions and leads to 1,2,3-triphosphaindenyl anion (**7b**) in 49% yield.

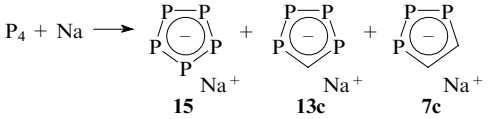
Scheme 10



14 **7b**

Elemental (white) phosphorus and alkali metal polyphosphides are widely used as reagents for synthesis of phospholide anions. In particular, formation of sodium pentaphosphacyclopentadienide (**15**) was detected for the first time in the reactions of white phosphorus with sodium metal (Scheme 11).[41] According to ^{31}P NMR, the reaction mixture contained also other phosphacyclopentadienides, such as 1,2,3,4-tetraphospholide (**13c**) and 1,2,3-triphospholide (**7c**) anions.

Scheme 11



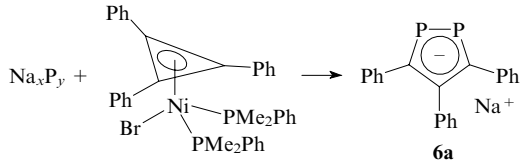
15 **13c** **7c**

Later, variation of the Na : P_4 ratio, the use of dibenzo-18-crown-6 (DBC-6) as a phase-transfer catalyst, as well as the use of sodium dihydrophosphide in THF, have made it possible to obtain a solution containing only sodium penta-

phosphacyclopentadienide (**15**).[42] The major products of this reaction are highest polyphosphides, which are precipitated and are not dissolved anymore, and the yield of compound **15** can be as large as 10%. A significant increase in the yield of sodium pentaphosphacyclopentadienide (**15**) has been achieved through careful selection of reaction conditions, in particular, the solvent and phase-transfer catalyst. Heating sodium and white phosphorus in diethylene glycol dimethyl ether in the presence of catalytic amounts of DBC-6 affords **15** in a yield of up to 22%.[43]

Using the products of the reaction of white phosphorus with sodium, alkali metal polyphosphides, has enabled the development of a radically new approach to the synthesis of phospholide anions. In particular, it has been shown that sodium polyphosphides react with 1,2,3-triphenylcyclopropenyl nickel complex to give exclusively sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**6a**) in high yield (Scheme 12).[44, 45]

Scheme 12

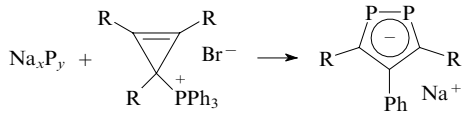


6a

Na_xP_y = NaP_5 (**15**), Na_3P_7

The reaction of sodium polyphosphides with cyclopropenylphosphonium salts represents a more convenient method of synthesis of 1,2-diphospholide anions **6** (Scheme 13).[46] This method has made it possible to synthesize new sodium 3,4,5-trisubstituted 1,2-diphosphacyclopentadienides **6** containing various aryl[47] or dialkylamine moieties.[48]

Scheme 13

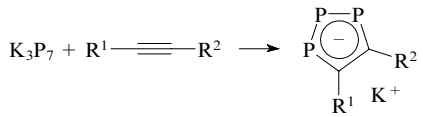


6

Na_xP_y = NaP_5 (**15**), Na_3P_7;
R = $NAlk_2$, Ph, 4-XC_6H_4 (X = F, Cl, Me, MeO)

Alkali metal polyphosphides are also convenient for synthesis of 1,2,3-triphospholide anions. In particular, it has been demonstrated that tripotassium heptaphosphide reacts with alkynes to form potassium 1,2,3-triphosphacyclopentadienides **7** (Scheme 14).[49, 50] The reaction occurs at room temperature and affords compounds **7** in 20% to 70% yield depending on the alkyne nature.[51]

Scheme 14



7

R^1, R^2 = H, Ph, Py; Py is 2-pyridyl

III. Chemical properties of phospholide anions

The stability and reactivity of phospholide anions are determined first of all by the aromaticity of the phospholide system. In all phospholide anions characterized by X-ray crystallography, the phosphorus–phosphorus or phosphorus–carbon bonds are equalized, which is evidence of considerable electron density delocalization inside the ring and of the aromatic character of phospholide anions.[52] According to quantum chemical calculations, the NICS criterion (nucleus independent chemical shift) of phospholide anions [NICS(0) = −13.2 to −15.9] is comparable with or larger than the analogous parameter of the cyclopentadienide anion [NICS(0) = −13.9; NICS(0) is the value of the criterion at the centre of the ring].[53] Theoretical analysis of aromaticity of these systems enabled the conclusion that successive substitution of a phosphorus atom for a CH moiety in the cyclopentadienide anion leads to an increase in aromaticity is the series of polyphosphacyclopentadienide anions **A**–**G** (see Scheme 1).[54]

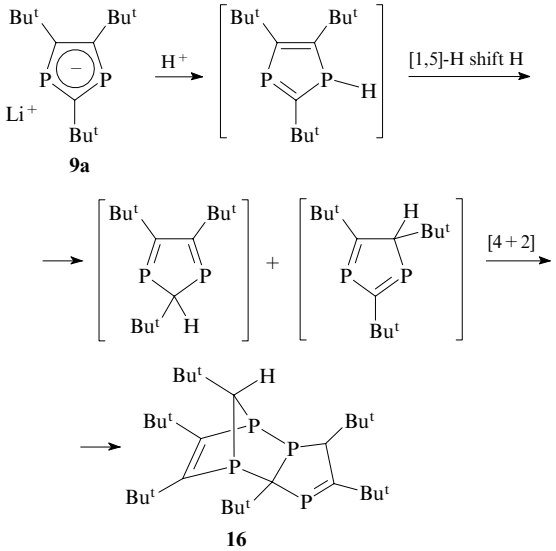
Compound	$C_5H_5^-$	**A**	**B**	**C**	**D**	**E**	**F**	**G**
NICS(0)	−13.9	−13.2	−13.9	−12.3	−14.2	−13.0	−14.5	−15.9

The aromaticity of phospholides, on the one hand, and the presence of a negative charge, on the other hand, predetermine their high reactivity toward organic and organometallic electrophiles.

1. Interaction of phospholide anions with electrophiles

Phospholide anions readily react with organic and organometallic electrophiles. The reaction always involves the phosphorus atom. Concurrently, a 4π-electron diene system is formed, which determines the stability and reactivity of phospholes. In particular, protonation of sodium mono-, di- and triphosphacyclopentadienides (for example, of compound **9a**) occurs through the formation of PH-phospholes at the first stage; even at room temperature, the latter undergo rearrangement *via* [1,5]-sigmatropic shift to give CH-phospholes, which undergo a [4 + 2]-cycloaddition reaction to form cage phosphines **16** (Scheme 15).[55]

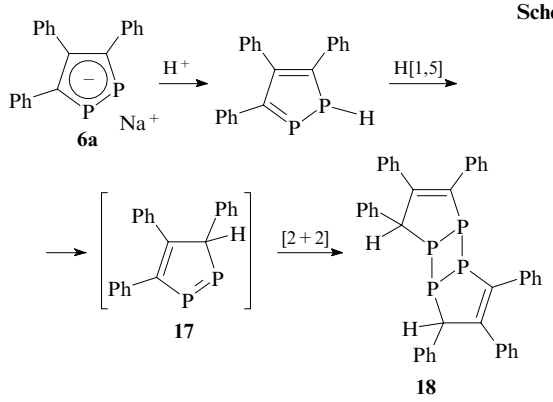
Scheme 15



16

Noteworthy is the anomalous protonation of sodium 1,2-diphospholide **6a**: the presence of the highly reactive P=P bond in CH-phosphole **17** is responsible for the formation of exclusively phosphine **18** as the [2 + 2]-cycloaddition product (Scheme 16).[56]

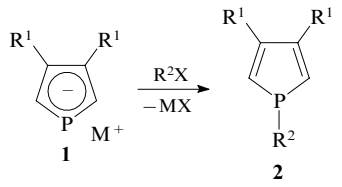
Scheme 16



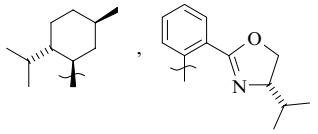
At the same time, alkylation of phospholide anions, as a rule, leads to the formation of stable phospholes — phosphorus analogues of cyclopentadiene, which attract the interest of researchers as starting compounds for synthesis of polycyclic phosphorus-containing compounds and metal complexes, as well as building blocks for design of efficient homogeneous catalysts, phosphorus-containing electro-optical materials and drugs.[57, 58]

In particular, the alkylation of monophosphacyclopentadienide anion **1** leads to stable 1*H*-phospholes **2** with an aryl, alkyl, pyridyl,[59] pyrrolidine,[60] alkenyl,[61] alkynyl,[62] ester,[63] phosphine,[64] chiral neomenthyl and oxazoline[65] or another substituent with functional groups at the phosphorus atom (Scheme 17).[58]

Scheme 17

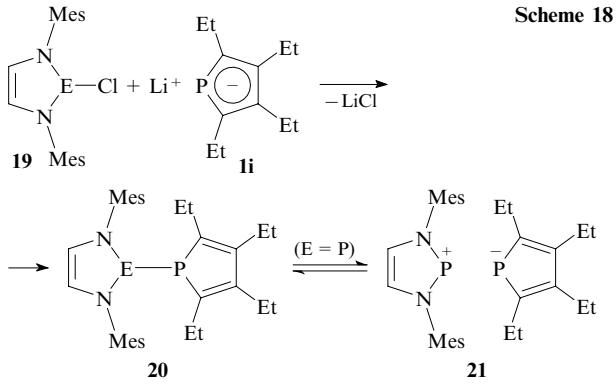


X = Cl, Br; R^1 = Me, Bn, Ph; R^2 = CN, CH_2Py, SiR^3_3, SnR^3_3, $CH_2CH_2CH{=}CH_2$, $CH_2C{\equiv}CPh$, CH_2CO_2Et, CH_2CH_2CN, CH_2Ar, $CH_2PR^3_2$ (R^3 = Alk, Ar),



The reaction of monophospholide anions (for example, **1i**) with different organometallic electrophiles (for example, with compounds **19**) leads to new monophospholes **20** with

Scheme 18

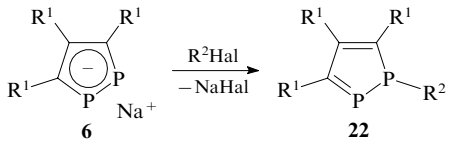


E = P, As, Sb; Mes = 2,4,6-$Me_3C_6H_2$

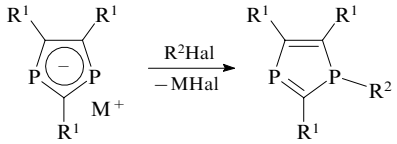
P–P, P–As, P–Sb[66, 67] and P–B bonds.[68] In diphosphines (E = P), the P–P bond is strongly polarized so that phosphenium–phospholide contact ion pair **21** is formed (Scheme 18).[69]

The reaction of corresponding polyphosphacyclopentadienide anions **6**, **9** and **8** with electrophilic reagents (alkyl, silyl, stannyl halides) is the only method of synthesis of 1,2-diphospholes **22**,[70–72] 1,3-diphospholes **23**[33, 73, 74] and 1,2,4-triphospholes **24** (Scheme 19).[75–77] In each case, the electrophilic species attacks the less sterically hindered phosphorus atom. The presence of bulky substituents (Bu^t, Mes*, $SiMe_3$) (Mes* = 2,4,6-$Bu^t_3C_6H_2$) favours the kinetic stabilization of the P=C bond, while electron density delocalization inside the ring leads to the thermodynamic stabilization of this bond. In the case of tin-containing derivatives **22** and **24**, the fluctuating behaviour of the Me_3Sn group is observed due to its shift between the phosphorus atoms of the P–P moiety.[70, 77]

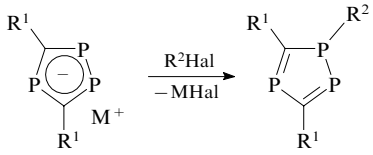
Scheme 19



Hal = Br, I; R^1 = Ph, 4-MeC_6H_4, 4-FC_6H_4, $NAlk_2$;
R^2 = Me, Et, Pr^n, Pr^i, Bu^n Bu^i, Cy, $SiMe_3$, SnR^3_3 (R^3 = Alk, Ar), $(CH_2)_nCH{=}CH_2$; Cy is cyclohexyl



Hal = Cl, Br; R^1 = Bu^t, CMe_2Et, $SiMe_3$; R^2 = Me, Pr^n, Bu^n, PPh_2, $SnPh_3$



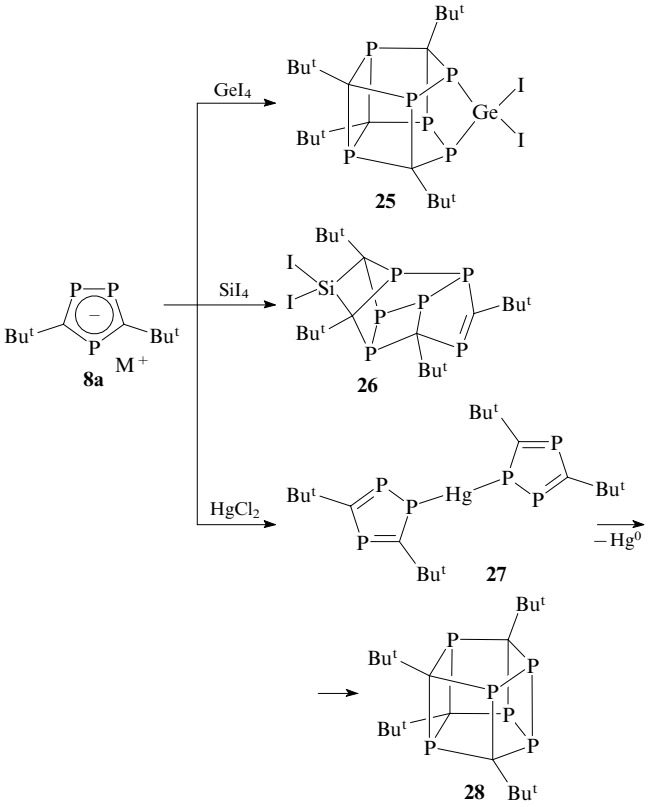
Hal = Cl, Br; R^1 = Bu^t, Mes*, $SiMe_3$; R^2 = Me, Bn, $CH(SiMe_3)_2$, SnR^3_3 (R^3 = Alk, Ar)

