Translated from *Uspekhi Khimii*, 52 1648-1675 (1983) U.D.C. 547.257.1/258.83

Advances in the Chemistry of σ-Derivatives of Group IVB–VIB Transition Metals

G.A.Razuvaev and L.I.Vyshinskaya

A systematic account is given of the literature data on the methods of synthesis and reactivities of transition metal σ-derivatives R_nM and R_nMX_{m-n} (X = halogen, OR′, acac, or NR'_2; R′ = Me, Et, or Ph; n = valence of the metal) for transition metals in the Ti, V, and Cr subgroups. The influence of the nature of the central atom and of the character of the σ-substituents on the mode of thermal decomposition is discussed. The mechanisms of reactions involving insertion in the transition metal-carbon σ-bond are considered.
The bibliography includes 124 references.

CONTENTS

I. Introduction 944
II. The synthesis of σ-derivatives of transition metals 944
III. Thermal decomposition of the σ-derivatives 951
IV. Reactions involving insertion in the transition metal-carbon σ-bond 954

I. INTRODUCTION

The chemistry of organometallic compounds (OMC) involving transition metals is at present one of the most rapidly and successfully developing branches of coordination chemistry.

The beginning of the development of the chemistry of σ-derivatives of transition metals was associated with attempts to obtain compounds of the type R_nM (R = Me, Et, or Ph; M = metal; n = valence of the metal), which were known for non-transition elements. The failure of these attempts led Krause and Grosse to postulate in 1937, in their detailed monograph on OMC chemistry, that transition metals with *d* orbitals cannot form a σ-bond with carbon.

However, studies carried out in the 1950's–1960's showed that R_nM (R = Me, Et, or Ph) derivatives of transition metals exist in solutions at low temperatures, decomposing when the temperature is increased. The results led to the erroneous hypothesis that the transition metal–carbon σ-bond is weak and that σ-derivatives of the type R_nM cannot be isolated. At this time attention was therefore concentrated on the study of the thermally stable complexes $R_nM.xL$ containing "stabilising" ligands such as CO, PR_3, or π-C_5H_5(Cp). The existing theory of the stability of the transition metal–carbon σ-bond postulated that the role of these ligands consists in increasing the energy of the σ-bond. However, subsequent numerous experimental data and their theoretical analysis demonstrated that the transition metal–carbon σ-bond is not weak. In his report at the Vth International Congress on Organometallic Chemistry, Wilkinson justified the view generally accepted at the present time; the thermal instability of the R_nM σ-derivatives is due to their kinetic instability associated with the low activation energy for the decomposition reaction. Since one of the main pathways leading to the decomposition is elimination of the alkene as a result of the transfer of a β-hydrogen atom to the metal atom, the compounds R_nM with σ-substituents which do not contain β-hydrogen atoms should be kinetically stable. Such substituents include the benzyl, neopentyl, trimethylsilylmethyl, mesityl, methyladamantyl, and other groups. The introduction of the electronegative perfluoroalkyl or perfluorophenyl σ-substituents into the molecule increases the activation energy for the decomposition reaction. In addition, it has been established that the successful isolation of the compounds R_nM depends on the correct choice of the method and conditions of the synthesis[1–4].

On the basis of the principles of kinetic stability, major advances have been achieved during the last decade on the isolation of individual σ-derivatives of transition metals of the type R_nM or R_nMX_{m-n} [X = halogen (Hal), OR′, acac, or NR'_2; R′ = alkyl or aryl]. They are as a rule extremely sensitive to oxygen and moisture but, in the absence of the latter, can exist for a long time at room temperature in the solid state or in solution without decomposition.

The reactivity of the transition metal–carbon σ-bond is being vigorously investigated. Attention has been concentrated on insertion reactions which take place in many catalytic processes. Instead of the compounds R_nM, many investigators have frequently used in the study of these reactions cyclopentadienyl derivatives of the type $Cp_2M(\sigma\text{-}R)_z$ (R = Me, Ph, CH_2Ph, or C_6H_5; z = 1 or 2) instead of the compounds R_nM. They are convenient objects of study, since the Cp_2M group is not involved in the reactions and the insertion products are fairly easy to identify.

The latest advances in the synthesis, isolation, and investigation of the chemical properties of individual σ-derivatives of Group IVB–VIB transition metals of the type R_nM or R_nMX_{m-n} (R = CH_2Ph, CH_2SiMe_3, CH_2CMe_3, Mes, adme, or C_6F_5; X = Hal, OR′, acac, NR'_2; R′ = alkyl or aryl; n = the valence of the metal; $m > n$)† will be examined in this review. The results of studies on the σ-derivatives of manganese, iron, cobalt and nickel as well as $Cp_2M(\sigma\text{-}R)_2$ will be resorted to in some cases in the discussions of the reactivity of the transition metal–carbon σ-bond.

II. THE SYNTHESIS OF σ-DERIVATIVES OF TRANSITION METALS

The main method of synthesis of the σ-derivatives involves the reaction of transition metal salts with organometallic compounds of lithium, magnesium, and zinc and, more rarely, mercury and aluminium. All these syntheses are usually carried out at low temperatures and with careful elimination of oxygen and moisture. The choice of the solvent has an appreciable influence on the yield of the product. The

† Mes = mesityl, adme = adamantylmethyl, and acac = acetylacetonate.

Table 1. Benzyl derivatives R_nM ($R = CH_2Ph$).

R_nM	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	R_nE	solvent	t, °C		m.p., °C	colour	
R_4Ti	$TiCl_4$	RMgCl	Et_2O	−20	40	71	dark-red	[5]
R_4Zr	$ZrCl_4$	RMgCl	Et_2O	−20	30	134	yellow	[5]
R_4Hf	$HfCl_4$	RMgCl	Et_2O	−90	60	114	pale-yellow	[6]
R_4V	VCl_4	R_2Mg	Et_2O	−70	25	80[a]	black-green	[9, 10]
R_5Ta	R_3TaCl_2	R_2Mg	toluene	−70	93	—[b]	red	[12]
R_4Cr[c]	$CrCl_3 \cdot 3THF$	RLi	THF + benzene	−20	5	—[e]	red-brown	[13]
R_4Mo	$MoCl_4 \cdot 2Et_2O$	R_2Mg	Et_2O	−40	75[d]	75[d]	black-brown	[15]
R_4W	$WCl_4 \cdot 3THF$	R_2Mg	Et_2O	−20	40	90[d]	red-brown	[14]
R_3Ti[c]	R_3Ti	EtLi	xylene	0	93	—	yellow	[18]
R_3V[c]	$VCl_3 \cdot 3THF$	RLi	THF	−70	88	—	blue	[21]
$R_2Ti \cdot 3Et_2O$	Cp_2TiR_2	RLi	Et_2O	+20	40	200[d]	black	[22]

Remarks: [a] melts with decomposition; [b] m.p. not determined; [c] obtained in solution; [d] decomposes without melting; [e] yield not indicated.

alkylating agents cannot always be interchanged. The most reactive alkylating agents are organolithium compounds. With their aid and at fairly low temperatures, it is possible to obtain fully substituted derivatives R_nM. It is noteworthy that, when organolithium compounds are used, it is necessary to maintain rigorously the stoichiometry of the reactions, since an excess of the organolithium compound entails the formation of ate-complexes, which reduces the yield and hinders the isolation of R_nM in a pure form.

The magnesium derivatives RMgHal and R_nMg are most widely used as alkylating agents as a result of their ready availability. However, when RMgHal is employed, the transition metal is sometimes reduced owing to the presence in the reaction mixture of the partly soluble $MgCl_2$, which forms relatively unstable complexes with R_nM. To prevent this process, dioxane, which binds magnesium chloride in the insoluble complex $MgCl_2.diox$, is added to the reaction mixture. Virtually complete separation of $MgCl_2$ from R_nM, which remains preferentially in solution, is then achieved. Organozinc compounds behave as mild alkylating agents. They do not reduce the transition metal, but, even in the presence of an excess of R_2Zn, the complete alkylation of MX_n is not observed. They are therefore used successfully for the synthesis of alkyl(aryl)metal halides R_nMHal_{m-n} ($n = 1, 2, 3$; $m = 4, 5$).

The metal chlorides and their complexes with Et_2O or tetrahydrofuran (THF) are usually employed as the transition metal compounds. In some cases it is desirable to use metal alkoxides, which are more soluble in organic solvents than the corresponding halides.

Thus the decisive factors for the isolation of individual R_nM are the character of the initial transition metal compound and the alkylating agent, the reaction stoichiometry, the absence of Lewis acid impurities from the reaction mixture, and the nature of the solvent. In the present review the above factors were chosen as the basis for the discussion of various methods of synthesis of the σ-derivatives. In each Section the compounds are grouped in terms of types of σ-substituents and in each Subsection compounds of the highest valences of Group IV–VII metals are considered initially and then compounds of the lowest valences of the metals in the same sequence within the Groups.

1. Synthesis of R_nM

Benzyl Derivatives (Table 1)

The tetrabenzyl derivatives of metals of the titanium subgroup have been synthesised by the classical procedure—the double decomposition reaction of the metal chloride with a Grignard reagent in ether at a low temperature[5,6].

In contrast to this, the double decomposition reaction of VCl_4 with $PhCH_2MgCl$ is accompanied by a decrease of the valence of vanadium regardless of the initial reactant ratio, the nature of the solvent, and temperature[7]. The optimum method of synthesis of $(PhCH_2)_4V$ proved to be the reaction of VCl_4 with $(PhCH_2)_2Mg$ in Et_2O at −70 °C.[8–10] The benzyl derivatives of niobium have not so far been obtained. Benzylation of $NbCl_n$ ($n = 5, 4$) not only with a Grignard reagent but also with $(PhCH_2)_2M$ (M = Mg, Zn, or Hg) was accompanied by the formation of complexes of low-valence niobium[11]. Similarly, in the benzylation of $TaCl_5$ by $(PhCH_2)_2Mg$, tantalum(V) was reduced[12]. However, by selecting the appropriate conditions of synthesis, it was possible to obtain $(PhCH_2)_5Ta$. $TaCl_5$ is initially treated with $(PhCH_2)_2Zn$, which does not reduce the transition metal. The reaction results in the isolation of the mixed derivative $(PhCH_2)_3TaCl_2$. The subsequent substitution of the residual chlorine atoms by benzyl groups takes place under the influence of $(PhCH_2)_2Mg$ in toluene. The employment of toluene and the addition of dioxane enabled the authors to eliminate $MgCl_2$ completely from the reaction zone and to obtain $(PhCH_2)_5Ta$ in an almost quantitative yield[12].

The compound $(PhCH_2)_4Cr$ has been obtained only in solution and has been identified by its EPR spectrum[13]. The influence of the conditions of synthesis on the formation of the benzyl derivatives of molybdenum and tungsten has been studied in detail. It has been established that the tetrabenzyl derivatives of molybdenum and tungsten can be isolated as a result of the interaction of $MoCl_4.2Et_2O$ and $WCl_4.2THF$, which are readily soluble in ether, with $(PhCH_2)_2.Mg$.[14,15]

Organic σ-compounds of tervalent metals are known only for titanium, vanadium, and chromium. The probable explanation is that the initial low-valence derivatives are difficult to obtain for the remaining Group IV–IVB metals.

Table 2. Neopentyl and trimethylsilylmethyl derivatives R_nM and R'_nM ($R = CH_2CMe_3$; $R' = CH_2SiMe_3$).

R_nM, R'_nM	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	RE, R'E	solvent	t, °C		colour	m.p., °C	
R_4Ti	$TiCl_4$	RLi	hexane	—70	26	yellow	105[a]	[24, 25]
R_4Zr	$ZrCl_4$	RLi	hexane + Et_2O	0	68	colourless	108[a]	[24, 25]
R_4Hf	$HfCl_4$	RLi	hexane + Et_2O	0	59	colourless	115	[24, 25]
R_4Cr	$CrCl_3 \cdot 3THF$	RMgCl	Et_2O	+20	30	chestnut	110	[13]
$R_4'Ti$	$TiCl_4$	R'MgCl	Et_2O	—20	65	yellow	+1	[26]
$R_4'Zr$	$ZrCl_4$	R'Li	Et_2O	0	89	colourless	10	[26]
$R_4'Hf$	$HfCl_4$	R'Li	hexane + Et_2O	0	96	colourless	10	[26]
$R_4'V$	VCl_4	R'Li	hexane	—60	10	green	42	[27]
$R_4'Cr$	$CrCl_3 \cdot 3THF$	R'MgCl	Et_2O	20	30	purple	40	[27]
R'_3Ti[b]	$R_4'Ti$	R'Li	toluene	0	50	yellow	—	[18]
$R'_3V.THF$	$VCl_3 \cdot 3THF$	R'MgCl	THF	—60	60	violet	75	[21]
$R_2'Cr$	$CrCl_3$	R'Li	hexane	20	97	dark violet	—[c]	[33]

Remarks: [a] melts with decomposition; [b] obtained in solution from R'_4Ti and EtLi; [c] m.p. not determined.

The possibility of synthesising $(PhCH_2)_3Ti$ by several procedures has been investigated. The double decomposition reaction of $TiCl_3.3THF$ or $Ti(acac)_3$ with an organomagnesium compound in Et_2O at −30 °C results in the formation of $(PhCH_2)_3Ti$. The attempts to isolate this compound lead to its decomposition at 0 °C.[16,17] Success was achieved by another method of synthesis involving the decomposition of ate-complexes:

$$(PhCH_2)_4Ti + EtLi \xrightarrow[0°C]{\text{xylene}} [(PhCH_2)_4TiEt]^-Li^+ \rightarrow$$
$$\rightarrow [(PhCH_2)_3TiEt] + PhCH_2Li$$
$$\downarrow \qquad CO_2\downarrow -78°C$$
$$(PhCH_2)_3Ti + [Et^-]\ PhCH_2CO_2Li\ .$$

However, it has not so far been possible to isolate $(PhCH_2)_3Ti$ in a pure form; $(PhCH_2)_3Ti$ has only been obtained in the form of solutions in aromatic hydrocarbons[18,19].

