Hydrido Complexes of the Transition Metals

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1 Introduction

The ability of molecular hydrogen to interact with transition metals was first recognized in the early decades of the 19th century. In 1823 Döbereiner developed a spongy form of platinum capable of catalysing the combination of hydrogen and atmospheric oxygen at room temperature.[1] In the same year Dulong and Thenard achieved a similar effect with finely divided palladium and iridium.[2] The first well established binary hydride, CuH, was prepared by Wurtz in 1844[3] and the capacity of palladium metal to occlude large volumes of hydrogen gas was first explored by Graham in 1866.[4] From these and similar early observations rich areas of solid state chemistry, surface chemistry, and heterogeneous catalysis have developed. Binary hydride phases are now known for the early transition metals (Ti, Zr, Hf, V, Nb, Ta, and Cr), palladium, the lanthanides and most of the actinides.[5] The ability of transition metal surfaces to chemisorb and thus activate gaseous hydrogen has been intensively studied over many years and has found important applications in heterogeneous catalysis.[5] Finally, current interest in molecular hydrogen as a fuel has led to much recent work on the use of *d* and *f* block metal alloys as agents for its safe storage and transport in high concentrations.[6]

In marked contrast the discovery and characterization of molecular complexes containing hydride ligands co-ordinated to transition metals occurred relatively recently. Although earlier claims exist, the first fully authenticated complex hydrides appear to be the carbonyl hydrides $FeH_2(CO)_4$ and $CoH(CO)_4$, reported by Hieber in 1931 and 1934 respectively.[7] Following Hieber's initial discovery, almost 25 years elapsed before further examples were identified and characterized. During this period several new hydrido complexes were undoubtedly synthesized but, in

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[1] J. W. Döbereiner, *Ann. Chim. Phys.*, 1823, **24**, 91.

[2] P. L. Dulong and L. G. Thenard, *Ann. Chim. Phys.*, 1823, **23**, 440.

[3] A. Wurtz, *Compt. Rend.*, 1844, **18**, 702.

[4] T. Graham, *Philos. Trans. R. Soc. London*, 1866, **156**, 415.

[5] G. G. Libowitz, 'The Solid State Chemistry of Binary Metal Hydrides', Benjamin, New York, 1965; K. M. MacKay, 'Hydrogen Compounds of the Metallic Elements', E. and F. N. Spon Ltd., London, 1966; G. C. Bond, 'Catalysis by Metals', Academic Press, New York, 1962.

[6] J. J. Reilly and G. D. Sandrock, *Scientific American*, 1980, **242**, 98.

[7] W. Hieber and F. Leutert, *Naturwissenschaften*, 1931, **19**, 360; *Z. Anorg. Allg. Chem.*, 1932, **204**, 145; W. Hieber, *Z. Elektrochem.*, 1934, **40**, 158.

the absence of modern spectroscopic techniques, were incorrectly characterized and thus passed into the literature unrecognized.[8] Others were claimed but could not subsequently be confirmed.[9] Three seminal papers published in the mid 1950's changed this situation dramatically and initiated a period of rapid growth in the field which continues to this day. In 1955 Wilkinson and Birmingham prepared $ReH(C_5H_5)_2$ and were able to detect the hydride ligand using the newly emergent technique of n.m.r. spectroscopy.[10] The same year Fischer, Hafner, and Stahl reported the chromium and molybdenum hydrides $MH(C_5H_5)(CO)_3$.[11] Two years later Chatt, Duncanson, and Shaw described the remarkably stable platinum(II) hydride, *trans*-$PtHCl(PEt_3)_2$, and recognized the ability of phosphorus (and arsenic) donor ligands to 'stabilize' transition-metal hydrogen bonds.[12] Rapid progress followed these discoveries and within ten years literally hundreds of transition metal hydrido complexes had been characterized. Twenty-five years later the field is still expanding rapidly.

Structural characterization of the hydride ligand by diffraction methods proved difficult because of the small X-ray scattering cross-section of the H-atom and the close proximity of the heavy transition metal atom. Early diffraction studies[13,14] revealed 'vacant' co-ordination sites that were presumed to contain the hydride ligands. However, in 1963 LaPlaca and Ibers[15] succeeded in locating the hydride ligand in $RhH(CO)(PPh_3)_3$ by X-ray diffraction methods and found a Rh—H distance of 1.72(15) Å. The following year Ginsberg *et al.*[16] reported a neutron diffraction study of K_2ReH_9 that unequivocally located all nine hydrogen atoms bound to rhenium and finally settled the long-running controversy concerning the stoicheiometry of this salt. These structure determinations also established that the hydride ligand does exert a stereochemical influence, has a 'normal' metal–ligand distance and is not, as was previously suggested, buried in the metal orbitals. In 1957 Hieber, Behrens, and co-workers[17] prepared the first polynuclear metal hydrido complexes. Subsequent diffraction studies on these and related polynuclear species have revealed a multitude of complex structures containing μ_2- and μ_3-bridging hydride ligands. The first report of an interstitial hydride ligand encapsulated in a non-metallic solid appeared in 1967 when Simon[18] published the structure of polymeric $(Nb_6HI_{11})_\infty$. The H-atom was not located directly but its presence at the centre of the Nb_6 octahedron could be inferred. More recent

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[8] G. E. F. Lundell and H. B. Knowles. *J. Res. Nat. Bureau Standard*, 1937. **18**. 624: F. P. Dwyer and R. S. Nyholm, *J. Proc. R. Soc. New South Wales*, 1941, **75**. 122. 127; 1942. **76**, 133, and 1944, **77**. 116.

[9] W. Hieber and H. Stallmann. *Z. Elektrochem.*, 1943, **49**, 288; W. Hieber and H. Lagally. *Z. Anorg. Allg. Chem.*, 1940. **245**. 321; 1943, **251**. 96.

[10] G. Wilkinson and J. M. Birmingham. *J. Am. Chem. Soc.*, 1955, **77**, 3421.

[11] E. O. Fischer. W. Hafner. and H. O. Stahl, *Z. Anorg. Allg. Chem.*, 1955. **282**, 47.

[12] J. Chatt. L. A. Duncanson. and B. L. Shaw. *Proc. Chem. Soc.*, 1957. 343.

[13] P. G. Owston. J. M. Partridge. and J. M. Rowe. *Acta Crystallogr.*, 1960. **13**. 246.

[14] P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 1962. 333.

[15] S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, 1963, **85**. 3501.

[16] S. C. Abrahams. A. P. Ginsberg. and K. Knox. *Inorg. Chem.*, 1964. **3**, 558.

[17] W. Hieber and G. Brendel. *Z. Anorg. Allg. Chem.*, 1957, **289**. 324; H. Behrens and W. Klek. *Z. Anorg. Allg. Chem.*, 1957. **292**. 151.

[18] A. Simon, *Z. Anorg. Allg. Chem.*, 1967. **355**, 311.

neutron diffraction studies on M_6 and M_{12} molecular hydride clusters have permitted direct location of H atoms within the interstitial cavities of M_6 octahedra.[19] Although interstitial binary hydrides of the *f*-block elements have been known for many years[5] complex molecular hydrides of these metals have only recently been synthesized. The first actinide hydrido complexes were reported in 1978[20] and the first lanthanide hydrido complexes were characterized in 1982.[21] Finally, the ability of certain transition metal salts to activate molecular hydrogen in homogeneous solution was first reported by Calvin in 1938[22] and the involvement of hydrido complexes in many catalytic processes, notably olefin hydrogenation, has served to further stimulate interest in their chemistry.

2 Terminal Hydride Ligands

These were the first to be observed and are still the most numerous, examples are known for virtually all the *d*-block transition elements. The majority are stabilized by the presence of ancillary phosphine, arsine, or carbonyl ligands.

A. Preparative Methods.—These are both numerous and diverse[23] and a selection of the more important routes is given below:

(i) *Hydrogenation of Metal Complexes*. Examples are given in equations 1—3; in those instances where the complex is formed *in situ* (equations 2 and 3) the method constitutes a direct synthesis from the metal.

$$cis\text{-PtCl}_2(\text{PEt}_3)_2 + \text{H}_2 \longrightarrow trans\text{-PtHCl}(\text{PEt}_3)_2 + \text{HCl} \quad (1)$$

$$2\text{Co} + 8\text{CO} + \text{H}_2 \longrightarrow 2\text{CoH(CO)}_4 \quad (2)$$

$$\text{Fe} + 2\,o\text{-C}_6\text{H}_4(\text{PEt}_2)_2 + \text{H}_2 \longrightarrow trans\text{-FeH}_2\{(\text{Et}_2\text{P})_2\text{C}_6\text{H}_4\text{-}o\}_2 \quad (3)$$

(ii) *Hydrolysis of Complex Salts*. This method has been widely employed to prepare hydrido complexes containing CO or PF_3 ligands (equations 4 and 5).

$$\text{Na}_2[\text{Fe(CO)}_4] \xrightarrow{\text{H}_2\text{SO}_4} \text{FeH}_2(\text{CO})_4 \quad (4)$$

$$\text{Na}[\text{Rh(PF}_3)_4] \xrightarrow{\text{H}_2\text{SO}_4} \text{RhH(PF}_3)_4 \quad (5)$$

(iii) *From Metal Salts and Reducing Agents*. The 'reduction' of metal halide, carboxylate, or acetylacetonate complexes with a variety of reducing agents notably $LiAlH_4$, $NaBH_4$, N_2H_4, and EtOH–base has been widely employed in hydride synthesis (equations 6—9 respectively).

$$mer\text{-IrCl}_3(\text{AsEt}_2\text{Ph})_3 + \text{LiAlH}_4 \xrightarrow{\text{THF}} fac\text{-IrH}_3(\text{AsEt}_2\text{Ph})_3 \quad (6)$$

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[19] R. W. Broach, L. F. Dahl, G. Longoni, P. Chini, A. J. Schultz, and J. M. Williams, *Adv. Chem. Ser.*, 1978, **167**, 93.

[20] J. M. Manriquez, P. J. Fagan, and T. J. Marks, *J. Am. Chem. Soc.*, 1978, **100**, 3939.

[21] W. J. Evans, J. H. Meadows, A. L. Wayda, W. E. Hunter, and J. L. Atwood, *J. Am. Chem. Soc.*, 1982, **104**, 2008, 2015.

[22] M. Calvin, *Trans. Faraday Soc.*, 1938, **34**, 1181; *J. Am. Chem. Soc.*, 1939, **61**, 2230.

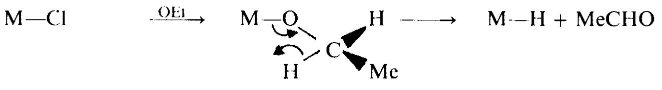
[23] For a fuller discussion of preparative methods see H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231; M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 115.

$$CoCl_2.6H_2O + PEtPh_2 + NaBH_4 \xrightarrow{EtOH} CoH_3(PEtPh_2)_3 \qquad (7)$$

$$cis\text{-}PtCl_2(PPh_3)_2 + N_2H_4.H_2O \xrightarrow{EtOH} trans\text{-}PtHCl(PPh_3)_2 \qquad (8)$$

$$IrCl_3(CO)(PEt_2Ph)_2 + EtOH + KOH \longrightarrow IrHCl_2(CO)(PEt_2Ph)_2 \qquad (9)$$

Other reducing agents employed include HCO_2H, H_3PO_2, $H_2S_2O_4$, and dialkyl aluminium compounds R_2AlX ($X = H$ or OR). The ethanol–base and formic acid reactions involve β-elimination (equation 10) and carbon dioxide extrusion (equation 11) steps respectively.



(10)

$$M{-}Cl \xrightarrow{HCO_2H} M{-}OC(O)H \longrightarrow M{-}H + CO_2 \qquad (11)$$

(iv) *Protonation by Strong Acids**. This reaction was first noted in 1955 by Wilkinson *et al.*[10] who found that $ReH(C_5H_5)_2$ displays a base strength similar to that of ammonia and is protonated by HCl to yield the cation $[ReH_2(C_5H_5)_2]^+$. A variety of strong protonic acids including HSO_3F and $BF_3.H_2O$ have been used.

(v) *Oxidative Addition of Weak Acids*. Weak acids, HX, where the conjugate base X^- is a halogen, oxygen, sulphur, nitrogen, phosphorus, carbon, silicon, germanium, or tin donor frequently generate hydrides by oxidative addition across unsaturated metal centres. These reactions are particularly common for complexes containing d^8 metal ions (notably Ru^0, Os^0, Rh^I, Ir^I). A few illustrative examples are given below:

$$RhCl(PPh_3)_3 + HSiCl_3 \longrightarrow RhHCl(SiCl_3)(PPh_3)_2 + PPh_3 \qquad (12)$$

$$Pt(PPh_3)_3 + HCN \longrightarrow PtH(CN)(PPh_3)_2 + PPh_3 \qquad (13)$$

$$[Ir(dppe)_2]Cl + PH_3 \longrightarrow cis\text{-}[IrH(PH_2)(dppe)_2]Cl \qquad (14)$$

Carbon acids usually participate in these reactions only if the C—H bonds are activated by adjacent electron-withdrawing groups (*i.e.* $MeNO_2$, $HC{\equiv}CR$)[24] or, in the case of cyclometallation reactions,[25] are held in close proximity to the metal as part of a co-ordinated ligand (equation 15).

$$IrCl(PPh_3)_3 \longrightarrow IrHCl\{P(C_6H_4)Ph_2\}(PPh_3)_2 \qquad (15)$$

However, recent work involving very electron-rich complexes has yielded a few

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*Since the hydride ligand and the proton are formally assigned oxidation states of −1 and +1 respectively, hydride formation by protonation involves an increase of two units in the formal oxidation state of the metal concerned.

[24] D. M. Roundhill, *Adv. Organomet. Chem.*, 1975, **13**, 273 and references therein.

[25] G. W. Parshall, *Acc. Chem. Res.*, 1970, **3**, 139 and references therein.

examples involving cleavage of C—H bonds in simple aromatic[26] (equation 16) and aliphatic[27] hydrocarbon substrates (equation 17).

$$W(C_5H_5)_2(CO) + C_6H_6 \xrightarrow{h\nu} WH(C_6H_5)(C_5H_5)_2 + CO \qquad (16)$$

$$Ir(C_5H_5)(CO)_2 + CH_3CMe_3 \longrightarrow IrH(CH_2CMe_3)(C_5H_5)(CO) + CO \qquad (17)$$

B. Characterization.—For obvious reasons the classical technique of elemental analysis by combustion does not afford a practicable method of detecting or estimating hydride ligands in metal complexes. Chemical reactions with halogens, mineral acids, and halogenated hydrocarbons (see Section 2F) have been employed for this purpose but cannot be relied upon to give a quantitative answer. Thus $IrH_5(PEt_2Ph)_2$ was originally formulated as $IrH_3(PEt_2Ph)_2$ on the basis of the volume of hydrogen liberated by treatment with hydrochloric acid.[28] In contrast, the hydride ligands in $Cu_6H_6(PPh_3)_6$ were estimated by acidolysis after diffraction and spectroscopic methods failed to detect their presence.[29] Molecular stereochemistry in metal hydride complexes can often be deduced from dipole moment measurements (the M—H bond has a small dipole moment)[30] or chemical lability studies (hydride ligands process a very strong *trans* effect). However, the overwhelming majority of hydride ligands are now detected and characterized by infrared and n.m.r. spectroscopy. The application of these and other spectroscopic techniques is discussed in the following section.

C. Spectroscopic Properties.—These are of paramount importance in transition-metal hydride chemistry and the rapid development of the field in the past 25 years owes much to the parallel emergence of modern spectroscopic techniques, particularly nuclear magnetic resonance. Spectroscopic data have been collected and tabulated in several major review articles.[31]

(i) *Vibrational Spectroscopy*. The infrared spectra of most hydrido complexes show M—H stretching and bending modes in the ranges *ca.* 2300—1600 and *ca.* 900—600 cm^{-1} respectively. The stretching mode is usually the easiest to observe and affords a valuable diagnostic test for hydride ligands, particularly in complexes unsuited to n.m.r. spectroscopy because of paramagnetism or low solubility. In those instances where the M—H bond is of low polarity a weak or undetectable band in the infrared spectrum is often matched by a strong Raman absorption. Synthesis and examination of the corresponding deuteride offers a means of distinguishing ν(M—H) from other infrared active modes—notably ν(CO), ν(CN), and ν(NN)—that occur in the same region of the spectrum. Accord-

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[26] K. L. Tang Wong, J. L. Thomas, and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1974, **96**, 3694.

