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Agostic Hydrogen Atoms in Transition Metal Complexes

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The methods of formation, the structures in the crystal and in solutions, the properties, and the reactions of complexes with a bridging hydrogen atom and three-centre M...H-C bonds in which the electrons of the C-H bonds play the role of two-electron ligands at the metal atom are examined.
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I. INTRODUCTION

The following types of binding of hydrogen have been known until recently in the chemistry of transition metal hydride complexes (see the relevant reviews[1-7]): (1) terminal hydrido-ligands in the complexes $LnMH_x$ ($x = 1-9$); (2) bridging μ^2-H ligands in the dinuclear and polynuclear complexes $L_nM(\mu^2\text{-}H)_xML_n$ ($x = 1-4$); (3) triply bridging μ^3-H ligands where the μ^3-hydrogen atom is located above the triangular face of the polyhedron (which is characteristic of the chemistry of clusters). In the FeH_6^{4-} anion, the Fe atom is in the centre of an octahedron made up of six H atoms.[8] A whole series of clusters have been obtained where 1-3 hydrogen atoms are located within a skeleton made up of metal atoms [the so called "inner cavity" or "encapsulated" ("interstitial") hydrido-ligands], for example, in the anions $HCo_6(CO)_{15}^-$, $H_2Ni_{12}(CO)_{21}^{2-}$, etc. (see the relevant reviews[6,7]).

The aliphatic C-H bonds in the molecules of CH_4 and other alkanes have been regarded traditionally as chemically inert and incapable of interacting with the metal centre in organometallic complexes. However, during the last 8-10 years fairly numerous examples of the activation of C-H bonds and of the oxidative addition to low-valence rhodium and iridium complexes have been found; numerous instances of the coordination of aliphatic and aromatic C-H bonds to transition metals have been observed and complexes with an H_2 molecules as the η^2-ligand have been obtained. The interest in compounds where the C-H bond is coordinated to a metal is indissolubly linked to the problem of the search for new effective catalysts for the activation of C-H bonds and organic synthesis on the basis of alkanes. This problem has attracted much attention and is being very vigorously investigated (see the relevant reviews[9-11]). Studies on these lines have been stimulated by advances in the field of both stoichiometric organometallic synthesis and in metal complex catalysis. These reviews consider complexes where hydrogen constitutes a bridge between the metal and carbon atoms with formation of two-electron, three-centre (2e, 3c) bonds M...H-C (CHB).† In such complexes, there is a new type of binding of hydrogen to transition metals. CHB of virtually all Group III-VIII transition metals, except vanadium and nickel,‡ have now been obtained and characterised by structural methods in the solid phase or by NMR methods in solutions. The formation of CHB proved to be characteristic not only of electron-deficient complexes of the elements at the beginning of the Periods (Sc, Y; Ti, Zr, Hf; Nb, Ta) but also of the lanthanides (Nd, Sm, Yb) and the elements in the middle of the Periods (Cr, Mo, W; Mn; Fe, Ru, Os; Co, Rh, Ir). Thus the ability to stabilise the electron-deficient centre by means of intramolecular coordination via C-H bonds, leading to the formation of a bridged M...H-C fragment, is a general property characteristic of the majority of transition metals. This phenomenon is apparently more general than was supposed previously. CHB formed with participation of aliphatic, olefinic, alkylidene (carbene), and aromatic C-H bonds are known.

All the CHB known at the present time are electron-deficient complexes whose metal centre formally has 12-16 electrons. The majority of CHB are cationic complexes or neutral molecules. The "driving force" and cause of the coordination of C-H bonds to the metal is the tendency to build up the electronic environment of the metal by means of the electron pair of the C-H bond to 18 electrons, or to decrease the electron deficiency by two electrons by increasing the number of electrons from 12 to 14 or from 14 to 16. The presence of an electron-deficient centre is an essential but not a sufficient condition for the formation of CHB. Apart from the electron deficiency, it is also necessary that the lowest unoccupied molecular orbital (LUMO) of the complex, used for the coordination with the C-H bond, should have the appropriate orientation in space. According to the results of X-ray diffraction analysis (XRD), in the case of the 16-electron complex $(\eta^7\text{-}C_7H_7)Ti(Dmpe).CH_2CH_3$,§ Ti...H-C bonds with the hydrogen of the CH_3 moiety of the ethyl group are not formed.[12] Quantum-chemical calculation has shown that in this case the LUMO consists mainly of the d_{z^2} orbital of titanium and is oriented along the z azis; owing to its unfavourable steric disposition, this orbital is incapable of effective overlap with the α- or β-CH bonds of the ethyl group and a bridge

†Complexes with hydrogen bridges. The corresponding Russian abbreviation is KMB (Translator).

‡According to the literature data for the period including December 1987, using also individual studies in 1988.

§Dmpe = $Me_2PCH_2CH_2PMe_2$.

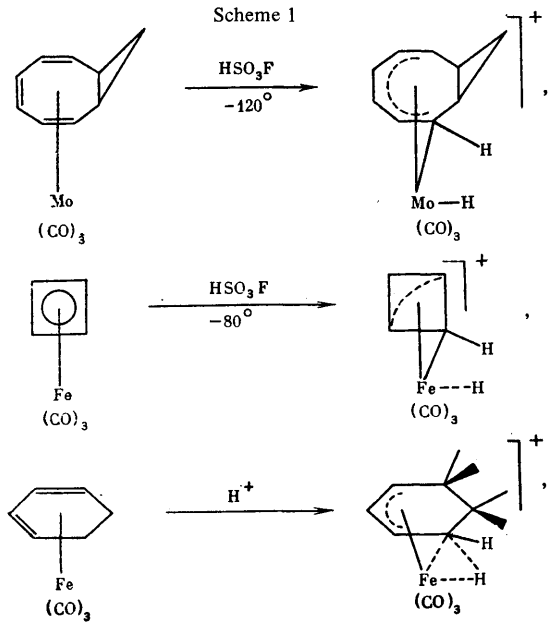
bond is not formed despite the presence of the electron-deficient centre. There exists a single brief review devoted to three-centre M...H−C bonds,[13] whose authors proposed a new term for such bonds and hydrogen atoms—"agostic" C−H bonds or hydrogen atoms. This term is frequently used in the foreign literature.

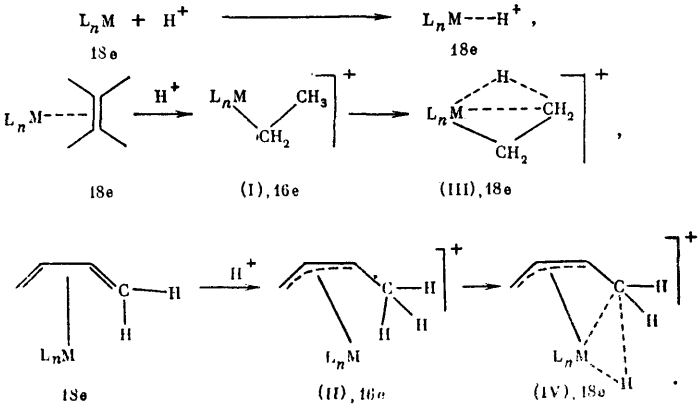
II. EARLY STUDIES

The first information about the possibility of the coordination of C−H bonds to transition metals appeared in 1968−1975. In many cases, the signals of the CH_2 and CH_3 protons in the H NMR spectra of the complexes were observed in the high field region (δ ranging from 0 to −12 p.p.m. and above), which is known to be characteristic of metal hydrides (see the review of Kaesz and Saillant[1]). It was shown on the basis of XRD data that in many cases there is a weak interaction in ruthenium, palladium, and platinum complexes between the metal and the hydrogen in the *ortho*-position in the arylphosphine ligands. On the other hand, owing to the insufficient accuracy of the XRD method, the positions of the hydrogen atoms could not be as a rule located by direct procedures. The conclusion that there is an interaction between the C−H bond and the metal was reached on the basis of the presence of short intramolecular M...H contacts, significantly shorter than the sums of the van der Waals radii of M and H. Interactions of this type have been described for the following complexes: $Ru(PPh_3)_3Cl_2$ (Ru...H distance 2.59 Å);[14] *trans*-$Pd(PPhMe_2)_2I_2$ (Pd...H 2.8 Å);[15] $Rh(PPh_3)_3^+ClO_4^-$ (Rh...H 2.56 Å);[16] $Pd(PPh_3)_2(Br)(CR{=}CR.CR{=}CHR)$, where R = COOMe (Pd...H 2.3 Å);[17] $Ni[Et_2B.(pyrazolyl)_2]_2$;[18] $Mo[Et_2B(pyrazolyl)_2](\eta^3\text{-}CH_2CHPhCH_2)(CO)_2$ [Mo...H 2.27 Å, δ(Mo−H) = 2.4 p.p.m.].[19]

More than 10 years ago, a series of studies were published[20-24] in which π,σ structures with protonation of the metal and the simultaneous formation of M−C σ-bonds were proposed for the protonated forms of the η-complexes solely on the basis of ^1H and ^{13}C NMR data (Scheme 1). Later these results were revised and it was concluded that an M−C σ-bond does not arise in such cases. The formation of the Fe...H−C 2e, 3c-bond was first postulated for the protonated form of the complex $(\eta^4\text{-}C_6H_8)Fe(CO)_3$.[25]

Scheme 1





During the last 8−10 years extensive experimental data have accumulated on the synthesis and properties of CHB both in the crystal (structural methods) and in solutions, a systematic account of which is given below.

III. METHODS OF FORMATION

An exceptionally wide variety of structures are characteristic of the complexes of the type considered. Their general property is that the metal atom is an electron-deficient centre. In the presence of electron-donating ligands or solvents (L), electron-deficient complexes are usually stabilised as a result of the addition of L to an unoccupied coordination site. However, if the system has no electron-donating ligands, then one of the possible ways in which the electron deficiency can be partially or completely made good and a stable 18-electron shell created involves the intramolecular coordination of an unoccupied orbital of the metal (LUMO) to one of the electron pairs of a C−H bond with formation of an M...H−C 2e, 3c-bond. In this case the C−H bond plays the role of a kind of two-electron "ligand". Depending on the geometry of the M...H−C fragment, such bonds can be divided by convention into "open" (M−H−C angle 120−130° and above), and "closed" (with an angle of 70−90°). There is no clear-cut boundary between these types.

Evidently, the formation of CHB is to be expected primarily among electron-deficient complexes of the elements at the beginning of the Periods (Sc, Ti, V, and their analogues), for which a large number of deviations from the 18-electron rule are known. Indeed, among the 12−16-electron complexes of Y, Ti, Zr, and Ta, numerous examples of the formation of M...H−C bridge bonds have been found. The formation of these bonds proved to be characteristic of a large group of 14- and 16-electron alkylidene complexes of Ta (and also Nb and W), typical representatives of which are the structurally characterised complexes $Ta(=CH-CMe_3)(\eta\text{-}C_5Me_5).(C_2H_4)(PMe_3)$, $[Ta(=CH-CMe_3)(PMe_3)Cl_3]_2$, and $W(=CH-CMe_3)(CO)(PMe_3)_2Cl_2$. Since the identification of the M...H−C bridge bonds in the crystal is based exclusively on structural research methods and in solutions mainly on NMR data, the properties and characteristics of the bridge bonds in the solid phase and in solutions will be examined in greater detail below in Sections IV and V.

Several reactions in which there is a possibility of the formation of CHB are known for compounds of the elements in the middle of the Period (Group VI−VIII) elements. The protonation and decarbonylation reactions have been studied in greatest detail.

Table 1. The formation of complexes with a bridging hydrogen atom on protonation or intramolecular isomerisation.

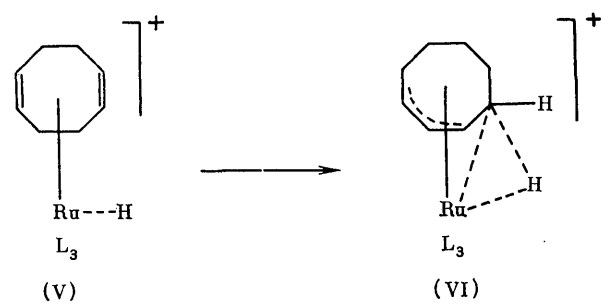
Precursor	Protonated form with bridging hydrogen atom	Acid	Refs.
$Mo_2(\eta\text{-}C_6Me_6)(\eta\text{-}Cp)_2$	$[Mo_2(\eta\text{-}C_6Me_6\text{-}\mu\text{-}H)(\eta\text{-}Cp)_2]^+$	$HBF_4\cdot Et_2O$, CF_3SO_3H	[29, 30]
$Mo(\eta^5\text{-}C_9H_7)(\eta\text{-}C_{12}H_{13})$	$[Mo(\eta^5\text{-}C_9H_7)(\eta\text{-}C_{12}H_{13}\text{-}\mu\text{-}H)]^+$	CF_3SO_3H	[31]
$Mo(\eta^4\text{-}C_4H_6)_2(PMe_3)_2$	$[Mo(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_4H_6\text{-}\mu\text{-}H)(PMe_3)_2]^+$	HBF_4/MeOH	[32]
$ReW(\mu\text{-}CHC_6H_4Me)(\mu\text{-Dppm})(CO)_7$ *	$[ReW(\mu\text{-}CH_2C_6H_4Me)(\mu\text{-Dppm})(CO)_7]^+$	$HBF_4\cdot Et_2O$	[33]
$[Mn(\eta^4\text{-}C_6H_8)(CO)_3]^-$	$Mn(\eta^3\text{-}C_6H_9\text{-}\mu\text{-}H)(CO)_3$	H_2O	[34]
$[Mn(\eta^4\text{-}C_6H_7R)(CO)_3]^-$	$Mn(\eta^3\text{-}C_6H_7R\text{-}\mu\text{-}H)(CO)_3$	H_2O	[35—38]
$Fe_2(\eta\text{-}Cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$	$[Fe_2(\eta\text{-}Cp)_2(CO)_2(\mu\text{-}CO)(\mu CH_2\text{-}\mu\text{-}H)]^+$	CF_3SO_3H, HBF_4	[39]
$Fe(\eta^4\text{-Dien})(P(OMe)_3)_3$	$[Fe(\eta^3\text{-Enyl-}\mu\text{-}H)(P(OMe)_3)_3]^+$		[40, 41]
Dien = cyclo-octa-1,3-diene	Enyl = cyclo-octenyl	HBF_4/MeOH, CF_3COOH/MeOH	[40, 41]
Butadiene	butenyl	»	[40, 41]
2-Methylbutadiene	2-methylbutenyl	»	[40, 41]
2,3-Dimethylbutadiene	2,3-dimethylbutenyl	»	[40, 41]
Cyclohexa-1,3-diene	cyclohex-1-en-3-yl	»	[40, 41]
Cycloheptа-1,3-diene	cyclohept-1-en-3-yl	»	[40, 41]
$Fe_2(\eta\text{-}Cp)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-Dppm})$	$[Fe_2(\eta\text{-}Cp)_2(\mu\text{-}CO)(\mu\text{-}CH_2\text{-}\mu\text{-}H)(\mu\text{-Dppm})]^+$	HPF_6	[42]
$[HFe_5C(CO)_{14}]^-$	$HFe_4(C\text{-}\mu\text{-}H)(CO)_{13}$	HCl	[43]
$[Ru(\eta^4\text{-}C_8H_{12})(H)(L)_3]^+$ L=P(OMe)$_2$Ph, P(OMe)Ph$_2$, PMe_3 PMePh$_2$; L_3=MeC(CH$_2$PPh$_2$)$_3$	$[Ru(\eta^3\text{-}C_8H_{12}\text{-}\mu\text{-}H)(L)_3]^+$	—	[44]
$Ru(\eta^6\text{-}Me_6C_6)(\eta^4\text{-}C_{10}H_{12})$	$[Ru(\eta^6\text{-}Me_6C_6)(\eta^3\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	HPF_6	[45]
$Ru(\eta^6\text{-}Me_6C_6)(\eta^4\text{-}C_8H_8)$	$[Ru(\eta^6\text{-}Me_6C_6)(\eta^3\text{-}C_8H_9\text{-}\mu\text{-}H)]^+$	HBF_4, HBF_6	[46]
$Ru(L_2)(L')(\eta\text{-}Me_4C_6(=CH_2)_2)$	$[Ru(L_2)(L')(\eta\text{-}Me_4C_6(CH_2)(CH_2\text{-}\mu\text{-}H)]^+$	HPF_6	[47]
L_2=Ph$_2$PCH$_2$CH$_2$PPh$_2$, L'=PMe$_2$Ph			
$Ru_3(\mu\text{-}H)_3(\mu\text{-CEt})(CO)_9$	$[Ru(\mu\text{-}H)_3(\mu\text{-EtC-}\mu\text{-}H)(CO)_9]^+$	CF_3SO_3H	[48]
$Os(\eta^6\text{-}Me_3C_6H_3)(\eta^4\text{-}C_{10}H_{12})$	$[Os(\eta^6\text{-}Me_3C_6H_3)(\eta^3\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CF_3SO_3H, FSO_3H	[45]
$Os_3(\mu\text{-}H)_3(\mu\text{-MeC})(CO)_9$	$[Os(\mu\text{-}H)_3(\mu\text{-MeC-}\mu\text{-}H)(CO)_9]^+$	CF_3SO_3H	[48]
$Co(\eta^5\text{-}C_5Me_4R)(\eta^3\text{-}C_3H_4)_2$, R=Me, Et:	$[Co(\eta^5\text{-}C_5Me_4R)(\eta^3\text{-}C_3H_4)(\sigma\text{-}C_3H_4\text{-}\mu\text{-}H)]^+$	HBF_4	[49]
$Co(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_2H_4)P(C_6H_4Me)_3$	$[Co(\eta^5\text{-}C_5Me_5)(\sigma\text{-}C_2H_4\text{-}\mu\text{-}H)P(C_6H_4Me)_3]^+$	HBF_4	[50, 52]
$Co(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_3H_3R)P(OMe)_3$, R=Me, Et	$[Co(\eta^5\text{-}C_5Me_5)(\sigma\text{-}C_3H_3R\text{-}\mu\text{-}H)P(OMe)_3]^+$	HBF_4	[51]
$Rn(\eta^5\text{-}C_5R_5)(\eta^4\text{-}C_{10}H_{12})$, R=H, Me;	$[Rh(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	HPF_6	[45]
$Rh(\eta^4\text{-}C_7H_8)(\eta^5\text{-}Me_2C_2B_9H_9)^-$	$Rh(\eta^3\text{-}C_7H_9\text{-}\mu\text{-}H)(\eta^5\text{-}Me_2C_2B_9H_9)$	CF_3COOH	[53]
$Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4H_6)$	$[Rh(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_4H_6\text{-}\mu\text{-}H)]^+$	HBF_4	[54]
$Ir(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_{10}H_{12})$	$[Ir(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	HPF_6	[45]

*Dppm = $Ph_2PCH_2PPh_2$.

