HYDRIDE COMPLEXES OF THE TRANSITION METALS

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I. The General Chemistry of Transition Metal Hydride Complexes

A. INTRODUCTION AND CLASSIFICATION

The transition metal hydrides considered here are those discrete complexes which contain one or more hydrogen atoms bonded directly to a transition metal by an essentially covalent, two-electron bond.* For many years, the only known complexes in this class were the unstable and reactive carbonyl hydrides of iron and cobalt and, by virtue of their novelty, the hydride ligand acquired a unique status in the minds of many chemists. Today that status is no longer generally acceptable in view of the number and diversity of presently known hydride complexes, many of which possess

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* For previous reviews on various aspects of transition metal hydride chemistry, see references (*5*, *24*, *33*, *47*, *98*, *136*, *137*, *140*, *180*, *242*, *271*).

high thermal stability, and chemical behavior allowing the hydride ligand to be compared with halide and alkyl ligands. The interest in hydride complexes per se is due to the wide variety of their chemical reactions (for example, in the field of homogeneous catalysis) and the simplicity of the hydride ligand, which thus lends itself to theoretical treatment.

It is convenient and to some extent chemically significant to classify hydrides according to the nature of the other ligands attached to the metal. Accordingly, the following classes are recognized:

1. Complex hydrides with tertiary phosphines and related ligands
2. Carbonyl hydrides: (a) mononuclear, (b) polynuclear
3. π-Cyclopentadienylcarbonyl hydrides
4. Bis(π-cyclopentadienyl) hydrides
5. Cyanide hydrides
6. Hydride complexes containing nitrogen ligands
7. "Pure" hydrides: complexes with hydride as the sole ligand

A general account of preparative routes and of the chemical and physical properties of the metal-hydrogen system precedes the discussion of the specific chemistry of these complexes.

B. General Preparative Methods

Examples of preparative methods are given for a wide variety of complexes in order to illustrate their common chemistry.

1. *Direct Hydrogenation*

A suitable complex of the metal is treated with hydrogen under pressure. In some cases, e.g., Eqs. (1) and (2), the necessary complex is prepared *in situ* when the method amounts to direct synthesis from the metal:

$$Co_2(CO)_8 \xrightarrow[25°C]{H_2,\ 30\ atm.} HCo(CO)_4 \xleftarrow[180°C]{250\ atm.} Co + 4CO + \tfrac{1}{2}H_2 \qquad (1)$$

$$Fe + 2\,o\text{-}C_6H_4(PEt_2)_2 \xrightarrow[200°C,\ 60\ hr]{under\ H_2,} trans\text{-}FeH_2[o\text{-}C_6H_4(PEt_2)_2]_2 \qquad (2)$$

$$cis\text{-}PtCl_2(PEt_3)_2 \xrightarrow[ethanol,\ 95°C]{H_2,\ 50\ atm.} trans\text{-}PtHCl(PEt_3)_2 \qquad (3)$$

$$[(C_5H_5)Cr(CO)_3]_2 \xrightarrow[60°C]{H_2,\ 150\ atm.} (C_5H_5)Cr(CO)_3H \qquad (4)$$

2. *Reduction of Metal Halide Complexes*

Suitable reducing agents are alkali metal borohydrides and aluminohydrides, hydrazine (*44*), sodium dithionite, sodium hypophosphite (*76a*, *198*), formic acid (*44*), and alcohols in the presence of alkali (*257*) (see Section I,B,3).

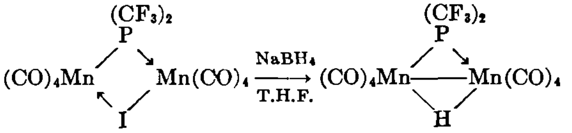
In many cases the reduction is only formal: if the hydrogen be considered as exhibiting the −1 state in the hydride complexes, some reactions may be envisaged as simple hydride/halide exchange or replacement reactions.

(*a*) Reductions using the hydride complexes of Group III metals are usually performed in polar solvents such as alcohol or tetrahydrofuran (T.H.F.):

$$[(C_5H_5)_2WCl_2]^+Cl^- \xrightarrow[\text{T.H.F.}]{\text{LiAlH}_4} (C_5H_5)_2WH_2 \xleftarrow[\text{T.H.F.}]{\text{LiAlH}_4} (C_5H_5)_2WCl_2 \qquad (5)$$

$$IrHCl_2(PPh_3)_3 \xrightarrow[\text{T.H.F.}]{\text{LiAlH}_4} IrH_3(PPh_3)_3 \qquad (6)$$

$$[en_2RhCl_2]^+ \xrightarrow[\text{water}]{\text{NaBH}_4} [en_2RhHCl]^{+*} \qquad (7)$$



(*113*)(8)

The course of a reaction depends to some extent on the nature of the nonhalogen ligands present; thus, for example, the reduction of *trans*-$FeCl_2[o\text{-}C_6H_4(PEt_2)]_2$ with lithium aluminohydride in tetrahydrofuran affords directly the dihydride derivative in 70% yield, whereas reduction of *trans*-$FeCl_2[C_2H_4(PEt_2)_2]_2$ may be arrested at the chlorohydride stage. For certain complexes, especially those of platinum, lithium aluminum hydride is too severe a reagent and the complex may be reduced to the metal.

(*b*) Hydrazine has been used as a reducing agent only in a few cases. The formation of intermediate hydrazine complexes has been suggested (*44*):

$$\begin{array}{l} cis\text{-}PtCl_2(PEt_3)_2 \xrightarrow[\text{N}_2\text{H}_4\cdot\text{H}_2\text{O, 90°C}]{\text{dil. aq. solution}} [PtCl(N_2H_4)(PEt_3)_2]^+Cl^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \big\downarrow \textit{ proposed intermediate} \\ \qquad\qquad\qquad\qquad\qquad trans\text{-}PtHCl(PEt_3)_2 + N_2 + NH_4Cl + NH_3 \qquad (9) \end{array}$$

3. Hydride-Transfer and Reverse Carbonylation Reactions

Base-catalyzed reductions using alcohols have been widely used in the preparation of hydrides with tertiary phosphine ligands (*45*, *46*, *257*, *258*). A number of reactions may occur, yielding among other products solvates,

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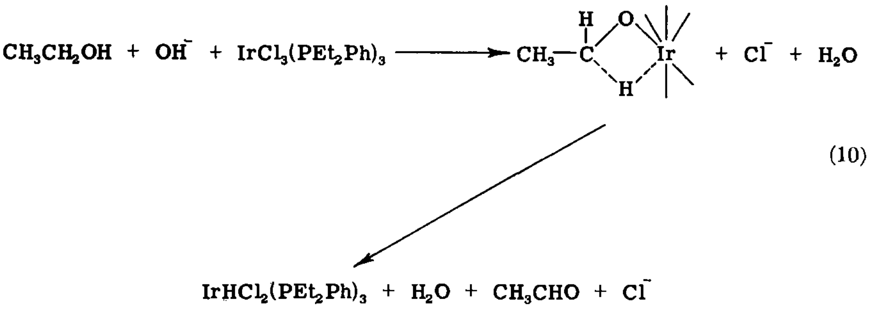
* en indicates ethylenediamine.

e.g., $MX_3L_2CH_3OH$ (*258*), alkoxides, carbonyls (*261*), hydrides (*257*, *260*, *262*), and carbonyl hydrides, depending on the conditions and the particular complex which is being reduced.

For the simplest cases involving the use of ethyl alcohol, the formation of a hydride is thought to proceed via the displacement of the halogen from the metal by the ethoxide ion, followed by transfer of the hydrogen from the ethyl group. Studies using CH_3CD_2OH show that the hydride hydrogen was originally attached to the α-carbon (*262*).



(10)

All three chlorines may be replaced by using excess of reagent and yields are usually high. Other alcohols such as isopropyl alcohol, allyl alcohol, and 2-methoxyethanol may be used.

In some cases a novel "reverse carbonylation" reaction may also occur, affording carbonyl hydride complexes, for example:

$$(NH_4)_2OsBr_6 + (\text{excess})\ PPh_3 \xrightarrow[190°C,\ 4.5\ hr\ (92\%)]{2\text{-}(\beta\text{-methoxyethoxy})\text{ethanol}} OsHBr(CO)(PPh_3)_3 \quad (11)$$

The origin of the carbon monoxide from the alcohol has been shown by syntheses employing radiocarbon-labeled ethylene glycol (*257*) and, as before, the hydride ligand is presumed to originate from the α-carbon of the reacting alcohol (*257*, *262*). The alcohols may therefore form aldehydes or ketones (*44*, *45*, *47*, *262*) and a proton (*260*) in the hydride transfer reaction:

$$RCH_2OH \rightarrow RCHO + H^+ + \text{H-metal complex} \quad (12)$$

or, in the "reverse carbonylation" reaction, an alkane is formed:

$$RCH_2OH \rightarrow RH + H^+ + \text{H(CO)-metal complex} \quad (13)$$

Although potassium hydroxide is frequently used, it is not essential and, as shown in Eq. (11), reactions in which the only "base" present is the tertiary phosphine give excellent yields of the hydride. It appears, in fact, that the phosphine ligand may also act as a reducing agent; the overall stoichiometry of the reaction shown in Eq. (11) is

$$(NH_4)_2OsBr_6 + 4PPh_3 + RCH_2OH \rightarrow OsHBr(CO)(PPh_3)_3 + RH + 2HBr + Ph_3PBr_2 + 2NH_4Br \quad (14)$$

An example of a reaction affording only a carbonyl complex (*261*) is

$$IrCl_3\ (aq.) + PPh_3 + alcohol \xrightarrow{reflux} \underset{(I)}{trans\text{-}IrCl(CO)(PPh_3)_2} \quad (15)$$

The complex (I) reacts readily with hydrogen halides and molecular hydrogen yielding hydride-halide complexes (see Section III,A,3).

4. Hydrolysis of Alkali Metal Salts of Complex Carbonyls

The majority of the carbonyl hydrides may be prepared by this method, e.g.,

$$\begin{tikzcd} Fe(CO)_5 \arrow[r, "Na/Hg", "T.H.F."'] \arrow[rr, bend right, "NaOH(aq.)"'] & Na_2[Fe(CO)]_4 \arrow[r, "aq."] & Na^+[HFe(CO)_4]^- \arrow[r, "H^+"] & H_2Fe(CO)_4 \end{tikzcd} \quad (16)$$

Complete hydrolysis is effected by using acids such as orthophosphoric or acetic acid. Further examples are

$$Cr(CO)_6 + 3OH^- \rightarrow Cr(CO)_5H^- + CO_3^{2-} + H_2O \quad (\mathit{139})(17)$$

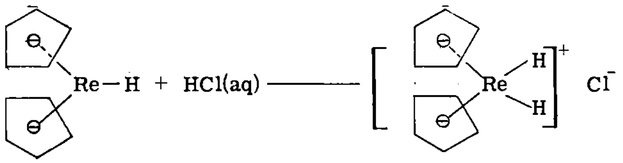
$$Fe_3(CO)_{12} + base \rightarrow [Fe_3(CO)_{11}]^{2-} \xrightarrow{H^+} H_2Fe_3(CO)_{11} \quad (18)$$

$$Na^+C_5H_5Mo(CO)_3^- \xrightarrow{H^+\ aq.} C_5H_5Mo(CO)_3H \quad (19)$$

The hydroxycarbonyl hydrides are prepared similarly (see Section III,B,4,*c*).

5. Protonation

A number of neutral complexes may be protonated, forming cationic hydride complexes (see Section III,E).



(20)

Weaker bases require strong acids such as concentrated sulfuric acid or boron trifluoride hydrate.

$$Fe(CO)_5 \xrightarrow{BF_3 \cdot H_2O} [HFe(CO)_5]^+ \tag{21}$$

$$(C_5H_5)_2Fe \xrightarrow{BF_3 \cdot H_2O} [(C_5H_5)_2FeH]^+ \tag{22}$$

6. *Unique Methods*

Certain hydrides, e.g., K_2ReH_9, have been prepared by specific methods; these preparations are discussed under the particular compound concerned.

C. CHEMICAL PROPERTIES

1. *Stability*

Chatt and co-workers have suggested (*48*) that the stability to dissociation of metal-carbon σ-bonds depends *inter alia* on the energy separation, ΔE, between the highest occupied electronic level in the molecule and the lowest unoccupied level. The larger the energy difference, the more likely is the complex to be stable, because the energy necessary to dissociate the metal-carbon bond is that required to promote the bonding electrons to unoccupied orbitals. The energy difference, ΔE, is markedly dependent upon which ligands are attached to the metal; the greater the field strength of the ligands, the greater is ΔE. In view of the marked analogy between the occurrence and chemistry of transition metal alkyls and hydrides, it is considered appropriate to use similar arguments to interpret the stability of hydride complexes.

In general agreement with the above theory, the most stable hydrides contain strong field ligands such as cyanide or tertiary phosphines. Also, where suitable series of homologous complexes are known, the thermal stability appears to increase with increasing atomic number of the metal, e.g.,

$C_5H_5Cr(CO)_3H$	dec. 57°C	$(PEt_3)_2NiHCl$	not isolable
$C_5H_5Mo(CO)_3H$	dec. 57°C	$(PEt_3)_2PdHCl$	dec. rapidly in solution
$C_5H_5W(CO)_3H$	dec. 180°C	$(PEt_3)_2PtHCl$	may be distilled at 130°C, 0.01 mm, without decomposition

The simple carbonyl hydrides of Group VIII metals appear to be an exception to this general rule, pointing to a limitation in the above argument.

The thermal stability of the known hydrides varies widely from the stable tertiary phosphine complexes (whose decomposition temperatures are frequently above 250°C) to the notoriously unstable mononuclear carbonyl hydrides. Although there are no thermodynamic data, it seems probable that many hydrides, particularly the latter, are thermodynamically unstable relative, for example, to hydrogen and a dimeric species. Thus $C_5H_5Fe(CO)_2H$ and $HCo(CO)_4$ decompose at room temperature to hydrogen and $[C_5H_5Fe(CO)_2]_2$ and $[Co(CO)_4]_2$, respectively.

2. Exchange or Replacement Reactions

The hydride ligand may readily undergo replacement, e.g.,

$$ReH_3(PPh_3)_4 \xrightarrow[\text{ether}]{\text{HCl}} ReCl_4(PPh_3)_2 \qquad (23)$$

Since most of the reactions have been demonstrated with the tertiary phosphine complexes, they are discussed fully under that heading (see Section III,A,3). A characteristic reaction of hydrides with halogenated hydrocarbons yields the metal halide derivatives:

$$(C_5H_5)_2WH_2 + HCBr_3 \rightarrow (C_5H_5)_2WBr_2 \qquad (24)$$

$$C_5H_5Mo(CO)_3H + HCCl_3 \rightarrow C_5H_5Mo(CO)_3Cl \qquad (25)$$

$$(PR_3)_2PtHCl + CCl_4 \rightarrow (PR_3)_2PtCl_2 \qquad (26)$$

See also Eq. (49). Reaction with halogens may result in replacement, but oxidation may also occur.

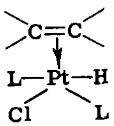
3. The Addition of Metal Hydride across Unsaturated Systems

The addition of M—H across olefins has been demonstrated for a number of different systems; however, the simplest example, namely addition to ethylene, has been found only in two cases.

$$trans\text{-}(PEt_3)_2PtHCl + C_2H_4 \underset{180°\text{C}}{\overset{\text{cyclohexane, 95°C, 40 atm.}}{\rightleftharpoons}} trans\text{-}(PEt_3)_2PtClEt \qquad (27)$$

$$Co(CO)_4H + C_2H_4 \rightleftharpoons Co(CO)_4Et \qquad (28)$$

It is interesting that both these reactions are reversible; the ethyl compounds decompose thermally to the hydride and ethylene. It has been shown that alkyl groups attached to transition metals may readily lose a hydride ion from the 2-carbon (*101*), so both the addition and decomposition reactions may well proceed via an unstable intermediate such as (II).

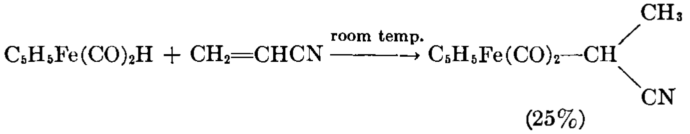


(II)

A more detailed discussion of the reactions of $CoH(CO)_4$ is given in the section on catalysis (Section IV,A,2).

Rather surprisingly, in contrast to ethylene, tetrafluoroethylene reacts readily with a number of metal hydrides at room temperature and atmospheric pressure, affording M-CF_2-CF_2-H complexes (*254*, *255*).

Addition of M—H across olefins, e.g., acrylonitrile and butadiene, also proceeds readily for hydrides such as $HCo(CO)_4$ (*185*) and $C_5H_5Fe(CO)_2H$ (*6*):



$$C_5H_5Fe(CO)_2H + CH_2{=}CHCN \xrightarrow{\text{room temp.}} \underset{(25\%)}{C_5H_5Fe(CO)_2{-}CH(CH_3)(CN)} \qquad (29)$$

The course of the above reaction indicates a hydridic nature for the hydrogen in $C_5H_5Fe(CO)_2H$.

$$C_5H_5Fe(CO)_2H + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\text{room temp.}} C_5H_5Fe(CO)_2{-}CH_2{-}CH{=}CH{-}CH_3 \qquad (30)$$

In reaction (30), the addition of the Fe—H to butadiene gives a *cis-trans* isomeric mixture of the Fe-but-2-enyl complex which is the 1:4 addition product. There is no evidence for the formation of either the 1:3 or 1:2 addition product (*102*).

A number of hydrides also react readily with diazomethane, affording methyl derivatives, e.g., (*173*, *230*):

$$C_5H_5Mo(CO)_3H + CH_2N_2 \xrightarrow[\text{ether}]{\text{room temp.}} C_5H_5Mo(CO)_3CH_3 + N_2 \qquad (31)$$

4. Acid-Base Characteristics

Certain hydrides behave as acids in aqueous solution, in particular the simple carbonyl hydrides. This property in aqueous solution, however, does not necessarily indicate the direction of polarity of the M—H bond in the neutral hydride. For example, in some addition reactions of $HCo(CO)_4$ to olefins the behavior of the hydrogen is sometimes "protonic" and sometimes "hydridic" (see Section III,B,3). Therefore it is unwise to classify metal hydrides as "acidic" or "basic" without reference to the particular conditions.

II. Physical Properties of the Metal-Hydrogen Bond

A. X-RAY AND NEUTRON DIFFRACTION STUDIES

These studies have shown that the hydrogen atoms in metal-hydride complexes occupy accepted coordination positions, and the most reliable determinations indicate M—H distances compatible with an essentially normal covalent bond.

The structure determination on *trans*-$PtHBr(PEt_3)_2$ (*228*) (Fig. 1), which does not locate the hydrogen, indicates an approximately T-shaped configuration for the other ligands about the platinum, and the hydrogen is assumed to occupy a position *trans* to the bromine atom.

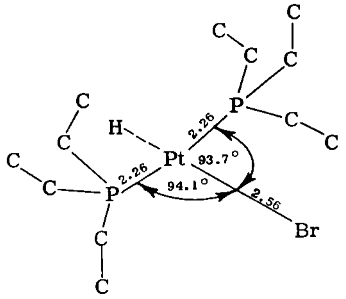


Fig. 1. Ligand atoms and C skeleton of *trans*-$PtHBr(PEt_3)_2$.