[27] J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 3723.

[28] B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1970, 703.

[29] S. A. Bezman, M. R. Churchill, J. A. Osborn, and J. Wormald, *J. Am. Chem. Soc.*, 1972, **93**, 2063.

[30] J. Chatt and G. J. Leigh, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 400.

[31] A. P. Ginsberg, *Transition Met. Chem.*, 1965, **1**, 111; H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231; G. L. Geoffroy and J. R. Lehman, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 189; D. M. Roundhill, *Adv. Organomet. Chem.*, 1975, **13**, 273; M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 115.

ing to the diatomic oscillator approximation the ratio ν(M—H)/ν(M—D) should equal $\sqrt{2}$; observed shifts are roughly in agreement with this prediction. For complexes containing carbonyl *trans* to hydride the Fermi resonance interaction between the two ligands leads to shifts in ν(CO) and anomalous values of ν(M—H)/ν(M—D).[32] In those instances where ν(M—D) is obscured by other absorptions the assignment must be based on the absence or reduced intensity of the ν(M—H) absorption for the deuteriated sample. The value of ν(M—H) reflects the nature of the ligand in the *trans* position, and is therefore a useful adjunct in the determination of stereochemistry; ligands with high *trans* influence weaken the M—H bond and produce a concomitant reduction in the M—H stretching frequency (Table 1).[33, 34] The effect is particularly marked in *trans*-dihydrides where $\nu(\text{M—H})_{\text{asym}}$ can be as low as *ca.* 1600 cm^{-1}. The nature of the *trans*-ligand also affects the solvent dependency of ν(M—H).

Table 1 *Infrared and proton n.m.r. data*[a] *for the complexes trans-*$PtHX(PEt_3)_2$

X	I	Br	NO_3	Cl	SCN	NO_2	CN
ν(Pt—H)/cm^{-1}	2156	2178	2242	2183	2112	2150	2041
τ(Pt—H)/p.p.m.	22.65	25.55	33.6	26.8	22.95	29.4	17.6
^1J(Pt—H)/Hz	1369	1346	1322	1275	1233	1003	778
K(Pt—H)/C.U.[b]	204.1	200.7	197.1	190.1	183.8	149.5	116.0

[a] Data from *ref.* 33 (i.r.) and *ref.* 34 (n.m.r.). [b] C.U. = coupling units, see *ref.* 41.

Thus, changing from chloroform to hexane (a less polar solvent) causes a shift of *ca.* 30 cm^{-1} to lower frequencies for hydride *trans* to halogen but no shift for hydride *trans* to P or As donor ligands.[35] Changes in the nature of the *cis*-ligands can also produce surprisingly large shifts in ν(M—H). Thus, in *trans*-RuHCl(chelate)$_2$, ν(Ru—H) ranges from 1804 to 1978 cm^{-1} for a series of closely related P and As donor chelates.[36]

The bonding mode δ(M—H) is frequently masked by ligand vibrations and has therefore attracted much less attention.

(ii) *Nuclear Magnetic Resonance Spectroscopy.* The most reliable spectroscopic evidence for the presence of hydride ligands in transition metal complexes is provided by the resonances observed to high field of TMS in the proton n.m.r. spectrum. These are readily detected by modern instruments except in a small minority of complexes where poor solubility or broadening of the signal due to inter- or intra-molecular exchange, nuclear quadruple interactions (*i.e.* ^{59}Co), or the presence of paramagnetic centres may cause problems. For terminal hydride ligands the high-field resonance is typically in the region τ 15—35 but can range

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[32] P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1967, **89**, 2851.

[33] P. W. Atkins, J. C. Green, and M. L. H. Green, *J. Chem. Soc. (A)*, 1968, 2275.

[34] J. Powell and B. L. Shaw, *J. Chem. Soc.*, 1965, 3879.

[35] D. M. Adams, *Proc. Chem. Soc.*, 1961, 431.

[36] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 2605.

from *ca.* $\tau 5$ to *ca.* $\tau 60$ in special circumstances.[37, 38] These high-field shifts, which are almost exclusive to hydride ligands in transition metal complexes, arise principally from two effects, a paramagnetic shielding term attributed to the mixing of excited electronic states into the ground state, and a diamagnetic shielding term. The latter becomes increasingly important for shorter M—H distances.[39, 40] The chemical shift τ(M—H) is sensitive to the nature of the ligand *trans* to the hydride; low values are associated with hydride ligands *trans* to groups having high *trans* influence (see Table 1). The highest recorded values are found for hydride ligands *trans* to the vacant co-ordination sites in tetragonal pyramidal complexes, *e.g.* *ca.* $\tau 60$ for $IrHCl_2(PBu^t_2R)_2$ (R = Me, Et, or Pr^n).[38] The multiplicity of the hydride resonance can be particularly informative. For hydride ligands bound to magnetically active transition-metal nuclides—notably ^{103}Rh (100% abundance, $I = \frac{1}{2}$), ^{183}W (14%, $I = \frac{3}{2}$) ^{189}Os(16.1%, $I = \frac{1}{2}$) and ^{195}Pt(33.7%, $I = \frac{1}{2}$)—the spin–spin coupling ^1J(M—H) provides strong evidence for the presence of a metal–hydrogen bond. The values obtained, which can range from > 1000 Hz (^{195}Pt—H) to < 15 Hz (^{103}Rh—H), reflect the magnetogyric ratio of the metal concerned, the co-ordination number of the metal and the nature of the *trans*-ligand, and can yield information concerning the oxidation state and stereochemistry of the complex. Since the magnetogyric ratios, γ, differ from nucleus to nucleus it is desirable in comparative studies to eliminate them from ^1J(M—H). To do this Pople and Santry[41] have defined reduced coupling constants $K_{(M-H)} = (2\pi/h\gamma_M\gamma_H)J(M\text{—}H)$ which are expressed in coupling units (Table 1).

Since the majority of terminal hydride complexes contain phosphorus donor ligands the coupling ^2J(PH) between phosphorus (^{31}P 100%, $I = \frac{1}{2}$) and hydride ligands is particularly useful in rigid planar or octahedral complexes, $^2J(PH)_{trans}$ is usually larger than $^2J(PH)_{cis}$; typical values for octahedral iridium(III) complexes are 100—180 Hz and 10—30 Hz respectively.[42] However, in a few complexes, usually involving first row transition metals, where ligand geometry leads to significant distortion of the co-ordination sphere the magnitudes of these couplings are reversed.[43] The majority of hydride resonance patterns are first order; analysis of second order spectra where they are found reveals that $^2J(PH)_{trans}$ and $^2J(PH)_{cis}$ are of opposite sign.[44] Many polyhydrido complexes of general form $MH_n(PR_3)_m$ display stereochemical non-rigidity in solution: all hydride ligands appear equivalent and couple equally to all the phosphorus nuclei present.[45] In these systems the number of phosphorus donor atoms and hydride ligands can be determined directly from the multiplicities of the ^1H and ^{31}P (organic ^1H narrow band decoupled) n.m.r. patterns respectively. The coupling $^2J(^{13}C\text{—}^1H)$ has been

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[37] B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *Inorg. Chem.*, 1967, **6**, 1979.

[38] H. D. Empsall, E. M. Hyde, E. Mentzer, B. L. Shaw, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1976, 2069.

[39] A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 2747 and 4583.

[40] L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, 1964, **3**, 22 and references therein.

[41] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[42] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231.

[43] F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1970, **92**, 1068.

[44] K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 1968, **7**, 546.

[45] J. P. Jesson in 'Transition Metal Hydrides', ed. E. L. Muetterties, Dekker, New York, 1971.

observed for a range of ^{13}C enriched carbonyl[46, 47] and cyanide[46] hydrides. For rigid multihydrido complexes containing chemically non-equivalent hydride ligands, small couplings [$^{2}J(HH') = ca.\ 5$—10 Hz] are usually observed.

Broad line n.m.r. data on $MnH(CO)_5$,[48] $FeH_2(CO)_4$,[49] and $CoH(CO)_4$[50] have been used to determine M—H bond distances; the very small values originally obtained (*ca.* 1.1—1.4 Å) were subsequently revised[51] to take account of quadrupole effects and are now in accord with results from other sources.

Electronic Spectroscopy. Analysis of the visible and ultra-violet spectra recorded for the species $RuX_2(Me_2PCH_2CH_2PMe_2)_2$ (X = Cl, Br, I, or CN) and $RuRCl(Me_2PCH_2CH_2PMe_2)_2$ (R = H, Me, Ph, or *p*-tolyl) placed hydride alongside alkyl, aryl, and cyanide groups as a high-field ligand.[52] This conclusion is supported by spectra data for $[CoH(CN)_5]^{3-}$ (*ref.*53) and $[ReH_9]^{2-}$ (*ref.*16) and is in keeping with the high *trans*-influence of the hydride ligand, the Mössbauer spectra of iron(II) hydrides[54] and the pale colours displayed by most mononuclear hydrido complexes. An examination of the electronic spectra of the rhodium(III) amine complexes $[RhX_2(en)_2]^+$ and $[RhXCl(en)_2]^+$ (X = H, Cl, Br, I, N_3, or NO_2) has, however, indicated a somewhat lower position for hydrogen in the spectrochemical series, somewhere between ammonia and water ligands.[55] In an attempt to rationalize this apparent anomaly it has been suggested that the hydride ligand, because of its unique nature, is highly polarizable and has a variable ligand field strength which is unusually dependent upon the co-ordination environment in which it is situated.[56]

Miscellaneous Spectroscopic and Physical Techniques. Mass spectroscopy has been extensively employed in the study of volatile hydride complexes containing PF_3 [57] and/or CO [58] ligands. Parent molecular ions are usually detected and competitive loss of hydride and carbonyl ligands is observed.[58] Polyhydrido complexes tend to lose hydride ligands in pairs.

The scarcity of authentic paramagnetic hydrido complexes has severely restricted the application of e.s.r. spectroscopy in this field. However, the high sensitivity of the technique has permitted the detection and characterization of paramagnetic hydrides present in solutions at low concentrations.[59, 60] Hyperfine

[46] G. M. Whitesides and G. Maglio, *J. Am. Chem. Soc.*, 1969, **91**, 4980.

[47] J. W. Faller, A. S. Anderson, and C.-C. Chen, *J. Chem. Soc., Chem. Commun.*, 1969, 719.

[48] T. C. Farrar, W. Ryan, A. Davison, and J. W. Faller, *J. Am. Chem. Soc.*, 1966, **88**, 184.

[49] E. O. Bishop, J. L. Down, P. R. Emtage, R. E. Richards, and G. Wilkinson, *J. Chem. Soc.*, 1959, 2484.

[50] T. C. Farrar, F. E. Brinckman, T. D. Coyle, A. Davison, and J. W. Faller, *Inorg. Chem.*, 1967, **6**, 161.

[51] G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1967, 751.

[52] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 772.

[53] W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 1959, 2757.

[54] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc. (A)*, 1970, 956.

[55] J. A. Osborn, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 1964, 3168.

[56] K. M. MacKay, 'Hydrogen Compounds of the Metallic Elements', E. and F. N. Spon Ltd., London, 1966, p. 141.

[57] F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *J. Am. Chem. Soc.*, 1968, **90**, 3684.

[58] B. F. G. Johnson, J. Lewis, and P. W. Robinson, *J. Chem. Soc. (A)*, 1970, 1684.

[59] V. V. Saraev, F. K. Shmidt, N. M. Ryutina, V. A. Makarov, and V. A. Gruznykh, *Koord. Khim.*, 1977, **3**, 1364; *Sov. J. Coord. Chem. (Engl. Transl.)*, 1977, **3**, 1064.

[60] I. H. Elson, J. K. Kochi, U. Klabunde, L. J. Manzer, G. W. Parshall, and R. N. Tebbe, *J. Am. Chem. Soc.*, 1974, **96**, 7374.

coupling constants have been measured and spin density distributions calculated. A fuller discussion is given in Section 2G.

X-Ray photoelectron spectroscopy has been used to investigate charge distribution within metal hydrido complexes, data for $MnH(CO)_5$, $FeH_2(CO)_4$, and $CoH(CO)_4$ indicated H-atom charges of −0.8, −0.3, and −0.75 respectively.[61] Similar measurements on polyhydrido complexes indicate that the hydride ligands carry little negative charge.[62] Mössbauer studies on iron(II) hydrides place hydride near or above cyanide in the spectrochemical series.[54]

D. Diffraction Studies.—Work on this area commenced in 1939 with a report by Ewens and Lister[63] on the molecular structures of $CoH(CO)_4$ and $FeH_2(CO)_4$ as determined by gas phase electron diffraction methods. The tetrahedral arrangement of carbonyl ligands about the metal centre was established but the hydride ligands could not be located. Similar difficulties were encountered in the first *X*-ray diffraction studies on metal hydrido complexes reported in the early 1960's. Thus the positions of the hydride ligands in *trans*-$PtHBr(PEt_3)_2$,[13] $MnH(CO)_5$,[64] and $OsHBr(CO)(PPh_3)_3$[14] were inferred from the presence of 'vacant' co-ordination sites. The first location of a hydride ligand by *X*-ray diffraction methods was reported in 1963 by LaPlaca and Ibers.[15] In a classic study they reasoned that since the *X*-ray scattering from hydrogen is largely confined to low angle data it should be possible to enhance hydrogen peaks in the difference-Fourier maps by removing the high angle reflections from the calculation. Using this approach a Rh—H distance of 1.72(15) Å was determined for $RhH(CO)(PPh_3)_3$. A neutron diffraction study completed in the following year[16] finally established the true stoicheiometry of K_2ReH_9 and revealed a Re—H bond length of 1.68 Å. These results are consistent with the presence of normal covalent M—H bonds and did much to resolve the long-running controversy concerning the nature of the metal hydrogen linkage in complex metal hydrides.

Location of hydride ligands by *X*-ray diffraction methods still poses problems except in the most favourable circumstances when sufficient low angle data are available. Consequently neutron diffraction, though requiring larger crystals and access to a suitable neutron source, remains the preferred method for accurate structure determination.[65] Neutron diffraction offers important advantages over *X*-ray diffraction for the determination of hydride structures. Since neutrons, unlike *X*-rays, are diffracted by most elements with very similar efficiencies, the hydride ligand is not masked by the adjacent heavy metal atom and can therefore be more easily located. However, this equality of diffracting power precludes the use of heavy atom methods and most neutron diffraction studies are preceded by an *X*-ray structure determination to locate all atoms save hydrogen. It should also be noted that since neutron diffraction locates true nuclear positions whereas *X*-ray

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[61] H.-W. Chen, W. L. Jolly, J. Kopf, and T. H. Lee, *J. Am. Chem. Soc.*, 1979, **101**, 2607.

[62] G. J. Leigh, *Inorg. Chim. Acta*, 1975, **14**, L35.

[63] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, 1939, **35**, 681.

[64] S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, 1964, **3**, 1491.