The benzylation of $VCl_3.3THF$ or $V(acac)_3$ by $PhCH_2MgCl$, $(PhCH_2)_2Mg$, and $(PhCH_2)_3Al$ in Et_2O does not go to completion[17,20]. The reaction of $VCl_3.3THF$ with three moles of $PhCH_2Li$ in THF results in a complete exchange of chlorine atoms for benzyl groups. However, $(PhCH_2)_3V$ could not be isolated in a pure form: at 0 °C the compound decomposes rapidly in solution[21].

The attempts to synthesise $(PhCH_2)_3Cr$ have so far been unsuccessful[17].

Among the benzyl derivatives of bivalent metals, only $(PhCH_2)_2Ti.3Et_2O$ has so far been isolated; it is obtained on decomposition of the ate-complex formed from $Cp_2Ti(CH_2Ph)_2$ and $PhCH_2Li$.[22] The complex $(PhCH_2)_2Ti.3diox$ has been obtained by the oxidative-reduction symmetrisation of benzyl derivatives of titanium(III).[23]

The Neopentyl and Trimethylsilylmethyl Derivatives (Table 2)

These substituents belong to the single type CH_2EMe_3 (E = C, Si, Ge, or Sn) and are more bulky than the benzyl derivatives.

The neopentyl derivatives of the titanium subgroup are obtained by the double decomposition reaction of the metal halides MCl_4 with Me_3CCH_2Li.[24,25] The trimethylsilylmethyl derivatives of the titanium subgroup metals are formed as a result of the reaction of MCl_4 with both a Grignard reagent and an organolithium compound. It has been established that the best alkylating agent for $ZrCl_4$ and $HfCl_4$ is Me_3SiCH_2Li. A high yield of $(Me_3SiCH_2)_4M$ (M = Ti, Zr, or Hf) is achieved in the presence of a 5% excess of MCl_4. When the initial reactant ratio is exactly 1 : 4, the complexes $(Me_3SiCH_2)_4M.(Me_3SiCH_2)_2Mg$, which are difficult to separate, arise in the reaction mixture, while in the presence of an excess of MCl_4 greater than 5% the stable compounds $(Me_3SiCH_2)_3MCl$ are produced.[26]

Among the neopentyl and trimethysilylmethyl derivatives of the Group VB metals, only $(Me_3SiCH_2)_4V$ has been isolated[27]. It has been established that the preparation of niobium and tantalum derivatives is hindered by steric factors. When attempts were made to synthesise $(Me_3ECH_2)_5M$, the alkylidene or alkylidyne complexes of these metals were isolated[25,28,29]. It was possible to synthesise the compound $Me_3Ta(CH_2SiMe_3)_2$, since the small methyl substituents are distributed in its molecule around the Ta atom, together with the Me_3SiCH_2 groups[30].

Virtually the same features have been observed for the metals of the chromium subgroup as for the Group VB metals. The interaction of the ether-soluble $CrCl_3.3THF$ with four equivalents of Me_3ECH_2MgCl (E = C or Si) under identical conditions yields the tetrasubstituted derivatives $(Me_3ECH_2)_4.Cr$ (E = C or Si) with identical yields[13,27]. The reactions of molybdenum and tungsten halides ($MoCl_5$ and WCl_5) with Me_3SiCH_2MgCl in Et_2O at 20 °C result in the formation of the dimeric bridged complexes $(Me_3SiCH_2)_6M_2$.[27] An analogous complex with neopentyl ligands has been obtained from $MoCl_5$ and Me_3CCH_2Li in Et_2O at 20 °C;[25] after the exchange of all the chlorine atoms in WCl_6 for the neopentyl groups, the carbyne complex $(Me_3CCH_2)_3W(\equiv C-CMe_3)$ is obtained from WCl_6 with the aid of Me_3CCH_2Li.[31]

The trimethylsilylmethyl derivatives of tervalent titanium and vanadium have been synthesised. The compound $(Me_3SiCH_2)_3Ti$ has been obtained in solution in toluene on decomposition of the ate-complex $[(Me_3SiCH_2)_4TiEt]^-Li^+$.[18]

After the alkylation of $VCl_3.3THF$ with Me_3SiCH_2MgCl, the complex $(Me_3SiCH_2)_3V.THF$, which is stable at room temperature, was isolated in a pure state[21]. It has been established that the successful alkylation of $VCl_3.3THF$ depends on the nature of the solvent and temperature.

A considerable stabilisation of the tervalent states is attained when the substituents $(Me_3Si)_2CH$ are used. The reaction of $[(Me_3Si)_2CH]Li$ with a suspension of MCl_3 in Et_2O at −60 °C afforded low yields of the derivatives $[(Me_3Si)_2CH]_3M$ (M = Ti, V, or Cr).[32] An interesting fact has been observed in relation to vanadium—the coordination number of the metal depends on the bulk of the substituent: tricoordinate compounds are obtained with the bulky substituent $(Me_3Si)_2CH$, while tetracoordinate derivatives are isolated with the less bulky substituent Me_3SiCH_2.

Among the bivalent Group IV–IVB metal derivatives, only $(Me_3SiCH_2)_2Cr$ has been described hitherto. On the other hand a quadrivalent chromium derivative R_4Cr is obtained

Table 3. Mesityl, 1-methyladamantyl, and pentafluorophenyl derivatives (R = Mes; R′ = 1-adme; R″ = C_6F_5).

R_nM, R'_nM, R''_nM	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	reagent	solvent	t, °C		colour	decomp. temp. °C	
R_4Ti	$[R_4Ti]Li$	O_2	—	20	—[a]	chrome-yellow	159	[34]
R_4V	$[R_4V]Li$	O_2	Et_2O + THF	20	90	dark-red	152	[35]
R_4Cr	$[R_4Cr]Li$	O_2	Et_2O	20	56	dark-brown	110	[36]
R_4Mo	$[R_4Mo]Li$	O_2	Et_2O	20	90	black-green	276	[37]
$R_3V.THF$	$VCl_3 \cdot 3THF$	RMgBr	THF	—30	45	blue	125	[39]
$R_3Cr.3THF$	$CrCl_3$	RMgBr	THF	—20	a	dark blue	80	[40]
$R_2Cr.3THF$	$CrCl_2$	RMgBr	THF	0	25	violet	50	[41]
$R_4'Ti$	$Ti(OPr\text{-}iso)_4$	R′Li	PE	—20	60	yellow	145	[43]
$R_4'Zr$	$ZrCl_4$	R′MgBr	Et_2O	—50	39	cream	130	[43]
$R_4'V$	$V(OPr\text{-}iso)_4$	R′Li	PE	—60	54	blue-green	80	[43]
$R_4'Cr$	$Cr(OBu\text{-}t)_4$	R′Li	PE	—60	45	chestnut	164	[43]
$R_4''Ti \cdot Et_2O$	$TiCl_4$	R″MgBr	Et_2O + hexane	—70	30	orange	119	[44]
$R_4''Zr \cdot Et_2O$	$ZrCl_4$	R″Li	Et_2O + hexane	—70	73	yellow	100[b]	[45]
$R_4''V \cdot 2Et_2O$	VCl_4	R″Li	Et_2O + hexane	—70	70	violet	220[b]	[46]
$R''_3Ti.3THF$	$TiCl_3.3THF$	R″MgBr	THF	0	45	dark-green	122[b]	[48]
$R''_3V.THF$	$VCl_3.3THF$	R″Li	THF	—70	85	brown	10	[21]

Remarks: [a]yield not indicated; [b]melts with decomposition; PE = petroleum ether.

when $CrCl_3.3THF$ is treated with an excess of RLi or RMgCl (R = CH_2Ph or CH_2EMe_3),[13,27] while the reaction of $CrCl_3$ with a deficiency of Me_3SiCH_2Li results in the formation of $(Me_3SiCH_2)_2Cr$; the reaction mechanism has not been established[33].

The Mesityl Derivatives (Table 3)

The tetramesityl derivatives cannot be obtained by the usual double decomposition reaction between metal halides and a Grignard reagent or RLi. In view of the large bulk of the ligand, only three chlorine atoms are substituted in these reactions even in the presence of the arylating agents. A novel method of synthesis has been developed, consisting in the oxidation of the ate-complexes and the tervalent metals, which give rise to derivatives of the quadrivalent metals after careful choice of oxidation conditions[34–37]:

$$MCl_3 \cdot 3THF + 4MesLi \xrightarrow[20°C]{THF+Et_2O} [Mes_4M]^- Li^+ \cdot 4THF + 3LiCl$$
$$\downarrow \tfrac{1}{2}O_2$$
$$Mes_4M + LiO + 4THF$$

Derivatives of titanium, chromium, vanadium, and molybdenum have been obtained in this way. The difficulties in synthesising the tetramesityl derivatives of zirconium, hafnium, niobium, tantalum, and tungsten are associated with the fact that the initial MCl_3 are at present difficult to obtain.

Mesityl derivatives of tervalent metals have been obtained for vanadium and chromium. Unfortunately attempts to synthesise Mes_3Ti have not been described, although in the synthesis of Mes_4Ti the compound $TiCl_3.3THF$ was mesitylated[34]. Mes_3V was isolated in a pure form after the reaction of $VCl_3.3THF$ with three moles of MesMgBr, but not with MesLi, since interaction with the latter results in the preferential formation of the ate-complex of vanadium(III), rather than the neutral compound[38,39]. $Mes_3Cr.THF$, which cannot be converted into an arene complex because of the characteristic features of the mesityl group, proved to be easy to synthesise[40]. For the same reason, it has been possible to obtain and investigate the σ-mesityl derivatives of chromium(II).

The complex $Mes_2Cr.3THF$ can be obtained from anhydrous $CrCl_2$ and MesMgBr.[41] It is of interest that Mes_2Cr can give rise to complexes with coordination numbers ranging from 3 to 5. If the pentacoordinate complex $Mes_2Cr.3THF$ is dissolved in hexane at 20 °C. the colour of the solution changes, after 15–20 min from violet to green and a green deposit having the composition $Mes_2Cr.3THF$ is precipitated. Three molecules of the coordinated THF are readily substituted by one molecule of the bidentate bipyridyl ligand with formation of dark-blue crystals of the tetracoordinate chromium complex $Mes_2Cr.bipy$.[41] The formation of Mes_2Mo was unexpected; the authors[42] believe that the interaction of Mes_2MoO_2 with MeLi involves reduction:

$$Mes_2MoO_2 + 2MeLi \xrightarrow[0°C]{Et_2O} Mes_2Mo \cdot 2Et_2O + 2MeOLi$$

However, a change in the valence of molybdenum was not demonstrated analytically and the properties of this compound were not investigated.

The Adamantylmethyl Derivatives (Table 3)

The 1-adamantylmethyl (adme) ligand has a large bulk. It has been established that the peralkyl compounds R_nM incorporating this ligand decompose above 100 °C. In the synthesis of $(adme)_4M$ (M = Ti, V, or Cr), the alkoxides and not the halides were used as the initial transition metal compounds (the use of MCl_4 leads to an extremely low yield of the final products). The employment of soluble derivatives $M(OR)_4$ made it possible to carry out the reaction in saturated hydrocarbons at low temperature.

The compound $(adme)_4Ti$ crystallises in an analytically pure form from the $Ti(OPr\text{-}iso)_4$ + 4(adme)Li system in petroleum ether at 20 °C.[43] In view of the difficulty of obtaining the initial reagent $Zr(OPr\text{-}iso)_4$, $ZrCl_4$ was used in the synthesis of $(adme)_4Zr$. The isolation in a pure state of the compound $(adme)_4Zr$ obtained from $ZrCl_4$ and (adme)MgBr therefore requires repeated crystallisation in order to eliminate the admixture of magnesium halide salts[43].

Treatment of $V(OPr\text{-}iso)_4$ with an excess of (adme)Li gives the unexpected product $(adme)_4V$.[43] The attempts to obtain the peradamantylmethyl derivatives of niobium and tantalum ended in failure, whose only cause was the steric hindrance resulting from the disposition of the five bulky groups around the Nb and Ta atoms. Treatment of $Nb(OBu\text{-}t)_5$ with an excess of (adme)Li resulted in the formation of a mixture of the di- and tri-alkylated products. When $TaCl_5$ was allowed

Table 4. Benzylmetal halides R_nMHal_{m-n} ($R = CH_2Ph$; $n = 1, 2, 3$; $m = 4, 5$).

Benzylmetal halide	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	R_nM	reagent	solvent	t, °C		colour	m.p., °C	
R_3TiF	R_4Ti	BF_3 (gas)	toluene	—10	40	red-brown	100[a]	[5]
R_3TiCl	R_4Ti	HCl (gas)	toluene	—10	86	red-brown	100[a]	[5]
R_3TiBr	R_4Ti	HBr (gas)	toluene	—10	89	red	100[a]	[5]
R_3TiI	R_4Ti	I_2	toluene	—20	70	dark-red	—[b]	[50]
R_2TiBr_2	R_4Ti	$TiBr_3$	toluene	—10	60	red	80	[5]
R_3ZrCl	R_4Zr	HCl (gas)	toluene	—10	80	yellow	89	[5]
R_2ZrCl_2	R_4Zr	HCl (gas)	toluene	—10	60	orange-yellow	60[c]	[5]
$R_3TaCl_2 \cdot$ bipy	$TaCl_5$	R_2Zn	toluene	20	55	orange	—[b]	[12]
$R_2TaCl_3 \cdot$ bipy	$TaCl_5$	R_2Zn	PE	—50	—[d]	brown	110	[10]
R_3TaCl_2	$TaCl_5$	R_2Zn	hexane	20	—[d]	yellow-brown	—[b]	[10]
$RTaCl_4$	$TaCl_5$	R_2Mg	PE	20	—[d]	yellow-brown	—[b]	[10]

Remarks: [a] melts with decomposition; [b] m.p. not determined; [c] decomposes without fusion; [d] yield not indicated.

to react with (adme)MgBr in Et_2O, only three chlorine atoms were substituted with formation of $(adme)_3TaCl_2$.[43]

The Pentafluorophenyl Derivatives (Table 3)

These derivatives have a much higher thermal stability than the phenyl compounds. While the Ph_4M (M = Ti, Zr, or V) derivatives cannot be isolated in a pure state, the corresponding pentafluorophenyl compounds are stable on heating to 100 °C and above.

