Translated from *Uspekhi Khimii*, **51** 507-534 (1982) U.D.C. 541.44

Monometal Hydrido-complexes of Transition Metals

G.L.Soloveichik and B.M.Bulychev

Published information on the chemistry of these complexes stabilised by cyclopentadienyl and other ligands is systematised, and modes of formation of a metal-hydrogen bond in their synthesis are discussed. Consideration is given to the influence on this bond of the structure of various types of transition-metal hydrides containing one, two, or three cyclopentadienyl groups in the coordination sphere. The possibility of stabilising the bond with σ-donor ligands is discussed. The chemical properties of these compounds and the possibility of their use as catalysts are examined. A list of 160 references is included.

CONTENTS

I. Introduction 286
II. Methods of preparation of cyclopentadienyl hydrides of transition metals 287
III. Transition-metal hydrides stabilised with cyclopentadienyl and σ-donor ligands 291
IV. Chemical properties of transition-metal cyclopentadienyl hydrides 297

I. INTRODUCTION

Intensive research has been undertaken during recent years on the preparation and properties of molecular hydrides of transition metals. The unfailing interest taken in them is associated with the development of modern views on the nature of the chemical bond and the stereochemistry of complexes containing a hydrido-ligand, as well as the theory and practice of homogeneous and heterogeneous catalysis of the reactions of unsaturated compounds. One of the most interesting and least studied aspects is catalysis on systems of the Ziegler–Natta type. Hydrido-complexes containing a transition metal together with a non-transition metal can be taken as models of the active centres in these systems. In most cases such complexes can be regarded as derivatives of individual transition-metal hydrides.

The most effective electron-donor ligands stabilising a metal–hydrogen bond are π-accepting (carbonyl, nitrosyl, phosphines, phosphites, arsines, etc.) and π-donor groups (η-cyclopentadienyl, related groups, and to a less extent arsines). π-Accepting ligands form coordinatively saturated mononuclear compounds (phosphorus- or arsenic-containing hydrides) or cluster compounds (carbonyl hydrides), which with rare exceptions do not yield complexes with compounds of non-transition metals, Lewis acids. These hydrides have been studied in some detail, and surveyed in reviews[1-5].

Most of the dimetal hydrido-complexes reported contain cyclopentadienyl ligands. Dicyclopentadienyl hydrides of transition metals have been covered in previous reviews[1,6,7]. During the past five to six years, however, results of fundamental importance have been obtained on the structure of known compounds of this type and on the synthesis of new ones, especially dinuclear complexes containing ($\eta:\sigma=C_5H_4$) groups or a fulvalene ligand (η-C_5H_4–η-C_5H_4). In this connection definite interest attaches also to the less stable monocyclopentadienyl hydrides of type $C_5H_5ML_3H_n$ and $C_5H_5ML_2H_n$, which are isoelectronic with the dicyclopentadienyl hydrides $(C_5H_5)_2M'H_n$, as well as the recently prepared transition-metal hydrides stabilised with σ-donor ligands (groups containing nitrogen or oxygen).

Hydrides have been described containing one, two, or three cyclopentadienyl groups attached to a transition-metal atom. The most stable and most thoroughly studied are dicyclopentadienyl hydrides, which can be subdivided into two main groups—the true dicyclopentadienyl hydrides of general formula $(\eta\text{-}C_5H_5)_2MH_n$ ($n = 1-3$) and the so called bismetallocene hydrides—in the latter of which the metal–hydrogen bond is formed by rearrangement, accompanied by dimerisation, in an unstable metallocene $(C_5H_5)_2M$ with migration of hydrogen from a cyclopentadienyl group to the metal atom. Dimerisation is effected either through a bridging fulvalene ligand η-C_5H_4–η-C_5H_4 (structures of the "stable titanocene" type[8]) or by two $\eta:\sigma=C_5H_4$ groups (structures of niobocene type[9]).

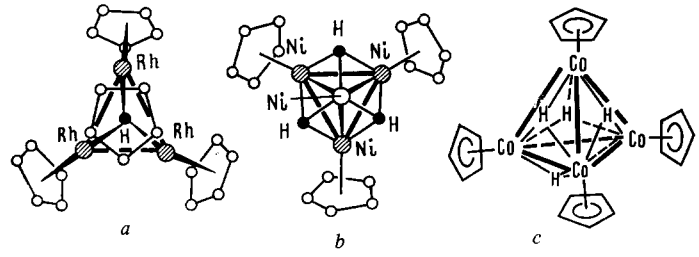


Figure 1. Structure of monocyclopentadienyl hydrides: *a*) $(C_5H_5)_4Rh_3H$;[10] *b*) $(C_5H_5)_4Co_4H_4$;[11] *c*) $(C_5H_5)_4Ni_4H_3$.[12]

The unstable monocyclopentadienyl hydrides of transition metals are stabilised either by the addition of two-electron and in some cases one-electron ligands or by the formation of clusters, among which $(C_5H_5)_4Rh_3H$,[10] $(C_5H_5)_4Co_4H_4$,[11] and $(C_5H_5)_4Ni_4H_3$[12] are known. In all these compounds the hydrogen atoms are attached to three transition-metal atoms, and are located above the plane of the triangle formed by the latter (Fig.1). Stabilisation by means of electron-donor ligands results in the formation of complexes of type $C_5H_5M(ArH)H_n$, $C_5H_5ML_3H_n$, $C_5H_5ML_2H_n$, and $C_5H_5MLXH_n$, where $n = 1-3$, L is a two-electron ligand, and X a one-electron ligand. These compounds are isoelectronic with dicyclopentadienyl hydrides $(C_5H_5)_2MH_n$ of the metals on the right or on the left in the Periodic Table.

Descriptions have appeared not only of neutral cyclopentadienyl hydrides but also of anionic (of metals in Groups IV and V) and cationic (in Groups VI–VIII) complexes.

II. METHODS OF PREPARATION OF CYCLOPENTADIENYL HYDRIDES OF TRANSITION METALS

Methods of obtaining cyclopentadienyl hydrides are in general the same as those for other transition-metal hydrides stabilised with π-accepting ligands. Possible sources of hydrido-hydrogen are molecular hydrogen, cyclopentadienyl groups, hydrides and alkyl compounds of non-transition metals and boron, compounds containing mobile hydrogen atoms, in particular Brønsted acids, and also apparently solvent molecules in certain cases. Our survey of general methods for synthesising cyclopentadienyl hydrides of transition metals will be based on the classification suggested in Ref.7†.

1. Reactions with Molecular Hydrogen

(1a) Oxidative addition

Hydrogen adds reversibly to permethyltitanocene to give the corresponding titanium(IV) dihydride[13]:

$$(C_5Me_5)_2Ti + H_2 \rightleftarrows (C_5Me_5)_2TiH_2 . \qquad (1)$$

Chromocene reacts with carbon monoxide and hydrogen under high pressures to yield[14] $C_5H_5CrH(CO)_3$. Formation of an anionic complex $Na^+(C_5H_5)_2TiH_2^-$ in the system comprising dicyclopentadienyltitanium dichloride with sodium naphthalide in an atmosphere of hydrogen also probably involves oxidative addition of hydrogen to unstable dicyclopentadienyltitanium followed by reduction[15].

We may note also the displacement of π-bonded ligands by hydrogen, reported for dinitrogen complexes of zirconium (II)[16] and molybdenum(0)[17]:

$$[(C_5Me_5)_2Zr(N_2)]_2N_2 + H_2 \xrightarrow[25°C]{\text{toluene}} (C_5Me_5)_2ZrH_2 + N_2 .$$

(1b) Hydrogenolysis of Metal–Carbon σ-bond

In some cases a metal–alkyl bond is very readily split by hydrogen with formation of metal–hydrogen bond. Thus dicyclopentadienyldimethyltitanium reacts with hydrogen even under low pressures, but the reaction becomes explosive when the pressure is raised above 250 mmHg[18] [Cp = C_5H_5]:

$$2Cp_2TiMe_2 + 3H_2 \xrightarrow[pH_2 \leqslant 250\ mmHg]{\text{solid phase}} (Cp_2TiH)_2 + 4CH_4 .$$

A similar reaction has been reported for bispentamethylcyclopentadienyldimethyl compounds of uranium and thorium[19]:

$$2(C_5Me_5)_2MMe_2 + 4H_2 \xrightarrow[25°C]{\text{toluene}} [(C_5Me_5)_2MH_2]_2 + 4CH_4 .$$

(1c) Hydrogenolysis of Metal–Metal Bond

Fission of a metal–metal bond by hydrogen has been reported only for cyclopentadienyl carbonyls of Group VI metals. Tricarbonylcyclopentadienylchromium hydride is formed[20] by the action of hydrogen on bis(tricarbonylcyclopentadienylchromium) at 150 atm and 70 °C. The corresponding reaction with the molybdenum compound takes place under still more severe conditions[14].

2. Oxidative Addition of H–Z Compounds

Compounds containing a sufficiently mobile hydrogen atom can add to low-valency transition-metal complexes to form M–H and M–Z bonds. The H–Z compounds may be hydrocarbons or hydrides of elements of the germanium subgroup.

(2a) Oxidative Addition of Hydrocarbons

Reduction of dicyclopentadienylzirconium dichloride with metallic sodium in the presence of naphthalene in oxolan forms a naphthyl hydrido-complex

$$(C_5H_5)_2Zr\mu(H)\mu(2\eta^1 : 2\eta^2\text{-}C_{10}H_7)Zr(C_5H_5)_2$$

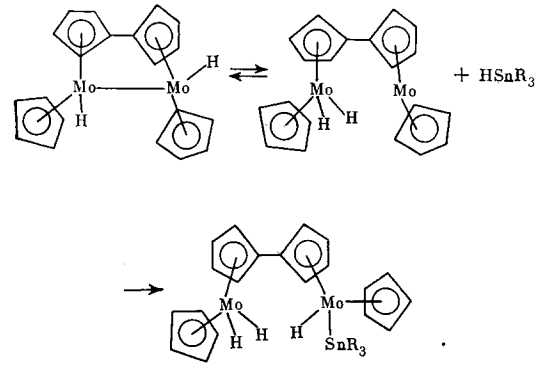
apparently by addition of naphthalene to the metastable dicyclopentadienylzirconium[21].

Cyclopentadienyl hydrides of transition metals have been obtained also by the oxidative addition of cyclopentadiene. Thus photoreaction of the latter with $C_5H_5Nb(P(C_6H_5)_3)_2(CO)_2$ gives the dihydride $C_5H_5Nb(P(C_6H_5)_3)_2(CO)H_2$, which is isoelectronic with $(C_5H_5)_2MoH_2$.[22] An analogous reaction has been reported for $Ni(P(C_6H_{11})_3)_2$[23] and $M(CO)_3(NCCH_3)_3$, where M = Cr, Mo, W.[24–26] The respective reaction products are $C_5H_5NiP(C_6H_{11})_3H$ and $C_5R_5M(CO)_3H$ (R = H, CH_3).

The action of atomic molybdenum and tungsten on excess of cyclopentadiene forms the dicyclopentadienyl dihydrides, with yields of 40–50% from the latter metal. Subliming the products of the reaction of atomic tungsten with a mixture of cyclopentadiene and an arene gives the complexes $C_5H_5W(ArH)H$.[27]

(2b) Oxidative Addition of Hydrides of the Germanium Subgroup

The photochemical action of trichlorosilane on cyclopentadienyl carbonyls of manganese, iron, and cobalt and also on arene carbonyls of chromium is accompanied by the evolution of carbon monoxide and the formation of cyclopentadienyl hydrides containing a metal–silicon bond[28]. The action of trialkylstannanes on $(C_5H_5MoH)_2(C_5H_4\text{–}C_5H_4)$ yields $C_5H_5MoH_2\text{-}\mu\text{-}(C_5H_4)C_5H_5Mo(H)SnR_3$, probably by oxidative addition to molybdenum(II)[29]:



† The numbering in the columns denoting "preparation" in Tables 1, 5, and 7 corresponds to the subheadings in this Section.

3. Protonation of Cyclopentadienyl Compounds of Transition Metals

Cyclopentadienyl hydrides of Groups VI–VIII transition metals possess lone pairs of electrons, and react with Brønsted acids to form metal–hydrogen bonds (oxidative addition of protons). The acids usually employed are tetrafluoroboric, hexafluorophosphoric, concentrated sulphuric, and anhydrous hydrohalic. Protonation of neutral complexes yields cationic hydrides. Dicyclopentadienyl hydrides $(C_5H_5)_2MH_n$ (M = Mo, W, Re, Tc) and also ferrocene give stable ionic complexes $(C_5H_5)_2MH_{n+1}^+X^-$. The carbonyl complexes $C_5H_5W(CO)_2H$[30] and $C_5H_5Ir(CO)_2P(C_6H_5)_3$[31] undergo analogous reactions, forming unstable hydrido-cations. Protonation accompanied by ligand substitution has been reported[32]:

$$CpRh(C_2H_4)_2 + BF_3\cdot H_2O + PPh_3 \xrightarrow{CH_3OH} [CpRh(PPh_3)_2H]^+[BF_4]^- .$$

Protonation of dinuclear cyclopentadienyl carbonyls of transition metals yields dinuclear hydrido-complexes $[C_5H_5M(CO)_3]_2H^+X^-$ (M = Mo, W) and $[C_5H_5M(CO)_2]_2H^+X^-$ (M = Fe, Ru).[30] A complex $[(C_5H_5)_2WH]_2H^+ClO_4^-$ has been obtained by the cathodic reduction of dicyclopentadienyltungsten dihydride in acetonitrile[33]. All these complexes apparently[33] contain a linear M–H–M bridge.

Anionic cyclopentadienyl carbonyls of molybdenum and tungsten also undergo protonation, forming neutral hydrides. Deuteroacetic acid yields the corresponding deuterides[14–34]:

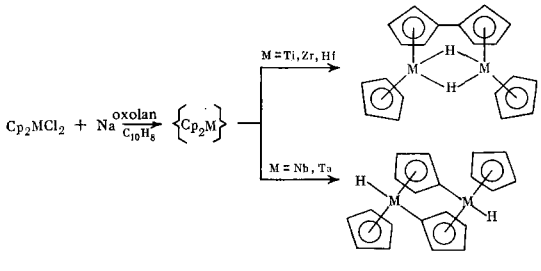
$$CpM(CO)_3^-Na^+ + CH_3COOD \rightarrow CpM(CO)_3D + CH_3COONa$$
$$M=Mo, W .$$

4. Reduction of Cyclopentadienyl Compounds of Transition Metals

Mild reduction of dicyclopentadienyl hydrides $(C_5H_5)_2MH_n$ (n = 2,3) in some cases yields the compounds $(C_5H_5)_2MH_{n-1}$. Further reduction results in unstable metallocenes $(C_5H_5)_2M$, which undergo rapid rearrangement with incorporation of metal at a carbon–hydrogen bond of a cyclopentadienyl group to give dimeric bismetallocene hydrides.