1. Protonation

It is well known that the η-complexes and low-valence carbonyl complexes of transition metals constitute a new class of bases—polyfunctional organometallic Lewis bases. They interact readily with various electrophiles (E)—including protic and aprotic acids, the attack by E being as a rule directed to the centre with the highest basicity. In complexes of the type L_nM, there is a possibility of the addition of E both to the metal atom and to the ligands (L). The relative basicities of the different centres and the direction of attack by E depend on the structure of the complex, the nature of the metal, the character and type of the ligand environment, and the nature of E (see the relevant reviews[26-28]). If the 18-electron complex L_nM is protonated at the metal atom, then the product is the cation $[L_nM-H]^+$, where the metal retains the 18-electron environment and there are no grounds to expect the formation of a CHB. However, if the proton adds to the carbon atom of the C=C bond in the coordinated olefin or diene ligand, then the number of electrons supplied by the ligand for binding to the metal diminishes by one. η^2-Olefins or η^4-dienes (donors of two or four electrons) are then converted respectively into η^1-alkyl or η^3-allyl ligands (donors of one and three electrons). Taking into account the positive charge, the formal electronic environment of the metal in the monocationic complexes (I) and (II) arising on protonation can be stabilised as a result of the coordination of the unoccupied orbital of the metal to the electrons of a suitably directed C—H bond with conversion into cationic or neutral (if an anionic complex has been protonated) CHB (III) and (IV). The instances of the formation of CHB on protonation of 18-electron precursors are compiled systematically in Table 1.

The intramolecular isomerisation of hydride complexes, known in relation to the cationic dieneruthenium hydride complexes,[44] bears a close analogy to protonation by acids (HBF_4, HPF_6, CF_3SO_2OH, etc.). The isomerisation of the dienemetal hydride complexes to CHB can be regarded as "intramolecular protonation":



The cationic η^4-dieneruthenium hydride complexes (V) have been isolated and characterised; they are stable in solution at temperatures below −10 °C, while in the temperature range 0—60 °C (depending on the size of L and the type of the donor atom), compounds (V) isomerise spontaneously and irreversibly to the η^3-allyl complexes (VI) with a bridging hydrogen atom as a result of the intramolecular proton transfer from the metal to the cyclo-octadiene ligand.[44] From this it follows that in the given case the η^3-allyl

CHB of type (VI) are thermodynamically more favourable than their η^4-dienemetal hydride precursors. The rate of isomerisation (V) → (VI) depends on the size of L and decreases in the following sequence of groups L: $P(OCH_2CMe_3)_3$ > $P(OMe)Ph_2$ ≃ PMe.Ph_2 > PMe_2Ph > $MeC(CH_2PPh_2)_3$ > $P(OMe)_2Ph$ > PMe_3 ≃ $AsMePh_2$. When L = $P(OMe)_3$, $AsMe_3$, or $AsMe_2Ph$, there is no isomerisation.[44]

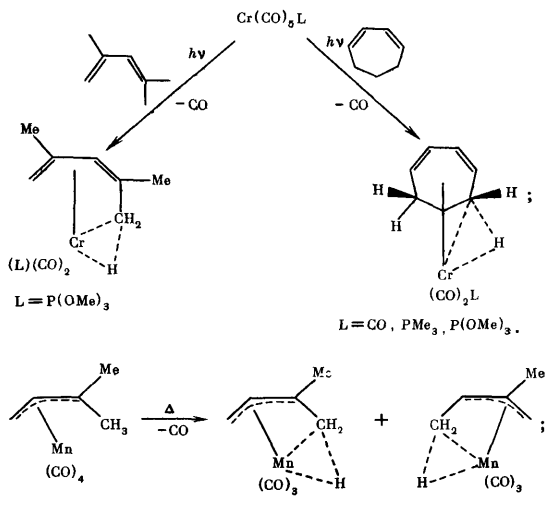
An important feature is that in the reactions involving the protonation of the η-complexes by strong acids, unstable olefin- or diene-metal hydride intermediates are formed initially as a result of the kinetically controlled rapid attack by H^+ on the metal atom. As a consequence of the subsequent migration of hydrogen from the metal to a carbon of the olefin or diene ligand, the intermediates are converted into thermodynamically more favourable cationic CHB. The dieneruthenium hydride complexes having the general formula $[(\eta^4\text{-}C_8H_{12})RuL_3H]^+$ proved to be sufficiently stable to be isolated and and characterised, but in the case of other metals they can be kinetically or thermodynamically unstable. In the reaction of the cationic dihydride complex $[Ir(H)_2(PPh_3)_2(Me_3CO)_2]^+$ with 2,3-dimethylbutadiene, the η^3-allyl CHB $[Ir(H)(PPh_3)_2(\eta^3\text{-}CH_2CMeCMe.$ $.CH_2\text{-}\mu\text{-}H)]^+$ (VII) was isolated as the final product. Apparently initially two acetone molecules are substituted by the diene ligand with formation of the thermodynamically unstable dieneiridium hydride complex $[IrH_2(PPh_3)_2(\eta^4\text{-}CH_2 = CMeCMe = CH_2)]^+$, which then affords compound (VII) as a result of the rapid intramolecular proton transfer from iridium to the diene.[55]

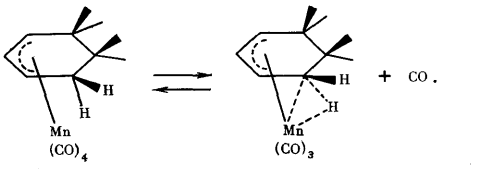
Protonation by strong acids is most characteristic of complexes of metals in the middle of the Periods (Mo, Mn, Fe, Co). Such reactions are unknown for the elements at the beginning and end of the Periods.

2. Decarbonylation

The second type of processes leading to the formation of CHB involves photochemical or thermal decarbonylation of the carbonyl complexes. On irradiation with UV light or on heating, the abstraction of one or several CO groups results in the formation of electron- and coordination-unsaturated intermediates, which can afford CHB in the presence of diene ligands, as shown in Scheme 2 for manganese and chromium complexes.

Scheme 2



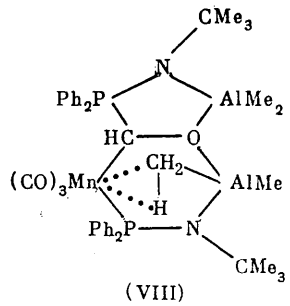


UV irradiation of $Cr(CO)_5L$ [L = P(OMe)] in pentane at 293 K in the presence of 2,4-dimethylpenta-1,3-diene did not yield the expected complex $Cr(CO)_3(L)(\eta^4\text{-}C_7H_{12})$, as in the reactions with other dienes.[56] Instead, the elimination of three CO groups and coordination of the $Cr(CO)_2(L)$ fragment to the diene led to the isolation of a CHB having the structure $Cr(CO)_2(L)(\eta^4\text{-}C_7H_{11}\text{-}\mu\text{-}H)$, in which the diene ligand is linked to chromium via two C=C bonds and the bridging hydrogen atom.[57] The photochemical decarbonylation of $Cr(CO)_5L$, where L = CO, PMe_3, or $P(OMe)_3$, in the presence of cyclohepta-1,3-diene, affording the complexes $Cr(CO)_2(L)(\eta^4\text{-}C_7H_9\text{-}\mu\text{-}H)$, proceeds analogously.[58] In both cases, the CHB isolated were characterised structurally. Thermolysis of the η^3-allyl complex $Mn(CO)_4(\eta^3\text{-}CH_2CHCMe_2)$ in toluene at 110 °C leads to the abstraction of CO with formation of a mixture of isomeric complexes with a bridging hydrogen atom: $Mn(CO)_3$. $.(\eta^3\text{-}CH_2CHCMe\text{-}CH_2\text{-}\mu\text{-}H)$.[59] The thermal decarbonylation of the enyl complex $Mn(\eta^3\text{-cyclohexenyl})(CO)_3L$, where L = phosphine or phosphite, proceeds analogously[59] (Scheme 2).

3. Ligand Substitution

A number of instances of the formation of CHB as a result of ligand substitution are known. One of them involves the displacement of two acetone molecules by 2,3-dimethylbutadiene in an iridium complex, which was already mentioned above. The interaction of salts of the square-planar cation $[Ir(PPh_3)_2(\eta^4\text{-}C_8H_{12})]^+A^-$ (A = PF_6, BF_4, or SbF_6) with gaseous H_2 in the presence of 8-methylquinoline (in CH_2Cl_2 at 0 °C) yielded, as a result of the oxidative addition of H_2 with simultaneous displacement of cyclooctadiene, cationic iridium(III) complexes having the composition $[IrH_2(PPh_3)(\mu\text{-}H\text{-}CH_2C_9H_6N)]^+A^-$ in which 8-methylquinoline is linked to iridium via a nitrogen atom and one bridging H atom in the methyl group.[60]

The substitution of one of the ligands L = PMe_3 and the abstraction of NaCl in the interaction Of $Mo(CO)(CO)(\eta^2\text{-}C,O\text{-}C(O)CH_2SiMe_3)L_3$ with sodium dimethyldithiocarbamate results in the formation of the complex $Mo(CO)(S_2CNMe_2)(L)_2\text{-}C(O)CH_2\text{-}\mu\text{-}H$, where the acetyl group is linked to Mo via a Mo–C σ-bond and a bridging H atom.[61] The above cationic dieneruthenium hydride complexes $[Ru(H)(L)_3(\eta^4\text{-}1,5\text{-}C_8H_{12})]^+$ or the products of their intramolecular isomerisation, namely CHB with the cyclooctenyl fragment $[Ru(\eta^3\text{-}C_8H_{12}\text{-}\mu\text{-}H)L_3]^+$ are converted into the corresponding cationic CHB of the type $[Ru(L)_3(\eta^3\text{-Enyl-}\mu\text{-}H)]^+$, where L = PMe_2Ph, PMe_3, $P(OMe)_2Ph$, or $P(OMe)Ph_2$, in reactions with 1,3-dienes (cyclohepta-1,3-diene, cyclohexa-1,3-diene, butadiene) as a result of the displacement of cyclo-octa-1,3-diene.[62] CHB formed in the following reactions have been obtained and characterised structurally: cocondensation of chromium vapour with cyclo-octa-1,3-diene or cyclo-octa-1,5-diene in the presence of PF_3 leading to the formation of the complex $Cr(\eta^5\text{-}C_8H_{10}\text{-}\mu\text{-}H)(PF_3)_3$;[63] the reaction of $Mn(CO)_5H$ with two moles of the ligand $Ph_3PN(CMe_3)$. $.AlMe_2$ leading to the formation of the bicyclic complex (VIII):[64,65]



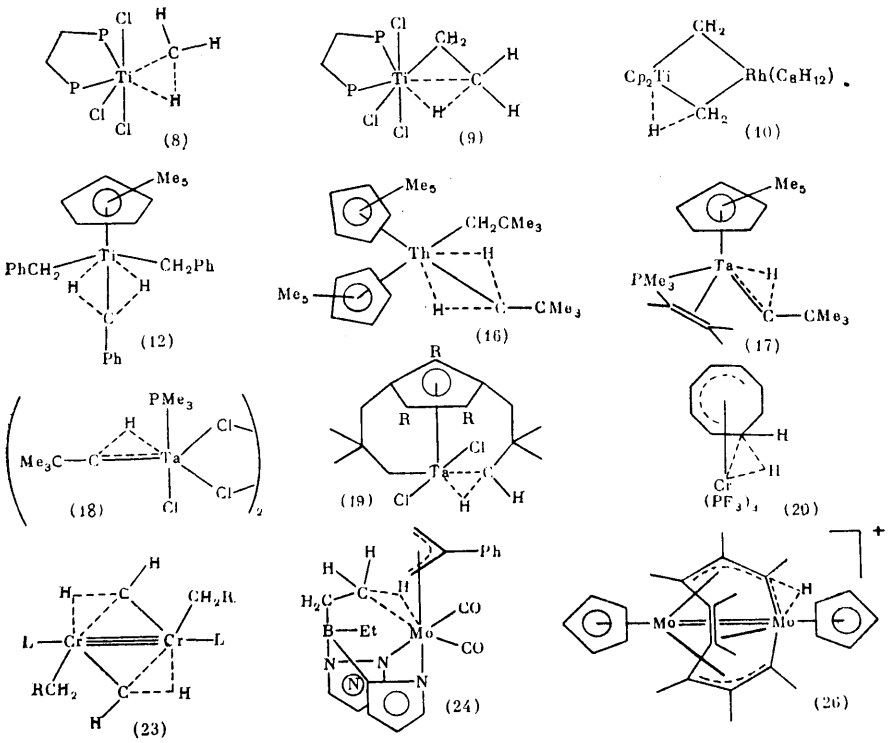
(VIII)

It has been suggested that the 17-electron radical-cations, formed in the one-electron electrochemical oxidation of the 18-electron complexes $(\eta\text{-Cp})_2W(R)(R')$, where R and R′ are an alkyl or an aryl group, can be stabilised via the formation of three-centre three-electron W...H−C bonds with the α- or β-hydrogen atom of the residue R.[66] The formation of cationic or neutral CHB in the protonation reactions is summarised in Table 1. The converse reaction is also known, namely the deprotonation of a neutral cluster with formation of an anionic CHB. It has been shown that the neutral tetrahedral cluster $Fe_3(CO)_9(\mu\text{-H})_3(\mu^3\text{-HC})$, not containing agostic H atoms, exists in solution in equilibrium with a further two isomeric clusters $Fe_3(CO)_9(\mu\text{-H})_2(\mu^3\text{-HC-}\mu\text{-}\textit{H})$ [isomer (A)] and $Fe_3(CO)_9(\mu\text{-H})(\mu^3\text{-HC-}\mu\text{-}\textit{H}_2)$ [isomer (B); the agostic hydrogen atoms are distinguished by being italicised]. In the isomers (A) and (B), there are respectively one and two Fe...H−C 2e, 3c-bonds. Deprotonation of $Fe_3(CO)_9(\mu^3\text{-HC})$ by treatment with an excess of $(PPh_3)_2N^+Cl^-$ leads to the formation of the anionic CHB $Fe_3(CO)_9$. $.(\mu\text{-H})(\mu^3\text{-HC-}\mu\text{-H})^-$.[67]

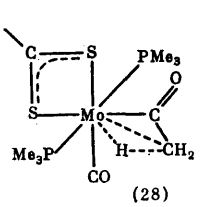
IV. THE STRUCTURE IN THE CRYSTAL ACCORDING TO DATA OBTAINED BY STRUCTURAL METHODS

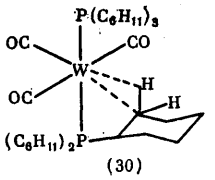
The identification of the M...H−C bridge 2e, 3c-bonds in the crystal is based exclusively on data obtained by structural research methods—X-ray diffraction analysis and neutron diffraction (ND). Scheme 3 presents formulae for a series of structurally characterised CHB and Table 2 summarises certain crystal-chemical data for the M...H−C bridged fragments: the M...H, C−H, and M−C distances and the M−H−C angle. It was not until 1979−1981 that it became possible to understand the fine features of the structure of the CHB as a whole class of complexes with a new type of coordination of the hydrogen atom in a C−H bond to the metal in connection with the considerable improvement of the accuracy of the XRD method and the publication of a series of pioneering studies in which the structures of CHB containing tantalum,[84,85] manganese,[35,95] and iron[100,101] were established.

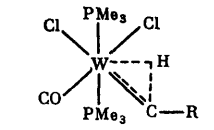
Scheme 3

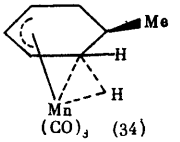


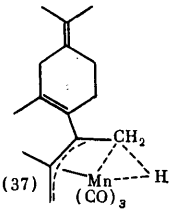
the numbering of the compounds is the same as in Table 1

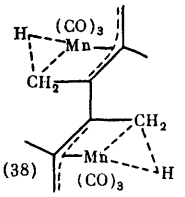

(28)

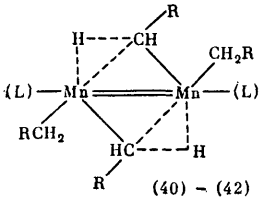

(30)

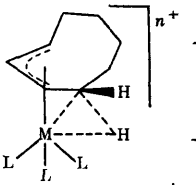

(32) R = CMe_3; (33) R = Ph


(34)

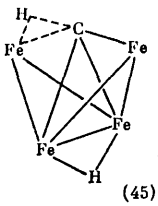

(37)

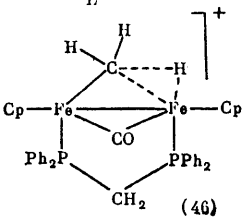

(38)

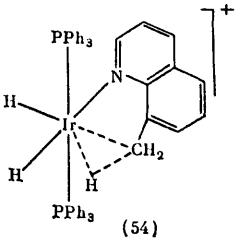

(40) – (42)



M	L	n	№
Fe	$P(OMe)_3$	1	(43)
Fe	$P(OMe)_3$	0	(44)
Ru	$P(OMe)Ph_2$	1	(47)


(45)


(46)


(54)

It is possible to differentiate the following characteristic features of the bridged M...H–C fragments. The M...H distances involving the bridging hydrogen atoms in the CH_n fragment (n = 2,3) are greater on average by 10–20% compared with the usual ranges of M–H bond lengths for terminal hydrido-ligands (according to data in the review of Teller and Bau[7]). The C–H distances determined from XRD data are known to be always too low by 0.1–0.15 Å by virtue of the characteristics of the method itself. One can therefore compare only the C–H distances obtained by the ND method, from which it follows that the C–H bonds coordinated to the metal are extended (loosened). According to ND data, the C–H distances in CHB are 1.10–1.19 Å, which is approximately 5–10% greater than the average C–H distances involving sp^3-carbon atoms (1.08 to 0.19 Å).

