Translated from *Uspekhi Khimii*, 52 72-103 (1983) U.D.C. 541.444 + 541.486 + 541.57

Bimetallic Transition Metal Hydride Complexes

G.L.Soloveichik and B.M.Bulychev

The literature data on bimetallic transition metal hydride complexes containing metal-hydrogen bonds and non-transition metal atoms are described systematically and discussed. The principal methods of synthesis of these compounds and ways of stabilising them in the lowest oxidation state by cyclopentadienyl and other electron-donating ligands are considered. The characteristics of the changes in the transition metal-non-transition metal and metal-hydrogen bond types as a function of the electronic configuration and the ligand environment of the metal atoms forming part of the bimetallic hydride complex are noted. The influence of complex formation on the geometrical parameters and spectrochemical characteristics of the metal-hydrogen bond are discussed.
The bibliography includes 191 references.

CONTENTS

I. Introduction 43
II. Classification of bimetallic hydride complexes 43
III. Methods of synthesis of bimetallic hydride complexes 44
IV. Transition metal tetrohydroaluminates 45
V. Biscyclopentadienyl bimetallic hydride complexes 46
VI. Mono- and tris-cyclopentadienyl bimetallic hydride complexes 55
VII. Bimetallic transition metal hydride complexes stabilised by other electron-donating ligands 56

I. INTRODUCTION

The successful preparation of catalytic systems of the Ziegler–Natta (Z–N) type for the hydrogenation and isomerisation reactions of olefins at the beginning of the 1960s led to a rapid increase in the number of publications, mainly patents, devoted to studies and applications of a wide variety of catalysts and cocatalysts for these reactions. At the present time there is no doubt that the active centres of the catalysts contain metal–hydrogen bonds[1–3]. The individual hydrides of Group VIII metals catalysing the hydrogenation of olefins have been studied in fair detail, particularly the rhodium, iridium, and ruthenium compounds. Their structures and the mechanisms of their hydrogenation have been considered in a number of reviews[4–6].

At the same time the reaction mechanism and the structure of the active centres of the classic Z–N system have not so far been finally elucidated.

This is because of the high sensitivity of the systems to oxidation and the consequent considerable scatter and poor reproducibility of the experimental data. Furthermore, several catalytic reactive complexes containing the transition metal (TM) in the lowest oxidation states[3] are as a rule formed in the course of the reaction[7,8].

It has been suggested that the low-valence state is stabilised as a result of the formation of a complex with the cocatalyst—a non-transition metal compound[3,9]. Since usually alkyl or hydride derivatives of aluminium and more rarely lithium alkyls and Grignard reagents are used as the cocatalyst, the active centres in such cases may be bimetallic hydride complexes (BHC) containing both a transition and a non-transition metal.

Complexes of this type have been studied in solutions. A comparatively small number of BHC have been isolated in a pure state and investigated. However, on the basis of the available data one cannot reach any definite conclusion concerning the relation between the structure of the BHC and their catalytic activity because the individual compounds have not as a rule been used in catalytic processes.

In monographs[10] and review articles[4,5] devoted to transition metal hydrides and also the application of the Z–N catalysts in the hydrogenation reactions of unsaturated compounds[2,3] little attention has been devoted to the BHC. Admittedly, recently a detailed review has been published on transition metal hydroborates belonging to the class of BHC.[11] In the present study these comparatively thoroughly investigated compounds will therefore be considered only in relation to the hydroaluminates. It is noteworthy that the M–H–B bridge bond in the transition metal hydroborate is not apparently involved in the catalytic steps and the activity of the compounds $M(BH_4)_nL_m$ or the MX_n–$M'(BH_4)_m$ systems is probably related to the products of their reactions or decomposition with formation of the M–H bond[12].

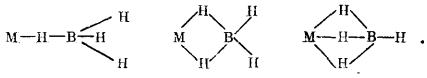
II. CLASSIFICATION OF BIMETALLIC HYDRIDE COMPLEXES

As regards the nature of the metal–hydrogen bond, BHC can be divided into four main types. In the first three the transition metal is linked to the non-transition metal via a hydrogen atom, while in the fourth there is a direct linkage.

The first type includes ionic or similar "inorganic" transition metal tetrahydroaluminates having the general formula $M(AlH_4)_m$, for example, $Y(AlH_4)_3$ [13] and $Nb_2(AlH_4)_5$.[14] The

tetrahydroaluminate group in these compounds consists of a more or less distorted isolated $[AlH_4]^-$ tetrahedron. This type includes also the ionic complexes of Group VIII metals such as $L_nFe^+[AlH_2X_2]^-$.[15]

An increase in the strength of the M–H bond leads to the formation of covalent three-centre bridge bonds. The most striking representative of the second type of BHC are the thoroughly investigated transition metal tetrahydroborates. All the possible varieties of bridges with one[16], two, and three[11] hydrogen atoms are known for these compounds:



Among the aluminium-containing BHC, compounds are known with both single bridges, such as $[Cp(C_5H_4).TiHAlEt_2]_2$ [17] and $Cp_2Ta(H)_2HAlMe_3$,[18] and double bridges, such as $Cp_2TiH_2AlEt_2$ [19] and $Cp_2NbH_2AlH_2$.[20]

A further increase in the strength of the M–H bond together with a weakening of the H–E bond lead to the formation of ionic compounds of the third type containing a transition metal linked to hydrogen atoms in the anion ($Cp_2TiH_2^-MgHal^+$) [21] or the cation $\{[L_mNiH]^+[AlCl_4]^-\}$.[22]

The fourth type includes complexes containing direct (covalent or donor–acceptor) metal–metal bonds, such as, for example, the "inorganic Grignard reagents" $Cp_2Mo(H).MgBr.2THF$ (THF = tetrahydrofuran) [23] or the adducts of Cp_2MoH_2 with halogenoalanes[24].

Naturally the proposed classification of BHC is fairly arbitrary. The real compounds may contain features of two types [for example, the compounds $M(AlH_4)_n$ have the features of both the first and second types] or may contain different types of bonds [for example, there are both terminal and bridging hydrogen atoms in $Cp_2Zr(H)BH_4$].[25]

III. METHODS OF SYNTHESIS OF BIMETALLIC HYDRIDE COMPLEXES

The sources of hydride hydrogen in the formation of the M–H bond in BHC may be individual hydrides of transition and non-transition metals, molecular hydrogen, alkyl groups, etc. The M–H bonds are then formed directly during the synthesis of the BHC or as a result of the substitution of alkyl groups, halogens, etc. in the bimetallic non-hydride complexes by the hydrido-ligand.

1. Reactions Involving Individual Transition Metal Hydrides

Stable binary transition metal hydrides MH_x, where x is usually 0.5–2, with a "metallic" metal–hydrogen bond are inactive in the synthesis of BHC. A directed two- or three-centre M–H bond is formed only in compounds containing stabilising electron-donating ligands (phosphines, carbon monoxide, cyclopentadienyl groups, etc.). However, since phosphine and carbonyl complexes are as a rule coordination-saturated, they are involved only extremely rarely in complex formation reactions with transition metal compounds (see Section VII below).

The cyclopentadienyl compounds Cp_2MH_n, whose interaction with Lewis acids leads to the formation of BHC of various types, constitute an exception.

The reaction of $(Cp_2ZrH_2)_x$ with $AlMe_3$ in benzene gives rise to a compound having the composition $(Cp_2ZrH_2.AlMe_3)_2$,[26] which may contain terminal Al–H bonds in the anion $[AlHMe_3]^-$:

$$(Cp_2ZrH_2)_x + xAlMe_3 \xrightarrow{20°,C_6H_6} \frac{x}{2}[Cp_2ZrH(HAlMe_3)]_2 \quad (1)$$

BHC containing the M–H–Al bridge bond have been obtained by an analogous reaction with participation of Cp_2TaH_3:[8]

$$Cp_2TaH_3 + AlEt_3 \xrightarrow{20°,C_6H_6} Cp_2Ta(H)_2HAlEt_3 \quad (2)$$

Direct M–E bonds are formed on interaction of Lewis acids with compounds of Group VI and VII metals having an unshared pair: Eqn.(3),[27] Eqn.(4),[24–28] and Eqn.(5).[29,30] The reduction of the metal to a lower oxidation state does not then take place:

$$Cp_2WH_2 + AlEt_3 \xrightarrow{20°,C_6H_6} Cp_2W(H)_2AlEt_3 \quad (3)$$

$$Cp_2ReH + BF_3 \xrightarrow{33°,\text{several days}} Cp_2Re(H)BF_3 \quad (4)$$

$$Cp_2MoH_2 + ZnCl_2 \rightarrow Cp_2MoH_2ZnCl_2 \quad (5)$$

Sometimes reactions of this kind are accompanied by the elimination of a hydrocarbon:

$$Cp_2MoH_2 + \text{iso-PrMgBr} \xrightarrow[-C_6H_6]{Et_2O} [Cp_2Mo(H)Mg(\text{iso-Pr})\mu\text{-}Br_2Mg(OEt_2)]_2 \xrightarrow{THF} 2Cp_2Mo(H)MgBr\cdot 2THF + 2\ \text{iso-PrMgBr} \quad (6)$$

A non-transition metal hydride may be involved in such reactions: Eqn.(7),[31] Eqn(8),[32] and Eqn.(9):[24]

$$(Cp_2TiH)_2 + B_2H_6 \xrightarrow{0°,THF} Cp_2TiBH_4 \quad (7)$$

$$(Cp_2ZrH_2)_x + x\,HAl(\text{iso-Bu})_2 \xrightarrow{20°,C_6H_6} Cp_2Zr(H)_2HAl(\text{iso-Bu})_2 \quad (8)$$

$$Cp_2MoH_2 + AlH_{3-n}Cl_n \xrightarrow{C_6H_6} Cp_2Mo(H)_2AlH_{3-n}Cl_n \quad (9)$$

2. Reactions with Participation of Non-Transition Metal Hydrides

This constitutes the most effective and promising methods of synthesis of BHC. Non-transition metal (mainly aluminium) hydrides undergo exchange reactions and addition reactions with transition metal salts or complexes to form BHC. With a rare exception[33], these reactions are carried out in ethyl ether or THF. Transition metals in the highest oxidation states are then usually reduced, for example, Fe^{III} is reduced to Fe^{II} [Eqn.(10)],[34] Ta(V) is reduced to Ta(IV) [Eqn.(11)],[35] and Ti(IV) is reduced to Ti(III) [Eqn.(12)]:[36,37]

$$FeCl_3 + LiAlH_4 \xrightarrow{-80°,Et_2O} Fe(AlH_4)_2\downarrow + H_2 + AlH_3 + LiCl\downarrow \quad (10)$$

$$TaBr_5 + LiAlH_4 \xrightarrow{-80°,Et_2O} [TaH_n(AlH_4)_{4-n}\cdot n\,AlH_3]\downarrow + H_2 + AlH_3 + LiBr \quad (11)$$

$$Cp_2TiCl_2 + LiAlH_4 \xrightarrow{20°,Et_2O} Cp_2TiAlH_4 + AlH_3 + LiCl \quad (12)$$

When the salts of transition metals in the lowest oxidation states are employed, the usual exchange reactions [reactions (13) [38] and (14) [39,40]] take place:

$$Li_2MnBr_4 + LiAlH_4 \xrightarrow{-80°,Et_2O} Mn(AlH_4)_2 + LiBr \quad (13)$$

$$(Cp_2TiCl)_2 + NaAlH_4 \xrightarrow{20°,THF} Cp_2TiH_2AlH_2 + NaCl \quad (14)$$

The 1,1′-methylenebiscyclopentadienyltitanium hydroaluminate $CH_2(C_5H_4)_2TiH_2AlH_2$, which is almost insoluble in ethyl ether and THF, has been obtained in a pure state only via the exchange reaction[41]

$$CH_2(C_5H_4)_2TiBH_4 + LiAlH_4 \rightarrow CH_2(C_5H_4)_2TiAlH_4\downarrow + LiBH_4 \quad (15)$$

Other hydroaluminates, insoluble or only slightly soluble in organic solvents, for example, $Zr(AlH_4)_4$, can also be obtained by this method.

The interaction of $Al(iso\text{-}Bu)_3$ and $AlH(iso\text{-}Bu)_2$ with Cp_2TiCl_2 or Cp_2VCl_2 leads to the formation of $Cp_2TiHClAl(iso\text{-}Bu)_2$ and $Cp_2TiH_2Al(iso\text{-}Bu)_2$ even for the ratios Al/Ti = 2 : 1 and 3 : 1:[42–47]

$$Cp_2Ti(V)Cl_2 + HAl(iso\text{-}Bu)_2 \rightarrow Cp_2Ti(V)H_2Al(iso\text{-}Bu)_2 + H_2 + ClAl(iso\text{-}Bu)_2. \quad (16)$$

It has been suggested that these compounds are formed either owing to the presence of admixtures of hydrides in AlR_3 or as a result of the disproportionation reaction

$$Al(C_2H_5)_3 \rightleftarrows AlH(C_2H_5)_2 + C_2H_4 \quad . \quad (17)$$

$Cp_2TiH_2AlMe_2$ has been obtained in a different way, via the reaction of $(Cp_2TiCl)_2$ with $NaAlH_2Me_2$ in ArH.[48,49]

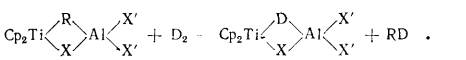
Reactions involving the addition of the aluminium hydride derivatives $AlH_nX_{3-n}.mL$, where $n = 1–3$, $m = 0$ or 1, and X = Hal, to biscyclopentadienyltitanium chloride, which are carried out in inert and, more rarely, solvating solvents, have been described[36,45,50,51]:

$$Cp_2TiX + AlH_nX_{3-n}\cdot L \xrightarrow{Et_2O,\ ArH} Cp_2TiH_nAlX_{4-n}\cdot L \quad . \quad (18)$$

These BHC are formed as intermediates in the interaction of Cp_2TiCl_2 with $LiAlH_4$.[37]

3. Activation of Molecular Hydrogen

It has been noted in a number of studies that the formation reactions of BHC in catalytic systems based on Cp_2TiCl_2 and alkali metal[52] and aluminium[44] alkyls are appreciably accelerated in a hydrogen atmosphere. The role of molecular hydrogen as a source of hydride hydrogen has been confirmed by experiments with deuterium[44] and in the hydrogenation of olefins in the presence of the $(Cp_2TiCl)_2$–$LiAlH_4$ system[53]:



$$+ RD \quad . \quad (19)$$

Reaction (19) can be regarded as the model reaction of the regeneration of the active centre in the catalytic hydrogenation of olefins.

4. The Cleavage of the Metal–Alkyl Bond

The cleavage of the M–Alk bond with formation of the M–H bond and an olefin [reaction (20)] has, with rare exceptions [for example, reactions (21) and (22)], no preparative value in the synthesis of BHC:[54,55]

$$M\text{–}Alk \rightleftarrows M\text{–}H + \text{olefin}; \quad (20)$$

$$(C_{10}H_8)(CpTiH)_2 + Al(C_2H_5)_3 \xrightarrow{C_6H_6} (C_{10}H_8)[CpTi(H)H_2Al(C_2H_5)_2TiCp] + C_2H_4; \quad (21)$$

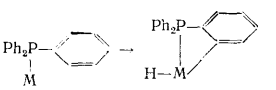
$$Cp_2TiCl_2 + C_2H_5MgCl \rightarrow Cp_2TiH_2^-MgCl^+ + MgCl_2 + C_2H_4 + C_2H_6 \quad . \quad (22)$$

However, reaction (20) plays an important role in catalytic isomerisation, polymerisation, and possibly metathetical reactions of olefins[56,57]. The alkyl groups are the source of hydride hydrogen in these substances[56]. It has been suggested that the $Cp_2TiH_2^-$ anion is formed via a stage involving the formation of the unstable anion $Cp_2TiR_2^-$.[58] Indeed a complex having the composition $[Na(THF)_x]^+[Cp_2TiR_2]^-$ has been obtained recently by the reduction of Cp_2TiR_2 with sodium naphthalide in THF.[59]

5. Transfer of Hydrogen from the Ligands to the Metal Atom

When Cp_2TiCl_2 is reduced with metallic magnesium in the presence of MgI_2 and also by lithium and sodium naphthalides in ether or THF, BHC with a double hydrogen bridge are formed[60–62]. The source of hydride hydrogen is in this instance the C_5H_5 group[61]. The formation of Cp_2TiH_2MgCl has also been noted in the reduction of Cp_2TiCl_2 with metallic magnesium in ethyl ether[58]. The reaction with metallic sodium in THF in the presence of $AlCl_3$ leads to the formation of $Cp_2TiH_2AlCl_2$ in 60% yield[63]. The same compound is formed on reduction of Cp_2TiCl_2 with metallic aluminium in THF.[64]

The reaction involving hydrogen transfer from the ligand is known to lead to the formation of "metallocene" hydrides {the "stable titanocene" $(C_{10}H_8)(CpTiH)_2$ and the "niobocene" $[Cp(C_5H_4)NbH]_2$} and also BHC such as $[Co(C_5H_4)TlHAlEt_2]_2$[17] and $(C_{10}H_8)[(C_5H_4)TiHAlEt_2]_2$.[54] These reactions proceed as a rule at elevated temperatures and lead to the formation of compounds with σ-π-linked cyclopentadienyl rings. The reaction mechanism is in all cases obscure. An analogous reaction has been described for arylphosphine complexes of transition metals[65]:



(23)

6. Reactions with Participation of the Solvent

In the extensive reduction of transition metals the source of hydrogen used for the formation of the M–H bond may also be the solvent, for example, ethyl ether in the reduction of Cp_2TiCl_2 with metallic magnesium [reaction (24)] and in the interaction of LiC_2H_5 with "metastable titanocene" [reaction (25)]:[58]

$$2Cp_2TiCl_2 + 5Mg + 4(C_2H_5)_2O \rightarrow 2Cp_2TiH_2^-MgCl^+ + MgCl_2 + 2Mg(OC_2H_5)_2 + 4C_2H_4; \quad (24)$$

$$(Cp_2Ti)_2 + 4C_2H_5Li + 2(C_2H_5)_2O \rightarrow 2Cp_2TiH_2^-Li^+ + 2LiOC_2H_5 + 5C_2H_4 + C_2H_6 \quad (25)$$

Nor can one rule out the possibility that the solvent "supplies" the hydride hydrogen in the synthesis of $Cp_2TiH_2AlCl_2$ from Cp_2TiCl_2 and Na in the presence of $AlCl_3$ in THF.[63]

IV. TRANSITION METAL TETRAHYDROALUMINATES

Transition metal tetrahydroaluminates without stabilising organic ligands, having the general formula $M(AlH_4)_n$, are known for Cu, Ag, Ce, V, Ti, Zr, Nb, Ta, Mn, Fe, and possibly Co.