(4a) Reduction by Alkali Metals

Reduction of dicyclopentadienyl dichlorides $(C_5H_5)_2MCl_2$ by alkali metals (sodium and to a less extent potassium) in the form of amalgams or naphthalene complexes is the principal method of preparation of bismetallocene hydrides of titanium[35–37], zirconium and hafnium[38,39], and niobium and tantalum[9,40]:



This reaction can be accomplished with catalytic quantities of naphthalene[39]. At −80 °C it leads to formation of the complex $C_5H_5Ti\mu$-(σ : η-C_5H_4)$Ti(C_5H_5)_2.C_4H_8O$,[41] treatment of which with toluene gives the non-solvated complex. A titanium–hydrogen bond may[41] be present. Intermediate formation of monomeric $(C_5H_5)_2M$ has been demonstrated by electron spin resonance in the case of niobocene[40]. Treatment of niobocene $C_5H_5Nb(H)(\mu = C_5H_4)_2Nb(H)(C_5H_5)_2$ with sodium naphthalide gives the anionic complex $Na_2[C_5H_5Nb(H)\mu$-$C_5H_4]_2$.[42] An analogous reaction has been reported for the titanium compounds $(C_5H_5)_2TiR_2$.[43]

(4b) Photochemical and Thermal Decomposition of Dicyclopentadienyl Hydrides and Alkyls of Transition Metals

Photolysis and thermal decomposition of $(C_5H_5)_2MR_2$ (M = Ti, Zr) and $(C_5H_5)_2MH_2$ (M = Mo, W) lead to the formation of bismetallocene hydrides. The course of the reaction and the composition of the final products are significantly influenced by the nature of the solvent.

Thermolysis of $(C_5H_5)_2MR_2$ (M = Ti, Zr, V) is usually accompanied by migration of hydrogen atoms of the cyclopentadiene ring to transition-metal atoms and elimination of an RH group[44–47]. A mixture of products is formed, containing π,σ-bound C_5H_4 groups and perhaps metal–hydrogen bonds[45]. Partial retention of the dicyclopentadienyl structure has been noted only with vanadium[47]. In contrast to thermolysis, the photolysis of $(C_5H_5)_2Ti(C_6H_5)_2$ has a radical mechanism[48]. In solvating solvents dicyclopentadienyltitanium hydride is formed, but in inert solvents the metastable dicyclopentadienyltitanium, which in an atmosphere of carbon monoxide is converted into the carbonyl $(C_5H_5)_2Ti(CO)_2$.[48]

Exposure (λ = 366 nm) of an iso-octane solution of $(C_5H_5)_2MoH_2$ gives a polymeric product $[(C_5H_5)_2Mo]_x$ of undetermined structure[49]. Replacement of iso-octane by ethanol[50] or toluene[51] as solvent yields a dinuclear compound

$$C_5H_5Mo\mu\text{-}[\sigma : \eta\text{-}C_5H_4)_2MoC_5H_5$$

perhaps by stabilisation of the intermediate monomeric compound $(C_5H_5)_2Mo$ by the solvent. Photolysis of $(C_5H_5)_2WH_2$ in diethyl ether gives $(C_5H_5WH)_2\mu = (\sigma : \eta = C_5H_4)_2$, but in tetramethylsilane *cis*- and *trans*-$(C_5H_5WH)\mu$-$(\sigma : \eta\text{-}C_5H_4)_2$. $.(C_5H_5WCH_2Si(CH_3)_3)$ are formed[50,51]. Furthermore, the thermal decomposition of $(C_5H_5)_2W(CH_3)H$ in cyclohexane yields the isomers $(C_5H_5WH)\mu$-$(\sigma : \eta\text{-}C_5H_4)_2(C_5H_5WCH_3)$.[51]

(4c) Cathodic and Other Reductions

Tervalent tungsten hydride $(C_5H_5)_2WH$ has been obtained as a complex with phenanthraquinone by electrolysis of $(C_5H_5)_2WH_2$ at a controlled potential. The cations $[(C_5H_5)_2W(R)H]^+$ and $[((C_5H_5)_2WH)_2H]^+$ have been obtained similarly[33].

Niobium(IV) and tantalum(IV) hydrides identified by electron spin resonance, have been obtained[52] by treating the $(C_5H_5)_2MH_3$ with di-t-butyl peroxide:

$$Cp_2NbH_3 + BuO^{\cdot} \xrightarrow[-80^\circ C]{h\nu} Cp_2NbH_2 + BuOH .$$

(4d) Reactions of Compounds of Transition Metals in Lower States of Oxidation

Double decomposition between cyclopentadienylsodium and low-valency transition-metal compounds can be used to obtain bismetallocene hydrides with intermediate formation of the dicyclopentadienyl compounds. Thus reactions involving titanium(II) chloride and dimeric molybdenum(II) acetate

yield fulvalene complexes containing methyl–hydrogen bridges (in the case of titanium)[53] and terminal bonds (molybdenum)[54].

5. Use of Alkyl and Hydride Compounds of Non-transition Metals and of Boron

Alkyl and hydride derivatives of Groups I–III metals (usually lithium, magnesium, or aluminium) and also hydroborates are the most frequent reactants for obtaining cyclopentadienyl hydrides of transition metals. The most convenient are hydro-aluminates and -borates, mostly solutions of lithium tetrahydroaluminate in ether or oxolan or of sodium tetrahydroborate in alcohol. The recent availability of new reagents such as $NaBH(C_2H_5)_3$, $LiAlH(OC_4H_9\text{-}t)_3$, and $NaAlH_2(OCH_2CH_2OCH_3)_2$ has extended significantly the range of solvents employed (in particular to aromatic hydrocarbons) and the overall possibilities of the method. The starting materials usually employed are transition-metal complexes containing bonds between metal and halogen or pseudohalogen, which is exchanged for an ElH_4^- group or a hydride anion. In all cases the reaction involves intermediate formation of more or less stable dimetal complexes containing M–C–El or M–H–El bridges. A metal–hydrogen bond is formed by three principal mechanisms—elimination of an alkene from a metal–carbon σ-bond, homolytic elimination of a hydro-borate or -aluminate group ElH_4^-, and hydrolysis of M–H–El bridges or direct M–El bonds.

(5a) Elimination of Alkene from Alkyl–Metal Complexes

In the reaction between dicyclopentadienyltitanium di- or mono-chloride and organo-lithium or -magnesium compounds electron spin resonance has revealed the presence in solution of anionic complexes $(C_5H_5)_2TiH_2^-M^+$ (M = Li, Na, MgX)[55–57]. The hydrogen originates in alkyl groups[57].

Successive treatment of $C_5H_5Co(P(CH_3)_2C_6H_5)I_2$ with isopropylmagnesium bromide and hexafluorophosphoric acid in oxolan gives the cationic complex $[C_5H_5Co(P(CH_3)_2C_6H_5)H]^+.[PF_6]^-$.[58] The tetraphenylcyclobutadiene complex $C_5H_5Mo(CO)(C_4(C_6H_5)_4)H$ is obtained similarly[59]. An unusual photochemical reaction of tungsten hexachloride with cyclohexa-1,3-diene, cyclopentadienylmagnesium bromide, and isopropylmagnesium bromide in ether yields the complex $C_5H_5W(\eta\text{-}C_6H_6)H$.[60]

(5b) Splitting of Tetrahydro-borate and -aluminate Groups

The action of hydroborates and especially of alkali-metal hydroaluminates on complexes of transition metals in higher states of oxidation usually involves reduction of the transition metal (except zirconium). Thus the reaction of triscyclopentadienyluranium monochloride with lithium triethylhydro-borate or tetrahydroaluminate yields solvated triscyclopentadienyluranium, presumably via an unstable intermediate $(C_5H_5)_3UH.L$.[61]

The complicated reaction of higher chlorides of niobium, tantalum, molybdenum, tungsten, rhenium, and technetium with the tetrahydroborate and the cyclopentadienyl of sodium in oxolan provides a general method for obtaining dicyclopentadienyl hydrides of those metals[62–65]. Although it requires precise observance of the procedure, it does not always give high yields. Application to the preparation of dicyclopentadienylniobium trihydride requires a high pressure of hydrogen (800 atm) over the reaction mixture[63], but that of dicyclopentadienyl-molybdenum or -tungsten dihydride needs low temperatures of −(100–120) °C. Sodium tetrahydroborate has been used to obtain dicarbonylcyclopentadienyl-iron and -ruthenium monohydrides[66,34] from corresponding halides.

In some cases the transition-metal cyclopentadienyl tetrahydroborates formed undergo homolytic fission only under the influence of stronger Lewis bases:

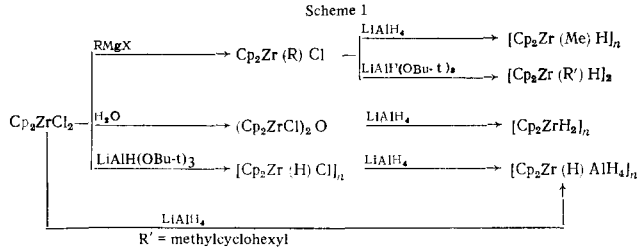
$$Cp_2M\left(\begin{array}{c}H\\ \diagup\ \diagdown\\ H\quad B\quad H\\ \diagdown\ \diagup\\ H\end{array}\right)_n + n\,L \rightarrow Cp_2MH_n + n\,BH_3\cdot L\ .$$

Thus dicyclopentadienylzirconium bistetrahydroborate forms the corresponding hydrido-monotetrahydroborate in the presence of an equimolecular quantity of trimethylamine, and the dihydride $[(C_5H_5)_2ZrH_2]_x$ with double that quantity[67]. Dicyclopentadienyltitanium tetrahydroborate does not undergo this reaction[67], although the tetrahydroborate group is decomposed by triethylamine in the presence of carbon monoxide, when dicarbonyldicyclopentadienyltitanium is obtained[68]. Use of excess of phosphine (phosphite) for this purpose yields phosphorus-containing hydrides: thus for the monocyclopentadienylchromium complex[69]

$$CpCrCl_2\cdot C_4H_8O \xrightarrow[\text{oxolan}]{NaBH_4} CpCr(BH_4)_2 \xrightarrow{P(OMe)_3} CpCr[P(OMe)_3]_3H\ .$$

Several dicyclopentadienyl hydrides of zirconium(IV) have been obtained by the action of lithium tetrahydroaluminate or tri-t-butoxyhydroaluminate on chlorine-containing complexes[70,71] (Scheme 1).

Scheme 1



The complexes $C_5H_5M(NO_2)H$ (M = Mo, W) have been obtained by treating the corresponding chlorides with sodium bismethoxyethoxydihydroaluminate in toluene[72]. An analogous method has been used to prepare $C_5H_5Mo(C_6H_6)H$[73] and $C_5H_5Mo(diphos)H_3$.[74] In several cases the resulting transition-metal (titanium, niobium, etc.) hydroaluminates are not decomposed by the solvent with formation of a metal–hydrogen bond and a solvated aluminium hydride: thus the TiH_2Al link is not broken even by triethylamine[75]. Conducting the reaction between dicyclopentadienyltitanium dichloride and lithium tetrahydroaluminate in non-solvating solvents (alkenes) gives fulvalene hydrides $(\eta\text{-}C_5H_4\text{–}\eta\text{-}C_5H_4)(C_5H_5Ti.(X)(Y)TiC_5H_5)$, where X, Y = H, Cl.[76]

A heterogeneous exchange reaction with sodium hydride has also been described. Thus triscyclopentadienyl- and also bisindenyl-cerium(IV) hydrides have been obtained from the chlorides heated in oxolan at 100 °C for 5–6 h.[77]

(5c) Hydrolysis of Compounds Containing Metal–Hydrogen–Element and Metal–Element Bonds

Reaction between $(C_5H_5)_2NbCl_2$ and $NaAlH_2X_2$ (X = H, C_2H_5, $CH_3OCH_2CH_2O$) gives an equimolecular mixture of $(C_5H_5)_2NbH_3$ and $(C_5H_5)_2NbH_2AlX_2$.[78] When X = H, only $(C_5H_5)_2NbH_2AlH_2$ is formed in the course of time, but conducting the reaction in the presence of carbon monoxide, a

trialkylphosphine, or ethylene gives the $(C_5H_5)_2Nb(H)L$ in at most 50% yield (trialkylphosphines do not react with $(C_5H_5)_2NbH_2AlH_2$). This reaction is assumed to involve disproportionation of the niobium(IV) dihydride[78]:

$$Cp_2NbCl_2 + NaAlH_2X_2 \xrightarrow[-NaCl,\ -AlHX_2]{\text{oxolan}} Cp_2NbH_2 \begin{cases} \longrightarrow Cp_2NbH_3 \\ \longrightarrow Cp_2NbH \xrightarrow{AlHX_2} Cp_2NbH_2AlX_2 \end{cases}$$

Hydrolysis of the reaction mixture and also of the individual $(C_5H_5)_2NbH_2AlH_2$ gives high yields of $(C_5H_5)_2NbH_3$. Hydrolysis takes place unsymmetrically: reaction with deuterium oxide yields $(C_5H_5)_2NbH_2D$ isomers and deuteroxy-groups attached to the aluminium atom[78].

Mild hydrolysis of the complex $[C_5H_5Ti\mu\text{-}(H)\mu\text{-}(H_2Al.(C_2H_5)_2)TiC_5H_5](C_{10}H_8)$ gives a 70% yield of stable titanocene[79]. The cation $(C_{10}H_8)(C_5H_5Mo(H)(OH)MoC_5H_5)^+$ has been obtained by treating "bismetallocene hydrides" of molybdenum with aqueous hexafluorophosphoric acid[51,80]. Transition-metal cyclopentadienyl hydrides are formed not only by hydrolytic fission of bridging hydrogen bonds but also by the fission of bonds between the transition metal and a non-transition metal, when hydroxo-groups combine with the more electropositive atom. Thus hydrolysis of the molybdenum complexes $[(C_5H_5)_2Mo(H)Li]_4$ $(C_5H_5)_2Mo(H)MgBr.2C_4H_8O$, and others containing molybdenum–magnesium and molybdenum–aluminium bonds gives high yields of $(C_5H_5)_2MoH_2$.[81–83] A similar reaction has been reported for $(C_5H_5)_2Ta(H)_2Li$.[84]

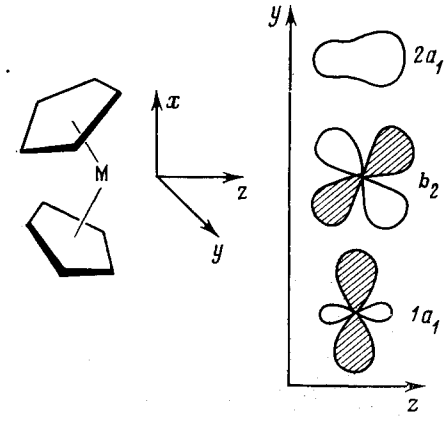


Figure 2. Schematic representation of valency orbitals of the metal atom in the $(C_5H_5)_2M$ group.[88]

Table 1. Physicochemical properties of dicyclopentadienyl hydrides of transition metals.