Thus the complex has a slightly distorted square-planar configuration. An interesting feature of the structure of this molecule is the unusually long Pt—Br distance of 2.56 Å (compare 2.43 Å, the sum of the Pt and Br covalent radii), that may be understood in terms of a high inductive *trans*-effect of the hydride ligand (*33*) and as providing supporting evidence for

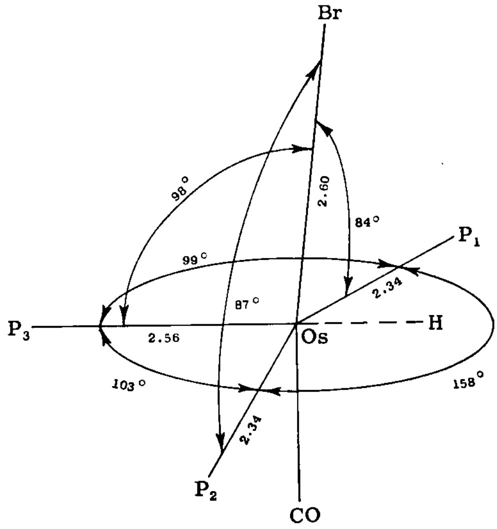


Fig. 2. $OsHBr(CO)(Ph_3P)_3$, fragment.

the location of the hydrogen. Further evidence that hydrogen fills an accepted ligand position is derived from the structures of $OsHBr(CO)(Ph_3P)_3$ (*227*) and $HMn(CO)_5$ (*197*) (Figs. 2 and 3, respectively), in which again the hydrogens are not located. Both show a distorted octahedral environment for the metal atom in which one position is vacant and is assumed to be occupied by a hydrogen. The structure of $HMn(CO)_5$ departs insignificantly from C_{4v} symmetry and the $Mn(CO)_5$ fragments are very similar in their geometry to that observed in $Mn_2(CO)_{10}$. Also the crystal structure is markedly similar to that of $Mn_2(CO)_{10}$; so much so, that in the crystal the hydrogen atoms, which lie between two manganese atoms, may be in intermolecular contact (*195b*, *197*). In each of the above examples, the distortion from regular symmetry in such that the ligands adjacent to the conjectured position of the hydrogen are slightly displaced toward it, due

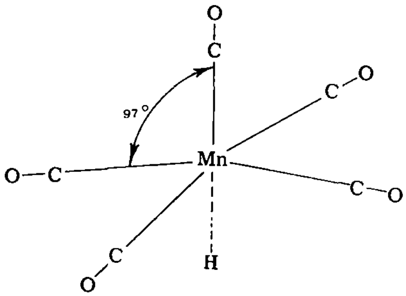


FIG. 3. $HMn(CO)_5$.

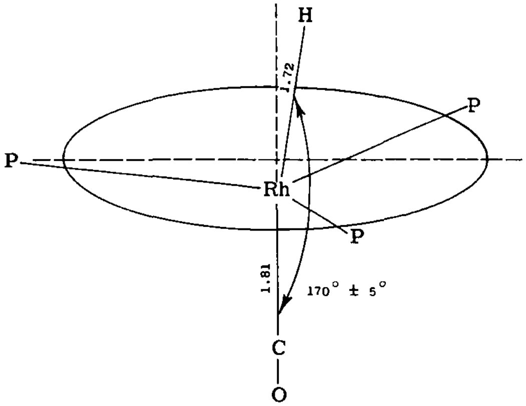


FIG. 4. $RhH(CO)(PPh_3)_3$, fragment. Rh—P = 2.31–2.34 Å; P—Rh—CO = 94.8 ± 0.8, 103.8 ± 0.8, 98.0 ± 0.8; P—Rh—P = 115.8 ± 0.3, 102.6 ± 0.3, 116.6 ± 0.3.

partly to the relatively small size of the hydrogen ligand. The structure of the osmium complex provides further evidence for a high *trans*-effect of the hydride ligand insofar as the Os—P bond *trans* to the hydrogen is approximately 0.22 Å greater than the other Os—P distances.

Recent structural determinations on $RhH(CO)(PPh_3)_3$ by X-ray (*196*, *196a*) and on potassium enneahydridorhenate, $K_2[ReH_9]$, by X-ray (*191*, *193*) and neutron diffraction (*1*), have located the hydrogen and have provided approximate metal-hydrogen distances, Rh—H = 1.60 ± 0.12 (*196a*); Re—H = 1.7 Å (Figs. 4 and 5, respectively).

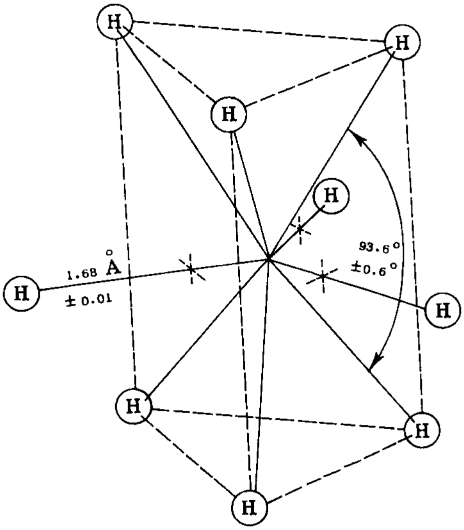


FIG. 5. H environment of Re atom in ReH_9^{2-}.

The structure of the rhodium complex has no features attributable to a high *trans*-effect of the hydride ligand. For the salt $K_2[ReH_9]$, there are three formula weights per unit cell (*192*), and the rhenium atoms are separated by large distances (minimum of 5.5 Å) so that discrete enneahydridorhenate anions must exist in the crystal. The anion has D_{3h} symmetry with six hydrogens at the corners of a trigonal prism and three beyond the centers of each equatorial face. The Re—H distance varies between 1.6 and 1.72 Å

Finally, an X-ray diffraction study on bis(π-cyclopentadienyl)molybdenum dihydride (*21*, *88a*) indicates the structure shown in Fig. 6. The reported Mo—H distance of 1.1 ± 0.2 Å is rather shorter than might be expected in view of M—H distances in the above complexes, and this result needs confirmation. It is interesting to note that in the complex $(\pi\text{-}C_5H_5)_2MoH_2$ the C_5H_5 rings do not have fivefold symmetry.

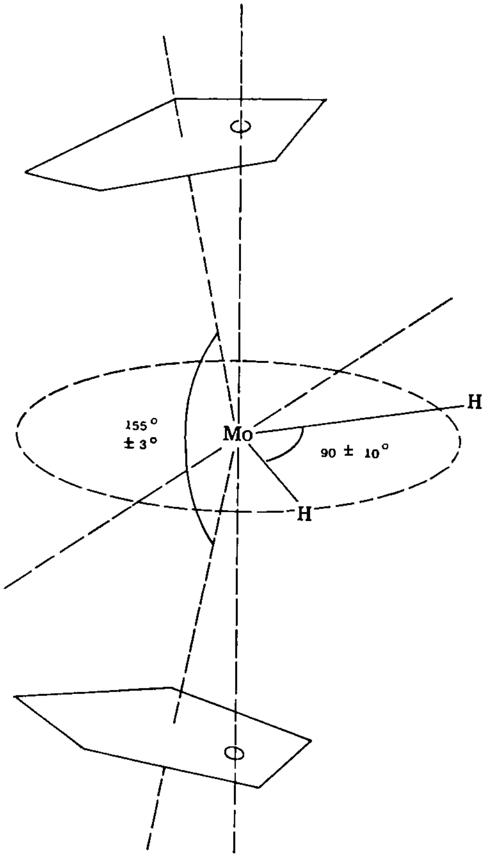


FIG. 6. (π = C_5H_5)MoH_2. Mo—C distances 2.22–2.40 Å. The angle between π-C_5H_5 rings is 34.1 ± 1°.

TABLE I
M—H BOND LENGTHS

Bond	Compound	M—H (Å)	Method[a]	Reference
Fe-H	$Fe(CO)_4H_2$	1.1–1.5	Calculated from broad-line n.m.r.	(*23*)
Mo-H	$(\pi\text{-}C_5H_5)_2MoH_2$	1.2 ± 0.3	X-ray (two-dimensional)	—
Rh-H	$RhH(CO)(PPh_3)_3$	1.60 ± 0.12	X-ray (1.72 ± 0.15) (*196*)	(*196a*)
Re-H	K_2ReH_9	1.6–1.72 (various)	Neutron diffraction	(*1*)
Mn-H	$MnH(CO)_5$	1.5–1.6	Estimated on basis of X-ray structure (1.4–1.9) (*197*)	(*195b*)

[a] Data in parentheses refer to earlier data from the same authors.

All reported M—H bond lengths are listed in Table I. It may be seen that the most reliable lie between 1.60 and 1.72 Å, which are acceptable values in terms of a normal covalent bond.

B. Nuclear Magnetic Resonance Studies

1. *Solid State Measurements*

Analysis of the broad-line proton magnetic resonance spectrum of $Fe(CO)_4H_2$ (*23*) indicates an interhydrogen distance in the molecule of 1.88 ± 0.05 Å.

It has been recently suggested, however, that the assumption of the observed second moment being due to interactions between the hydrogens in the same molecule only may be incorrect, and that there might also be a contribution from intermolecular contact (*197*). If a distorted tetrahedral configuration is taken for the $Fe(CO)_4$ fragment of $H_2Fe(CO)_4$ (chosen since Raman studies have indicated this configuration for the $[HFe(CO)_4]^-$ ion), and the hydrogens are allocated positions in the largest spaces produced by the distortion, the H-Fe-H bond angle may be estimated at between 109° and 125°. Then, taking the H—H distance as 1.88 Å, calculation yields Fe—H distances of 1.15–1.06 Å.

If a slightly distorted octahedral model be assumed for $H_2Fe(CO)_4$, however, then the calculated Fe—H distance becomes 1.5 Å (*252*), a more acceptable value in terms of the results given in the previous section.

2. *Solution Studies*

The rapid progress in the discovery and study of transition-metal hydride complexes is largely due to the characteristic high field shift (in the high resolution n.m.r. spectrum) exhibited to date by all hydrogens attached to transition metals.

The resonances of M-H hydrogens occur at $>12\tau$, are frequently in the range 20–30τ, and may come as high as 45τ. Only resonances arising from some paramagnetic complexes, porphyrins, and hydrogen iodide, occur in this region. The resonances from paramagnetic complexes are usually markedly broader than resonances due to hydrogens of diamagnetic complexes and thus may be distinguished. Anomalies may arise in the case of hydrogen ligands that are undergoing rapid exchange, for example with the solvent. In such cases the resonance may be broad or not even observable.

Where comparisons are appropriate, it appears that the high field shift of M-hydrogens is largest for first-row transition metals; the complexes of metals of the second and third transition series show shifts that are about

25% less than those of the lightest group members, e.g., for $MClHP_4$* where M = Fe, Ru, and Os, τ = 41.9, ~31, and ~34 p.p.m., respectively (*241*). The chemical shift data for many of the known hydride complexes are given in Tables III, IV, VI–VIII. Correlations of chemical shift of M-hydrogens with infrared stretching frequencies are discussed below (cf. *241*).

Spin-spin coupling of the M-hydrogens with other nuclei in the complex, in particular with the central metal, observable with the Rh^{103}, Pt^{195}, and W^{183} nuclei, provides strong evidence for direct M—H bonds. Coupling with other ligands attached to the central metal has also been observed. For example, in the phosphine hydrides the P^{31} nucleus will couple with the hydrogen; for the P ligand *trans* to H, $J_{P,H}$ = 80–160 cps, while for P *cis* to H, $J_{P,H}$ = 10–40 cps. Thus the phosphorus-hydrogen coupling constant can provide evidence for the configuration of various geometrical isomers (see Section III,A,5).

Some factors affecting the magnitude of metal-hydrogen coupling constants (J_{M-H}) have been considered (*97a*). The coupling constants J_{M-H} are dependent upon electronic effects and on the magnetogyric ratios of the nuclei concerned. As these magnetogyric ratios differ from nucleus to nucleus, it is convenient when comparing coupling constants in different compounds to eliminate them from the observed J_{M-H}. Thus Pople and Santry have defined a reduced coupling constant K_{AB} (*230a*), where $K_{AB} = (2\pi/h\gamma_A\gamma_B)J_{AB}$. In Table Ia are given reported values of J_{M-H} and the corresponding values of the reduced coupling constants; the latter are given in Sheppard-Lynden-Bell coupling units (c.u.) (*206a*), which are obtained by dividing the observed coupling constants in cycles per second by the product of the magnetogyric ratios $\gamma_A\gamma_B$. The reduced coupling constants thus obtained are a measure solely of the electronic environment on the nuclear spin-spin coupling. Pople and Santry propose that the dominant factor determining the magnitude of the coupling constant of hydrogen with another atom, (M), is the Fermi contact interaction (*230a*). The electronic factors on which this interaction depends are the *s*-electron densities at the two nuclei, the degree of *s* character in the M—H bond and on a mean excitation energy term. This energy term arises from a simplification of the perturbation theory used to derive the coupling constant which consists of replacing the electronic energies of all the triplet states interacting with the ground state by an appropriate average.

The *s*-electron density at the nucleus is affected by the effective nuclear charge. An increase in the latter quantity on the metal atom would increase J_{M-H}. The large value for J_{Pt-H} in platinum-hydride complexes has been attributed to the effective nuclear charge of the platinum (*239a*) and the striking increase in J_{M-H} with increasing atomic number for the

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* P indicates phosphine ligand.

Group IV hydrides may be associated with the corresponding increase in effective nuclear charge (*232a*). From Table Ia it may be seen that the reduced coupling constants of the 5*d* elements Pt and W are larger than those of the 4*d* element Rh.

The coupling constant will increase with increasing *s* character of the metal-hydrogen bond. This may be seen in the series acetylene, ethylene, and ethane where J_{C-H} decreases (*206a*). Thus J_{M-H} would be expected to decrease with increasing coordination number of the metal atom, for example, J_{N-H} in the NH_4^+ ion is smaller than in NH_3 despite the increase of effective nuclear charge (*232b*). The relative values of J_{W-H} for the complexes $(\pi\text{-}C_5H_5)_2WH_2$ and $[(\pi\text{-}C_5H_5)_2WH_3]^+$ may be similarly explained. It is expected that the mean excitation energy term would be dominated by the lowest singlet-triplet excitation energies, as it is the term associated with these energies which occur with greatest weight in the full perturbation treatment. Considering the series of compounds *trans*-$[Pt(PEt_3)_2HX]$ (see Table Ia), the ligand field strength of the ligand X will effect the lowest singlet-triplet transition excitation energy which will correspond to the ligand field splitting for the d^8 complexes. The reduced coupling constant K_{M-H} is inversely proportional to the mean excitation energy and, if the variation in this latter does correspond to variation in the ligand field

TABLE Ia
SOME METAL-HYDROGEN COUPLING CONSTANTS

A. For the complexes $[Pt(PEt_3)_2HX]$ (*239c*)

X:	I	Br	NO_3	Cl	−SCN	NCS	NCO	ONO	CN
J(cps):	1369	1346	1322	1275	1233	1086	1080	1003	778
K(c.u.):	204.1	200.7	197.1	190.1	183.8	161.9	161.0	149.5	116.0

B. Compound	J_{M-H} (cps)	K_{M-H} (c.u.)	Reference
$[HPt(CN)_4]^{3-}$	450	67.1	(*109*)
$(\pi\text{-}C_5H_5)_2WH_2$	73.2	57.0	(*62a*)
$[(\pi\text{-}C_5H_5)_2WH_3]^+$	47.8(A_2)	37.2	(*62a*)
$[(\pi\text{-}C_5H_5)W(CO)_3]_2H^+$	38.6	30.0	(*62a*)
$[(\pi\text{-}C_5H_5)_2MoW(CO)_6]H^+$	38	29.6	(*62a*)
$\pi\text{-}C_5H_5W(CO)_3H$	37.7	29.3	(*62a*)
cis-$[Rh(trien)H_2]^+$ [a]	30	30.6	(*89*)
cis-$[Rh(trien)HCl]^+$ [a]	27	27.5	(*89*)
trans-$[Rh(en)_2H_2]^+$ [b]	27	27.5	(*89*)
$[HRh(CN)_5]^{3-}$	13.1	13.3	(*108*)

[a] trien = triethylenetetramine.
[b] en = ethylenediamine.

strength of X, then an increase in the ligand field strength of X would be expected to decrease K_{M-H}. In Fig. 6a the ligand field strength, Δ, in the complexes $[Co(NH_3)_5X]^{2+}$ where X = CN^-, NCS^-, Cl^-, Br^-, and I^- (*183a*) is plotted against K_{M-H} for the corresponding platinum complexes. The value of Δ for the complex $[Co(NH_3)_5CN]^{2+}$ is estimated. The observed approximately linear relationship shown in Fig. 6a supports the above arguments.

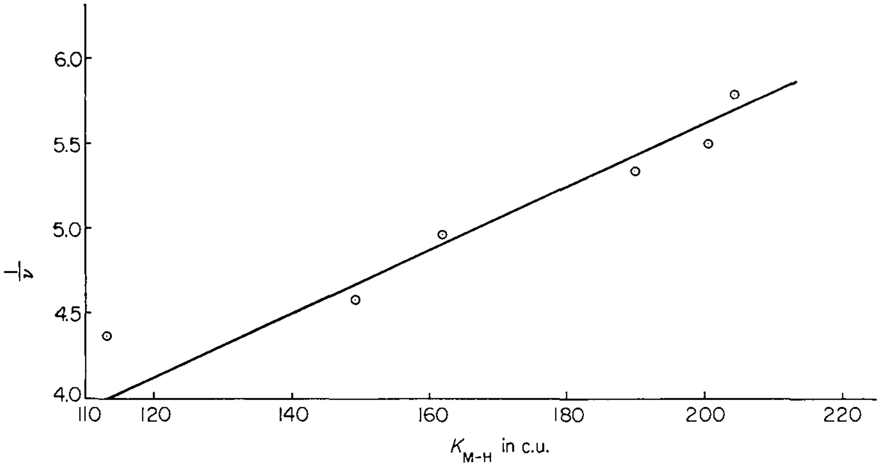


FIG. 6a. Plot of reciprocal of first ligand field transition $1/\nu$ in $[Co(NH_3)_5X]^{3+}$ against the reduced coupling constant K_{M-H} in *trans*-$[Pt(PEt_3)_2HX]$. $1/\nu$ in units of kK^{-1}.

It is interesting to consider other effects that the ligands in the complexes $[Pt(PEt_3)_2HX]$ might have on the magnitude of J_{Pt-H}. The effect of the change of electronegativity of the ligands is twofold. Increase in electronegativity would increase the effective nuclear charge on the platinum and hence increases K_{M-H}, i.e., for the halide complexes J_{M-H} would decrease Cl > Br > I. However, the polar nature of the Pt—X bond means that electron density is withdrawn from M to X. Thus the *s*-electron density at the platinum is reduced with increasing electronegativity of X. This consideration predicts K_{M-H} for the halides of I > Br > Cl. However, the presence of a more electronegative ligand *trans* to the M—H bond would be expected to increase the *s* character of the bond. This effect predicts K_{M-H}, Cl > Br > I. Thus the change in electronegativity is seen to result in several opposing effects and hence the relative sizes of the effects is crucial. In conclusion, the marked relationship between the K_{M-H} and the ligand field strength of the ligands X suggests that for the complexes $[Pt(PEt_3)_2HX]$, the change in the mean excitation energy term is dominant.

Finally, it may be noted that K_{M-H} is unusually low when there are unsaturated ligands attached to the metal such as cyanide, carbon monoxide, or the cyclopentadienyl ligand, the high ligand field strength of these ligands may be the major factor involved.

In some cyclopentadienyl hydrides, coupling of the M-hydrogen with the hydrogens of the π-cyclopentadienyl group may be observed. The coupling is usually small, (J_{H,C_5H_5} = 1–3 cps.). The fine structure arising from the π-cyclopentadienyl hydrogens may be used to determine structures (*105*), and in cases of low solubility may be diagnostic for the presence of M-hydrogens. Finally, in the trihydrides $(\pi\text{-}C_5H_5)_2TaH_3$ and $(\pi\text{-}C_5H_5)_2WH_3^+$, coupling between nonequivalent hydrogens has been observed, the spectra being typical for an A_2B system (*99*). Similar H—H coupling has been observed for the nonequivalent hydrogens in $IrH_2Cl(PEt_2Ph)_3$ (*241*).

As noted above, the chemical shifts for hydrogens attached directly to a transition metal are unique in that they are markedly greater than those of other hydrogens. Two theories have been put forward to account for the magnitude of these high field shifts, both of them invoking shielding by the nonbonding electrons of the metal. The essential difference between the theories lies in the consideration given to electrons in orbitals corresponding to an excited state of the metal atom. Stevens *et al.* (*252*) ignore this contribution and evaluate the chemical shift [in terms of diamagnetic shielding (σ^d) of the proton] from the calculated electron densities in environmental metal orbitals. Their studies have been confined to compounds of first-row transition metals, in particular $HCo(CO)_4$, and their results indicate the correct order of shift when the metal-hydrogen distances are taken as normal, i.e., the sum of the covalent radii. Thus this treatment is consistent with normal metal-hydrogen distances. The alternative and more refined theory of Buckingham and Stephens (*30*) incorporates the arguments of the above theory, but shows that contributions from excited states are significant for complexes in which the metal atom has partially filled *d* orbitals. These contributions are those responsible for temperature-independent paramagnetism and lead to the introduction of a paramagnetic shielding term (σ^P) which, according to the position of the H atom, may either increase or decrease the total σ. This contribution becomes especially significant for the second- and third-row transition metals. The success of the Stevens *et al.* treatment with $Co(CO)_4H$ may be due to the small contribution of the paramagnetic term (σ^P) for this molecule. The shielding ($\sigma = \sigma^d + \sigma^p$) of the proton is found to be very sensitive to anisotropy in the metal atom, so that neglect of distortions from regular symmetry could lead to appreciable errors in the calculation. In this connection it is important to note that all the hydrides whose structures have been investigated show marked deviation from the symmetrical models.