The general method of synthesis of these compounds involves the exchange reactions of the salts with $LiAlH_4$ in ethyl ether at low temperatures (between −110° and −80 °C). Since the $M(AlH_4)_n$ are insoluble in ethyl ether, like LiCl, the products investigated in the early studies were mixtures of two substances[66,67]. Pure transition metal tetrahydroaluminates were obtained using MBr_n or the bromide complexes Li_mMBr_{n+m}:

$$Li_mMBr_{n+m} + n\,LiAlH_4 \xrightarrow{\sim 110°,\ Et_2O} M(AlH_4)_n + (n+m)\,LiBr \quad . \quad (26)$$

In certain cases the starting materials were perchlorates[68,69] and tetrahydroborates[70]. Transition metal tetrahydroaluminates are substances insoluble in organic solvents, whose colour varies from yellow to red-brown with increase of the number of *d* electrons. The $M(AlH_4)_n$ are as a rule readily

oxidised and on contact with air ignite spontaneously [$Y(AlH_4)_3$ [13] and tantalum[35] and niobium[14] compounds]. They are vigorously hydrolysed by water with evolution of the entire hydride hydrogen. An exception is the tantalum tetrahydroaluminate $TaH_2(AlH_4)_2$, in which the metal–hydrogen bonds are retained after hydrolysis according to infrared spectroscopy data [ν(M–H) = 1650 cm^{-1}]. The residual hydrogen (three atoms per tantalum atom) is evolved on treatment with alkali[35].

When $NbCl_5$ is made to react with an excess of $LiAlH_4$, tetrahydroaluminates in different oxidation states are formed depending on the temperature. The yellow complex $LiNb_2 \cdot (AlH_4)_7$ was obtained in the range between −120° and −70 °C, being converted into the dark-red $LiNb_2(AlH_4)_5$ on raising the temperature[67]. The reaction at room temperature leads to the formation of the brown niobium(II) complex $LiNb \cdot (AlH_4)_3$.[67,71] Analogous binary compounds are formed also with LiCl.[72] A complex formation reaction with LiBr has likewise been noted for yttrium and ytterbium tetrahydroaluminates[72].

Zirconium tetrahydroaluminate apparently forms anionic complexes too, since a white deposit of this compound dissolves in an excess of zirconium(IV) tetrahydroborate[70]. However, it is noteworthy that the complex-forming atom in this instance can also be the aluminium atom which is known to form complex anions, for example, $[Al(BH_4)_4]^-$.[73]

The decomposition of the majority of the tetrahydroaluminates $M(AlH_4)_n$ begins already at −50° and below. This accounts for the virtually complete lack of data concerning the synthesis of the tetrahydroaluminates of metals such as V, Cr, Au, and Ag as well as data on the chemical and physicochemical properties of other compounds. The relatively stable tantalum and yttrium tetrahydroaluminates are an exception. The thermal stability increases consistently on passing from the First to the Third Series of transition elements (within a single Group), for example, Ti < Zr and Nb < Ta, although there is no explicit regularity on passing from Group to Group. One can only note that the stability of the tetrahydroaluminates varies in parallel with the thermal stability of the corresponding tetrahydroborates and that its maximum corresponds to Groups I–V.

The use of differential thermal analysis (DTA) in combination with gas-volumetric measurements made it possible to determine the mechanisms of the thermolysis of certain tetrahydroaluminates. The instances described in the literature can be combined in four groups.

1. The reduction of the metal to the lowest oxidation states with retention of the metal–tetrahydroaluminate group bond:

$$M^n(AlH_4)_n \rightarrow M^{n-m}(AlH_4)_{n-m} + m\,AlH_3 + \frac{m}{2}\,H_2 \quad (27)$$

Examples are provided by the reduction of Nb(V) to Nb(III) [14] or Nb(II).[71] It has also been suggested that the synthesis of iron(II) and tantalum(IV) tetrahydroaluminates proceeds via a stage involving the formation of the unstable $Fe(AlH_4)_3$ [34] and $Ta(AlH_4)_5$.[35,66,67]

2. The decomposition to the free metal and aluminium hydride is most frequently encountered:

$$M(AlH_4)_n \rightarrow M + n\,AlH_3 + \frac{n}{2}\,H_2 \quad (28)$$

Certain niobium tetrahydroaluminates[67,71], $AgAlH_4$,[68] $Fe(AlH_4)_2$,[74] and possibly $Zr(AlH_4)_4$ [70] decompose in this way.

3. The decomposition to the free transition metal and aluminium has been observed for $Ce(AlH_4)_3$,[75] $Mn(AlH_4)_2$, $Co(AlH_4)_2$,[38] and $AgAlH_4$.[69] However, it is known that thoroughly dispersed transition metal powders catalyse the decomposition of aluminium hydride:

$$M(AlH_4)_n \rightarrow M + n\,Al + 2n\,H_2 \quad (29)$$

It is therefore extremely likely that reaction (29) proceeds via a stage involving the formation of AlH_3, which is unstable under the given conditions, and is a special case of reaction (28).

4. The decomposition to the transition metal hydride and aluminium hydride, which takes place without a change in the valence state of the transition metal, has been observed for tantalum [Eqn.(30)] [35] and copper[38] tetrahydroaluminates:

$$Ta(AlH_4)_n \rightarrow TaH_2(AlH_4)_2 + 2AlH_3 \quad (30)$$

The individuality of $CuAlH_4$ has been confirmed by the synthesis from it of an Na_3AlH_6 analogue—copper(I) hexahydroaluminate Cu_3AlH_6—by the low-temperature (−40 °C) treatment of the tetrahydroaluminate with THF.[76]

There are no literature data concerning the direct or indirect determination of the structures of transition metal tetrahydroaluminates. The only physicochemical method used in the study of these compounds is infrared spectroscopy, but the data thus obtained are very scanty. This is evidently associated with the considerable difficulties in the low-temperature measurement of the spectrum. The infrared spectra of the transition metal tetrahydroaluminates contain absorption bands in the range 1500–1850 cm^{-1} which can be assigned to the stretching vibrations of the terminal Al–H bonds. The wave numbers ν for these vibrations in $Nb_2(AlH_4)_5$ (1500 cm^{-1}) [72] (1850 cm^{-1}),[67] $Ti(AlH_4)_4$ (1615 cm^{-1}),[77] $TaH_2(AlH_4)_2$ (1600 cm^{-1}), $Fe(AlH_4)_2$ (1690 cm^{-1}), $Y(AlH_4)_3$ (1840 cm^{-1}), and $Yb(AlH_4)_2$ (1800 cm^{-1}) [72] are close to the values of ν(Al–H) for ionic lithium (1780 cm^{-1}), sodium (1680 cm^{-1}), tetramethylammonium (1660 cm^{-1}),[78] and magnesium (1850 cm^{-1}) [79] tetrahydroaluminates.

Bearing in mind the physical and spectroscopic characteristics of the transition metal tetrahydroaluminates $M(AlH_4)_n$, one can assume that, in contrast to the corresponding tetrahydroborates, these are compounds with predominantly ionic M–AlH_4 bonds and slightly distorted tetrahedral anions $[AlH_4]^-$, i.e. apparently have structures similar to those of alkali and alkaline earth metal tetrahydroaluminates.

V. BISCYCLOPENTADIENYL BIMETALLIC HYDRIDE COMPLEXES

The biscyclopentadienyl complexes of transition metals, which can be regarded as products of the addition of transition metal biscyclopentadienyl hydrides[80,81] to Lewis acids or bases are most interesting from the theoretical and practical points of view.

Two types of transition metal biscyclopentadienyl hydride derivatives have been described in the literature: the biscyclopentadienyl hydrides proper with the general formula $(\eta^5\text{-}C_6H_5)_2MH_n$ and the so-called "metallocene hydrides" in which the metal–hydrogen bond is formed as a result of a rearrangement in an unstable "metallocene" Cp_2M with transfer of a hydrogen atom from the Cp ring to the metal atom.

According to quantum-chemical calculations on Cp_2ML_n molecules, where n = 1–3,[82–85] the metal atom in the Cp_2M fragment with inclined rings has three hybrid orbitals, used in the formation of bonds with ligands and located in a plane with yz symmetry.

The 18 electron rule holds for the majority of the compounds investigated[85].

1. Group IVA

BHC of the first three types are known for the elements of the titanium subgroup. The greatest number of compounds have been described for titanium owing to the vigorous

studies of the Cp_2TiCl_2—reductant systems with catalytic activity in the fixation of molecular nitrogen and the polymerisation and hydrogenation of olefins. However, one should note that in the vast majority of cases individual compounds were not isolated and they were identified solely by indirect methods, mainly by EPR. Only recently have studies been published in which these substances and systems have been investigated by other physicochemical methods.

Thus it has been shown[39,40] that the interaction of $(Cp_2TiCl)_2$ with $NaAlH_4$ in THF leads to the formation of Cp_2TiAlH_4 [Eqn.(14)]. Indeed, according to calorimetric titration (CT) data, this reaction proceeds in a single stage, whose heat is 140 kJ mol^{-1}, terminates following the attainment of the ratio Al : Ti = 1 : 1,[86] and differs from the analogous reaction involving $LiBH_4$ [reaction (31)], which leads to the formation of a complex with the ratio B : Ti = 2 : 1:[87]

$$Cp_2TiCl + LiBH_4 \xrightarrow{Et_2O} LiCl + Cp_2TiBH_4 \underset{-LiBH_4}{\overset{LiBH_4}{\rightleftarrows}} Li[Cp_2Ti(BH_4)_2] \quad . \qquad (31)$$

However, in a study of the catalytic properties of the $(Cp_2TiHal)_2$–$LiAlH_4$ system[53] it was established that the reaction results also in the formation of a catalytically active unstable BHC having the composition $(Cp_2Ti)_2AlH_4Cl$, which is not manifested on the CT curves.

The reaction of $(Cp_2TiCl)_2$ with the chloroalanes AlH_nCl_{3-n} [Eqn.(18)], proceeds according to CT data, with a heat change of 171 kJ mol^{-1} for n = 3 and 92 kJ mol^{-1} for n = 2.[36] In the latter case the reaction proceeds in two stages and terminates for the ratio Al : Ti = 2 : 1 with formation of the unstable complex $Cp_2TiH_2AlCl_2.AlH_2Cl$.[51] The study of the interaction in the $(Cp_2TiCl)_2$–AlH_2Cl system by dielectrometric titration[36,51] showed that $Cp_2TiH_2AlCl(H)$ is formed also via an intermediate stage involving the formation of an unusual conducting compound with the ratio Al : Ti = 1 : 3.

Analogous complexes, also detected by the CT method, exist likewise in the $(Cp_2TiCl)_2$–$AlH_nCl_{3-n}.L$ systems with n = 0 and 1.[88] The heats of reaction (32) are 58.5 kJ mol^{-1} for n = 0 and 44.9 kJ mol^{-1} for n = 1:

$$3Cp_2TiCl + AlH_nCl_{3-n}\cdot L \xrightarrow{C_6H_6} (Cp_2Ti)_3AlH_nCl_{6-n},\ n = 0, 1 \quad . \qquad (32)$$

Since the dipole moments of these complexes are close to zero[88], the latter apparently have symmetrical structures with a hexacoordinate aluminium atom in the centre of an octahedron, i.e. they resemble the structures of the known complexes of Cp_2TiCl with zinc, beryllium[89,90], and manganese[91] chlorides having the composition $(Cp_2Ti)_2M'Cl_4$. The proposed model has been confirmed by EPR [64,88] and infrared spectroscopic[50] data. Although further interaction of $(Cp_2Ti)_3AlH_n.Cl_{6-n}$ (n = 0 and 1) with $AlH_nCl_{3-n}.L$ does take place, it does not entail a heat change[88]. The EPR signal characteristic of the BHC $Cp_2TiH_2AlCl_2$ gradually appears in reaction (32) with an excess of dichloroalane in solution[51,88], i.e. a reaction analogous to reaction (33) takes place[42,43]:

$$Cp_2TiCl_2AlR_2 \underset{-ClAlR_2}{\overset{+HAlR_2}{\rightleftarrows}} Cp_2TiCl(H)AlR \underset{-ClAlR_2}{\overset{+HAlR_2}{\rightleftarrows}} Cp_2TiH_2AlR_2 \quad . \qquad (33)$$

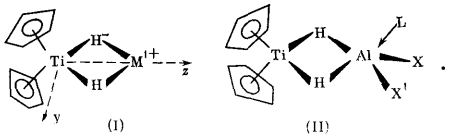
Solutions of the BHC Cp_2TiH_2M', where M' = Li, Na, MgHal, or AlX_2 have the intense violet colour characteristic also of other titanium(III) compounds containing two hydrogen bridges in the molecule—$(Cp_2TiH)_2$ [31] and $Cp_2TiH_2BH_2$.[92] In contrast to the halide and alkyl bridges, the hydride bridges are not decomposed by Lewis bases, which indicates their high strength. This is also confirmed by the displacement of the equilibrium in reaction (33) to the right even in the presence of a 50–100-fold excess of AlR_3 [42] and by direct thermochemical measurements.[37,51,86,88] The most informative method for the study of the paramagnetic BHC of titanium(III), vanadium(IV), iron(I), etc. in solution is EPR. The EPR spectra of BHC with the mixed bridges  are doublets as a consequence of the splitting by a single ^1H nucleus (J = 1/2) with a hyperfine coupling constant (HFC) a_H = 3.5–9.1 G (Table 1). The hyperfine structure (HFS) of the spectra of BHC with a double hydrogen bridge is due to the interaction of the unpaired electron with two equivalent hydrogen nuclei, which gives rise to the splitting of the spectral lines into a triplet in which the intensity ratios are 1 : 2 : 1 (observed, for example, in the spectra of magnesium-containing BHC [21,49,52,60,61]), and with the magnetic nucleus of the non-transition metal. The fundamental motif in the EPR spectrum is then a quartet for the lithium- and sodium-containing compounds ($J_{^7Li} = J_{^{23}Na}$ = 3/2) [40,52,58,60,95] and a sextet for the hydroaluminate complexes Cp_2TiH_2AlXX' ($J_{^{27}Al}$ = 5/2). The form of the spectrum is determined by the ratio of the HFC constants a_H and a'_M. In certain cases it is impossible to resolve the HFS of the spectrum despite the presence of hydrogen bridges, established by independent methods, for example, for the BHC with tetrahydroborate groups[53], $CH_2(C_5H_4)_2TiH_2AlH_2$,[41] and $(Cp_2Ti)_2AlH_4Cl$.[99] In the last case this is attributed to an intramolecular exchange interaction[99].

The correctness of the interpretation of the EPR spectrum can be readily (in most cases) checked by substituting the hydride hydrogen by deuterium. An increase in the number of components (J_{2D} = 1) [21,61] is then observed for the sodium- and magnesium-containing BHC of titanium(III) [for example, when $(C_5H_5)_2TiCl_2$ is replaced by $(C_5D_5)_2TiCl_2$, the reduction with sodionaphthalene gives rise to a 20-component multiplet instead of the 11-component multiplet[61]]. On the other hand, the HFS of Cp_2TiD_2AlXX' due to the nuclei is usually unresolved and the EPR spectrum shows a well-resolved sextet[39,51] (Table 1).

In some cases, it has proved possible to resolve the super-HFS of the EPR spectrum of Cp_2TiH_2M' due to the protons of the C_5H_5 groups (a_{HCp} = 0.2–0.6 G) and also the ^{47}Ti(J = 5/2) and ^{49}Ti(J = 7/2) nuclei, manifested as "satellites" at the edges of the spectrum.