[65] R. Bau and T. F. Koetzle, *Pure Appl. Chem.*, 1978, **50**, 55.

diffraction methods measure electron density distribution, M—H bond lengths determined by the former technique are often significantly shorter than those measured by the latter.[66] Thus values for the Zn—H bond in $\{ZnH(MeNCH_2CH_2NMe_2)\}_2$ as determined by *X*-ray and neutron diffraction methods are 1.70 and 1.60 Å respectively.[67]

E. Nature of the Terminal M—H Bond.—(i) *Historical Perspectives. Stereochemical properties.* Many of the early physical measurements on the simple carbonyl hydrides gave results consistent with the conclusion that the stereochemical influence of the hydride ligand was minimal. Thus the electron diffraction studies on the cobalt and iron carbonyl hydrides $CoH(CO)_4$ and $FeH_2(CO)_4$ established tetrahedral arrangements for the carbonyl ligands about the metal atoms.[63] Likewise the physical properties of $MnH(CO)_5$, including the infrared spectrum which was initially interpreted in terms of a molecule of C_S or C_{2V} rather than C_{4V} symmetry,[68, 69] appeared consistent with a trigonal bipyramidal structure similar to that found for $Fe(CO)_5$. To account for these observations, structures in which the hydrogen atom was buried in the electron cloud of the metal atom[70] or attached to a carbonyl ligand (linear C—O—H group)[63] were proposed. The second of these theories received no support from infrared evidence[71] and fell from favour but the first, originally proposed by Hieber, enjoyed wide acceptance until the late 1950's. According to Hieber the groups 'CoH' and 'FeH_2' functioned as pseudo-nickel atoms and were tetrahedrally co-ordinated by carbonyl ligands in the same manner as nickel in $Ni(CO)_4$.[70] This idea was compatible with broad line n.m.r. data for $FeH_2(CO)_4$ which indicated a H·····H distance of 1.88 ± 0.05 Å and an Fe—H bond length of 1.1 Å—slightly less than the covalent radius of iron.[49] It also appeared to explain, in terms of shielding by '*d*'-electrons, the high-field proton resonances observed for hydride ligands in the early solution n.m.r. studies.[10]

This situation changed dramatically when *X*-ray and neutron diffraction studies located the hydride ligands and revealed 'normal' covalent bond lengths, essentially equal to the sum of the metal and hydrogen covalent radii. Around the same period Buckingham[39] and Lipscomb[40] were able to show that the high-field proton n.m.r. shifts associated with metal hydrides could be explained without recourse to very short M—H distances. These results finally disproved the 'buried proton' model and led to recognition of the metal–hydrogen linkage as a normal covalent bond.

Although the hydride ligand occupies a normal co-ordination site its small volume (~ 7 Å^3) relative to more bulky carbonyl and phosphine ligands (CO ≈ 45 Å^3; $PPh_3 \approx 370$ Å^3) leads to sterically induced distortion within the

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[66] For a discussion of this problem see J. L. Petersen and J. M. Williams, *Inorg. Chem.*, 1978, **17**, 1308.

[67] P. T. Moseley, H. M. M. Shearer, C. B. Spencer, *Acta Crystallogr.*, 1969, **A25**, S169.

[68] W. E. Wilson, *Z. Naturforsch., Teil B*, 1958, **13**, 349.

[69] F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 1959, 833.

[70] W. Hieber, *Die Chemie*, 1942, **55**, 24; W. Hieber. K. Kramer, and H. Schulten, *Angew. Chem.*, 1936, **49**, 463.

[71] W. F. Edgell, C. Magee, and G. Gallup, *J. Am. Chem. Soc.*, 1956, **78**, 4185.

co-ordination spheres of many hydrido complexes.[72] Distortions are present in four, six, seven, and eight co-ordinate structures but are most readily quantified in five co-ordinate trigonal bipyramidal complexes MHL_4 where the equatorial ligands are displaced toward the small hydride ligand to form a pseudo-tetrahedral ML_4 skeleton.[73]

Whereas most hydrido complexes are stereochemically rigid the five co-ordinate species MHL_4, some six and many seven, eight, or nine co-ordinate polyhydrides MH_nL_m (L = P donor ligand) display stereochemical non-rigidity in solution. Variable temperature n.m.r. is particularly suited to the study of this phenomenon and has yielded much information concerning the kinetics and mechanisms of the rapid polytopal rearrangements occurring within these systems.[45] Under conditions of fast rearrangement all the hydride ligands become magnetically equivalent and couple equally to all ^{31}P nuclei present in the molecule. On several occasions failure to recognise this phenomenon has led to incorrect interpretation of n.m.r. data and wrong assignment of structure. For the tetraphosphine complexes $MH_n(PR_3)_4$ (n = 1, 2, 3, or 4) the rearrangements are thought to involve rapid intra-molecular migration of the hydride ligands between trigonal faces of the $M(PR_3)_4$ tetrahedron. All distinct permutational isomerization reactions of these complexes have been determined and their importance for the interpretation of temperature dependent line shape behaviour has been discussed.[74] Retention of internuclear couplings $^1J(MH)$ and $^2J(PH)$ eliminates dissociative mechanisms. Activation energies are usually less than 60 kJ mol^{-1}.[75]

(ii) *Stability of M—H Bonds.* The stability of transition metal hydrido complexes ranges from extremely high [*i.e.* $PtHCl(PEt_3)_2$, distils at 130 °C, 0.01 mm] to notoriously low [*i.e.* $CoH(CO)_4$, decomposes −20 °C]. The high stability displayed by many phosphine-containing hydrido complexes and by the binary hydrido anion $[ReH_9]^{2-}$ can in part be ascribed to kinetic factors.[76, 77] According to this theory a large energy gap ΔE between the highest occupied molecular orbital and the lowest unoccupied anti-bonding molecular orbital prevents promotion of electrons to the latter and thus stabilizes the complex. The observation that hydrides of highest stability usually involve the heavier members of a given metal triad and ligands of high-field strength lends support to this idea.

Data on the thermodynamic stability of M—H bonds are sparse even today. However, those now available indicate that the strengths of M—H bonds are significantly greater than those of $M—CH_3$ bonds and do not fall far short of the values recorded for M—Cl bonds in comparable complexes[78] (see Table 2).

(iii) Trans-*influence and* trans-*effect of Hydride.* In keeping with its high position

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[72] B. A. Frenz and J. A. Ibers, in 'Transition Metal Hydrides', ed. E. L. Muetterties, Dekker, New York, 1971.

[73] R. W. Baker and P. Pauling, *J. Chem. Soc., Chem. Commun.*, 1969, 1495.

[74] W. G. Klemperer, *Inorg. Chem.*, 1972, **11**, 2668.

[75] P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson, *J. Am. Chem. Soc.*, 1973, **95**, 1467.

[76] J. Chatt, *Proc. Chem. Soc.*, 1962, 318.

[77] A. P. Ginsberg, *Transition Met. Chem.*, 1965, **1**, 111.

[78] J. A. Connor, *Top. Curr. Chem.*, 1977, **71**, 71.

Table 2 *Enthalpy contributions $\bar{D}(M—X)$ for M—X bonds (X = H, Me, or Cl) in some transition metal complexes*

Complex	$\bar{D}(M—X)$ *kJ mol*$^{-1}$ X = H	Me	Cl	*Ref.*
$TiX_2(C_5Me_5)_2$	242			*a*
$MoX_2(C_5H_5)_2$	258.7			*b*
	251.4	149.5	304.2	*c*
$WX_2(C_5H_5)_2$	286.8			*b*
	305.2	197.8	346.0	*c*
$MnX(CO)_5$	*ca.* 300	*ca.* 130	*ca.* 300	*d*
$[FeX(CO)_4]^-$	*ca.* 310			*d*
$CoX(CO)_4$	*ca.* 290			*d*
$IrX_2Cl(CO)(PR_3)_2$	*ca.* 240—255			*e*

[a] J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1972, **94**, 1219. [b] V. I. Tel'noi, I. B. Rabinovich, K. V. Kir'yanov, and A. S. Smirnov, *Dokl. Acad. Nauk, Ser. Khim.*, 1976, **231**, 903. [c] J. C. G. Calado, A. R. Dias, J. A. Martinho-Simoes, and M. A. V. Ribeiro Da Silva, *J. Organomet. Chem.*, 1979, **174**, 77. [d] J. A. Connor, *Top. Curr. Chem.*, 1977, **71**, 77. [e] L. Vaska, *Trans. New York Acad. Sci.*, 1971, **33**, 70.

in the spectrochemical series (see Section 2C) the terminal hydride ligand exerts a strong *trans*-influence and *trans*-effect. The former is demonstrated by long M—L bond distances[79, 80] and low ν(M—L) values[80] for ligands (L) *trans* to hydride; the latter by the facile exchange of phosphine or halide ligands *trans* to hydride in many Group VIII metal complexes.[81, 82] The high *trans*-influence of the hydride ligand is attributed to its inductive effect in drawing a large amount of *p*-orbital character into the M—H σ-bond and thus weakening the σ-bond to the *trans*-ligand.[83] The high *trans*-effect is thought to arise largely from ground-state destabilization and thus follows from the high *trans*-influence.[84]

(iv) *Acidity of Metal Hydrides.* It has long been known that many transition metal hydrides display Brønsted acid character in polar media; acid strengths range from very strong to immeasurably weak.[85] Thus $FeH(SiCl_3)_2(\eta\text{-}C_5H_5)(CO)$ is reported to be a very strong acid in MeCN solution, comparable with $HClO_4$,[86] whereas $IrHCl_2(CO)(PMe_2Ph)_2$ (H *trans* to CO) does not lose HCl even in boiling sodium methoxide.[87] On the basis of the modest number of quantitative data available it appears that hydride acidity increases on crossing the transition metal block from

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[79] R. Mason, R. McWeeny, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, **47**, 20.

[80] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335 and references therein.

[81] P. G. Douglas and B. L. Shaw, *J. Chem. Soc. (A)*, 1970, 1556.

[82] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

[83] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York, 1965, Chapter 2.

[84] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 1707.

[85] R. G. Pearson and P. C. Ford, *Comments Inorg. Chem.*, 1982, **1**, 279.

[86] W. Jetz and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1159.

[87] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. (A)*, 1968, 1887.

left to right and decreases on moving down a metal triad.[85] Replacement of strong π-acceptor ligands with weaker ones also produces a marked decrease in acidity thus pK_a values for the complexes $CoH(CO)_3L$ ($L = CO$, $P(OPh)_3$, and PPh_3) are <2, 1.13×10^{-5}, and 1.09×10^{-7} respectively.[88] Finally there is evidence to suggest that for some iridium(III) complexes, acid strength is proportional to Ir—H bond strength; complexes with high ν(Ir—H) values tend to release protons most readily.[87]

F. Chemical Reactions.—In this section some of the more important chemical reactions displayed by terminal hydride ligands are discussed and representative examples given. Since the reactivities of individual hydrido complexes vary very widely it should not be assumed that any particular reaction type discussed is general to all, or even most, transition metal hydrido complexes.

(i) *Isomerization.* Some rigid octahedral hydrido complexes of the platinum group metals have been shown to undergo geometrical isomerization on photolysis. A dissociative mechanism involving rearrangement of five-co-ordinated intermediates, formed by photo-induced loss of a phosphine ligand *trans* to the hydride, has been proposed.[89]

(ii) *Hydrogen–deuterium Exchange.* Hydrido complexes that are susceptible to protonation, oxidative addition, and 'insertion' reactions undergo H–D exchange with D^+–D_2O (equation 18),[90] D_2 (equation 19),[91,92] and C_2D_4 (equation 20)[92] respectively. In combination with a reversible cyclometallation reaction (equation 21) these processes can affect H–D exchange at selected sites in the organic moieties of co-ordinated ligands (*i.e.* the *ortho* sites in triarylphosphine and phosphite ligands).[93]

$$(Et_3P)_2PtHCl + DCl \longrightarrow (Et_2P)_2PtHDCl_2 \longrightarrow (Et_3P)_2PtDCl + HCl \qquad (18)$$

$$(Ph_3P)_3(CO)IrH + D_2 \longrightarrow (Ph_3P)_2(CO)IrHD_2 + PPh_3 \longrightarrow (Ph_3P)_3(CO)IrD + HD \qquad (19)$$

$$(dppe)_2IrH + C_2D_4 \longrightarrow (dppe)_2IrCD_2CD_2H \longrightarrow (dppe)_2IrD + C_2HD_3 \qquad (20)$$

$$\{(PhO)_3P\}_4IrH \longrightarrow \{(PhO)_3P\}_2\overline{IrH_2\{P(OC}_6H_4)(OPh)_2\} + P(OPh)_3 \qquad (21)$$

(iii) *Reactions with Acids.* A wide variety of acids ranging from strong mineral acids to very weak carbon or silicon acids (*i.e.* $HC{\equiv}CR$, $HSiR_3$) can react with hydrido complexes. Strong acids with weakly co-ordinating conjugate bases usually form salts (equation 22)[94] whereas weak acids with strongly co-ordinating conjugate bases generally afford oxidative addition products (equation 23).[95]

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[88] W. Hieber and W. Hubel, *Z. Elektrochem.*, 1953, **57**, 235; W. Hieber and E. Lindner, *Chem. Ber.*, 1961, **94**, 1417.

[89] P. R. Brookes, C. Masters, and B. L. Shaw, *J. Chem. Soc. (A)*, 1971, 3756.

[90] C. D. Falk and J. Halpern, *J. Am. Chem. Soc.*, 1965, **87**, 3523.

[91] L. Vaska, *Inorg. Nucl. Chem. Lett.*, 1965, **1**, 89.

[92] R. A. Schunn, *Inorg. Chem.*, 1970, **9**, 2567.

[93] E. K. Barefield and G. W. Parshall, *Inorg. Chem.*, 1972, **11**, 964.

[94] L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 1965, 6974.

[95] F. Glockling and J. G. Irwin, *Inorg. Chim. Acta*, 1972, **6**, 355.

These reactions are frequently accompanied by reductive elimination of dihydrogen and afford a clean, convenient route for the introduction of the conjugate bases (*i.e.* $C{\equiv}CR$, SiR_3, acac, SPh, O_2CR) into the co-ordination sphere of the metal (equation 24).[96]

$$IrH(CO)(PPh_3)_3 + HClO_4 \longrightarrow [IrH_2(CO)(PPh_3)_3]ClO_4 \qquad (22)$$

$$IrH(CO)(PPh_3)_3 + HSnMe_3 \longrightarrow IrH_2(SnMe_3)(CO)(PPh_3)_2 + PPh_3 \qquad (23)$$

$$MHL_n + HX \longrightarrow MH_2XL_n \longrightarrow MXL_n + H_2 \qquad (24)$$

Treatment with trityl fluoroborate can lead to hydride abstraction and salt formation (equation 25).[97]

$$RuH_2(PPh_3)_4 + (Ph_3C)BF_4 \longrightarrow [RuH(PPh_3)_4]BF_4 + Ph_3CH \qquad (25)$$

(iv) *Reactions with Bases.* Many of the more acidic hydrides react with KOH or, failing this, with stronger bases such as LiR (R = alkyl or aryl)[98] or KH[99] to form salts (equations 26 and 27).

$$ReH(C_5H_5)_2 + LiBu \longrightarrow Li[Re(C_5H_5)_2] + BuH \qquad (26)$$

$$CoH\{P(OMe)_3\}_4 + KH \longrightarrow K[Co\{P(OMe)_3\}_4] + H_2 \qquad (27)$$

These reactions afford useful routes to salts of complex anions.

(v) *Reactions with Halogens and Organic Halides.* Most transition metal hydrides react readily with halogens and halogenated hydrocarbons to yield the corresponding metal halide complexes. The reactivity of the hydrocarbon increases with the degree of halogenation $CH_3Cl < CH_2Cl_2 < CHCl_3 < CCl_4$. Treatment of a complex hydride with CCl_4 and subsequent detection of $CHCl_3$ is a useful but not totally reliable method for establishing the presence of hydride ligands. Conversely, caution should be exercised in the use of halogenated hydrocarbon solvents when the presence of labile hydride ligands is suspected.

(vi) *'Insertion' (Hydrogen Migration) Reactions.* This large and diverse group of reactions, many of which participate in important catalytic cycles, are of the general form:

$$L_nMH + X \longrightarrow L_nM{-}X{-}H$$

The reverse reaction is termed extrusion. A selection of the more important examples is given in Table 3; the classification is self-explanatory. A number of the reactions listed merit special mention. The 'insertion' of carbon monoxide into M—H bonds, though much sought because of its probable participation in Fischer–Tropsch chemistry,[100] has only recently been detected and the example given in the table was the first to be reported. Insertion of carbonyl ligands into

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[96] K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1974, 1205; A. Dobson, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1975, 370.