The compound $(C_6F_5)_4Ti$ can be isolated in the form of the hexacoordinate complex $(C_6F_5)_4Ti.2Et_2O$ as a result of the double decomposition reaction between $TiCl_4$ and C_6F_5MgBr.[44] The best alkylating agent for the zirconium salt proved to be C_6F_5Li. In contrast to the titanium compound, the σ-derivative of zirconium can be isolated in the form of the pentacoordinate complex $(C_6F_5)_4Zr.Et_2O$.[45]

The interaction of VCl_4 with C_6F_5Li leads to the formation of the complex $(C_6F_5)_4V.2Et_2O$.[46] A brief communication (without description of experimental conditions) concerning the synthesis of the light-sensitive and volatile compound $(C_6F_5)_4Nb$ has been published[47].

The pentafluorophenyl derivatives $(C_6F_5)_3Ti.3THF$ and $(C_6F_5)_3V.THF$ have been synthesised by the reaction of $MCl_3.3THF$ with C_6F_5MgBr or C_6F_5Li. The authors of the present review established that the reaction conditions play a major role in the successful isolation of the compounds: the use of THF as the solvent, the optimum temperature range from 0° to +5 °C, and the order in which the reactants are added (it is essential that transition metal halide be added to the Grignard reagent)[21,48].

2. The Synthesis of Alkyl(aryl) Metal Halides

The main method of synthesis of organometallic halides involves the interaction of transition metal halides with alkylating (arylating) agents using different ratios of the initial reactants. The importance of the synthesis of compounds of the type R_nMHal_{m-n} is due to the possibility of their being used for the synthesis of other classes of substances.

The Benzyl Derivatives (Table 4)

The possibility of obtaining benzylmetal halides by the double decomposition reaction between MCl_4 and $PhCH_2MgCl$ has been investigated in relation to titanium. The reaction of $TiCl_4$ with different amounts of $PhCH_2MgCl$ in Et_2O at −20 °C leads to the reduction of titanium and the formation of bibenzyl[49]. Other methods of synthesis of benzyl titanium and benzylzirconium halides have therefore been used. A novel electrochemical method of synthesis of complexes of dibenzylmetal dihalides with bipyridyl or acetonitrile, having the general formula $(PhCH_2)_2MHal_2.L$ (M = Ti, Zr, or Hf; Hal = Cl, Br, or I; L = bipy or 2MeCN), has been proposed recently[51]. It consists in the chemical oxidation of the titanium subgroup metals in an electrolytic cell containing $PhCH_2Hal$ and acetonitrile or α,α-bipyridyl. The reactions are carried out in solution at a constant current of 30 mA (25 V). The process terminates with the precipitation of the insoluble complexes indicated above.

Benzylvanadium(IV) halides and benzylniobium(V, IV) have not been isolated in a pure state, since they decompose in the reaction solution at the instant of formation[7,52]. It proved possible to isolate certain benzyltantalum halides as a result of double decomposition reactions[10,12].

Particular attention has been devoted to the problem of the synthesis and investigation of the reactivities of benzyltitanium(III) halides, because it is believed that such titanium(III) derivatives enter into the decomposition of the active centres in various catalytic systems based on organotitanium compounds. In connection with the synthesis of $(PhCH_2)_n.TiHal_{3-n}$, a method for the substitution of the benzyl group in $(PhCH_2)_3Ti$ by a halogen involving treatment with HCl or I_2 was employed. The reaction of $(PhCH_2)_3Ti$ with gaseous HCl (in proportions of 1 : 1 and 1 : 2) was carried out in *o*-xylene at −20 °C. The reaction of $(PhCH_2)_3Ti$ with I_2 in toluene at −20 °C yields products with various degrees of alkylation depending on the initial reactant ratio[19]. It has been established that benzyltitanium(III) halides undergo quantitatively the oxidative-reductive disproportionation reaction on raising the temperature to 20 °C. However, the composition of the disproportionation products changes on passing from the chlorides to the iodides:

$$2\,(PhCH_2)_2\,TiCl \rightarrow TiCl_2 + (PhCH_2)_4\,Ti\,,$$
$$2\,(PhCH_2)_2\,TiI \rightarrow PhCH_2TiI + (PhCH_2)_3\,TiI\,.$$

The Trimethylsilylmethyl and Neopentyl Derivatives (Table 5)

The double decomposition reaction between $TiCl_4$ and Me_3SiCH_2MgCl or Me_3SiCH_2Li was used to synthesise $(Me_3SiCH_2)_nTiCl_{4-n}$ ($n = 1, 2, 3$); depending on the initial reactant ratio, it led to the isolation of $Me_3SiCH_2TiCl_3$ and $(Me_3SiCH_2)_2TiCl_2$.[53] The attempts at the synthesis of

Table 5. Neopentyl- and trimethylsilylmethyl-metal halides R_nMCl_{m-n} (R = CH_2CMe; R' = CH_2SiMe_3; n = 1, 2, 3, 4; m = 4, 5).

Alkylmetal halide	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MCl_n	R_nE, R'_nE	solvent	t, °C		colour	m.p., °C	
$R_2'TiCl_2$	$TiCl_4$	R'Li	hexane	—3	14	red-brown	—(65/1.5 mm)[a]	[53]
$R'TiCl_3$	$TiCl_4$	R'MgCl	hexane + Et_2O	—20	40	red-orange	—(45/1.5 mm)[a]	[53]
$R_2ZrCl_2 \cdot PMe_3$	$ZrCl_4$	RLi	Et_2O+PMe_3	20	90	yellow	50[b]	[54]
$[(Me_3Si)_2CH]_3ZrCl$	$ZrCl_4$	$(Me_3Si)_2CHLi$	Et_2O	20	45	colourless	–[c]	[32]
$[(Me_3Si)_2CH]_3HfCl$	$HfCl_4$	$(Me_3Si)_2CHLi$	Et_2O	20	53	colourless	–[c]	[32]
R_4TaCl	$TaCl_5$	RLi	pentane	—78	—[d]	yellow	25[d]	[28]
R_3TaCl_2	$TaCl_5$	R_2Zn	pentane	20	85	yellow	—(110/1 mm)[f]	[28]
R_2TaCl_3	$TaCl_5$	R_2Zn	toluene	20	d	yellow	25[d]	[28]
$RTaCl_4$	$TaCl_5$	R_2Zn	toluene	20	92	yellow	25[d]	[56]
$R_3'TaCl_2$	$TaCl_5$	$R_2'Zn$	Et_2O	0	77[d]	yellow	68	[55]
$R_2'TaCl_3$	$TaCl_5$	$R_2'Zn$	Et_2O	10	74	yellow	70	[55]
$R'TaCl_4$	$TaCl_5$	$R_2'Zn$	Et_2O	20	65	yellow	59	[55]
R_3NbCl_2	$NbCl_5$	R_2Mg	Et_2O	20	35	orange	70[d]	[28]
R_2NbCl_3	$NbCl_5$	R_2Zn	pentane	20	80	red-orange	25[d]	[57]
$R_3'NbCl_2$	$NbCl_5$	$R_2'Zn$	Et_2O	—10	53	orange-red	70	[55]

Remarks: [a]liquid, b.p. is indicated; [b]decomposes in benzene; [c]m.p. not determined; [d]yield not indicated; [e]melts with decomposition; [f]sublimation temperature.

Table 6. Mesityl- and pentafluorophenyl-metal halides R_nMCl_{m-n} (R = Mes; R' = C_6F_5; n = 1, 2, 3; m = 4, 5).

Arylmetal halide	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MCl_n	R_nE, R'_nE	solvent	t, °C		colour	m.p., °C	
$RTiCl_3$	$TiCl_4$	R_2Zn	pentane	20	56	red-orange	82	[61]
$RTiBr_3$	$TiBr_4$	R_2Zn	pentane	20	74	red	62	[61]
R_3NbCl_2	R_2NbCl_3	RLi	toluene	20	10	orange	—[a]	[62]
R_2NbCl_3	$NbCl_5$	R_2Zn	toluene	20	84	red	—[a]	[62]
$RNbCl_4$	$NbCl_5$	R_2Zn	pentane	20	85	dark-red	25[b]	[62]
R_3TaCl_2	R_2TaCl_3	RLi	toluene	20	71	yellow	—[a]	[62]
R_2TaCl_3	$TaCl_5$	R_2Zn	toluene	20	74	orange	—[a]	[62]
$RTaCl_4$	$TaCl_5$	R_2Zn	pentane	20	93	orange-red	25[c]	[62]
$RVCl_2 \cdot 2THF$	$VCl_3 \cdot 3THF$	RMgBr	THF	—30	36	brown-yellow	91[b]	[65]
$R_3'VCl \cdot THF$	VCl_4	R'Li	hexane	—70	70	red-violet	200[b]	[63]
$R_2'VCl_2 \cdot THF$	VCl_4	$R_2'V$	THF	—70	57	red	220[b]	[63]
$R'VCl_3 \cdot THF$	VCl_4	$R_2'V$	THF	—70	54	raspberry red	125	[63]

Remarks: [a]m.p. not determined; [b]decomposes without melting; [c]stable at 25 °C.

$(Me_3SiCH_2)_3.TiCl$ were unsuccessful, since this compound readily disproportionates in solutions[53]:

$$2\,(Me_3SiCH_2)_3\,TiCl \xrightarrow[20^\circ C]{\text{hydrocarbons}} (Me_3SiCH_2)_4\,Ti + (Me_3SiCH_2)_2\,TiCl_2\ .$$

Trialkylmetal halides which do not undergo disproportionation have been synthesised using the $(Me_3Si)_2CH$ bulky substituent. The double decomposition reaction of MCl_4 even with an excess $[(Me_3Si)_2CH]Li$ always leads to the isolation of $[(Me_3Si)_2CH]_3MCl$ (M = Zr or Hf). When attempts were made to obtain the analogous titanium compound, reduction with formation of $[(Me_3Si)_2CH]_3Ti$ was observed[32]. Neopentylzirconium chlorides have been obtained recently[54]: the reaction of $ZrCl_4$ with two moles of Me_3CCH_2Li in Et_2O yields $(Me_3CCH_2)_2ZrCl_2.Et_2O$ in the form of an oil, while crystalline products are isolated on formation of complexes with phosphines and amines. Procedures whereby the symmetrical $(Me_3CCH_2)_2ZrCl_2$ is converted into mono- or tri-neopentylzirconium chloride are being investigated[54].

It has been shown that trimethylsilylmethylvanadium(IV) halides as well as $(PhCH_2)_nVCl_{4-n}$ are unstable in solution and decompose with formation of low-valence vanadium complexes[21].

Organozinc compounds can be used successfully to isolate a whole series of derivatives of the type $(Me_3ECH_2)_nMCl_{5-n}$ (M = Nb or Ta; E = C or Si; n = 1, 2, 3, 4). With the aid of organozinc compounds, it is possible to substitute in succession the chlorine atoms in MCl_5 for the Me_3ECH_2 groups[28,55–57]. For the Group IVB metals, only the molybdenum complex $(Me_3SiCH_2)_3MoCl.PMe_3$ has been isolated[58].

The methods of synthesis of the compounds $(Me_3SiCH_2)_n.TiCl_{3-n}$ have been investigated by analogy with $(PhCH_2)_n.TiCl_{3-n}$. It has been established that they exist in solutions at temperature not exceeding –5 °C. When attempts were made to isolate them, oxidative-reductive disproportionation to the titanium(II) and Ti(IV) complexes was always observed[59,60].

The Mesityl Derivatives (Table 6)

Attempts to obtain mesitylmetal halides have now been described for titanium(IV), niobium(V), tantalum(V), and vanadium(III). Mes_2Zn is the best arylating agent. The reaction of $TiCl_4$ with Mes_2Zn in proportions of 2 : 1 yields $MesTiCl_3$.[61]

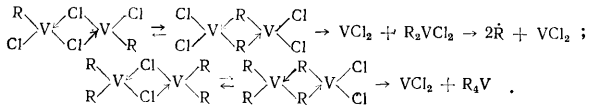
Depending on the initial reactant ratio, it is possible, as for the Me_3ECH_2 substituents, to replace in succession the chlorine atoms by the Mes groups by the reaction of MCl_5 (M = Mb or Ta) with Mes_2Zn. $MesMCl_4$ and Mes_2MCl_3 have been obtained in this way[62]. The substitution of the third chlorine atom by the mesityl group is possible when MesLi is used. It has been established that the thermal stability of mesitylmetal chlorides diminishes with increase of the degree of arylation. Thus $MesTaCl_4$ sublimes without signs of decomposition, $MesNbCl_4$ decomposes in the solid state at 25 °C after several days, while Mes_2NbCl_3 decomposes faster than the monosubstituted product under these conditions: Mes_3TaCl_2 and Mes_3NbCl_2 always contain decomposition products[62].

The Pentafluorophenyl Derivatives (Table 6)

Compared with other compounds, the σ-C_6F_5-substituted derivatives have been investigated to only a fairly slight extent. A series of pentafluorophenylmetal chlorides have now been investigated for Group VB metals[63].

The reactions of MCl_5 (M = Nb or Ta) with C_6F_5Li in various proportions (ranging from 1 : 3 to 1 : 6) in hexane at −78 °C give rise to solid variable-composition products $(C_6F_5)_nMCl_{5-n}$, where n = 2, 3; the molecular weight is intermediate between those of the monomer and the dimer[64].