The form and parameters of the EPR spectra of the isotypical BHC in inert and solvating solvents differ only slightly. Since the Lewis base is not removed on crystallisation of the BHC, there is no doubt that the latter are solvated also in solutions. One can therefore postulate that the molecules of the solvating solvent are not linked to the Ti atoms but are coordinated to the Al atom.

It follows from the data presented that all the BHC Cp_2TiH_2M', where M' = Li, Na, MgHal, or AlX_2, have in solution a structure of type (I) and (II) with two bridging H atoms occupying two equivalent orbitals of the Ti atom:



(I) (II)

The non-transition metal atoms lie on the z axis of the Cp_2Ti fragment. The question of the orientation of the orbital occupied by the unpaired electron (on the z axis[40] or at right angles to it, as for the orbital with the unshared electron pair[100]) remains open.

Table 1. Parameters of the EPR spectra of bimetallic cyclopentadienyltitanium complexes.

Compound	Method of synthesis	Solvent	Factor	Form of signal (intensity)	a_H, G	$a_{M'}$, G	a_{Tl}, G	a_{HCp}, G	References
$Cp_2TiCl \cdot C_4H_8O$		THF	1,979	Singlet	—	—	—	—	[52]
$Cp_2TiCl_2Li(Na)$	I	Toluene	1,977	ditto	—	—	—	—	[52]
Cp_2TiCl_2MgBr	I	Et_2O	1,977	»	—	—	—	—	[52]
$Cp_2TiClBCl_2$	—	C_6H_6	1,975	Quartet (1:1:1:1)	—	5.8	—	—	[93]
$Cp_2TiCl_2AlCl_2$	I	C_6H_6	1,975	Sectet (1:1:1:1:1:1)	—	6.7	3.8	—	[47]
$CpTi(Cl_2AlCl_2)_2$	—	C_6H_6	1,972	11 Components	—	5.7	—	—	[94]
$(Cp_2Ti)_3AlCl_3$	—	C_6H_6	1,973	Sextet (1:1:1:1:1:1)	—	7.0	—	—	[64]
$Cp_2TiCl_2AlClMe$	I	C_6H_6	1,975	Unresolved sextet	—	3.7	—	—	[47]
$Cp_2TiCl_2AlClEt$	I	C_6H_6	1,975	ditto	—	3.2	—	—	[46, 47]
$Cp_2TiCl_2 \cdot AlEt_2$	I	C_6H_6	1,976	»	—	1.8	—	—	[47, 59]
Cp_2TiCl_2AlClH	IV	Oct-1-ene	1,979	Sextet	—	4.0	—	—	[33]
$Cp_2TiH \cdot C_4H_8O$	II	THF		Doublet	11.6	—	—	—	[31]
$Cp_2TiHClLi$	II	Toluene	1,983	ditto	7.0	—	—	—	[52]
$Cp_2TiHClNa$	II	THF	1,983	»	9.1	—	—	—	[52]
$Cp_2TiHClMgBr$	II	Et_2O	1,984	»	3.6	—	—	—	[52]
$Cp_2TiHClAlEt_2$	I, II	Toluene	1,985	ditto	6.3	—	—	—	[43, 44]
Cp_2TiH_2Li	II	Et_2O	1,992	Multiplet	9.5	2.9	—	—	[52, 95]
Cp_2TiH_2Li	I	Et_2O	1,992	Triplet	8	—	—	—	[58]
Cp_2TiH_2Li	III	THF	1,994	Triplet of quartets	9.8	2.3	—	0.27	[60]
Cp_2TiH_2Na	II	THF	1,993	Multiplet	10.1	6.9	—	—	[52]
Cp_2TiH_2Na	III	THF	1,994	»	9.8	6.7	7.2	—	[40, 60]
Cp_2TiH_2MgBr	I, II	Et_2O	1,993	Triplet (1:2:1)	7.8—8.1	—	7.4	0.39	[21, 52, 40]
Cp_2TiH_2MgI	III	THF	1,994	ditto	7.9	—	—	—	[61]
Cp_2TiD_2MgBr	I	Et_2O	1,993	Quintet (1:2:3:2:1)	2.4	—	—	—	[21]
$Cp_2TiH_2AlMe_2$	IV	Toluene	1,992	Multiplet	4.65	6.9	—	0.3	[48, 49]
$Cp_2TiH_2AlEt_2$	I	»	1,987	Octet (1:3:4:4:4:4:3:1)	3.9	3.9	—	41	[47]
$Cp_2TiH_2Al(iso\text{-}Bu)_2$	IV	»	1,988	ditto	4	4	—	—	[42, 43]
$Cp_2TiH_2AlH_2$	IV	THF Et_2O	1,991	«	5.5	5.5	4.0	0.48	[39, 40]
$CH_2(C_5H_4)_2TiH_2AlH_2$	V	Et_2O	1,989	Singlet					
Cp_2TiH_2AlHBr	IV	Et_2O	1,989	13-Component multiplet (1:2:2:2:2:2:2:2:2:2:2:2:1)	— 3.8	— 7.6	— —	— —	[41] [51]
$(Cp_2TiH_2AlHCl)_2$	IV	Et_2O	1,989	17-Component multiplet	6.5 29.5	3.5	—	—	[37, 51, 96]
$Cp_2TiH_2AlCl_2$	III	THF	1,993	Sextet of triplets	3.1	10.8	—	0.57	[63, 64]
$Cp_2TiH_2AlCl_2$	IV	2-Methyl-THF Et_2O	1,992	ditto »	3.0 3.3	10.5 10.1	5.4 —	0.50 —	[40] [51]
$Cp_2TiH_2AlBr_2$	IV	Et_2O		»	3.4	10.0	—	—	[51]
$(Cp_2Ti)_2AlH_4Cl$	IV	Et_2O	1,989	Singlet	—	—	—	—	[99]
$Cp(Cl)TiH_2MgI$	III	THF	1,994	Triplet (1:2:1)	8.0	—	—	—	[53]
$[Cp_2VH_2AlEt_2]^+$	I	Toluene	1,990	Octet of octets	3.3	3.3	65	—	[47]
$Cp_2V(Cl)Cl_2AlCl_2$	I	CH_2Cl_2	1,968	Octet	—	—	73.9	—	[97]
$Cp_2V(H)Cl_2AlEt_2$	I	Pentane	1,996	Octet of doublets	5.7	—	41.1	1.6	[98]

It has also been suggested[63] that the TiH_2Al bridge may be asymmetric, as in the molybdenum complexes $[Cp_2MoH_2CuI]_2$.[101] The greatest strength of the hydride bridges compared with other types of bonding is consistent with the increase of the spin density of the unpaired electron at the aluminium atom in the sequence $Cp_2TiCl_2AlR_2 < Cp_2TiHClAlR_2 < Cp_2TiH_2 \cdot AlR_2$.[43,46,47] The amount of ionic character of the compounds increases in the sequence $M' = AlH_2 < AlCl_2 < MgBr < Li < Na$, which should apparently lead to an increase of the H–Ti–H angle[40].

One must note that the successive replacement of the terminal atoms in $Cp_2TiX_2AlX'_2$ by more electron-accepting ligands leads to a linear increase of the HFC constants a_{Al} and to a decrease of a_H for the BHC, the constants being linked by the simple relations $a_H = a_{Al}$ for $X = X' = H$,[38,39,51] Et,[44] or iso-Bu,[43] $a_H = \frac{2}{3}a_{Al}$ for $X' = X = Me$,[48,49] $a_H = \frac{1}{2}a_{Al}$ for $X = H$ and $X' = Br$,[51] and $a_H = \frac{1}{3}a_{Al}$ for $X = X' = Cl$[49,58,90] or Br.[51] The linear variation of properties such as the dipole moment μ and the standard enthalpy of formation ΔH_f^0 with increasing n was noted previously for $AlH_nCl_{3-n} \cdot L$,[102,103] where $n = 0$ and 3 and $L = NR_3$, Et_2O or THF.

Very few BHC of this type have been isolated in a pure state, although the alkyl derivatives $Cp_2TiX_2AlR_2$, where $X = Cl$ or Me,[104] and the complexes $Cp_2LnR_2AlR_2$ with similar properties, where Ln = Y, Yb, Sc, or Ho, are known[105]. The isolation of $Cp_2TiH_2Al(iso\text{-}Bu)_2$ in the form of a red-violet oily substance[40] has been reported but none of its characteristics are quoted in the above communication.

When an excess of $AlEt_3$ was allowed to act on Cp_2TiCl_2 [104,106] or on Cp_2TiPh_2 and Cp_2TiCl,[17] a red diamagnetic substance was obtained, melting without decomposition at 169–191 °C and readily soluble in water and hydrocarbons. It has been established by X-ray diffraction that in this compound the titanium and aluminium atoms are linked by hydrogen bridges and the compound is described by the formula $[Cp(C_5H_4) \cdot TiHAlEt_2]_2$.[17] A further two compounds are formed on

treating the "stable titanocene" with triethylaluminium. BHC with the compositions $[(CpTi)_2H.(H_2AlEt_2)](C_{10}H_8)$ and $[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8)$ crystallise at 20° and 100 °C respectively[54]. Analogous compounds are also formed when $AlEt_3$ is replaced by $AlMe_3$.[107]

"Zirconocene" reacts in a more complex manner and the composition of the products of the addition of $AlEt_3$ to it has not therefore been established[107].

The structures of the BHC considered (Fig.1) are derivatives of two types of structures: the structure of "niobocene" containing π,σ-linked $\eta^5:\eta^1$-C_5H_4 groups (III) and the structure of "titanocene" containing the fulvalene ligand $\eta^5:\eta^5$-$C_{10}H_8$ (V). In the BHC (IV) the features of both types of structures are observed. The close relation between "titanocene" and the BHC obtained from it is also indicated by the finding that they are formed with a high yield on treating compounds (V) with an equivalent of water[54]. The Ti–Ti distance in these compounds (2.91–3.37 Å) is significantly greater than the sum of the covalent radii (2.72 Å), which indicates the absence of a direct metal–metal bond [with the possible exception of compounds (IV)]. Consequently, the titanium in these compounds is in the +3 oxidation state. The diamagnetism of the BHC considered is evidently of the same type as in "titanocene" and its derivatives[108]. The Al–C and Ti–C distances are close to the sums of the covalent radii (1.95 Å and 2.13 Å), i.e. the Ti–C_{ring}–Al bond can apparently be described as a three-centre bond analogous to, for example, the Al–C–Al bond in Al_2Me_6.

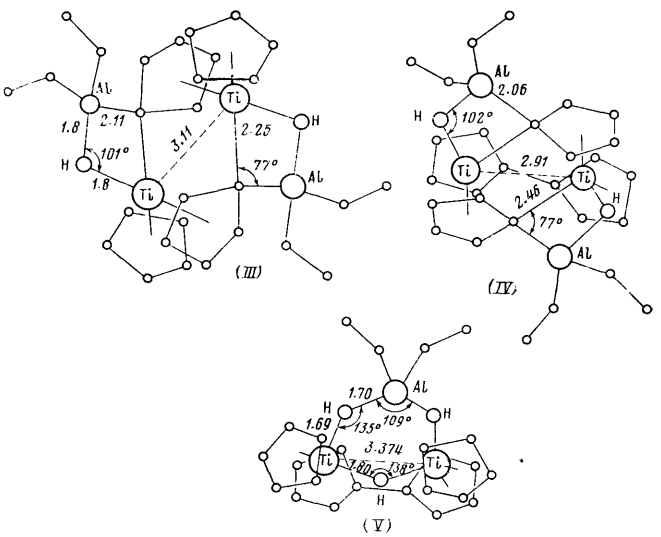
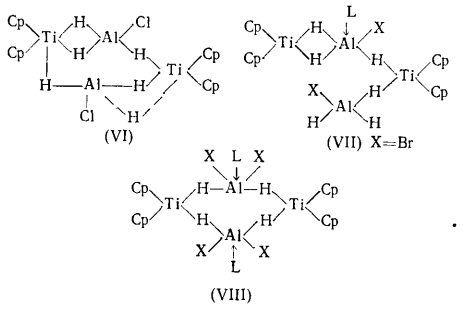


Figure 1. The structures of the bimetallic hydride complexes $[Cp(C_5H_4)TiHAlEt_2]_2$ (III), $(C_{10}H_8)[(C_5H_4)TiHAlEt_2]_2$ (IV), and $(C_{10}H_8)[Cp_2Ti_2(H)(H_2AlEt_2)]$ (V) according to X-ray diffraction data[17,54].

The ^1H NMR data for these compounds agree well with the results of X-ray diffraction analysis (Fig.1). The chemical shift of the protons in the Ti–H–Al bridge is in the range 16.6τ–21.6τ, whereas the chemical shift of the protons in the homonuclear Ti–H–Ti bridge is significantly greater and equal to 31.8τ.[17,54]

The interaction of zinc aryls and alkyls with titanium(IV) biscyclopentadienylalkyls (or the corresponding aryls) and the "metastable titanocene" leads to the formation of the diamagnetic complexes $(C_{10}H_8)(C_5H_4)(C_5H_3R)Ti_2(H)(R')Zn$, where R = H or Ph and R′ = Ph or Me.[109] The presence of the metal–hydrogen bond is confirmed by the formation of HD in the reaction with DCl, although the ν(Ti–H) bands were not observed in the infrared spectra. Structural formulae incorporating bridge or terminal Ti–H and Ti–R bonds and a dicoordinate zinc atom have been proposed for these compounds[109]. We believe that these formulae are unlikely bearing in mind the fact that the compounds are non-solvated. The "stable titanocene", which has two bridging hydrogen atoms[110], decomposes $ZnPh_2$ to metallic zinc and benzene, evidently as a result of the decrease of the stability of the complex on passing from the alkyl hydride to zinc hydride[109].

When the complexes $Cp_2TiAlH_nHal_{4-n}.L$ (n = 2–4, L = NEt_3 or OEt_2) are isolated from solutions, rearrangements take place and are in some cases accompanied by the loss of hydrogen (n = 4).[104] The structure (II) persists apparently only for $Cp_2TiH_2AlHal_2.NEt_3$.[111] The compounds obtained contain 0.5 or 1 (n = 2) mole of a Lewis base per gram atom of titanium and are paramagnetic intensely coloured substances moderately soluble in ethyl ether and benzene and extremely sensitive to oxidation and hydrolysis[111,112]. Infrared spectroscopic study of these compounds revealed the presence of three groups of ν(M–H) absorption bands, one of which was assigned to the vibrations of the terminal Al–H bonds (1750–1900 cm^{-1}) and the other two to vibrations of different types of hydrogen bridges, apparently the double TiH_2Al bridges (1150–1260 cm^{-1}) and the single TiHal bridges (1350–1500 cm^{-1}).[111] The halogen atoms are in all cases terminal[111]. The tendency towards rearrangements diminishes with decrease of n, on replacement of Cl by Br and of OEt_2 by NEt_3, and also on reducing the temperature of the synthesis. $Cp_2TiAlH_3.0.5OEt_2$ apparently contains $\eta^1:\eta^5$-C_5H_4 groups and its structure resembles structure (III). The structural formulae (VI)–(VIII) have been proposed[111] for the compounds $Cp_2TiAlH_3.OEt_2$ and $Cp_2TiAlH_2Hal.OEt_2$ on the basis of EPR and infrared spectroscopic data[51,111], as well as CT data[37,51]. The authors[111] do not rule out the possibility of the dimerisation of compounds (VI)–(VIII) via bridging $\eta^5:\eta^1$-C_5H_4 groups, as in the study of Tebbe and Guggenberger[17]:



On crystallisation of $Cp_2TiAlH_nCl_{4-n}.L$ with n = 0 and 1, only Ti : Al = 3 : 1 complexes with chloride bridges mixed with the solvates $AlCl_3.L$ (n = 0) or complexes of unknown composition with AlHCl.L (n = 1) were detected in the solid phase by infrared spectroscopy[89]. The compounds $Cp_2TiH_{2-n}.AlX_{2+n}$ are formed as intermediates also in the more complex reaction involving the reduction of Cp_2TiCl_2 by lithium tetrahydroaluminate[37]. According to EPR and CT data, the reaction then proceeds via a series of intermediate stages[34–37]

and terminates with formation of the unstable compound $Cp_2TiH_2.AlH_2.AlH_3$, which decomposes in accordance with Eqn.(38):

$$Cp_2TiCl_2 + LiAlH_4 \rightarrow [Cp_2TiH_2AlCl_2 \cdot Cp_2TiCl] + LiCl + H_2 \; ; \quad (34)$$

$$Cp_2TiH_2AlCl_2Cp_2TiCl + LiAlH_4 \rightarrow [Cp_2TiH_2AlH(Cl)]_2 \; ; \quad (35)$$

$$[Cp_2TiH_2AlHCl]_2 + LiAlH_4 \rightarrow [Cp_2TiH_2]_2\,Al_2H_3Cl + AlH_3 + LiCl \; ; \quad (36)$$

$$[Cp_2TiH_2]_2\,Al_2H_3Cl + AlH_3 + LiAlH_4 \rightarrow 2Cp_2TiH_2AlH_2 \cdot AlH_3 + LiCl \; ; \quad (37)$$

$$Cp_2TiH_2AlH_2 \cdot AlH_3 \rightarrow Cp_2TiH_2AlH_2 + Al + \tfrac{3}{2}H_2 \; . \quad (38)$$

Isagawa et al.[113] believe that the final product of these reactions is the complex $Cp_2Ti(AlH_3)_2$, but they do not take into account the instability of the entire system with respect to decomposition reaction and $Cp_2Ti(AlH_3)_2$ can therefore be regarded also as a partly decomposed form of $Cp_2TiH_2AlH_2.AlH_3$.

