HYDRIDE COMPLEXES OF THE TRANSITION METALS

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Contents

I. Introduction and Historical Development 231
II. Synthesis of Transition Metal Hydrides 232
  A. Reactions with Molecular Hydrogen 232
    1. Direct Hydrogenation 232
    2. Replacement by H_2 of Coordinated Ligands 233
    3. Oxidative Addition of H_2 to Coordinatively Unsaturated Species 233
    4. Hydrogenolysis of Transition Metal–Group IV Derivatives 234
  B. Reactions of Metal Complexes with Saline and Complex Hydrides 234
  C. Hydrogen Transfer from Solvent or Metal-Coordinated Group 236
    1. Reactions with Alcohols, Hydrazine, and Metal Alkyls 236
    2. Oxidative Addition of Hydrogen Compounds 238
    3. Reduction by and Oxidative Addition of Group IV Hydrides 240
    4. Intramolecular Oxidative Addition of C–H Bonds 242
  D. Hydrolyses and Dehydrohalogenation 243
    1. Hydrolysis of Alkali Metal Salts of Transition Metal Complexes 244
    2. Dehydrohalogenation of Alkyl Halides by Metal Anions 244
    3. Hydrolysis of Metal Carbonyl Cations 244
  E. Protonation 245
  F. Oxidative Addition of H_2 and HX to Cationic Metal Complexes 246
III. Chemical Properties and Chemical Reactions of Transition Metal Hydrides. Survey by Metal Triads 247
  A. Stability 247
  B. Trans Effect of Hydride 247
  C. Elimination of H_2 248
  D. Acid–Base Characteristics 248
  E. Reaction of Metal Hydrides with Halogens, Mercuric Halides, and Halocarbons 248
  F. Reaction of Metal Hydrides with Unsaturated Derivatives 249
    1. Addition of Metal Hydrides to Unsaturated Compounds 249
    2. Isomerization of Olefins 250
    3. Hydrogenation 250
    4. Hydroformylation 251
    5. Hydrosilation 252
  G. Titanium, Zirconium, and Hafnium 252
  H. Vanadium, Niobium, and Tantalum 253
  I. Chromium, Molybdenum, and Tungsten 254
  J. Manganese, Technetium, and Rhenium 255
  K. Iron, Ruthenium, and Osmium 258
  L. Cobalt, Rhodium, and Iridium 263
  M. Nickel, Palladium, and Platinum 269
  N. Zinc, Cadmium, and Mercury 271
IV. Spectroscopic Characterization of Transition Metal Hydrides 271
  A. Infrared and Raman 271
  B. Nuclear Magnetic Resonance 274
  C. Miscellaneous Instrumental Studies 278
V. Structure Determinations of Transition Metal Hydride Complexes 279

I. Introduction and Historical Development

In this article we shall deal only with the class of compounds which contain hydrogen bound to a transition metal and, in most cases, other stabilizing ligands in a discrete molecular or ionic species. We shall not include in this review those substances involving the adsorption of hydrogen in metallic or semimetallic phases which in many cases are nondiscrete, nonstoichiometric, and do not lend themselves to the same type of study as that for the discrete complexes.

Beginning in the early 1930's with the discovery by Hieber of the unstable hydridocarbonyls, $H_2Fe(CO)_4$ and $HCo(CO)_4$, hydride complexes of the transition metals remained a laboratory curiosity for a relatively long period of time. Three further examples of hydride complexes were reported in 1955, namely $HRe(C_5H_5)_2$ by Wilkinson and Birmingham and $HM(C_5H_5)(CO)_3$ (M = Cr, Mo) by Fischer, Hafner, and Stahl. It was not until 2 years later, however, after the discovery of *trans*-$HPtCl(PEt_3)_2$ by Chatt, Duncanson, and Shaw that a rapid development began. By 1965 there were some 300 original papers on this subject, 200 known derivatives, and two comprehensive review articles by Ginsberg[1] and by Green and Jones[2] among others (see references cited in these works). Transition metal hydrides were also coming to be recognized as intermediates or catalysts in reactions such as hydroformylation, olefin isomerization, and hydrogen exchange. These developments were discussed in two further reviews, one by Green[3] in 1967 and the other by Chatt[4] in 1968. In the 6-year period 1965–1970, there have appeared some 400 articles covering about 500 new derivatives. For the present work, we have limited ourselves to this

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(1) A. P. Ginsberg, *Transition Metal Chem.*, **1**, 112 (1965).