[97] J. R. Sanders, *J. Chem. Soc., Dalton Trans.*, 1973, 743.

[98] D. Baudry and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1979, 895.

[99] E. L. Muetterties and F. J. Hirsekorn, *J. Chem. Soc., Chem. Commun.*, 1973, 683.

[100] C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 61.

Table 3 *Hydride migration (insertion) reactions*

Reaction			*Ref.*
1/1 *Insertions*			
(Octaethylporphyrin)RhH	+ CO	→ (octaethylporphyrin)Rh(CHO)	*a*
$(dmpe)_2TaH(\equiv C{\cdot}CMe_3)I$		→ $(dmpe)_2Ta(=CH{\cdot}CMe_3)I$	*b*
$(\eta\text{-}C_5H_5)_2WH(CH_2PMe_2Ph)$		→ $(\eta\text{-}C_5H_5)_2W(CH_3)(PMe_2Ph)$	*c*
$(\eta\text{-}C_5H_5)(CO)_3MoH$	+ CH_2N_2	→ $(\eta\text{-}C_5H_5)(CO)_3MoMe + N_2$	*d*
$(\eta\text{-}C_5H_5)(CO)_3MoH$	+ SnR_2 ($R = CH_2SiMe_3$)	→ $(\eta\text{-}C_5H_5)(CO)_3Mo(SnR_2H)$	*e*
1/2 *Insertions*			
$(Me_3P)_3Co(C_2H_4)H$		→ $(Me_3P)_3CoC_2H_5$	*f*
$(Ph_3P)_2Cl_2RhH$	+ C_2H_2	→ $(Ph_3P)_2Cl_2Rh(CH=CH_2)$	*g*
$(\eta\text{-}C_5H_5)_2MoH_2$	+ $EtO_2C{\cdot}N=N{\cdot}CO_2Et$	→ $(\eta\text{-}C_5H_5)_2MoH(EtO_2C{\cdot}N\text{—}NH{\cdot}CO_2Et)$	*h*
trans-$[Rh(en)_2H(OH)]^+$	+ O_2	→ *trans*-$[Rh(en)_2(OH)(OOH)]^+$	*i*
$(Ph_3P)_3CoH_3$	+ CO_2	→ $(Ph_3P)_3Co(O_2CH) + H_2$	*j*
$(Ph_3P)_3(CO)ClRuH$	+ CS_2	→ $(Ph_3P)_2(CO)ClRu(S_2CH) + PPh_3$	*k*
1/3 *Insertions*			
$(\eta\text{-}C_5H_5)(CO)_3MoH$	+ $N_2CHSiMe_3$	→ $(\eta\text{-}C_5H_5)(CO)_2Mo(N_2CH_2SiMe_3) + CO$	*l*
1/4 *Insertions*			
$(\eta\text{-}C_5H_5)(CO)_2FeH$	+ $CH_2=CH\text{—}CH=CH_2$	→ $(\eta\text{-}C_5H_5)(CO)_2Fe(CH_2CH{:}CHCH_3)$	*m*

[a] B. B. Wayland and B. A. Woods, *J. Chem. Soc., Chem. Commun.*, 1981, 700. [b] M. R. Churchill, H. J. Wasserman, H. W. Turner, and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104**, 1710. [c] N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1974, 761. [d] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104. [e] J. D. Cotton, P. J. Davison, D. E. Goldberg, M. F. Lappert, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1974, 893. [f] H-F. Klein, R. Hammer, J. Gross, and U. Schubert, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 809. [g] M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 1347. [h] S. Otsuka, A. Nakamura, and H. Minamida, *J. Chem. Soc., Chem. Commun.*, 1969, 1148. [i] R. D. Gillard, B. T. Heaton, and D. H. Vaughan. *J. Chem. Soc. (A)*, 1970, 3126 and references therein. [j] L. S. Pu, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, 1968, **90**, 3896. [k] S. D. Robinson and A. Sahajpal, *Inorg. Chem.*, 1977, **16**, 2718. [l] M. F. Lappert and J. S. Poland, *J. Chem. Soc., Chem. Commun.*, 1969, 1061. [m] M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 1963, 189.

M—H bonds has also been cited as a possible explanation for the lability of certain carbonyl hydrides to ligand substitution.[101]

Hydrogen migration reactions involving carbene ligands have been postulated as intermediate steps in alternative mechanisms for the stereospecific polymerization of olefins by Ziegler–Natta catalysis.[102] Hydrogen migration onto co-ordinated olefin (or acetylene) ligands is a key step in hydrogenation reactions[103] and in one established mechanism for olefin isomerization.[104] The formation of hydro-peroxides is crucial in many transition metal mediated reactions for the oxidation of organic substrates.[105] Finally, the 'insertion' of carbon

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[101] R. G. Pearson, H. W. Walker, H. Mauermann, and P. C. Ford, *Inorg. Chem.*, 1981, **20**, 2741.

[102] K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 1978, 604.

[103] B. R. James, *Adv. Organomet. Chem.*, 1979, **17**, 319; 'Homogeneous Hydrogenation', Wiley-Interscience, New York, 1973.

[104] D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 3133.

[105] M. T. Atlay, M. Preece, G. Strukul, and B. R. James, *J. Chem. Soc., Chem. Commun.*, 1982, 406.

dioxide into M—H bonds to yield formates is a first step in one possible mechanism for the conversion of this abundant source of carbon into useful C_1 organic compounds.[106]

(vii) *Reductive Elimination Reactions*. These lead to the elimination of dihydrogen, hydrocarbons RH, or acids HX and require that the metal involved has a stable oxidation state two units below that existing in the parent complex (unless metal–metal bond formation occurs). Reductive elimination of dihydrogen from polyhydrides can readily be achieved by thermal or photolytic methods,[107] the presence of a donor ligand capable of reacting with the product often promotes the reaction. The species produced are electron deficient and are frequently highly reactive. Some are capable of taking up dinitrogen (equation 28)[108] or cleaving C—H bonds to form organo-hydrido complexes (equation 29).[109]

$$\mathrm{MoH_4(dppe)_2 + 2N_2 \xrightarrow{h\nu} Mo(N_2)_2(dppe)_2 + 2H_2} \quad (28)$$

$$\mathrm{WH_2(C_5H_5)_2 + C_6H_6 \xrightarrow{h\nu} WH(C_6H_5)(C_5H_5)_2 + 2H_2} \quad (29)$$

The instability of $CoH(CO)_4$ can be attributed in part to the formation of $Co_2(CO)_8$ by facile intermolecular elimination of dihydrogen. Reductive elimination of alkanes occurs readily, particularly if the participating hydride and alkyl ligands are mutually *cis*, and is a key step in the catalytic hydrogenation of olefins. The process can proceed by inter- or intra-molecular pathways. Thus, elimination of methane from *cis*-$OsH(Me)(CO)_4$ in the absence of added ligand affords $(OC)_4HOsOs(Me)(CO)_4$ whereas in the presence of a ligand L the mononuclear species $Os(CO)_4L$ is produced.[110] The ease with which alkane elimination occurs in many systems accounts for the scarcity of organo-hydrido complexes.

G. Complexes of Particular Interest.—(i) *Binary Hydride Species*. There are several reports in the early literature purporting to describe simple binary hydride species. In 1926 Weichselfelder[111] reported on the hydrogenation of PhMgBr/first row transition metal halide mixtures in ethereal suspensions and described black oily solid products which were formulated as the simple hydrides CrH_3, FeH_2, FeH_6, CoH_2, and NiH_2. Later workers confirmed the dihydrogen uptake but characterized the black solids as mixtures probably containing organometallic hydrides. However, a recent *X*-ray diffraction study on one of these products $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$ has revealed a FeH_6^{4-} anion surrounded by a tetrahedral arrangement of magnesium ions (Figure 1).[112]

An extensive series of solid state ternary hydrides, prepared by heating together powdered alkali metal hydrides and transition metals under hydrogen at *ca.* 600 —

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[106] R. Eisenberg and D. E. Hendriksen, *Adv. Catal.*, 1979, **28**, 79.

[107] G. L. Geoffroy, *Prog. Inorg. Chem.*, 1980, **27**, 123.

[108] G. L. Geoffroy, unpublished results cited in *ref.* 107.

[109] C. Giannotti and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1972, 1114.

[110] J. Halpern, *Acc. Chem. Res.*, 1982, **15**, 332.

[111] T. Weichselfelder and B. Thiede, *Liebig's Ann. Chem.*, 1926, **447**, 64.

[112] S. G. Gibbins, *Inorg. Chem.*, 1977, **16**, 2571 and references therein; R. Bau, D. M. Ho, and S. G. Gibbins, *J. Am. Chem. Soc.*, 1981, **103**, 4960.

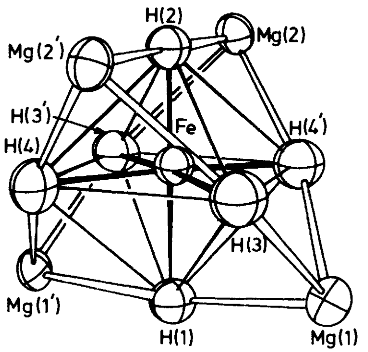

Figure 1 *View of the* $[FeH_6]^{4-}$ *anion surrounded by a tetrahedral array of magnesium cations*

800 °C appear to contain covalent transition metal – hydrogen linkages.[113] Diffraction studies on 'Sr_2RuD_6' and 'Li_4RhH_4' reveal the presence of RuD_6 octahedral (Ru—D = 1.69 Å) and RhH_4 square planar units respectively.[114] However, further work on these interesting products is required before their true

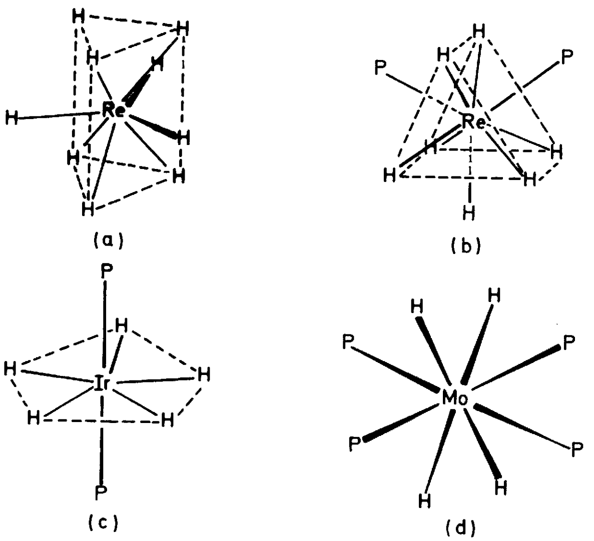

Figure 2 *Structures adopted by polyhydrides* (a) ReH_9^{2-}, (b) $ReH_7(PR_3)_2$, (c) $IrH_5(PR_3)_2$, (d) $MoH_4(PR_3)_4$ (P = phosphine)

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[113] J. D. Farr, *J. Inorg. Nucl. Chem.*, 1960, **14**, 202; A. F. Graefe and R. K. Robeson, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2917; R. O. Moyer, R. Lindsay, and D. N. Marks, *Adv. Chem. Ser.*, 1978, **167**, 366.

[114] L. B. Lundberg, D. T. Cromer, and C. B. Magee, *Inorg. Chem.*, 1972, **11**, 400; R. O. Moyer, C. Stanitski, J. Tanaka, M. I. Kay, and R. Kleinberg, *J. Solid State Chem.*, 1971, **3**, 541.

nature becomes fully apparent. In contrast the celebrated rhenium complex K_2ReH_9 and its technetium analogue have been very thoroughly characterized. Their structure (Figure 2a), fluxional character, stability, and chemical properties have been noted elsewhere in this review. The existence of isoelectronic species such as $[WH_9]^{3-}$ and $[OsH_9]^-$ has been speculated upon[56] but to date none has been isolated.

(ii) *Polyhydrides.* The small size of the hydride ligand favours high co-ordination numbers and although few binary polyhydrides have been reported a wide range of other polyhydrido complexes is known. Two particularly extensive series containing tertiary phosphine and cyclopentadienyl ligands respectively merit special mention. Phosphine-stabilized polyhydrido complexes, $MH_n(PR_3)_m$ (see Table 4a), are generally prepared by 'reduction' of metal halide complexes with $NaBH_4$ or $LiAlH_4$, often in the presence of dihydrogen. They are all white or pale yellow solids of moderate stability. All obey the 18-electron rule but most undergo photolytic or thermolytic loss of dihydrogen (see Section 2F). The variable temperature n.m.r. spectra and fluxional character of phosphine-stabilized polyhydrides in solution has been discussed above (Section 2C). Diffraction studies confirm that the solid-state structures are dominated by the bulky P donor ligands

Table 4 *Polyhydrido Complexes*

(a) MH_nL_m ($n \geqslant 3$; $L = PR_3$; $m = 1$—4)[a]

			FeH_4L_3	CoH_3L_3
NbH_5L_4	MoH_4L_4		*RuH_2L_4*	*$RhHL_4$*
			RuH_4L_3	RhH_3L_3
TaH_5L_4	WH_4L_4	ReH_3L_4	*OsH_2L_4*	*$IrHL_4$*
	$[WH_5L_4]^+$	$[ReH_4L_4]^+$	$[OsH_3L_4]^+$	
	WH_6L_3	ReH_5L_3	OsH_4L_3	IrH_3L_3
		ReH_7L_2	OsH_6L_2	IrH_5L_2
		$[ReH_8L]^-$		

(b) $MH_n(cp)_2$ ($n = 2,3$; cp = η-C_5H_5 or η-C_5Me_5)[a]

$TiH_2(cp)_2$				*$[FeH(cp)_2]^+$*
$ZrH_2(cp)_2$				
	$NbH_3(cp)_2$	$MoH_2(cp)_2$	*$TcH(cp)_2$*	
		$[MoH_3(cp)_2]^+$	$[TcH_2(cp)_2]^+$	*$[RuH(cp)_2]^+$*
	$TaH_3(cp)_2$	$WH_2(cp)_2$	*$ReH(cp)_2$*	
		$[WH_3(cp)_2]^+$	$[ReH_2(cp)_2]^+$	

[a] Also included (in italics) where known, are the mono and dihydrido complexes which complete the various series of compounds.

(Figures 2b—d). The chemistry of these compounds has recently been reviewed.[115]

Cyclopentadienyl-stabilized polyhydrides (Table 4b) have been prepared by numerous methods including hydrogenation of bis(cyclopentadienyl) complexes, 'reduction' of cyclopentadienyl metal halides, and treatment of anhydrous metal halides with NaC_5H_5 and $LiAlH_4$; the cationic species are usually obtained by protonation with strong acids. The simple mononuclear complexes $MH_n\ (C_5H_5)_2$ ($n = 1, 2,$ or 3) have an 'oblique' structure (Figure 3) with three chemically active orbitals in the equatorial plane. These orbitals can each accommodate a hydride ligand or a lone pair of electrons. The presence of a lone pair bestows base character and permits protonation or formation of adducts with Lewis acids (*i.e.* BF_3). Electron deficient species often adopt more complex hydrogen bridged binuclear structures. Some members of this group of polyhydrides are paramagnetic (see Sub-section V) others lose dihydrogen on photolysis to yield highly reactive unsaturated intermediates (see Section 2F). They are usually non-fluxional, thus the trihydrides $MH_3(C_5H_5)_2$ display AB_2 patterns in their high field proton n.m.r. spectra. Cyclopentadienyl metal hydrides have recently been reviewed.[116]

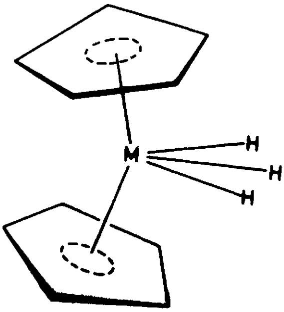

Figure 3 *'Oblique' structure adopted by bis(cyclopentadienyl)metal hydrides* $MH_n(\eta\text{-}C_5H_5)_2$ ($n = 1, 2,$ or 3)

(iii) *Cyanide Hydrides.* Although the cyanide anion is a strong field ligand and ought to 'stabilize' M—H bonds, remarkably few cyanide hydride complexes have been reported. The best known examples are the cobalt(III) anion $[CoH(CN)_5]^{3-}$ and its rhodium(III) and iridium(III) analogues. The ability of cobalt(II) cyanide solutions to absorb dihydrogen and catalyse the hydrogenation of activated olefins has been known since 1942.[117] However detection and characterization of the $[CoH(CN)_5]^{3-}$ anion in these solutions was first accomplished in 1958 using n.m.r.