In contrast to the titanium compounds, the BHC of zirconium(IV) and hafnium(IV) are not reduced by complex hydrides, so that only BHC containing the metal in the +4 oxidation state (mainly zirconium) have been described in the literature, although one can assume that in the future zirconium compounds analogous to the titanium(III) BHC examined above will be obtained (for example, on the basis of "zirconocene" isomorphous with the stable "titanocene"), namely $(C_{10}H_8)(CpTiH)_2$.[114]

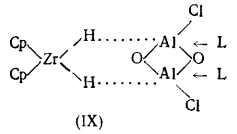
Biscyclopentadienylzirconium(IV) hydride tetrahydroaluminate has been obtained by the exchange reaction[115]

$$[Cp_2Zr(H)Cl]_x + x\,LiAlH_4 \xrightarrow{THF,\,C_6H_6} [Cp_2Zr(H)AlH_4]_x + x\,LiCl \; . \quad (39)$$

The solubility of the compound thus obtained is higher than that of the polymeric zirconium hydride complexes $[Cp_2Zr(H)X]_x$, where X = Cl or Me,[115] which may indicate a lower degree of association of the tetrahydroaluminate.

The reaction of $LiAlH_4$ with $(Cp_2ZrCl)_2O$ [Eqn.(40)], which terminates with the formation of the polymeric $(Cp_2ZrCl)_2O$,[115] may proceed via a stage involving the formation of the unstable complex (IX), decomposing on crystallisation:

$$(Cp_2ZrCl)_2O + LiAlH_4 \rightarrow 2/x\,[Cp_2ZrH_2]_x + LiCl + 1/2\,\{AlOCl\} \; ; \quad (40)$$

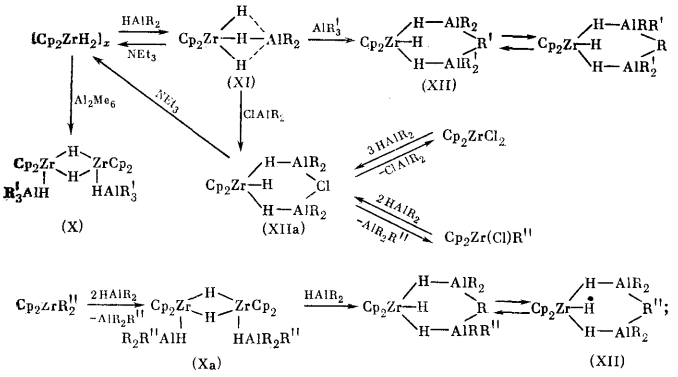


(IX)

The interaction of $(Cp_2ZrH_2)_x$ with Al_2Me_6 [26] leads to the formation of the molecular dimeric adduct $[Cp_2ZrH_2AlMe_3]_2$, which is fairly soluble in benzene. The adducts of $[Cp_2Zr.(H)Cl]_x$ with Al_2Me_6 are much less stable[26].

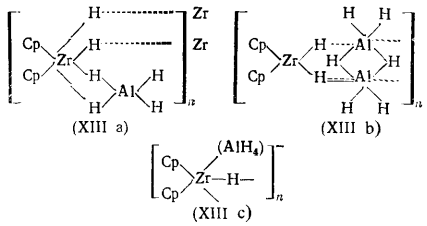
Several BHC of zirconium have been isolated in the form of pale-blue or pale-violet oily substances on treatment of biscyclopentadienyl compounds of zirconium(IV) with di-isobutylaluminium hydride[32]. The BHC of zirconium obtained were identified and their structure postulated on the basis of measurements of molecular weights and NMR data (Scheme 1):[26,32,115]

Scheme 1



R = t-Bu, R′ = Me, R″ = neohexyl.

Two models of the structure of biscyclopentadienylzirconium hydride tetrahydroaluminate have been proposed[115]: the bridged tetrahydroaluminate (XIIIa) (bidentate AlH_4 group) and the adduct with aluminium hydride (XIIIb):



(XIII a) (XIII b)

(XIII c)

The model (XIIIb) is inconsistent with the frequency ν(Al–H) (1790, 1700 cm^{-1}), which is characteristic of a tetracoordinate and not hexacoordinate aluminium atom[116]. Bearing in mind the method of synthesis of $[Cp_2Zr(H)AlH_4]_x$,[115] one can postulate that the polymeric skeleton of $[Cp_2Zr(H)Cl]_x$ persists [the frequencies ν(Zr–H–Zr) are respectively 1425 and 1390 cm^{-1}]. Since the bidentate AlH_4 group is a four-electron ligand like the BH_4 group[117], the zirconium atom in compound (XIIIa) has formally a 20-electron configuration. On the other hand, its tetrahydroborate analogue $Cp_2Zr(H)BH_4$ is monomeric and has an 18-electron configuration[25]. Although the 20-electron complexes of zirconium and hafnium are known, for example, $Cp_2Hf(BH_4)_2$ [118] and Cp_3ZrH,[119] it is also necessary to consider the 18-electron analogue (XIIIa) with a monodentate or ionic AlH_4 group, as in model (XIIIc). This is also indicated by the absence of the ν(Zr–H–Al) absorption bands in the range 1100–1500 cm^{-1},[26,115] which are characteristic covalent titanium tetrahydroaluminates[111].

The signal of the methyl protons in $(Cp_2ZrH_2AlMe_3)_2$ (0.41τ) is displaced downfield relative to Al_2Me_6 as a consequence of the formation of the Al–H bond[26]. The frequency of ν(Al–H) in the spectrum of the BHC (1780 cm^{-1}) corresponds to a tetracoordinate Al atom[116] and H in the terminal position. NMR data show that the CH_3 groups are also terminal[26]. Consequently, the zirconium atoms in both $[Cp_2Zr(H)AlH_4]_x$ and $[Cp_2ZrH_2AlMe_3]_2$ are linked by two hydride bridges and each is joined to the $AlHMe_3$ or $(AlH_4)^-$ group by an ionic bond, as in (XIVb).

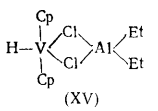
The butyl complex $(Cp_2ZrH_2Al(iso\text{-}Bu)_2C_6H_{13})_2$ evidently has a structure analogous to (Xa).

The chemical shift of the hydride protons in compounds (X)–(XII) (10.3τ–11.2τ for Zr–H and 12.0τ–12.9τ for Zr–H–Al) hardly changes, i.e. the nature of the Zr–Al bond is probably the same in all the complexes. The NMR data are satisfactorily consistent with the structural formulae (X) to (XII),[32] (Scheme 1) in which the zirconium atoms are coordination saturated.

The zirconium tetrahydroaluminate complexes are thermally unstable and decompose at room temperature[26,32], while $[Cp_2Zr(H)AlH_4]_x$ decompose above 60 °C in solution[107]. The main gaseous decomposition product of the latter is hydrogen, while in the case of $[Cp_2Zr(D)AlD_4]_x$ almost pure HD is formed[107]. According to infrared spectroscopic data, the Zr–H–Zr linkages are then retained, while the ν(Al–H) vibrations disappear. Consequently the tetrahydroaluminate and cyclopentadienyl groups participate in the elimination of H_2 and an $Al–C_5H_4$ σ-bond is then formed, as in the case of $[Cp(C_5H_4)TiHAlEt_2]_2$.[17] Hydrogen and methane are evolved on decomposition of $[Cp_2ZrH_2AlMe_3]_2$, but the Cp groups are apparently not involved[26].

2. Group VA

The biscyclopentadienyl BHC of vanadium are almost unknown. In the study of the Cp_2VCl_2–$AlH(iso\text{-}Bu)_2$ system by EPR, it was noted that, after the introduction of a small amount of oxygen to the system containing reduced vanadium, an eight-component EPR signal appears with broadened (ΔH = 30 G) lines[44]. The authors explained the broadening by the presence of an unresolved HFS associated with the splitting by two protons and the aluminium atom (as in the $Cp_2TiH_2AlR_2$ complexes[40,42–44]) and the EPR signal is attributed to the complex $Cp_2VH_2Al(iso\text{-}Bu)_2$, i.e. one can assume that BHC having the compositions $Cp_2VHClAl(iso\text{-}Bu)_2$ and $Cp_2VH_2Al(iso\text{-}Bu)_2$ with structure (I) are formed in the Cp_2VCl_2–$AlH(iso\text{-}Bu)_2$ system. BHC are also formed in the Cp_2VCl_2–Et_2AlCl system in an amount of approximately 10% of the initial Cp_2VCl_2 concentration. Differentiation of the EPR spectrum showed that each line of the octet ($J_{^{51}V}$ = 7/2) with a_V = 41.1 G is split into a doublet (a = 5.7 G), which may be due to the interaction of the unpaired electron of vanadium(IV) with a proton[98]. The following structural formula was attributed[88] to the BHC observed on the basis of data for the anisotropic splitting:



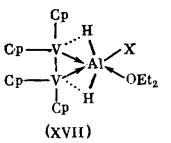
(XV)

The physical and physicochemical properties of biscyclopentadienylvanadium(III) tetrahydroborate Cp_2VBH_4 are very close to those of Cp_2TiBH_4, although the former compound is less stable[121]. The tetrahydroaluminate complexes obtained by the reaction of Cp_2VCl with lithium tetrahydroaluminate in diethyl ether are also less stable in solution[122]. The reaction proceeds in two stages: the first stage proceeds up to the ratio $Cp_2VCl : LiAlH_4$ = 2 : 1 and involves a heat change of 126.7 kJ mol^{-1}, which is close to the heat of the analogous reaction involving Cp_2TiCl (140 kJ mol^{-1}),[37] while the second stage, leading to the complete removal of chlorine from solution, is not accompanied by the evolution of heat.

The evolution of 0.5 mole of H_2 per mole of Cp_2VCl in the first stage indicates the reduction of vanadium(III) to vanadium(II). It has been suggested[122] that the vanadocene formed gives rise to a diamagnetic complex with monochloroalane:

$$2Cp_2VCl + LiAlH_4 \xrightarrow{Et_2O} (Cp_2V)_2AlH_2Cl + LiCl + H_2 . \quad (41)$$

According to infrared spectroscopic data, this substance contains bridging hydrogen atoms and a terminal chlorine atom [$\nu(Al–Cl_{term})$ = 440 cm^{-1}] and has the composition $(Cp_2V)_2AlH_2Cl.OEt_2$. The structural formula (XVIa) has been proposed for this substance. The unstable complex (XVIb) with aluminium hydride is apparently formed in the second stage of the reaction:



(XVII)

(a) X=Cl;

(b) X=H.

A series of BHC are known for niobium(III) and niobium(IV), these being formed on interaction of aluminium, gallium, and zinc alkyls with biscyclopentadienylniobium and biscyclopentadienyltantalum hydrides[123]:

$$Cp_2TaH_3 + MEt_n \underset{20°}{\overset{C_6H_6}{\rightleftharpoons}} Cp_2Ta(H)_2HMEt_n,\ M=Al,\ Ga,\ Zn,\ Cd ; \quad (42)$$

$$Cp_2NbH_3 + AlEt_3 \underset{-50°}{\overset{C_6H_5CH_3}{\rightleftharpoons}} Cp_2Nb(H)_2HAlEt_3 ; \quad (43)$$

$$Cp_2Nb(L)H + AlEt_3 \xrightarrow{20°,\ C_6H_6} Cp_2Nb(L)HAlEt_3,\ L=C_2H_4,\ CO,\ PMe_3 ; \quad (44)$$

$$[Cp(C_5H_4)NbH]_2 + 2AlEt_3 \xrightarrow{20°,C_6H_6} [Cp(C_5H_4)NbHAlEt_3]_2 . \quad (45)$$

The BHC have been isolated in a crystalline form. They are readily soluble in benzene, which made it possible to demonstrate the correspondence between the molecular weights and the proposed formulae, decompose in the light at room temperature, and are stable in the dark in the course of a week. The complexes with gallium, zinc, and cadmium alkyls are less stable and exist in equilibrium with the initial compounds only in solution; on crystallisation, equilibrium (42) shifts to the left. In contrast to tantalum, niobium(V) is reduced by metal alkyls and the adducts $Cp_2NbH_3.MEt_n$ have been detected by NMR only between −40° and −50 °C, splitting off alkanes on raising the temperature and giving rise to the BHC of niobium(III):[56]

$$Cp_2Nb(H_2)HAlEt_3 \xrightarrow{C_6H_6} Cp_2NbH_2AlEt_2 + C_2H_6 ; \quad (46)$$

$$2Cp_2Nb(H_2)HZnEt_2 \xrightarrow{C_6H_6} (Cp_2NbH_2)_2Zn + ZnEt_2 + C_2H_6 . \quad (47)$$

The BHC of this type are also formed on interaction of Cp_2NbCl_2 with $Na(Li)AlH_4$ and its derivatives $NaAlH_2X_2$ (X = Et or $OCH_2CH_2OCH_3$) [reaction (47)].[20] The reaction may proceed via a stage involving the disproportionation of the unstable niobium(IV) hydride[20]:

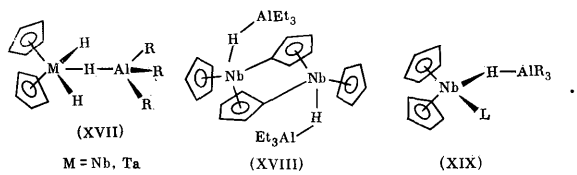
$$Cp_2NbCl_2 + NaAlH_2X_2 \xrightarrow{C_6H_6,\ THF} \underset{\downarrow}{Cp_2NbH_3} + \underset{\downarrow}{Cp_2NbH} + \underset{\downarrow}{AlHX_2} + NaCl$$
$$Cp_2NbH_3 \quad Cp_2NbH \quad AlHX_2 \rightarrow Cp_2NbH_2AlX_2 . \quad (48)$$

The interaction between Cp_2TaCl_2 and $NaAlH_2(OCH_2CH_2.OCH_3)_2$ proceeds analogously[124]. Although the intermediates have not been isolated, hydrolysis results, as in the study of Labinger and Quai Sam Wong,[20] in a satisfactory yield of Cp_2TaH_3.[124] In contrast to the tetrahydroborate Cp_2NbBH_4, the compounds $Cp_2NbH_2AlX_2$ do not react with

PR_3, CO, and C_2H_4 and do not form the complexes $Cp_2Nb.(H)L$.[20] The signal due to the hydride hydrogen atoms gradually appears in the benzene solution of $Cp_2NbD_2AlD_2$, which has been explained by the H/D exchange between the C_5H_5 rings and the AlD_4^- group. Only the bridging hydrogen atoms are exchanged and in THF the exchange is retarded evidently owing to the blocking of the coordination site by the solvent.

Treatment of a solution of Cp_2TaH_3 in toluene with LiBu [124] give rise to an insoluble orange substance containing, together with Ta–H bonds, apparently also Ta–Li bonds and having chemical properties resembling those of the BHC $[Cp_2Mo(H)Li]_4$ (see subsection 3 below).

The coordination of a non-transition metal alkyl or hydride leads to an upfield shift of the hydride proton signal by 3–7 p.p.m. and to a bathochromic shift of ν(M–H) (Table 2). In the case of the coordination-saturated trihydrides Cp_2MH_3 the shift is selective, i.e. mainly the signal of the central proton A (in the AB_2 system) is displaced[20,124]. Consequently, the structure of the BCH with the composition $Cp_2MH_3.AlR_3$ can be described by the structural formula (XVII) incorporating a single M–H–Al hydrogen bridge. Single hydrogen bridges are evidently present also in the BHC based on the "niobocene" (XVIII) and the hydrides $Cp_2Nb(L)H$ (XIX),[123] whereas structures with double hydrogen bridges of type (I) are more likely in the complexes of Cp_2NbH with aluminium and zinc hydrides[20,123]. This has been confirmed by NMR data, which have been satisfactorily interpreted on the hypothesis that the non-transition metal atom is located on the symmetry axis *z* of the Cp_2NbH_2 fragment[123].



(XVII) (XVIII) (XIX)

Table 2. ^1H NMR and infrared spectroscopic data for the biscyclopentadienyl BHC of vanadium, niobium, and tantalum.