Compound	Prep.	M.p., °C (decomp., °C)	Solvent	ν(M–H) (ν(M–D)), cm^{-1}	τ_{M-H}, ppm A	τ_{M-H}, ppm B	Ref.
$(Cp_2TiH)_2$	1b	(>70)	Et_2O, oxolan(—70°)	1450(1260, 1050)	—	—	[18]
$(Cp_2TiH)_x$	1b	(>60)	*	1140(800—850)	—	—	[18, 89]
$(Cp_2TiN)_2H_3$	2		PhMe	1585**	—	—	[90]
$(Cp_2ZrH_2)_x$	1b	(120)	*	1520, 1300 (1100, 960)	—	—	[67, 91]
$[Cp_2Zr(R)H]_2$***	5b	—	C_6H_6, Et_2O	1500, 1313	12.35	—	[71]
$Cp_2Zr(H)BH_4$	5b	—	C_6H_6	1945	5.47	—	[67]
$[Cp_2Zr(H)AlH_4]_x$	5b	(>60)	*	—	—	—	[70]
$Cp_2Zr(H)(C_{10}H_7)ZrCp_2$	2a	—	oxolan	—	19.3	—	[21]
Cp_2NbH_3	5b, 5c	(>80)	C_6H_6	1710	12.73	13.72	[63]
Cp_2TaH_3	5b, 5c	(>80)	C_6H_6	1735	11.63	13.02	[84, 92]
Cp_2MoH_2	5b	183—185	C_6H_6, oxolan	1853	—	18.17	[62, 93, 94]
Cp_2WH_2	5b	163—165	C_6H_6, oxolan	1912	—	22.28	[62, 93, 94]
$Cp_2W(H)GePh_3$	5b	235	—	—	21.50	—	[95]
$Cp_2W(H)SnPh_3$	5b	209	—	—	22.24	—	[95]
$Cp_2W(H)PbPh_3$	5b	(198)	—	—	22.78	—	[95]
$Cp_2WH_3{}^+Cl^-$	3	—	—	1943	16.08	16.44	[34]
$[(Cp_2W)_2H_3]^+ClO_4^-$	4c	—	—	2030	26.2	—	[33]
Cp_2TcH	5b	130—155	oxolan C_6H_6, hexane	1923	17.8	—	[65]
$[Cp_2TcH_2]^+PF_6^-$	3	—	—	1984	—	19.7	[65]
Cp_2ReH	5b	161—162	oxolan C_6H_6	2032, 2000	23.0	—	[65, 93]
$[Cp_2ReH_2]^+PF_6^-$	3	—	—	2058	24.6	—	[65]
$[Cp_2ReH]^+AlCl_4^-$	3	(125)	—	—	—	—	[96]
$(C_5Me_5)_2TlH_2$	1a	(>25)	C_6H_6, heptane	1560	—	—	[13]
$(C_5Me_5)_2ZrH_2$	1a	—	C_6H_6, heptane	1555(1100)	—	—	[16]
$[(C_5Me_5)_2UH_2]_2$	1b	(>20)	PhMe	1215, 1114(873, 802)	—	—	[19]
$[(C_5Me_5)_2ThH_2]_2$	1b	—	PhMe	1406, 1361(1020, 979)	—	—9.25	[19]

* Almost insoluble in organic solvents.
** Probably ν(M–H–N) absorption band.
*** R = methylcyclohexyl.

III. TRANSITION-METAL HYDRIDES STABILISED WITH CYCLOPENTADIENYL σ-DONOR AND LIGANDS

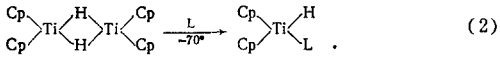
1. Dicyclopentadienyl Hydrides of Transition Metals

Quantum-chemical calculations indicate that the metal atom associated with the inclined rings in $(C_5H_5)_2ML_n$ molecules ($n = 1-3$)[85-88] has three hybrid orbitals, used in forming bonds with ligands and lying in the plane of symmetry yz. According to modern views[87,88] these orbitals have the form depicted in Fig.2. The highest is the $2a_1$ orbital. In the case of a single σ-bonding ligand such as hydrido, with orbitals $1a_1$ (and b_2) filled with electrons, a symmetrical structure is observed with the ligand located on the z axis. In the case of unfilled orbitals overlapping with lower orbitals is energetically more favourable, and the ligand is located between y and z axes[88]. When two ligands are present, the $2a_1$ and b_2 orbitals give two equivalent molecular orbitals, which is closely similar to Alkock's model[86]. With $n = 3$ the ligands form an AB_2 system, which is consistent with the earlier model of Ballhausen and Dahl[85]. Most of the compounds studied conform to the eighteen-electron rule[88].

The complexes $(C_5H_5)_2MH_n$ ($n = 1-3$) are typical covalent compounds. Their physicochemical properties are listed in Table 1.

Group IV

Dicyclopentadienyltitanium(III) hydride exists in two modifications: the grey–green form is polymeric[89], and the violet form apparently dimeric[18]. Association of the electron-deficient $(C_5H_5)_2TiH$ molecules is facilitated by energetic factors[88], and is apparently effected by hydrogen bridges. Absorption bands due to terminal titanium–hydrogen bonds are absent from the infrared spectra, but bands at 1450 and 1140 cm^{-1} are assigned to unsymmetrical stretching vibrations of Ti–H–Ti bridges in dimer and polymer respectively[18]. The action of electron donors (oxolan, triphenylphosphine) stronger than hydride hydrogen results in homolytic fission of hydrogen bridges and formation of unstable monomeric hydrides $(C_5H_5)_2Ti(H)L$:[18]



(2)

The presence of a vacant orbital is the obvious reason why dicyclopentadienylzirconium(IV) hydride $(C_5H_5)_2ZrH_2$ and the related compounds $(C_5H_5)_2Zr(H)X$ (X = Cl, CH_3, AlH_4) are formed as polymers. They are almost non-volatile and insoluble in organic solvents[67,70], except in the cases of the sterically hindered $(C_5H_5)_2Zr(H)R$ (R = methylcyclohexyl)[71] and $(C_5H_4C(CH_3)_3)_2ZrH_2$ (dimer in benzene).[91] The vibrational bands due to the metal–hydrogen bond in the compounds correspond to bridging hydrogen atoms (Table 1): they are located at 1390 cm^{-1} for X = Cl, and at 1500 and 1310 cm^{-1} for X = CH_3.[70] The compound $(C_5H_5)_2Zr(H)BH_4$ is a monomer containing terminal zirconium–hydrogen bonds[67].

Absorption bands ν(Zi–H) are absent[21] from the infrared spectrum of the dinuclear naphthyl hydrido-complex

$$(C_5H_5)_2\overline{Zr\mu\text{-}(H)\mu\text{-}(2\text{-}\eta^1:1\text{-}2\eta^2\text{-}C_{10}H_7)Zr}(C_5H_5)_2 .$$

X-Ray determination of the structure (Fig.3*a*) could not locate the hydrogen atom[21], but its presence follows from stereochemical considerations, nuclear magnetic resonance data (Table 1), and chemical properties (reactions with iodomethane and hydrogen chloride)[21,97].

The unusual complex $((C_5H_5)_2TiN)_2H_3$ is obtained by treating $(C_5H_5)_2Ti\mu(\sigma:\eta\text{-}C_5H_4)TiC_5H_5$ with ammonia, when one mole of hydrogen is evolved, or with a primary or secondary amine[90,98]. X-Ray structural analysis indicates[90] that a molecule of the complex contains the usual wedge-shaped $(C_5H_5)_2Ti$ sandwiches and a planar metal ring TiN_2Ti (the hydrogen atoms could not be located). A band at 1585 cm^{-1}, which is displaced when nitrogen-14 is replaced by nitrogen-15 and hydrogen by deuterium in the original ammonia, is apparently due to vibration of a Ti–H–N bond. The chemical properties of the complex undoubtedly indicate the hydride character of all the hydrogen atoms not present in cyclopentadienyl groups[99]. This, together with the presence of only one unpaired electron per molecule, suggested[90] that the hydrido-atoms were present at the positions indicated in Fig.3*b*.

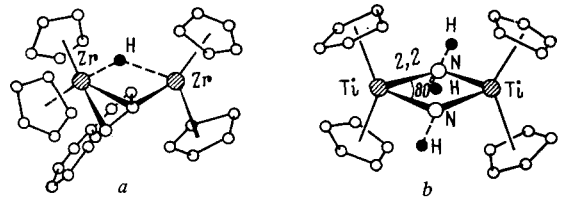


Figure 3. Molecular structure of: *a*) $(C_5H_5)_2\overline{Zr(H)(C_{10}H_7)Zr}.(C_5H_5)_2$;[21] *b*) $((C_5H_5)_2TiN)_2H_3$.[90]

Besides neutral dicyclopentadienyltitanium(III) hydrides electron spin resonance has detected the formation of anionic complexes $(C_5H_5)_2TiH_2^-M^+$ (M = Li, Na)[55-57,100] and $(C_5H_5)_2.TiHCl^-M^+$.[15] The Ti–H–M bond in them is largely covalent in character, the degree of covalency increasing in the sequence Na < Li < MgX < $AlCl_2$ < AlH_2.[100]

The parameters of the e.s.r. spectra of dicyclopentadienyltitanium(III) hydrides are listed in Table 2. The e.s.r. method is extremely useful also for investigating paramagnetic dicyclopentadienyl hydrides of other transition metals, in particular of niobium(IV) and tungsten(III) (below), which exist only in solution.

The dicyclopentadienyl trihydrides of niobium and tantalum are quite similar in properties, differing only in reactivity: the former is far more active than the latter, which is consistent with the fairly severe conditions for its preparation[63]. All three valency orbitals of the $(C_5H_5)_2M$ group in these compounds are involved in forming metal–hydrogen bonds. As a consequence, the complexes are monomeric, and are not protonated in strong acids[92].

Because of the abnormally intense absorption bands ν(Ta–H) of terminal bonds it was assumed[92] that the tantalum–hydrogen bond in the trihydride is largely ionic in character. The nuclear magnetic resonance spectrum of the trihydrides in the high-field region consists of a triplet (A) and a doublet (B_2) (Table 1) with the intensity ratio 1 : 2, which corresponds to the AB_2 system of protons[92]. The spectroscopic data have recently been confirmed by structural investigations[102] (Fig.4*a*, Table 3).

Both hydrides develop a strong tendency to eliminate a hydrogen molecule[107], which is consistent with a mass-spectrometric study of the tantalum complex (the main peak corresponds to the ion $C_{10}H_{11}Ta^+$).[108]

Table 2. Parameters of e.s.r. spectra of dicyclopentadienyl hydrides of transition metals.

Compound	Solvent	g-Factor	Multiplicity	a_H, G	a_M, G	a_H^{av}, G	Ref.
$Cp_2TiH \cdot OC_4H_8$	oxolan	—	doublet	11.6	—	0.4	[18]
$Cp_2TiH \cdot PPh_3$	oxolan	1.992	doublet of doublets	10.5	—	0.41	[15, 18]
$Cp_2TiH \cdot P(n\text{-}Bu)_3$	C_6H_6	1.992	doublet of doublets	10.7*	—	0.40	[15]
Cp_2TiHCl–Li+	C_6H_6	1.983	doublet	7.0		—	[15]
Cp_2TiHCl–Na+	C_6H_6	1.983	doublet	9.1	—	—	[15]
Cp_2TiH_2–Li+	oxolan	1.994	triplet of quartets	9.8	—	0.27	[56]
Cp_2TiH_2–Li+	Et_2O	1.994	triplet of quartets	9.5	—	—	[15]
Cp_2TiH_2–Li+	Et_2O	1.992	triplet	8	6.5	—	[55]
Cp_2TiH_2–Na+	oxolan	1.993	multiplet	10.1	7.2	—	[15]
Cp_2TiH_2–Na+	oxolan	1.994	multiplet	9.8	7.4	—	[56]
Cp_2TiH_2–MgBr+	Et_2O	1.993	triplet	7.8**	—	0.39	[15, 101]
Cp_2NbH_2	C_6H_6	2.010	decet of triplets	11.7***	45.9	—	[52]
$Cp_2Nb(H)$ Bu-t	C_6H_6	2.001	decet of doublets	11.6	68.5	—	[52]
Cp_2TaH_2	C_6H_6	2.006	octet	****	66	—	[52]
Cp_2WH *****	CH_3CN	—	—	1.9	—	—	[33]

* a_D = 1.7 G.
** a_D = 2.4 G (quintet).
*** a_D < 2 G.
**** Hyperfine structure of lines due to hydrido-protons not resolved.
***** In phenanthraquinone complex.

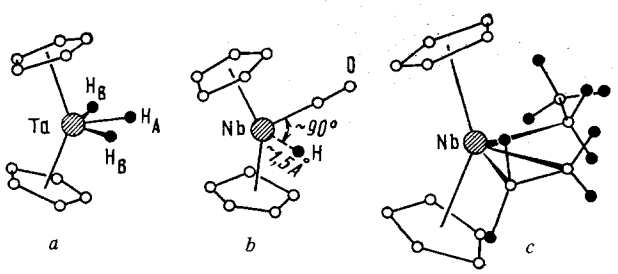
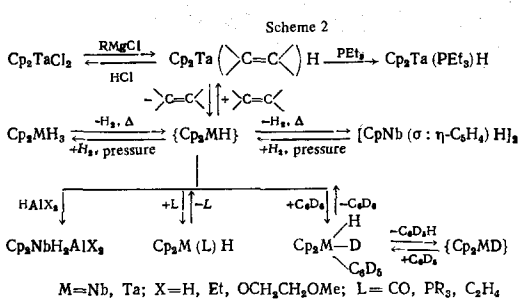


Figure 4. Molecular structure of: *a*) $(C_5H_5)_2MH_3$ (M = Nb, Ta)[102]; *b*) $(C_5H_5)_2Nb(CO)H$;[103] *c*) $(C_5H_5)_2Nb(C_2H_4)C_2H_5$.[104]

Scheme 2



M=Nb, Ta; X=H, Et, OCH_2CH_2OMe; L= CO, PR_3, C_2H_4

Heating the niobium trihydride in the absence of a ligand leads to formation of niobocene[63]. This reaction, like the others in Scheme 2, involves intermediate formation of unstable $(C_5H_5)_2NbH$.[63,78] This explains also the hydrogen–deuterium exchange of hexadeuterobenzene with molecular hydrogen in the presence of the trihydride[63,107].

Heating the trihydrides with a trialkylphosphine, carbon monoxide, or an alkene gives complexes $(C_5H_5)_2M(H)L$, in which the lone pair of electrons occupies one of the valency orbitals (obviously $1a_1$) of the $(C_5H_5)_2M$ group[63,109]. In the niobium and tantalum complexes $(C_5H_5)_2MHL$ with L = PR_3, CO (π-accepting ligands) the chemical shift of the hydrido-protons is observed upfield relative to the initial hydrides (similarly for $(C_5(CH_3)_5)_2Z(L)H_2$), but ν(M–H) is displaced to longer wavelengths. With a π-donor ligand (ethylene) the opposite shifts are observed (Table 4).