The Stephens and Buckingham theory shows that the "paramagnetic" shielding term (σ^p) is dependent on ΔE (the energy separation of the ground and excited states), R_{H} (the metal-hydrogen internuclear distance), and k, the exponent of the d orbitals. The latter was taken to be constant over any particular row of transition metals.

For complexes of approximately O_h symmetry, e.g., MX_5H, and a metal of d^6 configuration, the calculations yield values of approximately 30 p.p.m. for $R_{\mathrm{H}} = 1.1$ Å, σ^p being the principal contributor. A large change in k or a slight increase in R_{H} causes appreciable changes in the total shielding; σ decreases with increasing R_{H} $[\sigma \alpha (1/R_{\mathrm{H}}^3)]$. However, σ^p appears not to be very sensitive to changes in ΔE and therefore changes in ΔE cannot alone account for the much larger changes in τ occurring in a series of complexes of the type MX_4HZ, for example, where M = Co, Rh, or Ir. In passing from the first to the third transition series, ΔE increases and, although σ^d and σ^p would also show a corresponding increase for a given value of R_{H}, since in fact R_{H} also increases, σ is expected to decrease somewhat.

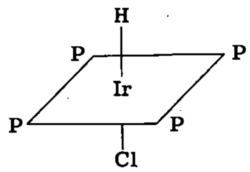
For molecules such as MX_4HY and *cis*- and *trans*-MX_4H_2, assuming R_{H} and k remain constant, increase in ligand field strength *trans* to H will cause σ^p to decrease, while an increase in the ligand field strength *cis* to H will cause an increase in σ^p. In conclusion, the Stephens and Buckingham theory is thus in accord with the experimental findings in that:

(*i*) in *trans*-$Fe(P—P)_2HX$, τ decreases from X = halogen to X = hydrogen (increasing ligand field strength)

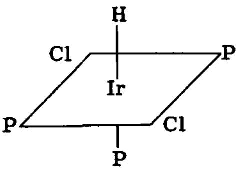
(*ii*) in *trans*-$M(P—P)_2HX$, X = halogen, τ decreases from M = Fe to M = Ru (increase in ΔE, but increase in R_{H})

(*iii*) in $HM(CN)_5^{3-}$, τ decreases from M = Co to M = Rh (increase in ΔE, but increase in R_{H})

(*iv*) τ decreases in passing from



to



where P = PEt_3. There are, however, some observations not in accord with the theory; for example, in the series *trans*-M(P—P)$_2$HX, where M = Fe, Ru, or Os, there is a decrease in τ for X = Cl, Br, I which is the reverse of the normal order of ligand field strengths. These and other anomalies may be due to uncertainties in the correct value of k to be assumed. Thus the Stephens and Buckingham theory is in essence satisfactory, although uncertainties in the appropriate values of k and R_H, and in the actual symmetry of the molecules, make detailed calculations and correlations unreliable.

C. INFRARED STUDIES

The spectra of most hydrides show bands in the region 1700–2200 cm^{-1}, which are assigned to the metal-hydrogen stretching frequency. Originally, this assignment was confirmed by comparison of the spectra with those of the metal-deuteride analogs; the spectra of the deuterides showed absence of the band at 1700–2200 cm^{-1} and appearance of a new band at lower frequency. The ratio of the frequencies of the two bands ($\nu_{M-H}/\nu_{M-D} = 1.4$) is in accord with simple theory.

The occurrence of the metal-hydrogen stretching frequencies in the given region is consistent with a covalent metal-hydrogen single bond of sensible average strength (e.g., force constant of Co—H in $HCo(CO)_4$ = 22.2 mdynes/Å). The intensity of the band varies from very weak, e.g., as in $(\pi\text{-}C_5H_5)_2ReH$, to very intense as in $(\pi\text{-}C_5H_5)_2WH_2$, where it is the strongest band in the spectrum and would normally be called a very strong band. For insoluble complex hydrides of high molecular weight the detection of ν_{M-H} may provide the only easily obtainable direct evidence for the presence of a metal-hydrogen system. Metal-hydrogen deformations occur in the region 700–950 cm^{-1} as expected (*57*, *68*, *73*). The bands are, in general, of weak to medium intensity. Many of the reported metal-hydrogen stretches are given in Tables III, IV, VI–VIII.

A study of the series *trans*-$(LR_3)_2PtHX$, where L = P or As, and R = Me or Et, shows that the Pt—H bond is remarkably sensitive to the nature of the other ligands. In general, substitution in the *trans* position with ligands of increasing *trans*-effect causes a decrease in the Pt—H stretching frequency, and hence a decreased bond strength (*35*, *44*) (see Table II). Similarly, for the complexes *trans*-$RuHX[C_2H_4(PEt_2)_2]_2$, ν_{Ru-H} falls in the order: X = Hal > NO_2 > CN > H (*42*).

In this latter series, the halogens are in the reverse order to that found for the platinum complexes above; this may be due to a change in π-bonding contributions by the halogens (*42*).

The M-H stretching frequency depends to some extent on the solvent

TABLE II

Pt—H STRETCH FOR THE COMPLEXES *trans*-$[(PEt_3)_2PtHX]$

X =	NO_3	Cl	Br	I	NO_2	SCN	CN
ν_{Pt-H} = (cm^{-1})	2242	2183	2178	2156	2150	2112	2041

used for the determination of the spectrum; for a solvent change from chloroform to hexane, a shift of ~30 cm^{-1} to lower frequencies has been observed when the hydride is *trans* to halogen; when the hydride is *trans* to phosphorus or arsenic, however, the M-H stretch is almost solvent-insensitive (*2*).

There is a loose correlation between the M-H stretching frequency and the resonance position in the proton magnetic resonance spectrum. Complexes with the more highly shielded protons frequently show higher M-H stretches (*241*).

D. FIELD STRENGTH OF THE HYDRIDE LIGAND

Studies of the ultraviolet spectrum of the anion $[Co(CN)_5H]^{3-}$ show a lowest energy *d-d* transition at 305 mμ. This band is coincident with the $^1T_{1g}$ band in the spectrum of $[Co(CN)_6]^{3-}$ and therefore, since the hydride is unlikely to have a ligand field strength substantially greater than cyanide, it is presumably of the same order (*108*, *231*).

The ultraviolet spectra of the complexes *trans*-$Ru[C_2H_4(PEt_2)_2]_2XY$ (III), where X = Cl and Y = Cl, H, R, or Ar, show from the shifts in position of a band assigned to the lowest *d-d* transition that the order of field strengths for the ligands Y is $Cl \ll H \leqslant R, Ar \sim CN$ (*41*). For Y = CN, the energy of the transition was estimated by averaging the lowest band for complexes in which X = Y = Cl and X = Y = CN, since the complex (III), where X = Cl, Y = CN, could not be made. It has been pointed out that this estimate might be in error (*247*) since, although in all the complexes except where X = Y = CN the lowest first excited state is ^1E, in the latter case the lowest state would be expected to be the $^1A_2$. Also, an inherent inaccuracy in the above studies arises from the difficulty in detecting the ^1E band owing to its partial coverage by charge-transfer bands.

Interpretations of the thermal stability of, e.g., $FeH_2[o\text{-}C_6H_4(PEt_2)_2]_2$, in relation to that of the hydride-halide derivative have been made on the basis of a greater ligand field strength of hydride relative to halide ligands (*40*).

Recent studies of *d-d* transitions shown in the ultraviolet spectra of some rhodium(III) hydrides have suggested a rather lower ligand field strength for the hydride, placing it between that of water and ammonia

(*227a*). Thus this work shows that the hydride ligand is spectrochemically more akin to a halide ligand.

It is concluded that in most cases to date the hydride behaves as a strong-field ligand, but that for the weak-field nitrogen-ligand rhodium hydrides (*89*, *227a*) the hydride behaves as a weak-field ligand.

This anomaly may be understood in that the hydride ion ($1s^2$) is a unique ligand for which π-bonding is impossible and the ligand would be expected to be highly polarizable. Thus the field strength of the hydride ligand would be more dependent on its environment in particular complexes than most other ligands. In complexes where back-donation from the metal via π-bonding is not possible (e.g. with N-ligands), it seems reasonable that the H should carry a larger negative charge than, for example, in the tertiary phosphine complexes and hence exhibit a weaker ligand field strength.

The hydride ligand shows a strong *trans*-effect. Kinetic studies (Section III,A,3) have shown that the hydride ligand causes more rapid substitutions in the position *trans* to itself than any other anionic ligand (*8*). Correlations with X-ray and infrared studies (Section II,B and C) supply corroborative evidence.

III. The Chemistry of Particular Hydride Complexes

A. COMPLEX HYDRIDES WITH TERTIARY PHOSPHINES AND RELATED LIGANDS

Transition-metal hydride complexes which also contain tertiary phosphines as stabilizing ligands are among the most numerous and stable of presently known hydride complexes. Their relative ease of preparation, and their thermal and oxidative stability, make them suitable materials for carrying out detailed studies of the metal-hydrogen system. As shown in Table III, a considerable range of complexes in this class has been prepared and their infrared and proton magnetic resonance spectra have been studied. The results of these studies are discussed in Section II,B and C, respectively.

1. *Historical Introduction; Occurrence*

The first known complex in this class, *trans*-bis(triethylphosphine)-platinum chlorohydride, was prepared by Chatt and co-workers (*36*). In the light of other hydrides known at that time, in particular the carbonyl hydrides of iron and cobalt and bis(π-cyclopentadienyl)rhenium hydride, the great stability of this complex was quite unique. It rapidly became clear that tertiary phosphine ligands were markedly effective in stabilizing the metal-hydrogen bond, and ligands such as Ph_3P, Et_3P, o-$C_6H_4(PMe_2)_2$,

TABLE III
COMPLEX HYDRIDES WITH TERTIARY PHOSPHINES AND RELATED LIGANDS

Compound[a]	Color	M.P. (°C)	References to preparation	Infrared, ν_{M-H} (cm^{-1})	NMR chemical shift of M-hydrogen τ(p.p.m.)	Notes
Mn						
$MnH(CO)_4(P^{IV})$	Very pale yellow	70	*(147)*	—	—	—
$MnH(NO)_2(P^{IV})_2$[b]	Lemon yellow	153–154	*(170)*	—	—	—
$Mn_2H(CO)_8(\mu\text{-}PPh_2)$	Yellow	154–155	*(100)*	*(100)*	26.8 $J_{H,P}$32cps *(100)*	—
$Mn_2H(CO)_8[\mu\text{-}P(CF_3)_2]$	Yellow	—	*(113)*	—	—	—
Re[c]						
$ReH_5(P^{IV})_2$	—	—	*(211)*	—	—	—
$ReH_4(P^{IV})_3$	—	—	*(211)*	—	—	—
$ReH_3(P^{IV})_4$	Yellow	144	*(208, 211)*	~2050*(208)*	—	Properties *(212)*
$ReH_3(P^{IV})_2\cdot 2EtOH$	Red	155	*(208)*	~2000*(208)*	—	—
$ReH_3(P^{IV})_2$	Red	178/193 dec.	*(208)*	~2000*(208)*	—	—
Fe						
trans-$FeH_2(PP^{VI})_2$	Orange	248–249.5	*(37, 38, 40)*	1726; δ_{Fe-H} = 716 *(38, 40)*	23.0 *(38, 241)*	Dipole moment = 1.8D *(40)*
trans-$FeHCl(PP^{VI})_2$	Red	214–218 *(40)* 230.5–231.5	*(37, 40)*	1870 *(40)*	40.7 *(40, 241)*	—
trans-$FeHCl(PP^{III})_2$	Red	180 dec.	*(37, 40)*	1810 *(40)*	—	—
trans-$FeHCl(PP^{IV})_2$	Red	154.5–155.5	*(37, 40)*	1849 *(40)*	41.9 *(40, 241)*	—
trans-$FeHI(PP^{IV})_2$	Red-brown	173 dec.	*(37, 40)*	1872 *(40)*	38.6 *(40, 241)*	—
$[FeH(CO)_3(P^{IV})_2]^+$[d]	Red-brown	—	*(60, 63)*P[e]	—	17.75 doublet $J_{H,P}$ 35.3cps *(63)*	—
$[FeH(CO)_4(P^{IV})]^+$[d]	Red-brown	—	*(60, 63)*P	—	17.78 triplet $J_{H,P}$ 30.2cps *(63)*	—
$[FeH(CO)_3(As^{IV})_2]^+$[d]	Red-brown	—	*(63)*P	—	18.11 *(63)*	—
$[FeH(CO)_4(As^{IV})_4]^+$[d]	Red-brown	—	*(63)*P	—	18.11 *(63)*	—
$Fe_2H(C_5H_5)(CO)_2(\mu\text{-}PMe_2)$	Dark brown	137–140	*(125)*	—	28.73 $J_{H,P}$43.5cps *(125)*	—
$Fe_2H(C_5H_5)(CO)_2(\mu\text{-}PPh_2)$	Dark brown	153–157	*(125)*	—	28.67 $J_{H,P}$41.0cps *(125)*	—

Ru						
trans-RuH$_2$(PP^{VI})$_2$	Yellow	276–278.5	(*39*)	1617 (*39*)	—	Dipole moment = 1.2D (*39*)
trans-RuH$_2$(PP^{IV})$_2$	Colorless	147–153 280 dec.	(*39*)	1615 (*39*)	—	Dipole moment = 2.1D (*39*)
trans-RuHCl(PP^{III})$_2$	Colorless	217–221 dec.	(*39*)	1891 (*39, 42*)	—	UV (*41*); dipole moment = 4.8D (*39*)
trans-RuHBr(PP^{III})$_2$	Yellow	215–220 dec.	(*39*)	1895 (*39, 42*)	—	UV (*41*)
trans-RuHI(PP^{III})$_2$	Yellow	322 dec.	(*39*)	1898 (*42*)	—	UV (*41*)
trans-RuH(SCN)(PP^{III})$_2$	Colorless	240 dec.	(*39*)	1870 (*39*)	—	—
trans-RuH(CN)(PP^{III})$_2$	Yellow	230 dec.	(*39*)	1754 (*39*)	—	UV (*41*)
trans-RuH(NO$_2$)(PP^{III})$_2$	Yellow	240 dec.	(*39*)	1858 (*39*)	—	—
trans-RuHCl(PP^{IV})$_2$	Colorless	175; 310 dec.	(*39*)	1938 (*42*)	32.5 (*39, 42*)	—
trans-RuHBr(PP^{IV})$_2$	Yellow	188–190 dec.	(*39*)	1945 (*42*)	31.7 (*39, 42*)	—
trans-RuHI(PP^{IV})$_2$	Yellow	212–224 dec.	(*39*)	1948 (*42*)	30.0 (*39, 42*)	—
trans-RuH(SCN)(PP^{IV})$_2$	Colorless	245–249 dec.	(*39*)	1919 (*42*)	—	—
trans-RuH(CN)(PP^{IV})$_2$	Colorless	Impure	(*39*)	1803 (*42*)	—	—
trans-RuHCl(PP^{I})$_2$	—	—	—	1891 (*2*)	—	Dipole moment = 4.95 (*39*)
trans-RuHCl(PP^{II})$_2$·½C$_6$H$_6$	Yellow	283–284.5	(*39*)	1978br (*39*)	—	—
trans-RuHCl(PP^{VI})$_2$	Yellow	250–256 dec.	(*39*)	1978br (*39*)	—	Dipole moment = 4.45 (*39*)
trans-RuHI(PP^{VI})$_2$	Brown	278–283 dec.	(*39*)	1976br (*39*)	—	—
trans-RuHMe(PP^{V})$_2$	—	—	(*42*)	1884 (*42*)	—	—
trans-RuHEt(PP^{V})$_2$	—	—	(*42*)	1873 (*42*)	—	—
trans-RuHPr^{n}(PP^{V})$_2$	—	—	(*42*)	1867 (*42*)	—	—
trans-RuHCl[*o*-C$_6$H$_4$(AsMe$_2$)$_2$]$_2$	—	190 dec.	(*39*)	1804 (*39*)	—	—
cis-RuH(2-C$_{10}$H$_7$)(PP^{III})$_2$	—	—	(*34*)	1802 (*34*)	18.6 (*34*)	—
cis-RuH(CH$_2$(Me)P(CH$_2$)$_2$P(Me)CH$_2$)(PP^{III})$_2$	—	—	(*39*)	—	—	—
RuHCl(CO)(PEt$_2$Ph)$_3$	Colorless	102.5–103.5	(*45, 240*)	—	17.0 (*45, 241*)	—
RuHBr (CO)(PEt$_2$Ph)$_3$	—	—	—	—	17.7 (*241*)	—
RuHCl(CO)(P^{IV})$_3$	—	139	(*46, 258, 263*)	2020 (*263*)	—	—
Os						
trans-OsH$_2$(PP^{VI})$_2$	Lemon	293–297	(*39*)	1720 (*39*)	—	—
trans-OsH$_2$(PP^{IV})$_2$	Colorless	150–155	(*39*)	1721 (*39*)	—	—
trans-OsHCl(PP^{II})$_2$·C$_6$H$_6$	Yellow	294.5–298.5 dec.	(*39*)	2045 (*39*)	—	—
trans-OsHCl(PP^{V})$_2$·C$_6$H$_6$	Yellow	313.5–318 dec.	(*39*)	2046 (*42*)	—	—

TABLE III (*Continued*)

Compound^a	Color	M.P. (°C)	References to preparation	Infrared, ν_{M-H} (cm^{-1})	NMR chemical shift of M-hydrogen τ(p.p.m.)	Notes
trans-$OsHCl(PP^{III})_2$	Colorless	190–205 dec.	(*39*)	2014 (*39*)	—	—
trans-$OsHCl(PP^{IV})_2$	Colorless	171–315 dec.	(*39*)	2039 (*39*)	36.7 (*39*)	—
trans-$OsHI(PP^{IV})_2$	Yellow	224–231	(*39*)	2051 (*39*)	31.5 (*39*)	—
trans-$OsH(SCN)(PP^{IV})_2$	Colorless	200 dec.	(*39*)	2009 (*39*)	—	—
$OsHCl(CO)(P^{IV})_3$	—	—	(*263*)	2100 (*263*)	—	—
$OsHBr(CO)(P^{IV})_3$	White	276	(*258*)	2105 (*263*)	—	X-ray (*227*)
$OsHCl(CO)(PhEt_2P)_3$	—	—	(*46*)	—	17.1 (*241*)	—
$OsHBr(CO)(As^{IV})_3$	Tan	195–243 dec.	(*257*)	2087 (*257*)	—	δ_{M-H}822,801 cm^{-1} (*257*)
$OsHCl(CO)(As^{IV})_3$	Colorless	200; 247 dec.	(*257*, *263*)	2085 (257)	—	δ_{M-H}823,807 cm^{-1} (*257*)
Co						
$HCo(P^{IV})_3{}^d$	—	—	(*273*)	—	—	—
$HCo(PP^{V})_2$	Red	—	(*273*)	1884 (*273*)	—	—
$HCo(CO)_3(P^{IV})$	Yellow	70 dec.	(*162*)	—	—	—
$HCo(CO)_3P(OPh)_3$	Dark yellow	0 dec.	(*162*)	—	—	—
Rh						
$RhHCl_2(AsMePh_2)_3$	Yellow	172	(*67*, *198*)	2677 (*198*)	—	—
$RhHBr_2(AsMePh_2)_3$	Orange	175	(*198*)	2073 (*198*)	—	—
$RhHI_2(AsMePh_2)_3$	Deep orange	164	(*198*)	2058 (*198*)	—	—
$RhH(CO)(P^{IV})_3$	Yellow	—	(*9*)	2004 (*9*)	19.9 (*9*)	X-ray (*196*)
Ir						
$IrH_3(P^{IV})_3$	Colorless	227–229 dec.	(*124*)	2100, 1745 (*124*)	—	Isomers not distinguished; dipole moment = 4.95D
α	Colorless	176 225 dec.	(*208*)	2124, 1745 (*208*)	—	Light-sensitive; dipole moment = 2.7D
α	Colorless	173	(*210*)	2130, 1750 (*210*)	—	Dipole moment = 2.75D
β	Colorless	149–152 217 dec.	(*208*, *209*)	2083 (*208*)	—	Dipole moment = 4.3D
β	Colorless	152–153	(*209*, *210*)	2075 (*210*)	—	Dipole moment = 4.75D