Compound	ν (M–H), cm^{-1}	$\tau_{C_5H_5}$	τ_{MH}	$\Delta\tau_{M-H}$	References
$(Cp_2V)_2AlH_2Cl\cdot OEt_2$	1575	—	—	—	[122]
$Cp_2Nb(H_2)\cdot AlHEt_2$	—	5.12	15.0 (A) 14.5 (B_2)	+2.4 +1.0	[20]
$Cp_2Nb(PMe_3)HAlEt_3$	—	—	23.12	+5.28	[123]
$Cp_2Nb(C_2H_4)HAlEt_3$	—	—	19.63	+6.68	[123]
$Cp_2Nb(CO)HAlEt_3$	—	—	21.51	+5.12	[123]
$Cp_2Nb(CO)HZn(BH_4)_2$	1400	—	—	—	[125]
$Cp_2Nb(CO)HFe(CO)_4$	1720	—	16.4	−0.1	[126]
$Cp_2Nb(H)(\mu\text{-}C_5H_4)Fe(CO)_2$	1780	—	—	—	[127]
$Cp_2NbH_2AlEt_2$	—	—	22.78	+9.0 *	[123]
$Cp_2NbH_2AlEt_2$	—	5.37	21.4	+7.9 *	[20]
$Cp_2NbH_2Al(OCH_2CH_2OCH_3)_2$	—	5.40	20.2	+6.7 *	[20]
$Cp_2NbH_2AlH_2$	1680 **	5.15	19.8	+6.3 *	[20]
$(Cp_2NbH_2)_2Zn$	—	—	19.05	+5.32 *	[123]
$[(C_5H_4)CpNbHAlEt_3]_2$	—	—	17.02	+4.95	[123]
$Cp_2Ta(H_2)HAlEt_3$	—	—	14.68 (A) 1.46 (B_2)	+3.05 −0.57	[123]
$[Cp_2TaH_{3-n}Li_n]$	1590 ***	—			[124]

*Relative to the signals of the H_2 protons in Cp_2NbH_3.
**The centre of a broad band with shoulders.
***The centre of a broad band.

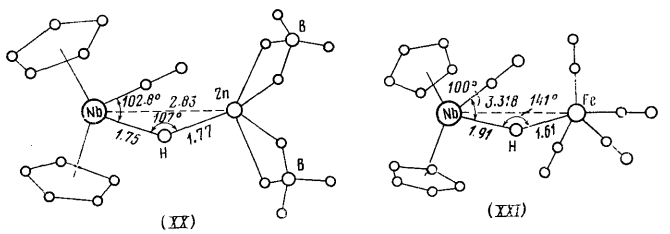
The reduction of "niobocene" with sodium naphthalide yielded the red anionic complex $Na_2[CpNb(\eta^1:\eta^5\text{-}C_5H_4)H]_2$.[128] An analogous complex containing cyclopentadienyl rings linked via a siloxane bridge has been obtained by the reduction of $[C_5H_4Si(Me_2)OSi(Me_2)C_5H_4]NbCl_2$ with sodium in toluene and subsequent treatment with diethyl ether. According to X-ray diffraction data, it retains the geometry of "niobocene" with isolated sodium ions solvated by two diethyl ether molecules. The Nb–Nb distance then increases (to 3.93 Å) and the Nb–H distance decreases together with an increase of the ν(Nb–H) frequency.

In the BHC of niobium(III) having an unshared electron pair, there is a possibility of the formation, in addition to the Nb–H–Al bridge bonds, also of a direct Nb → Al donor–acceptor bond. Indeed, according to the X-ray diffraction data for the unusual BHC $Cp_2Nb(CO)HZn(BH_4)_2.0.5C_6H_6$, obtained in accordance with Eqn.(4),[120,125,129] the niobium atom in this compound is linked to the electron-deficient molecule of zinc tetrahydroborate via both the Zn–H–Nb hydrogen bridge and the direct Nb–Zn bond (the Nb–Zn distance is close to the estimated sum of the covalent radii, namely 2.7 Å) (Fig.2). The stretching vibration frequency of the metal–hydrogen bond in compound (XX) undergoes a bathochromic shift on complex formation by ~350 cm^{-1}:[125]

$$NbCl_5 + CpNa + Zn \xrightarrow{THF,\,CO} \{Cp_2Nb(CO)ZnCl_2\} \xrightarrow{NaBH_4} Cp_2Nb(CO)HZn(BH_4)_2 \quad (49)$$

(XX)

An analogous complex containing niobium and iron and having the composition $Cp_2Nb(CO)HFe(CO)_4$ (XXI) has been obtained on treatment of Cp_2NbH_3 with $Fe(CO)_5$.[130] In view of the short metal–hydrogen bond distances (Fig.2), the authors postulate the presence of the Nb–H–Fe linkages and not of the direct Nb–Fe bond. The similarity of the spectroscopic characteristics of the Nb–H bond in $Cp_2Nb(CO)HFe(CO)_4$ to the analogous parameters in the monomeric $Cp_2Nb(CO)H$ (Table 2) and also the application of the 18 electron rule indicate a low probability of the existence of the Nb–H–Fe bridge. A terminal Nb–H bond has been postulated in the complex $Cp_2Nb(H)(\eta\text{-}C_5H_4)Fe(CO)_2$.[127]



(XX) (XXI)

Figure 2. The molecular structures of $Cp_2Nb(CO)HZn(BH_4)_2$ (XX) [129] and $Cp_2Nb(CO)HFe(CO)_4$ (XXI).[130]

3. Groups VIA and VII

As a consequence of the filling of all the unoccupied orbitals by the unshared electron pairs on formation of the metal–hydrogen bond, the biscyclopentadienyl derivatives of Group VIA (Mo, W) and VIIA (Te, Re) metal hydrides are bases and readily form 1 : 1 adducts with Lewis acids (H^+, boron and aluminium alkyl and halides, transition metal salts, etc.).

The adducts of magnesium and transition metal compounds with the halides of boron (diborane and BMe_3 do not react) and aluminium are almost insoluble in diethyl ether and aromatic hydrocarbons. The complexes with transition metals are

soluble in THF, dimethyl sulphoxide (DMSO), dimethylformamide (DMF), and pyridine[30] and those with aluminium alkyls are soluble also in aromatic hydrocarbons[27,82,131]. According to cryoscopic data, the latter are monomeric in solution[27]. As in the protonation reaction[126,132], Cp_2ReH combines with only one molecule of the Lewis acid[28,133].

The unstable adduct $Cp_2WH_2.AlH_3$ is apparently formed on interaction of Cp_2WH_2 and aluminium hydride[27], but all attempts to isolate it as well as the complex $Cp_2WH_2.AlHMe_2$ were unsuccessful. The reaction does not proceed at all with gallium hydride, although $GaMe_3$ gives rise to an unstable adduct[131].

The more stable complexes of Cp_2MoH_2 with aluminium halides and dihalogenoalanes have been obtained by the reaction[24]

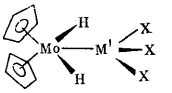
$$Cp_2MoH_2 + AlHal_{3-n}H_n \cdot OEt_2 \rightleftarrows Cp_2MoH_2 \cdot AlHal_{3-n}H_n + Et_2O,\ n = 0, 1. \quad (50)$$

Reaction (50) has been investigated in solvents with different solvating capacities and it has been concluded that the basicity of Cp_2MoH_2 exceeds only slightly that of diethyl ether[24]. The earlier view that the basicities of Cp_2MoH_2 and pyridine are comparable[82] is apparently wrong.

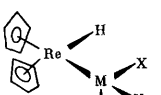
The equilibrium in the reaction of Cp_2MH_2 with transition metal compounds is fully displaced to the right, which can be accounted for either by the greater acidity of these compounds or by the formation of a different type of bond between the components.

These adducts as a rule crystallise from solutions in strongly solvated solvents in the form of the monosolvates $Cp_2MH_2.M'X_n.L$.[29,30,134–136]

The spectroscopic characteristics of the M–H bonds in the adducts $Cp_2MH_2.M'X_n$ are presented in Table 3. It follows from these data that the parameters of the metal–hydrogen bond hardly change on formation of adducts with compounds of Group IIIA elements. The chemical shift of the methyl protons (there is a downfield shift[26]), in $Cp_2MH_2.AlMe_3$ and the frequencies ν(B–Hal) in the complexes with $BHal_3$ correspond to tetracoordinate aluminium and boron atoms[27,28]. Hence it follows that in the adducts obtained the transition metal has two terminal hydrogen atoms and is linked to the non-transition element (B and Al) by a direct donor–acceptor bond (BHC of the fourth type):



(XXIIa)



(XXIIb)

A bathochromic shift of ν(Al–H) has been observed for the complexes of Cp_2MoH_2 with dihalogenoalanes[24] (Table 3) and is apparently associated either with a change in the C.N. of aluminium to 5 (the halogen bridge bond) or, what is more likely, with a significant decrease of the strength of the Al–H bond.

The adducts of $Cp_2Mo(W)H_2$ with aluminium alkyls are thermally unstable and gradually decompose in solution with liberation of alkanes and precipitation of solid products. As was to be expected, tungsten compounds are more stable than molybdenum compounds and the methyl complexes are more stable than the ethyl complexes[132].

The decomposition of $Cp_2WH_2.AlMe_3$ can proceed simultaneously via two pathways: the elimination of hydrogen from the Cp group formation of an Al–C σ-bond, and the elimination of the hydride hydrogen atom from tungsten with formation of a direct W–Al bond[132]. These reactions are common to strong alkylating agents—aluminium and lithium alkyls and Grignard reagents.

When the reaction between Cp_2MoH_2 and Al_2Me_6 is carried out in toluene at 80 °C, the orange crystals of the compound $C_{25}H_{35}Al_3Mo_2$ (XXIIIa) are formed[137]. Cp_2WH_2 reacts similarly, giving rise to the yellow crystals of $C_{25}H_{35}Al_3W_2$, which, however, is not isomorphous with the molybdenum compound[138]. Prolonged refluxing of the reagents makes it possible to obtain the yellow crystals of the compound $C_{26}H_{34}Al_4Mo_2$ (XXIIIb) (Scheme 2)[137].

Scheme 2

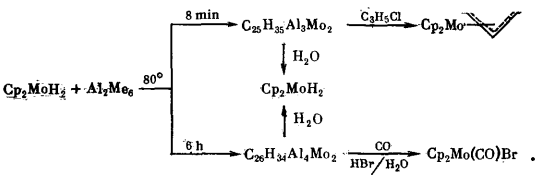


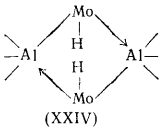
Table 3. The changes in the spectroscopic characteristics of the M–H bond on formation of complexes by Cp_2MH_2 (M = Mo or W) with Lewis acids.

Lewis acid	$\Delta\tau_{MH}$	ν (M–H), cm^{-1}	$\Delta\nu$ (M–H), cm^{-1}	References
		Complexes with Cp_2MoH_2		
BF_3	—	1855	+5	[28]
$AlHCl_2$ *	—	1855	+5	[30]
$AlCl_3$	—	1850	0	[24]
$AlHBr_2$ **	—	1850	0	[24]
$AlEt_3$	+0.27	—	—	[27]
$ZnCl_2$	+1.3 ***	1810, 1780	—55	[30]
ZnI_2	—	1795, 1740	—80	[30]
$ZnI_2 \cdot$ THF	—	1830, 1780	—45	[30]
$FeCl_2$	—	1760, 1720	—110	[29, 135]
$FeBr_2$	—	1750, 1680	—135	[29, 135]
FeI_2	—	1703, 1653	—170	[29, 135]
$FeI_2 \cdot$ THF	—	1820, 1740	—70	[29, 135]
CoI_2	—	1708	—142	[29, 135]
$Rh(PPh_3)_3$	+5.52	—	—	[136]
CuCl	—	1690, 1650	—180	[29, 135]
CuI	—	1660, 1650	—195	[29, 135]
		Complexes with Cp_2WH_2		
BF_3	—	1937	+17	[28]
$AlHCl_2$ *	—	1952	+32	[24]
$AlCl_3$	—	1945	+25	[24]
$AlHMe_2$	+0.19	—	—	[131]
$AlMe_3$	+1.00	1905	—15	[131]
$ZnCl_2$	+0.7 ***	1895, 1855	—45	[30]
ZnI_2	+0.2 ***	1885, 1845	—55	[30]
$ZnI_2 \cdot$ THF	—	1920, 1870	—25	[30]
$FeCl_2$	—	1860, 1807	—85	[29, 135]
FeI_2	—	1830	—90	[29, 135]
$FeI_2 \cdot$ THF	—	1900, 1825	—55	[29, 135]
$CoCl_2$	—	1868	—52	[29, 135]
CuCl	—	1775, 1723	—170	[29, 135]
$Rh(PPh_3)$	+5.83	—	—	[136]

*ν(Al–H) = 1910 cm^{-1}. **ν(Al–H) = 1890 cm^{-1}. ***Solution in DMF.

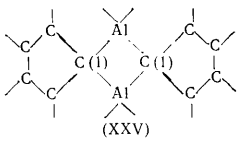
The structure of both molybdenum complexes was established by X-ray diffraction (Fig.3).[139,140] Although it was not possible to establish the positions of the hydrogen atoms, the larger Mo–Al distance (2.95–3.00 Å) compared with the Mo–Al distance in the "non-hydride" component of the molecule (2.65 Å) and the presence of an absorption band at 1825 cm^{-1} in the infrared spectrum enabled the authors[137,139,140] to postulate that the hydrogen atoms are located between the Mo and Al(3) atoms [formula (XXIIIa)], which are thus linked by hydrogen bridges. However, ν(M–H) is closer to ν(Mo–H) in Cp_2MoH_2 (1853 cm^{-1}) than to ν(Al–H) (1750

cm^{-1}) [116] and is not characteristic of bridging hydrogen atoms. One can therefore assume that terminal hydrogen atoms linked to molybdenum are present in the $C_{25}H_{35}Al_3Mo_2$ structure. The Mo–Mo distance (4.75 Å) is entirely sufficient to accommodate two hydrogen atoms [formula (XXIV)].



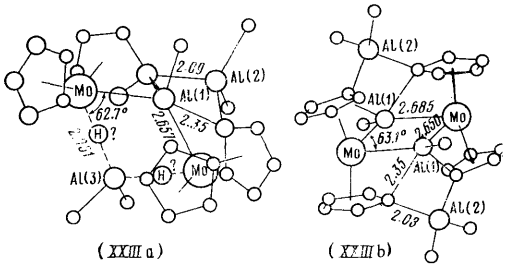
(XXIV)

It is of interest that the cyclopentadienyl group C_5H_4 is tridentate, as in aluminium titanium hydrides[17,54], forming, apart from the σ-bond with the transition metal atom, also a four-centre σ-bond with two aluminium atoms [formula (XXV)].



(XXV)

All the aluminium atoms and the C(1) carbon atom are then in one plane[139,140]. An analogous type of bond has been observed in the ferrocenylalanes $Me_2Al(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4Fe\text{-}\eta^5\text{-}C_5H_5)AlMe_2$.[141,142]

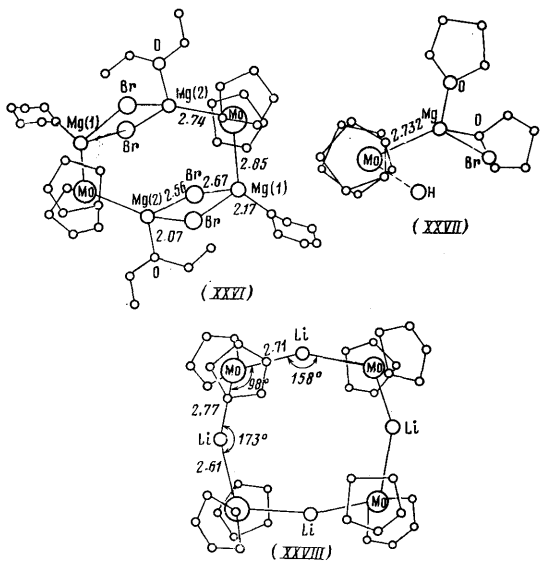


(XXIIIa) (XXIIIb)

Figure 3. The structures of the $C_{25}H_{35}Al_3Mo_2$ (XIIIa) and $C_{26}H_{34}Al_4Mo_2$ (XXIIIb) molecules according to X-ray diffraction data[139,140].

When solutions of Cp_2MoH_2(Cp_2WH_2) interact with an excess of a Grignard reagent RMgX in ether, yellow crystals of $[Cp_2Mo(H)Mg(R)\text{–}\mu\text{-}X_2Mg(OEt_2)]_2$ (XXVI) are deposited[138,143,144]. An X-ray diffraction study has been made of the compound with R = cyclohexyl [144] (Fig.4). The positions of the hydride hydrogen atoms have not been established. The infrared spectrum of the compound contains absorption bands at 1740 and 1720 cm^{-1}, which are displaced to 1260 cm^{-1} on deuteration. It has been suggested that the terminal hydrogen atoms are in the Mg_aMoMg_b plane, i.e. as in the complex with trimethylaluminium[73], and do not form a bond with the Mg atom. All three orbitals of Cp_2Mo are used up in the formation of bonds with hydrogen and two magnesium atoms (the length of the covalent Mo–Mg bond is shorter by ~0.1 Å than the coordinate bond)[144].