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[115] A. P. Borisov, V. D. Makhaev, and K. N. Semenenko, *Koord. Khim.*, 1980, **6**, 1139; *Sov. J. Coord. Chem. (Engl. Transl.)*, 1980, **6**, 549.

[116] G. L. Soloveichik and B. M. Bulychev, *Usp. Khim.*, 1982, **51**, 597; *Russ. Chem. Rev.*, 1982, **51**, 286.

[117] M. Iguchi, *J. Chem. Soc. Jpn.*, 1942, **63**, 634, 1752.

methods.[118] All three anions $[MH(CN)_5]^{3-}$ have now been isolated as stable alkali metal salts.[119]

(iv) *Hydrides Stabilized by Weak Field Ligands.* The majority of hydrido complexes owe their stability to the presence of high field ligands. A few hydrido complexes are now known, however, in which the ancillary ligands are nitrogen, oxygen, sulphur, or halogen donors. A representative selection of these complexes, some of which display moderate stability is given in Table 5.

(v) *Paramagnetic Hydrides.* Since most hydride complexes obey the 16- or 18-electron rule, paramagnetic hydrides are comparatively rare. However, in the past decade a few fully authenticated examples have been isolated and others, including some very unstable intermediates, have been detected and characterized in solution by e.s.r. spectroscopy. Hyperfine couplings to the hydride ligands and, in appropriate cases, to the central metal nuclei have been detected and electron spin density distributions have been calculated. A representative selection of complexes, together with magnetic data and attendant references, is given in Table 6.

3 M—H····X and M····H—X Interactions

Numerous structures are now known in which terminal hydride ligands bound to transition metals interact with a second (non-transition) element. Conversely, there

Table 5 *Hydrido complexes stabilized by weak field ligands*

Complex	*Comments*	*Ref.*
$[CrH(H_2O)_5]^{2+}$	transient intermediate generated photochemically in solution. Similar species reported for Fe^{3+}, Ti^{4+}, and Ag^{2+}	*a*
$[RuHCl_5]^{3-}$	product from heterolytic cleavage of H_2 by $[RuCl_6]^{3-}$	*b*
$[OsH_2(en)_2][ZnCl_4]$		*c*
$[RhH(NH_3)_5]^{2+}$ *cis*/*trans*-$[RhHX(en)_2]^+$ (X = H or halide)	examples from substantial range, stability due in part to kinetic inertness of Rh^{III}	*d*, *e*
$IrHCl_2(Me_2SO)_3$	hydrogen transfer catalyst	*f*

[a] D. A. Ryan and J. H. Espenson, *Inorg. Chem.*, 1981, **20**, 4401. [b] P. J. Brothers, *Prog. Inorg. Chem.*, 1981, **28**, 1 and references therein. [c] J. Malin and H. Taube, *Inorg. Chem.*, 1971, **10**, 2403. [d] R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 1963, 3594. [e] J. A. Osborn, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 1964, 3168. [f] Y. M. Y. Haddad, H. B. Henbest, and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 1*, 1974, 592.

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[118] W. P. Griffith, L. Pratt, and G. Wilkinson, *Nature*, 1958, **182**, 466.

[119] I. B. Baranovskii, *Zh. Neorg. Khim.*, 1978, **23**, 2579; *Russ. J. Inorg. Chem.*, 1978, **23**, 1429 and references therein.

Table 6 *Paramagnetic hydrides*

Complex	*E.s.r. data*		*Magnetic data*	*Ref.*
	g-value	*H-hyperfine* (G)	μ_{eff}(BM)	
$TiH(C_5H_5)_2(PPh_3)$	1.992	10.0	—	*a*
$NbH_2(C_5H_5)_2$	2.010	11.7	—	*b*
$TaH_2(C_5H_5)_2$	2.060	—	—	*b*
$ReHCl_2(acac)(PPh_3)_2$	—	—	2.99	*c*
$FeH(dppe)_2$	2.085	—	1.80	*d*
$[FeHCl(dppe)_2]BF_4$	2.086	—	2.16	*d*
$[CoH\{P(OPh)_3\}_4]BF_4$	—	—	2.19	*e*
$CoH(BH_4)(PCy_3)_2$	2.025	—	2,15	*f*

[a] J. E. Bercaw and H. H. Brintzinger. *J. Am. Chem. Soc.*, 1969, **91**, 7301. [b] I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Manzer, G. W. Parshall. and F. N. Tebbe, *J. Am. Chem. Soc.*, 1974, **96**, 7374. [c] M. Freni. P. Romiti. and D. Giusto, *J. Inorg. Nucl. Chem.*, 1970, **32**, 145. [d] M. Gargano, P. Giannoccaro, M. Rossi, G. Vasapollo, and A. Sacco, *J. Chem. Soc., Dalton Trans.*, 1975, 9. [e] M. Nakajima, H. Moriyama. A. Kobayashi, T. Saito. and Y. Sasaki. *J. Chem. Soc., Chem. Commun.*, 1975, 80. [f] J. R. Sanders, *J. Chem. Soc., Dalton Trans.*, 1973, 748.

are many complexes in which a H atom in a co-ordinated ligand approaches to within bonding distance of the central metal atom. Only a very brief account of these structures can be given here; for a fuller discussion readers are referred to a recent excellent review article.[120]

A. M—H—B Linkages.—This type of bridge is encountered in borohydrido complexes where the tetrahedral BH_4^- anion can be bound to a transition metal in mono-, bi-, or tri-dentate manner. Examples of these three bonding modes have been confirmed by diffraction methods in $Cu(HBH_3)(PPh_2Me)_3$ (*ref.* 121), $Hf(H_2BH_2)(\eta\text{-}C_5H_4Me)_2$ (*ref.* 122), and $Zr(H_3BH)_4$ (*ref.* 123) respectively. In each case the bridging hydride ligands have been located by neutron or electron diffraction. Bidentate co-ordination of the BH_4^- anion is most common, mono- and tri-dentate co-ordination are relatively rare. The chemical and structural properties of these systems have recently been reviewed.[124] Transition metal complexes containing larger borane (*i.e.* B_3H_8, B_5H_8) or carbaborane (*i.e.* $C_2B_9H_{11}$) ligands co-ordinated through M—H—B bridges are also known.

B. M—H—Al Linkages. — These are still rather rare. A neutron diffraction study on $(\eta\text{-}C_5H_5)Ti(\mu\text{-}H)(\mu\text{-}H_2AlEt_2)(\mu\text{-}C_5H_4\text{-}C_5H_4)Ti(\eta\text{-}C_5H_5)$ confirmed the pres-

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[120] R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 1.

[121] C. Kutal, P. Grutsch, J. L. Atwood, and R. D. Rogers, *Inorg. Chem.*, 1978, **17**, 3558; F. Takusagawa, A. Fumagalli, T. F. Koetzle, S. G. Shore, T. Schmitkons, A. V. Fratini, K. W. Morse, C. Y. Wei, and R. Bau, *J. Am. Chem. Soc*, 1981, **103**, 5165.

[122] P. L. Johnson, S. A. Cohen, T. J. Marks, and J. M. Williams *J. Am. Chem. Soc.*, 1978, **100**. 2709.

[123] P. H. Bird and M. R. Churchill, *J. Chem. Soc., Chem. Commun.*, 1967, 403; V. Plato and K. Hedberg *Inorg. Chem.*, 1971, **10**, 590.

[124] T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.

ence of a H_2AlEt_2 bridge; molecular parameters within the Ti—H—Al linkages are Ti—H, 1.69 Å; Al—H, 1.70 Å; Ti····Al, 3.13 Å.[125] Similar M—H—Al bridges have been postulated for a number of early transition metal complexes.[116, 120]

C. M—H—C Linkages. — These are of considerable importance because of their possible implications in homogeneous catalysis. Their presence is usually detected by diffraction studies which reveal ligands arranged to bring one or more C—H groups within close proximity of the central metal atom. Early examples in which *X*-ray diffraction studies revealed short M····H—C interactions between the metal atom and an *ortho*-hydrogen of a phenyl phosphine ligand include $RuCl_2(PPh_3)_3$ (Ru···H, 2.59 Å)[126] *trans*-$PdI_2(PMe_2Ph)_2$ (red form Pd····H, 2.84, 2.85 Å; yellow form, Pd···H, 3.28 Å),[127] and $RhCl(PPh_3)_3$ (red form, Rh·····H, 2.77 Å; orange form Rh····H 2.84 Å).[128] More recently, structures involving much shorter M····H distances have been reported including $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3][BF_4]$ in which the Fe···H distance at 1.874(3) Å is only 0.1 Å longer than the normal terminal Fe—H bond, and the C—H bond involved is longer than usual [1.164(3) Å].[129] Other examples are found in metal clusters [*i.e.* $Fe_4(\eta^2\text{-}CH)H(CO)_{12}$][130] and in alkylidene complexes [*i.e.* Ta (=$CHBu^t$)(mesityl)$(PMe_3)_2$].[131] Finally, severe distortion or the alkyl ligands in the complexes $TiRCl_3$(dmpe) (R = Me or Et) has been attributed to the presence of strong intramolecular bonding interactions between the titanium atom and an α-H of the methyl group [Ti····H, 2.03(4) Å] or a β-H of the ethyl group (Ti····H, 2.29 Å).[132]

D. M—H···Si Linkages. — Although several complexes have been claimed to display M—H—Si bridges these claims have rarely been fully substantiated. The best established M—H—Si linkage is found in $W_2(\mu\text{-}HSiPh_2)_2(CO)_8$ where W—Si distances of 2.586 and 2.703 Å are attributed to W—Si and W····H····Si bonds respectively.[133] Structures of this type have been discussed in a recent review.[120]

4 Edge Bridging (μ_2) Hydrides

A. A Note on Polynuclear Clusters. — Unlike terminal hydrides which are confined largely, though not exclusively, to mononuclear complexes, μ_2, μ_3 and encapsulated hydride ligands are, of necessity, found only in polynuclear clusters where they occupy edge, face, and interstitial sites respectively. Therefore, before embark-

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[125] L. J. Guggenberger and F. N. Tebbe, *J. Am. Chem. Soc.*, 1973, **95**, 7870.

[126] S. J. LaPlaca and J. A. Ibers. *Inorg. Chem.*, 1965. **4**, 778.

[127] N. A. Bailey and R. Mason, *J. Chem. Soc. (A)*, 1968, 2594.

[128] M. J. Bennett and P. B. Donaldson, *Inorg. Chem.*, 1977, **16**, 655.

[129] J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel. *J. Am. Chem. Soc.*, 1978, **100**, 7407 and with R. L. Harlow. 1980. **102**, 981.

[130] M. A. Beno. J. M. Williams, M. Tachikawa, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1980, **102**, 4542.

[131] M. R. Churchill and W. J. Youngs, *Inorg. Chem.*, 1979, **18**, 1930.

[132] Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa, and K. Prout, *J. Chem Soc., Chem. Commun.*, 1982, 802 and 1410.

[133] M. J. Bennett and K. A. Simpson. *J. Am. Chem. Soc.*, 1971, **93**, 7156.

ing upon a discussion of these types of hydride ligand some reference to the properties of metal clusters seems appropriate. The structure and stoicheiometry of the smaller (2, 3, and 4 membered) clusters can usually be rationalized in terms of the E.A.N. (18-electron) rule. Larger clusters require more sophisticated treatments and these have been provided by Chini, Hoffmann, Mingos, Wade, and others.[134] A full account of this work is given in a recent review by Johnson and Lewis.[135] Turning to the more immediate question of stoicheiometry and structure in polynuclear metal hydrides we note the formal analogy between these systems and polynuclear boron hydride clusters. This relationship has recently been recognized by the extension of Lipscomb's 'styx' formulae for boranes[136] to cover polynuclear transition metal hydrido clusters.[137] The mechanistic features of dynamic rearrangements in metal cluster species including polynuclear complex hydrides have recently been reviewed.[138]

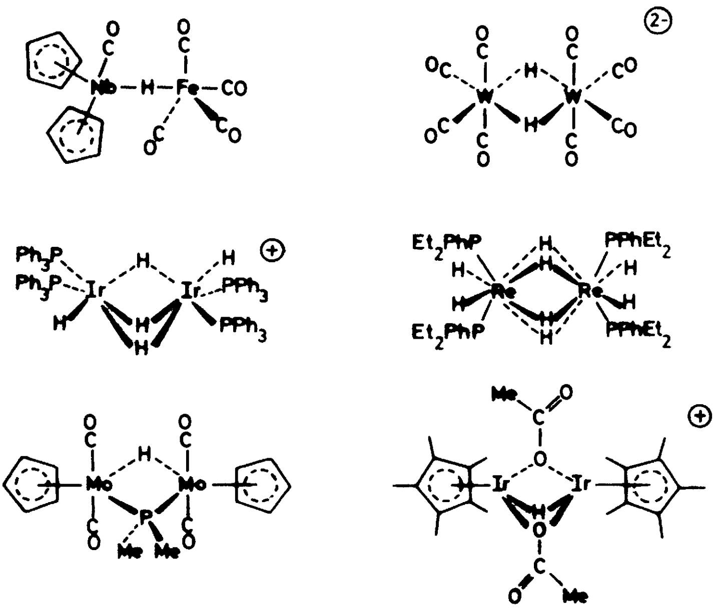

Figure 4 *Typical structures involving bridging* (μ_2) *hydride ligands*

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[134] P. Chini, *Inorg. Chim. Acta Rev.*, 1968, **2**, 31; P. Chini and B. T. Heaton, *Top. Curr. Chem.*, 1977, **71**, 1; P. Chini, G. Longoni, and V. G. Albano. *Adv Organomet. Chem.*, 1976, **14**, 285; M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058; D. M. P. Mingos, *Nature (London) Phys. Sci.*, 1972, **236**, 99; *J. Chem. Soc., Dalton Trans.*, 1974, 133; K. Wade, *Chem. Br.* 1975, **11**, 177; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

[135] B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 225; 'Transition Metal Clusters', ed. B. F. G. Johnson, Wiley, New York, 1980.

[136] W. N. Lipscomb, 'Boron Hydrides', Benjamin, New York, 1963.

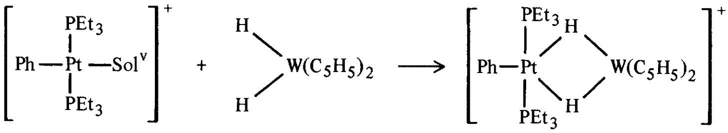
[137] J. C. Green, D. M. P. Mingos, and E. A. Seddon, *J. Organomet. Chem.*, 1980, **185**, C20; D. M. P. Mingos, *Pure. Appl. Chem.*, 1980, **52**, 705.

[138] E. Band and E. L. Muetterties, *Chem. Rev.*, 1978, **78**, 639.

B. Edge-bridging (μ_2) Hydrides. — Whereas the ability of hydrogen to bridge between boron atoms has been known since the 1940's, the formation of similar H-bridges between transition metal atoms was discovered relatively recently. However, following Hieber's synthesis[139] of the first polynuclear metal carbonyl hydrides, by treatment of metal carbonyls with base, a very extensive chemistry of μ_2-hydride bridged species has developed. Structures in which pairs of metal atoms are linked by mono-, di-, tri-, or tetra-hydride bridges, or by mixed bridges in which one or more hydrogens are replaced by other bridging groups (*i.e.* halide, OR, SR, PR_2, or CO) have now been established. A representative selection of examples is given in Figure 4.