The M...H distances obtained by the ND method are compared in Table 3 with the sum of the covalent radii of the M atoms (according to the data of Andrianov et al.[118] and Churchill[119]) and H atoms (0.37 Å) and the C–H bond lengths derived from ND data are also listed. Except for complexes of Group IV metals (Ti, Th), the M...H distances exceed by less than 10% the sum of the covalent radii of M and H. On this basis, one can apparently conclude that, at least in the cases quoted, the M...H bridge bonds, although extended, do not differ very greatly from the terminal M–H bonds in metal hydride complexes.

A method has been proposed[60] for the estimation of the strength of the interaction of the C–H bond with the metal and of the strength of the bond produced. The distance d_A between the metal atom and the point A, where according to the author's hypothesis the centre of the electron pair of the C–H bond is located and through which coordination to the unoccupied metal orbital takes place, is calculated from the experimental distances d(MH), d(MC), and the dimensionless constant a = 0.28 (the ratio of the covalent radius of the hydrogen atom to the length of the "usual" C–H sp^3-bond).

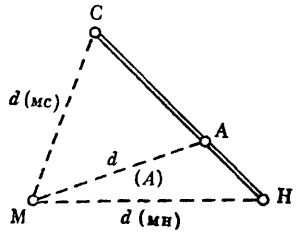


Table 2. Structural data for complexes with a bridging hydrogen atom.

No.	Compound	Method	Distance, Å			M...H–C angle, deg	r_A (Ref.60)	Refs.
			M···H	M–C	C–H			
1	Y (C_5Me_5)$_2$N($SiMe_3$)($SiMe_2CH_2$-μ-H)	XRD	2.45; 3.00	2,970	1.00; 1.06	110.4; 101.6	—	[68]
2	Y (C_5Me_5)$_2$C-μ-H ($SiMe_3$) ($SiMe_2CH$-μ-H_2)	XRD	2 53 (C-μ-H)	2,468	—	84	—	[68]
			2.45; 3.00 (SiCH-μ-H)	2,878	—	—	—	[68]
3	Nd (η^5, η^5-$C_5Me_4SiMe_2C_5Me_4$) C-μ-H ($SiMe_3$)$_2$	XRD	—	2,862	—	—	—	[69]
4	Sm (C_5Me_5)$_2$ (*o*, μ-HC_6H_4N=NC_5-*o*, μ-H) Sm (C_5Me_5)$_2$	XRD	2.29	—	—	—	—	[70]
5	Yb (C_5Me_5)$_2$ [(μ-H-)$_2$C=CH_2] Pt (PPh_3)$_2$	XRD	2.58; 2.64	2.770; 2.793	—	—	—	[71]
6	Yb (Dmpe) [N ($SiMe_3$)$_2$]$_2$	XRD	2.77; 2.86	3,04	—	—	—	[72]
7	Cl_2 (CH_3) Ti (μ-Cl)$_2$ Ti (CH_2-μ-H) Cl_2	XRD	1.92	2.068	1.19	78	—	[73]
8	Ti (CH_2-μ-H) (Dmpe) Cl_3	XRD	2.03	2.149	1.00	80	0.69	[74]
		ND	2,447	2.122	1.095	93.5		[75]
9	Ti (CH_2CH_2-μ-H) (Dmpe) Cl_3	XRD	2.22	2.524	1.04	88	0.98	[75, 76]
10	Ti (Cp)$_2$ (CH_2-μ-H) (μ-CH_2) Rh (C_6H_{12})	XRD	2.024	2.294	0.98	61	—	[77]
11	$TiMe_{1,3}Cl_{0,7}$ (Dmpe)$_2$	XRD	—	2.351	—	—	—	[78]
12	Ti (η-C_6Me_5) (CH_2Ph)$_3$	XRD	2.32; 2.37	2.081	—	—	—	79]
13	Zr (Cp)$_2$ (Cl) (μ-MeCH) Zr (Cl) (C_5H_4Me)$_2$	XRD	2.211	2.585	1.018	99.7	—	[80]
14	Zr (Dmpe) (CH_2SiMe_3)$_4$	XRD	2.48	2.215	—	—	—	[81]
15	[Hf (η-C_5Me_4) Cl—μ-($CHCH_2CMe$=$CMeCH_2$]$_2$	XRD	2.21	2.134	—	—	—	[82]
16	Th (η-C_5Me_5)$_2$ (CH_2CMe_3)$_2$	ND	2.597; 2.648	2.456	1.114; 1.122	—	—	[83]
17	Ta (η-C_5Me_5) ($CHCMe_3$) (η-C_2H_4) (PMe_3)	ND	2.042	1.946	1.135	—	0.61	[84. 85]
18	[Ta ($CHCMe_3$) (PMe_3) Cl_3]$_2$	ND	2.119	1.898	1,131	—	0.68	[84. 85]
19	Ta (η-C_5R_5) ($CH_2CMe_2CH_2$)$_2$ Cl_2	XRD	2.30	2.176	1.102	—	—	[86]
20	Cr (η-C_6H_{10}-μ-H) (PF_3)$_3$	XRD	1.8	2,352	—	—	—	[63]
21	Cr (η^4-C_7H_{11}-μ-H) (CO)$_2$ P (OMe)$_3$	XRD	1.94	2.399	—	101.1	—	[57]
22	Cr(η^4-1,3-cyclo-C_7H_9-μ-H)(CO)$_2$$PMe_3$	XRD	1.85	2.355	1.16	100.4	—	[58]
23	Cr_2 (CH_2SiMe_3)$_4$ (PMe_3)$_2$	XRD	2.236; 2.262	2.266 cp	0.910; 1.018	—	—	[87]
24	Mo [B (Pir)$_2^*$ (Et) (CH_2CH_2-μ-H)] (CO)$_2$ (η^3-C_3H_4Ph)	XRD	2.27	3.055	0.97	136	1.12	[19]
25	Mo ($Ph_2PCH_2CH_2PPh_2$)$_2$ (CO)	XRD	2.98	—	—	—	—	[88]
26	[Mo_2 (η-C_8Me_8-μ-H) (Cp)$_2$]$^+$	XRD	1.88	2.196	0.89	99	0.61	[29, 30]
27	[Mo (η-C_9H_7) (η, σ-$C_{12}H_{13}$-μ-H)]$^+$	XRD	1.80	2.391	1.08	110	—	[31]
28	Mo ($COCH_2$-μ-H) (S_2CNMe_2) (CO) (PMe_3)$_2$	XRD	2.06	2.60	1.00	111	0.84	[61]
29	WRe (μ-H-CHC_6H_4Me) ($Me_2PCH_2PMe_2$)(CO)$_7$	XRD	2.08	2,541	0.86	113	—	[33]
30	W [P (C_6H_{11})$_3$]$_2$ (CO)$_3$	XRD	2.27	2.945	0.95	127	—	[89 90]
31	W[P(iso-C_3H_7)$_3$]$_2$(CO)$_3$	XRD	—	3,027	—	—	—	[89]
32	W ($CHCMe_3$) (CO) (PMe_3)$_3$$Cl_2$	XRD	1.835	1,859	1.053	75	—	[91. 92]
33	W (CHPh) (CO) (PMe_3)$_3$$Cl_2$	XRD	—	1,860	—	—	—	[93. 94]
34	Mn (η^3-MeC_6H_8-μ-H) (CO)$_3$	XRD	1.86	2.301	1.07	100	0.75	[35]
		ND	1.84	2.34	1.19	99		[95]
35	Mn (CO)$_3$ (μ-σ:η^3-$CH_2CMeCHMe$) (μ-PPh_2) (μ-CO) MoCp	XRD	2.02	2.346	—	—	—	[96]
36	Mn (CO)$_3$ (μ-σ:η^4-$CHCHCH_2CHPPh_2$) Mo (CO) Cp	XRD	2.29	2.245	—	—	—	[96]
37	Mn (CO)$_3$ ($C_{15}H_{23}$)	XRD	2.296; 2.298	1.901; 1,880	—	98.1; 101.3	—	[97]
38	Mn_2 (CO)$_8$ ($C_{10}H_{16}$)	XRD	2 291	1.816	—	100,7	—	[97]
39	Mn (CO)$_3$$CHOAlMe_2N$ (CMe_3) Al (μ-H-CH_2) (Me)	XRD	1.91	2.45	0.80	124	—	[64, 65]
40	Mn_2 (CH_2Ph)$_4$ (PMe_3)$_2$	XRD	2.20	2.391	—	—	—	[99]
41	Mn_2 (CH_2SiMe_3)$_4$ (PMe_3)$_2$	XRD	2.29	2.369	—	—	—	[98, 99]
42	Mn_2 (CH_2SiMe_3)$_4$ ($PMePh_2$)$_2$	XRD	2.15	2.389	—	—	—	[99]
43	[Fe (η^3-C_8H_{12}-μ-H) (P (OMe)$_3$)$_3$]$^+$	XRD	1.95	2.384	1.07	100	0,79	[100, 101]
		ND	1,874	2.362	1.164	99.4		[101]
44	Fe (η^3-C_8H_{12}-μ-H) (P (OMe)$_3$)$_3$	XRD	2.77	2,983	0.99	93	—	[102]
45	Fe_4 (μ-CH) (H) (CO)$_{12}$	XRD	1.80	1,926	1,00	82	0.59	[103]
		ND	1,755; 1.747	1.927; 1 920	1 191; 1,176	84; 84	—	[104]
46	[Fe_2 (μ-CH_2-μ-H) (μ-CO) ($Ph_2PCH_2PPh_2$) (Cp)$_2$]$^+$	XRD	1.64; 1.78	2.108; 2,118	1 06; 0.83	101; 103	0.65	[42]
47	[Ru (η^3-C_8H_{12}-μ-H) (P (OMe) Ph_2)$_3$]$^+$	XRD	2.08	2 592	1.14	103	—	[105]
48	[Ru (η^3-C_4H_6-μ-H) (PMe_2Ph)$_3$]$^+$	XRD	1.84	2.38	—	—	—	[62]
49	RuCl ($C_{21}H_{34}$-μ-H)	XRD	2,10	—	1.04	118	—	[106]
50	[Os (η-$Me_5C_6H_3$) (η-$C_{10}H_{12}$-μ-H)]$^+$	XRD	1.81	2,30	0,95	110	—	[45]
51	[Co (η-C_6Me_5) (CH_2CH_2-μ-H) P (C_6H_4Me-*n*)$_3$]$^+$	XRD	1.46	2.128	1,31	—	—	[50]
52	Co (η^3-C_8H_9-μ-H) (C_6H_{11})$_2$$PCH_2CH_2P$ (C_6H_{11})$_2$	XRD	1.85	2.297	—	—	—	[107]
53	Rh (η-C_7H_8-μ-H) (η^5-1,2-$Me_2C_2B_9H_9$)	XRD	1.9	2.36	—	108	—	[53]
54	[IrH_2 (PPh_3)$_2$(N, C-8-CH_2—μ-H-C_9H_6N)]$^+$	XRD	2.08	2.69	0,96	119	0.91	[60]
55	Pd (N (NMePh)=CMe_2)$_2$$Cl_2$	XRD	2.36	—	—	—	—	[108]
56	Pd(1-methylcytosine)$_2$$Cl_2$	XRD	2.66	3,128 (Pd—N)	0 82 (N—H)	118	—	[109]
57	Pd (NMe=CHPh)$_2$$Cl_2$	XRD	2.44	3,22	1.01	131	1.30	[110]
58	Pd [(η^5-NC_4H_4)Mn (CO)$_2$$PPh_2C_6H_4$-μ-H]$_2$$Cl_2$	XRD	2.68	—	0.88	154	—	[111]
59	Pd (PPh_3)$_2$ (CR=CR—CR=CR-μ-H) Br, R = COOMe	XRD	2.30	3.19 [60]	—	137	1.26	[17]
60	[Pd (PPh_3CMe_3)$_2$]$_3$	XRD	2.70	3.45	1.05	128	1.56	[112]
61	[Pt (PPh_2CMe_3)$_2$]$_2$	XRD	2.77	3.46	0.97	126	1.60	[112]
62	*trans*- $PtCl_2$ [MeC_6H_3NN=C (μ-H) $C_6H_2Me_3$] ($AsEt_3$)	XRD	2.43	—	1.02	117	—	[113]
63	*cis*-Pt (*o*-$Ph_2PC_6H_4NC$ (O)C_6H_4) (*o*-$Ph_2PC_6H_4NHC$ (O) Ph)	XRD	2.318	3,24 (N—Pt)	1.04 (N—H)	—	—	[114]
64	[$PtCl_4$-*cis*-$PtCl_2(NH_2Me)_2$]$^{2-}$	ND	2.262	—	1.032(N—H)	167.1	—	[115]
65	Cu (C_7H_9-μ-H) ($H_2NCH_2CH_2NHCH_2CH_2NH_2$)	XRD	2.01	2.78	—	158	—	[116]
66	Au (PPh_3)C_5H_4C (=O) C_5H_4-μ-H	XRD	2,94	—	0.98	—	—	[117]

*Pir = pyrazolyl.

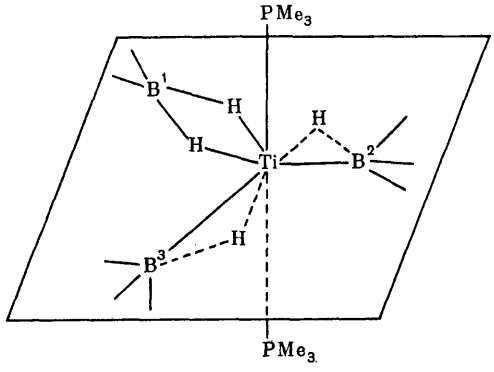
In order to be able to compare the complexes of different metals, the difference $r_A = d_A - r_M$, where r_M is the covalent radius of the metal, was adopted as a criterion of the estimate. It has been suggested that r_A be treated as a kind of "covalent radius" of the bonding electron pair. The greater the value of r_A, the weaker the M...H–C interaction. The values of r_A are listed in Table 2. One can differentiate arbitrarily three groups of compounds. Within the framework of the given approach, the bridge bonds are the strongest for Fe_4(μ-CH)(H)(CO)$_{12}$, [Mo_2(η-C_8Me_8-μ-H)(Cp)$_2$]$^+$, [Ta(CH. .CMe_3)(L)Cl_3]$_2$, and Ti(CH_2-μ-H)Cl_3($Me_2PCH_2CH_2PMe_2$) (the values of r_A are in the range 0.59–0.69). The bridging interaction in Mn(η^3-MeC_6H_7-μ-H)(CO)$_3$, [Fe(η^3-C_8H_{12}-μ-H) {P(OMe)$_3$}$_3$]$^+$,

$Mo(COCH_2\text{-}\mu\text{-}H)(S_2CNMe_2)(CO)(PMe_3)_2$, $[Ir(PPh_3)_2(H)_2(N,C\text{-}8\text{-}methylquinoline)]^+$, and $Ti(CH_2CH_2\text{-}\mu\text{-}H)Cl_3(Me_2PCH_2CH_2PMe_2)$ are less strong (the values of r_A are in the range 0.75–1.0). The bridge bonds in the complexes $Mo[BEt_2(pyrazolyl)_2](CO)_2(\eta^3\text{-}C_3H_4Ph)$, $Pd(PhCH{=}NMe)_2Cl_2$, and $[M(PPh_2CMe_3)_2]_2$ (M = Pd or Pt), where r_A = 1.0–1.6, are weakest.

Table 3. M...H and C...H distances in complexes with a bridging hydrogen atom according to neutron diffraction data.

Compound	M...H distance, Å	r_M, Å	r_M+r_H, Å	C–H distance, Å	Refs.
$Ti(CH_2\text{-}\mu\text{-}H)(Dmpe)Cl_3$	2.447 (3)	1.56	1.93	1.095 (3)	[75]
$Ta(\eta\text{-}C_5Me_5)(CHCMe_3)(C_2H_4)PMe_3$	2.042 (5)	1.66	2.03	1.135 (5)	[84, 85]
$Th(\eta\text{-}C_5Me_5)_2(CH_2CMe_3)_2$	2.597 (9); 2.648 (9)	1.73	2.10	1.114 (9); 1.122 (8)	[83]
$[Ta(CHCMe_3)(PMe_3)Cl_3]_2$	2.119 (4)	1.66	2.03	1.131 (3)	[84, 85]
$Mn(\eta^3\text{-}MeC_6H_7\text{-}\mu\text{-}H)(CO)_3$	1.84 (1)	1.38	1.75	1.19 (1)	[95]
$[Fe(\eta^3\text{-}C_9H_{12}\text{-}\mu\text{-}H)(P(OMe)_3)_3]^+$	1.874 (3)	1.34	1.71	1.164 (3)	[100, 101]
$Fe_4(\mu\text{-}CH)(H)(CO)_{12}$	1.753 (4)	1.34	1.71	1.191 (4)	[104]

Note. The average estimate of the covalent radius r_{Th} is based on Th–C bond lengths of 2.543(4) and 2.456(4) Å and the radius r_C = 0.77 Å.



The structure of the complex $(PMe_3)_2Ti(BH_4)_3$.[14]

In 1975–1982, Schrock and co-workers obtained a large number of electron-deficient niobium, tantalum, and tungsten complexes with alkylidene (carbene) ligands, namely :CH–CMe_3, :CH–Ph, etc.; the structurally characterised 14-electron and 16-electron complexes of this type are presented in Table 4, which includes also for comparison data for a series of 18-electron complexes. The following features of the coordination of the alkylidene ligands to the electron-deficient centre have been discovered. The character of the coordination (distances, angles) depends very strongly on whether the complex is of the 16-electron or 18-electron type. Alkylidene ligands contain an sp^2-carbon atom for which a trigonal-planar configuration with valence angles close to 120° is ideal. Deviations from the ideal geometry involving an increase in the M–C_α–C_β angles occur in both 16-electron and 18-electron complexes. However, the angles for the 18-electron complexes do not exceed 135 to 150°, whereas in the 16-electron complexes the distortion is significantly greater and the M–C_α–C_β angles are 160–170°. The M–C_α distances in the 18-electron complexes are 2.03–2.07 Å, while in the 16-electron complexes they are significantly smaller, amounting to 1.86–1.96 Å. In those cases where the locations of the hydrogen atoms have been determined and the M...H–C bridge fragments (carbene fragments) have been detected, the M–C_α–H angles are sharply diminished – from 90–110° to acute angles in the range 70–80°.