A Lewis base stronger than Cp_2MoH_2, for example, THF, displaces it from the complex with RMgX. Thus, when the BHC $[Cp_2Mo(H)Hg(Br)\mu\text{-}Br_2Mg(OEt_2)]_2$ was dissolved in THF, a red solution was formed, from which the monomeric BCH $Cp_2Mo(H)MgBr.2C_4H_8O$ (XXVII) was isolated[23,145,146]. X-Ray diffraction study of this compound demonstrated the presence of a direct Mo–Mg bond (Fig.4). The magnesium atom is solvated by two THF molecules and has C.N. = 4. The hydride hydrogen atoms are not localised, but ν(Mo–H) = 1850 cm^{-1} is very close to ν(Mo–H) for Cp_2MoH_2 (1853 cm^{-1}).[23] It has been suggested[108] that analogous compounds are formed on interaction of Cp_2MH_2 with RMgX in proportions of 1 : 1. According to Aripovskii et al.[143], the interaction of Cp_2MH_2 with Grignard reagents can proceed via three pathways (Scheme 3), depending on the conditions, with formation of solvated or non-solvated substances, but never leads to the formation of the adducts $Cp_2MH_2.RMgX$. The reaction of Cp_2MH_2 with BeX_2 in ether is significantly reversible.

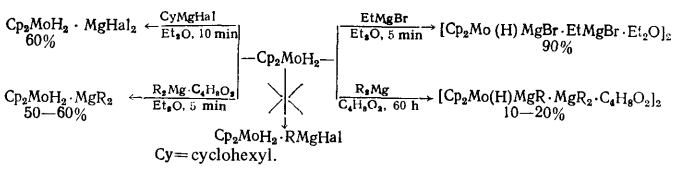


(XXVI) (XXVII) (XXVIII)

Figure 4. The molecular structures of $[Cp_2Mo(H)Mg(C_6H_{11}).(\mu\text{-}Br)_2Mg(OEt_2)]_2$ (XXVI),[144] $Cp_2Mo(H)MgBr.2C_4H_8O$ (XXVII),[23,145] and $[Cp_2Mo(H)Li]_4$ (XXVIII).[148]

Treatment of $Cp_2Mo(W)H_2$ with butyl-lithium in toluene at 50 °C gives rise to the yellow-orange crystals of $[Cp_2Mo(W).(H)Li]_4$ (XXVIII).[147]

Scheme 3



Cy = cyclohexyl.

It was established by X-ray diffraction that complex (XXVIII) is tetrameric and that association takes place via lithium bridges (Fig.4). The Li–Mo–Li angle (97–98°) is unduly large and suggests that hydrogen atoms are present in its bisector plane[148].

The fulvalene complex $[CpMo(H)]_2(\mu\text{-}C_{10}H_8)$ reacts analogously with LiBu, forming the lithium derivative $[CpMo(Li)]_2(\mu\text{-}C_{10}H_8)$, whose properties are similar to those of $[Cp_2Mo.(H)Li]_4$.[149] Like the magnesium derivatives, the compounds

$[(Cp_2Mo(W)(H)Li]_4$ are powerful nucleophiles whose properties are similar to those of organolithium compounds[147]. When they interact with $R_3M'Hal$ (M' = Ge or Sn; R = Me or Et), the BHC $Cp_2Mo(W)(H)M'R_3$, with a direct M–M' bond, are formed[150].

The compound Cp_2MH_2 react with ZnR_2 (R = Et or Bu) to form the polymeric complexes $[(Cp_2M)_2Zn]_n$ without M–H bonds[140]. Like all the BHC of molybdenum and tungsten with direct M–M' bonds, they regenerate the initial dihydride on hydrolysis[138,147,149].

A characteristic feature of the structures of the compounds formed by Cp_2MH_2 with compounds of non-transition Group IIIA and in certain cases Group IIA metals is the formation of a direct M–M' bond and the absence of hydrogen bridge bonds. The situation changes significantly on passing to Lewis acids formed by heavy transition metals.

Weakly soluble or insoluble adducts of Cp_2MH_2 with Zn, Cu, Ag, Co, Fe, Mo, and Rh compounds have been obtained in DMF, THF, diethyl ether, and benzene[29,30,134–136]. The reaction with strong bases results as a rule in the formation of the solvated complexes $Cp_2MH_2.M'Hal_{2-n}.L$ (n = 0 or 1); non-solvated substances crystallise from diethyl ether and benzene.

Table 3 shows that the formation of complexes by Cp_2MH_2 with the transition metal and zinc compounds investigated leads to a significant bathochromic shift of the ν(M–H) band (50–250 cm^{-1} and in the compounds with AgCl and $MoOCl_3$ not less than 350 cm^{-1}, since these bands are then masked by the bands of the solvents and the Cp rings) and its splitting into the ν_s and ν_{as} components[29,135], while τ_{M-H} is displaced upfield [$\Delta\tau_{M-H}$ = +5.5–+5.8 p.p.m. for $Rh(RPh)_3$][136]. This is undoubtedly characteristic of the formation of hydrogen bridge bonds analogous to the M–H–B bonds in transition metal hydroborates[11].

Table 4. Structural characteristics of the adducts of Cp_2MH_2 with transition metal and zinc compounds.

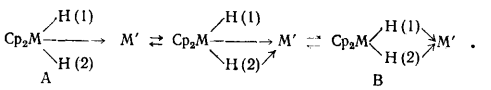
Compound	Interatomic distance r, Å						H(1)MH(2) angle, °	References
	$r_{M-H(1)}$	$r_{M-H(2)}$	$r_{M'-H(1)}$	$r_{M'-H(2)}$	$r_{M-M'}$	$r_{M'-X}$		
$Cp_2MoH_2 \cdot FeI_2 \cdot THF$	1.58	1.86	2.15	1.79	2.854	2.65	85.5	[151]
$[Cp_2MoH_2 \cdot CuI]_2$	1.32	1.97	2.02	1.57	2.73	2. 60, 2. 63	79	[101]
$[(Cp_2MoH_2)_2Cu]CuCl_2$	1.7	2.0	2.0	1.7	2.65	2.17	85	[152]
$Cp_2MoH_2 \cdot ZnBr_2 \cdot DMF$	1.40	1.75	1.78	1.59	2.793	2. 41; 2. 43	63.8	[134]
$Cp_2WH_2 \cdot Rh(PPh_3)_2$	—	—	—	—	—	2.16	—	[136]

X-Ray diffraction study of the compounds $Cp_2WH_2Rh(PPh)_3$,[136] $Cp_2MoH_2ZnBr_2.DMF$,[134] $[Cp_2MoH_2CuI]_2$,[101] $Cp_2MoH_2FeI_2.THF$,[151] and $[(Cp_2MoH_2)Cu].CuCl_2$ [152] confirmed the conclusions reached in other investigations[29,30,135] concerning the presence in these compounds of the bridge bonds

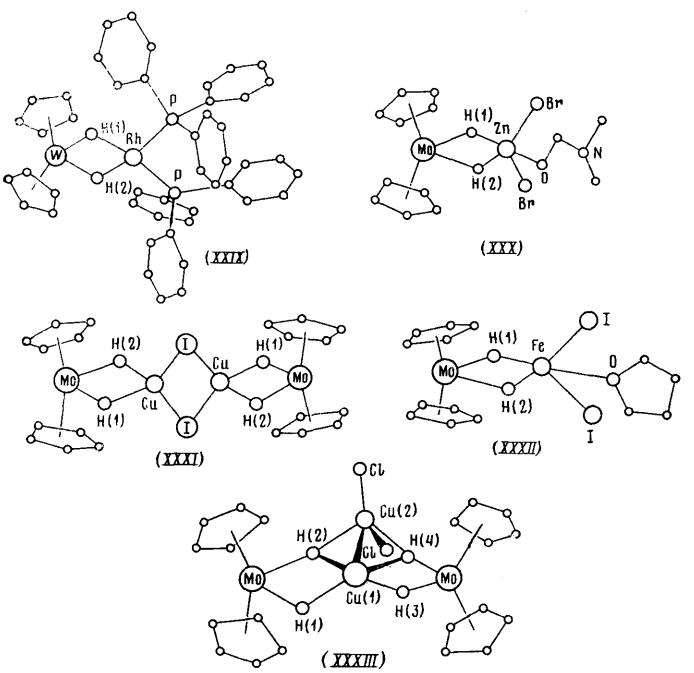


M' and, in contrast to the "classical" symmetrical bridge[11], in the last four compounds asymmetric hydrogen bridges were discovered (Table 4 and Fig.5; the coordinates of the hydrogen atom were not determined by Alcock et al.[136], while Grotty et al.[134] determined them with a large error).

The question of the degree of involvement of the d^2 electrons of the Mo and W atoms in the formation of a bond with the M' atoms remains open. On the basis of the theoretical model of Alcock and Green[85,86], some investigators[101,151,152] suggest that not only the interatomic distance but also the H(1)MH(2) angle is a measure of the degree of direct M–M' bonding. In compounds with an angle H(1)MH(2) > 90° (A), a direct intermetallic bond is formed preferentially (adducts with halogenoalanes). When the H(1)MH(2) angle is 80–90° (B) and for the corresponding interatomic distance, both a donor–acceptor bond and a hydrogen bridge bond can be formed, whereas in the case of an H(1)MH(2) angle less than 80° (C) the hydrogen bridge bond makes the main contribution to the bonding of the components and the complexes formed are of the chelate type (Cp_2MH_2 is a bidentate ligand) in which the d^2 electrons of the M atom occupy a non-bonding orbital. There is no doubt that the extreme cases are unlikely. Most probably both types of bond obtain to some extent in the compounds considered:



A B



(XXIX) (XXX) (XXXI) (XXXII) (XXXIII)

Figure 5. The molecular structures of $Cp_2MoH_2Rh(PPh_3)_2$ (XXIX),[136] $Cp_2MoH_2ZnBr_2.DMF$ (XXX),[134] $[Cp_2MoH_2CuI]_2$ (XXXI),[101] $Cp_2MoH_2FeI_2.C_4H_8O$ (XXXII),[151] and $[(Cp_2MoH_2)_2.Cu]CuCl_2$ (XXXIII).[152]

VI. MONO- AND TRIS-CYCLOPENTADIENYL BIMETALLIC HYDRIDE COMPLEXES

The introduction of even one π-C_5H_5 group into the coordination sphere of a transition metal atom increases significantly the stability of hydride compounds. The monocyclopentadienyl BHC have apparently a structure similar to that

of the biscyclopentadienyl complexes, although their stability is lower.

When $CpTiCl_3$ is reduced with metallic magnesium in the presence of MgI_2, the EPR spectrum exhibits a triplet with the intensity ratios 1 : 2 : 1, analogous to the signal of the compound $Cp_2Ti\begin{smallmatrix}H\\ \diagup\ \diagdown\\ H\end{smallmatrix}MgI$ [60] and apparently corresponding to the BHC $Cp(Cl)TiH_2^-MgI^+$. As in the case of the biscyclopentadienyl complex, the source of the hydride hydrogen is the Cp rings, since the EPR signal does not appear when $CpTiCl_3$ is replaced by $(C_5Me_5)TiCl_3$.[60]

The possibility of obtaining monocyclopentadienyltitanium BHC stable under ordinary conditions has been confirmed by the results of the calorimetric titration of $CpTiCl_3$ with lithium tetrahydroaluminate in diethyl ether: the reaction proceeds via the same stages as that involving Cp_2TiCl_2 and the enthalpy changes are similar[37]. It is of interest that the stage involving the substitution of the last chlorine atom by a hydrogen atom is not accompanied by an enthalpy change in this instance, as in the case of $(Cp_2V)_2ClAlH_2$.[122] The final reaction product is the complex $CpTi(AlH_4)_2.AlH_3$, which is extremely unstable and decomposes after 10–20 min with the complete evolution of hydrogen.

In the study of the polymerisation of ethylene in the presence of the Cp_4Zr–$AlEt_3$ system, the BHC (XXXV), stabilised by three C_5H_5 groups, was isolated[153]:

$$Cp_4Zr \xrightarrow[Cp_3AlEt_4]{AlEt_3} Cp_3ZrEt \xrightarrow[-C_2H_6]{AlEt_3} Cp_3ZrCH_2AlEt_2 \xrightarrow[-C_2H_6]{AlEt_3} Cp_3ZrCH_2CH\begin{smallmatrix}AlEt_2\\ \diagdown\\ \diagup\\ AlEt_2\end{smallmatrix}$$

$$Cp_3ZrCH_2CH_2AlEt_2 \rightarrow Cp_3ZrH\cdot Al(Et)CH=CH_2 \rightleftarrows (XXXIV) \rightleftarrows Cp_3ZrH + {}^1/_2(AlEt_3)_2. \quad (51)$$

The formula $Cp_3Zr{-}H{-}AlEt_3$ (XXXIV) was proposed on the basis of the chemical properties and preliminary X-ray diffraction data (Zr–Al = 3.66 Å). It may be that similar BHC are also formed in the Cp_2ZrX_2–$AlEt_3$ system[154,155].

Triscyclopentadienyluranium(IV) forms bimetallic complexes in solution with alkyl groups and halogen bridges of the type $Cp_3U\begin{smallmatrix}R\\ \diagup\\ \diagdown\\ U\end{smallmatrix}\begin{smallmatrix}R\\ \diagdown\\ Al\\ \diagup\\ R\end{smallmatrix}$,[156] but the BHC could not be isolated in a pure state owing to the rapid reduction of uranium(IV) to uranium(III).[157]

VII. BIMETALLIC TRANSITION METAL HYDRIDE COMPLEXES STABILISED BY OTHER ELECTRON-DONATING LIGANDS

Apart from the fairly numerous and comparatively thoroughly investigated biscyclopentadienyl BHC, there are extremely few data on BHC stabilised by other electron-donating ligands such as alkyl groups, olefins, and phosphorus- and oxygen-containing Lewis bases. The conclusion concerning the structure of the majority of the complexes formed under these conditions is exceptionally tentative and we shall therefore consider only briefly the available literature data on this question.

Thus the stabilisation of the transition metal hydride complexes has been noted in complex multicomponent catalytic systems of the Ziegler–Natta type, where the stabilisers are solvents, the substrate, and non-transition metal compounds.

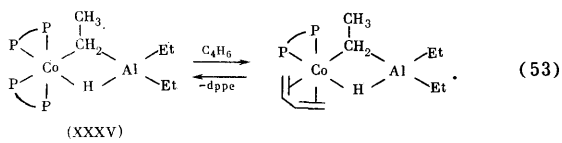
Although the majority of the transition metal hydrides obtained at the present time contain organophosphorus ligands, the BHC stabilised by phosphines or phosphites are almost unknown. The only reliably characterised BHC of this group is the compound $\{Ta[H_2Al(OC_2H_4OMe)_2](dmpe)_2\}$, where dmpe = bisdimethylphosphinoethane $Me_2PCH_2CH_2PMe_2$ obtained by reaction (52).[158] The complex is a dimer linked by Al–O–Al bridges:

$$TaCl_2(dmpe)_2 + NaAlH_2(OC_2H_4OMe)_2 \xrightarrow{Et_2O} [Ta\{H_2Al(OC_2H_4OMe)_2\}(dmpe)_2]_2 + NaCl + H_2 + AlH(OC_2H_4OMe)_2, \quad (52)$$

The P_4TaAl atomic group is a distorted square pyramid (as a consequence of the formation of the TaH_2Al bridge, the angle between the normal to the P_4 plane and the Ta–H bond is 16°). The H atoms are not localised but the infrared spectrum shows two equally intense bands at 1605 and 1640 cm^{-1}, which the authors attribute to the presence of two bridging hydrogen atoms.

A series of BHC have been obtained in Ziegler–Natta systems modified by phosphines. BHC having the composition $[Fe(dppe)_2]^+[AlH_2R_2]^-$ are formed in the $Fe(acac)_3$–$AlEt_3$–dppe system, where dppe = bisdiphenylphosphinoethane $Ph_2PCH_2CH_2PPh_2$ and acac = acetylacetone[15]. In contrast to the complex $[Fe(dppe)_2]^+[AlCl_2R_2]^-$, which has a similar composition, this compound does not decompose on treatment with diethyl ether[15], which indicates a more complex Fe–AlH_2R_2 interaction than was suggested on the basis of the ionic mechanism.

The codimerisation of ethylene and butadiene in the presence of $CoCl_2$–$AlEt_3$–dppe is believed to proceed in the presence of complex (XXXV), which readily splits off phosphines[159]:



(XXXV) (53)

The BHC having the general formula $[HNiL_n]^+AlX_4^-$ are formed in the NiX_2–$AlR_3(AlX_3')PR_3'$ systems, which are active in the dimerisation of olefins[22,160–162]. The non-transition metal compound plays the role of the Lewis acid and can be replaced by, for example, $TiCl_4$.[22]

The proposed structure of the BHC has been confirmed by specific synthesis from $HNiCl(PPr_3)_2$ and $AlCl_3$ [in this process $\nu(Ni{-}H_{ter})$ = 1937 cm^{-1} shifts slightly towards longer wavelengths[160]] and also from $Ni(dppe)_2$ and $HAlCl_4$.[163]. It is noteworthy that $\nu(Ni{-}H)$ = 1949 cm^{-1} and τ_{Ni-H} = 23 for the complex with dppe hardly change when the $AlCl_4^-$ anion is replaced by BF_4^-.[163] The isolation of the stable (up to 125 °C) BHC having the composition $Cp_2FeH^+AlCl_4^-$ has also been reported[164]. Only the BHC containing nickel(II) are active in the $NiCl_2$ + $AlEt_3$ + PR_3 system.[161,162] The formation of BHC has also been postulated in the $CoCl_2$–RMgCl–dppe system[165].