$IrH_3(As^{IV})_3$						
α	White	210 dec.	*(31a)*	2100 *(31a)*	—	Dipole moment = 5.2D
β	White	223 dec.	*(31a)*	2109, 1715 *(31a)*	—	—
$IrH_3(P^{IV})_2$	White	145 dec.	*(210a, 211)*	—	—	—
	White	140–145 dec.	*(5c)*	1945 *(5b)*	—	—
$IrH_3(As^{IV})_2$	White	143 dec.	*(31a, 211)*	1937 *(31a)*	—	—
$IrH_3(PEt_2Ph)_3$	—	—	*(240)*	—	J_{H-P} *trans* = 110–150 cps	—
				—	J_{H-P} *cis* = 15 cps *(240)*	—
$IrH_3(As^{IV})_3 \cdot C_5H_5N$	White	138 dec.	*(31a)*			
$[IrH_2(P^{IV})_3]^+ClO_4^-$	White	139–143	*(208, 209)*	2140, 2249 *(208)*	—	—
$[IrH_2(As^{IV})_3]^+ClO_4^-$	White	120 dec.	*(31a)*	2222, 2141 *(31a)*	—	—
$[IrH_2(P^{IV})_4]^+ClO_4^-$	White	207 dec.	*(5a)*	2250, 2225 *(5a)*	—	—
$IrH_2(P^{IV})_3$	Pale yellow	152–159	*(208)*	2210, 2083 *(208)*	—	—
$IrH_2Cl(PEt_2Ph)_3$	—	134–135	*(46, 240)*	2162, 2026 *(2, 33)*	33.3; 21.1 *(241)*	—
$IrH_2Cl(P^{IV})_3$	Colorless	218–220	*(124)*	2210, 2130 *(124)*	—	—
	Colorless	250 dec.	*(260)*	2215, 2110 *(260)*	—	Light-sensitive
		163	*(5a)*	2180, 2135 *(5a)*	—	—
$IrH_2Br(P^{IV})_3$	White	242 dec.	*(260)*	2240, 2090 *(260)*	—	Light-sensitive
	Ivory	168	*(208)*	2220, 2065 *(108)*	—	—
$IrH_2Br(As^{IV})_3$	—	234 dec.	*(31a)*	2188 *(31a)*	—	—
$IrH_2I(P^{IV})_3$	Yellow	190	*(5a)*	2210, 2080 *(5a)*	—	—
$IrH_2(OCOCH_3)(P^{IV})_3$	White	167	*(208)*	2200, 2150 *(208)*	—	—
	White	160	*(5a)*	2125, 2170 *(5a)*	—	—
$IrH_2(OCOCOOH)(P^{IV})_3$	White	184	*(5a)*	2210, 2260 *(5a)*	—	—
$IrH_2(OCOCH_2COOH)(P^{IV})_3$	White	157	*(208)*	2180, 2160 *(208)*	—	—
			(5a)	2190, 2195 *(5a)*	—	—
$[IrH_2NH_3(P^{IV})_3]^+ClO_4^-$	—	233–234 dec.	*(5a)*	2148, 2152 *(5a)*	—	—
$[IrH_2(P^{IV})_2(PP^V)]^+ClO_4^-$	—	182–184 dec.	*(5a)*	2100, 2150 *(5a)*	—	—
$[IrH_2(P^{IV})_2py_2]^+ClO_4^-$	—	224–226	*(5a)*	2150, 2155 *(5a)*	—	—
$[IrH_2(P^{IV})_3]^+NO_3^-$	Yellow	199	*(5a)*	2180 *(5a)*	—	—
$IrH_2NO_2(P^{IV})_3$	Colorless	141–143	*(5a)*	2130, 2180 *(5a)*	—	—
$IrH_2CN(P^{IV})_3$	—	231–234	*(5a)*	2090, 2180 *(5a)*	—	—
$IrHCl_2(PEt_2Ph)_3$	—	—	*(240)*	—	31.2 (α); 22.5 (β) *(241)*	Isomers
$IrHBr_2(PEt_2Ph)_3$	—	—	—	—	30.6 *(241)*	—
$IrHBr_2(P^{IV})_3$	Yellow	213	*(5a)*	2250 *(5a)*	—	—
$IrHBr_2(P^{IV})_3 \cdot C_6H_6$	Yellow	167	*(208)*	2220 *(208)*	—	—

TABLE III (*Continued*)

Compound[a]	Color	M.P. (°C)	References to preparation	Infrared, ν_{M-H} (cm^{-1})	NMR chemical shift of M-hydrogen τ(p.p.m.)	Notes
$IrHBr_2(AsPh_2Me)_3$	Yellow	248	(*198*)	2094 (*198*)	—	—
$IrHBr_2(P^{IV})_3$	—	—	—	—	23.6 (*241*)	—
$IrHCl_2(P^{II})_3$						
α	Yellow	81–84	(*45*)	2114 (*45*)	22.6 (*241*); 17.9 (*45*)	Dipole moment = 2.55D
β	White	99–100	(*45*)	2213 (*45*)	31.6 (*241*); 27 (*45*)	Dipole moment = 8.0D
				2090 (*33*)	—	Dipole moment = 2.5D
$IrHI_2(P^{IV})_3$	Yellow	220	(*5a*)	2270 (*5a*)	—	—
$IrHCl_2(As^{II})_3$	—	—	—	2099 (*2, 33*)	—	Dipole moment = 2.2D
$IrHCl_2(P^{IV})_3 \cdot C_6H_6$	Pale yellow	261–263 dec.	(*124*)	2230 (*124*); 2220 (*208*)	—	—
		145	(*5a*)	2200 (*5a*)		
$IrHCl_2(P^{IV})_3$	Yellow	256 dec.	(*260*)	2200 (*260*)	—	—
$IrHCl_2(As^{IV})_3$	Yellow	240 dec.	(*260*)	2170 (*260*)	—	—
		195 dec.	(*31a*)	2183 (*31a*)	—	—
$IrHCl_2(Sb^{IV})_3$	Yellow-orange	201 dec.	(*260*)	2100 (*260*)	—	—
$IrHBr_2(As^{IV})_3$	—	244 dec.	(*31a*)	2188 (*31a*)	—	—
$IrHBr_2(Sb^{IV})_3$	—	—	(*211*)	—	—	—
$IrH_3(CO)(P^{IV})_2$						
α	White	146	(*5c, 210a*)	—	—	—
β	—	138	(*5c, 210a*)	—	—	—
$[IrH_2(CO)(P^{IV})_3]^+ClO_4^-$						
α	Yellow	137	(*5c*)	2155, 2011 (*5c*)	—	—
β	White	210	(*5c*)	2185, 2011 (*5c*)	—	—
				2165, 2085, 2050 (*210*)	?	Isomers not separated
$[IrH_2(CO)(P^{IV})_2]^+ClO_4^-$	Yellow	103	(*5c*)	2165, 2080 (*5c*)	—	—
$IrH_2Cl(CO)(P^{IV})_2$	—	—	(*256*)	—	21.2 (*256a*)	—
$IrH_2Br(CO)(P^{IV})_2$	—	—	(*256a*)	—	17.5, 17.9 (*256a*)	—
$IrH_2I(CO)(P^{IV})_2$	—	—	(*256a*)	—	25.7, 19.0 (*256a*)	—
$IrH(CO)(P^{IV})_3$	Yellow	—	(*256a*)	2068 (*265a*)	21.2 J_{P-H} = 42 cps (*256a*)	—
	Yellow	187–188	(*5c*)	2120 (*5c*)	—	—

$IrH(CO)(P^{IV})_2$	Yellow	132	(*5c*)	2000, 1950 (*5c*)	—	—
$IrHCl_2(CO)(P^{IV})_2$	White	315–320 dec.	(*261*, *264a*)	2245 (*261*)	—	—
$IrHBr_2(CO)(P^{IV})_2$	Yellow	348–351 dec.	(*261*)	2230 (*261*)	—	—
$IrHI_2(CO)(P^{IV})_2$	Yellow	155	(*5c*)	2040 (*5c*)	—	Light-sensitive
$IrHCl(CO)(As^{IV})_2$	Yellow	249–252 dec.	(*261*)	2200 (*261*)	—	—
$IrHCl_2(CO)(PEt_2Ph)_2$						
α	Yellow	110–112	(*2*, *43*)	2008 (*43*), 2032 (*2*)	19.0 J_{P-H} = 16 cps (*43*)	—
β	Colorless	123–136 dec.	(*43*)	2194, 2205, 2237 (*43*)	26.05 J_{P-H} = 12 cps (*43*)	CO resonance not distinguished
$IrHBr_2(CO)(PEt_2Ph)_2$	Colorless	140–144 dec.	(*43*)	2232 (*43*)	—	—
$Ir_2H_2Cl_4(CO)_2(P^{II})_2$	Colorless	170–190 dec.	(*43*)	2242 (*43*)	—	—
Ni						
$NiHCl(P^{III})_2{}^d$	—	—	(*106*)	—	— (*106*)	—
Pd						
$PdHCl(P^{II})_2$	—	Impure	(*35*)	2035 (*35*)	—	—
Pt						
$PtH_2Cl_2(P^{II})_2$	Colorless	82–100 dec.	(*35*)	2254, 2265 (*35*)	—	—
$PtH_2(P^{IV})_4$	Pale yellow	116–118	(*50*)	—	—	—
$PtH_2(P^{IV})_3$	Yellow	125–130	(*50*)	—	—	—
trans-$PtH_2(P^{IV})_2$	Yellow-white	175–178	(*50*)	1670; δ_{MH} = 815 (*50*)	—	—
$[PtH(P^{IV})_3]^+X^f$	—	—	(*31a*)	—	—	—
trans-$PtHCl(P^{I})_2$	Colorless	132–137	(*44*)	2182 (*35*, *44*)	—	(*44*)
trans-$PtHCl(P^{II})_2$	Colorless	81–82	(*36*, *44*)	2183; δ_{MH} = 821 (*35*)	26.9 $J_{P,H}$ 14cps (*44*)	Dipole moment = 4.2D (*44*)
trans-$PtHBr(P^{II})_2$	Colorless	94–97	(*44*)	2178 (*35*)	25.6 $J_{P,H}$ 15cps (*44*)	Dipole moment = 4.45D; X-ray (*28*)
trans-$PtHI(P^{II})_2$	Colorless	73–75	(*44*)	2156 (*35*)	22.8 $J_{P,H}$ 13cps (*44*)	Dipole moment = 4.5D (*44*)
trans-$PtH(NO_2)(P^{II})_2$	Colorless	95–97.5	(*44*)	2150 (*35*)	29.6 $J_{P,H}$ 16.5cps (*44*)	Dipole moment = 5.8D (*44*)
trans-$PtH(NCS)(P^{II})_2$	Colorless	61–64	(*44*)	2112; δ_{MH} = 844 (*44*)	23.2, 27.9 $J_{P,H}$ 14cps (*44*)	Dipole moment = 7.4D (*44*)
trans-$PtH(CN)(P^{II})_2$	Colorless	106–107	(*44*)	2041; δ_{MH} = 826 (*44*)	17.9 $J_{P,H}$ 15.5 cps (*44*)	Dipole moment = 5.4D (*44*)
trans-$PtH(NO_3)(P^{II})_2$	Colorless	47–49	(*44*)	2242 (*35*)	33.8 $J_{P,H}$ 15.5cps (*44*)	—

TABLE III (*Continued*)

Compound[a]	Color	M.P. (°C)	References to preparation	Infrared, ν_{M-H} (cm^{-1})	NMR chemical shift of M-hydrogen τ(p.p.m.)	Notes
trans-$PtH(CNO)(P^{II})_2$	Colorless	65–66	(*44*)	2229; δ_{MH} = 840 (*44*)	—	—
trans-$PtHCl(P^{III})_2$	Colorless	47–49	(*44*)	2183 (*44*)	—	—
trans-$PtHCl(P^{V})_2$	Colorless	131–132.5	(*44*)	2206 (*44*)	—	—
trans-$PtHI(P^{V})_2$	Colorless	115–116	(*44*)	2189 (*44*)	—	—
trans-$PtHCl(P^{IV})_2$	Colorless	215–220 dec.	(*44*) (*316*)[g]	2220 (*44*)	—	—
trans-$PtHI(P^{IV})_2$	Colorless	195–212 dec.	(*44*)	2186 (*44*)	—	—
trans-$[PtH(NH_3)(P^{II})_2]^+Cl^-$	—	Impure	(*36*)	—	—	—
trans-$PtHCl(As^{II})_2$	Colorless	91–93 dec.	(*44*)	2174 (*44*)	—	—
trans-$PtHBr(As^{II})_2$	Colorless	107–110 dec.	(*44*)	2167 (*44*)	—	—
trans-$PtHI(As^{II})_2$	Colorless	109–112 dec.	(*44*)	2139 (*44*)	—	—
trans-$PtH(NCS)(As^{II})_2$	Colorless	56–57 dec.	(*44*)	2108 (*44*)	—	—

[a] Symbols used for phosphine ligands: $P^{I} = PMe_3$; $P^{II} = PEt_3$; $P^{III} = PPr_3^n$; $P^{IV} = PPh_3$; $P^{V} = PEtPh_2$. $PP^{I} = CH_2(PMe_2)_2$; $PP^{II} = CH_2(PPh_2)_2$; $PP^{III} = C_2H_4(PMe_2)_2$; $PP^{IV} = C_2H_4(PEt_2)_2$; $PP^{V} = C_2H_4(PPh_2)_2$; $PP^{VI} = o\text{-}C_6H_4(PEt_2)_2$; arsine ligands are coded analogously.

[b] Only known nitrosyl hydride.

[c] Compounds listed under Re are incompletely reported.

[d] Not isolated.

[e] P = obtained by protonation in strongly acid media.

[f] Where X = Cl^-, NO_2^-, ClO_4^-, BPh^-, BF_4, and $CH_3OSO_3^-$

[g] Complexes where Cl is replaced by CN or SCN.

and $C_2H_4(PEt_2)_2$ have been successfully employed for this purpose with this majority of the Group VIII metals. The hydrides of the heavier Group VIII elements seem to be more easily prepared than those of the first transition series; however, complexes of this type may be expected for the majority of the *d*-block elements, e.g., $(PP)Mo(CO)_3HX$.*

It is interesting to note that some complexes of Rh, Pt, and Ir, originally prepared a considerable time ago and formulated as low-oxidation state complexes, have recently been shown to be hydrides. For example a rhodium compound, prepared by Nyholm in 1941 (*67*) by treating rhodium trichloride with diphenylmethylarsine and hypophosphorous acid, has been shown to be the hydride $RhHCl_2(AsMePh_2)_2$ (*198*). These complexes were not recognized as hydrides at the time, since hydrides were unsuspected and the additional hydrogen is not detectable from the analytical figures. Also, Vaska, who was studying the reaction of osmium and ruthenium complexes with tertiary phosphines in alcoholic solutions, reported the products to be univalent complexes MXL_3 (*259, 264*). Later studies showed that these too were hydride complexes (*45, 46, 257, 258*).

2. Preparation and Properties

The important preparative methods, namely, reduction of phosphine metal halide complexes and the hydride-transfer and reverse carbonylation reactions, were discussed in Section I,B,2 and 3. Other routes are incidentally discussed below.

The complexes in this class are usually molecular ranging from colorless to yellow to red and having solubility characteristics similar to their halide analogs (frequently only slightly soluble in the more polar organic solvents).

In general the complexes are mild reducing agents and in solution will reduce silver nitrate to silver (*36*). The hydrides are not acidic in solution, nor will they form sodium salts analogous to those of the carbonyl hydrides (*40*).

3. Replacement of the Hydride Ligand

The lability of the M—H bond in these complexes varies widely. The complex $PtClH(PEt_3)_2$, for example, shows no exchange in hot D_2O; in acid solutions, however, exchange occurs moderately rapidly, which may be understood in terms of the protonation reaction (36). Despite the comparative inertness of the M—H system in some of these complexes, the replacement of the hydrogen by ligands such as halides may be achieved in many cases under a variety of conditions.

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* (PP) represents a chelating diphosphine ligand.

Many of the octahedral phosphine hydride and halogenohydride complexes undergo a stepwise hydride/chloride exchange with hydrohalides.

$$\underset{\text{(IV)}}{IrH_2Cl(PEt_3)_3} \xrightarrow{\text{dry HCl}} IrHCl_2(PEt_3)_3 \tag{32}$$

$$\underset{\text{(V)}}{ReH_3(PPh_3)_4} \xrightarrow[\text{benzene}]{\text{dry HCl}} ReCl_4(PPh_3)_2 \tag{33}$$

In reaction (32) only one of the hydride ligands undergoes exchange, whereas in the second case not only are all the hydrogens exchanged but phosphine ligands are expelled as well.

The complete replacement of the hydrogens in complex (IV) may be achieved by using chlorine in chloroform (*260*); again a phosphine ligand is removed:

$$IrH_2Cl(PEt_3)_3 \xrightarrow{Cl_2/CHCl_3} IrCl_4(PEt_3)_2 \tag{34}$$

In other complexes, however, total replacement of hydrogen may occur without the displacement of a phosphine ligand:

$$RhBr_2H(AsMePh_2)_3 + Br_2 \rightarrow RhBr_3(AsMePh_2)_3 + HBr \qquad (\mathit{198})(35)$$

In this case, the reaction is quantitative and may be used for the chemical determination of the number of hydrogens in the complex (*50*).

Treatment of the square-planar platinum complex $PtHCl(PEt_3)_2$ with hydrogen chloride results not in a replacement but in an addition reaction: the neutral six-coordinate platinum(IV) dihydride, (VI), is formed.

$$PtHCl(PEt_3)_2 + HCl \rightarrow \underset{\text{(VI)}}{PtH_2Cl_2(PEt_3)_2} \qquad (\mathit{44})(36)$$

This reaction may be compared with the remarkable addition reactions of the four-coordinate iridium(I) complex, $Ir(CO)Cl(PPh_3)_2$, demonstrated by Vaska (*256*) (Fig. 7a), and also with the addition of methyl iodide to the complex $PtMeI(PEt_3)_2$, affording $PtI_2Me_2(PEt_3)_2$.

Similar addition reactions of molecular hydrogen have been shown for the iridium hydride complex, $IrHCO(PPh_3)_2$ (*210a*), and a detailed study of the reactions of this complex with acids and carbon monoxide allows a comparison between the halide- and hydride-carbonyl complexes (see Fig. 7b).

Studies of hydrogen-deuterium exchange reactions of some of these iridium hydrides show that two mechanisms are apparently exhibited, one possibly involving seven- or eight-coordinate intermediates.

Replacement of the hydrogen by halogen in the square-planar plati-

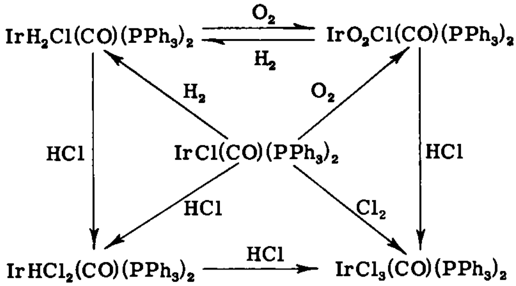
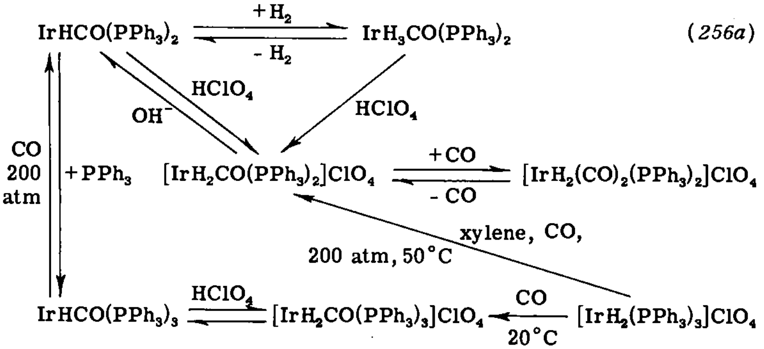


FIG. 7a. Some addition reactions of $IrCl(CO)(PPh_3)_2$.

num(II) complexes may be achieved by reaction with chloroform or alkyl halides (*44*). It may be noted that platinum(II) complexes, e.g., $PtHCl(PEt_3)_2$, undergo a rapid replacement of the *chloride* by ligands such as pyridine or ammonia to give cations $[PtH(PEt_3)_2(\text{nitrogen donor})]^+ Cl^-$. Kinetic studies show the reaction to be pseudo first-order, and the marked lability of the chloride ligand may be explained in terms of the high *trans*-effect of the hydride ligand (*8*).



(*256a*)

FIG. 7b. Some addition reactions of $IrHCO(PPh_3)_2$.