Table 4. Certain structural parameters of the carbene ligands :C(H)–CMe_3 and :C(H)–Ph in the 14-, 16-, and 18-electron tantalum and tungsten complexes.

Compound	Angles, deg		M–C_α distance, Å	$J(^{13}C\text{–}H)$, Hz	Refs.
	M–C_α–C_β	M–C–H			
Formally 14- and 16-electron complexes					
$Ta(\eta\text{-}C_5Me_5)(CHCMe_3)(C_2H_4)PMe_3$	170.0	78.1	1.946	74	[85]
$Ta(CHCMe_3)_2(\eta\text{-}C_5Me_3H_2)(PMe_3)_2$	168.9	*	1.932	91	[120]
	154.0		1.955	104	
$Ta(\eta\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$	166.0	*	1.883	82	[121]
$[Ta(CHCMe_3)(PMe_3)Cl_2]_2$	161.2	84.8	1.898	101	[85]
$[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2$ (N_2)	160.3	*	1.937	91 [123]	[122]
	158.5		1.932		
$W(CHCMe_3)(CO)(PMe_3)_2Cl_2$	168.7	72.2	1.859	73	[91, 92]
$W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(Dmpe)$	150.4	*	1.942	90 [125]	[124]
$W(CHPh)(CO)(PMe_3)_2Cl_2$	164.6	74.6	1.860	82	[93]
18-electron complexes					
$Ta(\eta\text{-}C_5H_5)_2(CHCMe_3)Cl$	150.4	111	2.030	121	[126]
$Ta(\eta\text{-}C_5H_5)_2(CHPh)(CH_2Ph)$	135.2	*	2.070	127	[127]
$Ta(\eta\text{-}C_5H_5)_2(CH_2)(CH_3)$	—	*	2.026	132	[128]
$W(CHPh)(PhC{\equiv}CPh)(PMe_3)_2Cl_2$	138	92.1	2.05	126	[93, 94]

*The locations of the hydrogen atoms have not been determined.

All the distortions in the geometry of the electron-deficient alkylidene complexes mentioned above have the same cause and are induced by the interaction of the α-hydrogen atom and the electrons of the C–H bond with the metal. Yet another parameter, which in the case of the carbene ligands :C(H)R depends greatly on whether the C–H hydrogen bond is of the bridge type, is the spin–spin coupling constant $^1J(^{13}C\text{–}H)$ for the ^{13}C NMR spectra. The constants for the C–H sp^3-bond are usually 120–125 Hz, while anomalously low values of the constant J, amounting to 50–110 Hz, are characteristic of the electron-deficient CHB (see below). This indicates a weakening (loosening) of the C–H bond when it is coordinated to the metal. The set of properties enumerated above constitutes characteristic features of the presence of M...H–C bridge 2e,3c-bonds.

An XRD study has been performed on the electron-deficient complexes $Mn_2(C_6H_{11})_4(Me_2PCH_2CH_2PMe_2)$,[129] $(\eta\text{-}C_5Me_5)_2ScCH_2CH_3$,[130] $(\eta^5\text{-}C_5Me_5)_2YCH_3.C_4H_8O$,[131] and also $(\eta^5\text{-}C_5Me_5)_2Th\overline{CH_2\text{-}(\eta^1{:}\eta^5\text{-}C_5R_2H_3)}M$ ($\eta^5\text{-}C_5R_2H_3$)Me, where M = Zr or Hf,[132] but, owing to the structural disorder in the crystal, it was not possible to reach clear-cut conclusions as to the presence or absence of an agostic hydrogen atom. For the same reason, it has not been possible to establish unambiguously whether the Co...H–C or the Co...H–B bond is formed in the complex $Co(\eta\text{-}C_5H_5)(\eta\text{-}Et_4C_2B_2CHMe)$.[133]

The possibility of the simultaneous coordination to the same metal atom of two bridging hydrogen atoms of the M–CH_2 fragment has been demonstrated in the complexes $Ti(\eta\text{-}C_5Me_5)(CH_2Ph)_3$ [79] and $Th(\eta\text{-}C_5Me_5)_2(CH_2CMe_3)_2$.[83] In these cases, there exist

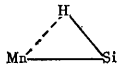
in the molecule both bridging and non-bridging CH_2 fragments whose parameters differ sharply. The M—C and C—H distances are significantly shorter precisely for the CH_3 group participating in the bridging interaction compared with the non-bridging CH_2 (Table 5).

Table 5. Structural data for complexes with two bridging hydrogen atoms.

Parameter	Method	Bridging CH_2 group	Non-bridging CH_2 groups
Ti (η-C_5Me_5) (CH_2Ph)$_3$ [79]			
Ti–C_α distance, Å	XRD	2.081 (10)	2 . (10); 2.140 (10)
Ti–H distance, Å	»	2.32 and 2.37	2.57—2 66
Ti–C_α–C_β angle, deg	»	139.0 (7)	114.0; 113.9
Th (η-C_5Me_5)$_2$ (CH_2CMe_3)$_2$ [83]			
Th–C_α distance, Å	ND	2.456 (4)	2.543 (4)
Th–H distances, Å	»	2 597 (9); 2.648 (9)	2.996 (9); 2.956 (9)
C_α–H distances, Å	»	1.114 (9); 1.122 (8)	1.079 (11); 1.095 (8)
Th–C_α–C_β angle, deg	»	158.2 (3)	132.1 (3)
Th–C_α–H angle, deg	»	84.1 (5); 87.1 (5)	104.2 (6); 101.1 (5)

Note. The numerals in square brackets denote references (Translator).

The formation of M...H—E 2e,3c-bonds by transition metals is not restricted to bonds with carbon alone. Whole series of cyclopentadienyl derivatives of manganese of the type $Mn(\eta\text{-}C_5H_5)(CO)_2\cdot(SiR_3)H$, in which there is a bridging hydrogen atom and the fragment



have been obtained and characterised structurally (Table 6). On passing from $SiCl_3$ to Si(Me) (naphthyl)Ph and $SiPh_3$, the Mn—Si and Mn—H distances increase somewhat, while the Si—H distances hardly change. The complexes $Ti(BH_4)_3(PR_2)_2$, where R = Me or Et, have been obtained recently. According to XRD data, the complex with PMe_3 contains two Ti...H...BH_3 2e,3c-bonds.[141] The molecule of this complex has the structure of a trigonal bipyramid with two PMe_3 ligands at the apical positions (see Figure). Of the three BH_4 groups in the equatorial plane, one is coordinated in the usual way, via two bridging H atoms [with the distances Ti—H = 1.90(7) Å, B(1)—H = 1.03(7) Å, and the non-bonding distance Ti...B(1) = 2.40(1) Å]. The other two BH_3 groups are linked to Ti by two three-centre Ti...H—B(2, 3) bonds involving one H atom from each BH_4 group: the distances Ti—B(2, 3) = 2.27(1) Å and Ti...H = 1.73(7) Å are shorter by 0.17 Å than in bonding of the type $Ti(\mu\text{-}H)_2B$. The distances from Ti to the other two H atoms in BH_3 are 2.25(7) and 2.68(7) Å, which exceeds by approximately 0.5 and 0.9 Å the distance to the bridging H atom. The M...H—B (where M = Mo, W, Fe, Ru, or Rh) bridge bonds are present in many transition metal complexes with carbaboranyl ligands of various types, which have been characterised by structural methods.[142–146]

V. THE STRUCTURE IN SOLUTIONS

The ^1H, ^{13}C, and ^{31}P NMR methods and in certain cases IR spectroscopy in the ν(C—H) frequency range are of principal importance for the identification and study of CHB in solutions. The hydrogen atoms of the CH_3, CH_2, and CH fragments involved in the bridge interaction with the metal give rise to ^1H NMR signals in strong fields (δ from 0 to -15 p.p.m.), i.e. in the region where there are signals due to terminal hydrido-ligands. It is therefore impossible to distinguish the two types of hydrogen atoms on the basis of ^1H NMR spectra. For the titanium, tantalum, and niobium complexes, where the metal atom has a small number of *d* electrons, the upfield shift of the signals due to the protons and ^{13}C nuclei in the M...H—CH_n fragments is usually weaker or is not observed at all. Anomalously low ^1J (^{13}D—H) constants for the ^{13}C NMR spectra, amounting to 50—110 Hz, are characteristic of the M...H—CH groups, which probably indicates a smaller strength of the C—H bridge bond compared with the usual bonds.

Table 6. Structural data for silylmetal hydride complexes with three-centre M...H—Si bonds.

Compound	Method	Distances, Å			Mn–H–Si angle, deg	Refs.
		Mn—H	Mn—Si	Si—H		
$Mn(\eta\text{-}MeC_6H_4)(CO)_2(SiCl_3)(\mu\text{-}H)$	XRD	1.47 (3)	2.254 (1)	1.79 (4)	—	[134]
$Mn(\eta\text{-}C_6H_5)(CO)_2(SiCl_2Ph)(\mu\text{-}H)$	XRD	1.49 (6)	2.310 (2)	1.79 (6)	—	[136]
$Mn(\eta\text{-}C_6H_4Me)(CO)_2(SiFPh_2)(\mu\text{-}H)$	ND	1,569 (4)	2.352 (4)	1 802 (5)	88	[135], [136]
$Mn(\eta\text{-}C_6H_4Me)(CO)(L)(SiHPh_2)(\mu\text{-}H)$ (L = PMe_3)	XRD	1.49 (4)	2.327 (1)	1 78 (4)	91	[136]
$Mn(\eta\text{-}C_6Me_5)(CO)_2(SiHPh_2((\mu\text{-}H)$	XRD	1.52 (3)	2.395 (1)	1.77 (3)	93	[136]
$Mn(\eta\text{-}C_5H_5)(CO)_2(SiPh_3)(\mu\text{-}H)$	XRD	1.55 (4)	2.424 (2)	1.76 (4)	—	[137]
$Mn(\eta\text{-}C_6H_4Me)Mn(CO)_2(SiR_3)(\mu\text{-}H)$ [SiR_3 = Si(Me)(Ph)(α-naphthyl)]	XRD	—	2,461 (7)	—	—	[138]
Mn (η-MeC_5H_4)(CO)× ×($Ph_2PCH_2CH_2SiMe_2$-μ-H)	XRD	1.53 (4)	2,547 (2)	1.75 (4)	97	[139]
$Cr(\eta\text{-}C_6Me_6)(CO)_3(SiPh_2H)(\mu\text{-}H)$	XRD	1.61 (4)	2.456 (1)	1,61 (4)	—	[140]

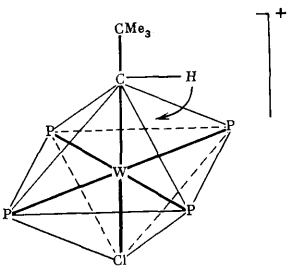
It follows from the XRD data (Table 2) that the C—H bonds coordinated to the metal in the CHB are extended and the hydrogen atom is close to the metal. The extension of the C—H bond weakens it and reduces the force constant of the C—H stretching vibration. The ν(C—H) frequencies for the bridging hydrogen in the CHB are 2200—2700 cm^{-1}, which is lower by 100—600 cm^{-1} than the usual value (2800—3000 cm^{-1}). The low constant $J(^{13}C—H)$ and the sharp decrease in the ν(C—H) frequencies indicate fairly reliably a decrease in the C—H bond orders on coordination to the metal. Both these effects are distinct in the NMR and IR spectra of the 14-electron and 16-electron alkylidene complexes of niobium, tantalum, and tungsten with the :CH—CMe_3 and :CH—Ph ligands and also the related angular sandwich complexes of titanium and thorium (Table 7). Several alkylidene complexes of tantalum and tungsten have been characterised structurally (Table 4) and bridging hydrogen atoms have been found in them. On the basis of the similar $J(^{13}C—H)$ constants and ν(C—H) frequencies, presumably the other complexes listed in Table 7 also have a distorted geometry with the α-hydrogen atom inclined relative to the metal and involving the formation of M...H—C bridge bonds.

Table 7. The constants $J(^{13}C-H)$ and the frequencies $\nu(C-H)$ of complexes with M...H−C bridge bonds.

Compound	$J(^{13}C-H)$, Hz	$\nu(C-H)$, cm^{-1}	Refs.
$Y(\eta\text{-}C_5Me_5)_2N(SiMe_3)(SiMe_2CH_2\text{-}\mu\text{-}H)$	116	—	[68]*
$Y(\eta\text{-}C_5Me_5)_2C\text{-}\mu\text{-}H(SiMe_3)(SiMe_2CH_2\text{-}\mu\text{-}H)$	84	—	[68]*
$Y(\eta\text{-}C_5Me_5)_2CH_2\text{-}\mu\text{-}H\cdot C_4H_8O$	108	2770	[131]*
$Sc(\eta\text{-}C_5Me_5)_2R$			
R=Me	111	—	[130]*
R=Et	122	2593, 2503, 2440	[130]*
R=Pr	117	—	[130]
$Nd(\eta\text{-}C_5Me_5)_2C\text{-}\mu\text{-}H(SiMe_3)_2$	90	—	[147]*
$TiMe_{1.3}Cl_{0.7}(Dmpe)_2$	—	2750	[78]*
$TiCp_2(CH_2\text{-}\mu\text{-}H)(\mu\text{-}CH_2)Rh(C_8H_{12})$	88	2460	[77]*
$[Hf(\eta\text{-}C_5Me_5)Cl{-}\mu\text{-}(CHCH_2CMe{=}CMeCH_2)]_2$	94	—	[82]*
$Hf(\eta\text{-}C_5Me_5)(C_6H_{10})R$			
R=Me	112	—	[148]
R=Et	121	2600, 2500, 2440	[148]
$R=CH_2CMe_3$	104	—	[148]
$Th(\eta\text{-}C_5Me_5)_2(CH_2SiMe_3)Cl$	104	—	[83]
$Th(\eta\text{-}C_5Me_5)_2(CH_2SiMe_3)_2$	99	—	[83]
$Th(\eta\text{-}C_5Me_5)_2(CH_2CMe_3)_2$	97	—	[83]*
$Th(\eta\text{-}C_5Me_5)_2\overline{CH_2{-}(\eta^1{:}\eta^5\text{-}C_5H_5)M(\eta\text{-}C_5H_5)}$			
M=Zr	89	—	[132]
M=Hf	84	—	[132]*
$Ta(\eta\text{-}C_5Me_5)(=CHCMe_3)(C_2H_4)PMe_3$	74	2605	[84, 85]*
$[Ta(=CHCMe_3)(PMe_3)Cl_3]_2$	101	2520	[84, 85]*
$Ta(=CHCMe_3)(CH_2CMe_3)_3$	90	—	[149]
$Nb(=CHCMe_3)(CH_2CMe_3)_3$	101	—	[149]
$Ta(=CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$	98 and 96	—	[150]
$Ta(\eta\text{-}C_5H_5)(=CHCMe_3)_2(PMe_3)$	97 and 90	—	[150]
$Ta(\eta\text{-}C_5H_5)(=CHCMe_3)(X)(Y)$	76—84	2420—2525	[151]
X, Y = Cl, Br, Me, CH_2CMe_3			
$M(=CHR)L_2X_3$, M = Nb, Ta, R = alkyl, Ph; L = phosphine, X = Cl, Br	70—100	2400—2700	[152]
$Ta(=CHCMe_3)(PMe_3)_2(Cl)(H)$	72	2440	[153]
$Ta(\eta\text{-}C_5Me_5)(=CHCMe_3)(PMe_3)(Cl)H$	72	2525	[153]
$Ta(=CHCMe_3)(PMe_3)_4Cl$	69	2200	[153]
$Ta(\eta\text{-}C_5H_5)(=CHPh)(X)(Y)$	82—91	—	[121]
X, Y = Cl or CH_2Ph			
$Ta(=CHCMe_3)(Dmpe)_2Cl$	57	2200	[154]
$Ta(=CHCMe_3)(C_2H_5)(PMe_3)_2Cl_2$	80	—	[155]
$W(=CCMe_3)(=CHCMe_3)(CH_2CMe_3)(Dmpe)$	90	—	[125]*
$W(=CHCMe_3)(PMe_3)_2Cl_3(H)$	84	2395	[91]
$W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$	73	—	[91, 92]*
$W(=CHCMe_3)(C_2H_4)(PMe_3)_2Cl_2$	70	—	[91]
$W(=CHPh)(CO)(PMe_3)_2Cl_2$	83	—	[93, 94]*
$W(CO)_3[P(C_6H_{11})_3]_2$	—	2552	[90]*
$W(\eta\text{-}C_6Me_5)Me_3(=CH_2)$	110	—	[156]
$Mn_2(CH_2R)_4L_2$ R = $SiMe_3$, CMe_3, Ph; L = PMe_3, $PMePh_2$	—	2700—2772	[99]*
$Fe_3(\mu\text{-}H)_2(CO)_9\text{-}\mu^3\text{-}(CH\text{-}\mu\text{-}H)$	89	—	[67]
$Fe_3(\mu\text{-}H)(CO)_9\text{-}\mu^3\text{-}(CH\text{-}\mu\text{-}H_2)$	98	—	[67]
$[Fe_3(\mu\text{-}H)(CO)_9\text{-}\mu^3\text{-}(CH\text{-}\mu\text{-}H)]^-$	60	—	[67]
$[Mn(\eta\text{-}C_5H_7\text{-}\mu\text{-}H)(Me_2PCH_2)_2CMe]^+$	118	2300—2360	[166]

*The structure has been established by structural methods.