Table 3. Structural data on dicyclopentadienyl hydrides of transition metals.

Compound	M to, A								Ref.
	$C_{C_5H_5}$	ring centre	α°	M–H_1, A	M–H_1, A	M–H_2, A	∠H_1MH_1, deg	∠H_1MH_2, deg	
Cp_2NbH_3	2.37	2.06	141	1.65	1.76	1.65	126	65	[102]
$Cp_2Nb(H)CO$	2.36	2.04	143	1.5	—	—	90	—	[103]
Cp_2TaH_3	2.39	2.07	140	1.77	1.78	1.78	125.8	63	[102]
Cp_2MoH_2	2.28	1.94	145.8	1.69	1.69	—	75.5	—	[105]
Cp_2WH_3+Cl−	2.26	1.87	148.2	—	—	—	—	—	[102]
$(Cp_2WH)_2H$+ClO_4−	—	—	145.6	—	—	1.8	—	—	[33]
$[(C_5Me_5)_2ThH_2]_2$	—	—	—	2.29	2.29	2.03	—	58	[106]

X-Ray structural analysis has shown[103] that in the $(C_5H_5)_2Nb(H)CO$ molecule the carbonyl group and presumably the hydrogen atom lie in the *yz* plane (Fig. 4b). According to n.m.r. data the structure of the $(C_5H_5)_2Nb(H)C_2H_4$ complex is closely similar to that of the ethyl complex $(C_5H_5)_2$.$Nb(C_2H_4)C_2H_5$, in which the ethylenic carbon atoms and the α-carbon atom of the ethyl group also lie in the *yz* plane[104] (Fig. 4c).

Because of the presence of a lone pair of electrons the compounds $(C_5H_5)_2M(H)L$ are Lewis bases. Thus treatment of $(C_5H_5)_2Nb(H)CO$ with hydrogen chloride at −30 °C is

stated[110] to give an unstable cationic complex $(C_5H_5)_2Nb(CO).H_2^+Cl^-$, which decomposes with the evolution of hydrogen. Donor–acceptor complexes containing metal–metal bonds have been reported to be formed by $(C_5H_5)_2Nb(H)CO$ with iron tetracarbonyl[111] and zinc tetrahydroborate[112].

Paramagnetic dicyclopentadienyl dihydrides of niobium and tantalum, isoelectronic with $[(C_5H_5)_2TiH_2]^-$, have been reported[52] (Table 2).

Table 4. Spectroscopic characteristics of complexes of dicyclopentadienyl hydrides of metals with π-acceptor and π-donor ligands.

Compound	ν(M–H), cm^{-1}	$\Delta\nu$(M–H), cm^{-1}	τ_{MH}, ppm	$\Delta\tau_{MH}$, ppm	Ref.
$Cp_2Nb(H)CO$	1695	−15	16.39	+2.67	[63]
$Cp_2Ta(H)CO$	1750	0	16.80	+2.62	[63]
$Cp_2Nb(H)PMe_3$	1635	−75	17.84	+4.12	[63]
$Cp_2Nb(H)PEt_3$	1650	−60	17.69	+3.97	[63]
$Cp_2Ta(H)PEt_3$	1705	−45	19.54	+6.52	[63]
$Cp_2Nb(H)(C_2H_4)$	1735	+25	12.95	−0.77	[63]
$Cp_2Ta(H)$ (Alkene)	1750–1700	0±50	—	—	[109]
$(C_5Me_5)_2ZrH_2(CO)$	—	—	8.93	+5.37	[16]
$(C_5Me_5)ZrH_2(PF_3)$	—	—	9.45	+5.89	[16]

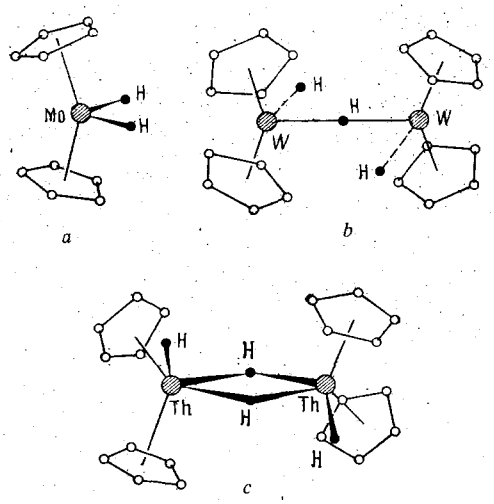


Figure 5. Molecular structure of: *a*) $(C_5H_5)_2MoH_2$;[105] *b*) $((C_5H_5)_2WH)_2H^+ClO_4^-$;[33] *c*) $[(C_5(CH_3)_5)_2ThH_2]_2$.[106]

Groups VI–VIII

According to the scheme of molecular orbitals of $(C_5H_5)_2ML_n$ in Fig. 2 the hydrides $(C_5H_5)_2MH_2$ (M = Mo, W) should possess a lone pair of electrons. In fact research shows[93–95,105,113] that these monomeric hydrides contain two equivalent terminal hydrogen atoms (Fig. 5*a*). The small HMoH angle (Table 3) is consistent with Alcock's model[86] (lone pair ~ 80% localised on *y* axis[105]). However, the structure of the protonated tungsten complex $[(C_5H_5)_2WH_3]^+Cl^-$ is closely similar to that of the niobium trihydride[102]: i.e. the central hydrogen atom is apparently situated on the *z* axis (hydrogen atoms not located).

The presence of the lone pair in the dihydrides determines their chemical behaviour. They are readily protonated by strong acids to cations $(C_5H_5)_2MH_3^+$ isoelectronic with the tantalum trihydride[62], and form donor–acceptor complexes with transition-metal carbonyls[114] and other Lewis acids (BX_3, AlX_3).[93,94,115,116] The spectroscopic characteristics of the M–H bond remain unchanged.

For tungsten a paramagnetic hydride $(C_5H_5)_2WH$ (Table 2) and a cationic hydrido-complex $((C_5H_5)_2WH)_2H^+ClO_4^-$ have also been described[33]. In the spectra of the cation ν(W–H) differs by 180 cm^{-1} and τ_{WH} by 3.9 ppm (all hydrogen atoms equivalent) from the values for the initial dihydride. X-Ray data indicate that the cation contains a linear W–H–W bridge (Table 3) (positions of hydrogen atoms estimated by analogy with the structure of the molybdenum dihydride) and terminal tungsten–hydrogen bonds[33] (Fig. 5*b*).

The rhenium and technetium monohydrides $(C_5H_5)_2MH$ contain two lone pairs, apparently occupying equivalent orbitals. However, only one orbital is protonated, which is attributed to weakening of the basic strength by acquisition of a positive charge. The ionic adduct $(C_5H_5)_2ReH_2^+Cl^-$ is completely stable, and sublimes in a vacuum at 140 °C without decomposition[64]. The two hydrogen atoms in the cation are equivalent, so that its structure is analogous to that of the isoelectronic molybdenum dihydride[105]. Adducts of the rhenium monohydride with BX_3 and with $Al(CH_3)_3$ have been described[93,115].

With Group VIII metals all valency orbitals in $(C_5H_5)_2M$ are occupied by lone electron pairs, and only formation of ions isoelectronic with the rhenium monohydride can be expected. Indeed ferrocene in strongly acid media gives a high-field ^1H n.m.r. signal corresponding to the $(C_5H_5)_2FeH^+$ ion[117], and a stable complex $(C_5H_5)_2FeH^+AlCl_4^-$ has been isolated[96].

Complete replacement by methyl groups of the hydrogen atoms in the cyclopentadienyl rings leads to significant stabilisation of the higher valency states. As an example, the titanium(IV) hydride $(C_5(CH_3)_5)_2TiH_2$ is stable at room temperature[13]; cryoscopic measurements indicate that this compound, like the zirconium derivative[16], is monomeric in benzene.

The low titanium–hydrogen and zirconium–hydrogen frequencies of terminal bonds (Table 1) indicate the instability of the latter. Indeed, equilibrium (1) is readily displaced to the left when the reaction mixture is heated above room temperature. The energy of a titanium–hydrogen bond in bispentamethylcyclopentadienyltitanium dihydride has been estimated[13] as 242.4 kJ mole^{-1}, which is comparable with those of the corresponding molybdenum–hydrogen and tungsten–hydrogen bonds (respectively 258.7 and 286.8 kJ mole^{-1}) obtained by combustion[118], or 251.4 and 305.2 kJ mole^{-1} from calorimetric measurements on the reactions of the dicyclopentadienyl dihydrides with tetrachloromethane in solution)[119].

The vacant orbital of the zirconium atom is involved in forming unstable complexes $(C_5(CH_3)_5)_2ZrH_2.L$, where L = CO, PF_3 (Table 4).[16]

Freezing-point measurements indicate that the thorium and uranium dihydrides are dimeric, which is related to the great size of the central atom[19]. The molecular structure containing terminal and bridging hydrogen atoms (thorium–hydrogen frequencies respectively 1410, 1360 and 1215, 1115 cm^{-1})[19] has been confirmed by X-ray examination[106] for $[(C_5(CH_3)_5)_2ThH_2]_2$ (Fig. 5*c* and Table 3). It is noteworthy that an *f*-element (thorium) departs from the classical geometry of $(C_5H_5)_2ML_3$: three hydrogen atoms do not lie in the single *yz* plane[106].

2. "Bismetallocene Hydrides" of Transition Metals

(a) Complexes Containing a Fulvalene Ligand

Bismetallocene hydrides containing a fulvalene (η-C_5H_4–η-C_5H_4) bridging ligand are now known for titanium, zirconium, hafnium, and molybdenum (Table 5).

Table 5. Physicochemical properties of bismetallocene hydrides of transition metals.

Compound	Prep.	ν(M–H), cm^{-1}	τ, ppm				Ref.
			C_5H_5	C_6H_5	C_5H_4	MH	
$(C_{10}H_8)(CpTiH)_2$	4a	1230	—	—	—	—	[35–37,53]
$(C_{10}H_8)(CpTiHClTiCp)$	5a	1222	—	—	—	—	[76]
$(C_{10}H_8)(CpZrH)_2$	4a	?	—	—	—	—	[38]
$(C_{10}H_8)(CpHfH)_2$	4a	?	—	—	—	—	[39]
$(C_{10}H_8)(CpMoH)_2$	4b,4d	1803	5.47	6.01	—	20.01	[54,80]
$(C_{10}H_8)(CpMoH)_2$	4b	1803	—	(6.53)	—	19.81	[51]
$(C_{10}H_8)[CpMo(H)(OH)MoCp]^+[PF_6^-]_2$	3	—	4.03	4.99; 4.30; 4.11; 3.10	—	21.15	[51,80]
$(C_{10}H_8)(CpMoH)_2H^+PF_6^-$	3	—	4.94	5.03; 5.11	—	22.22	[51]
$(C_{10}H_8)(CpMoH_2)_2$	5b	1815, 1841	—	—	—	—	[29]
$(C_{10}H_8)[CpMoH_2Mo(CO)Cp]$	5d	1805, 1820	—	—	—	18.38	[80]
$(C_{10}H_8)[CpMoH_2Mo(H)(SnR_3)Cp]$*	2b	1813, 1831	5.50; 5.64	5.50; 5.64	—	18.30(2); 17.91(1)	[29]
$[Cp(C_6H_4)NbH]_2$	4a	1650	5.11	—	5.60; 3.95	12.07	[9]
$Na_2[Cp(C_6H_4)NbH]_2$	4a	1720	—	—	—	—	[42]
$[Cp(C_5H_4)MoH]_2$	—	—	5.35; 5.32	—	5.35; 5.32	18.55; 18,66**	[51]
trans-$[Cp(C_5H_4)WH]_2$	4b	—	5.35	—	4.91; 5.36; 5.23; 6.28	20.51	[51]
cis-$[Cp(C_5H_4)WH]_2$	4b	—	5.32	—	4.81; 5.32; 6.27	20.59	[51]

* R = n-C_4H_9.
** Signals of *cis*- and *trans*-isomers.

Although no direct determination of the structure of "stable titanocene" has yet been made, infrared[37] and ^{13}C n.m.r.[8] spectroscopic data suggest the presence of bridging hydrogen atoms and a fulvalene ligand $(C_5H_5TiH)_2(C_{10}H_8)$ (Fig. 6*a*,*b*). It is consistent with X-ray data for the titanocene derivatives $(C_{10}H_8)(C_5H_5TiCl)_2$[120] and $(C_{10}H_8)(C_5H_5.TiOH)_2.C_4H_8O$[121] (Fig. 6*a*,*b*) and $(C_{10}H_8)(C_5H_5Ti(H)(H_2Al.(C_2H_5)_2)TiC_5H_5)$[79] obtained by the action of hydrogen chloride, water, and triethylaluminium respectively on $(C_{10}H_8).(C_5H_5TiH)_2$.

"Titanocene" and its derivatives $(C_{10}H_8)(C_5H_5TiX)_2$ are diamagnetic[36,120,121]. Coupling of the spins probably takes place through the fulvalene ligand, not through the bridging atoms[120]. A direct titanium–titanium bond, whose existence had been assumed[35], is obviously not formed, since for X = Cl, OH the Ti–Ti distance exceeds significantly the sum of the covalent radii (Table 6). Decreasing this distance would lead to excessive steric hindrance: in particular, with Ti–Ti = 2.7 Å the dihedral angle α (Fig. 6*a*) would be ~ 29°. Because of the presence of a single vacant orbital the complexes $(C_5H_5TiX)_2(C_{10}H_8)$ are Lewis acids, and give 1 : 1 complexes with oxolan[53,121].

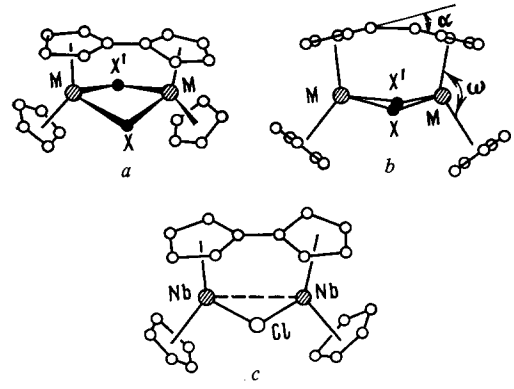


Figure 6. Molecular structure of complexes containing a fulvalene ligand: *a*) $(C_{10}H_8)(C_5H_5M(X)(X')MC_5H_5)$ (M = Ti, X = X' = Cl,[120] OH[121]); *b*) as (*a*) with (M = Mo, X = H, X' = OH[80]); *c*) $(C_{10}H_8)((C_5H_5)_2Nb_2Cl)$.[122]

Table 6. Structural characteristics of compounds of types (I) $(C_{10}H_8)(C_5H_5MX_2MC_5H_5)$ and (II) $C_5H_5M(X)(\mu\text{-}C_5H_4)_2.M(X)C_5H_5$.