4. *Addition Reactions of the M—H System*

Many of these complexes undergo typical addition reactions, e.g.:

$$PtHCl(PEt_3)_2 + CH_2N_2 \xrightarrow[\text{ether}]{} PtMeCl(PEt_3)_2 + N_2 \qquad (44)(37)$$

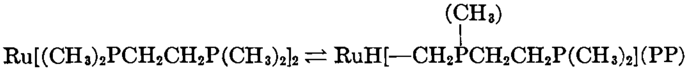
Other complexes, however, such as *trans*-$RuHCl(PP)_2$ will not undergo these reactions (*39*).

The reversible addition of olefins to metal-hydrogen bonds (see Section

IV,A,2a) has an interesting comparison in the behavior of the complex Ru(naphthalene)$(PP)_2$* (VII). Spectroscopic evidence has shown that in solution this complex is in equilibrium with the 2-naphthyl hydride (VIII) (*34*).

$$\underset{\text{(VII)}}{Ru(C_{10}H_8)(PP)_2} \rightleftharpoons \underset{\substack{\text{(VIII)} \\ \textit{(major component)}}}{RhH(2\text{—}C_{10}H_7)(PP)_2} \qquad (78)(38)$$

A related reaction also demonstrating the great affinity that the metals in these complexes have for hydrogen is shown in Eq. (39):



$$Ru[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2 \rightleftharpoons RuH[\text{—}CH_2\overset{\overset{(CH_3)}{|}}{P}CH_2CH_2P(CH_3)_2](PP) \qquad (39)$$

5. Occurrence and Identification of Isomers

A number of isomers are possible for complexes of the type MH_3L_3 or MHX_2L_3 and, as shown in Table III, some of these isomers have been prepared and separated, particularly those of the iridium complexes. The isomers may be differentiated and characterized by both their physical and chemical properties. Dipole moment determinations are frequently employed (*33*, *209*); however, unpredictable distortions of the molecules from regular symmetry may cause uncertainty. The most reliable information undoubtedly comes from proton magnetic resonance spectra. In the latter case the fine structure of the M-hydrogen resonance band, arising from coupling with P^{31} nuclei (spin $\frac{1}{2}$) and/or with other hydrogens, affords unequivocal data. In particular, it is possible to differentiate between hydrogens occupying a position *trans* to a phosphorus atom (coupling is large, $J = 80$–150 cps) and those *cis* to phosphorus (coupling is small, $J = 10$–40 cps) (*210*). The chemical differentiation of isomers depends largely on the labilizing effect of the hydrogen ligand. For example, for the complex RuHCl$(P\text{—}P)_2$ the chloride ligand is very labile and is therefore presumed to be in a position *trans* to the hydrogen (*39*). Such chemical studies must be interpreted with care, however, since in the complex *trans*-RuHCl$[CH_2(PPh_2)_2]_2$ ($\mu = 5$ D) the chloride is *not* labile, which may be due to steric effects (*39*).

As a further illustration of the above points and of preparative methods, the chemistry of some iridium isomers will be described.

The isomer (X) (L = PEt_2Ph) may be prepared by treating the complex (IX) with KOH in boiling ethanol (*43*).

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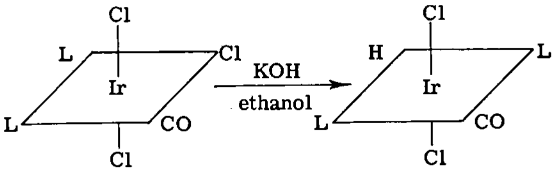
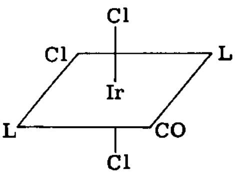
* PP represents $[(CH_3)_2PCH_2{\cdot}CH_2{\cdot}P(CH_3)_2]$.

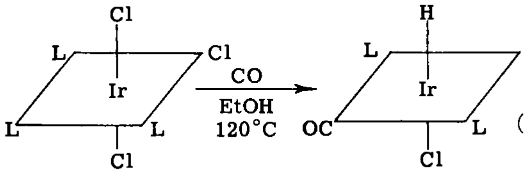


(IX) (X) (40)

In agreement with the proposed structure, the dipole moment is low ($\mu = 1.2$ D) and so is the P^{31}—H coupling constant ($J \sim 16$ cps). Surprisingly, the complex (XI) does not react with KOH and ethanol; chlorine ligands that are *trans* to either chlorine or carbon monoxide are inert to substitution by H with this reagent in these octahedral complexes. The isomer (XIII) may be prepared from (XII) by using the indicated conditions (*37*):



(XI)



(XII) (XIII) (41)

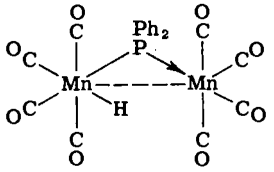
As expected, this isomer (XIII) has a high dipole moment ($\mu = 5.1$ D) and the P^{31}—H coupling constant is still low ($J = 12$ cps) (*43*).

Since in many of these phosphine complexes the ligands *trans* to the hydrogen are labile, many derivatives may be prepared by straight-forward metathetical replacement. The high lability of these *trans* ligands is well exemplified by the complex $IrCl_2H(PEt_3)_3$, the yellow isomer of which undergoes rearrangement in the crystalline state to the white isomer (*45*).

Finally, it may be noted from Table III that some of the complexes have unusual coordination numbers, e.g., $ReH_3(PPh_3)_4$ (*208*, *212*), $PtH_3(PPh_3)_{3,4}$ (*50*), and $IrH_2(PPh_3)_3$ (*208*, *209*). The occurrence of the higher coordination numbers may be due in part to the small size of the hydrogen ligand.

6. *Some Hydrides with Bridging Phosphine Ligands*

Treatment of sodium pentacarbonylmanganese with diphenylchlorophosphine surprisingly yields a hydride for which the structure (XIV) is proposed (*100*):



(42)

(XIV)

The carbonyl stretching frequencies in the infrared spectrum of the complex support an asymmetric configuration. Thus this suggests that the hydrogen is attached to one of the manganese atoms only, and spin pairing via a Mn—Mn bond is postulated to account for the observed diamagnetism. Other plausible but incorrect structures for complex (XIV) have been suggested (*126*). Similar complexes of Fe have been described (*125*); again the H is shown to be asymmetrically disposed and, on the basis of infrared and n.m.r. evidence, a metal-metal bond is proposed.

B. CARBONYL HYDRIDES

1. *The Mononuclear or Simple Carbonyl Hydrides*

The complexes $HCo(CO)_4$ and $H_2Fe(CO)_4$ are of historical interest in that they were the first reported complexes for which a transition metal-hydrogen bond was proposed. Prepared in the early 1930's by Hieber and his co-workers (*51, 136, 161*), these complexes were for many years unique and their structures and the nature of the metal-hydrogen bond intrigued and captured the interest of many chemists. The original intuitive concept by Hieber that the hydrogen was buried in the electronic core of the metal was upheld for many years. Later, partly to account for the strongly acidic properties of these hydrides, it was proposed that the hydrogen was attached to the oxygen of a carbon monoxide, giving an M—C—O—H system. This model was dismissed on the basis of infrared evidence which showed no O—H stretching frequency (*58, 72, 86*), and it was then postulated that the hydrogen lay about 2.0 Å from the cobalt and between three oxygens of the carbon monoxide groups with which interaction was suggested (*72, 86, 251*). Electron diffraction data (*74*) and a molecular orbital treatment (*69*) were argued to support this "bridged" model.

A more detailed examination of the infrared spectra (*58, 68, 251*), further theoretical treatments (*56, 199*), and Raman studies (*246*) discredited the "bridge" model, and the hydrogen was then proposed to be about 1.2 Å from the metal and directly attached to it. However, the precise structure of the simple carbonyl hydrides is still not known; and the latest evidence and arguments for the structures are now briefly discussed.

2. Structures of the Simple Metal Carbonyl Hydrides

The proton magnetic resonance and infrared spectra of the carbonyl hydrides of iron, cobalt, and manganese confirm that the hydrogens are directly bound to the metal in these complexes. As in other metal hydrides, the metal-hydrogen stretching frequencies occur in the region 2200–1700 cm^{-1}. For example, tetracarbonylcobalt hydride has its Co—H stretching frequency at 1934 cm^{-1} (*73*). Earlier assignments of the Co—H stretch to the band at 703 cm^{-1} were incorrect (*58, 68, 72*) and this band is almost certainly attributable to the Co—H deformation (*73*).

$Co(CO)_4H$. Detailed spectral studies, in particular infrared spectra, are best understood in terms of a molecule with C_{3v} symmetry (*68, 86, 246*). A possible structure is shown in Fig. 8. The structure may be regarded as being essentially a trigonal bipyramid where the equatorial carbonyl groups have bent toward the axial hydrogen.

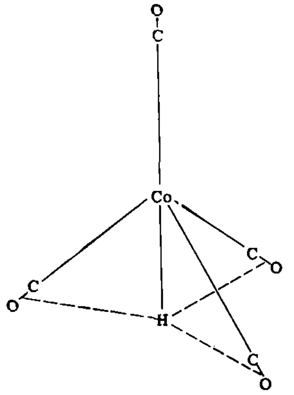


FIG. 8. $Co(CO)_4H$, showing suggested position of the H atom. The dotted lines are shown solely to indicate the Co–H direction.

$HMn(CO)_5$. Detailed infrared studies suggest a symmetry lower than octahedral (*57, 272*), and recent X-ray studies show that the molecule has essentially C_{4v} symmetry (*195b, 197*). The position of the hydrogen is not known; however, it seems reasonable that it should lie along the octahedral axis (see Fig. 3).

$H_2Fe(CO)_4$. Infrared studies on the neutral dihydride suggest a symmetry lower than octahedral (*68*). (For a discussion of the proton magnetic resonance data, see Section II,B.) The metal environment could be essentially octahedral with the carbonyl groups distorted slightly towards the sterically small hydrogens.

Qualitatively the structures may probably be regarded as the result of slight distortions from either regular octahedral symmetry in the case of

$H_2Fe(CO)_4$ and $HMn(CO)_5$, or from trigonal bipyramidal symmetry in the case of $HCo(CO)_4$. These distortions may arise from the disparity between the size and polarity of the ligands.

3. Preparation and Properties

All the simple carbonyl hydrides (Table IV) may be readily prepared by acidification of alkali metal salts derived from the simple carbonyls. Only the carbonyl hydrides of Mn, Re, Co, and Fe are well characterized. They form highly toxic volatile liquids and are unstable thermally and with respect to oxidation. Pentacarbonylmanganese hydride is stable to light and air for several hours at room temperature (*173*), while the very unstable cobalt and iron complexes decompose spontaneously at $\sim -20°C$ (*167*, *251*). It may be noted that solutions of these carbonyl hydrides in inert solvents undergo spontaneous decomposition much more slowly than the pure substances.

The carbonyl hydrides of Mn, Fe, and Co behave as acids. Aqueous solutions of $H_2Fe(CO)_4$ are slightly more acidic than acetic acid and the dissociation constants are $k_1 = 3.6 \times 10^{-5}$ and $k_2 = 1.1 \times 10^{-14}$ (*13*, *152*, *169*, *194*). The large difference between the first and second dissociation constants may be understood since the second hydrogen is attached directly to the iron atom, which must carry a considerable proportion of the uninegative charge of the $HFe(CO)_4^-$ anion (*152*, *153*). Tetracarbonyliron dihydride readily forms dibasic salts, in particular with the heavy metals (*76*, *146*, *150*, *177*). Tetracarbonylcobalt hydride dissolves only very slightly in water (3×10^{-3} moles/liter) (*47*); in the aqueous solution, however, the $HCo(CO)_4$ is highly dissociated and the solutions are strongly acidic, $k \sim 1$ (*151*, *153*). Measurements made in methanol, in which $HCo(CO)_4$ is quite soluble, show that this compound is as strong an acid as nitric acid (*151*). Cobalt carbonyl hydride thus exhibits the anomaly of behaving as a strong acid which is only slightly soluble in water, properties difficult to reconcile with one another.

The force constant of the Co—H bond is 22 mdynes/Å, indicating a stronger bond than in $HMn(CO)_5$, which is a very much weaker acid ($k = 0.8 \times 10^{-7}$) (*172*). The disparity must be interpreted in terms of the difference in solvation energies of the ions $Co(CO)_4^-$ and $Mn(CO)_5^-$. The dissociation constants of the series $HCo(CO)_3L$, where L = CO, $P(OPh)_3$, or PPh_3, are $k \cong 1$, 1.13×10^{-7}, and 1.09×10^{-7}, respectively (*162*).

Carbonyl hydrides are readily oxidized, and some redox potentials for carbonylate anions in aqueous alkaline solution are given in Table V.

The course of the addition of the Co—H in tetracarbonylcobalt hydride across C=C double bonds indicates an apparently variable polarity of the Co—H bond. Addition to 1- or 2-pentene indicates a protonic hydrogen

TABLE IV
THE SIMPLE CARBONYL HYDRIDES

Compound	Color	M.P. (°C)	References to preparation	Infrared, ν_{M-H} (cm^{-1})	NMR,[a] τ (p.p.m.)	Notes
$Cr(CO)_5H_2$[b,c]	—	—	(*138*)	—	—	Detected in mass spectra (*235*)
$[Cr(CO)_5H]^-$ salts	Yellow-orange	—	(*17, 139*)	—	—	—
$Mn(CO)_5H$	Colorless	−24.6	(*68, 172, 173, 181*[d])	1783 (*57, 68, 272*)	17.5 (*57*)	Chemical properties (*68, 254, 255, 269b*)
$Tc(CO)_5H$	—	—	(*175*)[b,c]	— (*175*)	—	—
$Re(CO)_5H$	Colorless	12.5, 100 dec.	(*141, 199*)	1832 (*199*)	15.66 (*62a*)	Chemical properties (*269a*)
$Fe(CO)_4H_2$ and salts	Pale yellow	−70	(*76, 116, 136, 137, 149, 151, 153, 154, 160, 161, 169, 171*)	(*71*)	21.1 (*23, 58, 87*)	Raman spectrum (*246*); pK_a (*151–153, 194*); redox studies (*152, 154*); chem. react. (*76, 134, 146, 150, 156, 233*)
$[Fe(CO)_5H]^+$ [b,c]	—	—	(*63*)P[e]	—	—	—
$Ru(CO)_4H_2$ [b,c]	—	—	Halide derivatives (*213*)	—	—	—
$Os(CO)_4H_2$ [b]	—	—	(*166*)	—	—	—
$Co(CO)_4H$	Yellow	−26	(*25, 51, 137, 148, 151, 164, 169, 251*)	1934 (*73*); other studies (*27, 58, 68, 72, 86, 251*)	20.7 (*58, 86*)	Chem. prop. (*5, 13, 69, 70, 72, 136, 153, 154, 167, 185, 189*); Raman studies (*246*); electron diffraction (*74*); redox studies (*152, 154*); pK_a (*151, 153*)
$Rh(CO)_4H$[c]	Yellow	~−10	(*158*)	—	—	—
$Ir(CO)_4H$[b,c]	—	—	(*159*)	—	—	—

[a] Chemical shift of hydrogen attached to the metal.

[b] Not isolated.

[c] Not fully characterized.

[d] Incorrect formulation proposed.

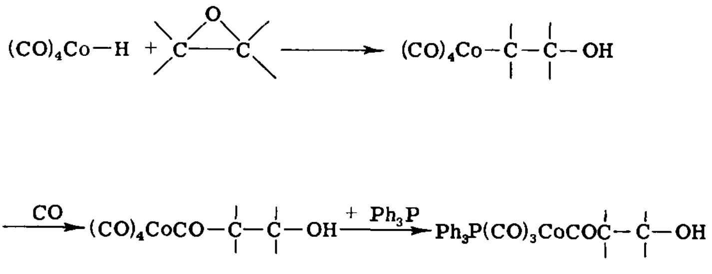
[e] P indicates preparation by protonation in strongly acidic media.

TABLE V
REDOX POTENTIALS

Carbonylate anion	E_0(volts, 20°C)	References
$2[Co(CO)_4]^- \rightleftharpoons Co_2(CO)_8 + 2e$	−0.4	(*152, 154*)
$2[Mn(CO)_5]^- \rightleftharpoons Mn_2(CO)_{10} + 2e$	−0.68	(*172*)
$3[HFe(CO)_4]^- \rightleftharpoons [Fe(CO)_4]_3 + 3H^+ + 6e$	−0.35	(*152, 154*)
$3[Fe(CO)_4]^{2-} \rightleftharpoons [Fe(CO)_4]_3 + 6e$	−0.74	(*152, 154*)

in Co—H; however, addition to $CH_2{=}CHCOOCH_3$, followed by addition of CO, affords as the major product $CH_3OOCCH(CH_3){-}COCo(CO)_4$, i.e., the Co-hydrogen has added to the most electropositive carbon, indicating a hydridic hydrogen. It therefore appears that the course of addition depends to some extent on the electron availability of the C═C system (*131*).

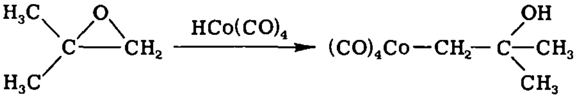
Treatment of epoxides with $HCo(CO)_4$ affords β-hydroxyacylcobalt complexes, which may be isolated as triphenylphosphine derivatives (XV) (*127*):



(XV)

(43)

The course of addition of Co—H to isobutylene oxide also indicates that the Co-hydrogen is hydridic. The addition of Re—H in $Re(CO)_5H$ to a



(44)

number of perfluorolefins has been demonstrated (*269a*) and the reaction of $(CO)_5ReH$ with perfluorobut-2-yne affords the complex (XVa).

$$Re(CO)_5H + CF_3CCCF_3 \rightarrow \underset{\text{(XVa)}}{CF_3CH{=}CCF_3Re(CO)_5} \qquad (44a)$$

A number of other simple carbonyl hydrides have been reported, but these are ill-characterized; they are listed in Table IV.

TABLE VI
POLYNUCLEAR CARBONYL HYDRIDES

Compound	Color	References to preparation	Notes
$HFeCo_3(CO)_{12}$[a]	Black-violet	(*49*)	Related polynuclear anions (*15*)
$[Cr_2(CO_{10}H]^-N(CH_3)_4^+$	Orange	(*14, 17, 18, 20*)	—
$[Mo_2(CO)_{10}H]^-$ salts	—	(*14, 16*)	—
$Fe_2(CO)_8H_2$ and salts[b,c,d]	Red-brown	(*142, 174*)	Related studies (*142, 149, 155, 156, 168*)
$Fe_3(CO)_{11}H_2$ and salts[b,c]	Cherry red	(*142, 174*)	—
$Fe_4(CO)_{13}H_2$ and salts[b,c]	Red	(*142, 174*)	—
$Ni_2(CO)_2H_2$[b,c]	Dark red	(*19*)	—
$[Ni_4(CO)_9H]^-$ salts	Dark red	(*157*)	—
$[Cr_2(CO)_6(OH)_3H]^-$ salts[c]	Orange	(*163*)	—
$[Cr_2(CO)_6(OH)_x(H_2O)_y]^{2-}$ salts[c]	Red orange	(*163*)[e]	—
$[Cr_2(CO)_6(OH)_x(CH_3O)_yH]^{2-}$ salts	Orange	(*163*)	—
$[Mo_2(CO)_6(OH)_3H_3]^0$ [b,c] salts	Pale yellow	(*145*)[e]	—
$[W(CO)_3(H_2O)H]^0$ salts[c]	Yellow	(*143*)	—
$[W_2(CO)_6(OH)_3H_3]^0$ [c]	Yellow	(*143*)	—
$[W_2(CO)_6(OH)_3H]^{4-}$ salts	—	(*144*) (*143*)[e]	—
$[W_3(CO)_9(OH)_2(H_2O)H_4]H_2O$[c]	—	(*144*)	—
$[W_4(CO)_{12}(H_2O)_4H_4]$[c]	Yellow	(*143*)[e]	—

[a] Decomposes at 100°C.

[b] Not isolated.

[c] Not fully characterized.

[d] NMR, chemical shift of M-hydrogen, τ(p.p.m.) = 14.9 (*61*).

[e] Also includes infrared data.

Acidification of salts of the anion $V(CO)_6^-$ does not afford a hydride (*31*).

4. Polynuclear Carbonyl Hydrides

The treatment of many of the metal carbonyls with bases affords complex polynuclear carbonylates (see (*140*) for a recent review). As is the case for the mononuclear carbonylate anions, hydrolysis of the anions, often with dilute acids, affords diamagnetic metal carbonyl hydride complexes (see Table VI). The majority of these complexes which are described below have not been studied by infrared and proton magnetic resonance spectroscopy; their formulations are based primarily on analysis and mode of decomposition, and thus remain tentative.