Reactions of polyphospholide anions with inorganic halides lead to more complicated products. In particular, the reaction of EI_4 (E = Si, Ge) with 1,2,4-triphosphacyclopentadienide anion **8a** (2 equiv.) yields derivatives of hexaphosphapentaprismane **25** and cage phosphine **26**, respectively (Scheme 20).[78]

The mechanism of these reactions remains unclear. It is presumed that first triphospholes with a P–Ge or P–Si bond are formed, which then undergo intramolecular cycloaddition reactions. Similar triphosphole **27** with a P–Hg bond and hexaphosphapentaprismane **28** were detected in the reaction of 1,2,4-triphosphacyclopentadienide anion **8a** with $HgCl_2$ (see Scheme 20). Elimination of mercury is observed in the course of this reaction, which is evidence of the occurrence of oxidative coupling.[79]

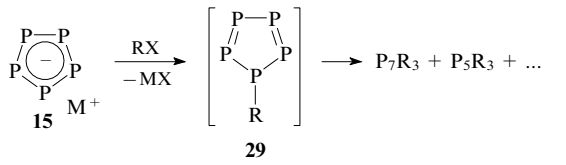
Currently, no data are available on the reactions of 1,2,3-triphospha- (**7**), 1,2,3,4-tetraphospha- (**13**) and penta-

Scheme 20



phosphacyclopentadienide anions (**15**) with electrophilic agents, which is likely due to the high reactivity and instability of the resulting polyphospholes. For example, an attempt of preparing pentaphosphole **29** by alkylation of sodium pentaphospholide (**15**) leads to a mixture of different polyphosphines, which can be explained by the high reactivity of the P=P bonds in molecule **29** (Scheme 21).[42]

Scheme 21



X = Cl, Br; R = Me, Et

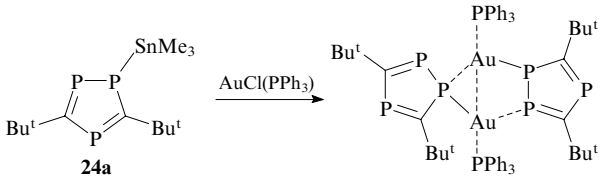
2. Complexing properties of phospholide anions

Phospholide anions are isolobal analogues of the cyclopentadienide anion — one of the most popular ligands in organometallic chemistry — and can act as 6π-electron donors to result in η^5 coordination to transition metal atoms. At the same time, the exchange of one or several carbon atoms in the five-membered ring for phosphorus atoms, which have LPE and are capable of additional coordination to a metal atom, considerably extends the potential of such ligands for design of novel polymetallic complexes and clusters.

a. Phospholide complexes of copper subgroup metals

A characteristic feature of Group I transition metal complexes is their propensity to form clusters with a metal–metal bond, as well as the occurrence of dynamic processes in solution accompanied by a change in the coordination mode of the ligand to the metal centre. In this context, the structure of the complex forming in the reaction of phosphacyclopentadienide anions with the metals of this group is difficult to predict. This fact has been demonstrated by the reaction of 1,2,4-triphospholes with gold(I) chloride. In particular, 3,5-di(*tert*-butyl)-1-trimethylstannyl-1,2,4-triphosphacyclopenta-2,4-diene (**24a**) reacts with $AuCl(PPh_3)$ to give binuclear complex **30** (Scheme 22).

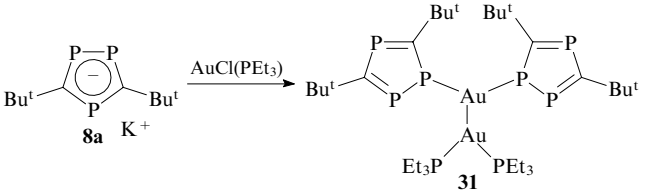
Scheme 22



In the solution of this compound, several complex species with different coordination modes of the 1,2,4-triphosphole ligand to the gold atom are at dynamic equilibrium. The low activation energy of mutual transformations prevented the identification of limiting structures of complex **30** in solution.[80] A striking feature of compound **30** is the short Au···Au distance (3.14 Å), which is shorter than the sum of the van der Waals radii (3.4 Å); this distance indicates a weak gold–gold interaction.

At the same time, varying the reaction conditions has led to another result. The reaction of potassium 1,2,4-triphosphacyclopentadienide **8a** with $AuCl(PEt_3)$ [rather than with $AuCl(PPh_3)$] also gives binuclear complex **31**. However, both phospholyl moieties in this compound are coordinated only to one gold atom, while the phosphine ligand migrates to the neighbouring gold atom (the Au–Au distance is 3.04 Å) (Scheme 23).[81]

Scheme 23

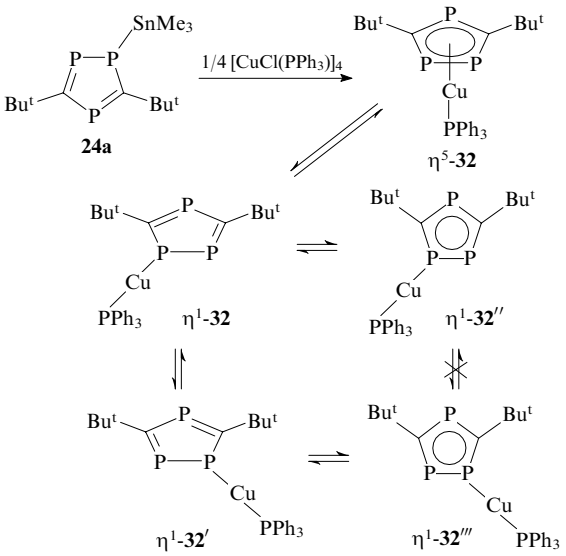


It should be noted that in solutions of complex **31**, there is a dynamic equilibrium between different species due to easy migration of the gold atom between two neighbouring phosphorus atoms.

The existence of dynamic equilibria has also been shown for solutions of copper complexes with 2,3-di(*tert*-butyl)-1,2,4-triphospholide **32**, which forms in the reaction of compound **24a** with triphenylphosphine adduct of copper(I) chloride (Scheme 24).[82] For compound **32**, the structures of isomers at equilibrium have been determined by means of variable-temperature NMR experiments. In particular, it has been demonstrated that compound **32** is a half-sandwich complex with η^5-coordination of the 1,2,4-triphosphacyclopentadienyl ligand to the metal atom as in the case of the Cp anion (see Scheme 24).[83]

However, the presence of phosphorus atoms with LPEs in the phosphole ligand promotes the change in the coordination mode of the phospholyl ligand to copper leading to the formation of the η^1-**32** isomer with η^1-coordination,

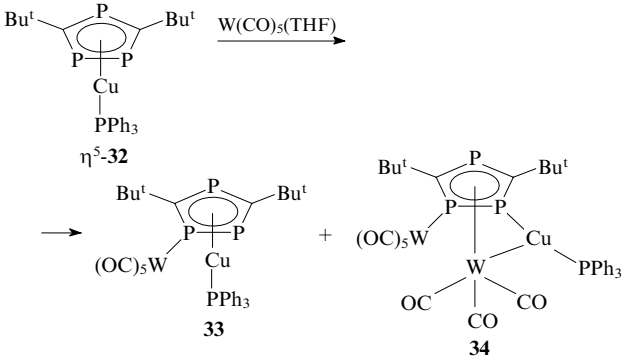
Scheme 24



which isomerizes with 1,2-sigmatropic shift into structure η^1-**32**′. In complexes η^1-**32** and η^1-**32**′, the phosphorus atom bonded to the Cu atom is sp^3-hybridized, and the π-system of the ring is localized. These species are at equilibrium with complexes η^1-**32**″ and η^1-**32**‴, in which the corresponding phosphorus atom is sp^2-hybridized, and its LPE is involved in the 6π-electron system of the ring.

The occurrence of this isomerization of complex **32** in solution has been indirectly confirmed by its reaction with tungsten carbonyl. The reaction yields two heterometallic complexes **33** and **34** with different coordination modes of the phospholyl ligand to the metal atom (Scheme 25).

Scheme 25

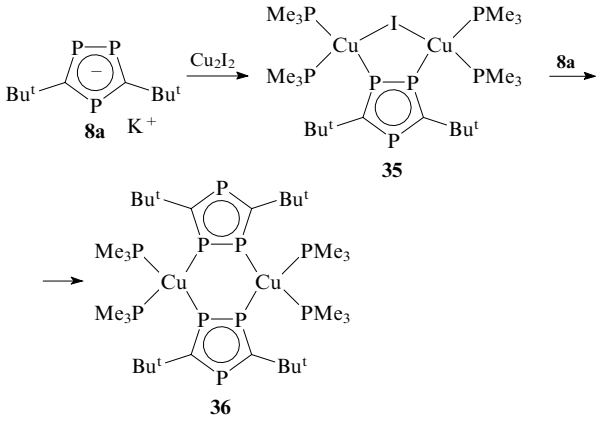


In particular, the η^5-coordination of the triphospholyl ligand to the copper atoms persists in major product **33** in which $W(CO)_5$ is coordinated through the LPE on one of the phosphorus atoms. At the same time, in second complex **34**, the $W(CO)_3$ moiety is involved in coordination with the π-system of the triphosphacyclopentadienyl ligand and is additionally bound to one phosphorus atom through the $CuPPh_3$ moiety.

It should be noted that in solutions, complexes **33** and **34** are also at dynamic equilibrium caused by migration of metal atoms between the phosphorus atoms.[82]

At the same time, the reaction of potassium salt **8a** (rather than corresponding tin derivative **24a**) with copper(I) iodide in the presence of PMe_3 taken in a 1 : 1 : 1 ratio yields complex **35** in which two copper atoms are linked through the C_2P_3 ligand and the iodine atom. When another equivalent of salt **8a** is added, complex **35** is converted into symmetric complex **36** with two bridging triphospholide moieties.[81] Complexes **35** and **36**, as distinct from corresponding gold derivatives **30** and **31**, are stable in solution (Scheme 26).

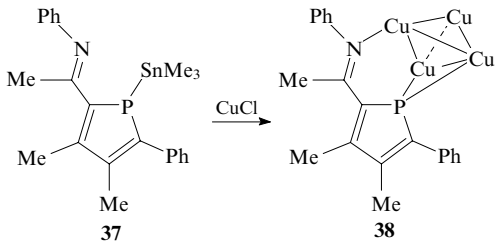
Scheme 26



Analogous binuclear copper complexes with 1,2-diphospholide ligands have also been synthesized.[84]

Complexation with chelating monophospholide forming from phosphole **37** and containing two different donor sites — the phosphorus atom and the nitrogen atom of the imino group — is more complicated (Scheme 27).[85] The major reaction product is the tetranuclear cluster $(CuL)_4$ (**38**), in which each ligand is coordinated to three copper atoms (Scheme 27 shows one of the four ligands).

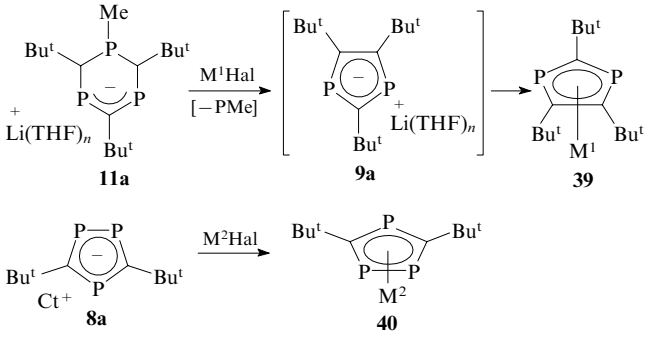
Scheme 27



b. Phospholide complexes of boron group metals

The complexation of boron group metals by phospholide anions is markedly different from that of copper and gold.

Scheme 1



M^1Hal = GaI, InI, TlCl; Ct = Li, M^2Hal = TlCl; Ct = K: M^2Hal = GaCl, InCl

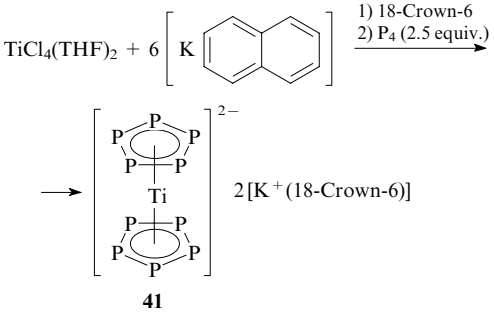
In particular, 1,3-di- (**9**) and 1,2,4-triphospholides (**8**) react with gallium(I),[86] indium(I)[87] and thallium(I)[88] halides to form stable complexes **39** and **40**, in which the phospholyl ligand acts as a 6π-electron donor (Scheme 28).

It should be noted that these compounds are salts and dissociate in solution so that the metal–ligand interactions occur only in the crystal.[89,90]

c. Phospholide complexes of titanium subgroup metals

Studying the complexing properties of phospholide anion derivatives in reactions with titanium and zirconium compounds has led to interesting results. In particular, with the pentaphospholide anion, the only representative of inorganic carbon-free phosphametallocenes **41** has been synthesized. For synthesis of this compound, an extraordinary method has been suggested consisting in *in situ* generation of the highly reactive complex bis(naphthalene)titanate(2−) and its introduction into further reaction with white phosphorus (Scheme 29).[91]

Scheme 29

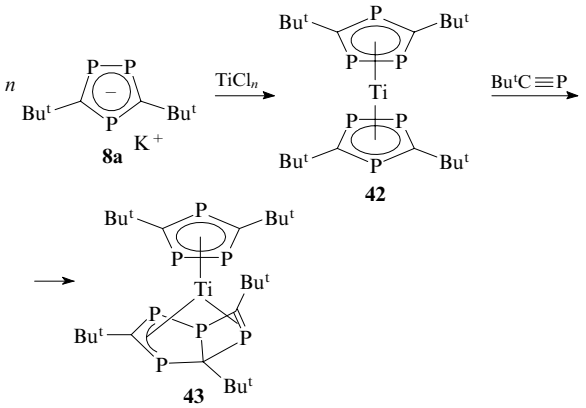


41

Decaphosphatitanocene **41** is a 16-electron dianionic complex in which titanium has a zero charge, and two potassium atoms linked to the crown act as counterions. Despite the presence of a large number of reactive sites, compound **41** is resistant to the action of 2,6-dimethylphenyl isocyanide, carbon monoxide, and oxygen for weeks and starts decomposing only in the presence of moisture.