Compound	M–X, Å	M–M, Å	Σ_r, Å*	M–C_5H_5, Å	M–C_6H_5, Å	M–C_6H_4, Å	ω, °	α, °	$\angle$XMX', °	Ref.
					type (I)					
$C_{10}H_8)(CpTiCl_2TiCp)$	2.51	3.64	2.72	2.05	2.06	—	134.4	2.5	81.3	[120]
$(C_{10}H_8)[CpTi(OH)_2TiCp]\cdot C_4H_8O$	2.10	—	2.72	2.08	2.08	—	133.5	15.1	—	[121]
$(C_{10}H_8)(CpNbClNbCp)$	2.56	3.27	—	—	—	—	—	—	—	[122]
$(C_{10}H_8)[CpMo(H)(OH)MoCp]^+(PF_6^-)_2$	—	—	—	—	—	—	—	18	—	[80]
					type (II)					
$Cp_2(\mu\text{-}C_6H_4)Ti(C_4H_8O)Cp$	—	3.37	2.72	—	—	2.19	—	—	—	[41]
$CpNb(H)(\mu\text{-}C_6H_4)_2Nb(H)Cp$	1.70	3.11	—	—	—	2.25	140.6	—	—	[9]
$[C_6H_4Si(Me)_2OSi(Me)_2C_6H_4NbH]_2Na_2]O(Et_2)_2$	1.62	3.93	—	—	—	2.31	133.7	—	—	[42]
trans- $CpW(H)(\mu\text{-}C_5H_4)W(H)Cp$	—	3.81	—	—	—	2.19	147	—	—	[123]
cis-$CpW(CH_2SiMe_2)(\mu\text{-}C_5H_4)_2W(H)Cp$	—	3.81	—	—	—	2.17	142	—	—	[123]

* Σ_r = sum of covalent radii.

"Zirconocene" and "hafnocene" are isomorphous with $(C_{10}H_8)(C_5H_5TiH)_2$, and possess similar chemical properties and physicochemical characteristics, which indicates similarity of structure between all three compounds[36,39].

Scheme 3

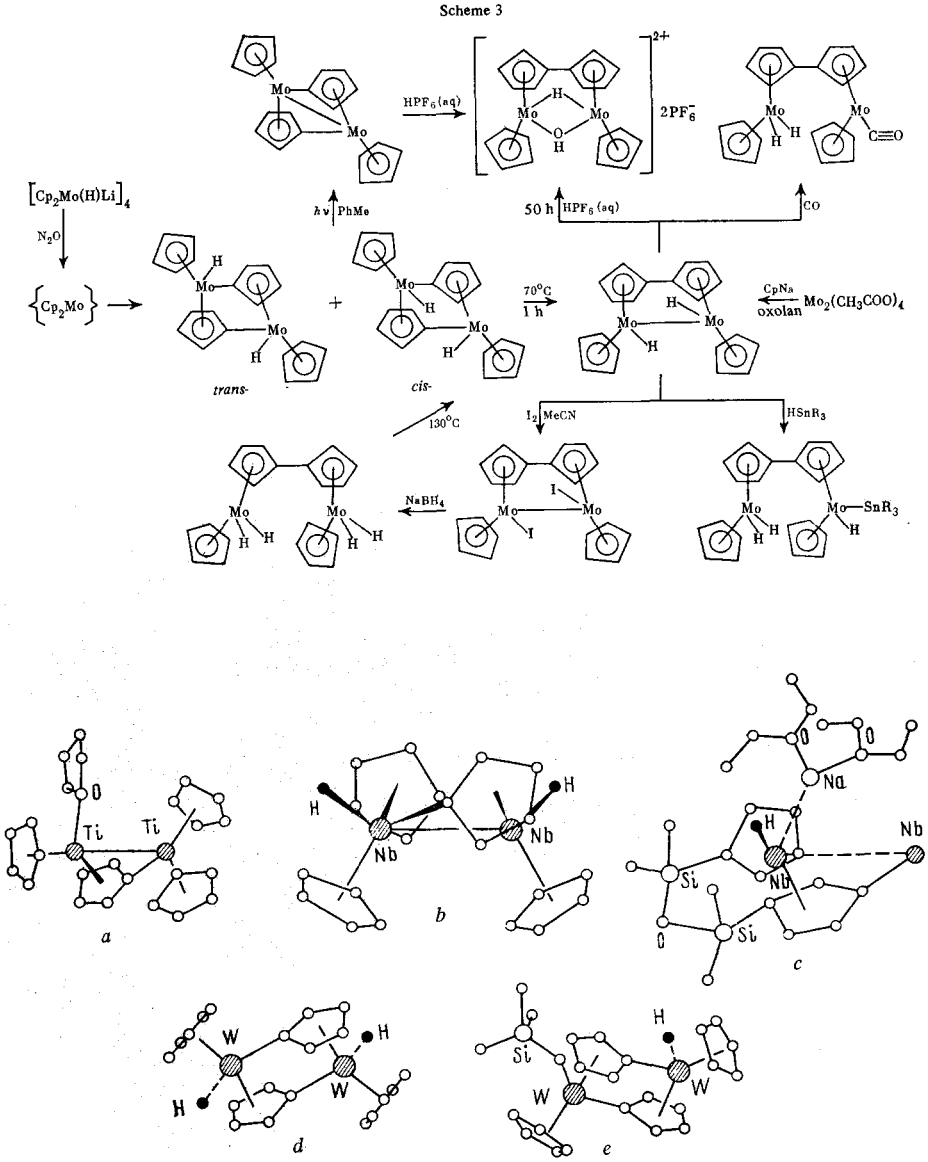


Figure 7. Molecular structure of complexes containing (σ : η-C_5H_4) bridging groups: *a*) $(C_5H_5)_2Ti(C_5H_4)Ti(C_5H_5).C_4H_8O$;[41] *b*) $C_5H_5(H)Nb(C_5H_4)_2Nb(H)C_5H_5$;[9] *c*) $Na_2(O(C_2H_5)_2)_2.[(C_5H_4Si(CH_3)_2OSi(CH_3)_2C_5H_3)NbH]_2$ (fragment)[42]; *d*) *trans*-$C_5H_5(H)W(C_5H_4)_2W(H)C_5H_5$; *e*) *cis*-$C_5H_5(H)W(C_5H_4)_2W(CH_2Si(CH_3)_3)C_5H_5$.[123]

Reactions involved in the synthesis and interconversion of molybdenum hydrides containing bridging ligands η-C_5H_4–η-C_5H_4 and σ : η-C_5H_4 are shown in Scheme 3 [29,51,54,80]. Neutral fulvalene hydrides of molybdenum contain terminal molybdenum–hydrogen bonds, whereas the cationic complexes are supposed to contain Mo–H–Mo bridges, with τ_{MoH} displaced upfield (Table 5). The metal–metal bond in molybdenum(III) hydrides is readily broken to give molybdenum(IV) dihydrides. Steric hindrance in the latter is apparently eliminated by the arrangement of two metal atoms on different sides of the plane of the fulvalene ligand[54].

(b) Complexes Containing Bridging (σ : η-C_5H_4) Groups

The paramagnetic complex $(C_5H_5)_2Ti\mu$-(σ : η-C_5H_4)TiC_5H_5 gives with oxolan an equimolecular adduct[41] (Fig. 7*a*), which may contain a bridging hydrogen atom according to X-ray examination, although infrared bands corresponding to the bridging bonds have not been detected. Indirect evidence of the presence of a hydrido-atom may be provided by the high catalytic activity of this compound in the hydrogenation and isomerisation of alkenes[124]. Under hydrogen pressures of 1–10 atm it absorbs one mole of the gas to form an unstable

Table 7. Monocyclopentadienyl hydrides of transition metals isoelectronic with $(C_5H_5)_2MH_n$.

Compound	Electronic configuration	Isoelectronic analogue	Prep.	M.p., °C (decomp., °C)	ν(M–H), cm^{-1}	τ_{MH}, ppm	J_{P-H}, G	Ref.
$CpW(NO)_2H$	d^4	Cp_2NbH	5b	52	1900	7.23	—	[72]
$diarsV(CO)_3H_3$	d^2	Cp_2NbH_3	3	(135)	—	8.86	—	[126]
$CpMo(diphos)H_3$	d^2	Cp_2NbH_3	5b	—	1800, 1780	25.15	3.8	[74]
$CpMo(diphos)[Sn(n\text{-}Bu)_3]H_2$	d^2	Cp_2MoH_2	2b	—	1815	16.15	36	[74]
$CpNb(CO)(PPh_3)_2H_2$	d^2	Cp_2MoH_2	2a	—	—	—	—	[22]
$(PhMe)Mo(PPh_3)_2H_2$	d^4	Cp_2MoH_2	1a	—	1740, 1720	14.32	50.2	[17]
$CpRe(CO)(NO)H$	d^5	Cp_2WH	*	liq.	—	18.2	—	[127]
$CpMo(C_6H_6)H$	d^4	Cp_2ReH	5b	(>20)	—	11.77	—	[73]
$CpW(C_6H_6)H$	d^4	Cp_2ReH	2a, 5b	—	1822	12.2	—	[27, 60]
$CpCr(CO)_3H$	d^4	Cp_2ReH	1b, 5b	(57)	—	15.46	—	[20, 34]
$CpCr[P(OMe)_3]_3H$	d^4	Cp_2ReH	5b	(>160)	—	19.70	75	[69]
$(C_6H_6)Cr(CO)_2(SiCl_3)H$	d^4	Cp_2ReH	2b	114	—	20.5	—	[28]
$CpMo(CO)_3H$	d^4	Cp_2ReH	1a, 5b	(110)	1790	15.52	—	[14, 34]
$CpMo(CO)_2(PMe_3)H$	d^4	Cp_2ReH	*	—	—	16.59**, 15.89***	66.6**, 23.0***	[128]
$CpW(CO)_3H$	d^4	Cp_2ReH	5b	(180)	1845	17.33	—	[34]
$CpW(CO)_2(PPh_3)H$	d^4	Cp_2ReH	*	—	—	16.77**, 17.19***	66.1**, 21.4***	[128]
$CpW(CO)_2(PMe_3)H$	d^4	Cp_2ReH	*	—	1860	18.31**, 17.15***	68.3**, 24***	[129]
$CpW(CO)_2[P(OMe)_3]H$	d^4	Cp_2ReH	*	—	1860	18.55**	73**	[129]
$CpW(CO)_2[P(OMe)_3]H$	d^4	Cp_2ReH				17.66***	26***	
$CpMn(CO)_2(SiCl_3)H$	d^4	Cp_2ReH	2b	83	—	19.7	—	[28]
$CpRe(CO)_2(SiCl_2Ph)H$	d^4	Cp_2ReH	2b	—	—	—	—	[130]
$CpFe(CO)_2H$	d^6	Cp_2ReH	5b	liq.	1835	21.91	—	[34, 66]
$CpFe(CO)(SiCl_3)_2H$	d^4	Cp_2ReH	2b	—		21.6	—	[28]
$CpRu(CO)_2H$	d^6	Cp_2ReH	5b	liq.	1835	20.92	—	[34]
$CpCo(CO)(SiCl_3)H$	d^6	Cp_2ReH	2b	33		23.3	—	[28]
$CpW(CO_3H_2)^+$	d^2	$Cp_2ReH_2^+$	3	unstable	—	11.9	—	[30]
$Cp_2Mo(dppm)H^+PF_6^-$	d^2	Cp_2FeH^+	3	—	1890	17.84	36	[74]
$CpRe(C_6H_6)H^+Cl^-$	d^4	Cp_2FeH^+	3	(118)	1705	16.17	—	[131]
$CpCo(PMe_2Ph)_2H^+PF_6^-$	d^6	Cp_2FeH^+	3	—		25.2	76.5	[58]
$(C_6H_6)Mo(PPh_3)_3H^+PF_6^-$	d^4	Cp_2FeH^+	3	—	1910	10.3	72.1	[132]
$(C_6H_6)Mo(PPh_3)_3H_2^{2+}(PF_6^-)$	d^2		3	—	1880	12.3	43.5	[132]

* Substitution of carbon monoxide in carbonyl cyclopentadienyl hydrides.

** Values for *cis*-isomer.

*** Values for *trans*-isomer.

grey–green deposit, which loses hydrogen when the pressure is released. The infrared spectrum of the deposit contains a broad band at 1140 cm^{-1}, corresponding to vibration of a bridging titanium–hydrogen bond[124].

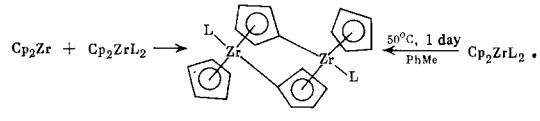
Niobocene (and obviously the isomorphous tantalocene) contain both the usual η^5-C_5H_5 groups and $\sigma:\eta$-C_5H_4 groups linking the niobium atoms in the dimer (Fig. 7*b*).[9] The length and spectrochemical characteristics of the niobium–hydrogen bond (Tables 5 and 6) are closely similar to the corresponding parameters of known transition-metal hydrides. Niobium–niobium bonds are apparently absent[9], as also in the fulvalene complex $(C_{10}H_8)(C_5H_5)_2Nb_2Cl$ (Fig. 6*c* and Table 6).[122] The corresponding hydrido-derivative has not been obtained.

Reduction of niobocene and its analogue containing Si–O–Si bridges between the rings gives the anionic complex $Na_2[C_5H_5Nb(H)(C_5H_4)]_2$.[42] On passing from the neutral compound to the dianion isoelectronic with tungstocene[123] the ν(Nb–H) frequency increases (Table 5) and the Nb–Nb distance (Fig. 7*c*, Table 6) increases, while the dihedral angle of the Nb–$C_{C_5H_4}$ bond diminishes[42].

An interesting reaction of $((C_5H_5)_2Mo(H)Li)_4$ with nitrous oxide gives a mixture of isomers $(C_5H_5MoH)_2(C_5H_4)_2$ (Table 5), which when heated or acidified form hydrido-complexes with a fulvalene ligand (Scheme 3).[80] In contrast to molybdenum, with which the fulvalene hydrides are the more stable[51], only the complexes containing bridging $(\sigma:\eta\text{-}C_5H_4)$ groups are known with tungsten (Tables 5 and 6 and Fig. 7*d*,*e*).

The above compounds are characterised by terminal metal–hydrogen bonds and exist as separable *cis*- and *trans*-isomers. The M, H, $C_{C_5H_4}$, and M′ atoms lie in the same plane[9], which is consistent with theoretical results on the nature of the bond in wedge-shaped sandwiches[85–88].

Besides hydrido-complexes bismetallocenes have been described containing μ-$(\sigma:\eta\text{-}C_5H_4)$ groups and no metal–hydrogen bond. A dark red diamagnetic complex isoelectronic with niobocene has been obtained[125]:



Hence it was assumed[125] that stable zirconocene, in contrast to titanocene, may contain $(\sigma:\eta\text{-}C_5H_4)$ groups. Formation of the corresponding molybdenum compound $C_5H_5Mo(C_5H_4)_2$.MoC_5H_5[51] is shown in Scheme 3.