Edge bridging (μ_2) hydride ligands are also frequently encountered in larger metal cluster polyhedra.

C. Preparative Methods. — Many of the early μ_2-hydrido complexes were the products of serendipitous reactions. However, as reactivity patterns in hydride chemistry have emerged more systematic approaches to synthesis have been developed. Thus, recognition of a formal scheme whereby mononuclear hydrido complexes act as donor 'ligands' binding through one or more hydride atoms to a co-ordinatively unsaturated acceptor complex has permitted the synthesis by design of many binuclear H-bridged species.[140] Examples of these reactions, some of which involve subsequent elimination of dihydrogen from the adduct, are given in equations 30—32.



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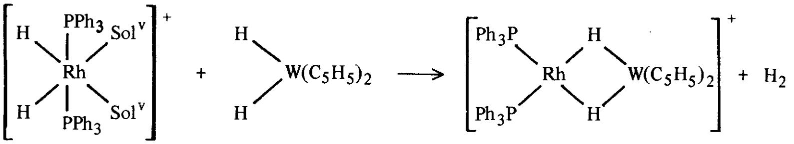
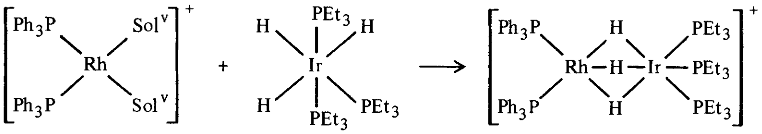


(31)



(32)

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[139] W. Hieber and G. Brendel, *Z. Anorg. Allg. Chem.*, 1957, **289**, 324; W. Hieber and R. Werner, *Chem. Ber.*, 1957, **90**, 286.

[140] L. M. Venanzi, *Coord. Chem. Rev.*, 1982, **43**, 251.

More complex polynuclear species have been synthesized from metal carbonyl cluster precursors by a diverse variety of highly specific reactions. These include protonation, oxidative addition of dihydrogen, activated hydrocarbons or functional organic molecules, cyclometallations, reactions with water, and base or borohydride 'reduction'. Some examples are given in equations 33—36, a fuller account may be found in a recent review.[141]

$$Ru_3(CO)_{12} \xrightarrow{\text{Conc. } H_2SO_4} [Ru_3H(CO)_{12}]^+ \tag{33}$$

$$Os_3(CO)_{12} + H_2 \longrightarrow Os_3H_2(CO)_{10} + 2CO \tag{34}$$

$$Os_3(CO)_{12} + C_2H_4 \xrightarrow[\text{octane}]{125\,^{\circ}C} Os_3H_2(C{=}CH_2)(CO)_9 + 3CO \tag{35}$$

$$Ru_3(CO)_{12} + H_2O \xrightarrow[24\,h]{135\,^{\circ}C} Ru_4H_2(CO)_{13} + Ru_4H_4(CO)_{12} \tag{36}$$

D. Characterization. — Bridging (μ_2) hydride ligands are usually more firmly bound than their terminal counterparts, consequently their detection and estimation by chemical means (reactions with halogenated hydrocarbons or halogen acids) is not usually feasible. Most bridging hydride ligands are characterized by one or more of the spectroscopic methods discussed below — notably n.m.r. and mass spectroscopy.

E. Spectroscopic Properties. — (i) *Vibrational Spectroscopy.* Bands due to ν(M—H—M) modes are frequently difficult to detect; they occur in a rather congested region of the spectrum (1700—700 cm^{-1}) and are usually broad ($\Delta\nu_{\frac{1}{2}} \sim 100\,cm^{-1}$) and weak.[142] However, in some instances, cooling of the sample to liquid nitrogen temperatures has been shown to effect a marked increase in intensity; a result which has been interpreted in terms of a double potential minimum for the M—H—M interaction.[143] The frequencies of ν(M—H—M) modes have been shown to correlate with the corresponding M—H—M angles;[144, 145] conversely the ν(Mo—H—Mo) frequencies of $[Mo_2HCl_8]^{3-}$ have been used to calculate $\angle$Mo—H—Mo and hence, given the Mo···Mo distance, the Mo—H bond length.[146] The dark colours and sensitivity to laser radiation associated with many cluster compounds have hindered Raman studies. Where work has been reported bands are described as broad, weak,[144] and numerous.[142] The literature on vibrational spectra of hydride bridged species has recently been surveyed.[142]

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[141] A. P. Humphries and H. D. Kaesz, *Prog. Inorg. Chem.*, 1979, **25**, 145.

[142] C. B. Cooper, D. F. Shriver, and S. Onaka, *Adv. Chem. Ser.*, 1978, No. 167, p. 232.

[143] D. C. Harris and H. B. Gray, *J. Am. Chem. Soc.*, 1975, **97**, 3073.

[144] H. D. Kaesz and S. W. Kirtley, *Abstracts 163rd Am. Chem. Soc. Meeting Boston Mass.*, 1972, Inorg. 131.

[145] M. W. Howard, U. A. Jayasooriya, S. F. A. Kettle, D. B. Powell, and N. Sheppard, *J. Chem. Soc., Chem. Commun.*, 1979, 18.

[146] V. Katović and R. E. McCarley *Inorg. Chem.*, 1978, **17**, 1268.

(ii) *Nuclear Magnetic Resonance Spectroscopy*. The application of high field n.m.r. spectroscopy to hydride bridged species is sometimes prevented by low solubility or by very long (or short) relaxation times.[147] Where spectra have been obtained resonances due to μ_2-bridging hydrides usually occur at rather higher field (*ca.* 25—35τ) than those of their terminal counterparts. Temperature-dependent n.m.r. spectroscopy has been employed to study dynamic equilibria involving rapid intramolecular exchange of μ_2-hydride ligands (see Section 4H). Preliminary results from solid state studies on several polynuclear carbonyl hydrides have been described, newer multiple-pulse techniques suppress the proton–proton dipolar interaction and allow data on the smaller interactions to be obtained.[148] Nematic phase n.m.r. studies coupled with structural information concerning heavy metal atoms have permitted the precise location of the hydride ligands in $Ru_3H_3(CMe)(CO)_9$.[149]

(iii) *Miscellaneous Spectroscopic and Physical Techniques*. Since many hydrido clusters contain numerous carbonyl ligands and are moderately volatile they are ideal candidates for study by mass spectrometry. Whereas terminal hydride ligands are frequently lost upon ionization, bridging hydride ligands are tenaciously retained — right down to the bare hydrido metal cluster in some instances.[147] Mass spectroscopy therefore offers a means of distinguishing between terminal and bridging hydride ligands.[150]

U.v. photoelectron spectra of $Re_3H_3(CO)_{12}$, $Os_4H_4(CO)_{12}$, and $Os_3H_2(CO)_{10}$ show broad ionization bands at *ca.* 11.9 — 12.7 eV that have been interpreted in terms of localized three centre, two electron (3*c*, 2*e*) bonds centred largely on the hydrogen atom.[137]

A combination of Mössbauer and diffraction methods was used to determine the structure of $Fe_3H(SPr^i)(CO)_9$. [151]Mössbauer spectroscopy has also been used to demonstrate the presence of two different iron environments in $Fe_3H(C{=}NMe_2)(CO)_{10}$.[152]

F. Diffraction Studies. — Because bridging hydrides are situated in close proximity to two or more heavy metal atoms the problems encountered in their location by *X*-ray diffraction methods are even more acute than those experienced with terminal hydrides. The situation can be improved by use of data treatment techniques, notably the elimination of high angle data and the application of Fourier averaging methods. However, even with these aids results are unpredictable. Therefore, in spite of the technical problems involved, neutron diffraction is the preferred method for location of bridging hydride ligands. A hybrid method, recently devel-

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[147] M. J. Mays and R. N. F. Simpson, *J. Chem. Soc (A)*, 1968, 1444.

[148] A. T. Nicol and R. W. Vaughan, *Adv. Chem. Ser.*, 1978, No. 167, p. 248.

[149] G. M. Sheldrick and J. P. Yesinowski, *J. Chem. Soc., Dalton Trans.*, 1975, 873 and references therein.

[150] B. F. G. Johnson, J. Lewis, and P. W. Robinson, *J. Chem. Soc., Dalton Trans.*, 1970, 1684.

[151] R. Bau, B. Don, R. Greatrex, R. J. Haines, R. A. Love, and R. D. Wilson, *Inorg. Chem.*, 1975, **14**, 3021.

[152] R. Greatrex, N. N. Greenwood, I. Rhee, M. Ryang, and S. Tsutsumi, *J. Chem. Soc., Chem. Commun.*, 1970, 1193.

oped by Sheldrick *et al.*[153] involves simultaneous least squares refinement of complementary *X*-ray and neutron diffraction data and thus reduces the number of neutron data required. In those instances where hydride ligands have not been located directly by diffraction methods, their positions can often be deduced from indirect evidence including M—M bond distances (see Section 4G), electron counts, and ligand orientations. A combination of *X*-ray diffraction studies, to establish the heavy atom framework, and potential energy calculations to optimise the position of hydride ligands within that framework has been used to predict hydride positions in several cluster structures.[154]

G. Nature of M—H—M Bridges. — (i) *Monohydride Bridged Species M—H—M.* Early *X*-ray diffraction studies on unsupported single bridged systems, notably $[Cr_2H(CO)_{10}]^-$ gave electron density projections which were taken to imply the presence of a linear M—H—M linkage. However, a later neutron diffraction study established that the bridging H position in $[Cr_2H(CO)_{10}]^-$ is two-fold disordered and that the angle Cr—H—Cr is in fact 158.9°.[155] Numerous systems of this type, including several hetero-bimetallic complexes, have all been shown to contain bent M—H—M linkages (∠M—H—M *ca.* 160° to 123°). Neutron diffraction studies on several molecules with 'unsupported' M—H—M bonds including $W_2H(CO)_9(NO)$[156] and $W_2H(CO)_8(NO)\{P(OMe)_3\}$[157] revealed that the bridging hydride ligands are located at 'off axis' positions (Figure 5). This arrangement is consistent with the presence of 'closed' three centre, two electron (3*c*, 2*e*) bonds (Figure 6) analogous to those found in borane chemistry and thus implies a certain degree of metal–metal bonding. Consequently the concept of bond order is difficult to quantify in these systems. Although most M—H—M systems are symmetrical, the presence of non-equivalent ligand sets can produce marked asymmetry. For example, the complex salt $[NEt_4][Mo_2(\mu\text{-}H)(CO)_9(PPh_3)]$ has Mo—H bond lengths of 1.68 and 2.19 Å.[158] More surprisingly, marked asymmetry of the

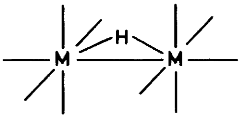

Figure 5 *Off-axis location of hydride ligand in 'unsupported'* M—H—M *linkage*

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[153] A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *J. Chem. Soc., Chem. Commun.*, 1978, 723; A. G. Orpen, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *Acta Cryst.*, 1978, **B34**, 2466.

[154] A. G. Orpen, *J. Organomet. Chem.*, 1978, **159**, C1; *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

[155] J. Roziere, J. M. Williams, R. P. Stewart, J. L. Petersen, and L. F. Dahl, *J. Am. Chem. Soc.*, 1977, **99**, 4497.

[156] J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, 1974, **96**, 6621.

[157] R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Whittlesey, and R. Bau, *J. Am. Chem. Soc.*, 1976, **98**, 4491.

[158] M. Y. Darensbourg, J. L. Atwood, R. R. Burch, W. E. Hunter, and N. Walker, *J. Am. Chem. Soc.*, 1979, **101**, 2631.

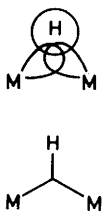

Figure 6 *'Closed'* M—H—M *bond* (a) *orbital representation* (b) *symbol*

W—H—W linkage in the 'symmetrical' complex anion $[W_2H(CO)_{10}]^-$ (W—H, 1.718 and 2.070 Å) has been found by low temperature (14 K) neutron diffraction.[159] This situation has been further complicated by the discovery that the $[W_2H(CO)_{10}]^-$ anion can adopt 'linear'/eclipsed (Figure 7a) or 'bent'/staggered (Figure 7b) structures depending upon the nature of the cation present.[160] In addition to the mounting number of binuclear species containing 'unsupported' hydride bridges there are numerous examples of H atoms occupying edge-bridging sites in larger polynuclear structures. Indeed, the growing body of diffraction data indicate that edge bridging is the most common form of attachment for hydride ligands in metal clusters.

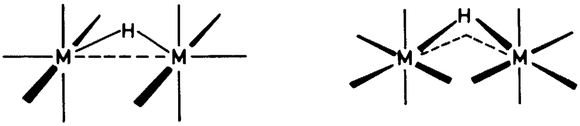

Figure 7 *Structures adopted by* $[W_2H(CO)_{10}]^-$ *anion,* (a) *linear/eclipsed and* (b) *bent/staggered*

(ii) *Dihydride Bridged Species* $M—(\mu\text{-}H)_2—M$. Binuclear structures containing the $M—(\mu\text{-}H)_2—M$ unit including $Re_2H_2(CO)_8$[161] and $[W_2H_2(CO)_8]^{2-}$ (*ref.* 162) were first characterized by diffraction methods in the early 1970's, the first heterobimetallic structure of this type $[(C_5H_5)_2W(\mu\text{-}H)_2Rh(PPh_3)_2]^+$ was reported in 1979.[163] Dihydride bridges have also been observed in a small number of metal cluster species including $Os_3H_2(CO)_{10}$.[164] In contrast to the hydrogen atoms in single bridged complexes which are found to lie 'outside' the intersection point of the *trans*-ligand vectors, the hydrogen atoms in $M—(\mu_2\text{-}H)_2—M$ systems lie within the intersection region of the ligand-metal vectors (Figure 8). The arrangement is usually discussed in terms of a four centre, four electron (4*c*,4*e*) bond.[164]

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[159] D. W. Hart, R. Bau, and T. F. Koetzle, unpublished work cited in *ref.* 120.

[160] R. D. Wilson, S. A. Graham, and R. Bau, *J. Organomet. Chem.*, 1975, **91**, C49.

[161] M. J. Bennett, W. A. G. Graham, J. K. Hoyano, and W. L. Hutcheon, *J. Am. Chem. Soc.*, 1972, **94**, 6232.

[162] M. R. Churchill and S. W.-Y. Chang, *Inorg. Chem.*, 1974, **13**, 2413.

[163] N. W. Alcock, O. W. Howarth, P. Moore, and G. E. Morris, *J. Chem. Soc., Chem. Commun.*, 1979, 1160.

[164] R. W. Broach and J. M. Williams, *Inorg. Chem.*, 1979, **18**, 314.

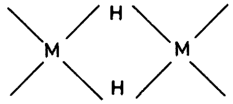

Figure 8 $M(\mu_2\text{-H})_2M$ *linkage; location of hydrogen atoms within the intersection region of the metal–ligand vectors*

(iii) *Trihydride Bridged Species $M—(\mu_2\text{-}H)_3—M$.* Complexes containing this grouping are still relatively rare, the first structurally characterized examples $[Fe_2(\mu_2\text{-H})_3(\text{triphos})_2][PF_6]$ and $[Co_2(\mu_2\text{-H})_3(\text{triars})_2][BPh_4]$ were reported in 1973.[165] Other more recently characterized structures include $[Ir_2(\mu_2\text{-H})_3(C_5Me_5)_2][BF_4]$,[166] the isoelectronic species $[Ir_2(\mu_2\text{-H})_3H_2(PPh_3)_4][PF_6]$,[167] and the heterobimetallic complex $[(Et_3P)_3Ir(\mu_2\text{-H})_3Rh(\text{dppe})][BF_4]$.[168] In each case the bridging hydrogen atoms lie 'within' the intersection region of the metal ligand vectors.