A decrease in the number of phosphorus atoms in the phospholyl ligand reduces its aromaticity, which leads to the increase in the reactivity of titanocene. The introduction of potassium 1,2,4-triphosphacyclopentadienide **8a** into the reaction with titanium(II) chloride affords hexaphosphatitanocene **42** in a yield of up to 30% (Scheme 30).[92] The distance between the phospholyl ligands in molecule **42** is larger than in complex **41**, which essentially influences the reactivity of the former.

Scheme 30



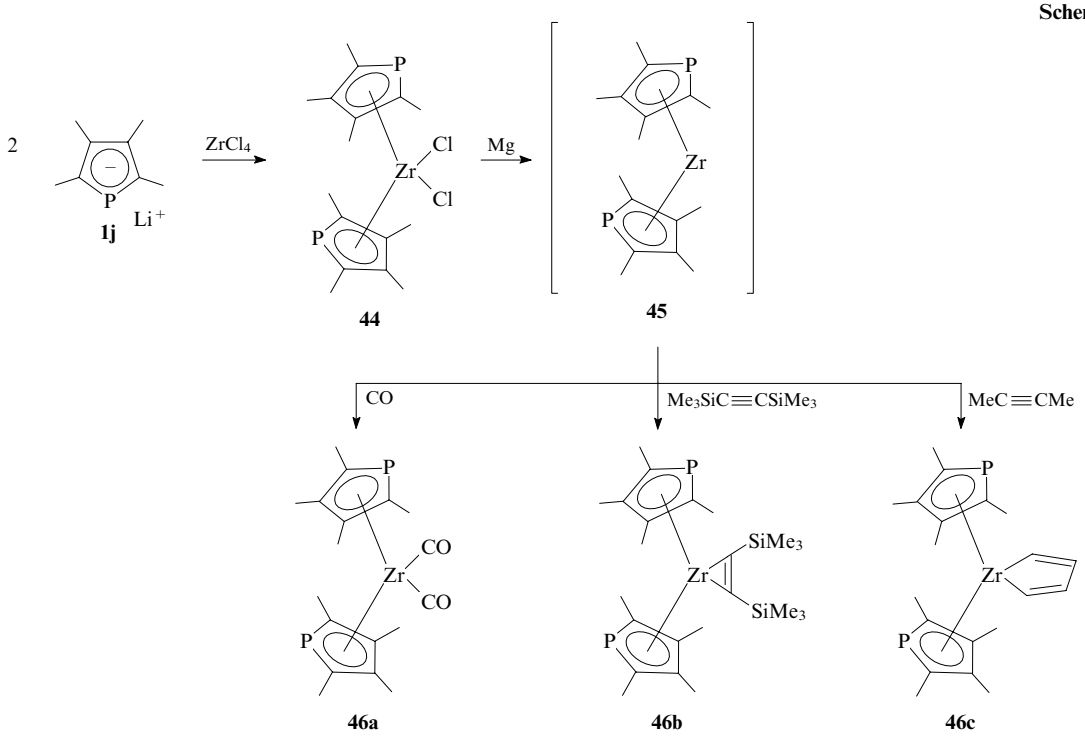
8a **42** **43**

n = 2, 3

In particular, hexaphosphatitanocene **42** is sensitive to air oxygen and moisture and easily undergoes an unusual [2 + 2] cycloaddition reaction with *tert*-butylphosphaalkyne to form **43** (see Scheme 30).[92]

Reduction of 1,1′-diphosphazirconocene dichloride **44** by magnesium leads to highly reactive 1,1′-diphosphazirconocene **45**, which has been characterized as adducts with

Scheme 31

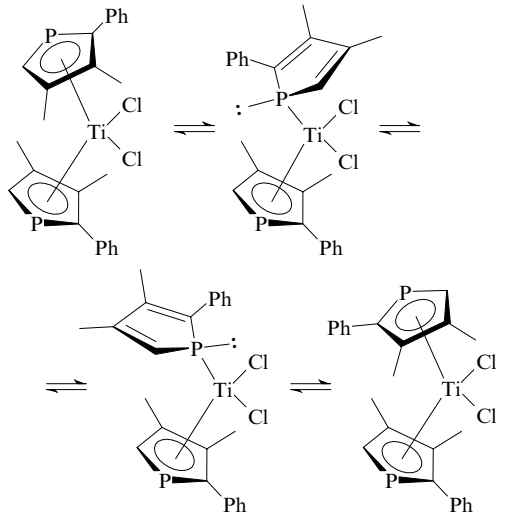


1j **44** **45** **46a** **46b** **46c**

carbon monoxide (**46a**), bis(trimethylsilyl)acetylene (**46b**) and but-2-yne (**46c**) (Scheme 31).[93]

The high reactivity of titanium and zirconium phospholides toward different substrates, as well as the existence of the lone pair of electrons on the phosphorus atom, makes these compounds promising candidates for designing novel catalysts of various processes, including asymmetric catalysis.[94] At the same time, the use of these compounds in asymmetric catalysis has been doubted since they readily undergo isomerization accompanied by inversion of configuration (Scheme 32). Isomerization can result not only from rotation around the metal – ring bond but also can be accompanied by a change in the metal – phospholyl ligand coordination mode involving the LPE on the phosphorus atom. Similar isomerization has been studied for titanium(IV)[95,96] and zirconium(IV)[97] complexes with monophospholyl ligands.

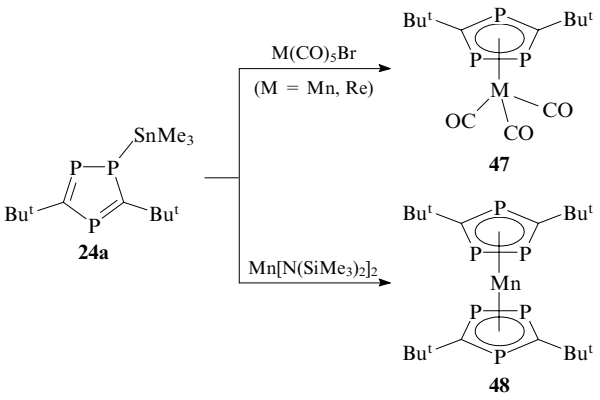
Scheme 32



d. Phospholide complexes of manganese subgroup metals

A classical example of synthesis of organometallic compounds is the reaction of the cyclopentadienide anion with manganese(II) halides and manganese(I) carbonyls yielding, respectively, sandwich and half-sandwich complexes with η^5-coordination of the Cp ligand. A similar behaviour is exhibited by 3,5-di(*tert*-butyl)-1-trimethylstannyl-1,2,4-triphosphole (**24a**), which reacts with $M(CO)_5Br$ (M = Mn, Re) and $Mn[N(SiMe_3)_2]_2$ to form half-sandwich (**47**) and sandwich (**48**) complexes, respectively (Scheme 33).[98 – 100]

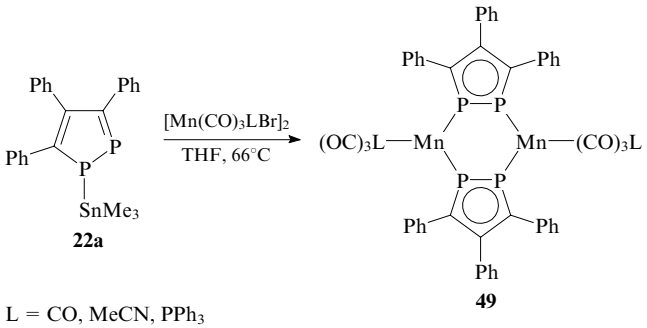
Scheme 33



As distinct from high-spin manganocene Cp_2Mn, hexaphosphamanganocene **48** is a low-spin complex due to the presence of phosphorus atoms in the ring which directly affect the energy of frontier orbitals. In triphosphacymantrene **47**, the major contribution to the formation of the metal – phospholide bond is made by ligand-to-metal π-donation, whereas metal-to-ligand back π-donation occurs in hexaphosphamanganocene **48**.

An unusual result has been obtained when studying the complexing properties of 1,2-diphosphole **22a** toward manganese carbonyl complexes under similar conditions: the reaction yields binuclear complexes **49** with bridging $\mu,\eta^1{:}\eta^1$-coordination metal – diphospholyl ligand (Scheme 34).[101]

Scheme 34



L = CO, MeCN, PPh_3

EPR spectroscopy and static magnetic susceptibility measurements have demonstrated that binuclear complexes **49** show magnetic properties characteristic of Mn^{II} in the low-spin state, which is caused by considerable electron density redistribution in the molecule. Moreover, magnetic properties can be efficiently controlled by varying ligands L at the manganese atoms.[102, 103]

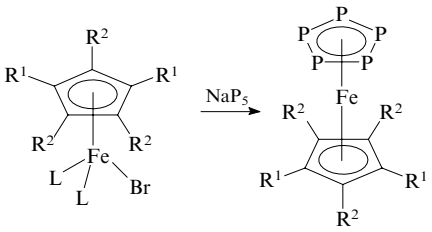
e. Phospholide complexes of iron group metals

Phosphaferrocenes are convenient models for studying electron density distribution in phospholide complexes by quantum chemical methods to evaluate the effect of phosphorus atoms in the cyclopentadienyl ligand on the metal – ligand bond character and the properties of resulting complexes. In particular, quantum chemical calculations have shown that substitution of phosphorus atoms for the carbon atoms of the cyclopentadienyl ring[104] strengthens the π-bonding of the ligand to the metal proportionally to the number of introduced heteroatoms.[105 – 107] In addition, it has been calculated for pentaphosphaferrocene derivatives as an example that the introduction of methyl substituents into the cyclopentadienyl ligand also leads to the strengthening of the Fe – (P_5-cyclo) bond.[108] Indeed, pentamethylpentaphosphaferrocene (**50a**) is highly stable, and the distance from the Fe atom to the centroid of the P_5 ring is rather short (1.52 Å) as compared with other phosphaferrocenes.[109, 110]

The more so, it has been experimentally shown that the stability of pentaphosphaferrocenes depends on the nature of substituents in the ring. In particular, pentaphosphaferrocene **50a** was obtained in 70% yield by heating to 110 °C a mixture of a solution of NaP_5 (**15**) in diglyme with $Cp^*Fe(CO)_2Br$ ($Cp^* = \eta^5$-C_5Me_5) (Scheme 35).[111] The yield of 1,3-di(*tert*-butyl)pentaphosphaferrocene (**50b**)

under the same conditions was only 2% because of the occurrence of the side reaction of formation of homoleptic 1,1′,3,3′-tetra(*tert*-butyl)ferrocene. The decrease in reaction temperature by using an iron complex containing two molecules of a tertiary phosphine instead of CO groups made it possible to increase the yield of product **50b** to 80%.[111]

Scheme 35

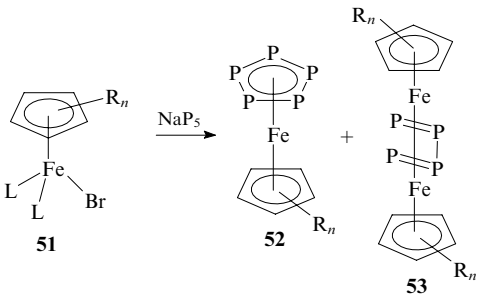


50a,**b**

L = CO, PMe_3; $R^1 = R^2 = Me$ (**a**); $R^1 = Bu^t$, $R^2 = H$ (**b**)

The effect of substituents in the CP ring on the occurrence of this reaction has been additionally studied for trimethylsilyl derivatives of cyclopentadienyl iron complex **51**. In particular, the reaction of an excess of complex **51** with NaP_5 (**15**) under mild conditions yields, in addition to expected pentaphosphaferrocene **52**, triple-decker complex **53**, in which tetraphosphabutadiene molecule is coordinated between two iron atoms (Scheme 36).[112]

Scheme 36



51 **52** **53**

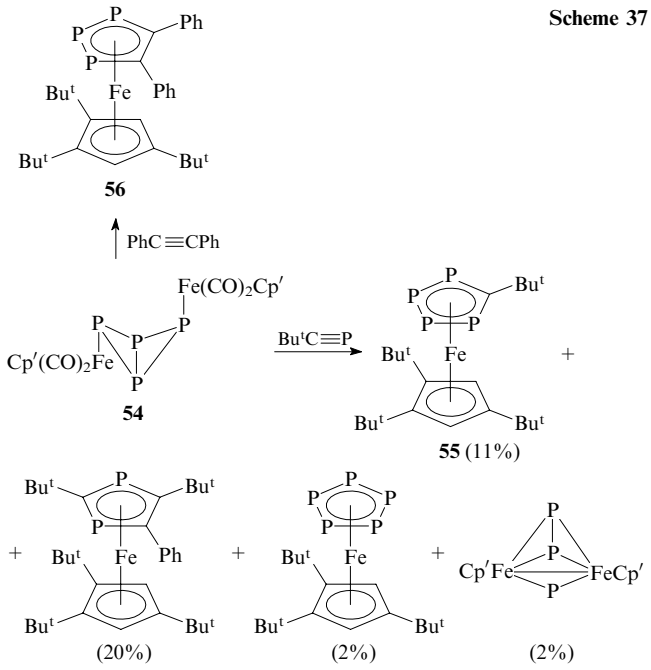
L = $PPhMe_2$; R_n = 1,3-$(SiMe_3)_2$, 1,3,4-$(SiMe_3)_3$

An original method of synthesis of phosphaferrocenes has been developed on the basis of binuclear iron carbonyl complex **54**, containing the bridging P_4^{2-} ligand. In particular, compound **54** readily reacts with *tert*-butylphosphaalkyne to form 1,2,3,4-tetraphosphaferrocene **55** in 11% yield in mixture with other products (Scheme 37).[113]

The use of diphenylacetylene rather than *tert*-butylphosphaalkyne has made it possible to synthesize, for the first time, 1,2,3-triphosphaferrocene **56** isolated by column chromatography in 40% yield (see Scheme 37).[114]

The development of a convenient and efficient method of synthesis of 1,2,3-triphospholide anion (**7c**) has made it possible to preliminarily study its complexing properties on the basis of the reaction with $[Ru(cod)\{\eta^3\text{-}MeC(CH_2)_2\}_2]$ (cod is cycloocta-1,5-diene).[49] The reaction affords anionic ruthenium complex **57** with η^5-coordination of the triphospholyl ligand to the metal. The reaction is accompanied by the change in the coordination mode of one of the 2-methylallyl ligands (from η^3 to η^1) and formation of the stable 18-electron complex (Scheme 38).