3. Monocyclopentadienyl Hydrides of Transition Metals

Monocyclopentadienyl hydrides of transition metals are known, stabilised with arenes, carbon monoxide, nitric oxide, phosphines, phosphites, SiX_3, and SnX_3 (Table 7), isoelectronic with the dicyclopentadienyl hydrides $(C_5H_5)_2NbH$, $(C_5H_5)_2NbH_3$, $(C_5H_5)_2MoH_2$, $(C_5H_5)_2WH$, and $(C_5H_5)_2ReH$, and also the cation $(C_5H_5)_2FeH^+$ (Section III, 1).

Monocyclopentadienyl complexes of transition metals with ligands giving a total of four (three) electrons are formally analogous to dicyclopentadienyl hydrides of transition metals situated one (two) places to the left in the Periodic Table, but the monocyclopentadienyl hydrides possess an additional lone pair of electrons. Supplying five electrons ($C_5H_5ML_2XH_n$ complexes) changes neither the state of oxidation nor the electronic configuration of the transition metal

in comparison with $(C_5H_5)_2MH_n$. The coordination of one six-electron ligand (arene) or three two-electron π-accepting ligands yields hydrides isoelectronic with dicyclopentadienyl hydrides of immediate neighbours on the right in the Periodic Table.

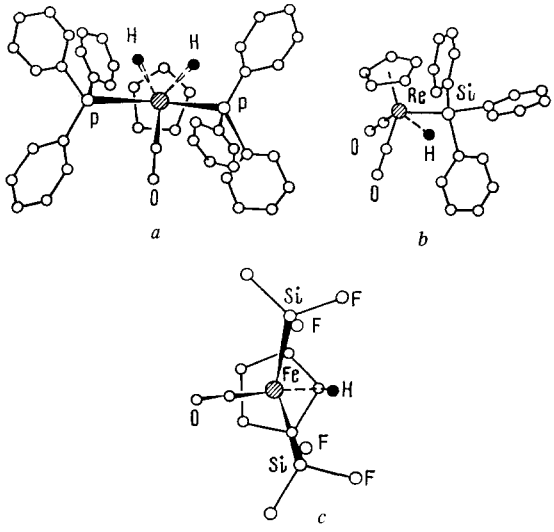


Figure 8. Molecular structure of: *a*) $C_5H_5Nb(CO)(P(C_6H_5)_3).H_2$;[22] *b*) $C_5H_5Re(CO)_2(SiCl_2C_6H_5)H$;[134] *c*) $C_5H_5Fe(CO)(Si.(CH_3)F_2)H$.[136]

It had previously been assumed that the ligand group $(CO)_3$, like an arene, should lead to the formation not only of electronic but also of structural analogues of $(C_5H_5)_2MH_n$[6,60,131]. However, X-ray examination of a series of complexes $C_5H_5M(CO)_2(SiX_3)H$ (M = Mn, Re)[133,134] and $C_5H_5Fe(CO).(SiX_3)_2H$[135,136] showed them to have a piano-stool configuration (Fig.8), in good agreement with n.m.r. results. The hydrogen atoms could not be located, and their positions were estimated from an analysis of non-bonded contacts. The length and spectroscopic characteristics of the metal–hydrogen bond (Table 7) are those usual for transition-metal hydrides.

In the case of $C_5H_5M(CO)_2(PR_3)H$ complexes *cis*- and *trans*-isomers have been obtained that differ markedly in spin–spin coupling constant (J_{P-H} ratio ~3, Table 7). Compounds containing two or more hydrogen atoms exhibit a rapid exchange of hydride protons on the n.m.r. time-scale: i.e. they are stereochemically fluximal.[17,74,126,132]

The chemical properties of monocyclopentadienyl hydrido-complexes of transition metals have been little studied, although their reactions with water, acids, halogens, and halogenated hydrocarbons are similar to those of the dicyclopentadienyl analogues. Thus $C_5H_5W(NO)_2H$ is hydrolysed by water with the evolution of hydrogen[72], whereas $C_5H_5W.(CO)_3H$ and electronic analogues of ferrocene are protonated in strong acids (Table 7).

Protonation of dinuclear complexes containing a metal–metal bond, of the types $(C_5H_5M(CO)_3)_2$ (M = Mo, W) and $(C_5H_5M(CO)_2)_2$ (M = Fe, Ru), form cationic complexes analogous to the dicyclopentadienyl complex $((C_5H_5)_2WH)_2H^+ClO_4^-$[33] and apparently containing M–H–M bridges[30]. Values of τ_{MH} in the cations $(C_5H_5M(CO)_3)_2H^+$ and $(C_5H_5M(CO)_2)_2H^+$ (some of the complexes were isolated as the fluorophosphates) are respectively 30.99, 34.8, 36.3, and 28.58 ppm for M = Mo, W, Fe, and Ru.[30]

It is interesting that protonation of the cation $(C_6H_6)M.(PR_3)_3H^+$, isoelectronic with $(C_5H_5)_2FeH^+$, gives the only known dinuclear cation $(C_6H_6)Mo(PR_3)_3H_2^{2+}$ (usually only one pair of electrons is protonated), which is attributed to the possibility of effective delocalisation of the positive charge[132].

4. Triscyclopentadienyl Hydrido-complexes of Transition Metals

Such hydrides are almost unknown. The brown complex $(C_5H_5)_3CeH$ has been reported[77], having an absorption line $\nu(Ce-H) = 2040\ cm^{-1}$. An attempt to isolate the corresponding uranium complex was unsuccessful[61]. The complex of the corresponding zirconium hydride with triethylaluminium has been isolated[137] from the $(C_5H_5)_4Zr-Al(C_2H_5)_3$ catalytic system; the link is formed by a single hydrogen bridge Zr–H–Al.

5. Transition-metal Hydrides stabilised with σ-Donor Ligands

Transition-metal hydrides stabilised with one-electron σ-donor ligands came to be studied comparatively recently. Hydrides of titanium, uranium, and thorium are known in addition to the relatively well studied zinc hydrides (configuration d^{10}) stabilised with nitrogen-containing ligands.

Reduction of diphenoxytitanium dichloride with alkali metals or sodium tetrahydroborate yields a series of hydro-complexes[138]:

$$(PhO)_2TiCl_2 \xrightarrow[oxolan]{NaBH_4} \{Ti(OPh)_2Cl(C_4H_8O)_2\}_2H$$
$$(PhO)_2TiCl_2 \xrightarrow[PhMe]{K} \{Ti(OPh)_2\}_3H$$
$$(PhO)_2TiCl_2 \xrightarrow[oxolan]{Na/Hg,\ N_2} \{Ti(OPh)_2\}_3(N_2)H\ .$$

Titanium–hydrogen absorption bands have not been detected in them, but their hydride character is confirmed by the formation of chloroform on treatment with tetrachloromethane. The titanium atoms are assumed to be linked by bridging hydrogen atoms and phenoxy-groups[138].

Stable complexes $[((CH_3)_3Si)_2N]_3MH$ (M = U, Th) have been obtained[139] by boiling the corresponding chlorides with $NaN(Si(CH_3)_3)_2$ in oxolan. The hydride hydrogen originates from the solvent, as is confirmed by experiments with octadeutero-oxolan. These hydrides can be obtained also by treating the chloride with t-butyl-lithium or lithium triethylhydroborate in pentane. The metal–hydrogen bond in them has a fairly low stretching frequency, 1430 and 1480 cm^{-1} for the uranium and thorium complexes respectively[139], close to that for the corresponding terminal bond in $[(C_5(CH_3)_5)_2.ThH]_2$ (Table 1).

IV. CHEMICAL PROPERTIES OF TRANSITION-METAL CYCLOPENTADIENYL HYDRIDES

Since in the work covered above attention has been paid mainly to preparing and establishing the structure of the hydrido-complexes, their chemical properties have remained almost uninvestigated. Reactions demonstrating the presence of a metal–hydrogen bond have been mainly studied.

1. Thermal Stability and Reaction with Oxygen

Almost all cyclopentadienyl hydrides of transition metals decompose when heated, with the evolution of hydrogen and often without melting. Published data on decomposition points are given in Tables 1 and 7. The dicyclopentadienyl complexes are more stable than hydrides containing a single cyclopentadienyl group. In a series of compounds of the same type the stability increases regularly with the atomic number of the metal. As a consequence, it has proved impossible to obtain molybdenum analogues of certain tungsten complexes[30,72]. Hardly any detailed study has been made of the thermolysis of cyclopentadienyl hydrides of transition metals. Quantitative evolution of hydrido-hydrogen has been reliably determined in only a few cases (for $(C_5(CH_3)_5)MH_2$ (M = Ti, Zr, U)[13,16,19], $C_5H_5M(CO)_3H$ (M = Cr, Mo, W), and $C_5H_5Fe(CO)_2H$[3,4]). In most cases the decomposition of dicyclopentadienyl hydrides apparently involves the cyclopentadienyl ligand, yielding bridging C_5H_4 or $C_{10}H_8$ groups.

Hardly any study has been made of the action of oxygen on cyclopentadienyl hydrides of transition metals, although many publications emphasise the great sensitivity of these compounds (especially of Groups IV and V) to oxidation.

2. Reactions of Hydrido-complexes with Water and Acids

The reactivity of cyclopentadienyl hydrides of transition metals towards water and aqueous acids, involving the evolution of hydrogen, diminishes regularly on passing from left to right along the Periodic Table: whereas compounds of Group IV transition metals are hydrolysed vigorously by water, those of Group V are moderately hydrolysed, and hydrides of Groups VI–VIII metals are not in general hydrolysed. This is due to diminution in the hydride character of the metal–hydrogen bond (or negative charge on the hydrogen atom). The reactivity of the dicyclopentadienyl hydrides towards the reduction of ketones varies similarly[140]. It is interesting that the complex $C_5H_5W(NO)_2H$, isoelectronic with $(C_5H_5)_2NbH$, is hydrolysed with the evolution of hydrogen, in contrast to $(C_5H_5)_2WH_2$.[72]

The composition of the hydrolysis products was not usually studied, but formation of a hydroxyl derivative of stable titanocene by the action of a stoichiometric quantity of water has been reported[121]. Reaction with hydrogen halides (aqueous or anhydrous) generally results in replacement of a hydrido-ligand by halogen[37,76,124]. Treatment of the dicyclopentadienyl hydrides of tervalent titanium, tantalum, and zirconium with hydrogen chloride leads to oxidation of the metal with evolution of hydrogen and formation of the dichlorides $(C_5H_5)_2MCl_2$.[18,21,109]. This reaction provides a method for identifying a metal–hydrogen bond (see also subsection 3) when n.m.r. investigation is impossible, while infrared metal–hydrogen absorption bands are overlapped by other bands or even are not observed. Evolution of hydrogen deuteride on reaction with deuterium oxide or chloride is regarded as a reliable criterion[7]. Thus this method has shown the presence of a titanium–hydrogen bond in the complex $((C_5H_5)_2.TiN)_2H_3$[90,99] and in the product of the action of diphenylzinc on $(C_5H_5)_2Ti(C_6H_5)_3$.[141] The latter is assumed to contain a fulvalene ligand and two η-C_5H_4 groups linked through the zinc atom[141].

In some cases acid hydrolysis apparently involves intermediate formation of a dihydrido-complex. Thus the cations $C_5H_5M(CO)_3H_2^+$ (M = Mo, W) are formed when the monohydrido-complexes are treated with hexafluorophosphoric acid. The complex tungsten cation evolves hydrogen rapidly, and its molybdenum analogue almost instantaneously[30].

It is assumed also that $(C_5H_5)_2NbH_2(CO)^+$ is formed by the action of hydrogen chloride on the monohydrido-complex[110]:

$$Cp_2NbCl_2 \xrightarrow[2)\ NEt_3,\ CO]{1)\ NaBH_4} Cp_2Nb(H)CO \xrightarrow[-30^\circ]{HCl} \rightarrow Cp_2NbH_2(CO)^+Cl^- \xrightarrow[-H_2]{\Delta} Cp_2Nb(Cl)CO\ .$$

It is noteworthy that its action on niobocene, in contrast to titanocene[37], gives the usual $(\eta$-$C_5H_5)_2NbCl_2$.[42] A similar course is shown by other reactions of oxidative addition involving niobocene[40] and also $(C_5H_5)_2Ti(\sigma:\eta$-$C_5H_4)TiC_5H_5$.[124] These reactions may be expected to apply generally to all hydrides containing μ-$(\sigma:\eta$-$C_5H_4)$ groups, but not to complexes having a fulvalene ligand.

The action of acids on cyclopentadienyl hydrides of Groups VI–VIII transition metals gives protonated complexes, which are discussed in the appropriate subsections.

3. Reactions of Hydrido-complexes with Halogens and Halogenated Hydrocarbons

The action of halogens on the cyclopentadienyl hydrides leads to replacement of a hydrido-ligand by halogen[72], often accompanied by oxidation of the transition metal. For example, "niobocene" gives with bromine dicyclopentadienylniobium dibromide[42], and iodine acts on $(C_5H_5MoH_2)_2(C_5H_4$–$C_5H_4)$ to give the molybdenum(IV) complex $(C_5H_5MoI_2)_2(C_5H_4$–$C_5H_4)$.[29]

The formation of chloroform when a complex is treated with tetrachloromethane also provides a reliable criterion of the presence of a metal–hydrogen bond[7]. The titanium–hydrogen bond in phenoxytitanium hydrides has been demonstrated in this way[138]. In the course of the reaction hydrogen is replaced by halogen with formation of corresponding complexes. Methods of preparation of cyclopentadienyl halides have been described for the complexes $[((CH_3)_3Si)_2N]_3MH$ (M = Th, U)[139] and $C_5H_5Mo(CO)_3H$[142] with tetrachloromethane, and for $(C_5H_5)_2MH_2$ (M = Mo, W)[143] and $C_5H_5Mo(diphos).H_3$[74] with bromoform. The reactivity of $CHal_nH_{4-n}$ diminishes as n decreases, but it has been reported[7] that dichloromethane acts on $(C_5H_5)_2MH_3$ (M = Nb, Ta). Iodomethane is an extremely effective agent, in some cases enabling the content of hydrido-hydrogen to be determined quantitatively (from the evolution of methane) on reaction with $((C_5H_5)_2TiN)_2H_3$,[90] $(C_5H_5)_2Zr(H)(C_{10}H_7)Zr(C_5H_5)_2$,[21] $C_5H_5MoH(\sigma:\eta$-$C_5H_4)_2Mo(H).(C_5H_5)_2$, and $(C_5H_5)_2MoH_2$,[143] and also the corresponding iodo-derivatives to be obtained[51,143].

4. Complex Formation with Lewis Acids

Lewis acids (BX_3, AlX_3, MgX_2, $M(CO)_n$, etc.) form with the cyclopentadienyl hydrides two types of complexes—either of donor–acceptor type containing a metal–metal bond involving the lone pair of a Group VI or VII transition-metal hydride or with a hydrogen bridge—which are the subject of a detailed survey[144]. Here we note merely that the formation of equimolecular adducts having an M–M′ bond hardly changes the spectrochemical characteristics of the metal–hydrogen bond. However, the involvement of hydrogen atoms in forming bridging bonds leads to considerable shifts, in the frequency of this bond (up to 100–350 cm^{-1}) to longer wavelengths, and in τ_{MH} (up to 3–6 ppm) upfield[144].