A detailed study has been made in order to synthesise alkylvanadium(III) chlorides R_nVCl_{3-n} (n = 1, 2) with substituents of different kinds (R = CH_2Ph, CH_2SiMe_3, Mes, or C_6F_5). For this purpose, the double decomposition reaction of VCl_3.3THF with RMgCl in proportions of 1 : 1 and 1 : 2 in Et_2O or THF as well as the reactions of R_3V.THF (R = CH_2. .$SiMe_3$ or C_6H_5) with gaseous HCl were investigated[21]. The attempts to isolate $RVCl_2$ and R_2VCl were unsuccessful. It has been established that the above derivatives undergo oxidative-reductive disproportionation in solutions at 0 °C. This process proceeds via a stage involving the formation of intermediate dinuclear complexes in which chlorine atoms are exchanged for the ligands R. The composition of the disproportionation products is determined by the ratio of the amounts of R and Cl in the initial reactant R_nVCl_{3-n}:



Evidently when a bulky ligand with structural rigidity is used, there is a possibility, on the one hand, that the monomeric form is stabilised and, on the other hand, that the exchange of a chlorine atom for a ligand R in the dinuclear complex, which subsequently decomposes, may be hindered. Such requirements are met by the mesityl ligand. Indeed the double decomposition reaction of VCl_3.3THF with MesMgBr in THF at a low temperature led to the isolation of the pure compound $MesVCl_2$.2THF, which is entirely stable on heating to 100 °C.[65]

3. The Synthesis of the Compounds R_nMX_{m-n} (X = OR', acad, or NR'_2; m = 3, 4, 5; n = 1, 2, 3)

The thermal stability of compounds of this type is determined not only by the characteristics of the σ-substituents considered in this review but also by the properties of the group X. The alkoxy-derivatives are thermally stable by virtue of the formation of dimers, since the R'O groups tend to associate. The acetylacetonate group reacts with the metal to form an intramolecular chelate. The R'_2N group promotes the coordination and saturation of the metal in the molecule. Furthermore, an increase of thermal stability is observed when bulky amide groups are used. The specific features of the above OR', NR'_2, and acac groups are responsible for the isolation of individual compounds containing methyl, ethyl, and phenyl groups (Tables 7 and 8).

The compounds $RTi(OPr\text{-}iso)_3$ (R = Me, Ph, or C_6H_5) and $R_2Ti(OEt)_2$ (R = CH_2Ph, or C_6H_{11}) have been obtained; they exist in the form of dimers[5,66,67,68].

The diphenoxides are monomeric and their thermal stability is determined to a large extent by the nature of the σ-substituent. The derivatives $(Me_3SiCH_2)_2Ti(OPh)_2$ is stable up to 100 °C, while the analogous dimethyl compound decomposes rapidly in solution at 20 °C.[69]

Studies of the synthesis of $(PhCH_2)_3TiOEt$, $RV(OR')_3$, and R_3VOR' have shown that they are readily symmetrised[5,70]. The compounds $R_2V(OR')_2$, which have been obtained in three different ways, proved to be thermally stable[70,71] (Table 7).

Table 7. Alkoxy-derivatives $R_nM(OR')_{4-n}$ and acetylacetonates $R_nM(acac)_{m-n}$.

Derivative	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	reagent	solvent	t, °C		colour	decomp. temp., °C	
$(PhCH_2)_2Ti(OEt)_2$	$(PhCH_2)_4Ti$	EtOH	benzene	+5	70	red-orange	110	[5]
$(Me_3SiCH_2)_2Ti(OPh)_2$	$Cl_2Ti(OPh)_2$	R_2Mg	Et_2O	−70	20	yellow	100	[69]
$C_6F_5Ti(OPr\text{-}iso)_3$	$ClTi(OPr\text{-}iso)_3$	C_6F_5Li	Et_2O	−70	17	colourless	135	[67]
$(PhCH_2)_2V(OBu\text{-}t)_2$	$(PhCH_2)_4V$	t-BuOH	hexane	−10	43	green	152	[70]
$(Me_3SiCH_2)_2V(OBu\text{-}t)_2$	$Cl_2V(OBu\text{-}t)_2$	RMgCl	Et_2O	−70	20	blue-green	148	[71]
$Mes_2V(OBu\text{-}t)_2$	$V(OBu\text{-}t)_4$	RMgBr	Et_2O	−70	80	green	176	[71]
$(C_6F_5)_2V(OBu\text{-}t)_2$	$(C_6F_5)_4V$	t-BuOH	Et_2O	−70	87	dark green	179	[71]
$(PhCH_2)_2Zr(acac)_2$	$(PhCH_2)_4Zr$	(acac)H	Et_2O	−40	71	yellow	125	[72]
$(PhCH_2)V(acac)_2$.THF	$V(acac)_3$	RMgCl	THF	−50	80	red-brown	100	[73]
$(Me_3SiCH_2)V(acac)_2$.THF	$V(acac)_3$	RMgCl	THF	−50	80	red-brown	112	[73]
$(C_6F_5)V(acac)_2$.THF	$V(acac)_3$	RMgBr	THF	−50	80	red-brown	128	[73]
$(PhCH_2)Cr(acac)_2$	$Cr(acac)_3$	RMgCl	Et_2O	−70	15	yellow-green	0	[17]

Table 8. Amido-derivatives $R_nM(NR''_2)_{4-n}$ and $R'_nM(NR''_2)_{4-n}$ ($R = CH_2Ph$, $R' = CH_2SiMe_3$).

Derivative	Initial compounds		Conditions of synthesis		Yield, %	Characteristics of the substance		Refs.
	MX_n	reagent	solvent	t, °C		colour	m.p., °C	
R_3TiNEt_2	Br_3TiNEt_2	RMgCl	Et_2O	—20	87	red	10[a]	[75]
$R_2Ti(NEt_2)_2$	$Br_2Ti(NEt_2)_2$	RMgCl	Et_2O	—20	38	red	—10[b]	[75]
$RTi(NEt_2)_3$	$BrTi(NEt_2)_3$	RMgCl	Et_2O	—20	78	red-orange	13	[75]
R_2TiPip_2	Br_2TiPip_2	RMgCl	Et_2O	—20	87	red	20[a]	[75]
$R_2Ti(CTS)_2$	$Br_2Ti(CTS)_2$	RMgCl	PE	—10	68	red	131	[76]
$R_2'Ti(NEt_2)_2$	$Br_2Ti(NEt_2)_2$	R'MgCl	Et_2O	—20	84	yellow-orange	0[b]	[75]
$R'Ti(NEt_2)_3$	$BrTi(NEt_2)_3$	R'MgCl	Et_2O	—20	91	yellow	0[a]	[75]
$R_2Zr(NPh_2)_2$	R_4Zr	Ph_2NH	benzene	+20	50	yellow	—[c]	[80]
$R_2'Hf[N(SiMe_3)_2]_2$	$Cl_2Hf[N(SiMe_3)_2]_2$	R'MgCl	Et_2O	0	89	colourless	91	[78]
Mes_3VNPh_2	$[Mes_3VNPh_2]Li$	O_2	—	+20	84	black	124	[81]

Remarks: [a]melts with decomposition; [b]decomposes in solution; [c]m.p. not determined. Pip = piperidine; CTS = octamethyl-2,4,6-trisila-1,3,5-triazacyclo-hex-1-yl.

The acetylacetonate derivatives have been investigated in relation to the zirconium and vanadium compounds (Table 7). While $(PhCH_2)_2Zr(acac)_2$ is fairly stable, $R_2V(acac)_2$ and also $RV(acac)_3$ undergo reductive elimination in solutions[72,73]. The derivatives $(Me_3SiCH_2)_3Zr(acac)$ and $R_3V(acac)$ are readily symmetrised. Systematic studies have been made of the synthesis and properties of mixed σ-derivatives of vanadium of the type R_nVX_{m-n} ($R = CH_2Ph$, CH_2SiMe_3, or C_6H_5; X = Cl, OBu-t, or acac; $n = 1, 2, 3$; $m = 3, 4$). It has been established that, regardless of the nature of the σ-substituent, the compounds RVX_3, RVX_2, and R_2VX_2 (X = Cl or acac) undergo reductive decomposition in Et_2O.[21] $RTi(OBu\text{-}t)_3$ and $R_2V(OBu\text{-}t)_2$ are exceptions owing to the large bulk and low electronegativity of the t-butoxy-groups. The derivatives RVX_3 are symmetrised, while the RVX_2 undergo oxidative-reductive disproportionation in solutions (regardless of the nature of X and R), which proceeds via a stage involving the formation of intermediate dinuclear complexes.

When the reaction mixture contains agents preventing the formation of dinuclear complexes and stabilising the monomeric form, stable products are isolated, for example, the compounds $RV(acac)_2.THF$, stabilised by the formation of the monomeric hexacoordinate complex, since the acetylacetonate group is a η^2-ligand.

Studies of a series of alkylamide derivatives of titanium established that the thermal stability of the compounds decreases in the sequence $RTi(NR'_2)_3 > R_3TiNR'_2 > R_2Ti(NR'_2)_2$. It was found that, in contrast to R_2TiX_2 (X = Hal or OR), the compounds $R_2Ti(NR'_2)_2$ readily disproportionate[74,75]:

$$3R_2Ti(NR'_2)_2 \xrightarrow[-20°C]{} 2RTi(NR'_2)_3 + R_4Ti \ .$$

The stabilisation of the symmetrical compounds has been achieved by employing rigidly fixed or bulky ligands (Table 8). X-Ray diffraction analysis of $MeHf[N(SiMe_3)_2]_3$ has shown that the $(Me_3Si)_2N$ groups are located in space in such a way that they fully shield the central atom from external influences[77]. By virtue of this spatial disposition of the $(Me_3Si)_2N$ groups, even the compound $Et_2Hf[N(SiMe_3)_2]_2$ (m.p. 65 °C) is thermally stable, although the ethyl derivatives of transition metals usually exist only at low temperatures because of the ease of β-elimination[78,79].

The amide derivatives of vanadium(IV) and vanadium(III) have been scarcely investigated. A single compound $Mes_3.VNPh_2$ has been synthesised by oxidising the corresponding ate-complex $[Mes_3VNPh_2]^-Li^+$.[81] The isolation of $MesV(NPh_2)_2$, formed by the reaction

$$VCl_3 \cdot 3THF + MesMgBr + 2KNPh_2 \rightarrow MesV(NPh_2)_2 \ ,$$

has been mentioned. No detailed description of the reaction conditions and the properties of the compounds is given[82].

III. THERMAL DECOMPOSITION OF THE σ-DERIVATIVES

The task of the study of the thermal decomposition of the individual σ-derivatives R_nM and R_nMX_{m-n} is the determination of the general features of this process as a function of the electronic configuration, coordination capacity of the central atom, and the decomposition conditions.

An attempt has been made at a theoretical justification of the modes of decomposition by analysing the correlation between the symmetry groups of the valence orbitals of the metal atoms in the initial σ-complex and its thermolysis products. On the basis of these correlations, the metal complexes with the electronic configurations $d - d^8$ should undergo reductive elimination. For the complexes with the electronic configurations d^0[Ti(IV), Zr(IV), and Hf(IV)] and d^1, d^2[V(IV), Cr(IV), Ti(III), and V(III)], the reductive elimination is prohibited and the σ-bond is homolysed[83]. The experimental results obtained by different workers are in good agreement with these theoretical postulates.

It has been established that reductive elimination is observed on thermolysis of the neophyl complexes of chromium(III) (d^3 system), Mn(II), Fe(III) (d^5 system), Fe(II), Co(III) (d^6 system), Co(II) (d^7 system), and Ni(II) (d^8 system) and leads to the formation of bineophyl and to a decrease of the valence of the central atom[84].

The elimination processes are varied. Apart from the reductive elimination, the complexes are decomposed via α-, β-, and γ-hydride elimination.

The classical compounds which decompose via α-elimination are the σ-derivatives of niobium and tantalum. The study of the kinetics of the thermal decomposition of $(PhCH_2)_5Ta$ in benzene at 40 °C in the presence of an initiator (azobisisobutyronitrile) or an inhibitor (the galvinoxy-radical) has shown that the decomposition of $(PhCH_2)_5Ta$ does not entail the homolysis of the M—C bond with formation of free radicals[85]. The authors believe that $(PhCH_2)_5Ta$ decomposes via intramolecular or intermolecular α-hydride elimination with formation of toluene and alkylidene complexes of quinquevalent tantalum. However, the individual compound could not be isolated in this instance. The neopentylidene complex $(Me_3CCH_2)_3Ta(CHCMe_3)$ proved to be thermally stable[28]. The analogous niobium complex is unstable. The authors[28] postulate the formation of the tantalum complex via the decomposition of the short-lived $(Me_3CCH_2)_5Ta$, whose molecules have a trigonal bipyramidal structure. Its relatively more acidic α-proton passes from the α-carbon atom of the equatorial alkyl group to the relatively more nucleophilic α-carbon atom of the axial alkyl group. This results in a rearrangement of the structure accompanied by the formation of Me_4C and the

final pseudotetrahedral complex. Schrock's investigations[12, 28,85] suggest that the decomposition of all the pentacoordinate niobium(V) and tantalum(V) complexes takes place via α-elimination with formation of tetracoordinate alkylidene complexes of formally quinquevalent niobium and tantalum[28].

The α-elimination process is dominant in the decomposition of alkylmolybdenum and alkyltungsten halides R_nMHal_{m-n} ($R = CH_2Ph$ or CH_2SiMe_3). The factor favouring this reaction pathway is the possibility of the stabilisation of carbenes on coordination to molybdenum and tungsten. The main evidence confirming the elimination of α-hydrogen is as follows: firstly, the Me_4Si formed on decomposition of $(Me_3.SiCH_2)_nMHal_{m-n}$ in deuterated solvents does not contain deuterium atoms and, secondly, the decomposition of the dry residues (after the decomposition of the compound) with heavy water results in the formation of considerable amounts of Me_3SiCHD_2 and $PhCHD_2$.[86-88]

Thus, in the decomposition of $Mes(Me)TaCl_3.PMe_3$ in toluene at 45 °C or of $Mes(Me)TaBr_3.PMe_3$ in $CHCl_3$ at 25 °C, the Me–Ta bond is cleaved homolytically and CH_4 is formed as a result of the abstraction of the γ-hydrogen from the Mes group. ^1H and ^{13}C NMR data made it possible to establish the formation of substituted benzylidene complexes and to put forward a γ-elimination mechanism[62]:

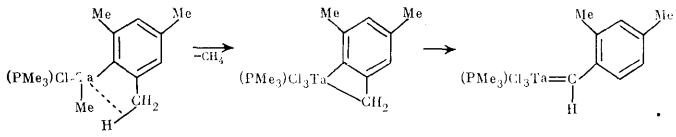


Table 9. Thermolysis of the benzyl and trimethylsilylmethyl derivatives of titanium, zirconium, and vanadium.