(iv) *Tetrahydride Bridged Species $M—(\mu_2\text{-}H)_4—M$.* The $M—(\mu_2\text{-H})_4—M$ core has been structurally characterized in $Re_2H_8(PEt_2Ph)_4$ (Figure 9)[169] — the

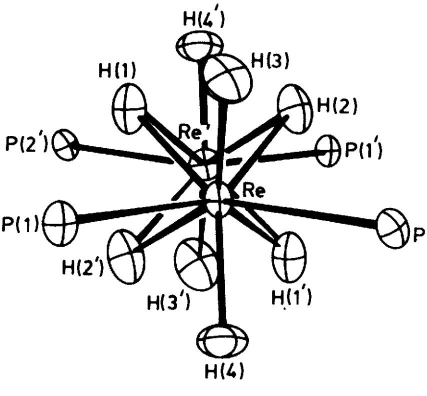

Figure 9 *The skeleton of the* $Re_2H_8(PEt_2Ph)_4$ *complex, viewed approximately along the* Re—Re *axis*

'agnohydride' $[ReH_n(PEt_2Ph)_2]_2$ of Chatt and Coffey.[170] The bonding has been rationalized in molecular orbital terms.[171] The only other example proposed to date has been postulated for $Ta_2Cl_4H_4(PMe_3)_4$.[172] The existence of the

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[165] P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Am. Chem. Soc.*, 1973, **95**, 2021; P. Dapporto, S. Midollini, and L. Sacconi, *Inorg. Chem.*, 1975, **14**, 1643.

[166] R. Bau, W. E. Carroll, D. W. Hart, and R. G. Teller, *Adv. Chem. Ser.*, 1978, **167**, 73.

[167] R. H. Crabtree, H. Felkin, and G. E. Morris, *J. Organomet. Chem.*, 1977, **141**, 205.

[168] A. Albinati, A. Musco, R. Naegeli, and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.* 1981, **20**, 958.

[169] R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, 1977, **99**, 3872.

[170] J. Chatt and R. S. Coffey, *J. Chem. Soc. (A)*, 1969, 1963.

[171] A. Dedieu, T. A. Albright, and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **101**, 3141.

[172] R. B. Wilson, A. P. Sattelberger, and J. C. Huffman, *J. Am. Chem. Soc.*, 1982, **104**, 858.

M—(μ_2-H)$_5$—M core has been speculated upon[171] but examples have yet to be found.

(v) *M—M and M—H Bond Distances.* Bridging M—H bonds tend to be significantly longer (*ca.* 0.15—0.20 Å) than their terminal counterparts, a situation parallel to that found in boranes. Typical values are *ca.* 1.6—1.9 Å for first row metals and *ca.* 1.7—2.1 Å for second and third row metals. In the absence of other bridging groups, the metal–metal distances in M(μ_2-H)M structures are *ca.* 0.1 to 0.4 Å longer than the M—M bonds in comparable non-bridged systems. Addition of further μ_2-H bridges decreases the M—M distance. Thus the observed trend in M—M distances is M(μ_2-H)M > M—M > M(μ_2-H)$_2$M > M(μ_2-H)$_3$M > M(μ_2-H)$_4$M. The introduction of non-hydridic (4-electron donor) bridging groups (*i.e.* Cl^-, OR^-, SR^-) leads to lengthening of M—M distances.[173] The short M—M distances in M(μ_2-H)$_n$M (n = 2, 3, or 4) linkages have been rationalized in terms of M—M multiple bonds.[162, 165, 166]

(iv) *Acidity of Bridging (μ_2) Hydrides.* Bridging hydride ligands in transition metal clusters are considerably more acidic than their terminal counterparts.[85] This observation, though rather anomalous at first sight, parallels that made for terminal and bridging hydrogen atoms in boranes.[174] In an early quantitative study Hieber[175] established the acidity order $Fe_3H_2(CO)_{11}$ > $Fe_2H_2(CO)_8$ > $FeH_2(CO)_4$; later workers[176] have shown that $Fe_3H_2(CO)_{11}$ is fully ionized in solution. Deprotonation is observed to occur with reagents of low nucleophilicity and high basicity (*i.e.* OH^-, OMe^-, or amines); very strong bases often cause degradation of the cluster.

H. Chemical Reactivity.—Bridging (μ_2) hydrides are generally less reactive than their terminal counterparts. However, the expanding organometallic chemistry of metal cluster complexes includes many reactions involving hydride ligands. Since these are beyond the scope of the present article, interested readers are referred to recent more specialized reviews.[135]

(i) *Dynamic Equilibria.* In polynuclear cluster structures fluxional behaviour involving rapid intramolecular exchange of hydride ligands between μ_2 and μ_3 or terminal sites is often observed.[138] Examples include $Re_2H_8(PEt_2Ph)_4$ (Figure 9) where terminal and bridging hydride ligands are equivalent on the n.m.r. time scale at temperatures down to 273 K,[169] $[Ir_3H_7(Ph_2PCH_2CH_2CH_2CH_2PPh_2)_3][BF_4]_2$ which undergoes rapid intramolecular scrambling of the μ_2 and μ_3 bridging hydride ligands,[177] and $Ru_4(\mu_2\text{-}H)_4(CO)_{11}\{P(OMe)_3\}$ in which μ_2-hydride ligands in non-equivalent sites participate in fast exchange down to below 173 K.[178] In binuclear systems dynamic isomerization processes involving *cis–trans* inter-

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[173] M. R. Churchill and R. A. Lashewycz, *Inorg. Chem.*, 1979, **18**, 1926, 3261; M. R. Churchill and S. A. Julis, *Inorg. Chem.*, 1977, **16**, 1488.

[174] E. L. Muetterties, 'Boron Hydride Chemistry', Academic Press, New York, 1975.

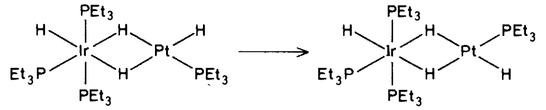
[175] W. Hieber and G. Brendel, *Z. Anorg. Allgem. Chem.*, 1957, **289**, 324.

[176] H. A. Hodali, D. F. Shriver, and C. A. Ammlung, *J. Am. Chem Soc.*, 1978, **100**, 5239.

[177] H. H. Wang and L. H. Pignolet, *Inorg. Chem.*, 1980, **19**, 1470.

[178] S. A. R. Knox and H. D. Kaesz, *J. Am. Chem. Soc.*, 1971, **93**, 4594.

changes (equation 37) and ligand migrations (equation 38) are also encountered.[140]



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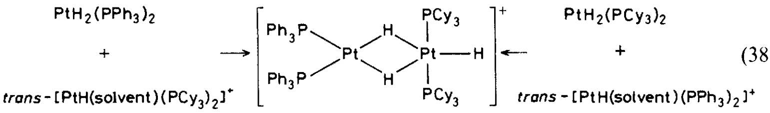
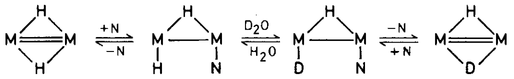


(38)

(ii) *Hydrogen–Deuterium Exchange.* Although bridging hydride ligands display considerable thermodynamic acidity they are frequently slow to undergo H–D exchange with D_2O or D_3PO_4. Exchange is much faster if terminal hydride ligands are also present or can be introduced. The catalysis of H–D exchange in these systems by chromatographic supports (Florisil) has been attributed to formation of terminal hydride ligands by nucleophilic attack on the cluster (equation 39).[179]



(39)

5 Face Bridging (μ_3) Hydrides

The face bridging mode of hydrogen binding, first reported in 1968,[180] is relatively rare and has only been fully established in metal-cluster chemistry where about twenty examples involving hydride ligands located above the triangular faces of metal or metal–boron polyhedra have been identified. There is also evidence that hydrogen chemisorbed onto metal surfaces exists as atoms bound in μ_3 manner to triangular groups of adjacent metal atoms.[181]

A. Preparative Methods.—Very few μ_3-bridged hydrido complexes have been synthesized by design and no simple systematic preparative routes are known at present. Some typical synthesis are shown in equations 40—42.

$$Re_3H_3(CO)_{12} \xrightarrow[\text{octane}]{\Delta, 1h} Re_4H_4(CO)_{12} \tag{40}$$

$$[Co(C_5H_5)(NO)]_2 \xrightarrow[\text{THF}]{\text{LiAlH}_4\text{-AlCl}_3} Co_4H_4(C_5H_5)_4 \tag{41}$$

$$[Ir(C_8H_{12})py(PCy_3)][PF_6] \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{H}_2, 273\text{ K}} [Ir_3H_7py_3(PCy_3)_3][PF_6]_2 \tag{42}$$

B. Characterization.—Hydride ligands bound in μ_3-bridging mode are rather inert and cannot therefore be readily detected by chemical means. Characterization by

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[179] M. A. Andrews, S. W. Kirtley, and H. D. Kaesz, *Adv. Chem. Ser.*, 1978, No. 167, p. 215.

[180] O. S. Mills and E. F. Paulus, *J. Organomet. Chem.*, 1968, **11**, 587.

[181] R. G. Teller, R. D. Wilson, R. K. McMullan, T. F. Koetzle, and R. Bau, *J. Am. Chem. Soc.*, 1978, **100**, 3071.

spectroscopic techniques is difficult, and location by diffraction methods is not without problems.

C. Spectroscopic Properties.—(i) *Vibrational Spectra.* The rather weak broad absorptions associated with the vibrational modes of μ_3-bridging hydride ligands occur in a crowded region of the spectrum (1200—600 cm^{-1}), consequently they have attracted relatively little attention.[42] However, in a recent study on carbonyl hydrido clusters assignments were made on the basis of deuteriation experiments and a vibrational model relating the ratio $\nu(\mathrm{M{-}H})_{\mathrm{asym}}/\nu(\mathrm{M{-}H})_{\mathrm{sym}}$ to the angular disposition of the three M—H bonds was successfully developed.[182]

(ii) *Nuclear Magnetic Resonance Spectroscopy.* Relatively few data are available since the small number of μ_3-bridged hydrido complexes known include several which for various reasons do not display high field proton resonances. Where high field signals have been recorded their positions range from *ca.* τ 15 for $Re_4H_4(CO)_{12}$ to *ca.* τ 33 for $Co_4H_4(C_5H_5)_4$ (*refs.* 183 and 184).

In several instances fluxional behaviour has been detected by n.m.r., thus ^{13}C n.m.r. spectra for the anion $[Os_6H(CO)_{18}]^-$ reveal rapid migration of the μ_3-H ligand between all eight faces of the octahedron above 188 K.[185] Rapid exchange of μ_2 and μ_3 hydride ligands has been noted earlier (Section 4H).

(iii) *Mass Spectroscopy.* Face bridging hydride ligands tend to be firmly bound, species containing this grouping usually afford parent molecular ions and frequently lose all other ligands in stepwise fashion to leave the naked metal hydrido cluster ion.[147]

D. Diffraction Methods.—Most known face bridged hydrido complexes have been characterized by *X*-ray diffraction methods. Usually the μ_3-hydride ligands cannot be located directly because of the adjacent heavy metal atoms and their positions have to be inferred from spectroscopic or structural evidence. Early examples solved in this way include $Rh_3H(C_5H_5)_4$, where the location of the hydride ligand centred over one face of the Rh_3 triangle was deduced from the high field proton n.m.r. quartet pattern[180] and $Ru_6H_2(CO)_{18}$ where carbonyl groups distorted away from enlarged Ru_3 faces betrayed the positions of the μ_3-hydride ligands.[186] However, location of μ_3-hydride ligands in the highly symmetrical pseudo-tetrahedral $Re_4H_4(CO)_{12}$ cluster was achieved directly from *X*-ray diffraction data by an image enhancement process involving superimposition of electron density functions calculated for all six mirror planes of the tetrahedron to yield composite difference maps.[187] Other clusters in which μ_3-hydride ligands have been located by *X*-ray or neutron diffraction methods include $Co_4H_4(C_5H_5)_4$ (*ref.* 188),

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[182] J. A. Andrews, U. A. Jayasooriya, I. A. Oxton, D. B. Powell, N. Sheppard, P. F. Jackson, B. F. G. Johnson, and J. Lewis, *Inorg. Chem.*, 1980, **19**, 3033.

[183] R. Saillant, G. Barcelo, and H. Kaesz, *J. Am. Chem. Soc.*, 1970, **92**, 5739.

[184] J. Müller and H. Dorner, *Angew. Chem., Int. Edn. Engl.*, 1973, **12**, 843.

[185] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1976, 302.

[186] M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, 1971, **93**, 5670.

[187] R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, 1976, **98**, 4687.

[188] G. Huttner and H. Lorenz, *Chem. Ber.*, 1975, **108**, 973.

$Ni_4H_3(C_5H_5)_4$ (*ref.* 189), and $FeCo_3H(CO)_9\{P(OMe)_3\}$ (*ref.* 181). Finally, face-bridging hydride ligands have been located in metalloborane clusters including $FeH_2(Me_2C_2B_4H_4)_2$ (H on FeB_2 face) and $Co_2(B_4H_6)(C_5H_5)_2$ (H on Co_2B face).[190]

E. Nature of Face Bridging Hydride.—Face bridging (μ_3) hydride ligands are generally located *ca.* 0.9—1.0 Å above the centre of a triangular M_3 face,[191] metal–hydrogen distances range from *ca.* 1.55 Å (Ni—H) to 1.77 Å (Re—H),[120] metal–metal distances are close to the inter-atomic separations in the bulk metal.[191] The metal hydrogen interaction can be described in terms of four centre, two electron (4*c*,2*e*) bonds; a rationalization of bonding in tetrahedral metal clusters containing μ_2 and μ_3 hydride ligands has been given by Hoffmann and co-workers.[192] Since the triangular M_3 groups involved in μ_3-hydride binding possess dimensions similar to those encountered in certain faces of solid metal crystals (notably {111} or {011} surfaces of CCP or HCP metals, respectively) several authors have drawn attention to possible analogies between μ_3-hydride ligands bound in metal cluster complexes and hydrogen atoms chemisorbed on metal surfaces.[191, 193, 194] The suggestion that hydrogen atoms chemisorbed on the Pt(111) face occupy threefold bridging sites has been supported by electron-energy-loss spectroscopy, which gave frequencies of 1230 and 550 cm^{-1} for $\nu(Pt—H)_{asym}$ and $\nu(Pt—H)_{sym}$ respectively.[194]

F. Chemical Reactions.—The few known μ_3-hydride complexes tend to be rather inert thus $Co_4H_4(C_5H_5)_4$ withstands heating to 300 °C under N_2.[184] In several instances intramolecular exchange of μ_2 and μ_3 hydride ligands has been observed but few chemical reactions involving μ_3-hydride ligands have been reported.

6 Encapsulated (Interstitial) Hydrides

Transition metal hydride chemistry came full circle in 1967 with the characterization of $\{(Nb_6HI_8)I_{6/2}\}_\infty$, the first non-metallic solid containing an interstitial hydrogen atom.[18] More recently, the upsurge in metal carbonyl cluster chemistry has revealed a growing range of polynuclear molecular complexes incorporating hydrogen atoms encapsulated or semi-encapsulated by four, five, or six metal atoms. These structures provide hydrogen environments akin to those found in binary metallic hydrides and promise to throw new light on the behaviour of hydrogen occluded in metals.

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[189] T. F. Koetzle, J. Müller, D. L. Tipton, D. W. Hart, and R. Bau, *J. Am. Chem. Soc.*, 1979, **101**, 5631.

[190] J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, 1979, **18**, 252 and 263.

[191] T. F. Koetzle, R. K. McMullan, R. Bau, D. W. Hart, R. G. Teller, D. L. Tipton, and R. D. Wilson, *Adv. Chem. Ser.*, 1978, **167**, 61.

[192] R. Hoffmann, B. E. R. Schilling, R. Bau, H. D. Kaesz, and D. M. P. Mingos, *J. Am. Chem. Soc.*, 1978, **100**, 6088.

[193] S. G. Louie, *Phys. Rev. Lett.*, 1979, **42**, 476.

[194] A. M. Baró, H. Ibach, and H. D. Bruchmann, *Surf. Sci.*, 1979, **88**, 384.