On protonation (with CF_3SO_3H or CF_3COOH), the 18-electron carbyne complex $L_4(Cl)W{\equiv}CCMe^3$ is converted into the cationic 16-electron carbene complex $[L_4(Cl)W{=}CH{-}CMe_3]^+$ (IX) (L = PMe_3 throughout), in which the α-hydrogen atom of the carbene ligand interacts with one of the C−P−P faces of the octahedron and the W atom:[157]



(IX)

The spectroscopic data for compound (IX) and the isoelectronic neutral complex $L_4(Cl)Ta{=}CH{-}CMe_3$ (X)[153] are similar:

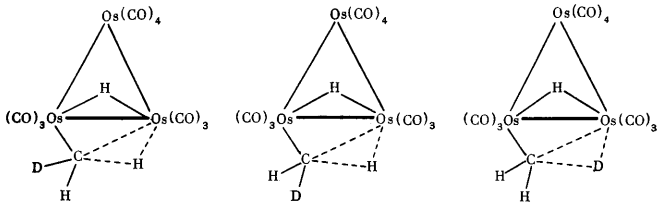
Compound	δ(CH) at 295 K, p.p.m.	$J(H-^{31}P)$, Hz	$J(^{13}C-H)$, Hz	Refs.
$[L_4(Cl)W{=}CH{-}CMe_3]^+$	−8.4 (quintet)	9	45	[157]
$L_4(Cl)Ta{=}CH{-}CMe_3$	−7.4 (quintet)	6	69	[153]

The complexes (IX) and (X) are stereochemically non-rigid compounds but at 295 K the rapid, in terms of the NMR time scale, migration of H between the four C−P−P faces leads to the apparent equivalence of the four P atoms.

In the 16-electron cations $[L_4(X)W{=}CH_2]^+$, where X = Cl[157] or I,[158] formed on protonation of the carbyne complexes $L_4(X)W{\equiv}CH$, at 298 K both hydrogen atoms of the methylene ligand give rise to a single averaged signal owing to rapid exchange (δ = −0.16 and −0.80 p.p.m.), which is split into a quintet. On cooling to 165 or 153 K, the two H atoms become non-equivalent and give rise to two different signals: the shifts δ are −7.67 and −9.00 p.p.m. for the H atoms interacting with the C−P−P face and the W atom; for the compound with X = Cl, the H atom not interacting with W produces a signal at δ = 7.05 p.p.m., while in the case where X = I the signal of this H atom is masked by the signal of the solvent. The complex with X=I has been studied by XRD, but the locations of the H atoms have not been determined.[159]

The majority of the CHB contain the CH_3 or CH_2 groups and are stereochemically non-rigid complexes (see below), whose NMR spectra exhibit reversible temperature variations (TV). Under the conditions of rapid exchange, the two or three protons of the CH_3 or CH_2 groups are equivalent and give rise to an average signal in the range δ = 0−−3 p.p.m., while the carbon nucleus in the ^{13}C NMR spectra is manifested by a binomial 1:2:1 triplet or a 1:3:3:1 quartet with an average constant J = 120−130 Hz. In slow exchange, the two protons of the CH^aH^b group are non-equivalent, form the AB (or AX) system, and give rise to two doublets with a geminal constant $J(H,H)$ = 15−30 Hz. The three non-equivalent protons in $CH^aH^bH^c$ form the ABC three-spin system and give rise to three multiplets, the signal of the bridging proton (H^a) usually having δ = −10−−15 p.p.m. The resonance signal of the carbon nucleus is split under the conditions of slow exchange respectively into a doublet of doublets (for CH^aH^b) or into a doublet of triplets ($CH^aH^{b,c}$) with different constants: $J(^{13}C-H^a)$ = 50−110 Hz for the bridging H^a atom and J = 130−150 Hz for the non-bridging H^b and H^c atoms. The ^1H and ^{13}C NMR data for CHB under the conditions of both rapid and slow exchange are compiled in Table 8.

When H is replaced by D in the M...H−CH_n (n = 1,2) groups, additional effects appear in the ^1H and also ^2H NMR. Deuteriation leads to an unusual upfield shift of the resonance signals of the CH_2D, CHD_2, and CHD groups relative to CH_3 and CH_2 (Δδ = 0.3−1.2 p.p.m.), although for the usual compounds geminal substitution of H by D in CH_3 or CH_2 is accompanied by only a very slight shift of the signals (Δδ = 0.01−0.3 p.p.m.). An appreciable influence of the H/D substitution on the constants $J(^{13}C-H)$ has been noted. The marked dependence of δ and Δδ on isotope substitution was first observed for the cluster complex $HOs_3(CO)_{10}\cdot(CH_2\text{-}\mu\text{-}H)$ and has been called the "isotope perturbation effect" or the chemical shift effect.[161] Three rotational isomers are possible for this cluster, in which the bridge position is occupied by either H [rotational isomers (XI) and (XII)] or by D [compound (XIII)]:



(XI) (XII) (XIII)

The equilibrium (XI) ⇄ (XII) ⇄ (XIII), whose position depends on temperature, exists in solution; the contributions of the individual rotational isomers are not the same and the distribution differs from the statistical distribution owing to the difference between the properties of H and D (isotope effect). Since the C–H and C–D bridge bonds are extended compared with the non-bridge bonds and also bearing in mind the difference between the zero-point energies of the C–H and C–D bonds, one may conclude that the bridge position is preferred for the light H atom compared with the heavier D atom. Each of the H-bridged forms will therefore contribute more than the D-bridged form.

Since the H atom linked to two M atoms should generate a signal in a stronger field than the non-bridging atom, for unequal amounts of the individual rotational isomers the signal due to the protons in CH_2D is located in a stronger field than the signal from CH_3. The observed strong temperature dependence of δ and Δδ is associated with the shift of the equilibrium between the rotational isomers. Data for the dependence of the chemical shifts on isotope substitution in CHB are presented in Table 9.

Table 8. ^1H and ^{13}C NMR data for complexes with bridging hydrogen atoms.

Compound	Group	^1H NMR spectra: rapid exchange		^1H NMR spectra: slow exchange			^{13}C NMR spectra				Refs.
		T, °C	δ(H), p.p.m.	T, °C	δ(H^a), p.p.m.	δ(H^b and H^c), p.p.m.	T, °C	δ(^{13}C), p.p.m. (multiplicity*)	J(^{13}C–H), Hz (H^a)	J(^{13}C–H), Hz (H^b and H^c)	
$Ti(CH_2\text{-}\mu\text{-}H)(Me_2PCH_2CH_2PMe_2)Cl_3$	CH_3	–90	2,29	—	—	—	–90	87.5 (q)	129.5		[75]
$Ti(Cp)_2(CH_2\text{-}\mu\text{-}H)(\mu\text{-}CH_2)Rh(C_8H_{12})$	CH_3	25	–3,13	–90	–12.15	1.28	–90	51.1 (dt)	88	127	[77]
$Ta(\eta^5\text{-}C_5R_3(CH_2CMe_2CH_2)_2)Cl_2$	CH_2	—	—	–70	0.33	4.03	—	—	—	—	[86]
$Cr(\eta^5\text{-}C_9H_{10}\text{-}\mu\text{-}H)(PF_3)_3$	CH_2	—	—	–50	–12.58	–0.09	–80	1.9 (dd)	88	144	[63]
$Cr(\eta^4\text{-}C_7H_{11}\text{-}\mu\text{-}H)(CO)_2P(OMe)_3$	CH_3	–33	–3.75	–148	–10.03	0.12 and –1.58	—	—	—	—	[57]
$Cr(\eta^4\text{-}1,3\text{-cyclo-}C_7H_9\text{-}\mu\text{-}H)(CO)_3$	CH_2	–33	–4.27	–143	–10.10	1.88	–33	26.43 (dd)	110	134	[58]
$Cr(\eta^4\text{-}1,3\text{-cyclo-}C_7H_9\text{-}\mu\text{-}H)(CO)_2PMe_3$	CH_2	–33	–5.67	–148	–10.66	1.70	–33	25.51 (dd)	107	133	[58]
$Cr(\eta^4\text{-}1,3\text{-cyclo-}C_7H_9\text{-}\mu\text{-}H)(CO)_2P(OMe)_3$**	CH_2	–33 –33	–5.04 –3.48	–148	–11.06 –10.86	1.84 1.64	–33 –33	25.63 (dd) 27.68	104 108	132 132	[58] [58]
$[Mo(\eta^3\text{-}CH_2CHCHCH_2\text{-}\mu\text{-}H)(C_4H_6)(PMe_3)_2]^+$	CH_3	23	–3.05	–90	–9.16	0.8 and –0.8	–90	–3.9 (dt)	84	144	[32]
$Mo(\eta^3\text{-}C_3H_5)_3(CHMeCH_2\text{-}\mu\text{-}H)$	CH_3	–50	–2.90	–120	–8.43	0.5 and –0.9	–60 –115	7.3 (q) 7.3 (dt)	122 88	138	[160]
$WRe(\mu\text{-}CHR\text{-}\mu\text{-}H)(Me_2PCH_2PMe_2)(CO)_7$	CH_2	—	—	–20	–3.69	3.25	–20	18.2 (dd)	81	131	[33]
$Mn(\eta^3\text{-}C_6H_8\text{-}\mu\text{-}H)(CO)_3$	CH_2	–9	–5.7	–99	–12.8	1.6	–100	14.0 (dd)	85	146	[35]
$Mn(\eta^3\text{-}CH_2CHCMeCH_2\text{-}\mu\text{-}H)(CO)_3$***	CH_3 CH_3	25 25	–4.4 –4.2	–100 –100	–12.0 –11.8	0.4 and –1.4 – and –1.3	–90 –90	–4.7 (dt) 0.5	89 —	139 —	[59] [59]
$Mn(\eta\text{-}C_{15}H_{23})(CO)_3$	CH_3	25	–4.27	–80	–11.82	0.19 and –1.37	—	—	—	—	[97]
$Mn_2(\mu,\ \eta\text{-}C_{10}H_{16})(CO)_6$	CH_3	25	–4.42	–80	–12.42	–0.9 and –2.2	—	—	—	—	[97]
$[Mn(\eta^5\text{-}C_9H_7\text{-}\mu\text{-}H)(Me_2PCH_2)_2CMe]^+$	CH_3	–30	–6,23	–130	–15.31	–0.3 and –3.0	–30	35.9 (q)	118		[166]
$[Fe(\eta^3\text{-}CH_2CHCHCH_2\text{-}\mu\text{-}H)(CO)_3]^+$	CH_3	–19	–4.7	–80	–14.6	1.0 and –1.0	–80	–3.0 (dt)	74	146	[21, 25]
$[Fe(\eta^3\text{-}C_6H_9\text{-}\mu\text{-}H)(CO)_3]^+$	CH_2	–15	–6,5	–86	–15.0	2.0	25	24 6 (dd)	78—88	130—140	[25]
$[Fe(\eta\text{-}CH_2CHCHCH\text{-}\mu\text{-}H)(P(OMe)_3)_3]^+$	CH_3	22	–5,92	–95	–15.2	–2.0 and –2.4	35 –120	–5.4 (t) –3.9 (dd)	129 100	140	[41]
$[Fe(\eta^3\text{-cyclo-}C_7H_{10}\text{-}\mu\text{-}H)(P(OMe)_3)_3]^+$	CH_2	22	–7.14	–80	–15.77	1.2	35 –80	5.0 (t) 7.3 (dd)	130 80	140	[41]
$[Fe(\eta^3\text{-}C_6H_4\text{-}\mu\text{-}H)(CO)_3]^+$	CH_2	—	—	–85	–11.16	3.45	–90	9 0 (dd)	81	191	[24]
$[Fe_2(\mu\text{-}CH_2\text{-}\mu\text{-}H)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$	CH_3	0	–1.88	—	—	—	0	23.4	120		[39]
$[Fe_3(\mu\text{-}H)_3(\mu\text{-}CH\text{-}\mu\text{-}H)(CO)_9]^-$	CH_2	—	—	–60	–10.1	6.6	–80	118.5 (dd)	67	155	[67]
$[Ru(\eta^3\text{-}C_8H_{13}\text{-}\mu\text{-}H)(P(OMe)Ph_2)_3]^+$	CH_2	34	–1.89	–80	–5.15	0.15	30	27.4	—	—	[44]
$[Ru(\eta^3\text{-}C_7H_{10}\text{-}\mu\text{-}H)(P(OMe)Ph_2)_3]^+$	CH_2	—	—	–90	–8.2	1.5	–20	18.1	—	—	[62]
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–10.13	–0.09	–80	2,52 (dd)	78	159	[45]
$[Os(\eta\text{-}C_6H_3Me_3)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–10.08	0.10	–80	–3.30 (dd)	66	160	[45]
$[Co(\eta\text{-}C_6Me_4Et)(\eta\text{-}CH_2{=}CH_2)(CH_2CH_2H)]^+$	CH_3	—	—	–80	–12,1	1.48 and 0.46	–90	26.6	67	155	[49]
$[Co(\eta\text{-}C_5Me_5)(CH_2CH_2\text{-}\mu\text{-}H)P(C_6H_4Me)_3]^+$	CH_3	–20	–4.94	–80	–12.67	–0.5 and –1.8	–80	–5.92	66	146	[50]
$[Co(\eta\text{-}C_5Me_5)(CH_2CHR\text{-}\mu\text{-}H)P(OMe)_3]^+$	CH_3	—	—	–70	–12.1	–0.1 and –0.2	–90	–5.8	61	152	[51]
$[Co(\eta\text{-}C_5Me_5)(CH_2CH_2\text{-}\mu\text{-}H)PPhMe_2]^+$	CH_3	25	–4.32	–85	–12.4	–0.13 and –0.55	—	—	—	—	[52]
$[Rh(\eta\text{-}C_5H_5)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–7,63	0,65	–80	2.20 (dd)	81	159	[45]
$[Rh(\eta\text{-}C_5Me_5)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–6.83	0.41	–80	6.10 (dd)	83	152	[45]
$[Ir(\eta\text{-}C_5Me_5)(\eta\text{-}C_{10}H_{12}\text{-}\mu\text{-}H)]^+$	CH_2	—	—	–80	–9.53	0,22	–80	9,02 (dd)	50	165	[45]
$[Ir(PPh_3)_2(H)_2(N,C\text{-}8\text{-methylquinoline})]^+$	CH_3	–43	1.1	—	—	—	—	–8.15	—	—	[60]

*Here q = quartet, dd = doublet of doublets, and dt = doublet of triplets.

**The complex is chiral and exists as a mixture of two diastereoisomers.

***Two isomers with different positions of the bridging H atom.

It has been suggested that there is a possibility of the coordination of the metal centre to the CH_4 molecule, which is isoelectronic with the BH_4^- anion, and also to other alkanes.[141] In a study of the photochemical reactions of the complexes $(\eta\text{-}C_5R_5)M(CO)_2$ (where R = H or Me; M = Co, Rh, or Ir) in matrices at 12 K by IR and UV spectroscopic methods, the formation of products of the oxidative addition of CH_4, and, furthermore, the formation of compounds of yet another type, for which the structure of complexes with an agostic hydrogen atom was proposed, i.e. $(\eta\text{-}C_5R_5)(CO)$. .M...H$-CH_2$, was noted.[162] In a number of investigations, the formation in solutions of CHB of different structure, containing Ta,[163] W,[164] Fe,[165] Mn,[166] Ru,[167,168] and Co,[169] has been observed or postulated on the basis of NMR, IR, and UV spectroscopic data as well as kinetic data.

Table 9. Dependence of the chemical shifts δ in the ^1H NMR spectra on isotope substitution.

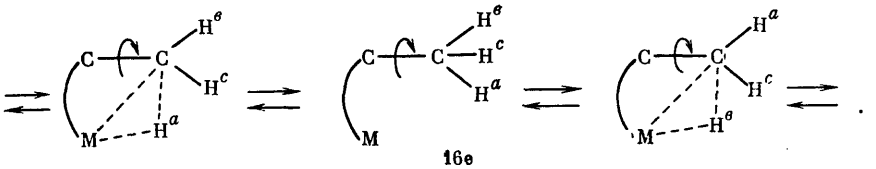
Compound	Group	δ, p.p.m.			Refs.
		CH_3	CH_2D	CHD_2	
$TiCl_3(Dmpe)(CH_2\text{-}\mu\text{-}H)$	CH_3	2.29	1.89	—	[75]
$[Mo(C_4H_8)(\eta\text{-}C_5H_4CH_2\text{-}\mu\text{-}H)(PMe_3)_2]^+$	CH_3	−3.05	−3.66	—	[32]
$[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2\text{-}\mu\text{-}H)(\eta\text{-}Cp)_2]^+$	CH_3	−1.88	−2.62	—	[39]
$[Fe_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(CH_2\text{-}\mu\text{-}H)Cp_2]^+$	CH_3	−2.90	−3.47	—	[42]
$[Ir(\eta\text{-}CH_2CMeCMeCH_2\text{-}\mu\text{-}H)(PPh_3)_2(H)]^+$	CH_3	−2.23	−2.54	−2.91	[55]
$[Ir(N,C\text{-}\mu\text{-}H\text{-}8\text{-methylquinoline})(PPh_3)_2N_2]^+$	CH_3	1.10	0.96	0.82	[60]
$Os(H)(CO)_{10}(CH_2\text{-}\mu\text{-}H)$	CH_3	−3.67	−4.02	−4.41	[161]
$Fe_2(CO)_8(\mu\text{-}H)(\mu^3\text{-}HC\text{-}\mu\text{-}H_2)$	CH_3	−8.49	−8.78	−9.05	[67]
		CH_2	CHD		
$[W(Cl)(PMe_3)_4(=CH\text{—}H)]^+$	CH_2	−0.16	−1.40		[157]
$Mn(\eta\text{-}C_5H_5\text{-}\mu\text{-}H)(CO)_3$	CH_2	−5.8	−7.0		[35]
$[Fe(\eta\text{-}C_5H_{12}\text{-}\mu\text{-}H)(P(OMe)_3)_3]^+$	CH_2	−6.5	−7.6		[41]

VI. PROPERTIES AND REACTIVITY

1. Stereochemical Non-rigidity

The majority of CHB are stereochemically non-rigid complexes characterised by different intramolecular rearrangements (IAR) associated with the migration of a hydrogen atom and/or ML_n fragments relative to the carbon atom of the skeleton of the η-ligand. These rearrangements can be degenerate (DIAR) or non-degenerate. Several (up to three) different IAR can occur simultaneously, whereupon the ^1H, ^{13}C, and ^{31}P NMR spectra exhibit reversible temperature variations. The following types of rearrangements with participation of the CH_3, CH_2, CH groups and ML_n fragments are typical for CHB.