Compound	Decomposition conditions (*t*, °C)	Amount of RH, mol/mol OMC	Refs
$(PhCH_2)_4Ti$	solid (100)	2.2	[89, 90]
$(PhCH_2)_4Ti$	in heptane (100)	2.5	[5]
$(PhCH_2)_4Zr$	solid (135)	2.5	[90]
$(PhCH_2)_4Zr$	in octane (100)	2.5	[5]
$(PhCH_2)_4Zr$	in toluene (100)	2.5	[5]
$(PhCH_2)_4V\cdot 2Et_2O$	solid[a] (80)	2.4	[91]
$(PhCH_2)_4V\cdot 2Et_2O$	in benzene (80)	3.8	[91]
$(PhCH_2)_4V\cdot 2Et_2O$	in ether (80)	3.8	[91]
$(PhCH_2)_3V\cdot THF$	in THF (0)	2.8	[91]
$(Me_3SiCH_2)_4V$	solid (95)	2.8	[91]
$(Me_3SiCH_2)_4V$	in benzene (90)	2.8	[91]
$(Me_3SiCH_2)_4V$	in THF (90)	2.8	[91]
$(Me_3SiCH_2)_3V\cdot THF$	solid[a] (75)	1.9	[91]
$(Me_3SiCH_2)_3V\cdot THF$	in hexane (75)	2.0	[91]
$(Me_3SiCH_2)_3V\cdot THF$	in ether (75)	2.0	[91]

Remarks: [a] the decomposition was carried out in a quasi-flow system permitting the removal of the eliminated ligand from the reaction zone.

It is nowadays regarded as generally accepted that the decomposition of the σ-derivatives of Ti, Zr, Hf, V, Cr, Mo, and W is accompanied by the homolysis of the σ-bond. The thermolysis of the benzyl derivatives $(PhCH_2)_4M$ (M = Ti, Zr, Hf, V, Mo, or W) in the solid state and in solutions entails the formation of mainly toluene. At the same time very small amounts of bibenzyl, benzene, diphenylmethane, methane, and ethane were detected. The metal-containing thermal decomposition products consist of dark involatile pyrophoric substances in which the metal is present in a low-valence state. Unfortunately quantitative data have been obtained only for titanium, zirconium, and vanadium[5,89,90,91] (Table 9).

The trimethylsilylmethyl and neopentyl compounds of the elements in the titanium and vanadium subgroups decompose to give Me_4E (E = C or Si) as the only volatile product. No detailed studies of the thermolysis of $(Me_3ECH_2)_4M$ (M = Ti, Zr, Hf) have so far been made. It has been established that the thermolysis of the trimethylsilylmethyl derivatives of vanadium(IV) and vanadium(III) under various conditions leads to the formation of black pyrophoric residues containing low-valence vanadium[91].

There are virtually no quantitative literature data on the thermolysis of mesityl derivatives. The high thermal stability of the compounds Mes_4M (M = Ti, V, Cr, or Mo), which decompose above 100 °C, has been noted[34-37]. The decomposition results in the formation of mainly mesitylene together with small amounts of xylene, toluene, and bimesityl. For example, in the decomposition of the Mes_4Ti the product ratios are $MesH : Me_2C_6H_4 : MeC_6H_5 : Mes_2 = 100 : 0.1 : 10 : 4.7$.[92] The decomposition of $Mes_3V.THF$ is accompanied by the elimination of THF followed by the splitting off of more than 90% of the σ-substituents. The decomposition products are mesitylene, xylene, toluene, and bimesityl in the proportions 100 : 6.3 : 2.3 : 6.3.[93]

Thus the first stage of the thermolysis is the homolysis of the R–M σ-bond regardless of the valence of the central atom. If the compound has a coordinated ligand, its decomposition usually begins with the elimination of the ligand molecule. It has been established by physicochemical methods that the eliminated σ-substituents do not become free radicals. Consequently their subsequent reactions take place intramolecularly or intermolecularly within a cage. The reaction products of the homolytic species are RH. The sources of hydrogen can be (1) the groups R bound to the metal, (2) the ligand coordinated to the central atom, and (3) the solvent molecules.

It has been established that Me_4Si is formed in the decomposition of the Me_3SiCH_2 derivatives only via the intramolecular or intermolecular elimination of the hydrogen atom from the groups R bound to the central atom. Neither the coordinated ligands nor solvent molecules serve as sources of hydrogen. After the elimination of THF in the first stage of the thermolysis of $(Me_3SiCH_2)_3V.THF$, a structural rearrangement takes place with formation of the dimer $[(Me_3SiCH_2)_6V_2]$. The large bulk of the Me_3SiCH_2 groups and the small radius of the vanadium atom hinder its coordination to THF or Et_2O in the dimer and also in $(Me_3SiCH_2)_4V$.[91,94]

The benzyl derivatives decompose in the solid state via the same mechanism as the Me_3SiCH_2 derivatives but in solutions a difference is observed. Since the $PhCH_2$ groups are less bulky than the Me_3SiCH_2 ligands, they do not hinder the coordination of the THF or Et_2O to vanadium. Although the thermolysis of the complexes $(PhCH_2)_4V.2Et_2O$ and $(PhCh_2)_3V.THF$ begins with the loss of the coordinated ligand, a mobile equilibrium exists in solutions:

$$(PhCH_2)_nV\cdot xL \rightleftharpoons (PhCH_2)_nV + xL \quad ;$$

$$n = 3, 4;\ L = Et_2O,\ THF;\ x = 1, 2 \quad .$$

The occurrence of the reversible reaction makes it possible to replace the ligand by a molecule of the solvent capable of coordination, which serves in its turn as a hydrogen donor. Consequently in the decomposition reaction in solutions, the sources of hydrogen for the formation of RH can be both the groups R bound to the metal and the molecules of the coordinated ligand. The occurrence of two pathways is confirmed by the quantitative yield of toluene and by the analysis of the solid residue. In the decomposition of organovanadium

Table 10. $(C_6F_5)_nM.xL$ decomposition products[48,91,95].

Compound	decomp. temp., °C	Decomposition conditions		Decomposition products, mol/mol R_nM				
		solvent	t, °C	C_6F_5H	$(C_6F_5)_2$	$C_6F_4-C_6F_6$	$(C_6F_4)_3$	MX_n
$(C_6F_5)_4Ti\cdot 2Et_2O$	130	THF	90	0.20	—	—	1.02	TiF_4+TiF_3
$(C_6F_5)_4Ti\cdot 2Et_2O$	130	benzene	100	0.20	0.10	2.80	—	TiF_4+TiF_3
$(C_6F_5)_3Ti\cdot 3THF$	122	solid[a]	130	—	—	—	0.81	TiF_3
$(C_6F_5)_3Ti\cdot 3THF$	122	THF	90	0.83	—	—	0.63	F_2TiOR
$(C_6F_5)_3Ti\cdot 3THF$	122	benzene	90	0.70	—	1.83	—	F_2TiOR
$(C_6F_5)_4V\cdot 2THF$	205	Et_2O	90	0.70	0.10	—	—	$(C_6F_5)_3V.THF$
$(C_6F_5)_4V\cdot 2THF$	205	Bu_2O	140	0.65	0.10	—	1.03	$VF_3.THF$
$(C_6F_5)_4V\cdot 2THF$	205	benzene	140	0.77	0.10	2.83	—	$VF_3.THF$
$(C_6F_5)_3V\cdot THF$	220	Bu_2O	140	—	—	—	0.96	$VF_3.THF$
$(C_6F_5)_3V\cdot THF$	220	benzene	140	—	—	2.93	—	$VF_3.THF$

Remarks: [a] decomposition in a quasi-flow system; amount of THF 2.75 mol/mol $(C_6F_5)_3Ti.3THF$. A dash indicates that the given compound was not detected in the decomposition products.

compounds the solid residue contains the V–OR fragments which have arisen from secondary oxygen-containing ether groups. The study of the thermal decomposition of $(PhCH_2)_4V.2Et_2O$ in di-isopropyl ether by EPR revealed the formation of the intermediate derivative $(PhCH_2)_2V(OPr\text{-}iso)_2$.

The solvent is not involved in the formation of RH in the thermolysis of the benzyl derivatives of titanium and zirconium in hydrocarbons. This is confirmed by data for the decomposition of $(PhCH_2)_4Zr$ in $C_6D_5CD_3$, which does not result in the formation of $PhCH_2D$. The thermolysis of the equimolar $(PhCH_2)_4Ti + (C_6D_5CD_2)_4Ti$ mixture in heptane leads to the formation of toluene deuterated to different extents. This indicates the existence of an intermolecular pathway leading to the elimination of hydrogen. Unfortunately the decomposition of $(PhCH_2)_4M$ (M = Ti or Zr) in solvents capable of coordination (Et_2O, THF) has not been studied in detail and it is therefore difficult to reach a general conclusion concerning the influence of the nature of the solvent on the RH formation pathways.

The influence of the nature of the σ-substituent and of solvent character is clearly manifested in the thermolysis of the pentafluorophenyl derivatives of titanium and vanadium[48, 91,95] (Table 10). The titanium compounds decompose without fusion in the temperature range 120–130 °C, while the vanadium compounds decompose at 205–220 °C. The thermograms of the titanium complexes show that the coordinated ligands are split off initially. In contrast to this, the thermograms of the vanadium complexes have no peaks corresponding to the elimination of THF. The difference between the first stages of the decomposition determines also the difference between the subsequent decomposition pathways.

In compounds with the C_6F_5 ligands there is a possibility of the interaction of the unshared electron pair of the fluorine atom in the *ortho*-position with the *d* orbital of the metal. In the complexes $(C_6F_5)_4Ti.2Et_2O$, $(C_6F_5)_3Ti.3THF$, and $(C_6F_5)_4V.2THF$, the central atom is coordination-saturated and there is therefore initially no additional coordination of the fluorine to the metal. Experimental data show that the coordinated Et_2O or THF ligands are split off initially in the decomposition of the titanium derivative and one of the C_6F_5 groups is the first to be split off in the case of vanadium. This is probably followed by a rearrangement of the coordination sphere of the central atom associated with the fact that the vacant sites in the octahedral configuration are occupied by fluorine atoms. This additional coordination weakens both the $C-F_{ortho}$ and the C–M bonds. Both bonds are therefore ruptured in the thermolysis, which is accompanied by a transfer of the fluorine to the metal atom and the formation of metal fluorides. The fluorinated ligand is split off in the form of tetrafluorodehydrobenzene and the subsequent reaction pathways of C_6F_4 depend only on the nature of the solvent. C_6F_4 does not react with ethers and trimerises, but it does enter into a reaction with benzene of the type of diene synthesis with formation of 5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene.

The C_6F_5 groups eliminated from vanadium in the thermolysis of $(C_6F_5)_4V.2THF$ are converted mainly into C_6F_5H as a result of the abstraction of hydrogen from the coordinated THF molecules. A small proportion of the C_6F_5 groups dimerise. The formation of small amounts of C_6F_5H in the decomposition of $(C_6F_5)_4Ti.2Et_2O$ shows that the loss of coordinated ligands is accompanied by the partial homolysis of the C_6F_5–Ti σ-bond. On thermal decomposition in solutions, the compound $(C_6F_5)_3Ti.3THF$ remains coordination-saturated and for this reason one observes under the given conditions in the first stage the elimination of the C_6F_5 group, which is converted into C_6F_5H as a result of the abstraction of hydrogen from THF. Owing to the octahedral configuration, two vacant sites are produced and are occupied by the fluorine atoms from the two remaining C_6F_5 groups. The subsequent decomposition leads to the elimination of two C_6F_4 groups and the transfer of two fluorine atoms to titanium. However, $F_2Ti(OR)$ is formed instead of TiF_2, since the alkoxy-group produced due to the decomposition of the dehydrogenated THF adds to titanium. In $(C_6H_5)_3V.THF$ there is a possibility of the expansion of the coordination sphere to an octahedron as a result of the coordination of fluorine to vanadium. The C_6F_4 and not C_6F_5 is therefore split off in the decomposition of $(C_6F_5)_3V.THF$ and $VF_3.THF$ is formed.

Thus the mode of the thermal decomposition of the pentafluorophenyl derivatives is determined by the electronic configuration of the central atom and the possibilities for the rearrangement of the coordination sphere in the decomposition process.

Studies of the thermal decomposition of the compounds R_nMX_{m-n} have been published recently[7,63,96]. They are of interest because they make it possible to follow the influence of the second substituent on the reaction pathway. Under comparable conditions, studies have been made of the decomposition of the halogeno-derivatives R_nVCl_{4-n} having substituents of different kinds (Table 11). R_3VCl decomposition products show that symmetrisation takes place initially in accordance with the equation

$$R_3VCl \rightarrow {}^1/_2R_4V + {}^1/_2R_2VCl_2 \ .$$

When R = CH_2Ph or CH_2SiMe_3, the corresponding products R_4V do not decompose under the experimental conditions and

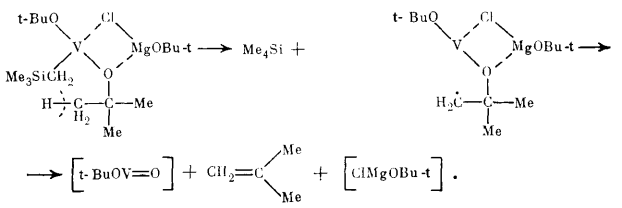
Table 11. R_nVX_{m-n} decomposition products[7,63,96].