(*a*) *Polynuclear Iron Carbonyl Hydrides.* Hieber and Werner (*174*) have reported a series of iron carbonyl hydrides of increasing stability:

$$H_2Fe(CO)_4 \quad H_2Fe_2(CO)_8 \quad H_2Fe_3(CO)_{11} \quad H_2Fe_4(CO)_{13}$$

Few studies have been made on these hydride complexes, although the preparation and chemistry of the corresponding anions have received considerable attention (*155*, *156*, *168*). The presence of Fe—H bonds in these complexes has been noted (*61*).

(*b*) *Hexacarbonyldinickel Dihydride.* Treatment of tetracarbonylnickel with sodium in liquid ammonia yields a very unstable, deep red, binuclear nickel dihydride (XVI) (*19*):

$$2Ni(CO)_4 + 2Na + 2NH_3 \rightarrow \underset{(XVI)}{[NiH(CO)_3]_2} + 2CO + 2NaNH_2 \qquad (45)$$

Little is known of this complex.

(*c*) *The Carbonyl Hydrides of the Group VI Metals.* Unlike the simple carbonyl hydrides of Co, Ni, and Fe, those of the Group VI metals have not been isolated since they decompose very readily and undergo polymerization, giving polynuclear carbonyl species with evolution of hydrogen (*20*, *138*). The sodium salts of the hydrides may be prepared by treatment of the metal hexacarbonyls with sodium in liquid ammonia:

$$M(CO)_6 + Na \xrightarrow{NH_3\ (liq.)} Na_2[M(CO)_5] \xrightarrow{H_2O} [M(CO)_5]_n + H_2 \qquad (46)$$

where M = Cr, Mo, W. As shown in Eq. (46), the sodium salts are readily hydrolyzed with evolution of hydrogen (*17*, *20*). In the case of the pentacarbonylchromium anion the hydrolysis may be arrested at the halfway stage, and the pentacarbonylchromium hydride anion may be isolated as the orange diamagnetic ferroin salt (*20*). A further reaction may occur on hydrolysis of the chromium anion, producing a binuclear carbonyl hydride anion (XVII) that has been isolated as the tetramethylammonium salt:

$$Cr(CO)_5H^- + H^+ \rightarrow Cr(CO)_5 + H_2 \xrightarrow{Cr(CO)_5H^-} \underset{(XVII)}{Cr_2(CO)_{10}H^-} \qquad (47)$$

The anion (XVII) may also be prepared via the reduction of hexacarbonylchromium with sodium borohydride in liquid ammonia (*14*):

$$\begin{array}{c} 2Cr(CO)_6 + 2NaBH_4 + 6NH_3 \rightarrow Na_2[Cr_2(CO)_{10}] + 2B(NH_2)_3 + 2CO + 7H_2 \qquad (48) \\ \downarrow H_2O \\ [Cr_2(CO)_{10}H]^- + OH^- \end{array}$$

It is interesting to note that the anion (XVII) reacts with ammonia, affording the monosubstituted amminopentacarbonylchromium (*17*), and with CN⁻:

$$[Cr_2(CO)_{10}H]^- \xrightarrow{CN^-} [Cr(CO)_5CN]^- \qquad (18)(49)$$

Treatment of the hexacarbonyls of chromium, molybdenum, and tungsten with ethanolic potash, contrary to earlier reports (*138*), does not yield the simple carbonylates, but in every case polynuclear hydroxy-aquo-carbonylate species are isolated (*143–145, 163*). A typical reaction scheme is (*163*):

$$\begin{aligned}&2Cr(CO)_6 + 6OH^- \rightarrow 2[Cr(CO)_5H]^- + 2CO_3^{2-} + 2H_2O\\&\qquad\qquad\qquad\qquad\quad \searrow 4OH^- + 3H_2O\\&\qquad\qquad\qquad\qquad\quad [Cr_2(CO)_6(OH_2)H]^{2-} + H_2 + 4HCOO^- \qquad (50)\end{aligned}$$

If methanolic potash is used then the products may contain methoxy groups, e.g., $K_3Mo_2(CO)_6(OH)_2(CH_3O)$ (*163*). Many of these complexes, which are listed in Table VI, are formulated as hydrides and give solutions of moderate acidity. However, proton magnetic resonance spectra have not been obtained and, since the protons may be attached to hydroxy groups, it remains uncertain whether these complexes are hydrides at all. It may be noted that the complex anion $[Re_2(CO)_8O_2H]^-$, prepared by the action of base on decacarbonyldirhenium (*165*), is not a hydride.

(*d*) *Miscellaneous*. Reaction between octacarbonyldicobalt and pentacarbonyliron affords the anion $[FeCo_3(CO)_{12}]^-$, which on acidification gives the violet-black hydride $HFeCo_3(CO)_{12}$ (*49*). It is postulated that the structure is analogous to that of $Co_4(CO)_{16}$, in which the metal atoms have a tetrahedral arrangement.

The first and only nitrosyl hydride has been prepared recently by the reduction of the complex $MnBr(NO)_2(PPh_3)_2$ with sodium borohydride (*170*). It may be noted that reduction of the nitrosylcarbonyl $(\pi\text{-}C_6H_6)Cr(CO)(NO)Br$ does not give a Cr—H complex. A possible polynuclear technetium hydride $[Tc(CO)_4]_3H$ has been discussed (*186*). Reduction of the complex $CH_3SCH_2CH_2SCH_3Mo(CO)_3I_2$ affords an unstable hydride (*215*).

C. π-CYCLOPENTADIENYLCARBONYL HYDRIDES

These complexes barely deserve a separate classification in that their chemistry is very similar to that of the simple carbonyl hydrides. All are diamagnetic and their formulation obeys the rare gas rule. Only rarely does the π-cyclopentadienyl group play a distinctive role in the chemistry of these complexes, and for the majority of the chemistry it may be regarded as an inert π-bonding ligand.

1. *Preparation and Properties*

The complexes may be prepared either by the acidification of the appropriate alkali metal salt of the anion (*79, 230*):

$$Mo(CO)_6 + Na^+C_5H_5^- \rightarrow Na^+[\pi\text{-}C_5H_5Mo(CO)_3]^- \rightarrow \pi\text{-}C_5H_5Mo(CO)_3H \qquad (51)$$

or by the reduction of suitable halide complex:

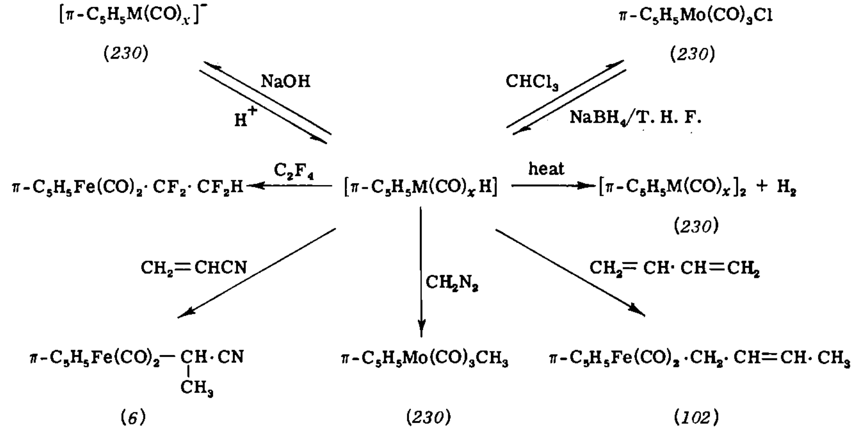
$$\pi\text{-}C_5H_5Fe(CO)_2Cl \xrightarrow[\text{T.H.F., }0°C]{NaBH_4} \underset{(XVIII)}{\pi\text{-}C_5H_5Fe(CO)_2H} \tag{52}$$

An easier preparative route to the complex (XVIII) (which is very unstable both thermally and with respect to oxidation) exploits the strongly basic nature of the anion $[\pi\text{-}C_5H_5Fe(CO_2)]^-$. Treatment of the sodium salt with *tert*-butyl chloride results in the standard elimination reaction (*101*).

$$Na^+[\pi\text{-}C_5H_5Fe(CO)_2]^- + H—CH_2—C(CH_3)_2—Cl \xrightarrow[\text{24 hr}]{\textit{room temp.}}$$
$$\pi\text{-}C_5H_5Fe(CO)_2H + NaCl + CH_2{=}C(CH_3)_2 \tag{53}$$

in greater than 50% yield. All known complexes in this class are shown in Table VII and all form volatile yellow crystals unstable with respect to oxidation.

Some typical reactions are exemplified in the diagram.



Detailed studies of the reduction with sodium borohydride of the cations $[\pi\text{-}C_5H_5Fe(CO)_2L]^+$, where L = CO or Ph_3P, have shown that when L = Ph_3P the cyclopentadiene complex $C_5H_6Fe(CO)_2Ph_3P$ is formed, and that when L = CO the hydride $\pi\text{-}C_5H_5Fe(CO)_2H$ is isolated (*62*). Whether these reductions proceed via the attack of the hydride ion on the π-cyclopentadienyl ring or on the metal atom is not known (*62*, *104*); whichever the case, however, if the reduction proceeds by the same mechanism, it is clear that a transfer of the hydrogen between the iron atom and the π-cyclopentadienyl ring must occur in one of the reactions. The transfer of hydrogen from a cyclopentadiene ring to the iron is a postulated step in the

TABLE VII

π-Cyclopentadienylcarbonyl Hydrides

Compound	Color	M.P. (°C)	References to preparation[a]	NMR chemical shift of M-hydrogen, τ (p.p.m.)	Notes
$C_5H_5Cr(CO)_3H$	Golden yellow	57–58 dec.	*(77–79, 230)*	15.46 *(62a)*	—
$C_5H_5Mo(CO)_3H$[b]	Pale yellow	50–57 dec.	*(77, 79, 230)*	15.52 *(62a)*	Reactions *(230, 254)*
$[C_5H_5Mo(CO)_3H_2]^+$ salts	Red-brown	—	*(60, 63)*P	30.99 *(63)*	—
$[(C_5H_5Mo(CO)_3)_2H]^+$	Red-brown soln.	—	*(63)*P	32.88 *(63)*	—
$C_5H_5W(CO)_3H$[c]	Pale yellow	66–67	*(77, 81, 230)*	17.33 *(62a)*	Reactions *(230, 254)*
$[(C_5H_5W(CO)_3)_2H]^+$ salts	Red-brown soln.	—	(63)P	34.77 *(63)*	Detailed NMR studies *(63)*
$[C_5H_5W(CO)_3CH_3H]^+$	Red-brown soln.	—	*(63)*P	— *(63)*	—
$[(C_5H_5W(CO)_3)_2Hg]H^+$	Red-brown soln.	—	*(63)*P	11.95 *(63)*	—
$C_5H_5Fe(CO)_2H$[d]	Yellow	−5	*(101, 106)*	21.91 *(62a)*	—
$[(C_5H_5Fe(CO)_2)_2H]^+PF_6^-$	Brown	—	*(60, 63)*P	36.3 *(63)*	Van't Hoff *i* factor in sulfuric acid *(115)*
$[C_5H_5FeMn(CO)_7H]^+PF_6^-$[e]	Orange	—	*(63)*P	38.3 *(63)*	—
$[(C_5H_5Ru(CO)_2)_2H]^+$	Red-brown soln.	—	*(63)*P	28.58 *(63)*	—
$C_5H_5Ru(CO)_2H$[f]	Yellow	—	*(62a)*	20.92 *(62a)*	—
Arene carbonyl hydrides prepared from					
$C_6H_6Cr(CO)_3$	*(63)*P	—	—	13.55 ± 0.3 *(63)*	—
(1,2-Diphenylethane)$Cr(CO)_3$	*(63)*P	—	—	14.06 ± 0.3 *(63)*	—
$CH_3C_6H_5Cr(CO)_3$	*(63)*P	—	—	13.98 ± 0.2 *(63)*	For analogous complexes see *(63)*

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[a] P = obtained by protonation in strongly acid media.

[b] ν_{Mo-H} 1790W *(62a)*.

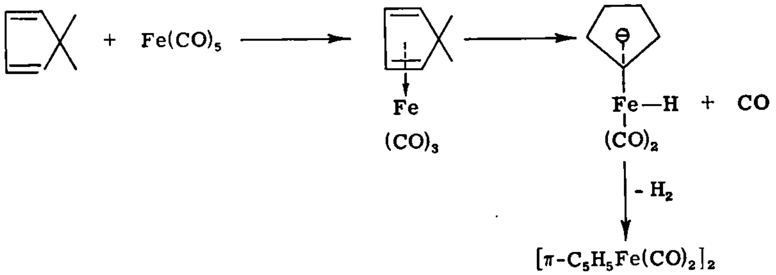
[c] ν_{W-H} 1845M *(62a)*.

[d] ν_{Fe-H} 1835W *(62a)*.

[e] ν_{Fe-H} 1760W *(62a)*.

[f] ν_{Ru-H} 1853W *(62a)*.

formation of the binuclear complex [π-$C_5H_5Fe(CO)_2]_2$ from cyclopentadiene and iron carbonyl (*62*):



(53a)

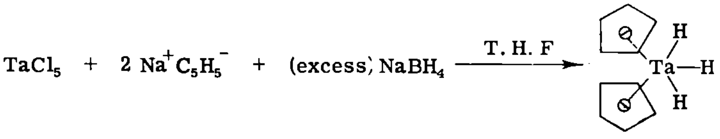
The reverse transfer of a hydrogen from the metal to a π-cyclopentadienyl ring presumably occurs in the formation of π-cyclopentadienylcyclopentadienedicarbonylrhenium from bis-(π-cyclopentadienyl)rhenium hydride and carbon monoxide (*56*, *107*). Cationic complexes in this class, prepared by protonation reactions, are discussed in Section III,E.

D. Bis(π-cyclopentadienyl) Hydrides

Bis(π-cyclopentadienyl)rhenium hydride was the first hydride to be recognized for 20 years after the isolation of the carbonyl hydrides of iron and cobalt (*22*). Within the last few years the related hydrides of molybdenum, tungsten, and tantalum have been isolated (*80*, *99*, *106*) (Table VIII).

1. Preparation and Properties

The neutral complexes (π-$C_5H_5)_2ReH$ (XIX), (π-$C_5H_5)_2MH_2$ (XX) where M = Mo and W, and (π-$C_5H_5)_2TaH_3$ (XXI) may all be prepared by treating solutions of sodium borohydride and sodium cyclopentadiene in tetrahydrofuran with anhydrous metal chlorides, e.g.,



(XXI)

(54)

The formation of the hydrides may proceed via bis(π-cyclopentadienyl)-metal halide complexes, since compounds such as (π-$C_5H_5)_2ReCl_2{}^+Cl^-$ and (π-$C_5H_5)_2WCl_2$ are known and are readily reduced to the neutral hydrides on treatment with lithium aluminum hydride (*54*) (Eq. 5). Treatment of technetium tetrachloride with sodium cyclopentadiene does not give a hydride analogous to that of rhenium. Molecular weight determina-

TABLE VIII
BIS-(π-CYCLOPENTADIENYL) HYDRIDES

Compound	Color	M.P. (°C)	References to preparation	Infrared ν_{M-H} (cm^{-1})	NMR chemical shift of M-hydrogen, τ (p.p.m.)	Notes
$(C_5H_5)_2TaH_3$	White	187–189 dec.	(*99, 207*)	1735 (*99*)	13.03(A_2); 11.63(B) (*99*)	—
$(C_5H_5)_2MoH_2$	Yellow	183–185	(*80, 99, 106*)	1847 (*80, 88, 99*)	18.76 (*99*)	Reactions (*54, 55*)
$[(C_5H_5)_2MoH_3]^+$ salts	Yellow	—	(*80,99*)	1915w (*62a*)	16.08 (*99*)	—
$(C_5H_5)_2WH_2$	Yellow	163–165	(*80, 99, 106*)	1912 (*80, 88, 99*)	22.2 (*99*)	Reactions (*54, 55*)
$[(C_5H_5)_2WH_3]^+$ salts	Golden yellow	>185 dec.	(*80, 99*)	1943w (*62a*)	—	—
$(C_5H_4Li)_2WH_2$	Golden yellow	—	(*55*)	—	—	—
$(C_5H_5)_2ReH$	Lemon yellow	161–162; 250 dec.	(*22, 105*)	2030 (*88, 105*)	22.8 (*59, 105*) 23.4 (*179*)	Reactions (*54, 55, 82, 107*) 1.17 D (*81*)
$[(C_5H_5)_2ReH_2]^+$ salts	White	—	(*105*)	2025w (*62a*)	—	—
$(C_5H_4Li)_2ReH$	Pale yellow	—	(*55*)	—	—	—
$(C_5H_4HgCl)_2ReH^a$	Pale yellow	—	(*55*)	—	—	—
$[(C_5H_4HgCl)_2ReH_2]^+Cl^{-a}$	Golden yellow	—	(*55*)	—	—	—
$[(C_5H_5)_2ReC(COOMe{=}CHCOOMeH]^+$	—	—	(*66a*)P^b	—	—	—
$[(C_5H_5)_2FeH]^+$ salts^a	Yellow	—	(*59, 236*)P^c	—	12.1; J = 1.5 cps (*59*)	—
$[(C_5H_5)_2RuH]^{+a}$	Yellow solution	—	(*59*)P	—	17.2 (*59*)	—
$[(C_5H_5)_2OsH]^{+a}$	Yellow solution	—	(*59*)P	—	—	—

[a] Not fully characterized.

[b] Hydride resonance at 10.6 p.p.m. relative to 3-trimethylsilyl-1-propane sulfonate (*66a*).

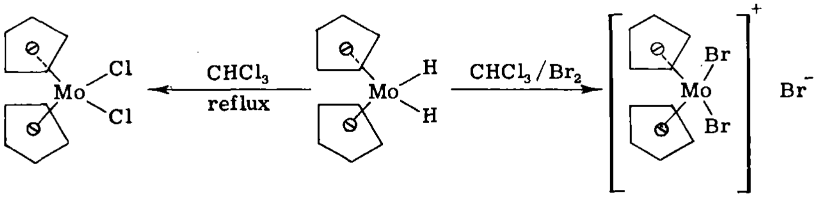
[c] P = obtained by protonation in strongly acid media.

tions show that the complex isolated is binuclear and is formulated as $[(\pi\text{-}C_5H_5)_2Tc]_2$ with a Tc—Tc bond (*179*).

The neutral complexes (XIX), (XX), and (XXI) are crystalline and sublime *in vacuo* at ~150°C. They are moderately soluble in the common organic solvents and are insoluble in and unaffected by water and strongly alkaline solutions. All the complexes are quite readily oxidized, and ethereal solutions exposed to air show signs of decomposition after a few minutes.

The neutral hydrides are to some extent atypical in that the metal hydrogens do not show the normal addition reactions with diazomethane or tetrafluoroethylene. The complexes $(\pi\text{-}C_5H_5)_2MH_2$ (XX), however, show characteristic substitution reactions with halogenated hydrocarbons such as $CHCl_3$, $CHBr_3$, and CH_3I, affording deep green halide derivatives $(\pi\text{-}C_5H_5)_2MX_2$; see Eq. (24).

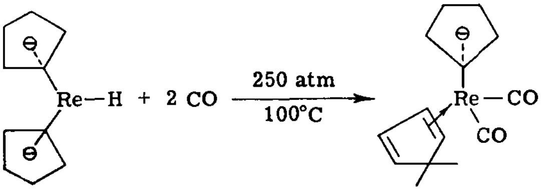
Treatment of chloroform solutions of the dihydrides (XX) or the rhenium hydride (XIX) with chlorine or bromine results in both oxidation of the metal and replacement of the hydrogens (*54*).



(XX) deep red-purple

(55)

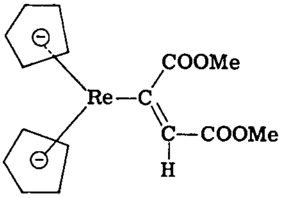
The rhenium hydride (XIX) reacts with carbon monoxide under pressure giving the olefin complex (XXII) (*107*); an original formulation of this complex as a hydride was incorrect (*82*).