1. The interchange of the positions of the bridging H^a and non-bridging H^b and H^c atoms in the CH_3 group (rotation about the $C-CH_2-\mu$-H bond) via a 16-electron intermediate—a type "A" rearrangement:

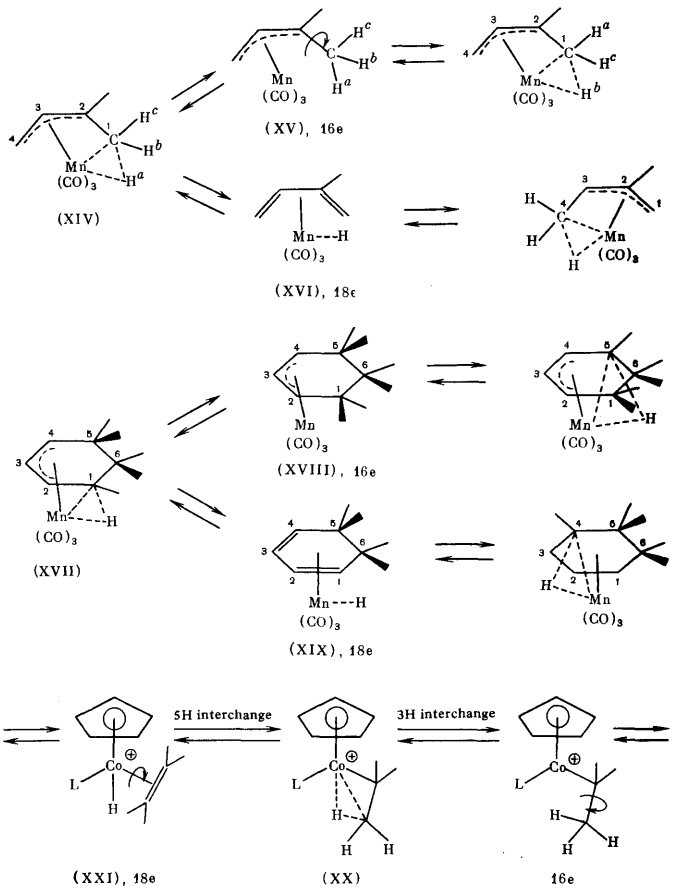


16e

The positions of the C atoms do not then change.

2. Two types of rearrangements, illustrated in relation to manganese compounds[35,59] (Scheme 4), are possible for η^3-allyl CHB.

Scheme 4



After the dissociation of the bridge bond, the μ-H atom can move either to a carbon atom with formation of the 16-electron intermediates (XV) and (XVIII) or to the metal atom with formation of 18-electron dienemetal hydride intermediates (XVI) and (XIX). For the non-cyclic CHB (XIV), the rearrangement via the 16-electron intermediate (XV) belongs to type "A" and leads to the exchange of the three protons H^a, H^b, and H^c. The rearrangement via the 18-electron intermediate (XVI) is non-degenerate owing to the presence of the methyl group at C(2) and leads to the exchange of the bridging hydrogen atom between the C(1) and C(4) atoms in the same ligand (a type "B" rearrangement).

For the cyclic CHB (XVII), rotation about the C−C bond is impossible and, after the formation of the 16-electron compound (XVIII), the bridging H atom is exchanged between C(1) and C(5) without change in the carbon skeleton (IAR) of type "B". The

rearrangement of compound (XVII) via the 18-electron intermediate (XIX) also leads to the migration of the bridge, but, in contrast to the rearrangement via the 16-electron intermediate, is accompanied by the 1,2-migration of $Mn(CO)_3$ relative to the carbon skeleton of the η-ligand. In a more general sense, all the IAE associated with the migration of ML_3 relative to the carbon skeleton of the ligand (rearrangements of type "C") can be assigned to this type.

In compounds (XVI) and (XIX) and analogous intermediates, the proton involved in the M—H bond is "acid" and readily enters into an exchange with the acid derived from the solvent. If the CHB are generated by treatment with deuterio-acids (Table 1), then deuterium is inserted under these conditions in the 1,4-positions for the non-cyclic system and in the 1,5-positions for the cyclic system.[41]

3. The cobalt complexes with the η^2-ethylene ligands (η-Cp)Co.(L)(η-CH_2=CHR), where L = phosphine, phosphite, or CH_2 = CH_2, produce on protonation the CHB $[(\eta\text{-Cp})Co(L)(CH_2CHR-\mu\text{-H})]^+$ (XX), where R = H or alkyl.[49–52] In this case, a type "A" rearrangement takes place (exchange of the three protons in $CH_2-\mu$-H) and also an IAR with the exchange of the five protons in $CH_2CH_2-\mu$-H via the intermediate (XXI) (Scheme 4) and rotation about the cobalt—ethylene bond (rearrangement of type "D").

4. Rearrangements associated with the interchange of the positions of the groups L in the ML_3 "tripod" (IAR of type "E") take place in CHB with the groups ML_3 = $Mn(CO)_3$, $Fe(CO)_3$, $Fe(P)_3$, $Ru(P)_3$, etc., where (P) = phosphite or phosphine.

5. In CH_3 having two or more identical structural elements (M atoms, C_2H_4 or C_4H_6 ligands, etc.) rearrangements take place with migration of the bridge between such elements (IAR of type "F"). The migration of μ-CH between two out of the four Fe atoms in $HFe_4(CO)_{12}(CH)$[43,104] as well as the alternate involvement of each of the four carbon atoms of the CH_2= groups of the protonated form $[Mo(PMe_3)_2(CH_2$=CHCH=$CH_2)_2H]^+$ in the formation of the Mo...H—C bond via an 18-electron metal hydride intermediate[32] are examples of such rearrangements. The migration of an α-hydrogen atom of the alkylidene ligand between the four C—P—P faces in the octahedral cationic complexes $[W(PMe_3)_4(X)(=CH-R)]^+$, where R = CMe_3 or H, can be assigned to IAR of type "F".[157] Apart from the rearrangement indicated, in the complex with R=H there is also a rearrangement involving the interchange of the positions of the two hydrogen atoms of the CH_2 ligand (type "B").

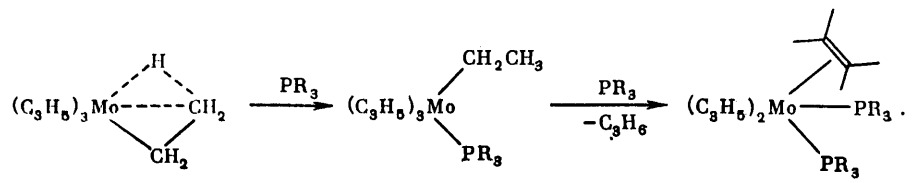
The rearrangements known for the CHB and the barriers $\Delta G^{\neq}$ obtained from the NMR data are listed in Table 10.

The chemical properties of the CHB have been little investigated. Their characteristic reaction involves the ready dissociation of the bridge bond. The M...H—C interaction is comparatively weak: on treatment with nucleophiles—the 2-electron ligands PR_3, $P(OR)_3$, CO, CNR, etc.—these bonds are readily cleaved with substitution of H by L, as shown below for tris-η^3-allylmolybdenum complexes:[160]

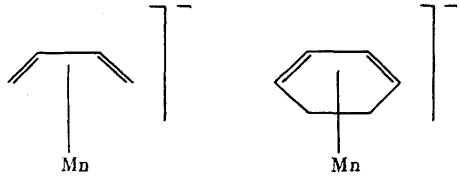
Table 10. Intramolecular rearrangements in complexes with three-centre M...H—C bonds.

Compound	Type of re-arrange-ment	ΔT, K	$\Delta G^{\neq}$, kJ mol^{-1}	Refs.
$Ti(Cp)_2(CH_2)(CH_2\text{-}\mu\text{-H})Rh(\eta\text{-}C_8H_{12})$	A	233 (T_c)	40.9	[77]
$Cr(\eta^4\text{-}C_7H_{11}\text{-}\mu\text{-H})(CO)_2P(OMe)_3$	A	124—240	28.6 (200 K)	[57]
	C	240—390	68.1 (300 K)	[57]
$Cr(\eta\text{-cyclo-}C_7H_{10}\text{-}\mu\text{-H})(CO)_2(L)$				
L = CO	B	125—240	27.9 (165 K)	[58]
	C	240—380	67.2 (350 K)	[58]
L = PMe_3	B	125—240	28.6 (165 K)	[58]
	C	240—380	64.1 (350 K)	[58]
L = $P(OMe)_3$	B	125—240	28.4 (165 K)	[58]
	C	240—380	61.4 (350 K)	[58]
$Cr(\eta\text{-}C_8H_{10}\text{-}\mu\text{-H})(PF_3)_3$	B	193—293	—	[63]
$[Mo(\eta\text{-}C_4H_8)(\eta\text{-}C_5H_4CH_2\text{-}\mu\text{-H})(PMe_3)_2]^+$	A	183—298	37.2	[32]
	F	183—298	77.2 and 81.0	[32]
$Mo(\eta^3\text{-}C_3H_5)_3CH(Me)CH_2\text{-}\mu\text{-H}$	A	153—243	—	[160]
$[W(PMe_3)_4(Cl)$=$CHCMe_3]^+$	F	153—295	41.8	[157]
$[W(PMe_3)_4(Cl)$=$CH_2]^+$	F	165—298	—	[157]
$Mn(\eta^3\text{-cyclo-}C_6H_8\text{-}\mu\text{-H})(CO)_3$ (XVII)	B	174—264	34.6	[35]
	E	233—313	54.9	[35]
	F	281—392	65.0	[35]
$Mn(\eta\text{-}CH_2CHCMeCH_2\text{-}\mu\text{-H})(CO)_3$ (XIV)	A	173—273	37.2	[59]
	B	323—384	72.2	[59]
$Mn(\eta\text{-}C_{15}H_{23})(CO)_3$	A	195—298	43.5	[97]
$Mn_2(\eta\text{-}C_{10}H_{16})(CO)_6$	A	195—298	41.7	[97]
$[Mn(\eta^5\text{-}C_5H_7\text{-}\mu\text{-H})(Me_2PCH_2)_3CMe]^+$	A	143—243	39.6	[166]
	B	243—303	69.0	[166]
	E	203—293	47.5	[166]
$[Fe(\eta\text{-enyl})(P(OMe)_3)_3]^+$				
Enyl = cyclohexenyl	B	183—308	41.8	[41]
	E	183—308	66.5	[41]
Enyl = cycloheptenyl	B	183—308	44.0	[41]
	E	183—308	70.0	[41]
Enyl = cyclo-octenyl	B	123—273	21	[41]
	E	183—308	59.9	[41]
$[Ru(\eta^3\text{-Enyl})(P)_3]^+$				
Enyl = butenyl	A	183—298	—	[62]
Enyl = cyclohexenyl, cycloheptenyl	B, C	183—298	—	[62]
	E			
$[Co(\eta^5\text{-}C_5H_4R)(\eta^3\text{-}C_2H_4)(CH_2CH_2\text{-}\mu\text{-H})]^+$	A	183—298	43.0	[49]
	D	183—298	51.1	[49]
$[Co(\eta^5\text{-}C_5Me_5)(P(C_6H_4Me)_3)(CH_2CHR\text{-}\mu\text{-H})]^+$	A	193—298	38.4	[51, 52]
	D	193—298	56.0	[51, 52]
$[Ir(PPh_3)_2(\eta^3\text{-}CH_2CMeCMeCH_2\text{-}\mu\text{-H})H]^+$	A, B	153—298	—	[55]

Depending on the type of complex and the nature of M, the ease of the dissociation of the bridge bond can be various. Thus $[Fe(\eta\text{-}C_8H_{12}\text{-}\mu\text{-H})\{P(OMe)_3\}_3]^+$ reacts with CO and $CNCMe_3$ but not with $P(OMe)_3$, the Fe...H—C bond being dissociated and the Fe—C_8H_{11} bond being retained.[41] On the other hand, the complexes $[Ru(C_8H_{12}\text{-}\mu\text{-H})L_3]^+$, where L is a tertiary phosphine or arsine, readily react with L, a process involving the dissociation of the Ru...H—C and Ru—C_8H_{12} bonds and the formation of the $RuHL_5^+$ cations.[44] The complexes (XIV) and (XVII) (Scheme 4) readily enter into a reaction with CO in which the Mn...H—C bond is dissociated, and



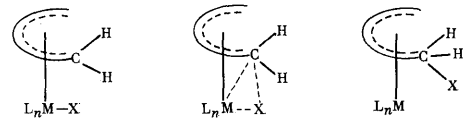
are converted into the complexes (η^3-allyl)$Mn(CO)_4$.[35,59] Compounds (XIV) and (XVII) are readily deprotonated on treatment with KH with evolution of H_2 and the formation of the anions (XXII) and (XXIII). When these are alkylated with MeI, the methyl group adds to the diene ligands and not to the Mn atom:[35,59]



(XXII) (XXIII)

The problems of the theoretical analysis of the structure and reactivity of CHB have attracted much attention. Several quantum-mechanical calculations have been made for the CHB both by the extended Hückel method (EHM) and by non-empirical methods. The characteristic features of the structure and of the unusual geometry of the alkylidene ligands in tantalum complexes and the characteristics of the activation of the C–H bond and of the hydrogen α-elimination reactions have been analysed.[170] In other studies by Hoffmann, the quantum-mechanical description of the activation of the C–H and H–H bonds by complexes having the d^n ($n > 0$) and d^0 configurations and also on the surface of the metal has been examined.[171,172] Calculations by the EHM have been performed for the model complexes $MeTiH_3$ and $Me_2TiH_5^{2-}$ and the influence of various factors and of the character of the ligands on the stabilisation of the 2e,3c-interaction in the methyl complexes has been discussed.[173] The electronic structures of the complexes $[Fe(\eta^3\text{-}C_8H_{12}\text{-}\mu\text{-}H)(CO)_3]^+$, $[Fe(\eta\text{-}C_8H_{12}\text{-}\mu\text{-}H)(PH_3)_3]^+$, $[Fe(C_6H_8\text{-}\mu\text{-}H)(CO)_3]^+$, $Mn(\eta\text{-}C_6H_8\text{-}\mu\text{-}H)(CO)_3$, and $Cr(\eta\text{-}C_8H_{10}\text{-}\mu\text{-}H)(PF_3)_3$ have been calculated[174] on the basis of the geometry obtained from XRD data.[35,41,63] The energy profile of the conversion of $[CpCo(PH_3)C_2H_5]^+$ into $[CpCo(PH_3)(C_2H_4)H]^+$ has been calculated and it has been concluded that the intermediate with the Co...H–C 2e,3c-bond is more stable than the ethylenemetal hydride complex.[175] *Ab initio* calculations have led to the optimisation of the geometry of the model complexes $Pd(Et)(H)(PH_3)$ and $Pd(H)_2(C_2H_4)(PH_3)$ and of the transition state between them, involving Pd...H–C 2e,3c-bonding, as well as the complexes $Pd(CH_3CHF_2)(H)(BH_3)$ and $Ni(Et)(H)(PH_3)$, and the role of the three-centre interactions in α-elimination reactions has been considered.[176] Optimisation of the geometry of the complex $Ti(Et)(PH_3)_2(Cl_2)(H)$(*ab initio* calculation) yielded a Ti–H distance of 2.23 Å and a Ti–C_α–C_β angle of 89°,[177] which agrees well with XRD data for $Ti(Et)(Dmpe)Cl_3$ (2.29 Å and 86° [75]). The most convenient structure of the complexes $Ti(Me)(PH_3)_2(X)_2(Y)$, which yielded a Ti–H distance of 2.51 Å and a Ti–C–H angle of 100° for X = Y = Cl,[178] which agrees well with experiment for $Ti(Me)(Dmpe)Cl_3$ (2.45 Å and 99° [75]), was calculated analogously. Calculations by the EHM have been performed for complexes containing molyb-denum[30] and cobalt.[52]

The survey of the structures and properties of CHB shows that a large number of complexes (B) (X = H) with M...H–C 2e,3c-bonds have already been obtained and characterised both in the crystal (more than 60 structures) and in solutions. The complexes are thermodynamically more stable than the corresponding alkene-, diene-, or polyenyl-metal hydride complexes (A) (X = H). The equilibrium (A) ⇄ (B) ⇄ (C), leading to the migration of hydrogen between the metal atom and the ligand, exists in solutions:



(A) (B) (C)

It has been suggested that there is an analogy between the complexes (B, X = H) and (B, X = alkyl) as regards structure, properties, and the dynamics of the migration of the group X and that in the complexes (B,X = alkyl) there is a possibility of the ready migration of the alkyl (Me, Et) group from the metal to the ligand.[51] A mechanism has been adopted for the polymerisation of olefins in the presence of Ziegler-Natta catalysts in which the key stage involves the migration of the alkyl group (R) from the metal atom to the olefin ligand and chain propagation via the insertion of R in the C–H bonds.[179] If such migration is possible in the complexes (B, X = alkyl), then they may be expected to manifest catalytic properties. It has been shown that the complexes $[(\eta\text{-}C_5Me_5)Co(L).(CH_2CHR\text{-}\mu\text{-}H)]^+$ do indeed catalyse the polymerisation of ethylene under mild conditions.[51]

In connection with the vigorous investigation of the activation of C–H and C–C bonds in alkanes,[10,11] new data have been obtained recently on the mechanisms of the reactions involving the oxidative addition (OA) of C–H bonds in the alkanes RH to low-valence rhodium, iridium, and rhenium complexes with formation of $R-(ML_n)-H$.[182–184] In the reactions of RH with rhodium compounds, intermediates of the type of CHB with the η^2-coordination of a C–H bond are apparently formed initially and then rapidly undergo intramolecular isomerisation to hydridoalkyl complexes.[184] A three-centre transition state with participation of M, C, and H atoms, preceding the dissociation of the C–H bond, has been proposed for the OA reactions.[185] The trajectories of the interaction of the M, C, and H nuclei in the course of the reactions have also been analysed:[60]

$$M + C\text{—}H \rightarrow C\text{—}(M)\text{—}H.$$

The data considered in the present review permit the conclusion that stable CHB with three-centre M...H–C bonds are apparently good models of the transition states in the OA reactions of alkanes.