5. Metallation of Hydrido-complexes at Metal–Hydrogen Bonds

Metallation of the metal–hydrogen bond in cyclopentadienyl hydrides has been effected by the action of butyl-lithium. The reaction with the dicyclopentadienyl dihydrides of molybdenum and tungsten gives cyclic tetramers $[(C_5H_5)_2M(H)Li]_4$ containing M–Li–M bonds.[81] Treatment of the molybdenum hydride with Grignard reagents and aluminium alkyls also results in fission of a molybdenum–hydrogen bond and formation of complexes containing bonds between molybdenum and respectively magnesium[82] and aluminium[83]. Analogous metallation by n-butyl-lithium has been described for $(C_5H_5MoH)_2(C_5H_4{-}C_5H_4)$[29] and $(C_5H_5)_2TaH_3$.[84] Apparently the metal–hydrogen bonds in the thorium and uranium complexes $[((CH_3)_3Si)_2N]_3MH$ also undergo metallation during preparation of the deuterated complexes[139]:

$$[(Me_3Si)_2N]_3ThH_2 \xrightarrow[2)\ Cl_3CCOD]{1)\ n\text{-}LiBu} [(Me_3Si)_2N]_3ThD\ .$$

All metallation products are strong nucleophiles, extremely sensitive to oxygen and readily hydrolysed with regeneration of the metal–hydrogen bond.

6. Reactions of Hydrido-complexes with Donor Molecules

Reaction with donor molecules may or may not involve a metal–hydrogen bond.

The presence of vacant orbitals on a transition-metal atom usually results in the formation of solvates. Stable titanocene gives an adduct with oxolan[35–37], and niobocene adducts with acetonitrile and aromatic hydrocarbons[40]. Monomeric $(C_5(CH_3)_5)_2ZrH_2$ gives unstable equimolecular complexes with carbon monoxide and phosphorus trifluoride[16]. The orbitals of Groups VI–VIII metals are filled with d-electrons, and the hydrido-complexes acquire basic properties. However, the reaction of carbon monoxide with $(C_5H_5MoH)_2(C_5H_4{-}C_5H_4)$ (Scheme 3) probably involves addition of the donor molecule to the isomer $C_5H_5MoH_2(C_5H_4{-}C_5H_4)C_5H_5Mo$ at the molybdenum(II) atom[54].

Ligand substitution not involving a metal–hydrogen bond

$$CpML_3H + L' \rightarrow CpML_2L'H + L$$

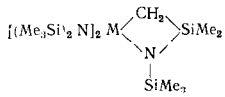
has been reported for L = CO, L′ = PR_3, $P(OR)_3$, and M = Mo, W[128] and for L = $P(OCH_3)_3$, L′ = CO, and M = Cr.[69]

A TiH_2Ti bridge undergoes homolytic fission by donor molecules (oxolan, PR_3)[15,19] (Eqn.2).

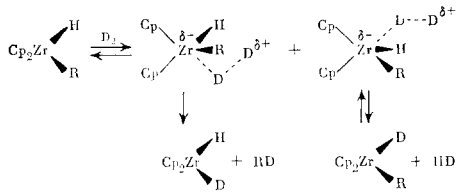
Hydrido-ligands are displaced from $(C_5H_5)_2Ti(\sigma:\eta\text{-}C_5H_4).TiC_5H_5.H_2$[124] and $(ArH)Mo(P(C_6H_5)_3)_2H_2$[17] by nitrogen to form dinitrogen complexes. Carbon monoxide "displaces" a hydrogen atom from a cyclopentadienyl group in $(C_5H_5)_2ReH$ to give the cyclopentadiene complex $C_5H_5Re(CO)(C_5H_6)$.[145] Such ligands as carbon monoxide, trialkylphosphines, and alkenes displace two hydrogen atoms from $(C_5H_5)_2MH_3$ (M = Nb, Ta) (Scheme 2)[63,109]. Reaction between $((C_5H_5)_2TiN)_2H_3$ and carbon monoxide is accompanied by partial evolution of hydrogen and formation of a complex, from which $(C_5H_5)_2Ti.(CO)_2$ can be obtained by pyrolysis[99].

7. Isotope Exchange

Solid $((C_5H_5)_2TiH)_2$ exchanges protons of its cyclopentadienyl rings for deuterium in an atmosphere of the latter. Subsequent treatment with hydrogen chloride yields $(C_5D_5)_2.TiCl_2$.[57] The reaction apparently involves a hydride-transfer stage. An analogous reaction has been described for $[((CH_3)_3Si)_2N]_3MH$ (M = U, Th).[146] Formation of the completely deuterated product $[((CD_3)_3Si)_2N]_3MD$ is assumed to involve an intermediate four-membered metallobutane ring derivative



isolated on pyrolysis of the hydride[146]. Deuterium exchange in $(C_5H_5)_2Zr(H)R$ apparently proceeds via an intermediate five-coordinated complex[71]:



On contact of $C_5H_5Cr[P(OCH_3)_3]_3H$ with deuterium more than 50% of the hydrogen atoms are exchanged, presumably via a hydrogen-detachment stage and oxidative addition of deuterium[69].

Catalytic isotope exchange has been reported[63,107] between benzene and deuterium or between hexadeuterobenzene and hydrogen in the presence of $(C_5H_5)_2TaH_3$ (Scheme 2). Isotope exchange with $(C_5H_5)_2ReH$ and $(C_5H_5)_2MH_2$ (M = Mo, W) in the presence of deuterium oxide is accelerated by acids (owing to formation of protonated complexes)[34,62,64].

8. Reactions of Hydrido-complexes with Unsaturated Molecules

Alkyl complexes are formed by the action of alkenes on cyclopentadienyl hydrides of transition metals. Titanocene absorbs an equimolecular quantity of an alkene[147,148], with disappearance of the band at 1230 cm^{-1}.[148] Zirconium(IV) hydrides such as $(C_5H_5)_2ZrH_2$ and $(C_5H_5)_2Zr(H)Cl$ respectively give the complexes $(C_5H_5)_2ZrR_2$ and $(C_5H_5)_2Zr(R)Cl$[91,149]. Addition of ethylene to $(C_5H_5)_2Nb(H)(C_2H_4$[63] and of tetrafluoroethylene to $C_5H_5M(CO)_3H$ (M = Mo, W)[150] and $C_5H_5Fe(CO)_2H$[151] yields the corresponding ethyl complexes.

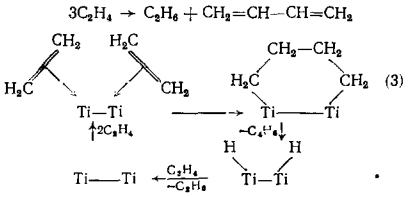
Conjugated dienes form the corresponding π-allyl complexes, as e.g. with $((C_5H_5)_2TiH)_2$[18] and $C_5H_5Mo(diphos)H_3$.[74] However, the complexes $C_5H_5M(CO)_3H$ (M = Cr, Mo, W) hydrogenate dienes selectively, and are converted into $(C_5H_5M(CO)_3)_2$.[152,153] Reaction between $(C_5H_5)_2WH_2$ and isoprene results in hydrogenation of the latter and formation of the complex $(C_5H_5)_2W(H)C_6H_5$, obviously by oxidative addition of benzene to dicyclopentadienyltungsten[154].

Dicyclopentadienylmolybdenum dihydride adds readily[155] at C:C and N:N bonds to give respectively $(C_5H_5)_2Mo(H).(CR{:}CHR)$ and $C_5H_5Mo(H)(RN.NHR)$.

9. Catalytic Activity of Hydrido-complexes

Catalytic activity is exhibited by cyclopentadienyl hydrides only of transition metals in Groups IV and V, mainly titanium and zirconium. It was reported[156] that titanocene was an effective catalyst for the hydrogenation of alkenes, but recent work has shown[15] that its activity is less by factors of 10^3–10^4 than that of systems comprising $(C_5H_5)_2TiCl_2$ with a metal alkyl. Alkenes are dimerised by titanocene in the presence of a methylhydropolysiloxane[157]. Titanocene and

$(C_5H_5)_2Ti(\sigma:\eta\text{-}C_5H_4)TiC_5H_5$ catalyse also the conversion of ethylene into butadiene, which probably involves double β-elimination:



Other hydrogenation catalysts are $(C_5H_5)_2Ti(\sigma:\eta\text{-}C_5H_4)\cdot TiC_5H_5$,[124] $((C_5H_5)_2TiN)_2H_3$,[99] and the zirconium compounds $(C_5H_5)_2ZrH_2$[91,149] and $(C_5H_5)_2Zr(H)(C_{10}H_7)Zr(C_5H_5)_2$,[21] which readily add alkenes at metal–hydrogen bonds (subsection 8).

The intermediate species $(C_5H_5)_2TiH$ (or $(C_5H_5)_2Ti(H)Cl$) is assumed to be the true catalyst, in systems based on $(C_5H_5)_2TiCl_2$ together with AlR_3, LiR, MgRX, $LiAlH_4$, or $HAl(N(C_3H_7)_2)_2$ (in non-solvating solvents), for hydrogenation[15], intramolecular cyclisation of cyclododecatriene[157], hydrometallation of alkenes[158], etc. This hypothesis is consistent with the catalytic activity of $(C_5H_5)_2TiCH_3$ after treatment with hydrogen[159]. In the case of systems containing aluminium hydrides, however, the catalytic activity of $(C_5H_5)_2TiH$ is doubtful, owing to the formation of very stable dimetal complexes having bridging hydrogen bonds[144].

Catalytic hydrogenation of ethylene on the complex $(C_5H_5)_2\cdot Nb(H)(C_2H_4)$ has been reported[63]. Blocking of the terminal hydrogen atom (by complex formation with triethylaluminium) inhibits the catalyst[160].

REFERENCES

1. M.L.H.Green and D.J.Jones, Adv.Inorg.Chem. Radiochem., 1965, **7**, 115.
2. H.D.Kaesz and R.B.Saillant, Chem.Rev., 1972, **72**, 231.
3. J.P.McCue, Coord.Chem.Rev., 1973, **10**, 265.
4. G.L.Geoffrey and J.R.Lehman, Adv.Inorg. Chem.Radiochem., 1977, **20**, 189.
5. A.P.Borisov, V.D.Makhaev, and K.N.Semenenko, Koord.Khim., 1980, **6**, 1139.
6. M.L.H.Green, "Organometallic Compounds—The Transition Elements" (Translated into Russian), Mir, Moscow, 1972.
7. E.L.Muetterties (Editor), "Transition Metal Hydrides" (Translated into Russian), Mir, Moscow, 1975.
8. A.Davison and S.S.Wreford, J.Amer.Chem.Soc., 1974, **96**, 3017.
9. L.Guggenberger, J.Inorg.Chem., 1973, **12**, 294.
10. O.S.Mills and E.F.Paulus, J.Organomet.Chem., 1968, **11**, 587.
11. J.Müller and H.Dorner, Angew.Chem.Int.Ed., 1973, **12**, 843.
12. T.F.Koetzle, J.Müller, D.L.Tipton, D.W.Hart, and R.Bau, J.Amer.Chem.Soc., 1979, **101**, 5631.
13. J.E.Bercaw, R.H.Marvich, L.G.Bell, and H.H.Brintzinger, J.Amer.Chem.Soc., 1972, **94**, 1219.
14. E.O.Fischer, Inorg.Synth., 1963, **7**, 136.
15. V.V.Saraev, F.K.Shmidt, N.M.Ryutina, V.A.Makarov, and V.A.Gruznykh, Koord.Khim., 1977, **3**, 1364.
16. J.M.Manriquez, D.R.McAlister, R.D.Sanner, and J.E.Bercaw, J.Amer.Chem.Soc., 1978, **100**, 2716.
17. M.L.H.Green and W.E.Silverthorn, Chem.Comm., 1971, 557.
18. J.E.Bercaw and H.H.Brintzinger, J.Amer.Chem. Soc., 1969, **91**, 7301.
19. J.M.Manriquez, P.J.Fagan, and T.Marks, J.Amer. Chem.Soc., 1978, **100**, 3939.
20. E.O.Fischer, W.Hafner, and H.O.Stahl, Z.anorg. allg.Chem., 1955, **282**, 47.
21. G.P.Pez, C.F.Putnik, S.L.Suib, and G.D.Sucky, J.Amer.Chem.Soc., 1979, **101**, p.6933.
22. N.I.Kirillova, A.I.Gusev, A.A.Pasynskii, and Yu.T.Struchkov, Zhur.Strukt.Khim., 1974, **15**, 288.
23. K.Jonas and G.Wilke, Angew.Chem.Int.Ed., 1969, **8**, p.519.
24. R.B.King and G.A.Fronzaglia, Chem.Comm., 1965, p.547.
25. R.B.King and G.A.Fronzaglia, Inorg.Chem., 1969, **5**, p.1837.
26. S.A.Keppie and M.F.Lapper, J.Organomet.Chem., 1969, **19**, p.15.
27. E.M.Van Dam, W.N.Brent, M.P.Silvon, and P.S.Skell, J.Amer.Chem.Soc., 1975, **97**, p.465.
28. W.Jetz and W.A.G.Graham, J.Amer.Chem.Soc., 1969, **91**, p.3375.
29. M.L.H.Green and S.J.Simpson, J.Organomet.Chem., 1979, **173**, p.287.
30. A.Davison, W.McFarlane, L.Pratt, and G.Wilkinson, J.Chem.Soc., 1962, p.3653.
31. A.J.Oliver and W.A.G.Graham, Inorg.Chem., 1970, **9**, p.2653.
32. R.R.Schrock and J.A.Osborn, Inorg.Chem., 1970, **9**, p.2339.
33. R.J.Klingler, J.C.Huffman, and J.K.Kochi, J.Amer.Chem.Soc., 1980, **102**, p.208.
34. A.Davison, J.A.McCleverty, and G.Wilkinson, J.Chem.Soc., 1963, p.1133.
35. J.J.Salzmann and P.Mosimann, Helv.Chim.Acta, 1967, **50**, 1831.
36. G.W.Watt, L.J.Baye, and F.O.Drummond, J.Amer. Chem.Soc., 1966, **88**, p.1138.
37. H.H.Brintzinger and J.E.Bercaw, J.Amer.Chem. Soc., 1970, **92**, p.6182.
38. G.W.Watt and F.O.Drummond, J.Amer.Chem.Soc., 1966, **88**, p.5926.
39. G.W.Watt and F.O.Drummond, J.Amer.Chem.Soc., 1970, **92**, p.826.
40. A.N.Nesmeyanov, D.A.Lemenovskii, V.P.Fedin, and E.G.Perevalova, Dokl.Akad.Nauk SSSR, 1979, **245**, 609.
41. G.P.Pez, J.Amer.Chem.Soc., 1976, **98**, p.8072.
42. V.P.Fedin, Candidate's Thesis, Moscow State University, 1980.
43. M.F.Lappert, P.I.Riley, and P.I.W.Yarrow, Chem.Comm., 1979, p.305.
44. C.P.Boekel, J.H.Teuben, and H.F.Liefde Meier, J.Organomet.Chem., 1974, **81**, p.371.
45. G.A.Razuvaev, V.P.Marin, and Yu.A.Andrianov, J.Organomet.Chem., 1979, **174**, p.67.
46. G.A.Razuvaev, V.N.Latyaeva, and L.I.Vyshinskaya, Dokl.Akad.Nauk SSSR, 1976, **231**, 114.
47. G.A.Razuvaev, V.P.Mar'in, S.P.Korneva, and Yu.A.Andrianov, Dokl.Akad.Nauk SSSR, 1976, **231**, 626.
48. M.Reng and C.H.Brubaker, Inorg.Chim.Acta, 1978, **26**, p.231.
49. G.L.Geoffrey and M.G.Bradley, J.Organomet.Chem., 1977, **134**, 27.