In the fixation of nitrogen in the presence of the $TiCl_3.(VCl_3)$–Mg–THF system, the nitride complex $[MNMg_2Cl_2.THF]$ is formed and reacts with H_2 in the presence of Mg to form the BHC $[TiH_2NMg_3Cl_{1.5}.(THF)_x]$.[166,167] The reduction of VCl_3 with magnesium in THF in an argon atmosphere gives rise to a BHC having a similar composition, namely $[VHMg_2.Cl_{1.5}(THF)_x]$, while reduction in an H_2 atmosphere results in the formation of $[VH_2MgCl(THF)_2](THF)_2$.[167,168] The $\nu(M{-}H)$ absorption band has not been observed in the infrared spectra of the two complexes[166]. Analogous BHC are apparently formed also in the MX_n–Mg systems for compounds of other transition metals[168]. These compounds catalyse the hydrogenation of olefins. It is of interest that the introduction of aluminium chloride into the VCl_3–Mg system up to the ratio Al : V = 1 : 1 increases the rate of hydrogenation[167], which is believed to be due to the substitution of Mg by aluminium in the BHC.

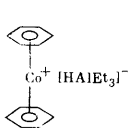
BHC containing a Group VIII metal and magnesium are formed in Ziegler–Natta systems with Grignard reagents. Thus the $FeCl_3$–PhMgBr system absorbs hydrogen, which is attributed to the formation of BHC of the second type[169]. Subsequently the complex $FeH_2MgX_4(THF)_8$ was isolated in a pure state in the form of a yellow crystalline substance[170]:

$$FeCl_3 + 7PhMgBr + 6H_2 \xrightarrow{THF} \tfrac{1}{2}\,Ph{-}Ph + 3MgX_2 + 6C_6H_6 + FeH_6Mg_4X_4(THF)_8. \quad (54)$$

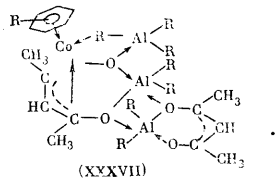
The existence of the catalytically active BHC with Co–H–Al bridge bonds and stabilised by THF has been postulated in the $CoCl_2$–$NaAlH_2(OMe)_2$ system prepared in an H_2 atmosphere[171].

A complex dihydride, active in the hydrogenation of olefins, is formed in the cobalt(nickel, iron) stearate–RMgX systems in diethyl ether; it is believed to be stabilised by the products of the interaction of the stearate and a Grignard reagent[172,173].

The interaction in cobalt chelates–AlR_3(LiR, RMgX) systems gives rise to a series of cobalt(I) and zerovalent cobalt complexes stabilised by aromatic hydrocarbons and transition metal compounds[174,175]. The formation of the BHC (XXXVI) [174] and of the alkyl complex (XXXVII),[175] which in the course of hydrogenation apparently gives rise to compounds (XL), has been postulated:



(XXXVI)



(XXXVII)

An unusual BHC, stabilised by an olefin and THF and having the composition $(COD)_{1.5}NiLi_2H_2(THF)_x$ (COD = cyclo-octadiene) has been obtained in accordance with Eqn. (55). The complex reacts with CO, liberating cyclo-octadiene but not H_2.[176] As regards chemical properties, it behaves as a lithium hydride transferring agent, its reaction with $AlEt_2$, for example, yielding $Li[AlHEt_3]$, but, in contrast to pure LiH, it reacts with olefins, forming lithium alkyls:

$$(COD)_2Ni + 2Li \xrightarrow{THF,\ -30^\circ} (COD)_2NiLi_2(THF) \xrightarrow{+H_2,\ -60^\circ} (COD)_{1.5}NiH_2Li_2(THF)_x. \quad (55)$$

It is of interest to consider the possible ways of seeking new BHC, which evidently involves their stabilisation by effective ligands other than the C_5H_5 groups. As stated above (Section III, Subsection 5), the stability of the transition metal tetrahydroaluminates $M(AlH_4)_n$ varies in parallel with the stability of the corresponding tetrahydroborates. The same behaviour has been observed also for other BHC: stable tetrahydroaluminates correspond to the stable monocyclopentadienyltitanium tetrahydroborate[177] and biscyclopentadienyltitanium, biscyclopentadienylzirconium, biscyclopentadienylvanadium, and biscyclopentadienylniobium tetrahydroborates[11]. Consequently stable transition metal tetrahydroborate complexes can be regarded as models in relation to the tetrahydroaluminate complexes. However, it is noteworthy that, since the coordinating capacity of the aluminium atom is greater than that of the boron atom and the AlH_4^- group is a stronger reductant than BH_4^-, it is to be expected that the structure of the tetrahydroaluminate BHC differs significantly in most cases from that of the tetrahydroborate BHC (see, for example, Erofeev et al.[122] and Marks and Kennelly[178]).

Transition metal tetrahydroborates stabilised by phosphines and also arsines have been described for cobalt, nickel, ruthenium, rhodium, iridium, palladium, copper, and silver[11] as well as molybdenum[179]. Carbonyl compounds are also known: the stable salt $[(Ph_3P)_4N]^+[Mo(CO)_4BH_4]^-$ and the unstable complex $Mn(CO)_5BH_4$.[11] The stable trisdialkylaminotitanium(IV) [180] and trisdialkylaminothorium(IV) [181] tetrahydroborates and uranium(III) tetrahydroborate, stabilised by crown-ether[182], are noteworthy.

Bearing in mind the synthesis in recent years of a large number of stable transition metal alkyls with substituents not containing β-hydrogen atoms, one may expect the synthesis of BHC containing such alkyl groups. Thus a series of zinc tetrahydroaluminate complexes having the general formula $MZn_nMe_{2n}AlH_4$, where M = Li, Na or K and n = 1 or 2, which are stable in solution in THF, have been obtained by Ashby and Watkins[183–185].

Another possible method of synthesis of stable BHC involves the interaction of non-transition metal compounds with molecular transition metal hydrides. Among these, we may note the familiar pentahydrides $MH_5(dmpe)_2$ of niobium[186] and tantalum[187], whose chemical properties resemble closely those of Cp_2MH_3: they catalyse the H–D exchange between D_2, on the one hand, and C_6H_6 and C_2H_4, on the other, and form the complexes $NHL_2(dmpe)_2$ with CO and C_2H_4. Analogous complexes having the composition $MH_3(dmpe)$ have also obtained for titanium and zirconium[188]. The synthesis of $CpNb(PPh_3)_2(CO)H_2$, isoelectronic with Cp_2MoH_2,[189] and of $CpMo(dppe)H_3$, isoelectronic with $CpNbH_3$,[190] has been reported. The chemistry of BHC involving the study of the complex-formation reactions of Cp_2MH_n and the isoelectronic compounds Cp_2NbH, $(PR_3)_4MH_4$,[191] etc. with transition metal compounds will apparently be fairly fruitful.

REFERENCES

1. R.S.Coffey, "Latest Advances in the Homogeneous Hydrogenation of Multiple Carbon–Carbon Bonds" in "Aspects of Homogeneous Catalysis" (Edited by R.Ugo) (Translated into Russian), Izd.Mir, Moscow, 1973.
2. B.R.James, "Homogeneous Hydrogenation" (Translated into Russian), Izd.Mir, Moscow, 1976.
3. D.V.Sokol'skii and N.F.Noskova, "Katalizatory Tipa Tsiglera–Natta v Reaktsii Gidrirovaniya" (Ziegler–Natta Catalysts in the Hydrogenation Reaction), Izd.Nauka, Alma-Ata, 1977.
4. H.D.Kaesz and R.B.Saillant, Chem.Rev., 1972, **72**, 231.
5. G.Dolcetti and N.W.Hoffman, Inorg.Chim.Acta, 1974, **9**, 269.
6. C.A.Tolman, "The Role of Transition Metal Hydrides in Homogeneous Catalysis", in "Transition Metal Hydrides" (Edited by E.L.Muetterties) (Translated into Russian), Izd.Mir, Moscow, 1975.
7. D.S.Breslow and N.R.Newburg, J.Amer.Chem.Soc., 1959, **81**, 81.
8. M.Uetsuki and Y.Fujiwara, Bull.Chem.Soc.Japan, 1976, **49**, 3530.
9. K.Tanai, Bull.Chem.Soc.Japan, 1965, **38**, 1575.
10. R.A.Schunn, "The Chemistry of Transition Metal Hydrides" in "Transition Metal Hydrides" (Edited by E.L.Muetterties) (Translated into Russian), Izd.Mir, Moscow, 1975.
11. T.J.Marks and J.R.Kolb, Chem.Rev., 1977, **77**, 263.
12. V.Kadlec, H.Kadlecova, and J.Masek, Chem.Listy, 1976, **70**, 673.

13. M.E.Kost and A.I.Golovanova, Zhur.Neorg.Khim., 1977, **22**, 832 [Russ.J.Inorg.Chem., 1977(3)].
14. M.E.Kost and A.I.Golovanova, Zhur.Neorg.Khim., 1977, **22**, 977 [Russ.J.Inorg.Chem., 1977(4)].
15. V.V.Saraev, F.K.Shmidt, V.A.Gruznykh, T.I.Bakunina, and L.V.Mironova, Koord.Khim., 1979, **5**, 1472.
16. J.B.Atwood, R.D.Rogers, C.Kutal, and P.A.Grutsch, Chem.Comm., 1977, 593.
17. F.N.Tebbe and L.J.Guggenberg, Chem.Comm., 1973, 227.
18. F.N.Tebbe, J.Amer.Chem.Soc., 1973, **95**, 5412.
19. A.E.Shilov, A.K.Zefirova, and N.N.Tikhomirova, Zhur.Fiz.Khim., 1959, **33**, 2113 [Russ.J.Phys.Chem., 1959(9)].
20. J.A.Labinger and Kwai Sam Wong, J.Organometal. Chem., 1979, **170**, 373.
21. H.H.Brintzinger, J.Amer.Chem.Soc., 1966, **88**, 4305.
22. N.V.Obeshchalova, Zhur.Org.Khim., 1968, **4**, 1014.
23. S.G.Davies, Chem.Comm., 1977, 135.
24. A.V.Aripovskii and B.M.Bulychev, Zhur.Neorg.Khim., 1980, **25**, 2191 [Russ.J.Inorg.Chem., 1980(8)].
25. B.D.James, P.K.Nanda, and M.G.H.Wallbridge, Inorg. Chem., 1967, **6**, 1979.
26. P.C.Wailes, H.Weigold, and A.P.Bell, J.Organometal. Chem., 1972, **43**, C29.
27. A.Storr and B.S.Thomas, Canad.J.Chem., 1971, **49**, 2504.
28. M.P.Johnson and D.F.Shriver, J.Amer.Chem.Soc., 1966, **88**, 301.
29. A.V.Aripovskii, B.M.Bulychev, L.B.Krivdin, and V.B.Polyakova, Zhur.Neorg.Khim., 1981, **26**, 409 [Russ.J.Inorg.Chem., 1981(2)].
30. A.V.Aripovskii and B.M.Bulychev, Zhur.Neorg.Khim., 1980, **25**, 1687 [Russ.J.Inorg.Chem., 1980(6)].
31. J.E.Bercow and H.H.Brintzinger, J.Amer.Chem.Soc., 1969, **91**, 7301.
32. L.J.Shoer, K.I.Gell, and J.Schwartz, J.Organometal. Chem., 1972, **136**, C19.
33. K.Mach, H.Antropiusova, V.Hanus, and A.Dosedlova, Trans.Met.Chem., 1980, **5**, 5.
34. H.Neumaier, D.Büchel, and G.Ziegelmaler, Z.anorg. Chem., 1966, **345**, 46.
35. A.I.Golovanova, M.E.Kost, V.I.Mikheeva, Izv.Akad. Nauk SSSR, Ser.Khim., 1973, 1448.
36. B.M.Bulychev, A.L.Kostenko, N.A.Yakovleva, G.L.Soloveichik, and E.V.Evdokimova, "Proceedings of the XIXth International Conference on Coordination Chemistry", Prague, 1978, Vol.2, p.24a.
37. B.M.Bulychev, S.E.Tokareva, G.L.Soloveichik, and E.V.Evdokimova, J.Organometal.Chem., 1979, **179**, 263.
38. G.Monnier, Ann.chim., 1957, [13], **2**, 14.
39. G.Henrici-Olivé and S.Olivé, J.Organometal.Chem., 1970, **23**, 155.
40. J.W.Kentworthy, J.Myatt, and M.C.R.Symons, J.Chem.Soc.A, 1971, 1020.
41. A.I.Sizov and B.M.Bulychev, Zhur.Neorg.Khim., 1981, **26**, 2652 [Russ.J.Inorg.Chem., 1981(10)].
42. A.E.Shilov, A.K.Zefirova, and N.N.Tikhomirova, Zhur.Fiz.Khim., 1959, **33**, 2113 [Russ.J.Phys.Chem., 1959(9)].
43. A.K.Zefirova, N.N.Tikhomirova, and A.E.Shilov, Dokl.Akad.Nauk SSSR, 1960, **132**, 1082.
44. F.K.Shmidt, V.V.Saraev, S.M.Krasnopol'skaya, and V.G.Lipovich, Kinetika i Kataliz, 1973, **14**, 617.
45. P.E.M.Allen, J.K.Brown, and R.S.M.Obaid, Trans. Faraday Soc., 1963, **59**, 1808.
46. A.H.Maki and E.W.Randall, J.Amer.Chem.Soc., 1960, **82**, 4109.
47. G.Henrici-Olivé and S.Olivé, J.Organometal.Chem., 1970, **21**, 377.
48. D.G.H.Ballard and R.Pearce, Chem.Comm., 1975, 621.
49. J.Holton, M.F.Lappert, D.G.H.Ballard, R.Pearce, J.L.Atwood, and W.E.Hanter, J.Chem.Soc., Dalton Trans., 1979, 45.
50. B.M.Bulychev, G.L.Soloveichik, A.L.Kostenko, and V.B.Polyakova, Zhur.Neorg.Khim., 1980, **25**, 2134 [Russ.J.Inorg.Chem., 1980(8)].
51. B.M.Bulychev, G.L.Soloveichik, A.L.Kostenko, and N.A.Yakovleva, Trans.Met.Chem., 1981, **6**, 32.
52. V.V.Saraev, F.K.Shmidt, N.M.Ryutina, V.A.Makarova, and V.A.Gruznykh, Koord.Khim., 1977, **3**, 1364.
53. E.V.Evdokimova, B.M.Bulychev, and G.L.Soloveichik, Kinetika i Kataliz, 1981, **22**, 170.
54. L.J.Guggenberger and F.N.Tebbe, J.Amer.Chem.Soc., 1973, **95**, 7870.
55. G.N.Nechiporenko, G.M.Tabrina, A.K.Shilova, and A.E.Shilov, Dokl.Akad.Nauk SSSR, 1965, **154**, 1062.
56. N.M.Chirkov, P.E.Matkovskii, and F.S.D'yachkovskii, "Polimerizatsiya na Kompleksnykh Metalloorganicheskikh Katalizatorakh" (Polymerisation in the Presence of Complex Organometallic Catalysts), Izd.Khimiya, Moscow, 1976.
57. D.T.Laverty, J.J.Roney, and A.Stewart, J.Catalysis, 1976, **45**, 110.
58. H.H.Brintzinger, J.Amer.Chem.Soc., 1967, **89**, 6871.
59. M.F.Lappert, P.I.Rilev, and P.I.W.Yarrow, Chem. Comm., 1979, 305.
60. G.Henrici-Olivé and S.Olivé, Angew.Chem.Int.Ed., 1968, **7**, 386.
61. M.E.Volpin, A.A.Belyi, V.B.Shur, Yu.I.Lyakhovetsky, R.V.Kudryavtsev, and N.N.Bubnov, J.Organometal. Chem., 1971, **27**, C5.
62. M.E.Vol'pin, A.A.Belyi, V.B.Shur, Yu.I.Lyakhovetskii, R.V.Kudryavtsev, and N.N.Bubnov, Dokl.Akad.Nauk SSSR, 1970, **194**, 579.
63. G.Henrici-Olivé and S.Olivé, J.Organometal.Chem., 1969, **19**, 309.
64. G.L.Soloveichik and B.M.Bulychev, "Tezisy IV Vsesoyuznoi Konferentsii 'Sintez i Issledovanie Neorganicheskikh Soedinenii v Nevodnykh Sredakh'" (Abstracts of Reports at the IVth All-Union Conference on 'The Synthesis and Study of Inorganic Compounds in Non-aqueous Media'), Ivanovo, 1980, Vol.1, p.117.
65. G.W.Parshall, Acc.Chem.Res., 1970, **3**, 139.
66. G.W.Schaeffer, J.S.Roscoe, and A.C.Stewart, J.Amer. Chem.Soc., 1956, **78**, 729.
67. E.Wiberg and H.Neumaier, Angew.Chem., 1964, **76**, 597.
68. E.Wiberg and W.Henle, Z.Naturforsch., 1952, **7b**, 250.
69. G.Jander and K.Kraffczyk, Z.anorg.Chem., 1956, **283**, 217.
70. W.E.Reid, J.J.Bish, and A.Brenner, J.Electrochem. Soc., 1957, **104**, 21.
71. E.Wiberg and H.Neumaier, Z.anorg.Chem., 1965, **340**, 189.
72. M.E.Kost and A.I.Golovanova, Izv.Akad.Nauk SSSR, Ser.Neorg.Materialy, 1978, 1732.
73. K.N.Semenenko, O.V.Kravchenko, S.P.Shilkin, and V.B.Polyakova, Dokl.Akad.Nauk SSSR, 1971, **201**, 1372.
74. M.E.Kost and A.I.Golovanova, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 991.
75. J.Aubry and G.Monnier, Bull.Soc.chim.France, 1954, **9**, 1037.
76. E.C.Ashby and R.A.Covar, Inorg.Chem., 1977, **16**, 1437.