It is important to emphasise that CHB can serve as intermediates in the various reactions of organometallic complexes with participation of acids. The H/D exchange reactions involving aromatic η-ligands in ferrocene, i.e. $(\eta\text{-}C_5H_5)M(CO)_{3-n}(P)_n$ [M = Mn or Re; (P) = phosphine; $n = 0-2$] and $(\eta\text{-}C_6H_6)Cr(CO)_2(L)$ (L = CO or phosphines), were studied in detail in 1962–1973 (see the relevant reviews[180,181]). A mechanism with protonation of the metal and the migration of an H atom to the η-ligand has been proposed for these reactions.[181] It is known that the complex $(\eta\text{-}C_4H_4)Fe(CO)_3$ (XXIV) is readily protonated[24] and rapidly exchanges H or D with $CF_3.COOD$.[186] It has been concluded[24] that the Fe atom is protonated, but it is clear on the basis of the set of ^1H and ^{13}C NMR data, presented above in Section V, that the form of these spectra for the protonated form (XXIV) [the chemical shifts δ and the constants $J(^{13}C-H)$] agrees only with the formation of a three-centre Fe...H–C bond and an agostic H atom. The insertion of deuterium in η-ligands on protonation of the complexes $(\eta\text{-Dien})Fe(P)_3$

by deuterioacids has already been mentioned above;[41] for -Dien = $\eta^4C_8H_{12}$, the CHB formed, with an Fe...H−C bond, was isolated and its structure was demonstrated by a structural method.[100,101] On the basis of the foregoing, it is logical to assume that the H/D exchange between the cyclic ferrocene ligands and the η-complexes of manganese, rhenium, and chromium, on the one hand, and acids, on the other, may also proceed via intermediates with bridging hydrogen.

During the preparation of the manuscript for the press, the following communications, describing the synthesis of complexes with agostic hydrogen atoms or postulating their formation as intermediates, were published. A review[187] deals with the activation of C−H bonds in alkanes by complex hydrides and organometallic compounds and the reactions and transformations of alkanes in the coordination sphere of the metal. The structure of $TiMeCl_3$ in the gas phase has been established by electron diffraction.[188] The following complexes with M...H−C bonds have been characterised by the XRD method; $Ru(SC_6H_2$-2,4,6-isoPr$_3)_4$ [189] and the cyclopalladised complexes $C_6H_4CHMe-NMe(Pr\text{-}iso)-Pd(L, L')$, where L, L′ = $(PPh_3)Cl$[190] or the acetylacetonato-group.[191] The agostic Fe...H−B bond in the complex $(PMe_3)_2(CO)FeCH(SR)S-BH_3$ has been detected by XRD.[192] Several polypyrazolylborate complexes with M...H−B bonds, including $[(Pir\text{¶})_2BH\text{-}\mu\text{-}H]Zr(Cp)Cl_2$,[193] $[(3,5\text{-}Me_2Pir)BH\text{-}\mu\text{-}H]Ru(\eta^4\text{-}C_8H_{12})H$,[194] and the complex $[(Pir)_2BH\text{-}\mu\text{-}H]_3Y$ containing three agostic Y...H−B bonds simultaneously have been characterised structurally.

In the studies quoted below, the conclusion that agostic hydrogen atoms are present was reached from ^1H and ^{13}C NMR spectra. The formation of the Li...H−C and Y...H−C bonds has been postulated for the complexes $Me_3CSC_6H_4Li(THF)_2$ [196] and $(C_5Me_5)_2YCH_2C_6H_3Me_2$.[197] The protonation of anionic (n = −1) or neutral (n = 0) η^4-diene complexes with acyclic and cyclic dienes of the type $[(\eta^4\text{-Dien})ML_x]^n$ leads to the formation of neutral or cationic η^3-allyl complexes with agostic hydrogen: $[(\eta^3\text{-allyl-}\mu\text{-H})\text{-}ML_x]^{n+1}$. The anionic complexes of manganese[198] and the neutral complexes of iron,[199,200] cobalt, rhodium, and iridium[201] (preliminary communication—see Buchmann and Salzer[54]) are protonated in this way. The Ru...H−C agostic bonds have been discovered in the complexes $[Ru(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_8H_{11}\text{-}\mu H)]^+$ [202] and $Ru(\eta^3\text{-}C_7H_{11}\text{-}\mu\text{-}H)(PPh_3)_2Cl$.[203] The synthesis and reactions of cationic dinuclear derivatives of biscyclopentadienylruthenium, where one of the hydrogen atoms of the bridging CH_3 group is coordinated to ruthenium, have been described.[204,205] The substitution of the agostic hydrogen atom in the dinuclear complex containing molybdenum and manganese by the isolobal fragment $Au(PMe_2Ph)$ has been carried out.[206] It was suggested that the reaction involving the dehydrogenation of alkanes to alkenes in the presence of $IrH_2(O_2 .CCF_3)[P(C_6H_4F)_3]_2$ results in the formation of the catalytically active intermediate withan Ir...H−C bond.[207] The pathways leading to the redistribution of hydrogen in the protonated form of the complex $Mo(C_2H_4)_2$(*cis*-$Ph_2PCH=CHPPh_2)_2$ have been discussed[208] and it has been suggested that this process does not necessarily proceed via a 16-electron σ-ethyl intermediate.

The formation of agostic bonds in clusters has been observed in a number of studies. In the aryne complex $H_2Os_3(CO)_9(\mu^2\text{:}\mu^4\text{-}C_6H_4)$, there is rapid proton exchange between the ring and the metal, apparently via an intermediate with agostic hydrogen;[209] analogous intermediates have been proposed for the hydrogen substitution and elimination reactions in $Fe_3(CO)_9(\mu\text{-}H)_3(\mu\text{-}CCH_3)$.[210] It has been shown by ^1H and ^{13}C NMR that the protonation of the heterometallic anionic carbido-clusters $MFe_3(CO)_{13}C^{2-}$ (M = Cr or W), $MnFe_3(CO)_{13}C^-$, and $RhFe_3(CO)_{12}C$ with the "butterfly" skeleton leads to the formation of agostic Fe...H−C bonds between the hydrogen of the methylidyne fragment and the iron atom.[211]

The interaction of CH_4 and CD_4 with organometallic complexes has been investigated by IR spectroscopy in matrices at 12−16 K. The formation of the relatively unstable compounds of the type $L_nM...H-CH_3$ has been postulated for Cp_2Ni, $(C_5Me_5)_2Ni$, $(C_5Me_5)_2Mn$, and (arene)$M(CO)_3$.[212] The quantum-chemical aspects of the electronic structure, the problem of the relative stabilities of the intermediate systems with M−H and M−C bonds, the coordination of methane, and the interaction of C−H bonds with the metal complex centre have been examined in a monograph[213] and in the literature quoted therein. The results of theoretical calculations of the electronic structure, stability, and reactivity of complexes with M...H−C,[214-218] Fe...H−E (E = B or C),[219] and Ti−Si−C[220] bonds have been described in a number of communications. Quantum-chemical calculations for compounds with Mn−H−Si bonds have been carried out.[221] Evidently both the experimental and the theoretical chemistry of complexes with agostic hydrogen atoms continues to develop very vigorously.

¶Pir = pyrazolyl (Translator).

REFERENCES

1. H.D.Kaesz and R.B.Saillant, Chem. Rev., 1972, **72**, 231.
2. R.Bau and T.F.Koetzl, Pure and Appl. Chem., 1978, **50**, 55.
3. R.Bau, Accounts Chem. Res., 1979, **12**, 176.
4. G.L.Soloveichik and B.M.Bulychev, Uspekhi Khim., 1982, **51**, 507 [Russ. Chem. Rev., 1982(3)].
5. G.L.Soloveichik and B.M.Bulychev, Uspekhi Khim., 1983, **52**, 72.
6. D.S.Moore and S.D.Robinson, Chem. Soc. Revs., 1983, **12**, 415.
7. R.G.Teller and R.Bau, Structure and Bonding, 1981, **44**, 1.
8. R.Bau, D.M.Ho, and S.G.Gibbins, J. Amer. Chem. Soc., 1981, **103**, 4960.
9. E.L.Muetterties, Chem. Soc. Rev., 1982, **11**, 283.
10. R.H.Crabtree, Chem. Rev., 1985, **85**, 245.
11. J.Halpern, Inorg. Chim. Acta, 1985, **100**, 41.
12. M.L.H.Green, N.Hazel, P.D.Grebenik, et al., J. Chem. Soc. Chem. Comm., 1983, 356.
13. M.Brookhart and M.L.H.Green, J. Organometal. Chem., 1983, **250**, 395.
14. S.J.La Placa and J.A.Ibers, Inorg. Chem., 1965, **4**, 778.
15. N.A.Bailey, J.M.Jenkins, R.Mason, and J.Shaw, J. Chem. Soc.A, 1968, 2594.
16. Y.W.Yared, S.L.Miles, R.Bau, and C.A.Reed, J. Amer. Chem. Soc., 1977, **99**, 1076.
17. D.M.Roe, P.M.Bailey, K.Moseley, and P.M.Maitlis, J. Chem. Soc. Chem. Comm., 1972, 1273.
18. S.Trofimenko, J. Amer. Chem. Soc.,1967, **89**, 6288.
19. F.A.Cotton, T.La Cour, and A.G.Stanislowsky, J. Amer. Chem. Soc., 1974, **96**, 754.
20. M.Brookhart, D.L.Harris, and R.C.Damman, J. Chem. Soc. Chem. Comm., 1973, 187.
21. M.Brookhart and D.L.Harris, Inorg. Chem., 1974, **13**, 1540.
22. G.A.Olah, S.H.Yu, and G.Liang, J. Org. Chem., 1976, **41**, 2383.
23. G.A.Olah, G.Liang, and S.H.Yu, J. Org. Chem., 1976, **41**, 2227.

24. G.A.Olah and G.Liang, J. Org. Chem., 1976, **41**, 2659.
25. M.Brookhart, T.H.Whiteside, and J.M.Crockett, Inorg. Chem., 1976, **15**, 1550.
26. B.V.Lokshin, A.G.Ginzburg, and E.B.Nazarova, Uspekhi Khim., 1980, **49**, 223 [Russ. Chem. Rev., 1980(2)].
27. H.Werner, Pure Appl. Chem., 1982, **54**, 177.
28. H.Werner, Angew. Chem. Intern. Ed., 1983, **22**, 927.
29. M.Green, N.C.Norman, and A.G.Orpen, J. Amer. Chem. Soc., 1981, **103**, 1269.
30. M.Green, N.C.Norman, A.G.Orpen, and C.P.Schaverian, J. Chem. Soc. Dalton. Trans., 1984, 2455.
31. D.G.Bourner, L.Brammer, M.Green, et al., J. Chem. Soc. Chem. Comm., 1985, 1409.
32. M.Brookhart, K.Cox, F.G.N.Cloke, et al., J. Chem. Soc. Dalton. Trans., 1985, 423.
33. J.C.Jeffery, A.G.Orpen, W.T.Robinson, et al., J. Chem. Soc. Chem. Comm., 1984, 396.
34. W.Lamanna and M.Brookhart, J. Amer. Chem. Soc., 1981, **103**, 989.
35. M.Brookhart, W.Lamanna, and M.B.Hamprey, J. Amer. Chem. Soc., 1982, **104**, 2117.
36. M.Brookhart, W.Lamanna, and A.R.Pinhas, Organometallics, 1983, **2**, 638.
37. M.Brookhart and A.Lucas, Organometallics, 1983, **2**, 649.
38. M.Brookhart and A.Lucas, J. Amer. Chem. Soc., 1984, **106**, 4161.
39. C.P.Casey, P.J.Fagan, and W.H.Miles, J. Amer. Chem. Soc., 1982, **104**, 1134.
40. S.D.Ittel, F.A.Van-Catlege, C.A.Tolman, and J.P.Jesson, J. Amer. Chem. Soc., 1978, **100**, 1317.
41. S.D.Ittel, F.A.Van-Catlege, and I.P.Jesson, J. Amer. Chem. Soc., 1979, **101**, 6905.
42. G.M.Dawkins, M.Green, A.G.Orpen, and F.G.A.Stone, J. Chem. Soc. Chem. Comm., 1982, 41.
43. M.Tachikawa and E.L.Muetterties, J. Amer. Chem. Soc., 1980, **102**, 4541.
44. T.V.Ashwort, A.A.Chalmers, E.Meintjies, et al., Organometallics, 1984, **3**, 1485.
45. M.A.Bennett, T.J.McMahon, S.Pelling, et al., Organometallics, 1985, **4**, 754.
46. M.A.Bennett and T.W.Matheson, J. Organometal. Chem., 1978, **153**, C25.
47. M.A.Bennett, I.J.McMahon, and T.W.Turney, Angew. Chem. Intern. Ed., 1982, **21**, 379.
48. J.B.Keister, J. Organometal. Chem., 1986, **312**, C33.
49. M.Brookhart, M.L.H.Green, and R.B.A.Pardy, J. Chem. Soc. Chem. Comm., 1983, 691.
50. R.B.Cracknell, A.G.Orpen, and J.L.Spencer, J. Chem. Soc. Chem. Comm., 1984, 326.
51. G.F.Schmidt and M.Brookhart, J. Amer. Chem. Soc., 1985, **107**, 1443.
52. R.B.Cracknell, A.G.Orpen, J.L.Spencer, J. Chem. Soc. Chem. Comm., 1986, 1005.
53. D.M.Speckman, C.B.Knobler, and M.F.Hawthorne, Organometallics, 1985, **4**, 1692.
54. B.Buchmann and A.Salzer, "XII International Conference on Organometallic Chemistry", Thesis, Vienna, 1985, p.196.
55. O.W.Howarth, C.H.McAlteer, P.Moore, and G.E.Morris, J. Chem. Soc. Chem. Comm., 1981, 506.
56. M.Kotzien, C.G.Kreiter, G.Michael, and S.Ozkar, Chem. Ber., 1983, **116**, 3637.
57. M.Gunter, J.Kaub, and C.G.Kreiter, Angew. Chem., 1985, **97**, 503.
58. M.Gunter, J.Kaub, and C.G.Kreiter, Chem. Ber., 1985, **118**, 3944.
59. F.Timmers and M.Brookhart, Organometallics, 1985, **4**, 1365.
60. R.H.Crabtree, E.M.Holt, M.Lavin, and S.A.Morehouse, Inorg. Chem., 1985, **24**, 1986.
61. E.Carmona, L.Sanchez, J.M.Marin, et al., J. Amer. Chem. Soc., 1984, **106**, 3214.
62. T.V.Ashworth, A.A.Chalmers, E.Meintjies, et al., J. Organometal. Chem., 1985, **286**, 237.
63. R.J.Blackborow, C.R.Eady, F.W.Grevels et al., J. Chem. Soc. Dalton. Trans., 1981, 661.
64. D.L.Grimmett, J.A.Labinger, J.N.Bonfiglio, et al., J. Amer. Chem. Soc., 1982, **104**, 6858.
65. D.L.Grimmett, J.A.Labinger, J.N.Bonfiglio, et al., Organometallics, 1983, **2**, 1325.
66. M.E.Asaro, S.R.Cooper, and N.J.Cooper, J. Amer. Chem. Soc., 1986, **108**, 5187.
67. T.K.Dutta, J.C.Vites, and S.B.Jacobsen, Organometallics, 1987, **6**, 842.
68. K.H.Haan, J.L.Boer, J.H.Teuben, et al., Organometallics, 1986, **5**, 1726.
69. J.Jeske, L.E.Schock, P.N.Swepston, et al., J. Amer. Chem. Soc., 1985, **107**, 8103.
70. W.J.Ewans, D.K.Drummond, S.G.Bott, and L.A.Jeffery, Organometallics, 1986, **5**, 2389.
71. C.J.Burns and R.A.Andersen J. Amer. Chem. Soc., 1987, **109**, 915.
72. T.D.Tiliey, R.A.Anderson, and A.Zalkin, J. Amer. Chem. Soc., 1982, **104**, 3725.
73. M.Yu.Antipin, S.I.Troyanov, Yu.T.Struchkov, and L.S.Bresler, Metalloorg. Khim., 1988, **1**(1), 111.
74. Z.Dawodi, M.L.H.Green, V.S.B.Mtetwa, and K.Prout, J. Chem. Soc. Chem. Comm., 1982, 1410.
75. Z.Dawodi, M.L.H.Green, V.S.B.Mtetwa, et al., J. Chem. Soc. Chem. Comm., 1986, 1629.
76. Z.Dawodi, M.L.H.Green, V.S.B.Mtetwa, and K.Prout J. Chem. Soc. Chem. Comm., 1982, 802.
77. J.W.Park, P.B.Mackenzie, W.P.Shaefer, and R.H.Grubbs, J. Amer. Chem. Soc., 1986, **108**, 6402.
78. G.S.Girolami, G.Wilkinson, A.M.R.Galas, et al., J. Chem. Soc. Dalton Trans., 1985, 1339.
79. M.Mena, M.A.Pellinghelli, P.Royo, et al., J. Chem. Soc. Chem. Comm., 1986, 1118.
80. G.Erker, W.Fromberg, K.Angermund, et al., J. Chem. Soc. Chem. Comm., 1986, 372.
81. J.Z.Cayias, E.A.Babaian, D.C.Harnar, et al., J. Chem. Soc. Dalton Trans., 1986, 2743.
82. B.Hessen, F.van Bolhius, and J.H.Teuben, Organometallics, 1987, **6**, 1352.
83. J.W.Bruno, G.M.Smith, T.J.Marks, et al., J. Amer. Chem. Soc., 1986, **108**, 40.
84. A.J.Schultz, J.M.Williams, R.R.Schrock, et al., J. Amer. Chem.Soc., 1979, **101**, 1593.
85. A.J.Schultz, R.K.Brown, J.M.Williams, and R.R.Schrock, J. Amer. Chem. Soc., 1981, **103**, 169.
86. H.V.Heijden, A.W.Gal, P.Pasman, and A.G.Orpen, Organometallics, 1985, **4**, 1847.
87. M.B.Hursthouse, K.M.A.Malik, and K.D.Sales, J. Chem. Soc. Dalton Trans., 1978, 1314.