Compound	Decomposition conditions		Decomposition products, mol/mol R_nVX_{m-n}		
	solvent	t, °C	RH	R–R	V-containing product (yield)
$PhCH_2VCl_3$	Et_2O	−18	—	0.45	VCl_3 (0.95)
$(PhCH_2)_2VCl_2$	Et_2O	−18	—	0.90	VCl_2 (0.94)
$(PhCH_2)_3VCl$	Et_2O	20	—	0.50	R_4V+VCl_2 (0.40+0.45)
$(Me_3SiCH_2)_3VCl$	Et_2O	20	0.80	—	R_4V+VCl_2 (0.46+0.45)
$C_6F_5VCl_3.THF$	Et_2O	20	0.10	0.45	VCl_3 (0.90)
$(C_6F_5)_2VCl_2.THF$	Et_2O	20	0.40	0.80	VCl_2 (0.90)
$(C_6F_5)_3VCl.THF$[a]	Bu_2O	140	0.67	0.33	VF_3+VCl_2 (0.60+0.33)
$Me_2V(OBu\text{-}t)_2$	Et_2O	90	0.94	—	V(III)+V(II) (0.75+0.15)
$Me_2V(OBu\text{-}t)_2$	heptane	90	0.90	—	V(III)+V(II) (0.75+0.15)
$(PhCH_2)_2V(OBu\text{-}t)_2$	Et_2O	90	0.80	—	V(III)+V(II) (0.75+0.15)
$(PhCH_2)_2V(OBu\text{-}t)_2$	heptane	90	0.70	—	V(III)+V(II) (0.75+0.15)
$Me_3SiCH_2V(OBu\text{-}t)_2.ClMgOBu\text{-}t$	solid[b]	200	0.89	—	V(IV) oxides (0.99)

Remarks: [a] amount of $(C_6F_4)_3$ found 0.60 mol/mol $(C_6F_5)_3VCl.THF$; [b] thermolysis in a quasi-flow system with removal of products from the reaction zone; iso-C_4H_{10} (0.45 mole), iso-C_4H_8 (1.95 mole) and t-BuOH (0.38 mole) were found. A dash indicates that the given compounds was not detected in the decomposition products.

can be isolated from the reaction mixture. The second symmetrisation product (R_2VCl_2) decomposes. The complex $(C_6F_5)_3VCl.THF$ also undergoes symmetrisation initially, but, since it decomposes at 198 °C and $(C_6F_5)_4V.2THF$ decomposes at 205 °C, in the given instance the processes are superimposed and a mixture of decomposition products of both compounds is obtained.

The study of the influence of the t-BuO group on the decomposition of alkylvanadium alkoxides (Table 11) makes it possible to establish that the reaction begins with the homolysis of the V–C σ-bond. At high temperatures (above 200 °C), the V–O and C–O bonds are cleaved. It is noteworthy that $V(OBu\text{-}t)_3$ and $V(OBu\text{-}t)_4$ decompose at 150° and 164 °C respectively. The amounts of RH formed in the decomposition of $R_2V(OBu\text{-}t)_2$ show that the neighbouring R ligands serve as a source of hydrogen. The formation of considerable amounts of CD_4 in the decomposition of $(CD_3)_2V.(OBu\text{-}t)_2$ may serve as confirmation of this finding. The formation of Me_4Si and the subsequent reactions can be represented schematically as follows:



The decomposition temperature determines the composition of the final vanadium-containing products. Below 100 °C, a mixture of alkoxides is produced, while at 200 °C the products consist of a mixture of vanadium oxides.

Regardless of the nature of R and R′, the thermolysis of the compounds $(RCH_2)_nTi(NR'_2)_{4-n}$ (n = 1, 2, 3; R = Ph or $SiMe_3$; R′ = Me or Et) leads to the formation of one mole of RH per RCH_2 group. The titanium remains quadrivalent in all cases[75] (Table 12). An ionic mechanism of the decomposition reaction with participation of the β-hydrogen of the NR_2 groups has been proposed[75]:

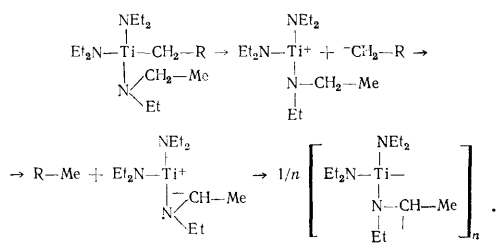


Table 12. Products of the decomposition of $(RCH_2)_n.Ti(NR'_2)_{4-n}$ in the solid state[75].

Compound	Decomp. temp.	RH, moles
$(PhCH_2)_3Ti(NEt_2)$	80	2.2
$(PhCH_2)_2Ti(NEt_2)_2$	80	1.5
$(PhCH_2)Ti(NEt_2)_3$	140	0.8
$(PhCH_2)Ti(NMe_2)_3$	105	0.8
$(Me_3SiCH_2)_2Ti(NEt_2)_2$	90	1.5
$(Me_3SiCH_2)Ti(NMe_2)_3$	90	0.9
$(Me_3SiCH_2)Ti(NEt_2)_3$	130	0.9

Data on the thermolysis of compounds containing bulky amide groups are consistent with the ionic mechanism[76]. The mechanism of the decomposition of the alkylamide compounds is significantly influenced by the presence of the alkylamide group and not by the character of the σ-substituent.

IV. REACTIONS INVOLVING INSERTION IN THE TRANSITION METAL–CARBON σ-BOND

The reactions of the σ-derivatives of transition metals with acids, alcohols, halogens, hydrogen halides, and metal salts have been investigated in fair detail. Numerous investigations established that the above reactions are independent of

the nature of the central atom—the M–C σ-bond is cleaved in all cases. The presence of bulky σ-ligands, such as the adamantyl, norbornyl, and mesityl groups, retards the bond cleavage but the reaction pathway remains unchanged.

An increasing number of studies on the chemistry of organic compounds of transition metals are nowadays devoted to the insertion reactions described by the general formula

$$M-[-R]_n + A \rightarrow M-[-AR]_n .$$

Many such reactions are known, since numerous monatomic and polyatomic species can be inserted in the M–C σ-bond. The reaction pathway is determined, on the one hand, by the nature of the transition metal–carbon σ-bond and, on the other, by the properties of the inserted molecules.

1. Reactions with Oxygen, Sulphur, and Selenium

Virtually all the σ-derivatives of transition metals are sensitive to molecular oxygen. Many compounds undergo spontaneous heating in air. However, if the substance contains bulky substituents, which shield the central atom from coordination with oxygen, it is usually resistant to oxidation. Indeed, Mes_4M and $(adme)_4M$ are not oxidised in air.

Organic compounds of non-transition metals are known to be oxidised via a radical mechanism with formation, depending on the conditions, of peroxides or alkoxides of the corresponding metals. Only preliminary data exist at present concerning the mechanism of the oxidation of organic compounds of transition metals. The oxidation of $(Me_3SiCH_2)_4$.Ti(Zr) or $(PhCH_2)_4$Zr(Hf) takes place at a higher rate at −78 °C. For example, the oxidation of $(PhCH_2)_4Hf$ in toluene for 3 min results in the quantitative formation of $(PhCH_2O)_4Hf$. In the presence of an excess of pyridine the initial rate of oxidation of $(PhCH_2)_4$Zr(Hf) diminishes, one mole of oxygen is then absorbed (at −78 °C), and $(PhCH_2)_2Hf(OCH_2Ph)_2$.Py is formed[97,98]. The authors suggest that organometallic peroxides are formed in the first stage of the oxidation reaction and either rearrange or react with another molecule of the organometallic compound, giving rise ultimately to alkoxides.

The insertion of elementary sulphur and selenium in the transition metal–carbon σ-bond has been described in only two instances. In contrast to the compounds RMgX, whose interaction with S_8 and Se yields the corresponding mercaptans and selenoalcohols, the compounds Cp_2NbR_2 (R = Me or α-thienyl) give rise to niobium(V) complexes and not insertion products on irradiation with ultraviolet light in benzene in the presence of S_8:[99]

$$Cp_2NbR_2 \xrightarrow[C_6H_6]{S_8,h\nu} Cp_2Nb\begin{matrix}R\\ \diagup\\ \diagdown\\ S\end{matrix}\!\!\begin{matrix}\\ \\ \\ S\end{matrix} .$$

An X-ray diffraction study of the complex $Cp_2Nb(S_2)Me$ showed that S_2 is a bidentate ligand and that the Mb–S distances are 2.515 and 2.432 Å.[100]

Analogously to Grignard reagents, a direct insertion of the Se atom in the M–C σ-bond has been observed for Cp_2MMe_2 (M = Zr or Hf). On refluxing with two equivalents of selenium, the derivatives thus produced give rise to a high yield of $Cp_2M(SeMe)_2$.[101]

2. Reactions with Carbon Monoxide

Numerous studies in this field during recent years established the mechanism of the coordination and subsequent insertion of the CO molecule as a function of the central atom and the character of the σ-substituent. The discovery of these features became possible when the cyclopentadienyl compounds $Cp_2M(R)X$, Cp_2TiR, and Cp_2MR_2 (R = Me, Ph, CH_2Ph, or C_6F_5; M = Ti, Zr, Hf, V, Nb, or Ta; X = Cl or OEt) were used[102–108]. It was established that the first stage involves the coordination of the CO molecule to the central atom. The secondary reactions leading to the final product depend on the nature of the central atom.

We shall consider how this situation arises in the few-reactions of compounds of the type R_nM with CO which have been investigated. The $(PhCH_2)_4Ti$ molecule absorbs only two CO molecules. The highest coordination number of titanium(IV) is six, so that only two ligands can be coordinated to the central atom in $(PhCH_2)_4Ti$ [in the analogous reaction of CO with the complex $(PhCH_2)_4Ti.NH(C_6H_{11})_2$, in which titanium-(IV) has a coordination number of 5, only one mole of CO is absorbed]. The infrared spectrum of the solution shows initially absorption bands at 1952 and 1873 cm^{-1}, which are characteristic of the coordinated CO group: subsequently these bands vanish and new bands due to the carbonyl group $\rangle C{=}O$ appear at 1640 and 1635 cm^{-1}. The acyl derivative $(PhCH_2)_2Ti(COCH_2Ph)_2$ was isolated as a result of the reaction. The process is reversible; when the solution is heated, CO is evolved and the initial compound $(PhCH_2)_4Ti$ reformed[109].

In contrast to $(PhCH_2)_4Ti$, the titanium(II) derivative $(PhCH_2)_2Ti.3Et_2O$ reacts slowly with CO in toluene (p_{CO} = 2 atm) at 20 °C and not more than two moles of CO are absorbed irreversibly. It has been established that 0.5 mole of CO is absorbed after 5 h, 1.0 mole after 10 h, and 2.0 moles after 24 h. The slow insertion is complicated by secondary reactions giving rise to a complex range of products[110].

The compound $(PhCH_2)_4Zr$ reacts with CO in decalin at 22 °C. Analysis of the zirconium-containing products demonstrated the presence of the Zr–CO–CH_2Ph, –Zr–O–C–CH_2Ph, and other fragments[111].

The vanadium(IV) and chromium(IV) compounds $(Me_3Si.CH_2)_4M$ and $(iso\text{-}Pr)_4Cr$ do not react with CO at 20 °C under normal pressure owing to the large bulk of the σ-substituents which obscure the central atom and prevent the coordination of the CO. However, at a CO pressure of 50 atm in THF, all the isopropyl groups are displaced from the $(iso\text{-}Pr)_4Cr$ molecule and $Cr(CO)_6$ is formed[27,112].

When the molybdenum complex $ClMo(CH_2SiMe_3)_3.PMe_3$ is acted upon by CO, two Me_3SiCH_2 groups are substituted by carbonyl groups and some of them migrate to a coordinated CO molecule, giving rise to an η^2-coordinated acyl group. The carbonylation product was identified on the basis of X-ray diffraction data as a dimer with hexacoordinate molybdenum $[ClMo(COCH_2SiMe_3)CO_2(PMe_3)]_2$.[58] The complexes $(C_6F_5)_2Co.2PR_3$ (R = Et, n-Bu, or Ph) combine reversibly with one CO molecule to form the pentacoordinate carbonyl complexes $(C_6F_5)_2Co.2PR_3(CO)$. An excess of CO induces the decomposition of the complexes accompanied by the formation of the dimer $[Co(CO)_3.PR_3]_2$.[113] When the dioxane complex is acted upon by CO, the dioxane is displaced and, in the presence of an excess of CO, cobalt is reduced to cobalt(I):[113]

$$(C_6F_5)_2Co\cdot 2diox \xrightarrow[-78°C]{CO} [(C_6F_5)_2Co(CO)_3] \xrightarrow[20°C]{CO} (C_6F_5)Co(CO)_4 .$$

When a stream of CO is passed through a tetrahydrofuran solution of $(C_6F_5)_2Ni.2diox$ for 8–10 h at 20 °C, the colour of the solution changes and the infrared spectra indicates the presence of a coordinated CO group. However, the attempts to isolate the carbonyl complex led only to the decomposition product $(C_6F_5)_2$ [114] (Table 13).

3. Reactions with Carbon Dioxide

Organolithium and organomagnesium compounds, which behave as sources of carbanions, readily react with various electrophiles, particularly with CO_2. This reaction can be formally represented as the insertion of the carbonyl group in the metal–carbon bond. This results in the formation of lithium or magnesium carboxylates, which give rise to the corresponding carboxylic acids after hydrolysis.

Table 13. Products of the reactions of R_nM with CO_2 and CO (p = 1 atm).