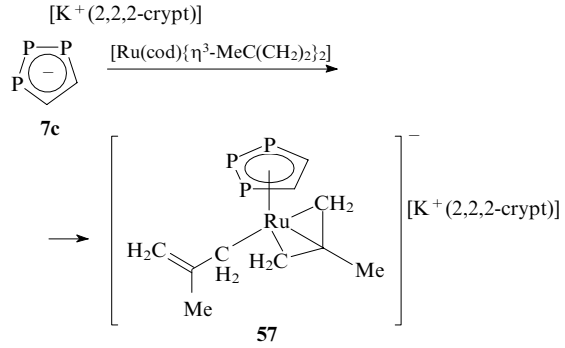
Scheme 37



56 **54** **55** (11%) (20%) (2%) (2%)

$Cp' = C_5H_2Bu^t_3$-1,2,4

Scheme 38

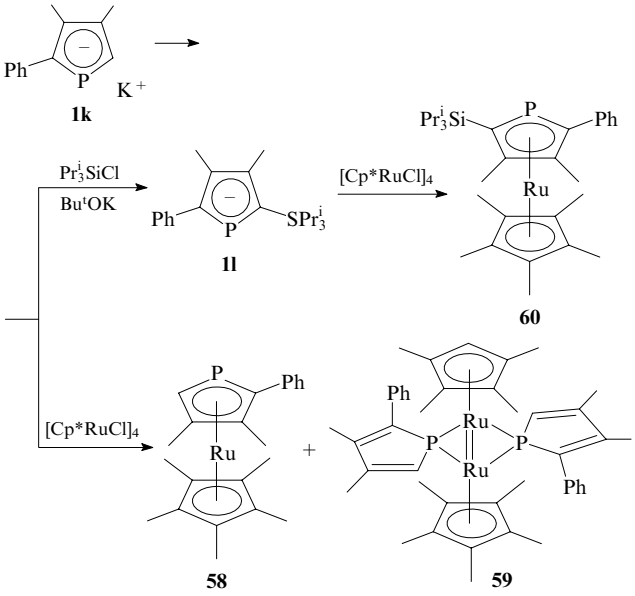


7c **57**

Stable 18-electron phosphaferrocenes and phospharuthenocenes are the most abundant products of reactions of different derivatives of monophospholide anion **1** with iron(II)[115–118] and ruthenium(II)[26,119,120] halides. At the same time, for ruthenium complexes with monophospholide anion **1**, the effect of substituents in the phospholide ring on the metal–phospholyl ligand coordination mode has been revealed. In particular, the introduction of potassium 3,4-dimethyl-2-phenylmonophospholide (**1k**) into the reaction with $[Cp^*RuCl]_4$ leads only to trace amounts (< 5%) of desired phospharuthenocene **58**, and the major product (> 80%) is binuclear complex **59**, in which the metal sites are linked by bridging phosphorus atoms of the phospholyl ligands (Scheme 39).[121] Long-term heat treatment of complex **59** does not afford phospharuthenocene **58**, and only leads to the decomposition of complex **59**.

At the same time, modification of the initial potassium 3,4-dimethyl-2-phenylmonophospholide (**1k**) by introducing the sterically crowded triisopropylsilyl substituent into the 5-position (anion **1l**) enables the synthesis of ruthenocene **60** in high yield under mild conditions in a similar reaction (Scheme 39).

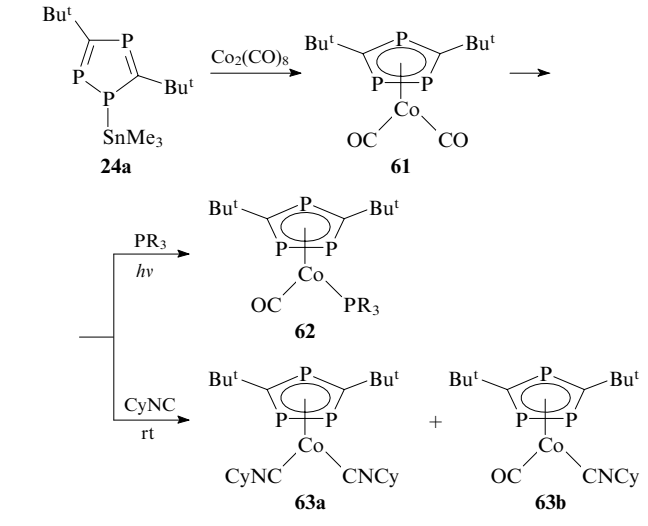
Scheme 39



f. Phospholide complexes of cobalt subgroup metals

The substitution of phosphorus atoms for the carbon atoms in the cyclopentadienyl ligand markedly influences the properties of the forming complexes, which has been shown by the example of 1,2,4-triphospholylcarbonylcobalt **61** (Scheme 40).[100] In particular, it has been demonstrated that compound **61** is more reactive as compared with its carbon analogue: in **61**, the carbonyl ligands can be substituted by tertiary phosphines or isonitriles under rather mild conditions, with retention of the half-sandwich structure of complexes **62** and **63a**,**b**.[100]

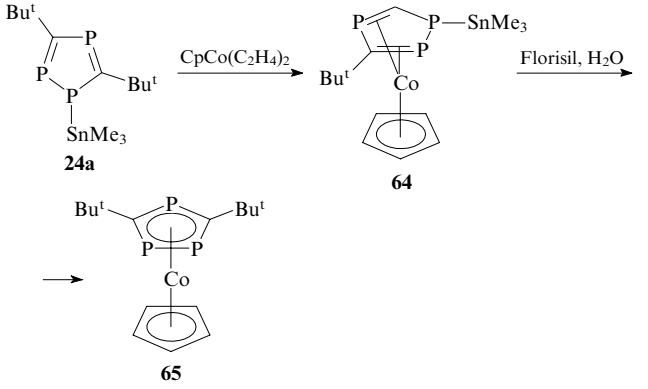
Scheme 40



R = Et, Ph

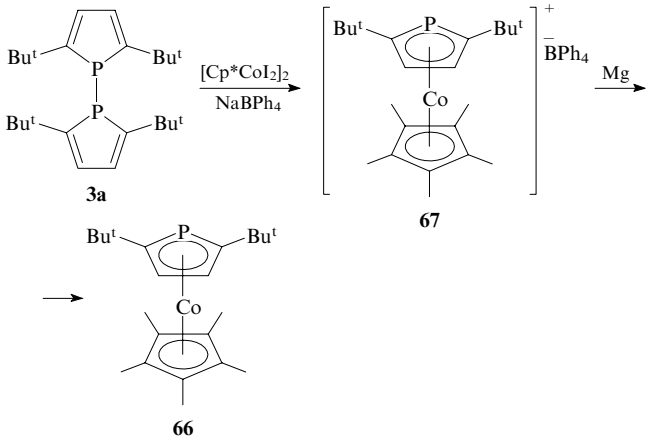
At the same time, the reaction of **24a** with $CpCo(C_2H_4)_2$ involves substitution of 1,2,4-triphosphole **24a** acting as a 4π-electron donor for the two ethylene molecules to form 18-electron complex **64** (Scheme 41).[122] Like the initial phosphole, compound **64** is subjected to hydrolysis resulting in phosphorus–tin bond cleavage to form paramagnetic triphosphacobaltocene **65**.[122]

Scheme 41



Another method has been suggested for synthesis of monophosphacobaltocene **66**. The method is based on the reduction of cationic complex **67**, obtained by the reaction of $[Cp^*CoI_2]_2$ with 2,2′,5,5′-tetrakis(*tert*-butyl)-1,1′-bimonophosphole (**3a**) (Scheme 42).[123, 124]

Scheme 42



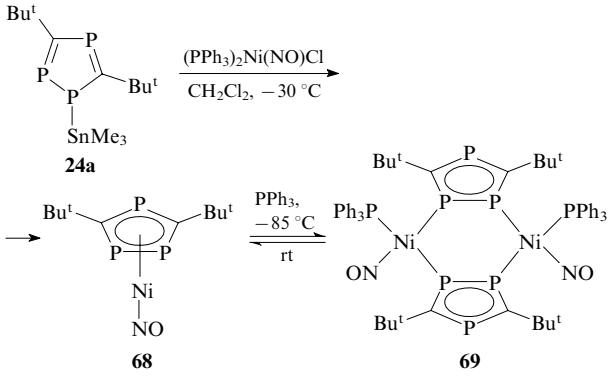
The most straightforward and convenient method of synthesis of cobaltocene complexes is the introduction of monophospholide anion **1** into the reaction with cobalt(II) complexes containing easily leaving groups (acetylacetone, acetonitrile, *etc.*).[125, 126] At the same time, it has been demonstrated for the reaction of derivatives of monophospholide anion **1** with rhodium and iridium compounds that the presence of sterically crowded substituents at the phosphorus atom makes it possible to prevent the metal coordination to the phosphorus LPE so that the phospholyl ligand is η^5-coordinated to the metal atom.[127]

g. Phospholide complexes of nickel group metals

Reactions of phospholide anion derivatives with nickel group metals clearly demonstrates the effect of the nature of a phospholyl ligand, metal centre and its ligand environment, as well as synthesis conditions, on the coordination mode of phospholyl ligand to the metal atom. For example, the reaction of 1-trimethylstannyl-1,2,4-triphosphole (**24a**) with a nitrosyl nickel complex yields half-sandwich complex **68** with η^5-coordination of the phospholide anion (Scheme 43). In this case, the coordination mode of the phospholyl ligand is essentially temperature dependent: with decreasing temperature, the metal–ligand coordina-

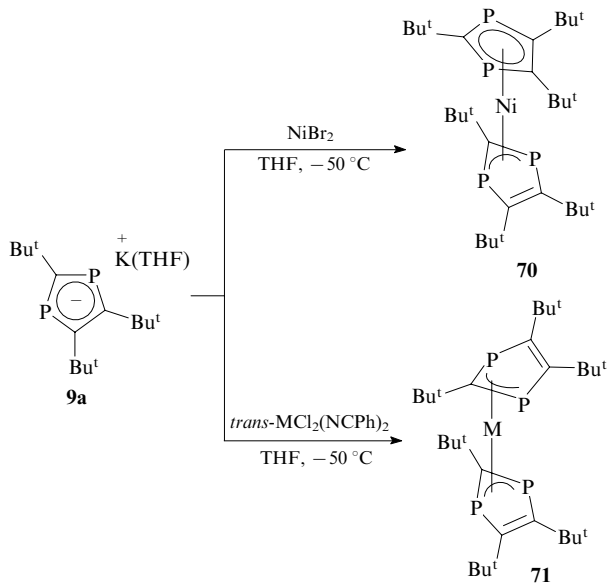
tion mode changes to give binuclear complex **69** (Scheme 43).[128]

Scheme 43



At the same time, the reaction of nickel(II), palladium(II) and platinum(II) halides with potassium 1,3-diphospholide **9a**, in which the phosphorus atoms are surrounded by bulky *tert*-butyl groups preventing the coordination of metals *via* the LPEs on the phosphorus atoms, leads to complexes **70** and **71** with exclusively π-coordination of 1,3-diphospholide to the metal (Scheme 44).[129] In the case of nickel, 18-electron complex **70** is formed in which one of the diphospholyl rings is a 6π-electron donor, and the second ring is a 4π-electron donor. Palladium and platinum derivatives give 16-electron complexes **71** with η^3-coordination of both phospholyl rings.

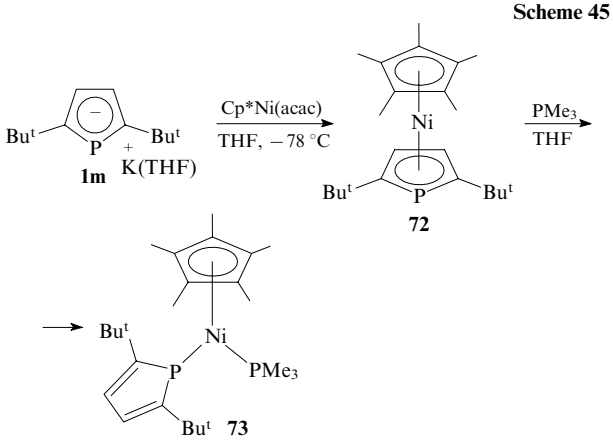
Scheme 44



M = Pd, Pt

To synthesize stable 20-electron phosphanickelocene **72**, monophospholide anion **1m** with sterically crowded phosphorus atom has been successfully used (Scheme 45). It is likely that, due to the steric crowdedness of the phosphorus atom in the phospholyl ligand, the η^5-coordination in this case is more favourable. At the same time, the addition of a tertiary phosphine to a solution of compound **72** leads to the change in the coordination mode of the monophospholyl ligand and formation of novel 18-electron complex **73**.[130]

Scheme 45

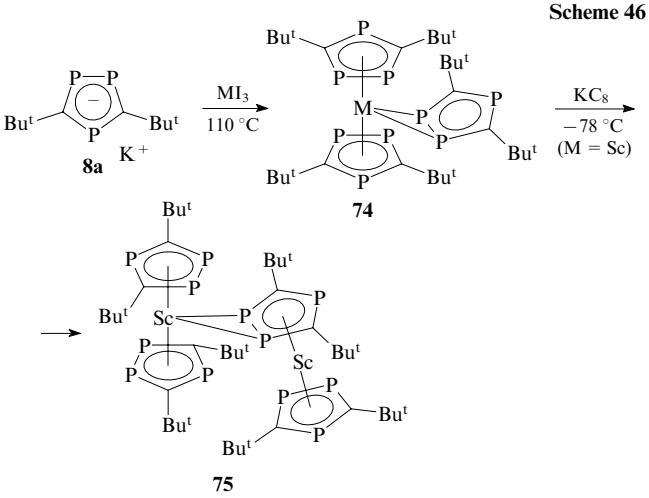


acac is acetylacetonate

h. Phospholide complexes of rare-earth metals

A specific feature of rare-earth metals is the tendency to form complexes with a coordination number exceeding 6. Therefore, in the reaction with phospholide anions, rare-earth metal atoms (Sc,[131] Y,[132] Sm,[133] Tm[134]) are often coordinated to three phospholyl ligands, whatever the oxidation state of the metal, two ligands being coordinated through the ring π-system and the third one, through the LPEs on phosphorus atoms (Scheme 46).