(XIX) (XXII)

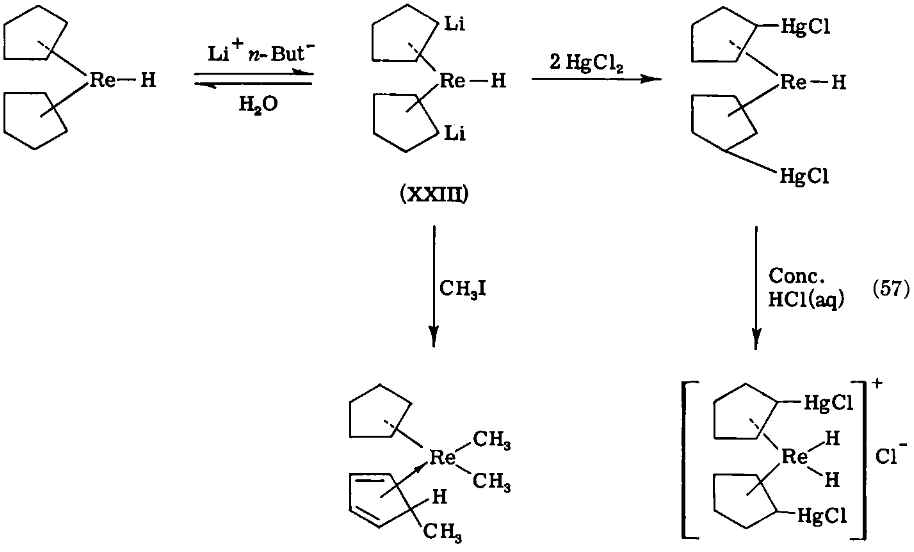
(56)

Recently the rhenium hydride (XIX) has been shown to undergo a smooth *cis*-addition reaction to dimethylacetylenedicarboxylate, affording the complex (XXIIa) for which *cis* and *trans* isomers may be isolated (*66a*). The complex (XXIIa) is a base and protonates in dilute sulfuric acid to give a cationic hydride complex (*66a*).



(XXIIa)

The hydrides $(\pi\text{-}C_5H_5)_2WH_2$ and $(\pi\text{-}C_5H_5)_2ReH$ have been shown to react readily with *n*-butyllithium in ether. Proton magnetic resonance studies have shown that the metal-hydrogen system is not thereby destroyed, and deuterolysis of the lithiated reaction products, which are involatile in vacuum at ~150°C, affords deuterated derivatives of the parent hydrides. Infrared and proton magnetic resonance studies show that the deuterium has substituted in the π-cyclopentadienyl rings. Detailed studies of some reactions of the lithiated products suggest that they are 1:1 dilithiated complexes, e.g., (XXIII) (see diagram) (*55*).



(XXIV)

As shown in the diagram, treatment of the dilithio complex (XXIII) with methyl iodide gives the diamagnetic crystalline complex (XXIV). The mechanism of this reaction is unknown.

Finally, the hydrides (XIX) and (XX) are unique in that they are bases slightly weaker than ammonia; they protonate readily and reversibly with dilute mineral acids to give cationic hydrides (see Section III,E).

2. Structure of the Complexes

An early proposal that the hydrogen in these complexes was embedded in the bonding between the metal and the π-cyclopentadienyl ring (*200*) has been discarded on the basis of proton magnetic resonance studies (*105*). Dipole moment measurements (*80, 81*), to some extent infrared spectra (*88*), and in particular the X-ray studies on the complex $(\pi\text{-}C_5H_5)_2MoH_2$ (*21, 88a*) (see Fig. 6) support the oblique ring structures shown in the equations above and in Fig. 9b. The structures of the trihydride cations $[(\pi\text{-}C_5H_5)_2MH_3]^+$ (XXa), where M = Mo or W, and of the complex $(\pi\text{-}C_5H_5)_2TaH_3$ (XXI) are unknown. Infrared studies have very tentatively suggested a parallel ring structure (*88*) for the cations; however, proton magnetic resonance studies show that in the trihydrides the three hydrogens are not equivalent and that they form an A_2B group. This evidence, supported by theoretical considerations (*7*) (see Section III,E), favors an oblique ring structure for the complexes (XXa) and (XXI), such as that shown in Eq. (55).

E. THE FORMATION OF TRANSITION METAL HYDRIDES BY PROTONATION IN STRONG ACIDS

The transition metals have nine atomic orbitals which are of suitable energy to take part in bonding. These orbitals are the ns, $(n - 1)d^5$, and np^3, where n, the principal quantum number, may have values 4, 5, or 6 for the "*d*-block" transition metals. Molecular orbital (MO) treatments of ferrocene show that, other than five metal orbitals which are principally involved in the iron-cyclopentadienyl ring bonding, there are four "nonbonding" orbitals, two of these in a plane through the iron atom parallel to the π-cyclopentadienyl rings (Fig. 9a). The latter two nonbonding orbitals contain an electron pair. Using a similar MO approach, Ballhausen and Dahl (*7*) have shown that the oblique-ring bis(π-cyclopentadienyl) metal hydrides have three orbitals not involved in the metal-ring bonding. These orbitals are either nonbonding or only partially involved in back-donation to the π-cyclopentadienyl ligands, and may be treated as "chemically active" (*7*). The configuration of these molecules and the position of the three orbitals are shown in Fig. 9(a). Consider the molecule bis(π-cyclopentadienyl)tungsten dihydride: the two hydrogens are bonded to two of the three orbitals and the third orbital contains a pair of electrons. This electron pair gives the molecule basic properties, and thus the neutral dihydride readily protonates to the trihydride cation $[(\pi\text{-}C_5H_5)_2WH_3]^+$, or will form weak 1:1 complexes with strong Lewis acids such as boron trifluoride (*241b*). Bis(π-cyclopentadienyl)rhenium hydride may be considered to be similar, but in this case there are two nonbonding electron pairs. As mentioned previously, the neutral complex behaves as a relatively strong base and is readily protonated, affording the dihydride cation $[(\pi\text{-}C_5H_5)_2ReH_2]^+$ (XXV). Only a single proton may be added and the cation (XXV) is too weak a base for a second proton to become attached to the positively charged rhenium. The neutral sandwich complexes $(\pi\text{-}C_5H_5)_2M$, where M = Fe, Ru, and Os, also protonate in strong acids giving metal-hydride cations (*59*, *222*, *237*). The proton must attach itself to one of the nonbonding electron pairs, and the protonated molecules may be expected to have an oblique-ring structure similar to that of the neutral bis(π-cyclopentadienyl)rhenium hydride (see Eq. 57). The importance of these hydride cations as intermediates in substitution reactions of the cyclopentadienyl ring has recently been discussed (*237*).

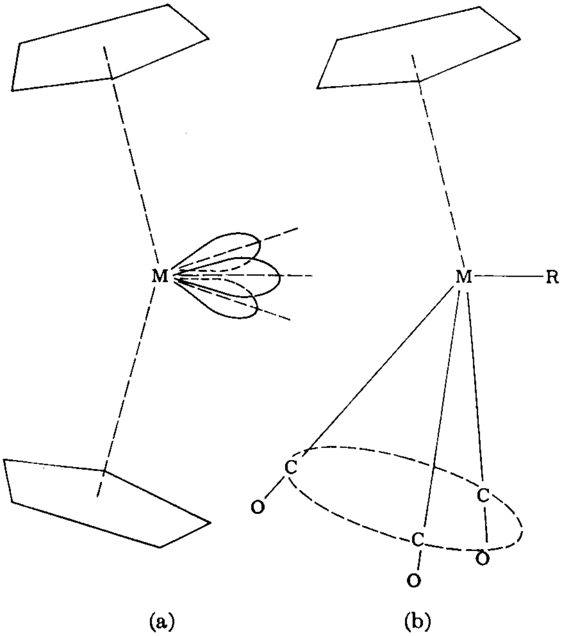


FIG. 9. (a) Configuration and position of these orbitals in the oblique-ring bis(π-cyclopentadienyl) metal complex. (b) Configuration of the monocyclopentadienyl tricarbonyl complexes.

An analogy may be drawn between the monocyclopentadienyl complexes such as $\pi\text{-}C_5H_5M(CO)_3R$ (XXVI), where M = Mo or W, and R = alkyl, and the bis(π-cyclopentadienyl) metal complexes. The three carbon monoxide groups in the complexes (XXVI) may be compared with a π-cyclopentadienyl group, in that they occupy three coordination positions of the metal contributing six electrons to the bonding, and the plane containing the three carbons of the carbon monoxide groups is at an angle to the π-cyclopentadienyl group [Fig. 9(b)]. Thus the complexes (XXVI) may be considered analogous to the neutral $(\pi\text{-}C_5H_5)_2ReH$ which contains two nonbonding electron pairs, one of which may be protonated in strongly acidic media. Similar arguments may be applied to the binuclear complexes $[(\pi\text{-}C_5H_5)M(CO)_3\text{—}(CO)_3M(\pi\text{-}C_5H_5)]$, i.e., (XXVI) where R = $(\pi\text{-}C_5H_5)M(CO)_3$. The latter complexes undergo monoprotonation even though there are two metal atoms; thus the protonated metal atom must exert a strong −I effect on the second metal atom. The structure of these protonated binuclear complexes is discussed below (Section III,E,1).

The protonation of nonbonding pairs in other complexes such as $Fe(CO)_5$, forming $[Fe(CO)_5H]^+$, has been demonstrated.

The four- and five-coordinate complexes $IrHCOL_2$ and $IrHCOL_3$, respectively (L = PPh_3), react reversibly with strong acids adding a proton (*210a*), e.g.,

$$IrHCOL_3 \underset{KOH}{\overset{HClO_4}{\rightleftharpoons}} [IrH_2COL_3]^+ClO_4^- \tag{57a}$$

The six-coordinate IrH_3COL_2, however, reacts quantitatively with perchloric acid evolving hydrogen (*210a*):

$$IrH_3COL_2 + HClO_4 = [IrH_2COL_2]^+ClO_4^- + H_2 \tag{57b}$$

Zero-valent platinum complexes of the general formula PtL_3, where L = PPh_3 or $AsPh_3$, have analogous basic behavior and the following reaction scheme has been demonstrated (*31b*).

$$PtL_3 \underset{KOH}{\overset{HX}{\rightleftharpoons}} [PtHL_3]^+X^- \underset{+L}{\overset{-L}{\rightleftharpoons}} PtHXL_2 \tag{57c}$$

Those hydride complexes that are formed by protonation reactions are listed in the tables and are designated P in the column headed "Preparation." Unfortunately, many transition metal complexes are decomposed by strongly acid solutions, e.g., (*63*):

$$\begin{array}{l} (\pi\text{-}C_5H_5)Mo(CO)_3CH_3 + CF_3COOH \rightarrow [(\pi\text{-}C_5H_5)Mo(CO)_3CH_3H]^+CF_3COO^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \pi\text{-}C_5H_5Mo(CO)_3CO{\cdot}OCF_3 + CH_4 \end{array} \tag{58}$$

Also, many of the protonated complexes that are stable in strongly acid solutions may not be isolated. Other than the bis(π-cyclopentadienyl) hydride cations, only the complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2H^+$ and $[\pi\text{-}C_5H_5Fe(CO)_2\text{—}Mn(CO)_5]H^+$ have been isolated, as the PF_6^- salts, and in an impure state. Solutions of the latter salts in aqueous acetone immediately revert quantitatively to the neutral complexes (*63*).

1. *Structure of the Protonated Binuclear (π-Cyclopentadienyl)carbonyls*

Detailed proton magnetic resonance studies on the protonated complexes $[(\pi\text{-}C_5H_5)M(CO)_3]_2H^+$, where M = Mo and/or W, have been made to resolve the question of whether the hydrogen is attached to a single metal atom, is exchanging rapidly between the two metal atoms, or is forming a symmetrically bridged system.

Despite elegant arguments based on *inter alia* the fine structure of the proton resonance bands of the W-H hydrogen due to coupling with the W^{183} nucleus (14.28% abundance, spin ½), a definite answer may not be given. However, a rapid exchange of the hydrogens between the two tungsten atoms is favored. Studies on the complex $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2H^+$ show that there are no longer bridging carbonyls as are found in the neutral complex. In this complex the proton appears to be attached to one of the iron atoms and is not undergoing exchange (*63*).

F. CYANIDE HYDRIDES

Aqueous solutions of cobalt salts containing cyanide ions have long been known to absorb molecular hydrogen (*11, 182, 218*). Only recently, however, has it been shown by proton magnetic resonance studies that under certain conditions these solutions contain cobalt-hydrogen species (*108, 111*). The concentration of the cobalt-hydride complex depends on the Co:CN⁻ ratio and reaches a maximum for a ratio of about 1:5 (3% if no hydrogenator, e.g., H_2 or BH_4^-, other than water is present) (*188*). Thus the hydrido complex may be formed in small concentration merely on dissolution of Adamson's salt, $K_6[Co_2(CN)_{10}]$, in water. Although no complex hydride ion has been isolated from these solutions, the results of potentiometric titrations (*11, 272a*), proton magnetic resonance, and ultra-

TABLE IX
CYANIDE HYDRIDES

Compound[b,c]	Color	References to preparation	NMR[a] τ (p.p.m.)
$[HCo(CN)_5]^{3-}$	Yellow solution	(*64,65,108, 111*)	~22.1 (*108*)
$[HRh(CN)_5]^{3-}$	Yellow solution	(*108*)	~20.3; J_{Rh-H} = 13.1 cps (*108*)
$[HIr(CN)_5]^{3-}$	—	(*109*)	~24
$[HPt(CN)_4]^{3-}$	—	(*109*)	~18; J_{Pt-H} = 450 cps (*109*)

[a] Chemical shift of M-hydrogen.
[b] Not isolated.
[c] Not fully characterized.

violet spectral studies favor the formulation $[Co(CN)_5H]^{3-}$ (*108*, *111*, *188*). An anomaly exists in that the UV spectra of solutions reduced with BH_4^- differ from those of solutions reduced in other ways (*188*, *231*). The work on these solutions is difficult owing to the sensitivity to oxidation (*10*, *108*, *111*) and the number of different complex species, e.g., $[Co(CN)_5H_2O]^{3-}$, $[Co(CN)_5]^{3-}$, which appear to be present. The complex $[Co(CN)_5H]^{3-}$ is analogous to the recently prepared stable σ-alkyl complexes $[Co(CN)_5CH_3]^{3-}$ and $[Co(CN)_5CH_2C_6H_5]^{3-}$ (*122*). In the absence of oxygen, solutions containing the proposed pentacyanocobalt hydride anion undergo only slow decomposition at room temperature. The stability of the Co—H system in such a complex may be understood in terms of the high ligand field strength of the CN^- and the well-known nonlability of low-spin d^6 complexes. In the latter connection, it has been shown that the hydrido-anion undergoes only slow exchange in D_2O solutions (*111*).

The kinetics of oxidation of these solutions has been the subject of a number of studies, and a likely postulated (*12*) mechanism is:

$$[Co(CN)_5H]^{3-} \xrightarrow{O_2} \underset{\text{(XXVII)}}{[Co(CN)_5OOH]^{3-}} \xrightarrow[\text{acid hydrolysis}]{H^+} [Co(CN)_5OH_2]^{2-} \qquad (59)$$

The complex (XXVII) has been isolated as the potassium salt by the hydrolysis of $K_6[(CN)_5Co—O—O—Co(CN)_5]$, and may be recognized by an absorption maximum at 272 mμ. Thus the ultraviolet spectrum of oxygenated solutions containing the hydride anion identifies the presence of the complex (XXVII).

As mentioned above, the cobalt cyanide solutions absorb molecular hydrogen and, although this reaction has been studied in some detail, much doubt remains concerning the actual mechanism. A possible mechanism is (*64*, *65*):

$$2[Co(CN)_5]^{2-} \rightleftharpoons [Co(CN)_{10}]^{6-} \overset{H_2}{\rightleftharpoons} [Co(CN)_5H]^{3-} \qquad (60)$$

Other mechanisms involving species such as $[Co(CN)_5H_2]^{4-}$ have been postulated (*65*, *188*).

An interesting application of these cobalt cyanide solutions arises in their ability to behave as homogeneous catalysts for the hydrogenation of unsaturated organic compounds (*64*, *65*, *182*, *188*, *195*, *218*, *220*). Thus these solutions, in the presence of hydrogen, reduce benzil to benzoin, 1:3 cyclohexadiene to cyclohexane, styrene to ethylbenzene, and octadeca-9,11,13-trienoic acid to octadeca-9,11-dienoic acid. Solutions containing a Co to CN^- ratio of 1:5 and about 0.15 *M* in strength were used. Solutions containing the Co—H species react with C_2F_4 affording the anion $[Co(CW)_5CF_2CF_2H]^{3-}$ (*217a*).

Proton magnetic resonance studies have also shown the presence of metal-hydrogen species in cyanide solutions of rhodium, platinum, and iridium (Table IX). In particular, the addition of CN^- to a boiled aqueous solution of rhodium trichloride, followed by reduction with sodium borohydride, yields a solution that contains an Rh—H complex in moderately high concentrations and is stable in the absence of oxygen for several years (*108*). The observed coupling of the proton with the Rh^{103} nucleus (spin $\frac{1}{2}$) confirms the presence of an Rh—H bond (*108*).

1. Vitamin B_{12}

Reduction of vitamin B_{12} with zinc in ammonium chloride solution or with aqueous solutions containing borohydride affords a gray-green reduction product called vitamin B_{12s} (*224*). It has been suggested that the reduced product is a hydride (*66*, *176*, *184*, *219*), since it has some reactions that are analogous to those of metal-hydrogen complexes (*26*) (see Fig. 10) and the method of preparation is similar to that for the postulated $[Co(CN)_5H]^{3-}$. However, despite careful examination of the proton magnetic resonance spectrum of the reduced vitamin B_{12} solutions, no band assignable to a Co—H hydrogen may be observed (*119*, *175a*). The absence of a suitable hydrogen resonance is not conclusive negative evidence, since broadening due to rapid exchange may occur. Recently (*239b*) the chemistry of some dimethylglyoxime cobalt complexes have been shown to be analogous to that of Vitamin B_{12s}, e.g., reaction with diazomethane yields a Co—Me complex. However, no physical evidence is given for the presence of a Co—H system in the dimethylglyoxime complexes.

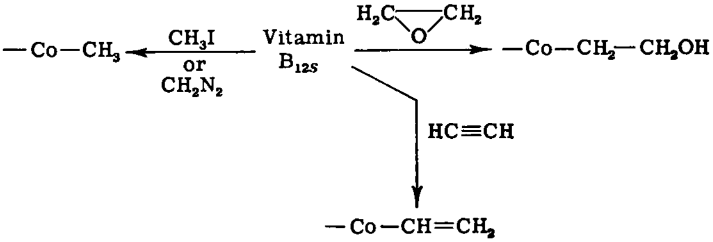


FIG. 10. Some reactions of vitamin B_{12s}.

Recent elegant studies using deuterated solutions of vitamin B_{12} are also inconsistent with a Co—H system in the reduced solutions (*52*). Further, the reactions in Fig. 10 may be interpreted in terms of a complex cobalt anion [compare $Co(CO)_4^-$], and therefore it must be concluded that the presence of a Co—H system in vitamin B_{12s} is not proven and that the evidence is rather against the postulate.

G. Hydride Complexes Containing Nitrogen Ligands

Treatment of aqueous solutions of bis(ethylenediamine)dichlororhodium(III) with sodium borohydride give solutions which the proton magnetic resonance spectrum shows to contain an Rh—H complex ($\tau \sim 31$ p.p.m., $J_{\text{Rh-H}} \sim 31$ c.p.s.). Also, the infrared spectrum of the precipitated tetraphenyl boronate shows a band at 2100 cm^{-1} assigned to an Rh—H stretch.

As shown in Table X, the reduction of a number of related rhodium complexes affords hydride complexes. None of these has been isolated in an analytically pure state and their formulations are not known. General evidence suggests that in the majority of cases the monohydride cations are formed, and the reaction may be regarded as a replacement reaction:

TABLE X
Hydride Complexes Containing Nitrogen Ligands

Compounds prepared from	References to preparation[a]	Infrared $\nu_{\text{M-H}}$ (cm^{-1})		NMR chemical shift of M-hydrogen τ (p.p.m.)	
$[trans\text{-Rh(en)}_2\text{Cl}_2]^+$	(*89, 227a, 270*)	2100	(*89*)	31; $J_{\text{Rh-H}} = 30.2$ c.p.s.	(*227a*)
$[cis\text{-Rh(en)}_2\text{Cl}_2]^+$	—	2093		31	(*89*)
$[\text{Rh(NH}_3)_5\text{Cl}]^+$	(*89, 227a*)	2079		—	
$[cis\text{-Rh(trien)Cl}_2]^+$	—	2081		28.5; 27.1; $J_{\text{Rh-H}} =$ 27 c.p.s.	
$[trans\text{-Rh(D.M.G.)}_2\text{Cl}_2]^+$	—	—		26.4	
$[trans\text{-RhPy}_4\text{Cl}_2]^+$	(*76a, 90*)	—		28.6	

[a] Complexes were prepared as yellow aqueous solutions.

$$[\text{en}_2\text{RhCl}_2]^+ + \text{H}^- \xrightarrow{\text{BH}_4^-} [\text{en}_2\text{RhClH}]^+ + \text{Cl}^- \tag{61}$$

In certain cases it appears that both chloride ligands may be replaced, affording dihydrido species from $\text{Rh(en)}_2\text{Cl}_2^+$; $\tau = 31.6$ p.p.m. (*227a*).