Initial compound	Reagent	Reaction conditions: solvent	t, °C	time, h	Reaction products	Yield, %	Refs.
$(PhCH_2)_2Ti\cdot 3Et_2O$	CO_2	THF	20	24	$(PhCH_2CO_2)_2Ti\cdot 3Et_2O$	99	[110]
$(PhCH_2)_4V\cdot 2Et_2O$	CO_2	pentane	0	96	$V(OCOCH_2Ph)_2$	95	[21]
$(PhCH_2)_4V\cdot 2Et_2O$	CO_2	Et_2O	−20	2	$V(OCOCH_2Ph)_3$	99	[21]
$(C_6F_5)_4V\cdot 2Et_2O$	CO_2	THF	20	150	$V(OCOC_6F_5)_3$	95	[21]
$(C_6F_5)_3V.THF$	CO_2	THF	20	150	$V(OCOC_6F_5)_3$	96	[21]
$(Me_2SiCH_2)_3V.THF$	CO_2	THF	−20	3	$V(OCOCH_2SiMe_3)_3$	83	[21]
$Me_2Ni.bipy$	CO_2	benzene	80	15	$Ni(OCOMe)_2\cdot bipy$	90	[117]
$Et_2Ni.bipy$	CO_2	benzene	50	15	$Ni(OCOEt)_2\cdot bipy$	52	[117]
$Et_2Hf[N(SiMe_3)_2]_2$	CO_2	pentane	20	24	$Et_2Hf[OCON(SiMe_3)_2]_2$	90	[78]
$(PhCH_2)_4Ti$	CO	pentane	−50	—[b]	$(PhCH_2)_2Ti(COCH_2Ph)_2$	80	[109]
$(iso\text{-}Pr)_4Cr$	CO	THF	20[a]	—[b]	$Cr(CO)_6$	66	[112]
$ClMo(CH_2SiMe_3)_3\cdot PMe_3$	CO	PE	20	—[b]	$[ClMo(COCH_2SiMe_3)\cdot (CO)_2(PMe_3)]_2$	99	[58]
$(C_6F_5)_2Co\cdot 2diox$	CO	hexane	20	—[b]	$(C_6F_5)Co(CO)_4$	60	[113]

Remarks: [a] p_{CO} = 50 atm; [b] time not indicated.

Systematic studies of the insertion of CO_2 in the transition metal–carbon σ-bond in derivatives of the type R_nM were begun quite recently. It was found that the compound $(PhCH_2)_4M$ (M = Ti or Zr) absorb slowly and irreversibly two moles of CO_2 per gramme-atom of the metal at 20 °C (p_{CO_2} = 13 atm), which is caused, as in the insertion of CO, by the coordinating capacity of Ti(IV) and Zr(IV). The hydrolysis of the reaction products yields in both cases $PhCH_2COOH$ as well as $(PhCH_2)_3COH$ as a result of secondary reactions[5]. The complex $(C_6F_5)_4Ti.2Et_2O$ does not react with CO_2 at 20 °C and p_{CO_2} = 2 atm.[44]

The derivatives R_3Ti (R = CH_2Ph or CH_2SiMe_3) are not carboxylated by gaseous CO_2 in toluene at −70 °C and p_{CO_2} = 1 atm.[21,48] The insertion of CO_2 in the Ti–C_6F_5 bond in $(C_6F_5)_3Ti$ has not been observed either at 20 °C (p_{CO_2} = 2 atm).[48]

It has been observed that, after 24 h at 20 °C (p_{CO_2} = 1 atm), the compound $(PhCH_2)_2Ti.3Et_2O$ absorbs two moles of CO_2 with formation of the complex $(PhCH_2CO_2)_2Ti.3Et_2O$. Analysis of the infrared spectrum showed that the carboxylate group in this complex has the η^1-coordination[110].

Detailed studies have been made of the character of the interaction of CO_2 with a series of vanadium(IV) and vanadium(III) compounds: $(Me_3SiCH_2)_4V$, $R_4V.2THF$ (R = CH_2Ph or C_6F_5), and $R_3V.THF$ (R = CH_2SiMe_3 or C_6F_5).[21] The compounds $(Me_3SiCH_2)_4V$ and $[(Me_3Si)_2CH]_3V$, in which the central atom is shielded, do not absorb CO_2.[21,32] The complexes $(PhCH_2)_4V.2Et_2O$ and $R_3V.THF$ (R = CH_2Ph or $CH_2.SiMe_3$) absorb CO_2 at −20 °C, while $(C_6F_5)_4V.2Et_2O$ and $(C_6F_5)_3V.THF$ react slowly with CO_2 at +20 °C.

Experimental data have shown that at the beginning of the reaction the CO_2 molecule is coordinated to the vanadium atom, which is accompanied by the displacement of the Et_2O or THF ligand species. Subsequently the σ-substituent migrates to the carbon atom with formation of the carboxylate. The multistage insertion of CO_2 in vanadium(IV) and vanadium(III) derivatives as well as the reactions of the carboxylates formed, which behave analogously to the mixed compounds R_nVX_{m-n} examined above, has been investigated[21]. The carboxylation of the test compounds with an excess of gaseous CO_2 leads to the formation of $V(OCOR)_3$. Analysis of the infrared spectra has shown that the carboxylate group in these compounds has the η^2-coordination (Table 13). The reactivity with respect to CO_2 of the remaining σ-derivatives described above in Section II has not been investigated. There are in the literature isolated examples of the insertion of CO_2 in the M–C σ-bonds in metal complexes (M = Mn, Fe, or Ni). For example, after reaction with CO_2 (20 °C, 2 h), $[R_3Mn]^-Li^+$ and $R_3MnMgCl$ give rise to RCO_2H (R = Ph or Mes) in quantitative yields after hydrolysis[115]. The complex $(Me_3P)(H)Fe(CH_2PMe_2)$ reacts with CO_2 in THF at 20 °C and yields an unusual product of insertion in the Fe–C bond[116]. The nickel derivatives $R_2Ni.bipy$ (R = Me or Et) readily absorb two moles of CO_2 with formation of the carboxylates $(RCO_2)_2Ni.bipy$.[117]

Thus the results obtained hitherto demonstrate that the general character of the reactions with CO_2 is the same for the organic compounds R_nM of lithium, magnesium, and transition metals. It is noteworthy that the reactivity of the transition metal–carbon σ-bond depends on the nature and valence of the metal and also on the character of the σ-substituent.

It has been shown in relation to $Et_2Hf[N(SiMe_3)_2]_2$ that, when M–C and M–N bonds are present in the molecule, CO_2 is inserted in the M–N bond with formation of $Et_2Hf[OCON.(SiMe_3)_2]_2$.[78,118]

4. Reactions with Aldehydes and Ketones

The addition of organolithium and organomagnesium compounds to the carbonyl group in aldehydes and ketones is one of the most important reactions in organic synthesis. The study of such reactions involving transition metal complexes is only just beginning.

It has been observed that $(PhCH_2)_4Ti$ readily interacts with one or two equivalents of ketones (acetone, benzophenone), yielding after hydrolysis the corresponding tertiary alcohols; the excess ketones do not react[119]. The reaction of $(PhCH_2)_2.Ti.3Et_2O$ with the above ketones results in the formation of the alkoxides $Ti[OCR_2(CH_2Ph)]_2$ (R = Me or Ph), which do not contain coordinated ether[110].

The reactivity of compounds of the type $R_nTi(OR')_{4-n}$ with respect to carbonyl compounds is lower than that of R_nTi. For example, $(PhCH_2)_2Ti(OME)_2$ does not react with acetone; one refluxing in Et_2O for 7 h, $PhTi(OPr\text{-}iso)_3$ reacts with PhCO to yield 19% of Ph_3COH after hydrolysis. At 20 °C the compound $PhTi(OPr\text{-}iso)_3$ reacts only with aldehydes[66,120,121]. Investigations have shown that the compounds $RTi(OPr\text{-}iso)_3$ (R = Bu or Ph) are more selective in relation to carbonyl compounds than the corresponding organolithium compounds [120–122]. In contrast to $PhTi(OPr\text{-}iso)_3$, $MeTi(OR')_3$ reacts with different ketones[120,123].

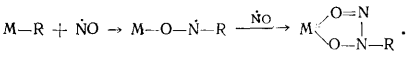
Like $(PhCH_2)_4Ti$, the compound $(PhCH_2)_4V$ reacts only with two moles of acetone, forming $(PhCH_2)_2V[OC(Me)_2CH_2Ph]_2$. It is known that $R_2V(OBu\text{-}t)_2$ derivatives do not react with acetone even on heating[21].

The data obtained for the titanium and vanadium compounds make it possible to put forward a general reaction mechanism. Analogously to organolithium and organomagnesium compounds, in the first stage oxygen is coordinated to the metal.

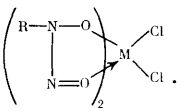
The alkoxy-groups formed are very bulky and tend to associate. These findings indicate the shielding of the central atom, so that coordination to the latter of other ketone molecules becomes virtually impossible. Steric effects are also responsible for the inertness of the compounds $R_2M(OR')_2$ (M = Ti or V) and $PhTi(OPr\text{-}iso)_3$ in relation to ketones. Bulky alkoxy-groups displace the coordinated Et_2O molecules from $(PhCH_2)_2Ti.3Et_2O$ in the alkoxide formation stage.

5. Reactions with Nitric Oxide

The mode of reaction with NO is determined by the nature of NO itself, which is a radical. Reactions with diamagnetic complexes lead to the formation of *N*-alkyl-*N*-nitrosohydroxylaminate derivatives[124]:

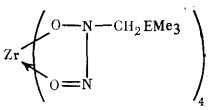


The compounds R_2MCl_2 ($R = CH_2CMe_3$ or CH_2SiMe_3; M = Ti or Zr) absorb four moles of NO in petroleum ether at 0 °C and give rise to octahedral complexes:



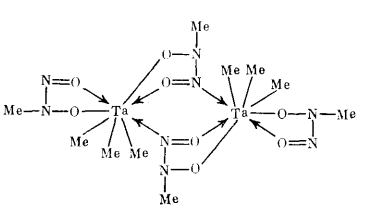
Analysis of the infrared spectra of these complexes indicates the *cis*-disposition of the Cl atoms relative to the metal atom and also the η^2-coordination of the two ON(R)NO groups. The compound $(Me_3CCH_2)_3TiCl$ absorbs six moles of NO, while $(Me_3SiCH_2)_4Ti$ absorbs eight moles of NO. Since titanium forms only hexacoordinate complexes, the ON(R)NO groups in the complexes are probably not equivalent; for example, $Ti[ON(CH_2SiMe_3)NO]_4$ has two chelate and two monodentate groups.

The reaction of $(Me_3ECH_2)_4Zr$ (E = C or Si) with NO results in the formation of monomeric octacoordinate complexes which are stable in air:



The observed difference between the structures of the products obtained from titanium and zirconium compounds is due to the different coordinating capacities of the above metal atoms.

Octacoordinate complexes are formed as a result of the reaction of Me_5Nb or Me_5Ta with NO. However, the nature of the central atom permits the existence of different structures of these metal complexes. It has been found that Me_5Nb gives rise to the monomeric complex $Me_2Nb[ON(Me)NO]_3$ with equivalent chelate ligands. A dimeric complex is formed from Me_5Ta and the following structure has been attributed to it on the basis of infrared and NMR spectra:



The paramagnetic complexes of transition metals with an unpaired electron at the metal atom react with NO to produce oxo-derivatives of the metals and azomethane[124]. The hypothesis that the initial stage in the reactions of paramagnetic complexes with NO involves the coordination of the NO molecule to the transition metal atom has been confirmed by the isolation of the complex $[(Me_3Si)_2CH]_3CrNO$, in which bulky ligands prevent further reactions[32].

---o0o---

It follows from the results of the analysis of the investigations carried out that considerable progress has now been achieved in the chemistry of the thermally stable σ-derivatives of transition metals. Extensive studies of the properties of the compounds R_nM and R_nMX_{m-n} have made a definite contribution to the development of theoretical organoelemental chemistry. The research prosecuted vigorously on these lines gives rise to good prospects for the practical utilisation of the σ-derivatives in metal complex catalysis, in the formation of biologically active preparations, and in the development of new methods for the preparation of protective coatings by the decomposition of organometallic compounds.

REFERENCES

1. F.A.Cotton, Chem.Rev., 1955, **55**, 551.
2. J.Davidson, M.F.Lappert, and R.Pearce, Chem.Rev., 1976, **76**, 219.
3. R.R.Schrock and G.W.Parshall, Chem.Rev., 1976, **76**, 243.
4. G.Wilkinson, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1972, **17**, 377.
5. U.Zucchini, E.Albizzati, and U.Giannini, J.Organometal.Chem., 1971, **26**, 357.
6. J.J.Felten and W.P.Anderson, J.Organometal.Chem., 1972, **36**, 87.
7. V.N.Latyaeva, A.N.Lineva, and V.V.Drobotenko, Trudy Khim.i Khim.Tekhnol.Gor'k.Gos.Univ., 1973(2), 35.
8. G.A.Razuvaev, V.N.Latyaeva, A.N.Lineva, and V.V.Drobotenko, Dokl.Akad.Nauk SSSR, 1973, **208**, 876.
9. G.A.Razuvaev, V.N.Latyaeva, L.I.Vyshinskaja, A.N.Linyova, V.V.Drobotenko, and V.K.Cherkasov, J.Organometal.Chem., 1975, **93**, 113.
10. E.Köhler, K.Jacob, and K.-H.Thiele, Z.anorg.Chem., 1976, **421**, 129.
11. K.Jacob, Z.Chem., 1976, **16**, 196.
12. R.R.Schrock, J.Organometal.Chem., 1976, **122**, 209.
13. W.Mowat, A.J.Shortland, N.J.Hill, and G.Wilkinson, J.Chem.Soc., Dalton Trans., 1973, 770.
14. K.-H.Thiele, A.Russek, R.Opitz, B.Mohai, and W.Brüser, Z.anorg.Chem., 1975, **412**, 11.
15. K.-H.Thiele, R.Opitz, and E.Köhler, Z.anorg.Chem., 1977, **435**, 45.
16. K.-H.Thiele and W.Schafer, Z.anorg.Chem., 1970, **379**, 63.
17. K.Jacob, K.H.Thiele, and V.Dimitrov, Z.anorg.Chem., 1978, **447**, 136.
18. S.I.Beilin, S.B.Gol'shtein, B.A.Dolgoplosk, A.M.Krapivin, E.I.Tinyakova, I.Sh.Guzman, and G.N.Bondarenko, Dokl.Akad.Nauk SSSR, 1977, **235**, 99.