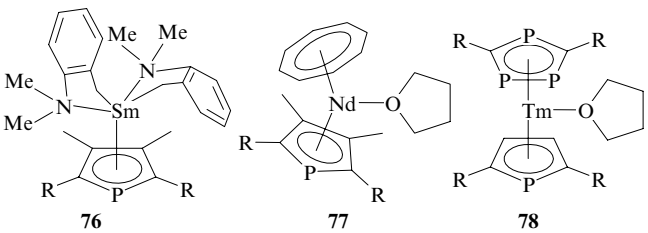
Scheme 46



M = Sc, Y, Tm

When treated with strong reducing agents, complex **74** (M = Sc) is converted into dimer **75**, in which the phospholyl ligand bridges two metal atoms. Using reactants with coordinatively unsaturated metal centres makes it possible to obtain complexes with one (**76**, **77**)[135–138] or two (**78**)[139]

Structures 76–78



R = Bu^t, SiMe3

phospholyl ligands and to prevent the association of complexes.

3. Coordination properties of phosphametallocenes

Among the known phosphametallocenes, the complexing properties of pentamethylpentaphosphaferrocene (**50a**) are best understood because of its synthetic availability and stability. The high aromaticity of the pentaphospholyl ligand, as well as the lack of substituents, enables the synthesis of not only stable triple-decker complexes[140–142] but also more complicated polynuclear structures.[143,144] In particular, unique polynuclear coordination polymers **79**–**83** and oligomer **84** have been synthesized by the reaction of pentamethylpentaphosphaferrocene (**50a**) with copper(I)[2] and silver(I) salts, respectively (Scheme 47).[145,146] Depending on the ratio of reactants, the pentaphospholyl ligand in the resulting coordination polymers is coordinated to two to six metal atoms.[147]

Selection and optimization of synthesis conditions have made it possible to synthesize, for the first time, an inorganic fullerene analogue from compound **50a** and copper(I) halides.[3,148] Studying these reactions suggests that formation of this type of nanoballs is driven by stacking of pentaphospholyl ligands and other aromatic molecules, such as pentaphosphaferrocene **50a**,[149–151] *ortho*-carborane[152] or fullerene C_{60}.[153] However, this hypothesis does not account for the formation of polymetallic supramolecular host–guest compounds encapsulating white phosphorus and yellow arsenic.[154]

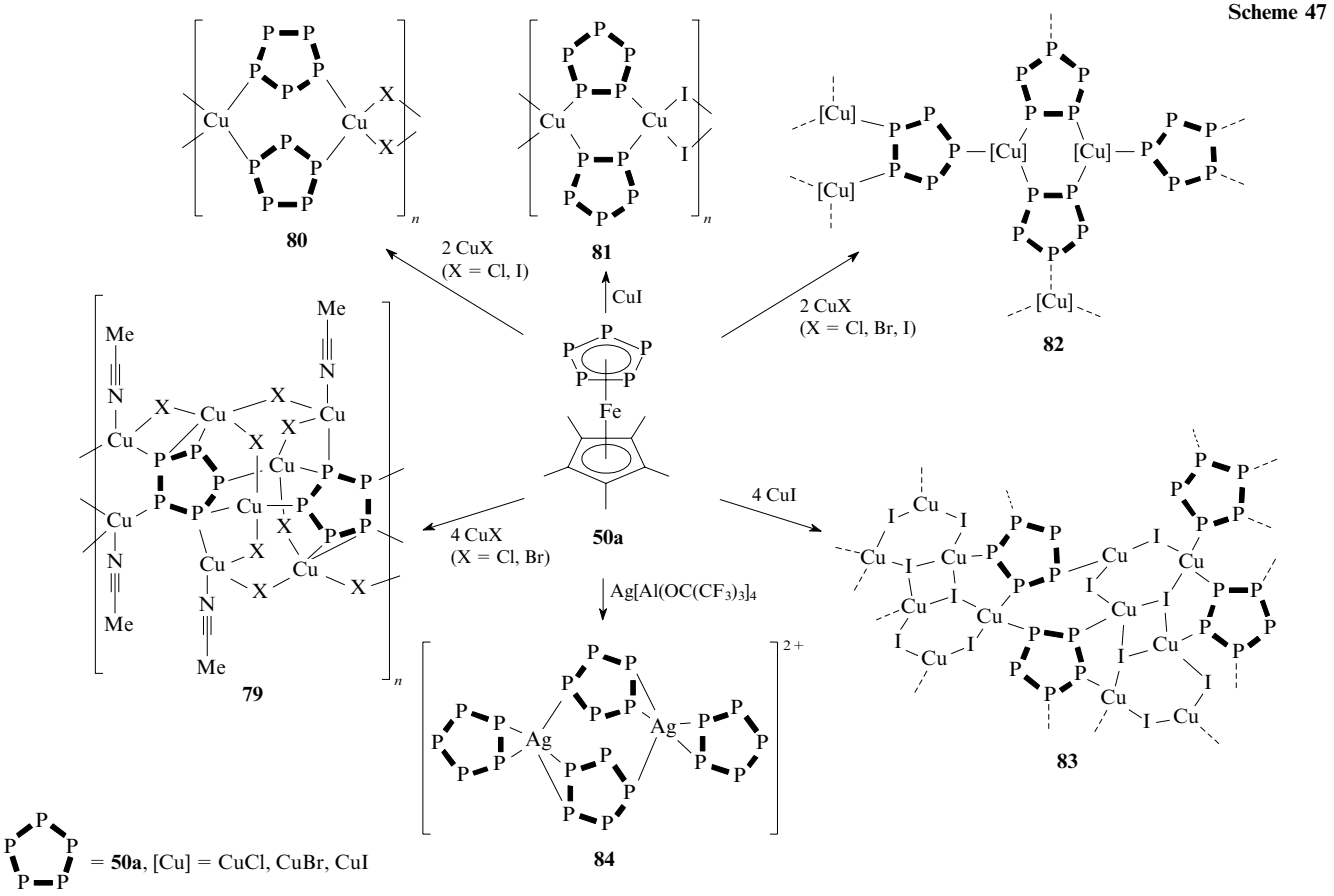
Phosphaferrocenes with a smaller number of phosphorus atoms in the phospholyl ligand have also been successfully used for synthesizing coordination polymers of different dimension. In particular, the reaction of 1,2,3-triphosphaferrocene **56** with copper(I) halides yields a one-dimensional polymer in which only the phosphorus atoms in the 1- and 3-positions of the triphospholyl ligand are involved in coordination.[155] At the same time, when compound **56** reacts with a tungsten carbonyl excess, all phosphorus atoms of the triphospholyl ligand are simultaneously involved in coordination.[156]

The structure of the products of the reaction of 1,3-di(*tert*-butyl)-1,2,4-triphosphaferrocene (**85**) with copper(I) salts appreciably depends on the reaction conditions. In particular, varying the reactant ratio, the substituents in the Cp ligand and the halogen atom in the initial salt makes it possible to obtain different oligomeric (**86**)[157] or polymeric (**87**) complexes (Scheme 48).[158–160]

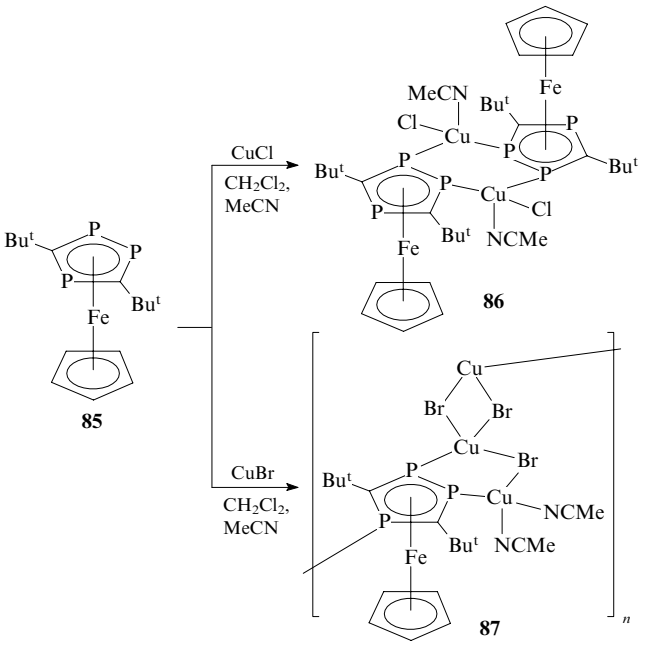
The high degree of electron density delocalization in the phospholyl ligand, as well as the more pronounced s-character of the LPEs on the phosphorus atoms in 1,2,4-triphosphaferrocene **85** as compared with 1,2,3-triphosphaferrocene **56**, leads to the unusual η^2-coordination to the rhodium(I) complex (Scheme 49).[161] It should be noted that, in a solution of complex **88**, there are no dynamic processes associated with migration of the rhodium atom between the neighbouring phosphorus atoms.

The complexing properties of monophosphaferrocenes and 1,1′-diphosphaferrocenes have been best studied. In particular, monophosphaferrocenes **89a**,**b** react with ruthenium hydride $RuH_2(H_2)_2(PCy_3)_2$ to give, depending on the reactant ratio, complexes with the ratio metal : ligand = 1 : 1 (**90**) or 1 : 2 (**91**) (Scheme 50).[162]

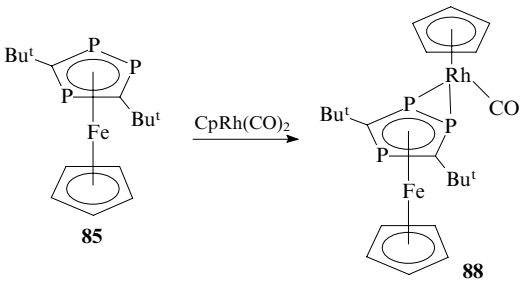
Scheme 47



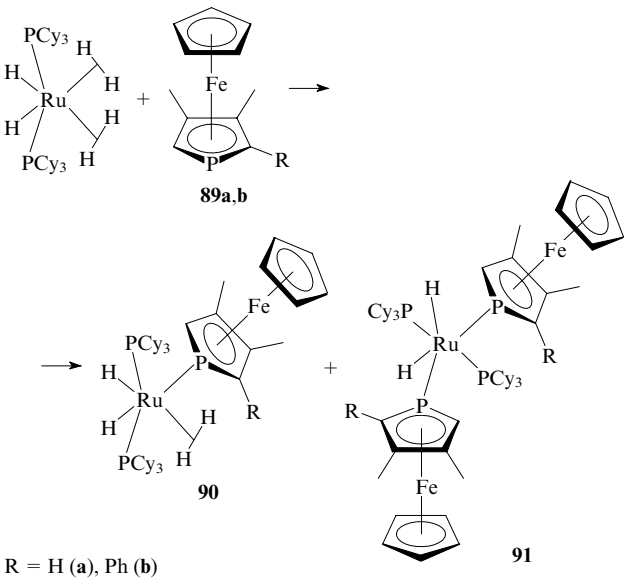
Scheme 48



Scheme 49



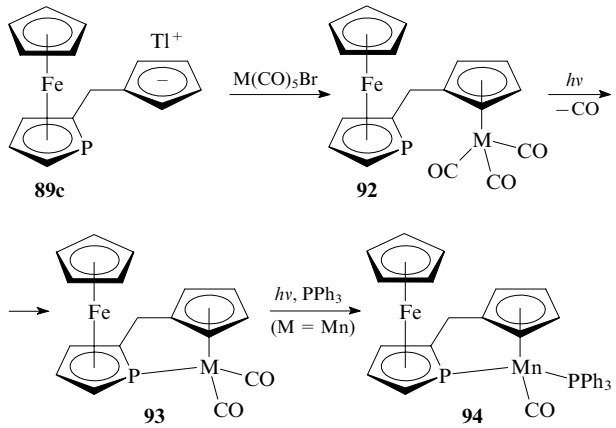
Scheme 50



R = H (**a**), Ph (**b**)

Monophosphaferrocenes containing substituents in the 2-position of the phospholide ring have been used for synthesis of enantiomerically pure complexes. For example, monophosphaferrocene **89c**, containing the cyclopentadienide anion in the substituent in the 2-position of the phospholide ring, readily reacts with $M(CO)_5Br$ (M = Mn, Re) to give half-sandwich complexes **92**, which lose one carbonyl ligand when exposed to UV light to form chelates **93** (Scheme 51).[163]

Scheme 51

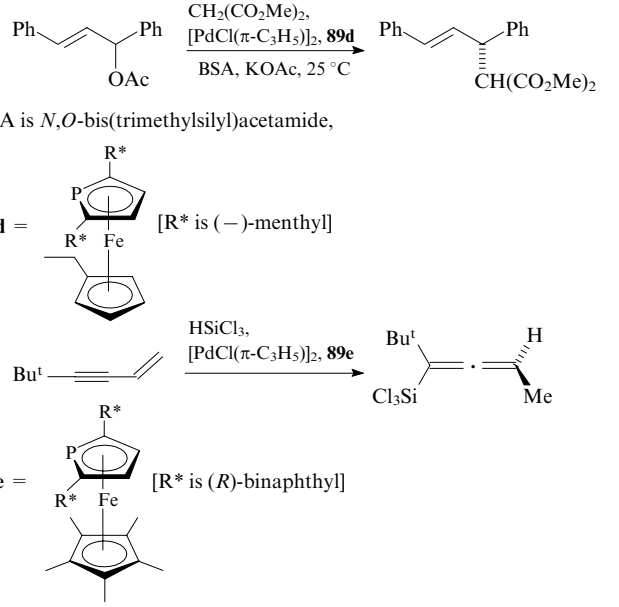


M = Mn, Re

The replacement of the second carbonyl ligand at the manganese atom in complex **93** is stereospecific: the diastereomeric ratio for complex **94** is 11 : 1 (the prevailing isomer is shown).[163] High stereoselectivity is also observed in the reactions of 2-oxophosphaferrocenes and -ruthenocenes.[164]

It should be noted that palladium(II) complexes with enantiomerically pure monophosphaferrocenes[165, 166] **89d**,**e** have shown high activity and selectivity in asymmetric synthesis.[167, 168] In particular, the use of a catalyst based on monophosphaferrocene **89d** in allyl alkylation reactions leads to the formation of the *R* isomer with an enantiomeric excess of 99% (Scheme 52).