A. Preparative Methods.—Encapsulated hydrides are often prepared by protonation or hydrogenation of metal carbonyl clusters. Typical syntheses for specific complexes are illustrated in equations 43—45.

$$[Co_6(CO)_{15}]^{2-} + H^+ \longrightarrow [Co_6H(CO)_{15}]^- \tag{43}$$

$$[Rh_{12}(CO)_{30}]^{2-} + H_2 \xrightarrow[10\,h,\,80\,^{\circ}C]{Pr^iOH} [Rh_{13}H_3(CO)_{24}]^{2-} \tag{44}$$

$$[Ni_3(\mu_2\text{-}CO)_3(CO)_3]_2^{2-} \xrightarrow[pH\,5.5]{H_2O\text{–}THF} [Ni_{12}H(CO)_{21}]^{3-} \tag{45}$$

B. Characterization.—Although the spectroscopic properties of interstitial hydrido complexes have been examined they do not at present afford a reliable means of characterization. Encapsulated hydride ligands are therefore usually detected using structural data provided by diffraction studies.

C. Spectroscopic Properties.—(i) *Vibrational Spectra.* Very little work has been done in this area. However, Ru—H/D stretching absorptions have been observed at low temperatures in the infrared spectra of the ions $[Ru_6H(CO)_{18}]^-$ and $[Ru_6D(CO)_{18}]^-$ near 825 cm^{-1} and 600 cm^{-1} respectively. The very low Ru—H stretching force constant (21 N m^{-1}) is attributed to the fact that the H to Ru bonding is equally shared between six metal atoms.[195]

(ii) *Nuclear Magnetic Resonance Spectroscopy.* Chemical shift values for encapsulated hydride ligands range from *ca.* -13τ to $+41\tau$ indicating that interstitial hydride environments differ substantially from structure to structure. Early suggestions[196] that the extremely low chemical shifts found for $[Ru_6H(CO)_{18}]^-$ (-6.5τ) and $[Co_6H(CO)_{15}]^-$ (-13.2τ) were indicative of hydrogen bound to carbonyl (formyl CHO group) or H-bonded to oxygen (O····H····O) have largely been refuted (for the solid state at least) by subsequent neutron diffraction studies.[197, 198] The high chemical shift values found for $[Ni_{12}H(CO)_{21}]^{3-}$ and $[Ni_{12}H_2(CO)_{21}]^{2-}$ (τ 34.0 and τ 28.0 respectively) are similar to those observed for some face-bridged (μ_3) hydride ligands and there is evidence from diffraction studies that the hydride ligands in these structures are offset toward one internal face of the Ni_6 octahedron and may indeed be bound in this manner.[199]

D. Diffraction Studies.—Despite the obvious difficulties encountered in detecting, by diffraction methods, a single hydrogen atom invested by four or more heavy metal atoms, advances in knowledge of encapsulated hydride ligands have depended heavily on *X*-ray and, in particular, neutron diffraction studies. In some

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[195] I. A. Oxton, S. F. A. Kettle, P. F. Jackson, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1979, 687.

[196] P. Chini, G. Longoni, S. Martinengo, and A. Ceriotti, *Adv. Chem. Ser.*, 1978, **167**, 1 and references therein.

[197] D. W. Hart, R. G. Teller, C.-Y Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, and T. F. Koetzle, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 80.

[198] P. F. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, M. McPartlin, W. J. H. Nelson, K. D. Rouse, J. Allibon, and S. A. Mason, *J. Chem. Soc., Chem. Commun.*, 1980, 295.

[199] R. W. Broach, L. F. Dahl, G. Longoni, P. Chini, A. J. Schultz, and J. M. Williams, *Adv. Chem. Ser.*, 1978, **167**, 93.

instances the hydride ligand has been located directly, in others its position has been deduced from structural evidence. Thus a slight enlargement of the metal atom polyhedron is often symptomatic of the presence of an interstitial hydride[197, 199] and the absence of localized distortions can often eliminate alternative (μ_2 or μ_3) modes of hydride co-ordination.

E. Nature of Encapsulated Hydrides.—The introduction of a hydride ligand into an interstitial site in a metal cluster usually leads to a small expansion of the metal polyhedron—metal–metal distances increase by 0.02 to 0.07 Å—similar to that found in metallic hydrides.[199] Conversely, diffraction studies on some octahedral M_6H clusters have revealed that the hydride ligands are located off-centre in the interstitial site and may have room to 'rattle around'. The conclusion is supported by the observation that in 'symmetrical' M_6H octahedra the M—H distances are rather long (*i.e.* Co—H, 1.82 Å; Ru—H, 2.04 Å). Marked similarities in the interatomic distances and interstitial site dimensions in nickel metal, $NiH_{0\cdot6}$ and $[Ni_{12}H(CO)_{21}]^{3-}$ emphasize the close structural relationship between metallic hydrides and interstitial complex hydrides.[199] Finally there is clear evidence (see below) that encapsulated hydride ligands have the ability to migrate within the larger metal clusters and, in solution, to leave the cluster entirely. These observations may have important implications for our understanding of hydrogen migration in metallic solids.

(i) *$M_4(\mu_4$-H) Clusters.* Although hydrogen atoms occupy tetrahedral interstitial sites in metallic hydrides of the early (larger) transition elements, the presence of such an arrangement in a molecular complex was unknown until very recently. Early suggestions that $FeCo_3H(CO)_{12}$ (*ref.* 147) and $[Fe_4H(CO)_{13}]^-$ (*ref.* 200) contained $M_4(\mu_4$-H) groups were subsequently refuted.[191] However, the first fully authenticated example $[Os_{10}H(C)(CO)_{24}]^-$ was reported in 1982 and more recently a similar structure with four $M_4(\mu_4$-H) groups has been proposed for $[Os_{10}H_4(CO)_{24}]^{2-}$ (*ref.* 201).

(ii) *$M_5(\mu_5$-H) Clusters.* This arrangement in which the hydride ligand sits at the base of a square pyramid and is semi-encapsulated by five metal atoms has recently been proposed for the twinned cubo-octahedral clusters $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (n = 2, 3, or 4) (Figure 10).[202, 203] Variable temperature n.m.r. has shown that the hydride ligands are migrating rapidly within the metal cluster[203] and chemical studies have revealed facile, reversible removal of protons by base.[202]

(iii) *$M_6(\mu_6$-H) Clusters.* Enclosure within an M_6 octahedron is the most common form of hydride encapsulation encountered in polyhedral metal carbonyl clusters. The hydride ligand may be centred in the M_6 cavity as in $[Ru_6H(CO)_{18}]^-$ (*ref.* 198) and $[Co_6H(CO)_{15}]^-$ (*ref.* 197) or may be offset, as if bound in μ_3 fashion to one

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[200] K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. (A)*, 1969, 2339.

[201] D. Braga, J. Lewis, B. F. G. Johnson, M. McPartlin, W. J. H. Nelson, and M. D. Vargas, *J. Chem. Soc., Chem. Commun.* 1983, 241. P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, *ibid.*, 1982, 49.

[202] V. B. Albano, G. Ciani, S. Martinengo, and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1979, 978.

[203] S. Martinengo, B. T. Heaton, R. J. Goodfellow, and P. Chini, *J. Chem. Soc., Chem. Commun.*, 1977, 39.

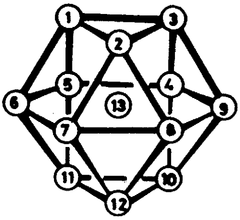

Figure 10 *Rhodium cluster in* $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (n = 2, 3, or 4) *anions; hydride ligands are thought to be located within the square faces*

internal face of the M_6 octahedron, as observed for $[Ni_{12}H(CO)_{21}]^{3-}$ (*ref.* 199). Those structures in which the hydride ligand is centred display remarkably low proton n.m.r. resonances (*ca.* $-15\,\tau$ to $-6\,\tau$). These signals which disappear reversibly when the sample is warmed have been taken to indicate that in solution the hydride ligand is able to migrate from the cluster and associate with solvent molecules.[197] Protonation and H–D exchange reactions also indicate that the interstitial proton can leave its 'cage' with considerable ease.[197]

7 Hydrides of the '*f*'-Block Metals

Binary and ternary metallic hydrides of the lanthanide and actinide elements have been actively studied for many years. In contrast the first molecular hydrido complexes are of very recent origin and their chemistry is largely unexplored.

A. Lanthanide Hydrides.—The synthesis of cerium(IV) cyclopentadienyl hydrides, $CeH(C_5H_5)_3$ and $CeH_2(C_5H_5)_2$, was claimed in 1974.[204] However, characterization of these products as hydrido complexes rests heavily on the presence of a band at *ca.* 2040 cm^{-1} in their infrared spectra and has not been confirmed. The first fully authenticated lanthanide hydrido complexes were prepared in 1982 using the reactions outlined in equations 46 and 47.[21]

$$2\,LnBu^t(C_5H_5)_2.THF + 2H_2 \longrightarrow [LnH(C_5H_5)_2(THF)]_2 + 2\,Bu^tH \qquad (46)$$

$$(Ln = Lu \text{ or } Er)$$

$$3\,ErBu^t(C_5H_5)_2.THF + LiCl \longrightarrow [Li(THF)_4][Er_3H_3Cl(C_5H_5)_6] \qquad (47)$$

All the complexes reported are extremely air and moisture sensitive. An *X*-ray diffraction study on the trinuclear erbium complex $[Li(THF)_4][Er_3H_3Cl(C_5H_5)_6]$ has established a triangular structure with μ_2 and μ_3 hydride ligands (Figure 11); μ_2-hydride structures have been proposed for the binuclear species.[205] Spectroscopic features include infrared modes ν(Ln—H) at *ca.* 1350—1200 cm^{-1} and proton n.m.r. resonances τ(Ln—H) at *ca.* 5—9 τ.

B. Actinide Hydrides.—N.m.r. evidence for the formation of hydridic intermediates during the reduction of $UCl(C_5H_5)_3$ with $LiAlH_4$ was reported in

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[204] S. Kapur, B. L. Kalsotra, and R. K. Multani, *J. Inorg. Nuclear Chem.*, 1974, **36**, 932.

[205] H. Marquet-Ellis and G. Folcher, *J. Organomet. Chem.*, 1977, **131**, 257.

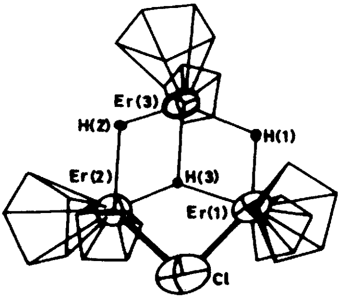

Figure 11 *Structure determined by diffraction methods for the anion in the salt* $[Li(THF)_4][Er_3H_3Cl(\eta\text{-}C_5H_5)_6]$

1977,[205] the first isolable actinide hydride complexes $[MH_2(C_5Me_5)_2]_2$ (M = Th or U) were obtained the following year by a hydrogenolysis reaction (equation 48).[20]

$$2\,MMe_2(C_5Me_5)_2 + 4H_2 \longrightarrow [MH_2(C_5Me_5)_2]_2 + 4CH_4 \qquad (48)$$

The thorium complex was subsequently shown by neutron diffraction methods to possess a hydride bridged structure $[Th(\mu_2\text{-}H)H(C_5Me_5)_2]_2$.[206] Terminal and bridging hydride ligands show infrared ν(Th—H) modes at 1406, 1361 cm^{-1} and 1215, 1114 cm^{-1} respectively. A low field ($-9.25\,\tau$) n.m.r. signal which remains a singlet down to 183 K is taken to indicate rapid exchange of bridging and terminal hydride ligands.[20] Mononuclear thorium and uranium hydrides $MH\{N(SiMe_3)_2\}_3$ have been prepared by treatment of the corresponding chlorides with $Na[N(SiMe_3)_2]$. For the thorium compound ν(Th—H) and τ(Th—H) occur at 1480 cm^{-1} and 9.1 τ respectively.[207] All of these complexes react readily with chlorinated hydrocarbons to generate the corresponding chlorides[20, 207] and undergo rapid H–D exchange.[207, 208] The high affinity of the actinide elements for O-donor ligands is reflected in the formation of dimeric enediolate derivatives [ThOC(H)=C(H)OTh] by facile insertion of CO into Th—H bonds at −78 °C.[209]

8 Conclusion

The developments of the past 50 years, summarized in this review, clearly demonstrate that the hydride anion, the smallest and simplest possible ligand, possesses quite unique chemical and physical properties. In addition to arousing great academic interest, it has established an exceptional position as a participant in many important homogeneous catalysis reactions. Continued interest in the field

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[206] R. W. Broach, A. J. Schultz, J. M. Williams, G. M. Brown, J. M. Manriquez, P. J. Fagan, and T. J. Marks, *Science*, 1979, **203**, 172.

[207] H. W. Turner, S. J. Simpson, and R. A. Andersen, *J. Am. Chem. Soc.*, 1979, **101**, 2782 and 7728.

[208] P. J. Fagan, J. M. Manriquez, E. A. Matta, A. M. Seyam, and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6650.

[209] P. J. Fagan, K. G. Moloy, and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6959.

of transition-metal hydrido complexes seems assured for the foreseeable future and must surely be rewarded with many more exciting and important discoveries. New work reported in the short period since the original typescript was submitted testifies to the pace of current progress. Novel complexes recently described include new paramagnetic hydrides $MH_2Cl_2(Me_2PCH_2CH_2PMe_2)_2$ (M = Nb, Ta),[210] $[Re_2H_8(PPh_3)_4][PF_6]$, $[Re_2H_7(PPh_3)_4(CNBu^t)][PF_6]_2$ and $[ReH(NCMe)_3(PPh_3)_2(py)][PF_6]_3$;[211] tetrahydrido-bridged ruthenium complexes $Ru_2H_8(PPh_3)_4$ and $Ru_2H_6(N_2)(PPh_3)_4$;[212] the trinuclear salt $[H_2(MePh_2P)_2Re(\mu\text{-}H)_3Cu(\mu\text{-}H)_3Re(PMePh_2)_2H_2][PF_6]$; a related species $[\{Re_2H_8(PMePh_2)_4\}_2Cu_2][PF_6]_2$ containing an unprecedented planar rhomboidal (Re_4Cu_2) metal array[213] and the remarkable *molecular* hydrogen complex $W(\eta^2\text{-}H_2)(CO)_3(PPr^i_3)_2$.[214] New reactions reported include facile intermolecular activation of aromatic C—H bonds by lutetium hydride complexes,[215] oxidative addition of dihydrogen reversibility to a metal cluster in $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)]$[216] and irreversibly across a Ta=Ta bond in $[Ta_2Cl_6(PMe_3)_4]$,[217] and the reversible conversion of $Cr(CH_3)(CO)_3(C_5H_5)$ into $CrH(CH_2)(CO)_2(C_5H_5)$.[218]

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[210] M. L. Luetkens, W. L. Elcesser, J. C. Huffman, and A. P. Sattelberger, *J. Chem. Soc., Chem. Commun.*, 1983, 1072.

[211] J. D. Allison and R. A. Walton, *J. Chem. Soc., Chem. Commun.*, 1983, 401.

[212] B. Chaudret, J. Devillers, and R. Poilblanc, *J. Chem. Soc., Chem. Commun.*, 1983, 641.

[213] L. F. Rhodes, J. C. Huffman, and K. G. Caulton, *J. Am. Chem. Soc.*, 1983, **105**, 5137.

[214] P. J. Vergamini and G. J. Kubas, *Chem. Eng. News*, 28th Mar. 1983, 4.

[215] P. L. Watson, *J. Chem. Soc., Chem. Commun.*, 1983, 276.

[216] L. J. Farragia, M. Green, D. R. Hankey, A. G. Orpen, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 310.

[217] A. P. Sattelberger, R. B. Wilson, and J. C. Huffman, *Inorg. Chem.*, 1982, **21**, 4179.

[218] K. A. Mahmoud, A. J. Rest, and H. G. Alt, *J. Chem. Soc., Chem. Commun.*, 1983, 1011.