No doubt many hydride complexes containing weak-field ligands may be prepared for the heavier transition metals (for which ligand field splittings are greater) and possibly even complexes such as $[\text{Cr(H}_2\text{O)}_5\text{H}]^{2+}$ might be moderately stable.

H. "Pure" Transition Metal Hydrides

The formation of transition metal hydrides using atomic hydrogen has been studied (*242*), and there is evidence for transient volatile hydrides of Co, Ag, and Au. The only well-defined solid hydride is CuH (dec. > 60°) (*196*), which neutron diffraction studies show to have the wurtzite structure with a Cu—H distance of 1.73 Å (*96*). It is well known that the majority of the transition metals form "interstitial" hydrides, which are often nonstoichiometric and have been regarded as "solutions of hydrogen in the metal" (*266*). In many cases, however, these systems may be complicated; for example, dimorphic α-UH_3 and β-UH_3 may contain weak U—U bonds, and the U/H system has been described in terms of delocalized bonding to account for the essentially metallic properties of the solid (*238a*). Also PdH_4 units are postulated to occur in palladium-hydrogen systems (*221*).

There are several reports in the literature of discrete transition metal hydrides. In 1926 Weichselfelder and Thiede studied the reaction between phenylmagnesium bromide in ether and the halides of the first-row transition metals (*265*). They found that the solutions absorbed molecular hydrogen forming oily black solids which, although not isolated in a pure state, were formulated as simple hydrides such as CrH_3, FeH_2, FeH_6, CoH_2, and NiH_2. A more recent examination of these reactions (*239*) shows that the products are complex mixtures containing also hydrocarbons, magnesium, and metal halides. They confirm, however, the earlier work in that similar metal to hydridic hydrogen ratios were found. The nature of these products remains obscure, although the recent isolation of complexes such as $Li_3[CrHPh_5]\cdot 3Et_2O$ and $Li_3[H_3CrPh_3]\cdot 3Et_2O$, formed by treatment of $Li_3[CrPh_6]\cdot 2.5Et_2O$ with molecular hydrogen (*135*) suggests that a similar hydrogenolysis of metal-carbon bonds may account for the absorption of hydrogen in the Weichselfelder studies and that his complexes may be similar.

Complex hydrides of rhodium, Li_4RhH_4, and Li_4RhH_5 have been described (*75*). They were prepared by treatment of rhodium metal powder with lithium hydride at 600°C. The presence of transition metal-hydrogen bonds in either the latter complexes or those of Weichselfelder has yet to be unequivocally shown. Recent studies using a time-of-flight mass spectrometer have identified TiH_4 and chlorohydride derivatives (*29*).

1. *Potassium Enneahydridorhenate(VII)*

Treatment with potassium metal of a suspension of potassium perrhenate in ethylenediamine containing a little water precipitates a brown powder that may be purified (with considerable difficulty) by repeated extraction with 2-propanol, followed by dissolution in potassium hydroxide and reprecipitation with 98% ethylenediamine (*28*, *95*, *112*). The final product is a diamagnetic white deliquescent solid that undergoes slow decomposition on exposure to the atmosphere.

An early formulation, $KRe\cdot 4H_2O$ (*84*), for this product, based on analysis of an impure sample and the mistaken identification of the substance with similarly formulated rhenide species produced by other modes of reduction (*201*, *202*, *204*) (see below), was dismissed when the proton magnetic resonance spectrum showed a high field line indicative of an M-hydrogen (*53*, *91*, *94*). The product was reformulated as $K_6Re_2H_{14}\cdot 6H_2O$ (*91*, *94*), $K_2ReH_4\cdot 2H_2O$ (*83*), and K_2ReH_8 (*95*, *114*).

Recently a clarification of this confusion has come from the very elegant and comprehensive studies by Ginsberg and co-workers, who have fully characterized the salt as the enneahydride complex K_2ReH_9 on the basis of X-ray and neutron diffraction studies (*1*, *192*, *193*).

In retrospect, comparison of infrared spectra show that the previously obtained products formulated as above (*83*, *84*) were the impure potassium enneahydridorhenate, as were earlier preparations (*28*, *95*).

The salts of the enneahydridorhenate anion are remarkably stable (up to 300°C). They are soluble in alkaline solutions which are stable in the absence of oxygen. Aqueous solutions are alkaline and on the addition of acid liberate hydrogen, and rhenium metal is deposited (*178*). The aqueous solutions have strong reducing properties (*238*) and cause the immediate reduction of complexes such as $[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^+$, and $[Bi(OH)_4]^-$ to the respective metals. Treatment with thallous ions gives initially a white precipitate that rapidly turns black, giving thallium metal. This reaction may be used as a test for the ReH_9^{2-} anion.

The structure of K_2ReH_9 has been discussed (Section II,A). The proton magnetic resonance spectrum of solutions of the ReH_9^{2-} anion shows a single high-field line ($\tau \sim 18.6$) assignable to the Re—H hydrogens; hence all the hydrogens appear to be equivalent; they are also equivalent with respect to exchange with alkaline D_2O. The equivalence of the hydrogens is understandable in terms of the similarity of the environment of the prism and equatorial hydrogens. Also it is possible that in solution there is an exchange of roles of the hydrogens by means of deformation modes which involve displacements of only $\sim$0.4 Å.

The infrared spectrum of the ReH_9^{2-} anion shows bands at 1846 and 735 cm^{-1} assigned to the Re—H stretch and bend, respectively (*95*).

The bonding in the ReH_9^{2-} anion has been described in terms of a molecular orbital theory, leading to the set of energy levels shown in Fig. 11. The lowest-energy symmetry-allowed electric dipole transition is $e'^{(1)} \rightarrow a_1'^{(1)*}$, which interprets the observed sole absorption at 46,080 cm^{-1}.

Ginsberg has also reported potassium enneahydridotechnecate (*92*, *192*); this compound has not been prepared in a pure state, but the similarity of the mode of preparation, chemical properties, and above all the infrared spectrum and X-ray powder photographs to those of the rhenium analog leaves no doubt as to its constitution. These two enneahydrides are

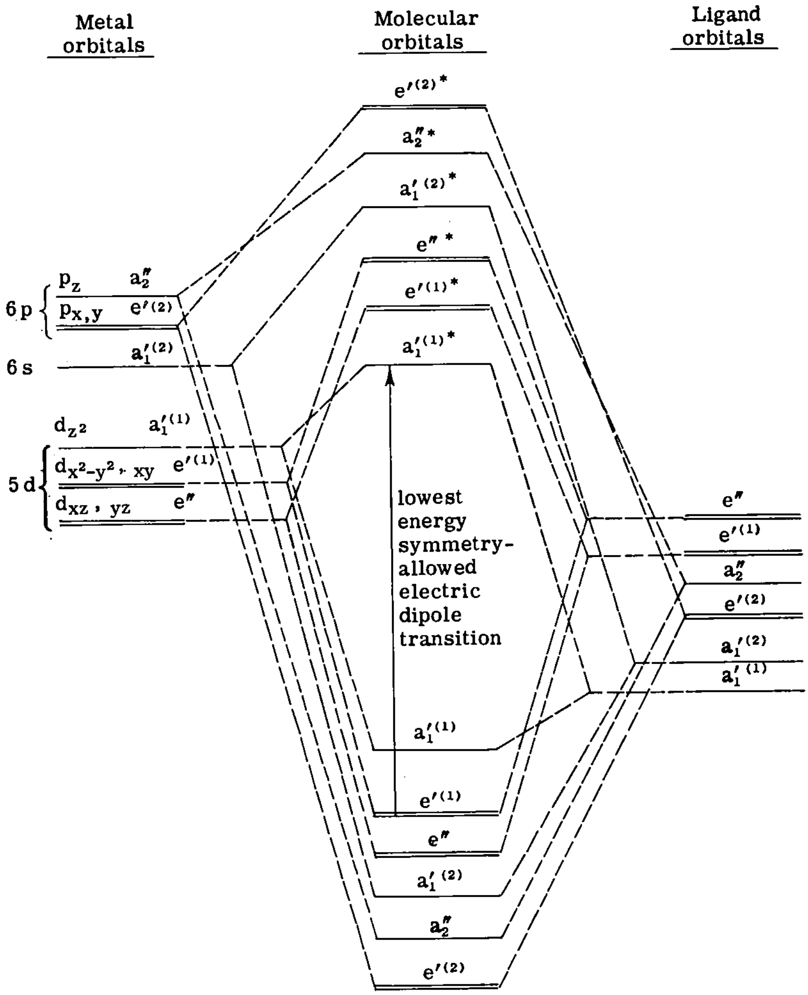


Fig. 11. Molecular orbital energy diagram for ReH_9^{2-} based on overlap considerations. (Note that the metal *6p*, *5d* and the ligand orbitals are degenerate sets and are separated here for clarity in showing which orbitals combine.)

the only simple transition metal hydride complexes known at present. However, anions such as $[CrH_6]^{3-}$ and $[CoH_6]^{3-}$ might well be stable.

2. Other Hydridorhenates

A number of aqueous "rhenide" solutions have been obtained, using reducing agents such as zinc in acid solution, zinc or sodium amalgam, or at the dropping mercury electrode (*204, 214, 253*), and Wilkinson showed that the solutions contain hydride species (*53*) which he tentatively suggested as $[ReH_3(OH)_3(H_2O)]^-$. The solutions do not contain the ReH_9^{2-} anion, as is shown by differences in ultraviolet spectra (*93*) and chemical properties (*214*). Polarographic reduction of the perrhenate anion, which may show up to an 8-electron reduction, as expected for the Re(—I) state, also shows other stages that may be due to rhenium hydride species (*53, 201, 202, 238*).

IV. The Role of Transition Metal Hydrides in Homogeneous Catalysis

A. CATALYTIC REACTIONS

It will by now be apparent that hydrogen very readily bonds to transition metals. Also a survey of the variety of routes employed in the formation of transition metal hydrides shows that the hydrogen may arise from many different sources such as water, alcohols, molecular hydrogen, and the hydrocarbon entities of nearby coordinating ligands. Metal-hydrogen systems are reactive and will add across unsaturated C=C systems, undergo homolytic dissociation, and may be readily replaced.

In view of these observations it is not surprising that there occur a wide variety of catalytic reactions, particularly involving hydrocarbons. For example, the isomerization of olefins, homogeneous hydrogenations, group substitution in the vicinity of double bonds, and polymerization reactions are all catalyzed by transition metal complexes.

The fields of organometallic chemistry and transition metal hydrides have grown together and are inextricably bound. A detailed coverage of the chemistry relating these two fields would be out of place here; however, a variety of examples are considered below that show the importance of transition metal hydrides in the field of catalysis and organometallic chemistry.

1. Examples of Catalytic Reactions That May Involve Metal Hydrides

(*a*) Certain metal ions such as Cu^{2+}, Ag^+, and Hg^{2+} can activate hydrogen homogeneously in aqueous solution (*116–119*). Kinetic studies suggest the presence of intermediates such as CuH, CuH^+, and AgH. Similar hydride species are postulated to account for the kinetics of oxidation and reduction of metal ions by hydrogen atoms (*120*) e.g.,

$$2Ag^+ + H_2 \rightarrow 2AgH^+ \qquad (62)$$

The observed activation energy of 15 kcal for this reaction implies a considerable stability for the AgH^+ species. The catalytic properties of cobalt cyanide solutions in hydrogenation reactions have been described in Section III,F; see also (*195, 195a*).

(*b*) The absorption of hydrogen on pure transition metals almost certainly affords M—H covalent bonds, and hydrogenations using Raney nickel, platinized asbestos, and various precious metals are well known. Pure metals such as Ni and Pt in active forms will also chemisorb olefins and cause isomerization reactions (*32, 130, 190, 217, 225, 243, 245, 248*).

(*c*) Ethylene platinous chloride in toluene or acetone solutions catalyzes the reduction of ethylene to ethane by molecular hydrogen at $-10°C$ without the deposition of platinum metal (*85*), and olefin-palladium chloride complexes may cause the isomerization of olefins (*244*). Similarly, hydrogen transfer reactions such as

$$2CH_2{=}CH{\cdot}CH_2OH \rightarrow CH_2{=}CHCH_3 + CH_2{=}CH{\cdot}CHO + H_2O \qquad (63)$$

are catalyzed by ruthenium, rhodium, and palladium salts (*223*), and ruthenium(II) will catalyze the homogeneous reduction of olefins (*121*).

(*d*) Finally, solutions of $(PR_3)_2NiCl_2$ in tetrahydrofuran which have been reduced with borohydride will catalyze the oligomerization of acetylene (*103, 205, 206*), and similar reactions of acetylenes in the presence of many other Group VIII metal complexes have been shown (*206*).

Few detailed studies on the mechanism of these reactions have been made; however, the essential steps of the mechanism might be expected to show strong similarities to those in the cobalt hydride reactions described below.

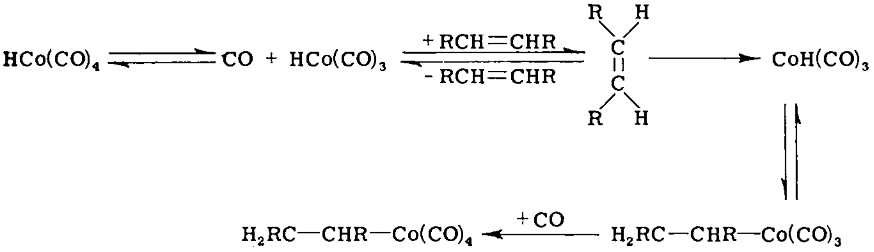
2. Catalytic Reactions Involving Cobalt Carbonyl Hydride Complexes

The reaction of olefins with carbon monoxide and hydrogen in the presence of cobalt carbonyl catalysis affords *inter alia* aldehydes, ketones, and alcohols. These reactions are of considerable industrial importance. The industrial reactions were originally called the Fischer-Tropsch or Oxo syntheses but now are described under the general title of hydroformylation reactions (*3, 224*).

The prediction that tetracarbonylcobalt hydride would act as a catalyst in hydroformylation reactions (*133, 224*) has been amply verified; for example, the stoichiometric hydroformylation, using $HCo(CO)_4$, of 1-pentene at room temperature affords a variety of isomeric aldehydes (*187*). Also, $HCo(CO)_4$ is formed under the high pressure (100 atm.; 1:1; H_2:CO) and temperature (100°–300°C) conditions of the hydroformylation reaction (*183, 226*).

Recent detailed studies of a number of the reactions of cobalt alkyls, cobalt acyls, and $HCo(CO)_4$, in particular by Heck and co-workers, have shown that there are some basic equilibria which account for many of the catalytic reactions.

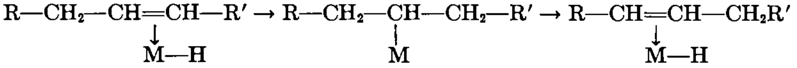
(*a*) Tetracarbonylcobalt hydride will add reversibly across olefinic C=C systems; the following equilibria are postulated:



$$\begin{tikzcd} \mathrm{HCo(CO)_4} \arrow[r, shift left] & \mathrm{CO} + \mathrm{HCo(CO)_3} \arrow[l, shift left] \arrow[r, shift left, "+\mathrm{RCH{=}CHR}"] & \mathrm{RHC{=}CHR} \arrow[l, shift left, "-\mathrm{RCH{=}CHR}"] \arrow[r] & \mathrm{CoH(CO)_3} \arrow[d, shift left] \\ & \mathrm{H_2RC{-}CHR{-}Co(CO)_4} & & \mathrm{H_2RC{-}CHR{-}Co(CO)_3} \arrow[u, shift left] \arrow[ll, "+\mathrm{CO}"'] \end{tikzcd} \qquad (64)$$

Evidence for the above reactions comes from kinetic studies (*130*), and from the thermal decomposition of ethyltetracarbonylcobalt which gives ethylene and tetracarbonylcobalt hydride (*130*). Earlier studies have eliminated possible free radical mechanisms (*4*). Supporting evidence arises from the demonstration of the reversible addition of ethylene to a platinum hydride (see Eq. 27) and from the observation that a number of transition metal alkyls have been shown to lose readily a hydride ion from the 2-carbon of the alkyl group (*101*).

The reversible addition and subtraction of the hydrogen from alkyls (shown above) can be used to account for the mechanism of isomerism of olefins. The scheme formally illustrated below has been postulated by several authors (*101*, *123*, *225*, *250*):



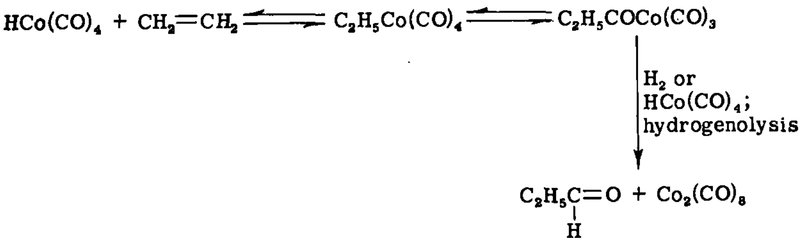
$$\underset{\downarrow\atop \mathrm{M{-}H}}{\mathrm{R{-}CH_2{-}CH{=}CH{-}R'}} \rightarrow \mathrm{R{-}CH_2{-}}\underset{|\atop \mathrm{M}}{\mathrm{CH}}\mathrm{{-}CH_2{-}R'} \rightarrow \underset{\downarrow\atop \mathrm{M{-}H}}{\mathrm{R{-}CH{=}CH{-}CH_2R'}} \qquad (65)$$

(*b*) Another equilibrium system postulated to account for the hydroformylation reactions is the reversible formation of acyl complexes from alkyls:

$$\mathrm{RCOCo(CO)_3} \rightleftharpoons \mathrm{RCo(CO)_4} \rightleftharpoons \mathrm{RCo(CO)_3} + \mathrm{CO} \qquad (66)$$

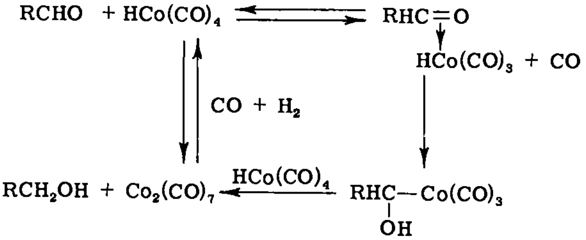
Evidence for this equilibrium comes from kinetic studies (*129*), from infrared spectra of the alkyl cobalt complexes which show bonds assignable to both terminal and acyl C—O stretches (*130*, *133*), and from the preparation of acyl complexes by treatment of the corresponding alkyls with carbon monoxide under pressure (*130–132*).

(*c*) Tetracarbonylcobalt hydride reacts readily with carbon monoxide, hydrogen, and 1-olefins to form aldehydes (*187*, *189*, *229*, *269*), and on the basis of the above equilibria the following mechanism has been postulated (*130*, *133*):



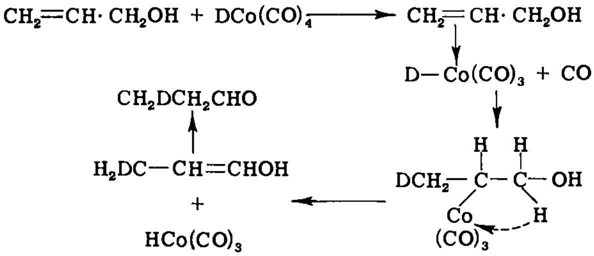
(67)

(*d*) During hydroformylation reactions some reduction of the aldehydes to alcohols or even paraffins occurs, and at 200°C these reductions become the major reactions (*3*, *267*, *268*). A mechanism suggested for the reaction is (*4*, *216*):



(68)

(*e*) A final example is the isomerization of allyl alcohol to propionaldehyde by $HCo(CO)_4$ (*97*). The reaction is very rapid, and studies using the deuteride $DCo(CO)_4$ have shown that CH_2DCH_2CHO is formed exclusively. The mechanism postulated is:



(69)

(*f*) Some related carbonylation reactions of nickel complexes have been postulated to proceed via Ni—H species (*128*), and reactions of acetylenes with iron carbonyls in alkaline solution (*233*, *234*) may proceed via Fe—H intermediates (*249*).

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