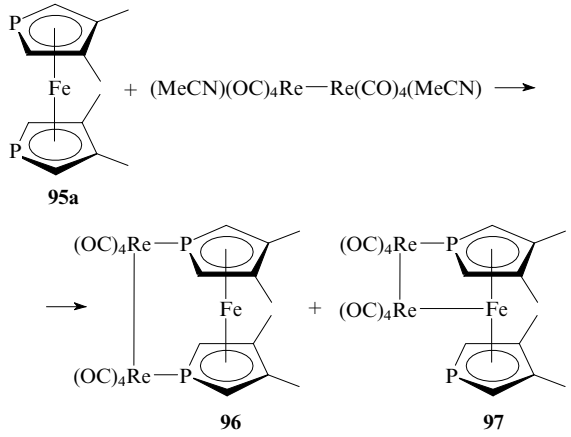
Scheme 52



For allyl silylation, a catalyst based on a palladium complex with monophosphaferrocene **89e** containing binaphthyl substituents in the 2- and 5-positions of the phospholyl ligand has been suggested (see Scheme 52).[23]

Complexation reactions involving 1,1′-diphosphaferrocenes **95** are more complicated because of a considerable increase in the number of possible coordination motifs. In particular, the reaction of 1,1′-diphosphaferrocene **95a** with the binuclear rhenium derivative $Re_2(CO)_8(MeCN)_2$ yields, along with expected complex **96**, unusual complex **97** with the iron – rhenium bond (Scheme 53).[169]

Scheme 53

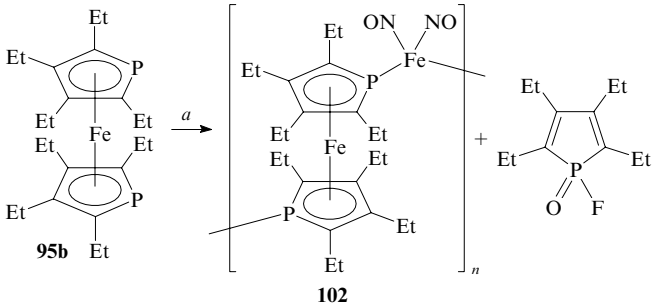


Weak interactions of the central iron atom with the other metal centre has been observed also for complexes **98** and **99**, synthesized by the reaction of 1,1′-diphosphaferrocenes **95** with gallium(I),[170] copper(I), gold(I)[171] and palladium(0) compounds (Scheme 54).[4] It should be noted that 1,1′-diphosphaferrocene acts as a chelating ligand since both phospholide rings are involved in coordination with metals.

At the same time, the reaction of monophosphaferrocene **95c** with $Pd(cod)Cl_2$ leads to dimeric complex **100**, in which common η^1-coordination of the phospholyl ligand to palladium is observed.[172] In the subsequent reaction of complex **100** with $[Pd(dba)_2]$, the Pd^0 atom is inserted between two diphosphaferrocenes to give pentanuclear complex **101**.[173] It should be noted that palladium complexes **99** and **100** show high activity as catalysts of the Suzuki[4] and Miyaura[5] reactions.

In the last years, close attention of researchers has been paid to the redox properties of phosphaferrocenes. In particular, the oxidation of 1,1′-diphosphaferrocene **95b** by nitrosonium tetrafluoroborate leads to a dark green precipitate poorly soluble in organic solvents. X-Ray crystallography has shown that product **102** is a coordination polymer in which phosphaferrocene **95b** molecules are bound by iron atoms (Scheme 55).[174]

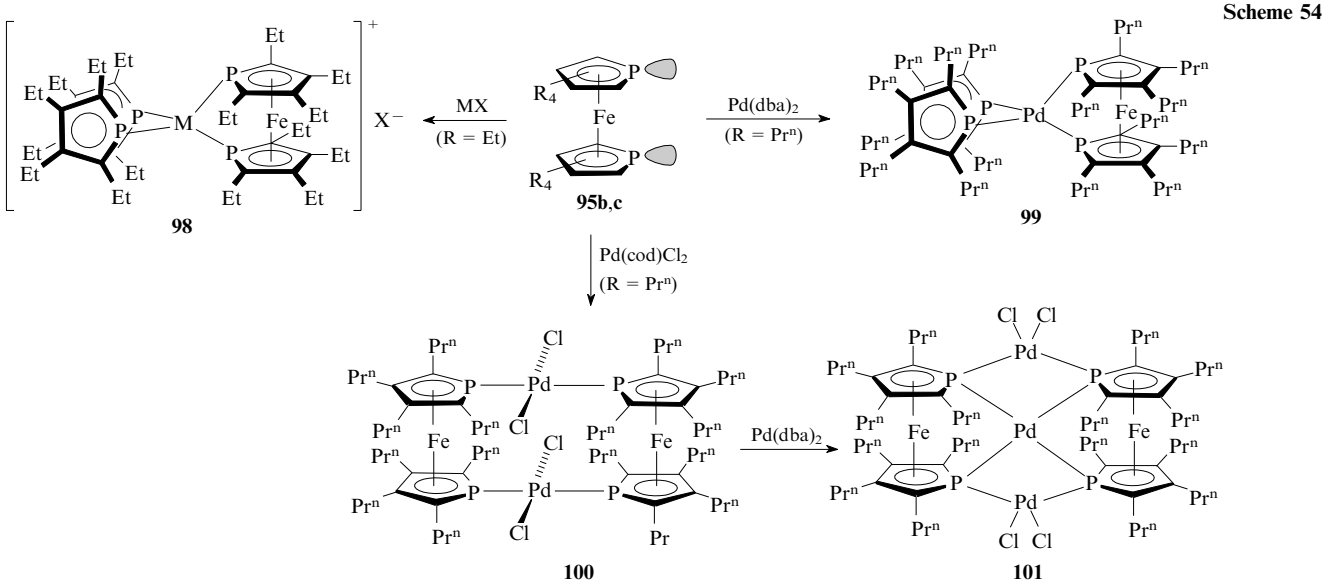
Scheme 55



It is likely that treatment of phosphaferrocene **95b** with nitrosonium tetrafluoroborate destroys the phosphaferrocene molecules, and the forming $Fe(NO)_2$ species are coordinated to the phosphorus atoms to give polymer **102**. Phosphaferrocene **95** also decomposes upon oxidation with molecular iodine.

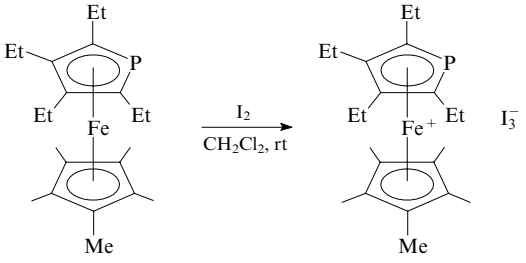
At the same time, the substitution of the pentamethylcyclopentadienyl ligand for one monophospholyl ligand of phosphaferrocenes considerably increases the stability of oxidation products. For example, monophosphaferrocene **89f** is easily oxidized with iodine to form phosphaferrocenium triiodide **103** in 95% yield (Scheme 56).[175] It is worth noting that the distance between the cyclopentadienyl rings and the iron atom in molecule **103** is elongated as compared with initial phosphaferrocene **89f**.

Scheme 54



R = Et (**b**), Pr^n (**c**); MX = $GaCl_3$, $[Cu(MeCN)_4]^+[PF_6]^-$, $AuCl(SMe_2)$; dba is dibenzylideneacetone

Scheme 56



89f **103**

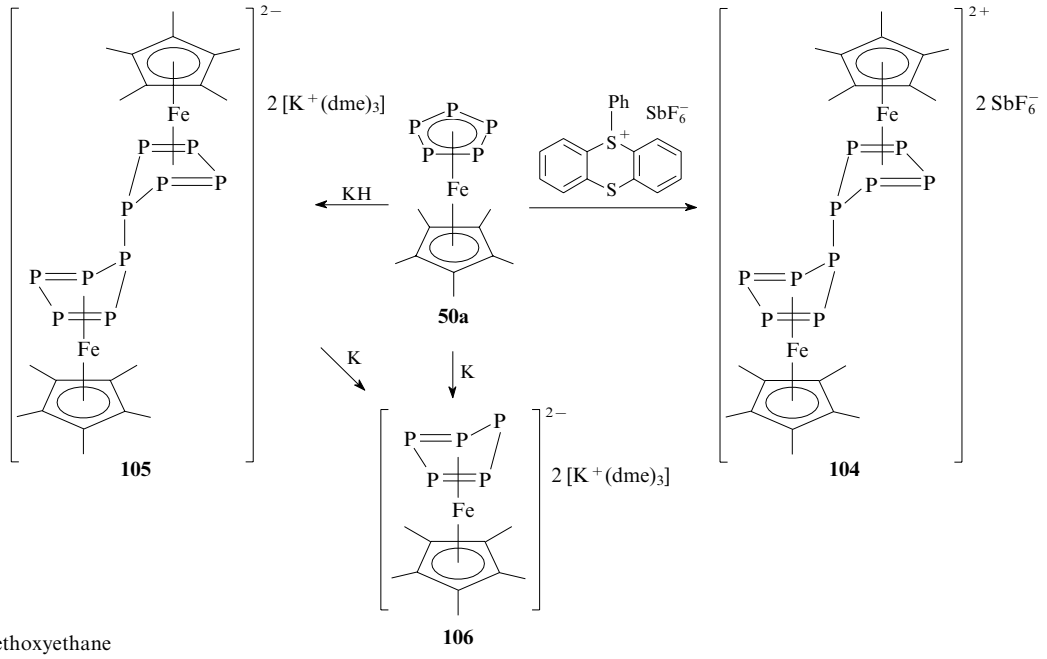
The stabilizing effect of the pentamethylcyclopentadienyl ligand has been spectacularly demonstrated for pentaphosphaferrocene **50a** as well. Cyclic voltammetry has shown that one-electron oxidation or reduction of compound **50a** is possible. However, as distinct from ferrocene, the reduction and oxidation of **50a** is irreversible since the resulting anion or cation of **50a** enters into the chemical reaction involving the pentaphospholyl moieties. EPR spectroscopy has revealed iron(I) compounds; on this basis, the authors have assumed the formation of dimeric compounds with a phosphorus–phosphorus bond.[176] However, the formation of dimers upon one-electron oxidation or reduction of pentamethylpentaphosphaferrocene **50a** has been experimentally proven only recently.[177]

In particular, the oxidation of compound **50a** with thianthrenium hexafluoroantimonate occurs under mild conditions to give dication **104**, containing decaphosphadifulvalene as a ligand (Scheme 57). According to Mössbauer spectroscopy data, the iron atoms in complex **104** are divalent. The density functional theory method has shown that each of the P_5 moieties donates six electrons, so that the rule of 18 electrons is valid for each of the iron atoms.

The reduction of phosphaferrocene **50a** with potassium hydride leads to dianionic complex **105**, also with a fulvalene-like ligand. At the same time, the more profound reduction of compound **50a** or product **105** with potassium metal yields mononuclear dianion **106**, which has not been detected by cyclic voltammetry.

Pentaphosphaferrocene **50a** exhibits similar chemical properties in the reactions with samarium(II) derivatives (Scheme 58).[178, 179] Complexes **107** and **108** are the products of, respectively, one- and two-electron reduction of penta-

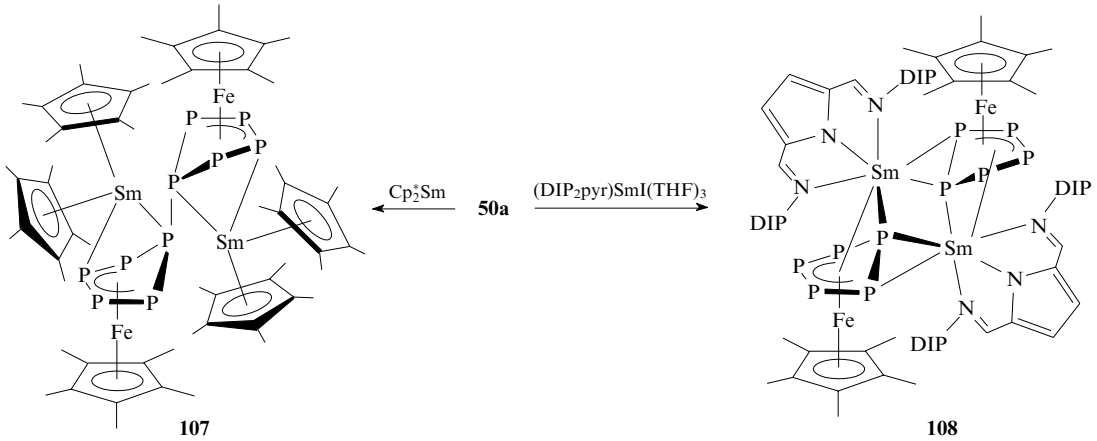
Scheme 57



105 **50a** **104** **106**

dme is dimethoxyethane

Scheme 58



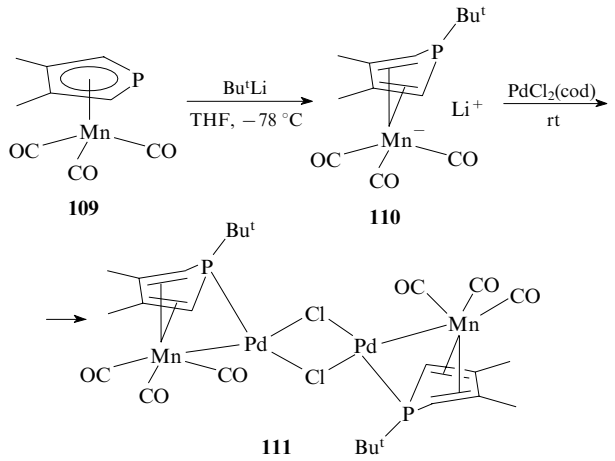
107 **108**

DIP_2pyr is 2,6-bis[N-(2,6-diisopropylphenyl)iminomethyl]pyrrol-1-yl

phosphaferrocene **50a**. The coordination mode of the phospholyl ligand changes from that in pentaphosphaferrocene to ($\mu:\eta^1;\eta^2;\eta^4$) in complex **108**.