50. M.L.H.Green, Eighth Preprint Congress on Organometallic Chemistry, Kyoto, Japan, 1977, 3B08.
51. M.Berri, N.J.Cooper, M.L.H.Green, and S.J.Simpson, J.Chem.Soc., Dalton Trans., 1980, p.29.
52. I.H.Elson, J.K.Kochi, U.Klabunde, L.J.Manzer, G.W.Parshall, and F.N.Tebbe, J.Amer.Chem.Soc., 1974, **96**, p.7374.
53. A.K.Fischer and G.Wilkinson, J.Inorg.Nuclear Chem., 1956, **2**, p.146.
54. J.C.Smart and C.I.Curtis, Inorg.Chem., 1978, **17**, p.3290.
55. H.H.Brintzinger, J.Amer.Chem.Soc., 1967, **89**, p.6871.
56. G.Henrici-Olive and S.Olive, Angew.Chem.Int.Ed., 1968, **7**, p.386.
57. M.E.Vol'pin, A.A.Belyi, V.B.Shur, Yu.I.Lyakhovetskii, R.V.Kudryavtsev, and N.N.Bubnov, J.Organomet.Chem., 1971, **27**, 5.
58. T.Avibs and M.L.H.Green, J.Chem.Soc., Dalton Trans., 1979, 1116.
59. R.B.King and A.J.Efrati, Chem.Comm., 1970, p.1370.
60. H.W.Wehner, E.O.Fischer, and J.Müller, Chem.Ber., 1970, **103**, 2258.
61. H.Marquet-Ellis and G.Folcher, J.Organomet.Chem., 1977, **131**, p.257.
62. M.L.H.Green, L.Pratt, J.A.McGleverty, and G.Wilkinson, J.Chem.Soc., 1961, p.4854.
63. F.N.Tebbe and G.W.Parshall, J.Amer.Chem.Soc., 1971, **93**, p.3793.
64. M.L.H.Green, L.Pratt, and G.Wilkinson, J.Chem. Soc., 1958, p.3916.
65. E.O.Fischer and M.W.Schmidt, Angew.Chem., 1967, **79**, 99.
66. A.Davison, M.L.H.Green, and G.Wilkinson, J.Chem. Soc., 1961, p.3172.
67. B.D.James, P.K.Nanda, and M.L.H.Wallbridge, Inorg.Chem., 1967, **6**, p.1979.
68. G.Fachinetti, G.Fochi, and G.Floriani, Chem.Comm., 1976, p.230.
69. J.D.Koola and H.H.Brintzinger, Chem.Comm., 1976, p.388.
70. P.C.Wailes and H.Weigold, J.Organomet.Chem., 1970, **24**, p.405.
71. K.J.Gell and J.Schwartz, J.Amer.Chem.Soc., 1978, **100**, p.3246.
72. P.Legzdins and D.T.Martin, Inorg.Chem., 1979, **18**, p.1250.
73. M.L.H.Green, J.Knight, and J.A.Segal, J.Chem.Soc., Dalton Trans., 1977, p.2189.
74. T.Aviles, M.L.H.Green, A.R.Dias, and C.Romao, J.Chem.Soc., Dalton Trans., 1979, p.1367.
75. B.M.Bulychev, G.L.Soloveichik, A.L.Kostenko, and N.A.Yakovleva, Trans.Met.Chem., in the press.
76. H.Antropiusova, V.Hanus, and K.Mach, Trans.Met. Chem., 1978, **3**, p.121.
77. S.Kapur, B.L.Kalsotra, and R.K.Multani, J.Inorg. Nuclear Chem., 1974, **36**, p.932.
78. J.A.Labinger and Kwai Sam Wong, J.Organomet. Chem., 1979, **170**, p.373.
79. L.J.Guggenberger and F.N.Tebbe, J.Amer.Chem. Soc., 1973, **95**, p.7870.
80. N.J.Cooper, M.L.H.Green, C.Couldwell, and K.Prout, Chem.Comm., 1977, p.145.
81. B.R.Francis, M.L.H.Green, T.Luong-Thi, and G.A.Moser, J.Chem.Soc., Dalton Trans., 1976, p.1339.
82. M.L.H.Green, T.Luong-Thi, G.A.Moser, J.Packer, F.Pettit, and D.M.Roe, J.Chem.Soc., Dalton Trans., 1976, p.1988.
83. F.W.Bentfield, B.R.Francis, M.L.H.Green, T.Luong-Thi, G.A.Moser, and J.C.Poland, J.Less-Common Met., 1974, **36**, p.187.
84. M.L.H.Green and J.J.E.Moreau, J.Organomet.Chem., 1978, **161**, 25.
85. C.J.Ballhausen and J.P.Dahl, Acta Chem.Scand., 1961, **15**, p.1333.
86. N.W.Alcock, J.Chem.Soc., (A), 1967, p.2001.
87. J.C.Green, M.L.H.Green, and C.K.Prout, Chem.Comm., 1972, p.421.
88. J.W.Lauher and R.Hoffman, J.Amer.Chem.Soc., 1976, **98**, 1729.
89. J.E.Bercaw, R.H.Marvich, L.G.Bell, and H.H.Brintzinger, J.Amer.Chem.Soc., 1972, **94**, 1219.
90. J.N.Armor, Inorg.Chem., 1978, **17**, p.203.
91. S.Couturier and B.Gautheron, J.Organomet.Chem., 1978, **157**, 61.
92. J.McCleverty and G.Wilkinson, Chem.and Ind., 1961, p.288.
93. M.P.Johnson and D.F.Shriver, J.Amer.Chem.Soc., 1966, **88**, p.301.
94. A.Storr and B.S.Thomas, Canad.J.Chem., 1971, **49**, p.2504.
95. N.V.Perevozchikova, A.S.Smirnov, Yu.A.Sorokin, R.V.Kaplina, and V.A.Dodonov, Zhur.Obshch.Khim., 1979, **49**, 945.
96. M.Rosenblum and J.O.Santer, J.Amer.Chem.Soc., 1959, **81**, 5517.
97. G.P.Pez, US P.3839381 (1973).
98. J.Armor and G.P.Pez, US P.4046790 (1977).
99. J.N.Armor, Inorg.Chem., 1978, **17**, 213.
100. J.J.Kenworthy, J.Myatt, and M.C.R.Symons, J.Chem.Soc., (A), 1971, 1020.
101. H.H.Brintzinger, J.Amer.Chem.Soc., 1966, **88**, 4305.
102. R.D.Wilson, T.F.Koestle, D.W.Hart, A.Kvick, D.L.Tipton, and R.Bau, J.Amer.Chem.Soc., 1977, **99**, 1775.
103. N.I.Kirillova, A.I.Gusev, and Yu.T.Struchkov, Zhur.Strukt.Khim., 1972, **13**, 473.
104. L.J.Guggenberger, P.Meakin, and F.N.Tebbe, J.Amer.Chem.Soc., 1974, **96**, 5420.
105. A.J.Schultz, K.L.Stearby, J.M.Williams, R.Mink, and G.D.Stucky, Inorg.Chem., 1977, **16**, 3303.
106. R.W.Broach, A.J.Schultz, J.M.Williams, G.M.Brown, J.M.Manriquez, and T.J.Marks, Science, 1979, **203**, No.4376, p.172.
107. F.K.Barfield, G.W.Parshall, and F.N.Tebbe, J.Amer.Chem.Soc., 1970, **92**, 5234.
108. F.Macašek, V.Mikulaj, and F.Drienwosky, Coll. Czech.Chem.Comm., 1970, **35**, 993.
109. A.H.Klasinga and J.H.Teuben, J.Organomet.Chem., 1978, **157**, 413.
110. E.E.H.Otto and H.H.Brintzinger, J.Organomet. Chem., 1978, **148**, 29.
111. J.A.Labinder, Kwai Sam Wong, and W.R.Schiedt, J.Amer.Chem.Soc., 1978, **100**, 3254.
112. M.A.Porai-Koshits, A.S.Antsyshkina, G.G.Sadikov, Yu.V.Skripkin, A.A.Pasynskii, and V.N.Ostrikova, Koord.Khim., 1979, **5**, 1103.
113. M.Gerloch and R.Mason, J.Chem.Soc., (A), 1965, p.304.
114. B.Deubzer and H.Kaesz, J.Amer.Chem.Soc., 1976, **98**, 3276.
115. H.Brunner, P.C.Wailes, and H.D.Kaesz, Inorg. Nuclear Chem., Lett., 1965, **1**, p.125.

116. A.V.Aripovskii and B.M.Bulychev, Zhur.Neorg. Khim., 1980, **25**, 2191 [Russ.J.Inorg.Chem., 1980, **25**(8)].
117. V.J.Kurney, J.Santer, M.Rosenblum, and J.H.Richards, J.Amer.Chem.Soc., 1960, **82**, p.5249.
118. V.I.Tel'noi, I.B.Rabinovich, K.V.Kir'yanov, and A.S.Smirnov, Dokl.Akad.Nauk SSSR, 1976, **231**, 903.
119. J.C.G.Calado, A.R.Dias, J.A.Martino, and M.Ribeiro da Silva, J.Organomet.Chem., 1979, **174**, 77.
120. J.Olthof, J.Organomet.Chem., 1977, **128**, 367.
121. L.J.Guggenberger and F.N.Tebbe, J.Amer.Chem. Soc., 1976, **98**, 4137.
122. Yu.T.Struchkov, Yu.A.Slovokhotov, A.I.Yanovskii, V.P.Fedin, and D.A.Lemenovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1421.
123. C.Couldwell and K.Prout, Acta Cryst., 1979, **35B**, 335.
124. G.P.Pez and S.S.Kwan, J.Amer.Chem.Soc., 1976, **98**, 8079.
125. K.I.Gell and J.Schwartz, Chem.Comm., 1979, 244.
126. J.E.Ellis, R.A.Faltynek, and S.G.Hentges, J.Amer. Chem.Soc., 1977, **99**, 626.
127. R.P.Stewart, N.Okamoto, W.A.G.Graham, J.Organomet.Chem., 1972, **42**, 32.
128. P.Kalck, R.Pince, R.Poieblanc, and J.Poussel, J.Organomet.Chem., 1970, **24**, 444.
129. P.Kalck and R.Poieblanc, J.Organomet.Chem., 1969, **19**, 115.
130. W.A.G.Graham and J.K.Hoyano, Chem.Comm., 1977, p.1029.
131. E.O.Fischer and H.W.Wehner, Chem.Ber., 1968, **101**, 454.
132. M.L.H.Green, J.Knight, L.C.Mitchard, G.G.Roberts, and W.E.Silverthorn, Chem.Comm., 1971, 1619.
133. K.A.Simpson, Doctoral Diss.Univ.of Alberta, 1973; see Acta Cryst., 1977, **33B**, 1113.
134. R.A.Smith and M.J.Bennet, Acta Cryst., 1977, **33B**, 1113.
135. L.Manoilovic-Muir, K.W.Muir, and J.A.Ibers, Inorg.Chem., 1970, **9**, 447.
136. R.A.Smith and M.J.Bennet, Acta Cryst., 1977, **33B**, 1118.
137. H.Sinn, W.Kaminsky, H.-J.Vollmer, and R.Woldt, Angew.Chem.Int.Ed., 1980, **19**, 390.
138. A.Flamini, D.J.Cole-Hamilton, and G.Wilkinson, J.Chem.Soc., Dalton Trans., 1978, 454.
139. H.W.Turner, S.J.Simpson, and R.A.Anderson, J.Amer.Chem.Soc., 1979, **101**, 2782.
140. J.A.Labinder and K.H.Kimadina, J.Organomet. Chem., 1978, **155**, 25.
141. G.A.Razuvaev, V.N.Latyaeva, L.I.Vishinskaya, and T.P.Samarina, J.Organomet.Chem., 1979, **164**, 41.
142. T.S.Piper and G.Wilkinson, J.Inorg.Nuclear Chem., 1956, **3**, 104.
143. P.L.Cooper and M.L.H.Green, Z.Naturforsch., 1964, **19**, 652.
144. G.L.Soloveichik and B.M.Bulychev, Uspekhi Khim., in the press.
145. M.L.H.Green and G.Wilkinson, J.Chem.Soc., 1958, 4314.
146. S.J.Simpson, H.W.Turner, and R.A.Andersen, J. Amer.Chem.Soc., 1979, **101**, 7728.
147. K.Shikata, K.Yogokawa, J.Matsumura, and K.Asuma, J.Chem.Soc., Japan, 1965, **68**, 1260.
148. G.P.Pez, Chem.Comm., 1977, 560.
149. P.C.Wailes, H.Weigold, and A.P.Bell, J.Organomet. Chem., 1972, **43**, 34.
150. P.M.Treichel, J.H.Morris, and F.G.Stone, J.Chem. Soc., 1963, 720.
151. M.L.H.Green and A.N.Stear, Z.Naturforsch., 1965, **20**, 812.
152. A.Miyake and H.Kondo, Angew.Chem.Int.Ed., 1968, **7**, 631.
153. A.Miyake and H.Kondo, Angew.Chem.Int.Ed., 1968, **7**, 880.
154. M.L.H.Green and P.J.Knowles, Chem.Comm., 1970, 1677.
155. S.Otsuka, A.Nakamura, and H.Minamida, Chem. Comm., 1969, 1148.
156. K.Shikata, K.Yokogawa, S.Nakao, and K.Asuma, J.Chem.Soc.Japan, Ind.Chem.Sect., 1965, **68**, 1248.
157. H.Antropiusova, K.Mach, V.Hanus, F.Turecek, and P.Sedmera, React.Kinet.Catal.Lett., 1979, **10**, 297.
158. E.C.Ashby and S.P.Noding, J.Organomet.Chem., 1979, **177**, 117.
159. E.Klei and J.H.Teuben, J.Organomet.Chem., 1980, **188**, 97.
160. F.N.Tebbe, J.Amer.Chem.Soc., 1973, **95**, 5412.

Institute of New Chemical Problems,
USSR Academy of Sciences,
Chernogolovka,
Moscow Region

Lomonosov Moscow State University