19. L.L.Afinogenova, I.Sh.Guzman, E.N.Tinyakova, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1980, **252**, 1408.
20. K.Jacob, Z.Chem., 1978, **18**, 227.
21. G.A.Razuvaev, V.N.Latyaeva, L.I.Vhysinskaya, and V.V.Drobotenko, J.Organometal.Chem., 1981, **208**, 169.
22. G.A.Razuvaev, V.N.Latyaeva, G.A.Vasil'eva, and L.I.Vyshinskaya, Synth.Inorg.and Metalorg.Chem., 1972, **2**, 33.
23. K.-H.Thiele, A.Röder, and W.Mörke, Z.anorg.Chem., 1978, **441**, 13.
24. P.J.Davidson, M.F.Lappert, and R.Pearce, J.Organometal.Chem., 1973, **57**, 269.
25. W.Mowat and G.Wilkinson, J.Chem.Soc., Dalton Trans., 1973, 1120.
26. M.R.Collier, M.F.Lappert, and P.Pearce, J.Chem.Soc., Dalton Trans., 1973, 445.
27. W.Mowat, A.Shortland, G.Yagupsky, N.J.Hill, M.Yagupsky, and G.Wilkinson, J.Chem.Soc., Dalton Trans., 1972, 533.
28. R.R.Schrock and J.D.Fellmann, J.Amer.Chem.Soc., 1978, **100**, 3359.
29. F.Hug, W.Mowat, A.C.Skapaki, and G.Wilkinson, Chem.Comm., 1971, 1477.
30. C.Santini-Scampucci and J.G.Riess, J.Organometal.Chem., 1980, **187**, 331.
31. D.N.Clark and R.R.Schrock, J.Amer.Chem.Soc., 1978, **100**, 6774.
32. G.K.Barker, M.F.Lappert, and J.A.K.Howard, J.Chem.Soc., Dalton Trans., 1978, 734.
33. I.F.Gavrilenko, N.N.Stefanovskaya, E.I.Tinyakova, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1978, **239**, 1354.
34. W.Seidel and I.Bürger, Z.Chem., 1977, **17**, 185.
35. W.Seidel and G.Kreisel, Z.Chem., 1976, **16**, 115.
36. W.Seidel and I.Bürger, Z.anorg.Chem., 1976, **426**, 155.
37. W.Seidel and I.Bürger, J.Organometal.Chem., 1979, **171**, C45.
38. G.Kreisel, P.Scholz, and W.Seidel, Z.anorg.Chem., 1980, **460**, 51.
39. W.Seidel and G.Kreisel, Z.Chem., 1974, **14**, 25.
40. G.Stolze, J.Organometal.Chem., 1966, **6**, 383.
41. G.Stolze and J.Hähle, J.Organometal.Chem., 1967, **7**. 301.
42. B.Heyn and R.Hoffmann, Z.Chem., 1976, **16**, 195.
43. M.Bochmann, G.Wilkinson, and G.B.Young, J.Chem.Soc., Dalton Trans., 1980, 1879.
44. G.A.Razuvaev, V.N.Latyaeva, G.A.Kilyakova, and G.Ya.Mal'kova, Dokl.Akad.Nauk SSSR, 1970, **191**, 620.
45. V.N.Latyaeva, A.N.Lineva, E.N.Shatalin, and G.A.Razuvaev, Zhur.Obshch.Khim., 1976, **46**, 931.
46. G.A.Razuvaev, V.N.Latyaeva, A.N.Linyova, and N.N.Spiridonova, J.Organometal.Chem., 1972, **46**, C13.
47. E.Kinsella, V.B.Smith, and A.G.Massey, J.Organometal.Chem., 1972, **34**, 181.
48. G.A.Razuvaev, L.I.Vyshinskaya, and S.Ya.Timoshenko, Zhur.Obshch.Khim., 1981(51), 2004.
49. K.S.Boustany, K.Bernauer, and A.Jacot-Guillarmod, Helv.Chim.Acta, 1967, **50**, 1080.
50. I.Sh.Guzman, O.K.Sharaev, E.N.Tinyakova, and B.A.Dolgoplosk., Dokl.Akad.Nauk SSSR, 1973, **208**, 856.
51. F.F.Said and D.G.Tuck, Canad.J.Chem., 1980, **58**, 1673.
52. K.Jacob, Z.Chem., 1974, **14**, 364.
53. S.I.Beilin, G.N.Bondarenko, V.I.Vdovin, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1974, **218**, 1347.
54. J.H.Wengrovius and R.R.Schrock, J.Organometal.Chem., 1981, **205**, 319.
55. S.Moorhouse and E.Wilkinson, J.Chem.Soc., Dalton Trans., 1974, 2187.
56. C.D.Wood, S.J.McLain, and R.R.Schrock, J.Amer.Chem.Soc., 1979, **101**, 3210.
57. R.R.Schrock, L.W.Messerle, C.D.Wood, and L.J.Guggenberg, J.Amer.Chem.Soc., 1978, **100**, 3793.
58. E.Carmona Guzman, G.Wilkinson, R.D.Rogers, W.E.Hunter, M.J.Zaworotco, and J.L.Atwood, J.Chem.Soc., Dalton Trans., 1980, 229.
59. N.A.Venediktova, E.N.Kropacheva, L.A.Smirnova, L.I.Vyshinskaya, and S.Ya.Timoshenko, Vysokomol.Soed., 1980, **22A**, 977.
60. S.I.Beilin, S.B.Gol'shtein, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1976, **229**, 351.
61. W.Seidel and E.Riesenberg, Z.Chem., 1980, **20**, 450.
62. P.R.Sharp, D.Astruc, and R.R.Schrock, J.Organometal.Chem., 1979, **182**, 477.
63. G.A.Razuvaev, L.I.Vyshinskaya, and V.V.Drobotenko, Zhur.Obshch.Khim., 1980, **50**, 1535.
64. G.Jamieson and W.F.Lindell, Inorg.Chim.Acta, 1978, **28**, 113.
65. W.Seidel and G.Kreisel, Z.anorg.Chem., 1977, **435**, 153.
66. D.F.Herman and W.K.Nelson, J.Amer.Chem.Soc., 1953, **75**, 3977.
67. M.D.Rausch and H.B.Cordon, J.Organometal.Chem., 1974, **74**, 85.
68. J.-B.Weber, J.Porret, and A.Jacot-Guillarmod, Helv.Chim.Acta, 1978, **61**, 2949.
69. A.Flamini, D.J.Cole-Hamilton, and G.Wilkinson, J.Chem.Soc., Dalton Trans., 1978, 454.
70. G.A.Razuvaev, V.N.Latyaeva, V.V.Drobotenko, A.N.Lineva, L.I.Vyshinskaya, and V.K.Cherkasov, J.Organometal.Chem., 1977, **131**, 43.
71. G.A.Razuvaev, A.A.Baulin, L.I.Vyshinskaya, S.S.Ivanchev, V.N.Latyaeva, E.V.Babaina, and V.V.Drobotenko, USSR P.738 656 (1978); Byul.Izobret., 1980(21), 34.
72. G.A.Razuvaev, L.I.Vyshinskaya, and A.M.Rabinovich, Zhur.Obshch.Khim., 1980, **50**, 1665.
73. G.A.Razuvaev, V.N.Latyaeva, L.I.Vyshinskaya, and V.V.Drobotenko, Dokl.Akad.Nauk SSSR, 1979, **245**, 1397.
74. H.Burger and H.-J.Neese, J.Organometal.Chem., 1969, **20**, 129.
75. H.Burger and C.Kluess, J.Organometal.Chem., 1976, **108**, 69.
76. D.J.Brauer, H.Burger, and K.Wiegel, J.Organometal.Chem., 1978, **150**, 215.
77. R.A.Andersen, Inorg.Chem., 1979, **18**, 1724.
78. R.A.Andersen, Inorg.Chem., 1979, **18**, 2928.
79. R.A.Anderson, J.Organometal.Chem., 1980, **192**, 189.
80. H.-O.Frohlich and S.Keiser, Z.Chem., 1975, **15**, 30.
81. G.Kreisel and W.Seidel, Z.anorg.Chem., 1981, **478**, 106.
82. H.-O.Fröhlich and U.Märkisch, Z.Chem., 1976, **16**, 82.
83. B.Akermark and A.Ljungqvist, J.Organometal.Chem., 1979, **182**, 47.
84. B.Akermark and A.Ljungqvist, J.Organometal.Chem., 1979, **182**, 59.
85. V.Malatesta, K.U.Ingold, and R.R.Schrock, J.Organometal.Chem., 1978, **152**, C53.

86. I.A.Kershenbaum, L.N.Grebenyak, I.A.Oreshkin, B.A.Dolgoplosk, and E.I.Tinyakova, Dokl.Akad.Nauk SSSR, 1978, **238**, 359.
87. S.A.Smirnov, I.A.Oreshkin, V.G.Zaikin, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1979, **245**, 1400.
88. L.S.Cherezova, V.A.Yakovlev, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1980, **245**, 1400.
89. K.Jacob, K.-H.Thiele, Ch.Keilberg, and R.Kiebuhr, Z.anorg.Chem., 1975, **415**, 109.
90. K.-H.Thiele, E.Köhler, and B.Adler, J.Organometal. Chem., 1973, **50**, 153.
91. G.A.Razuvaev, L.I.Vyshinskaya, V.V.Drobotenko, and V.N.Latyaeva, Dokl.Akad.Nauk SSSR, 1981, **259**, 127.
92. G.A.Razuvaev, V.N.Latyaeva, G.A.Kilyakova, and V.P.Mar'in, Trudy.Khim.i Khim.Tekhnol.Gor'k.Gos. Univ., 1973(4), 35.
93. W.Seidel and G.Kreisel, Z.anorg.Chem., 1977, **435**, 146.
94. V.M.Gorelik, A.Kh.Bagdasar'yan, and B.A.Dolgoplosk, Kinetika i Kataliz, 1979, **20**, 321.
95. V.N.Latyaeva, L.I.Vyshinskaya, and G.A.Kilyakova, Khim.Elementoorg.Soed.Gor'k.Gos.Univ., 1979(7), 71.
96. V.N.Latyaeva, V.V.Drobotenko, A.N.Lineva, L.I.Vyshinskaya, and G.Ya.Mal'kova, Khim.Elementoorg.Soed.Gor'k.Gos.Univ., 1977(5), 100.
97. P.B.Brindley and J.C.Hardson, J.Organometal.Chem., 1974, **65**, 57.
98. P.B.Brindley and M.F.Scotton, J.Chem.Soc., Perkin Trans.II, 1981, 419.
99. Yu.A.Ol'dekop and V.A.Knizhnikov, Izv.Akad.Nauk Beloruss.SSR, Ser.Khim., 1979(5), 78.
100. R.Mercier, J.Douglade, J.Amaudrut, J.Sala-Pala, and J.Guerchals, Acta Cryst., 1980, **36**, 2986.
101. B.Gautheron, G.Tainturier, and Ph.Meunier, J. Organometal.Chem., 1981, **209**, C49.
102. G.Fachinetti, C.Floriani, and H.Stoekli-Evans, J.Chem. Soc., Dalton Trans., 1977, 2297.
103. G.Erker and F.Rosenfeldt, J.Organometal.Chem., 1980, **188**, C1.
104. G.Fachinetti, C.Floriani, and C.Tochi, J.Chem.Soc., Dalton Trans., 1977, 1947.
105. J.A.Marsella, K.G.Moloy, and K.G.Caulton, J.Organometal.Chem., 1980, **201**, 389.
106. M.D.Rausch and W.H.Boon, J.Organometal.Chem., 1977, **141**, 299.
107. A.Dormond and A.Dahchour, J.Organometal.Chem., 1980, **193**, 321.
108. E.J.M.De Boer, L.C.Ten Cate, A.G.J.Staring, and J.H.Teuben, J.Organometal.Chem., 1979, **181**, 61.
109. A.Röder, K.-H.Thiele, G.Paliy, and L.Marko, J. Organometal.Chem., 1980, **199**, C31.
110. G.A.Razuvaev, L.I.Vyshinskaya, G.A.Vasil'eva, A.V.Malysheva, and A.M.Rabinovich, Zhur.Obshch. Khim., 1982, **52**, 1338,
111. C.J.Attridge, R.Dobbe, and S.J.Maddock, J.Organometal.Chem., 1973, **57**, C55,
112. J.Müller and W.Holzinger, Z.Naturforsch., 1978, **33b**, 1309.
113. P.Royo and A.Vazquez, J.Organometal.Chem., 1981, **205**, 223.
114. A.Arcas and P.Royo, Inorg.Chim.Acta, 1978, **31**, 97.
115. G.Friour, G.Cahiez, A.Alexakis, and J.F.Normant, Bull.Soc.chim.France, 1979, 515.
116. H.H.Karsch, Chem.Ber., 1977, **110**, 2213.
117. T.Yamamoto and A.Yamamoto, Chem.Letters, 1978, 615.
118. C.Blandy, R.Choukroom, and D.Gervais, Abstracts of VIII.Int.Conf.on Organometallic Chemistry, Kioto (Japan), 1977, 1A50.
119. J.Causse, R.Tabacchi, and A.Jacot-Guillarmod, Helv. Chim.Acta, 1972, **55**, 1560.
120. M.T.Reetz, R.Steibach, J.Westerman, and R.Peter, Angew.Chem., 1980, **92**, 1044.
121. M.T.Reetz, Angew.Chem., 1982, **94**, 133.
122. B.Weidmann, L.Widler, A.G.Olivero, C.D.Maycock, and D.Seebach, Helv.Chim.Acta, 1981, **64**, 357.
123. G.Blandy and D.Gervais, Inorg.Chim.Acta, 1981, **52**, 79.
124. R.A.Middleton and G.Wilkinson, J.Chem.Soc., Dalton Trans., 1980, 1888.

Institute of Chemistry at
the Gorky State University