For the first time, a similar coordination mode has been observed in binuclear complexes based on phosphacymantrene **109** (Scheme 59). The nucleophilic attack of Bu^{t}Li at the phosphorus atom of the phospholyl moiety leads to complex **110**, containing the η^4-coordinated phospholyl ligand. Treatment of compound **110** with a palladium complex gives tetranuclear complex **111**, in which the phospholyl ligand has $\mu:\eta^1;\eta^4$-coordination.[180]

Scheme 59



The coordination mode of the phospholyl ligand also changes in the reaction of phosphacymanterene with other nucleophilic reagents [KOH – crown ether,[181] $NR_3 - H_2O$ (R = H, Et, Pr^i)[182, 183]], as well as in the reaction of phospharuthenocenes with acyl halides in the presence of aluminium chloride.[184]

* * *

The above data on the chemical behaviour of phospholide anions suggests that this line of research, being at the intersection of different fields of modern chemistry, continues to attract attention of researchers, which is reflected in numerous publications. There are two important aspects that determine the interest of researchers in this field of chemistry. First, study of the chemical behaviour of phospholide anions, as well as their organic derivatives (phospholes) and metal complexes, in comparison with their carbon counterparts makes it possible to better understand the relationship between organic chemistry and phosphorus chemistry, draw some analogies and develop a theoretical basis for the preparation of novel phosphorus compounds. Second, phospholide anions, especially their organometallic derivatives, are of considerable interest for the design of novel supramolecular systems and materials with practically valuable properties. It is precisely the combination of fundamental and practical importance that will determine the development of this field of chemistry in the coming years.

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References

1. R Hoffmann *Angew. Chem., Int. Ed. Engl.* **21** 711 (1982)
2. J Bai, A V Virovets, M Scheer *Angew. Chem., Int. Ed.* **41** 1737 (2002)
3. J Bai, A V Virovets, M Scheer *Science* **300** 781 (2003)
4. X Sava, L Ricard, F Mathey, P Le Floch *Organometallics* **19** 4899 (2000)
5. M Melaimi, F Mathey, P Le Floch *J. Organomet. Chem.* **640** 197 (2001)
6. E J M de Boer, I J Gilmore, F M Korndorffer, A D Horton, A van der Linden, B W Royan, B J Ruisch, L Schoon, R W Shaw *J. Mol. Catal. A* **128** 155 (1998)
7. P Le Floch *Coord. Chem. Rev.* **250** 627 (2006)
8. D Gudat *Top. Curr. Chem.* **232** 175 (2004)
9. R K Bansal, J Heinicke *Chem. Rev.* **101** 3549 (2001)
10. V Caliman *Quimica Nova* **23** 346 (2000)
11. D Carmichael, F Mathey *Top. Curr. Chem.* **220** 27 (2002)
12. F Mathey *J. Organomet. Chem.* **646** 15 (2002)
13. V Caliman, P B Hitchcock, J F Nixon *Phosphorus, Sulfur, Silicon Relat. Elem.* **93 – 94** 375 (1994)
14. F Mathey *Coord. Chem. Rev.* **137** 1 (1994)
15. F Mathey, in *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain* (Ed. F Mathey) (Oxford: Pergamon Press, 2001)
16. K B Dillon, F Mathey, J F Nixon *Phosphorus, the Carbon Copy* (Chichester: Willey, 1998)
17. E H Braye, I Caplier, R Saussez *Tetrahedron* **27** 5523 (1971)
18. T Douglas, K H Theopold *Angew. Chem., Int. Ed. Engl.* **28** 1367 (1989)
19. E Deschamps, F Mathey *Chem. – Eur. J.* **11** 6829 (2005)
20. X Sava, N Mézailles, N Maigrot, F Nief, L Ricard, F Mathey, P Le Floch *Organometallics* **18** 4205 (1999)
21. L Zhang, M Hissler, H-B Bu, P Bäuerle, C Lescop, R Réau *Organometallics* **24** 5369 (2005)
22. M Ogasawara, K Yoshida, T Hayashi *Organometallics* **20** 1014 (2001)
23. M Ogasawara, A Ito, K Yoshida, T Hayashi *Organometallics* **25** 2715 (2006)
24. F Nief, L Ricard *J. Organomet. Chem.* **642** 208 (2002)
25. D Carmichael, J Klankermayer, L Ricard, N Seeboth *Chem. Commun.* 1144 (2004)
26. D Carmichael, X Le Goff, E Muller *New J. Chem.* **34** 1341 (2010)
27. D Carmichael, L Ricard, N Seeboth, J Brown, T Claridge, B Odell *Dalton Trans.* 2173 (2005)
28. N Maigrot, N Avarvari, C Charrier, F Mathey *Angew. Chem., Int. Ed. Engl.* **34** 590 (1995)
29. N Maigrot, M Sierra, C Charrier, F Mathey *Bull. Soc. Chim. Fr.* **131** 397 (1994)
30. R Bartsch, J F Nixon *Polyhedron* **8** 2407 (1989)
31. S Mansell, M Green, R Kilby, M Murray, C Russell *C.R. Chimie* **13** 1073 (2010)
32. F G N Cloke, P B Hitchcock, J F Nixon, D J Wilson *Organometallics* **19** 219 (2000)
33. J Steinbach, P Binger, M Regitz *Synthesis* 2720 (2003)
34. S Clendenning, P Hitchcock, M Lappert, P Merle, J Nixon, L Nyalszi *Chem. – Eur. J.* **13** 7121 (2007)
35. P Binger, T Wettling, R Schneider, F Zurmühlen, U Bergsträsser, J Hoffmann, G Maas, M Regitz *Angew. Chem., Int. Ed. Engl.* **30** 207 (1991)
36. J Lynam, M Copsey, M Green, J Jeffery, J McGrady, C Russell, J Slattery, A Swain *Angew. Chem., Int. Ed.* **42** 2778 (2003)
37. C Fish, M Green, J C Jeffery, R J Kilby, J M Lynam, C A Russell, C Willans *Organometallics* **24** 5789 (2005)
38. A S Ionkin,W J Marshall, B M Fish, A A Marchione, L A Howe, F Davidson, C McEwen *Eur. J. Inorg. Chem.* 2386 (2008)

39. A S Ionkin, W J Marshall, B M Fish, M F Schiffhauer, F Davidson, C N McEwen *Organometallics* **28** 2410 (2009)
40. C Butts, M Green, T Hooper, R Kilby, J McGrady, D Pantazis, C Russell *Chem. Commun*. 856 (2008)
41. M Baudler, D Duster, D Ouzounis *Z. Anorg. Allg. Chem*. **544** 87 (1987)
42. M Baudler, S Akpapoglou, D Ouzounis, F Wasgestian, B Meinigke, H Budzikiewicz, H Münster *Angew. Chem., Int. Ed. Engl*. **27** 280 (1988)
43. V A Milyukov, A V Kataev, O G Sinyashin, E Hey-Hawkins *Russ. Chem. Bull., Int. Ed*. **55** 1297 (2006) [*Izv. Akad. Nauk, Ser. Khim*. 1249 (2006)]
44. V Miluykov, A Kataev, O Sinyashin, P Lönnecke, E Hey-Hawkins *Organometallics* **24** 2233 (2005)
45. V A Milyukov, A V Kataev, O G Sinyashin, E Hey-Hawkins *Russ. Chem. Bull., Int Ed*. **56** 304 (2007) [*Izv. Akad. Nauk, Ser. Khim*. 294 (2007)]
46. I Bezkishko, V Miluykov, A Kataev, I Litvinov, D Krivolapov, O Sinyashin, E Hey-Hawkins *J. Organomet. Chem*. **693** 3318 (2008)
47. I Bezkishko, V Miluykov, O Sinyashin, E Hey-Hawkins *Phosphorus, Sulfur, Silicon Relat. Elem*. **186** 657 (2011)
48. V Miluykov, I Bezkishko, L Shakirova, D Krivolapov, O Sinyashin *Russ. Chem. Bull. Int. Ed*. **61** 1483 (2012) [*Izv. Akad. Nauk, Ser. Khim*. 1467 (2012)]
49. R Turbervill, J M Goicoechea *Chem. Commun*. **48** 6100 (2012)
50. R Turbervill, A R Jupp, P S B McCullough, D Ergöçmen, J M Goicoechea *Organometallics* **32** 2234 (2013)
51. R S P Turbervill, J M Goicoechea *Inorg. Chem*. **52** 5527 (2013)
52. L Nyulaszi *Chem. Rev*. **101** 1229 (2001)
53. L Wang, H Wang, W Dong, Q Ge, L Lin *Struct. Chem*. **18** 25 (2007)
54. A Dransfeld, L Nyulaszi, P Schleyer *Inorg. Chem*. **37** 4413 (1998)
55. V Caliman, P Hitchcock, J Nixon *J. Organomet. Chem*. **536** 273 (1997)
56. V Miluykov, A Kataev, O Sinyashin, P Lönnecke, E Hey-Hawkins *Mendeleev Commun*. 204 (2006)
57. F Mathey *Acc. Chem. Res*. **37** 954 (2004)
58. A A Zagidullin, I A Bezkishko, V A Miluykov, O G Sinyashin *Mendeleev Commun*. **23** 117 (2013)
59. C Thoumazet, M Melaimi, L Ricard, F Mathey, P Le Floch *Organometallics* **22** 1580 (2003)
60. J Hydrio, M Gouygou, F Dallemer, J-C Daran, G G A Balavoine *Tetrahedron: Asymmetry* **13** 1097 (2002)
61. E Mattman, F Mercier, L Ricard, F Mathey *J. Org. Chem*. **67** 5422 (2002)
62. N Maigrot, M Melaimi, L Ricard, P Le Floch *Heteroat. Chem*. **14** 326 (2003)
63. M Melaimi, L Ricard, F Mathey, P Floch *Org. Lett*. **4** 1245 (2002)
64. D H Nguyen, J Bayardon, C Salomon-Bertrand, S Jugé, P Kalck, J-C Daran, M Urrutigoity, M Gouygou *Organometallics* **31** 857 (2012)
65. X Sava, A Marinetti, L Ricard, F Mathey *Eur. J. Inorg. Chem*. 1657 (2002)
66. S Burck, D Gudat, M Nieger *Angew. Chem., Int. Ed*. **43** 4801 (2004)
67. S Burck, M Nieger, D Gudat *Z. Anorg. Allg. Chem*. **636** 1263 (2010)
68. G Belanger-Chabot, P Rioux, L Maron, F-G Fontaine *Chem. Commun*. **46** 6816 (2010)
69. S Burck, K Gotz, M Kaupp, M Nieger, J Weber, J Schmedt, D Gudat *J. Am. Chem. Soc*. **131** 10763 (2009)
70. V Miluykov, I Bezkishko, A Zagidullin, O Sinyashin, E Hey-Hawkins *Russ. Chem. Bull. Int. Ed*. **59** 1232 (2010) [*Izv. Akad. Nauk, Ser. Khim*. 1206 (2010)]
71. V Miluykov, I Bezkishko, A Zagidullin, O Sinyashin, P Lönnecke, E Hey-Hawkins *Eur. J. Org. Chem*. 1269 (2009)
72. A A Zagidullin, V A Miluykov, D B Krivolapov, S V Kharlamov, S K Latypov, O G Sinyashin, E Hey-Hawkins *Eur. J. Org. Chem*. 4910 (2011)
73. F Geoffrey, N Cloke, P Hitchcock, J Nixon, D Wilson, L Nyulászi, T Kvrpvti *J. Organomet. Chem*. **690** 3983 (2005)
74. S Ito, H Miyake, H Sugiyama, M Yoshifuji *Tetrahedron Lett*. **45** 7019 (2004)
75. A Elvers, F Heinmann, B Wrackmeyer, U Zenneck *Chem. – Eur. J*. **5** 3143 (1999)
76. A S Ionkin, W J Marshall, B M Fish, A A Marchione, L A Howe, F Davidson, C N McEwen *Organometallics* **27** 5118 (2007)
77. M Hofmann, T Clark, F Heinemann, U Zenneck *Eur. J. Inorg. Chem*. 2225 (2008)
78. A Avent, F G N Cloke, M Francis, P Hitchcock, J Nixon *Chem. Commun*. 879 (2000)
79. M M Al-Ktaifani, W Bauer, U Bergsträßer, B Breit, M D Francis, F W Heinemann, P B Hitchcock, A Mack, J F Nixon, H Pritzkow, M Regitz, M Zeller, U Zenneck *Chem. – Eur. J*. **8** 2622 (2002)
80. M Hofmann, F W Heinemann, U Zenneck *J. Organomet. Chem*. **643 – 644** 357 (2002)
81. M M Al-Ktaifani, P B Hitchcock, J F Nixon *J. Organomet. Chem*. **665** 101 (2003)
82. F W Heinemann, M Zeller, U Zenneck *Organometallics* **23** 1689 (2004)
83. H Werner, H Otto, T Ngo-Khac, C Burschka *J. Organomet. Chem*. **262** 123 (1984)
84. V A Miluykov, I A Bezkishko, O G Sinyashin, P Lönnecke, E Hey-Hawkins *Mendeleev Commun*. **20** 195 (2010)
85. J Grundy, B Donnadieu, F Mathey *J. Am. Chem. Soc*. **128** 7716 (2006)
86. M D Francis, P B Hitchcock, J F Nixon, H Schnöckel, J Steiner *J. Organomet. Chem*. **646** 191 (2002)
87. C Callaghan, G K B Clentsmith, F G N Cloke, P B Hitchcock, J F Nixon, D M Vickers *Organometallics* **18** 793 (1999)
88. M Brym, M D Francis, G Jin, C Jones, D P Mills, A Stasch *Organometallics* **25** 4799 (2006)
89. G K B Clentsmith, F G N Cloke, M D Francis, J C Green, P B Hitchcock, J F Nixon, J L Suter, D M Vickers *J. Chem. Soc., Dalton Trans*. 1715 (2000)
90. D A Wann, S L Hinchley, H E Robertson, M D Francis, J F Nixon, D W H Rankin *J. Organomet. Chem*. **692** 1161 (2007)
91. E Urngžius, W W Brennessel, C J Cramer, J E Ellis, P R Schleyer *Science* **295** 832 (2002)
92. F G N Cloke, J R Hanks, P B Hitchcock, J F Nixon *Chem. Commun*. 1731 (1999)
93. F X Buzin, F Nief, L Ricard, F Mathey *Organometallics* **21** 259 (2002)
94. C Ganter *J. Chem. Soc., Dalton Trans*. 3541 (2001)
95. T K Hollis, Y J Ahn, F S Tham *Chem. Commun*. 2996 (2002)
96. Y J Ahn, R J Rubio, T K Hollis, F S Tham, B Donnadieu *Organometallics* **25** 1079 (2006)
97. W P Freeman, Y J Ahn, T K Hollis, J A Whitaker, V C Vargas, R J Rubio, K D Alingog, E B Bauer, F S Tham *J. Organomet. Chem*. **693** 2415 (2008)
98. T Clark, A Elvers, F W Heinemann, M Hennemann, M Zeller, U Zenneck *Angew. Chem., Int. Ed*. **39** 2087 (2000)
99. M Al-Ktaifani, J C Green, P B Hitchcock, J F Nixon *J. Chem. Soc., Dalton Trans*. 1726 (2001)
100. F W Heinemann, H Pritzkow, M Zeller, U Zenneck *Organometallics* **20** 2905 (2001)
101. V Miluykov, I Bezkishko, D Krivolapov, O Kataeva, O Sinyashin, E Hey-Hawkins, A Parameswaran, Y Krupskaya, V Kataev, R Klingeler, B Büchner *Organometallics* **29** 1339 (2010)