77. V.I.Mikheeva and M.E.Kost, Zhur.Neorg.Khim., 1958, **3**, 260.
78. N.M.Alpatova, V.V.Gavrilenko, Yu.M.Kessler, O.R.Osipov, and D.N.Maslin, "Kompleksy Metallo-organicheskikh, Gidridnykh i Galoidnykh Soedinenii Alyuminiya" (Complexes of Organometallic, Hydride, and Halide Compounds of Aluminium), Izd.Nauka, Moscow, 1970.
79. B.M.Bulychev, K.N.Semenenko, and K.V.Bitsoev, Koord.Khim., 1978, **4**, 374.
80. M.L.H.Green and D.J.Jones, Adv.Inorg.Chem.and Radiochem., 1965, **7**, 115.
81. G.L.Soloveichik and B.M.Bulychev, Uspekhi Khim., 1982, **51**. 507 [Russ.Chem.Rev., 1982(3)].
82. C.J.Ballhausen and J.P.Dahl, Acta Chem.Scand., 1961, **15**, 1333.
83. N.W.Alcock, J.Chem.Soc.A, 1967, 2001.
84. J.C.Green, M.L.H.Green, and C.K.Prout, Chem. Comm., 1972, 421.
85. J.W.Lauher and R.Hoffmann, J.Amer.Chem.Soc., 1976, **98**, 1729.
86. B.M.Bulychev, S.E.Tokareva, G.L.Soloveichik, and K.N.Semenenko, Izv.Akad.Nauk SSSR, Ser.Neorg. Materialy, 1978, **14**, 1741.
87. G.L.Soloveichik, S.E.Tokareva, A.P.Savchenkova, K.N.Semenenko, and B.M.Bulychev, Koord.Khim., 1978, **4**, 1211.
88. B.M.Bulychev, G.L.Soloveichik, A.L.Kostenko, and N.A.Yakovleva, Zhur.Neorg.Khim.(in the press).
89. J.J.Salzmann, Helv.chim.Acta, 1968, **51**, 526.
90. R.Yungst, D.Sekutowski, and G.D.Stucky, J.Amer. Chem.Soc., 1974, **96**, 8108.
91. D.Secutowski, R.Yungst, and G.D.Stucky, Inorg. Chem., 1978, **17**, 1848.
92. H.Nöth and R.Hartwimmer, Chem.Ber., 1960, **93**, 2238.
93. G.Henrici-Olivé and S.Olivé, J.Organometal.Chem., 1969, **17**, 83.
94. G.Henrici-Olivé and S.Olivé, Makromol.Chem., 1969, **121**, 70.
95. F.K.Shmidt, N.M.Ryutina, V.V.Saraev, V.A.Gruznykh, and V.A.Makarov, React.Kinet.Catal.Letters, 1976, **5**, 101.
96. S.E.Tokareva, V.I.Pergushov, A.L.Kostenko, and B.M.Bulychev, Dokl.Akad.Nauk SSSR, 1979, **246**, 1384.
97. A.G.Evans, J.C.Evans, and E.H.Moon, J.Chem.Soc., Dalton Trans., 1974, 2390.
98. A.G.Evans, J.C.Evans, and J.Mortimer, J.Amer.Chem. Soc., 1979, **101**, 3204.
99. E.V.Evdokimova, G.L.Soloveichik, and B.M.Bulychev, Kinetika i Kataliz, 1982, **23**, 1053.
100. M.Gerloch and R.Mason, J.Chem.Soc.A, 1965, 304.
101. V.K.Bel'skii, E.B.Fomicheva, A.V.Aripovskii, and B.M.Bulychev, Dokl.Akad.Nauk SSSR, 1981, **258**, 1137.
102. K.N.Semenenko, A.P.Savchenkova, and B.M.Bulychev, Zhur.Fiz.Khim., 1975, **49**, 1882 [Russ.J.Phys.Chem., 1975(8)].
103. K.N.Semenenko, B.M.Bulychev, N.A.Yakovleva, and V.V.Belov, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1921.
104. G.Natta and G.Mazzanti, Tetrahedron, 1960, 86.
105. J.Holton, M.F.Lappert, G.R.Scollary, D.G.H.Ballarde, R.Pearce, J.L.Atwood, and W.E.Hanter, Chem.Comm., 1976, 425.
106. O.Corradini and A.Sirigu, Inorg.Chem., 1967, **6**, 601.
107. P.C.Wailes and H.Weigold, J.Organometal.Chem., 1970, **24**, 713.
108. J.Olthof, J.Organometal.Chem., 1977, **128**, 367.
109. G.A.Razuvaev, V.N.Latyaeva, L.I.Vishinskaya, and T.P.Samarina, J.Organometal.Chem., 1979, **164**, 41.
110. H.H.Brintzinger and J.E.Bercow, J.Amer.Chem.Soc., 1970, **92**, 6182.
111. B.M.Bulychev, A.L.Kostenko, G.L.Soloveichik, and V.B.Polyakova, Trans.Met.Chem., 1981, **6**, 240.
112. G.L.Soloveichik, A.P.Savchenkova, B.M.Bulychev, and K.N.Semenenko, "Tezisy XII Chugaevskogo Soveshchaniya po Khimii Kompleksnykh Soedinenii" (Abstracts of Reports at the XIIth Chugaev Conference on the Chemistry of Complex Compounds), Novosibirsk, 1975, Vol.3, p.466.
113. K.Isagawa, K.Tatsumi, H.Kosugi, and Y.Otsuji, Chem.Letters, 1977, 1017.
114. G.W.Watt and F.O.Drummond, J.Amer.Chem.Soc., 1966, **88**, 5926.
115. P.C.Wailes and H.Weigold, J.Organometal.Chem., 1970, **24**, 405.
116. H.Roszinski, R.Dautel, and W.Zeil, Z.phys.Chem. (Frankfurt), 1963, **36**, 26.
117. T.J.Marks, W.J.Konnely, J.R.Kolb, and L.A.Shimp, Inorg.Chem., 1972, **11**, 2540.
118. P.L.Johnson, S.A.Cohen, T.J.Marks, and J.M.Williams, J.Amer.Chem.Soc., 1979, **100**, 2709.
119. E.M.Brainina, L.I.Strunkina, B.V.Lokshin, and M.G.Ezernitskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 447.
120. A.A.Pasynskii, Yu.V.Skripkin, I.L.Eremenko, V.T.Kalinnikov, A.S.Antsyshkina, G.G.Aleksandrov, N.I.Kirillova, and Yu.T.Struchkov, "Tezisy XIII Chugaevskogo Soveshchaniya po Khimii Kompleksnykh Soedinenii" (Abstracts of Reports at the XIIIth Chugaev Conference on the Chemistry of Complex Compounds), Moscow, 1978, p.306.
121. T.J.Marks and W.J.Konnely, J.Amer.Chem.Soc., 1975, **97**, 1439.
122. A.B.Erofeev, B.M.Bulychev, and G.L.Soloveichik, Zhur.Neorg.Khim., 1980, **25**, 2634.
123. F.N.Tebbe, J.Amer.Chem.Soc., 1973, **95**, 5412.
124. M.G.H.Green and J.J.E.Moreau, J.Organometal.Chem., 1978, **161**, C25.
125. M.A.Porai-Koshits, A.S.Antsyshkina, G.G.Sadikov, Yu.V.Skripkin, A.A.Pasynskii, and V.V.Ostrikova, Koord.Khim., 1979, **5**, 1103.
126. Kwai Sam Wong, W.R.Schneidt, and J.A.Labinder, Inorg.Chem., 1979, **18**, 136.
127. Yu.V.Skripkin, Abstract of Candidate's Thesis in Chemical Sciences, MFTI, Dolgoprudnyi, 1978.
128. V.P.Fedin, Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1980.
129. M.A.Porai-Koshitz, A.S.Antsyshkina, A.A.Pasynskii, G.G.Sadikov, Yu.V.Skripkin, and V.N.Ostrikova, Inorg.Chim.Acta, 1979, **34**, L285.
130. J.A.Labinder, Kwai Sam Wong, and W.R.Schneidt, J.Amer.Chem.Soc., 1978, **100**, 3254.
131. H.Brunner, P.C.Wailes, and H.D.Kaesz, Inorg.Nuclear Chem.Letters, 1965, **1**, 125.
132. M.L.H.Green, L.Pratt, and G.Wilkinson, J.Chem.Soc., 1958, 3916.
133. O.M.Abu Salah and M.J.Bruce, Austral.J.Chem., 1977, **30**, 2293.
134. D.Grotty, T.J.Anderson, M.D.Glick, and J.P.Oliver, Inorg.Chem., 1977, **16**, 2346.
135. A.V.Aripovskii, B.M.Bulychev, and V.B.Polyakova, Zhur.Neorg.Khim., 1981, **26**, 2722.
136. N.W.Alcock, O.W.Howarth, P.Moore, and G.E.Morris, Chem.Comm., 1979, 1160.

137. F.W.Bentfield, B.R.Francis, M.L.H.Green, N.T.Luong-Thi, G.Moser, and J.C.Poland, J.Less-Common Metals, 1974, **36**, 187.
138. R.A.Forder, M.L.H.Green, R.E.McKenzie, J.C.Poland, and K.Prout, Chem.Comm., 1973, 426.
139. R.A.Forder and K.Prout, Acta Cryst., 1974, **B30**, 2312.
140. S.J.Pettig, A.Storr, B.S.Thomas, and J.Troffer, Acta Cryst., 1974, **B30**, 666.
141. R.D.Rogers, W.J.Cook, and J.L.Atwood, Inorg.Chem., 1979, **18**, 279.
142. J.L.Atwood and A.L.Shoemaker, Chem.Comm., 1976, 536.
143. A.V.Aripovskii, B.M.Bulychev, L.B.Krivdin, and V.B.Polyakova, Zhur.Neorg.Khim., 1981, **26**, 3282.
144. M.L.H.Green, G.A.Moser, J.Packer, F.Petit, R.A.Forder, and K.Prout, Chem.Comm., 1974, 839.
145. M.L.H.Green, N.T.Luong-Thi, G.S.Moser, J.Packer, F.Pettit, and D.M.Roe, J.Chem.Soc., Dalton Trans., 1976, 1988.
146. A.Coda, K.Prout, and D.Tazzoli, Acta Cryst., 1979, **B35**, 1597.
147. B.R.Francis, M.L.H.Green, T.Luong-Thi, and G.A.Moser, J.Chem.Soc., Dalton Trans., 1976, 1339.
148. R.A.Forder and K.Prout, Acta Cryst., 1974, **B30**, 2318.
149. M.L.H.Green and S.J.Simpson, J.Organometal.Chem., 1979, **173**, 287.
150. N.V.Perevozchikov, A.S.Smirnov, Yu.A.Sorokin, R.V.Kaplina, and V.A.Dodonov, Zhur.Obshch.Khim., 1979, **49**, 945.
151. V.K.Bel'skii, E.B.Fomicheva, A.V.Aripovskii, and B.M.Bulychev, Koord.Khim., 1981, **7**, 1722.
152. E.B.Lobkovskii, A.V.Aripovskii, V.K.Bel'skii, and B.M.Bulychev, Koord.Khim., 1981, **7**, 141.
153. H.Sinn, W.Kaminsky, H.-J.Vollmer, and R.Woldt, Angew.Chem.Int.Ed., 1980, **19**, 390.
154. W.Kaminsky, J.Kopf, and G.Thirese, Annalen, 1974, 1531.
155. W.Kaminsky, J.Kopf, H.Sinn, and H.-J.Vollmer, Angew.Chem.Int.Ed., 1976, **15**, 629.
156. V.K.Vasil'ev, V.N.Sokolov, and G.P.Kondratenkov, Dokl.Akad.Nauk SSSR, 1977, **236**, 360.
157. H.Marquett-Ellis and G.Folcher, J.Organometal.Chem., 1977, **131**, 257.
158. T.J.McNeese, S.S.Wreford, and B.M.Foxman, Chem. Comm., 1978, 500.
159. G.Henrici-Olivé and S.Olivé, J.Organometal.Chem., 1971, **35**, 381.
160. N.V.Petrushanskaya, A.I.Kuranova, N.M.Rodionova, and V.Sh.Fel'dblyum, Zhur.Org.Khim., 1974, **10**, 1402.
161. F.K.Shmidt, L.V.Mironova, V.V.Saraev, W.S.Tkach, and A.V.Kalabina, React.Kinet.Catal.Letters, 1976, **4**, 73.
162. V.V.Saraev, F.K.Shmidt, V.A.Gruznykh, L.V.Mironova, and T.I.Bakunina, Koord.Khim., 1979, **5**, 897.
163. R.A.Schunn, Inorg.Chem., 1970, **9**, 394.
164. M.Rosenblum and J.O.Santer, J.Amer.Chem.Soc., 1959, **81**, 5517.
165. G.Henrici-Olivé and S.Olivé, Chem.Comm., 1969, 1482.
166. A.Yamomoto, S.Go, M.Okawa, M.Takahashi, S.Ikeda, and T.Keii, Bull.Chem.Soc.Japan, 1972, **45**, 3110.
167. P.Sobota, B.Jeźowska-Trzebiatowska, and J.Utko, React.Kinet.Catal.Letters, 1976, **4**, 113.
168. P.Sobota, B.Jeźowska-Trzebiatowska, T.Pluzinski, and S.Rummel, J.Organometal.Chem., 1980, **185**, 69.
169. Y.Takegami, T.Ueno, K.Kawayiri, Bull.Chem.Soc. Japan, 1966, **39**, 1.
170. S.G.Giggins, Inorg.Chem., 1977, **16**, 2571.
171. T.Ueno and H.Mija, Chem.Letters, 1973, 39.
172. G.Speier, B.Babos, and L.Markó, Magyar.Kem.Foly, 1970, **76**, 59.
173. F.Ungvari, B.Babos, and L.Markó, J.Organometal. Chem., 1967, **8**, 329.
174. V.V.Saraev, F.K.Shmidt, V.G.Lipovich, and S.M.Krasnopol'skaya, Kinetika i Kataliz, 1973, **14**, 477.
175. F.K.Shmidt, V.V.Saraev, Y.S.Levkoskii, V.G.Lipovich, V.A.Gruznykh, G.V.Ratovskii, and T.V.Dmitrieva, React.Kinet.Catal.Letters, 1979, **10**, 195.
176. K.Jonas and K.R.Pörschke, Angew.Chem.Int.Ed., 1979, **18**, 488.
177. G.L.Soloveichik, B.M.Bulychev, and K.N.Semenenko, Koord.Khim., 1978, **4**, 1216.
178. T.J.Marks and W.J.Kennelly, J.Amer.Chem.Soc., 1975, **97**, 1439.
179. J.L.Atwood, W.E.Hunter, E.Carmona-Guzman, and G.Wilkinson, J.Chem.Soc., Dalton Trans., 1980, 467.
180. W.A.Korniker, E.P.Bensing, and W.C.Raleigh, US P.3 394 156, 1968.
181. H.W.Turner, R.A.Andersen, A.Zalkin, and D.H.Templeton, Inorg.Chem., 1979, **18**, 1221.
182. D.C.Moody, R.A.Penneman, and K.V.Salazar, Inorg. Chem., 1979, **18**, 208.
183. E.C.Ashby and J.J.Watkins, Inorg.Chem., 1977, **16**, 1445.
184. J.J.Watkins and E.C.Ashby, Inorg.Chem., 1977, **16**, 2062.
185. E.C.Ashby and J.J.Watkins, Inorg.Chem., 1977, **16**, 2070.
186. R.R.Schrock, J.Organometal.Chem., 1976, **121**, 373.
187. F.N.Tebbe, J.Amer.Chem.Soc., 1973, **95**, 5823.
188. F.N.Tebbe, US P.3 933 876, 1974.
189. N.I.Kirillova, Zhur.Strukt.Khim., 1974, **15**, 288.
190. T.Aviles, J.Chem.Soc., Dalton Trans., 1979, 1371.
191. A.P.Borisov, V.D.Makhaev, and K.N.Semenenko, Koord.Khim., 1980, **6**, 1139.

Institute of New Chemical Problems,
USSR Academy of Scineces,
Chernogolovka

Lomonosov Moscow State University