88. M.Sato, T.Tatsumi, T.Kodama, et al., J. Amer. Chem. Soc., 1978, **100**, 4447.
89. H.J.Wassermann, R.J.Kubas, and R.R.Ryan, J. Amer. Chem. Soc., 1986, **108**, 2294.
90. G.J.Kubas and R.R.Ryan, Polyhedron, 1986, **5**, 473.
91. J.H.Wengrovius, R.R.Schrouk, M.R.Churchill, and H.J.Wassermann, J. Amer. Chem. Soc., 1982, **104**, 1739.
92. M.R.Churchill and H.J.Wassermann, Inorg. Chem., 1983, **22**, 1574.
93. A.Mayr, K.S.Lee, M.A.Kjelsberg, and D.V.Engen, J. Amer. Chem. Soc., 1986, **108**, 6079.
94. A.Mayr, M.F.Asaro, M.A.Kjelsberg, et al., Organometallics, 1987, **6**, 432.
95. A.J.Schultz, R.G.Teller, M.A.Beno, et al., Science, 1983, **220**, 197.
96. A.D.Norton, M.J.Mays, and P.R.Raithby, J. Chem. Soc. Chem. Comm., 1985, 247.
97. C.G.Kreiter, M.Leyendecker, and W.S.Scheldrick, J. Organometal. Chem., 1986, **302**, 217.
98. J.I.Davies, C.G.Howard, A.C.Skapski, and G.Wilkinson, J. Chem. Soc. Chem. Comm., 1982, 1077.
99. C.G.Howard, G.Wilkinson, M.Thornbon-Pett, and M.B.Hursthouse, J. Chem. Soc. Dalton Trans., 1983, 2025.
100. J.M.Williams, R.K.Brown, A.J.Schultz, et al., J. Amer. Chem. Soc., 1978, **100**, 7407.
101. R.K.Brown, J.M.Williams, A.J.Schultz, et al., J. Amer. Chem. Soc., 1980, **102**, 7496.
102. R.L.Harlow, R.J.McKinney, and S.D.Ittel, J. Amer. Chem. Soc., 1979, **101**, 7496.
103. M.A.Beno, J.M.Williams, M.Tachikawa, and E.L.Muetterties, J. Amer. Chem. Soc., 1980, **102**, 4542.
104. M.A.Beno, G.M.Williams, M.Tachikawa, and E.L.Muetterties, J. Amer. Chem. Soc., 1981, **103**, 1485.
105. T.V.Ashwort, D.C.Liles, and E.Singleton, Organometallics, 1984, **3**, 1851.
106. K.Itoh, N.Oshima, G.B.Jameson, et al., J. Amer. Chem. Soc., 1981, **103**, 3014.
107. K.Jonas, Angew. Chem. Intern. Ed., 1985, **24**, 307.
108. G.Natile, F.Gasparatti, D.Misiti, and G.Perego, J. Chem. Soc. Dalton Trans., 1977, 1747.
109. E.Sinn, C.M.Flynn, and R.B.Martin, Inorg. Chem., 1977, **16**, 2403.
110. L.G.Kuzmina and Yu.T.Struchkov, Cryst. Structure Comm., 1979, **8**, 715.
111. N.I.Pyschnograeva, A.S.Batzanov, Yu.T.Struchkov, and A.G.Ginzburg, J. Organometal. Chem., 1985, **297**, 69.
112. S.Otsuka, T.Yoshida, M.Matsumoto, and K.Nakatsu, J. Amer. Chem. Soc., 1976, **98**, 5850.
113. A.Albinati, C.Are, and P.S.Pregosin, Inorg.Chem., 1987, **26**, 508.
114. D.Heyden, D.M.Roundhill, W.C.Fultz, and A.L.Rheingold, Organometallics, 1986, **5**, 336.
115. L.Brammer, J.M.Charchock, P.L.Goggin, et al., J. Chem. Soc. Chem. Comm., 1987, 443.
116. M.Pasqquali, C.Floriani, A.Gaetani-Manfredotti, and A.Chiese-Villa, J. Amer. Chem. Soc., 1978, **100**, 4918.
117. E.G.Perevalova, I.G.Bolesov, Yu.T.Struchkov, et al., J. Organometal. Chem., 1985, **286**, 129.
118. V.T.Andrianov, B.P.Biryukov, and Yu.T.Struchkov, Zhur. Strukt. Khim., 1969, **10**, 1129.
119. M.R.Churchill, "Perspectives in Structural Chemistry", New York–London, 1970, Vol.3, p.177.
120. M.R.Churchill and W.J.Young, Inorg. Chem., 1979, **18**, 1930.
121. L.W.Messerle, P.Jennische, R.R.Schrock, and G.D.Stucky, J. Amer. Chem. Soc., 1980, **102**, 6744.
122. M.R.Churchill and H.J.Wassermann, Inorg. Chem., 1981, **20**, 2899.
123. H.W.Turner, J.D.Fellmann, S.M.Rocklade, and R.R.Schrock, J. Amer. Chem. Soc., 1980, **102**, 7809.
124. M.R.Churchill and W.J.Youngs, Inorg. Chem., 1979, **18**, 2454.
125. D.N.Clark and R.R.Schrock, J. Amer. Chem. Soc., 1978, **100**, 6774.
126. M.R.Churchill and E.J.Hollander, Inorg. Chem., 1978, **17**, 1957.
127. R.R.Schrock, L.W.Messerle, C.D.Wood, and L.J.Guggenberger, J. Amer. Chem. Soc., 1978, **100**, 3793.
128. L.J.Guggenberger and R.R.Schrock, J. Amer. Chem. Soc., 1975, **97**, 6578.
129. G.S.Girolami, C.G.Howard, G.Wilkinson, et al., J. Chem. Soc. Dalton Trans., 1985, 921.
130. M.E.Thompson, S.M.Baxter, A.R.Bulls, et al., J. Amer. Chem. Soc., 1987, **109**, 203.
131. K.den Haan, J.L.de Boer, J.H.Teuben, et al., J. Organometal. Chem., 1987, **327**, 31.
132. G.M.Smith, M.Sabat, and T.J.Marks, J. Amer. Chem. Soc., 1987, **109**, 1854.
133. J.Edwin, M.C.Bohm, N.Chester, et al., Organometallics, 1983, **2**, 1666.
134. U.Schubert, K.Ackermann, and B.Worle, Z.Naturforsch, 1983, **38B**, 1488.
135. U.Schubert, K.Ackermann, and B.Worle, J. Amer. Chem. Soc., 1982, **104**, 7378.
136. U.Schubert, G.Scholz, J.Muller, et al., J. Organometal. Chem., 1986, **306**, 303.
137. W.A.G.Graham and M.J.Bennett, Chem. Eng. News, 1970, **48**(24), 75.
138. F.Carre, E.Colomer, R.J.P.Corriu, and A.Vioux, Organometallics, 1984, **3**, 1272.
139. U.Schubert, K.Bahr, and J.Muller, J. Organometal. Chem., 1987, **327**, 357.
140. U.Schubert, J.Muller, and H.G.Alt, Organometallics, 1987, **6**, 489.
141. J.A.Jensen, S.R.Wilson, and G.S.Girolami, J. Amer. Chem. Soc., 1988, **110**, 4977.
142. M.Green, J.A.K.Howard, A.P.James, et al., J. Chem. Soc. Chem. Comm., 1985, 1778.
143. P.E.Behnken, T.B.Marder, T.Baker, et al., J. Amer. Chem. Soc., 1985, **107**, 932.
144. K.Shelly, C.A.Reed, Y.J.Lee, and W.R.Scheidt, J. Amer. Chem. Soc., 1986, **108**, 3117.
145. M.Green, J.A.K.Howard, A.P.James, et al., J. Chem. Soc. Dalton Trans., 1987, 81.
146. M.O.Albers, S.F.A.Crosby, D.C.Liles, et al., Organometallics, 1987, **6**, 2014.
147. G.Jeske, H.Lauke, H.Mauermann, et al., J. Amer. Chem. Soc., 1985, **107**, 8091.
148. J.Blenkers, B.Hessen, F.van Bolhius, et al., Organometallics, 1987, **6**, 459.
149. R.R.Schrock and J.D.Fellmann, J. Amer. Chem. Soc., 1978, **100**, 3359.
150. J.D.Fellmann, G.A.Rupprecht, C.D.Wood, and R.R.Schrock, J. Amer. Chem. Soc., 1978, **100**, 5964.

151. C.D.Wood, S.J.McLain, and R.R.Schrock, J. Amer. Chem. Soc., 1979, **101**, 3210.
152. G.A.Rupprecht, L.W.Messerle, D.J.Fellman, and R.R.Schrock, J. Amer. Chem. Soc., 1980, **102**, 6236.
153. J.D.Fellman, H.W.Turner, and R.R.Schrock, J. Amer. Chem. Soc., 1980, **102**, 6608.
154. M.R.Churchill, H.F.Wasserman, H.W.Turner, and R.R.Schrock, J. Amer. Chem. Soc., 1982, **104**, 1710.
155. J.D.Fellman, R.R.Schrock, and D.D.Traficante, Organometallics, 1982, **1**, 481.
156. A.H.Liu, R.C.Murray, J.C.Bewan, et al., J. Amer. Chem. Soc., 1987, **109**, 4282.
157. S.J.Holmes, D.N.Clark, H.W.Turner, and R.R.Schrock, J. Amer. Chem. Soc., 1982, **104**, 6322.
158. S.J.Holmes, R.R.Schrock, M.R.Churchill, and H.J.Wassermann, Organometallics, 1984, **3**, 476.
159. A.J.Schultz, J.M.Williams, R.R.Schrock, and S.J.Holmes, Acta Cryst., 1984, **C40**, 590.
160. R.Benh, S.Holle, P.W.Jolly, et al.,Angew. Chem.,1986, **98**, 555.
161. R.B.Calvert and J.R.Shapley, J. Amer. Chem. Soc., 1978, **100**, 7726.
162. A.J.Rest, I.Whitwell, W.A.G.Graham, et al., J. Chem. Soc. Dalton Trans., 1987, 1181.
163. N.Hovnanian, L.C.Hubert-Pflazgraf, and G.Le Borgne, Inorg. Chem., 1985, **24**, 4647.
164. R.J.Kazlauskas and M.S.Wrighton, J. Amer. Chem. Soc., 1982, **104**, 6005.
165. M.L.H.Green and L.L.Wong, J. Chem. Soc.Dalton Trans., 1987, 411.
166. J.R.Bleeke, J.J.Kotuk, D.A.Moore, and D.J.Rauscher, J. Amer. Chem. Soc., 1987, **109**, 417.
167. B.E.Mann, P.W.Manning, and C.M.Spencer, J. Organometal. Chem., 1986, **312**, C64–C66.
168. T.P.Duggan, D.J.Barnett, M.J.Muscatella, and J.B.Keister, J. Amer. Chem. Soc., 1986, **108**, 6076.
169. K.Kanamori, W.E.Broderick, R.F.Jordan, et al., J. Amer. Chem. Soc., 1986, **108**, 7122.
170. J.R.Goddard, R.Hoffman, and E.D.Jemmis, J. Amer. Chem. Soc., 1980, **102**, 7667.
171. J.-Y.Saillard and R.Hoffmann, J. Amer. Chem. Soc., 1984, **106**, 2006.
172. H.Robaa, J.Y.Saillard, and R.Hoffmann, J. Amer. Chem. Soc., 1986, **108**, 4327.
173. O.Einstein and Y.Jean, J. Amer. Chem. Soc., 1985, **107**, 1177.
174. N.J.Fitzpatrick and M.A.McGinn, J. Chem. Soc. Dalton Trans., 1985, 1637.
175. P.N.Pavankumar, B.Ashok, and E.D.Jemmis, J. Organometal. Chem., 1986, **315**, 361.
176. N.Koga, S.Obara, K.Kitamura, and K.Morokuma, J. Amer. Chem. Soc., 1985, **107**, 7109.
177. N.Koga, S.Obara, and K.Morokuma, J. Amer. Chem. Soc., 1984, **106**, 4625.
178. S.Obara, N.Koga, and K.Morokuma, J. Organometal. Chem., 1984, **270**, C33.
179. E.G.Arlman and P.Cossee, J. Catal., 1964, **3**, 99.
180. V.N.Setkina and D.N.Kursanov, Uspekhi Khim., 1968, **37**, 1729 [Russ. Chem. Rev., 1968(10)].
181. V.N.Setkina, N.K.Baranetskaya, A.G.Ginzburg, et al., J. Organometal. Chem., 1973, **61**, 287.
182. T.T.Wenzel and R.G.Bergman, J. Amer. Chem. Soc., 1986, **108**, 4856.
183. W.C.McGhee and R.G.Bergman, J. Amer. Chem. Soc., 1986, **108**, 5621.
184. R.A.Periana and R.G.Bergman, J. Amer. Chem. Soc., 1986, **108**, 7332.
185. J.M.Buchanan, J.M.Stryker, and R.G.Bergman, J. Amer. Chem. Soc., 1986, **108**, 1537.
186. J.D.Fitzpatrick, L.Watts, G.F.Emerson, and R.Pettit, J. Amer. Chem. Soc., 1965, **87**, 3254.
187. G.L.Soloveichik, Metalloorg. Khim., 1988, **1**, 277.
188. A.Berry, Z.Dawody, M.L.H.Green, et al., J. Chem. Soc. Chem. Comm., 1986, 520.
189. S.L.Soong, H.J.Hain, M.Millar, and S.A.Koch, Organometallics, 1988, **7**, 557.
190. L.G.Kuz'mina, Yu.T.Struchkov, O.A.Zalevskaya, et al., Zhur. Obshch. Khim., 1987, **57**, 2499.
191. L.G.Kuz'mina, Yu.T.Struchkov, V.V.Dunina, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1986, 1807.
192. D.V.Khasnis L.Toupet, and P.H.Dixneuf, J. Chem. Soc. Chem. Comm., 1987, 230.
193. D.L.Reger, R.Mahtab, J.C.Baxter, and L.Lebioda, Inorg. Chem., 1986, **25**, 2046.
194. M.O.Albers, S.F.A.Crossby, D.C.Liles, et al., Organometallics, 1987, **6**, 2014.
195. D.L.Reger, R.Mahtab, J.C.Baxter, and L.Lebioda, Inorg. Chem., 1986, **25**, 2046.
196. W.Bauer, P.A.Klusener, S.Harder, et al., Organometallics, 1988, **7**, 552.
197. K.den Haan, Y.Wielstra, and J.H.Teuben, Organometallics, 1987, **6**, 2053.
198. M.Brookhart, S.K.Noh, and F.J.Timmers, Organometallics, 1987, **6**, 1829.
199. M.L.H.Green, D.O'Hare, and L.L.Wong, J. Chem. Soc. Dalton, 1987, 2031.
200. A.S.Howell, M.C.Tirvengadum , and G.Walton, J. Organometal. Chem., 1988, **338**, 217.
201. B.Buchmann, U.Piantini, W.von Philipsborn, and A.Salzer, Helv. Chim. Acta, 1987, **70**, 1487.
202. F.Bouchir, A.Chaudret, F.Dahan, and I.Tkatchenko, Nouv. J. Chem., 1987, **11**, 527.
203. M.Grassi, B.E.Mann, P.Manning, and C.M.Spencer, J. Organometal. Chem., 1986, **307**, C55.
204. D.L.Davies, B.P.Gracey, V.Guerchias, et al., J. Chem. Soc. Chem. Comm., 1984, 841.
205. N.G.Connelly, N.J.Forrow, B.P.Gracey, et al., J. Chem. Soc. Chem. Comm., 1985, 14.
206. A.D.Horton, M.J.Mays, and M.McPartlin, J. Chem. Soc. Chem. Comm., 1987, 424.
207. M.J.Burk and R.H.Crabtree, J. Amer. Chem. Soc., 1987, **109**, 8025.
208. M.L.H.Green and L.L.Wong, J. Chem. Soc. Chem. Comms., 1988, 677.
209. H.J.Kneuper and J.R.Shapley, Organometallics, 1987, **6**, 2455.
210. T.Dutta, X.Meng, J.C.Vites, and T.P.Fehlner, Organometallics, 1987, **6**, 2191.
211. J.A.Hriljac, S.Harris, and D.F.Shriver, Inorg. Chem., 1988, **27**, 816.
212. I.I.Grinval'd, B.V.Lokshin, E.K.Rudnevskii, et al., Dokl. Akad. Nauk SSSR, 1988, **298**, 366.
213. A.A.Bagatur'yants, "Kvantovaya Khimiya Metallokompleksnogo Kataliza. Itogi Nauki i Tekhniki. Ser. Kinetika i Kataliz" (Quantum Chemistry of Metal Complex

Catalysis. Advances in Science and Engineering. Kinetics and Catalysis Series), Izd. VINITI, Moscow, 1985, Vol.14, pp.66, 73.
214. J.Silvestre, M.J.Calhorda, R.Hoffmann, et al., Organometallics, 1986, **5**, 1841.
215. B.E.Bursten and R.H.Cayton, Organometallics, 1986, **5**, 1051.
216. M.J.Calhorda and J.A.M.Simoes, Organometallics, 1987, **6**, 1188.
217. K.Tatsumi and A.Nakamura, Organometallics, 1987, **6**, 427.
218. I.I.Grinval'd, B.V.Lokshin, I.A.Abronin, and V.A.Korsunov, Izv. Akad. Nauk SSSR, Ser. Khim., 1988, 594.
219. M.M.Lynam, D.M.Chipman, R.D.Barreto, and T.P.Felhner, Organometallics, 1987, **6**, 2405.
220. N.Koga and K.Morokuma, J. Amer. Chem. Soc., 1988, **110**, 108.
221. H.Rabaa, J.-Y.Saillard, and U.Shubert, J. Organometal. Chem., 1987, **330**, 397.

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