102. Y Krupskaya, R Zaripov, E Vavilova, V Miluykov, I Bezkishko, D Krivolapov, O Kataeva, O Sinyashin, E Hey-Hawkins, V Voronkova, K Salikhov, V Kataev, B Bmchner *Phys. Rev. B* **84** 092402 (2011)
103. R Zaripov, E Vavilova, V Miluykov, I Bezkishko, O Sinyashin, K Salikhov, V Kataev, B Büchner *Phys. Rev. B* **88** 094418 (2013)
104. J Frunzke, M Lein, G Frenking *Organometallics* **21** 3351 (2002)
105. G Frison, F Mathey, A Sevin *J. Phys. Chem. A* **106** 5653 (2002)
106. Ê D V Bruce, W R Rocha *Organometallics* **23** 5308 (2004)
107. E J Padma Malar *Eur. J. Inorg. Chem.* 2723 (2004)
108. T P Gryaznova, S A Katsyuba, V A Milyukov, O G Sinyashin *J. Organomet. Chem.* **695** 2586 (2010)
109. F Dielmann, R Merkle, S Heinl, M Scheer *Z. Naturforsch., B* **64** 3 (2009)
110. R Loschen, C Loschen, W Frank, C Ganter *Eur. J. Inorg. Chem.* 553 (2007)
111. V A Miluykov, O G Sinyashin, O Scherer, E Hey-Hawkins *Mendeleev Commun.* 1 (2002)
112. V A Miluykov, O G Sinyashin, P Lönnecke, E Hey-Hawkins *Mendeleev Commun.* 212 (2003)
113. M Scheer, S Deng, O J Scherer, M Sierka *Angew. Chem., Int. Ed.* **44** 3755 (2005)
114. O J Scherer, T Hilt, G Wolmershiuser *Angew. Chem., Int. Ed.* **39** 1425 (2000)
115. G Frison, L Ricard, F Mathey *Organometallics* **20** 5513 (2001)
116. A Escobar, F Mathey *Organometallics* **29** 1053 (2010)
117. A Escobar, B Donnadieu, F Mathey *Organometallics* **27** 1887 (2008)
118. E Deschamps, L Ricard, F Mathey *Organometallics* **20** 1499 (2001)
119. M Ogasawara, T Nagano, K Yoshida, T Hayashi *Organometallics* **21** 3062 (2002)
120. M Ogasawara, K Yoshida, T Hayashi *Organometallics* **22** 1783 (2003)
121. D Carmichael, F Mathey, L Ricard, N Seeboth *Chem. Commun.* 2976 (2002)
122. A Elvers, F Heinemann, S Kummer, B Wrackmeyer, M Zeller, U Zenneck *Phosphorus, Sulfur, Silicon Relat. Elem.* **144** 725 (1999)
123. C Burney, D Carmichael, K Forissier, J C Green, F Mathey, L Ricard *Chem. – Eur. J.* **9** 2567 (2003)
124. K Forissier, L Ricard, D Carmichael, F Mathey *Organometallics* **19** 954 (2000)
125. Y Cabon, D Carmichael, K Forissier, F Mathey, L Ricard, N Seeboth *Organometallics* **26** 5468 (2007)
126. E V Mutseneck, D A Loginov, D S Perekalin, Z A Starikova, D G Golovanov, P V Petrovskii, P Zanello, M Corsini, F Laschi, A R Kudinov *Organometallics* **23** 5944 (2004)
127. V Schnitzler, W Frank, C Ganter *J. Organomet. Chem.* **693** 2610 (2008)
128. F W Heinemann, H Pritzkow, M Zeller, U Zenneck *Organometallics* **19** 4283 (2000)
129. F G N Cloke, J C Green, P B Hitchcock, J F Nixon, J L Suter, D J Wilson *Dalton Trans.* 1164 (2009)
130. C Burney, D Carmichael, K Forissier, J C Green, F Mathey, L Ricard *Chem. – Eur. J.* **11** 5381 (2005)
131. G K B Clentsmith, F G N Cloke, J C Green, J Hanks, P B Hitchcock, J F Nixon *Angew. Chem., Int. Ed.* **42** 1038 (2003)
132. G K B Clentsmith, F G N Cloke, M D Francis, J R Hanks, P B Hitchcock, J F Nixon *J. Organomet. Chem.* **693** 2287 (2008)
133. D Turcitu, F Nief, L Ricard *Chem. – Eur. J.* **9** 4916 (2003)
134. F Jaroschik, F Nief, X-F Le Goff, L Ricard *Organometallics* **26** 3552 (2007)
135. M Visseaux, F Nief, L Ricard *J. Organomet. Chem.* **647** 139 (2002)
136. F Jaroschik, T Shima, X Li, K Mori, L Ricard, X-F Le Goff, F Nief, Z Hou *Organometallics* **26** 5654 (2007)
137. E Le Roux, F Nief, F Jaroschik, K W Törnroos, R Anwander *Dalton Trans.* 4866 (2007)
138. E Le Roux, Y Liang, K W Törnroos, F Nief, R Anwander *Organometallics* **31** 6526 (2012)
139. F Nief, B Tayart de Borms, L Ricard, D Carmichael *Eur. J. Inorg. Chem.* 637 (2005)
140. A R Kudinov, D A Loginov, Z A Starikova, P V Petrovskii, M Corsini, P Zanello *Eur. J. Inorg. Chem.* 3018 (2002)
141. D A Loginov, I D Baravi, O I Artyushin, Z A Starikova, P V Petrovskii, A R Kudinov *Russ. Chem. Bull. Int. Ed.* **59** 1312 (2010) [*Izv. Akad. Nauk, Ser. Khim.* 1282 (2010)]
142. D A Loginov, M M Vinogradov, Z A Starikova, P V Petrovskii, J Holub, A R Kudinov *Collect. Czech. Chem. Commun.* **75** 981 (2010)
143. S Welsch, L J Gregoriades, M Sierka, M Zabel, A V Virovets, M Scheer *Angew. Chem., Int. Ed.* **46** 9323 (2007)
144. P Sekar, S Umbarkar, M Scheer, A Voigt, R Kirmse *Eur. J. Inorg. Chem.* 2585 (2000)
145. M Scheer, L J Gregoriades, R Merkle, B P Johnson, F Dielmann *Phosphorus, Sulfur, Silicon Relat. Elem.* **183** 504 (2008)
146. M Scheer, L J Gregoriades, A V Virovets, W Kunz, R Neueder, I Krossing *Angew. Chem., Int. Ed.* **45** 5689 (2006)
147. F Dielmann, A Schindler, S Scheuermayer, J Bai, R Merkle, M Zabel, A V Virovets, E V Peresypkina, G Brunklaus, H Eckert, M Scheer *Chem. – Eur. J.* **18** 1168 (2012)
148. M Scheer, J Bai, B P Johnson, R Merkle, A V Virovets, C E Anson *Eur. J. Inorg. Chem.* 4023 (2005)
149. M Scheer, A Schindler, J Bai, B P Johnson, R Merkle, R Winter, A V Virovets, E V Peresypkina, V A Blatov, M Sierka, H Eckert *Chem. – Eur. J.* **16** 2092 (2010)
150. A Schindler, C Heindl, G Balázs, C Gröger, A V Virovets, E V Peresypkina, M Scheer *Chem. – Eur. J.* **18** 829 (2012)
151. S Welsch, C Gröger, M Sierka, M Scheer *Angew. Chem., Int. Ed.* **50** 1435 (2011)
152. M Scheer, A Schindler, C Gröger, A V Virovets, E V Peresypkina *Angew. Chem., Int. Ed.* **48** 5046 (2009)
153. M Scheer, A Schindler, R Merkle, B P Johnson, M Linseis, R Winter, C E Anson, A V Virovets *J. Am. Chem. Soc.* **129** 13386 (2007)
154. C Schwarzmaier, A Schindler, C Heindl, S Scheuermayer, E V Peresypkina, A V Virovets, M Neumeier, R Gschwind, M Scheer *Angew. Chem., Int. Ed.* **52** 10896 (2013)
155. S Deng, C Schwarzmaier, C Eichhorn, O Scherer, G Wolmershäuser, M Zabel, M Scheer *Chem. Commun.* 4064 (2008)
156. S Deng, C Schwarzmaier, M Zabel, J F Nixon, A Y Timoshkin, M Scheer *Organometallics* **28** 1075 (2009)
157. S Deng, C Schwarzmaier, U Vogel, M Zabel, J F Nixon, M Scheer *Eur. J. Inorg. Chem.* 4870 (2008)
158. A Schindler, M Zabel, J F Nixon, M Scheer *Z. Naturforsch., B* **64** 1429 (2009)
159. A Schindler, G Balázs, M Zabel, C Gröger, R Kalbitzer, M Scheer *C.R. Chimie* **13** 1241 (2010)
160. S Deng, C Schwarzmaier, M Zabel, J F Nixon, M Bodensteiner, E V Peresypkina, G Balázs, M Scheer *Eur. J. Inorg. Chem.* 2991 (2011)
161. C S J Callaghan, P B Hitchcock, J F Nixon *J. Organomet. Chem.* **584** 87 (1999)
162. A J Toner, B Donnadieu, S Sabo-Etienne, B Chaudret, X Sava, F Mathey, P Le Floch *Inorg. Chem.* **40** 3034 (2001)
163. J Bitta, S Fassbender, G Reiss, W Frank, C Ganter *Organometallics* **24** 5176 (2005)
164. D Carmichael, X-F Le Goff, E Muller, L Ricard, M Stankevič *Dalton Trans.* **41** 5155 (2012)

165. D Carmichael, G Goldet, J Klankermayer, L Ricard, N Seeboth, M Stankevič *Chem. – Eur. J.* **13** 5492 (2007)
166. D Carmichael, J Klankermayer, E Muller, K M Pietrusiewicz, L Ricard, N Seeboth, S Sowa, M Stankevič *Organometallics* **30** 1804 (2011)
167. M Ogasawara, K Yoshida, T Hayashi *Organometallics* **20** 3913 (2001)
168. B Deschamps, F Mathey *Heteroat. Chem.* **16** 458 (2005)
169. A Kłys, A Rybarczyk-Pirek, J Zakrzewski *J. Organomet. Chem.* **693** 1166 (2008)
170. X Sava, M Melaimi, N Mézailles, L Ricard, F Mathey, P Le Floch *New J. Chem.* **26** 1378 (2002)
171. X Sava, M Melaimi, L Ricard, F Mathey, P Le Floch *New J. Chem.* **27** 1233 (2003)
172. X Sava, L Ricard, F Mathey, P Le Floch *Chem. – Eur. J.* **7** 3159 (2001)
173. M Melaimi, L Ricard, F Mathey, P Le Floch *J. Organomet. Chem.* **684** 189 (2003)
174. X Sava, L Ricard, F Mathey, P Le Floch *J. Organomet. Chem.* **671** 120 (2003)
175. X Sava, L Ricard, F Mathey, P Le Floch *Inorg. Chim. Acta* **350** 182 (2003)
176. R F Winter, W E Geiger *Organometallics* **18** 1827 (1999)
177. M V Butovskiy, G Balázs, M Bodensteiner, E V Peresypkina, A V Virovets, J Sutter, M Scheer *Angew. Chem., Int. Ed.* **52** 2972 (2013)
178. T Li, M T Gamer, M Scheer, S N Konchenko, P W Roesky *Chem. Commun.* **49** 2183 (2013)
179. T Li, J Wiecko, N A Pushkarevsky, M T Gamer, R Köppe, S N Konchenko, M Scheer, P W Roesky *Angew. Chem., Int. Ed.* **50** 9491 (2011)
180. B Deschamps, L Ricard, F Mathey *J. Organomet. Chem.* **689** 4647 (2004)
181. V V Bashilov, A G Ginzburg, A F Smol'yakov, F M Dolguschin, P V Petrovskii, V I Sokolov *J. Organomet. Chem.* **694** 4121 (2009)
182. A G Ginzburg, V V Bashilov, F M Dolgushin, A F Smol'yakov, P V Petrovskii, V I Sokolov *Inorg. Chim. Acta* **370** 292 (2011)
183. A G Ginzburg *Russ. Chem. Rev.* **78** 195 (2009)
184. M Ogasawara, T Sakamoto, A Ito, Y Ge, K Nakajima, T Takahashi, T Hayashi *Organometallics* **26** 6698 (2007)