(2) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 115 (1965).

(3) M. L. H. Green, *Endeavour*, **26**, 129 (1967).

(4) J. Chatt, *Science*, **160**, 723 (1968).

period continuing where the reviews of Green and Jones[2] and Ginsberg[1] had terminated. A few noteworthy developments in 1971 which became known to us while this article was in preparation have also been added.

In the references, we have combined, whenever possible, the citation of a preliminary communication with that of the full paper appearing on the same subject.

A word is perhaps necessary on the nomenclature used in this review. Although the nomenclature committee of the IUPAC has stipulated "in formulas the symbol for the central atom(s) should be placed first" (Section 7.21, *J. Amer. Chem. Soc.*, **82**, 5523 (1960)), this has not been standard practice among transition metal hydride chemists (see reviews, ref 1 and 2). The committee itself (Section 7.323) has placed the hydrogen in hydrogen tetracarbonylcobaltate(−I) before the metal atom. That order is preferred, no doubt, because hydrogen ionizes as a proton. Since no unanimous preference exists and the complete ionization behavior of all the transition metal hydride complexes is unknown, we have elected to write the formulas throughout this review with the hydrogen symbol preceding that of the metal as explained on p 252.

ABBREVIATIONS

acac	acetylacetonate
AcO	acetate
Bu^n	*n*-butyl
Bu^t	*tert*-butyl
C_7H_8	norbornadiene
COD	1,5-cyclooctadiene
Cp	C_5H_5 (cyclopentadienide)
Cplx	complex multiplet
Cy	cyclohexyl
depe	bisdiethylphosphinoethane
diglyme	diethylene glycol dimethyl ether
diphos	bisdiphenylphosphinoethane
dipy	bipy = bipyridine = 2,2′-bipyridyl
dmpe	bisdimethylphosphinoethane
Et	ethyl
EtO	ethoxy
fac	facial
Me	methyl
MeO	methoxy
mer	meridional
Ph	phenyl
phen	1,10-phenanthroline
Pr^i	isopropyl
Pr^n	*n*-propyl
py	pyridine
QP	$P(o\text{-}C_6H_4P(Ph)_2)_3$
THF	tetrahydrofuran

II. Synthesis of Transition Metal Hydrides

The transition metal hydrides which were reported in the period 1965–1970 are summarized in the tables in section III, organized according to the groups of the periodic classification of the elements, accompanying discussion of these in that section.

Individual methods of synthesis are discussed in the sections below. Green and Jones[2] organized the known methods for the synthesis of transition metal hydrides into five general categories: (1) direct hydrogenation; (2) reduction of metal halide complexes; (3) hydride transfer and reverse carbonylation; (4) hydrolysis of alkali metal salts of complex carbonyls, and (5) protonation. We find this a convenient scheme and continue in this form with slightly modified and expanded classifications to incorporate new information.

A. REACTIONS WITH MOLECULAR HYDROGEN

1. Direct Hydrogenation

Molecular hydride complexes of transition metals can be formed by the direct union of elemental hydrogen with the metal in the presence of a suitable accompanying ligand at elevated temperatures and pressures. Thus, as summarized by Green and Jones,[2] this method affords the synthesis of $HCo(CO)_4$ from cobalt metal, CO, and H_2 at 250 atm and 180° or $H_2Fe(depe)_2$ from iron metal, ligand, and H_2 at 200°. The equilibrium at temperatures of 150–260° between gaseous carbonyls of cobalt and the metal (dispersed on pumice), CO and H_2 in the pressure range 100–300 atm, was studied by Bronshtein, *et al.*[5] The principal metal species in the gas phase was established to be $HCo(CO)_4$ ($p_{H_2} = 170$ atm, $p_{CO} = 130$ atm); the standard free energy and enthalpy of formation of this hydride from the elements were calculated to be respectively $\Delta G°_{298} = -127.55$ kcal/mol and $\Delta H°_{298} = -136.044$ kcal/mol.

Kruck and coworkers have extended the direct synthesis to the hydridometal trifluorophosphine complexes starting with metal salts, a halogen acceptor, the ligand, and H_2.[6,7]

$$CoI_2 + Cu + H_2\,(100\text{ atm}) + PF_3\,(250\text{ atm}) \xrightarrow{170°} HCo(PF_3)_3 \quad (1)$$

$$FeI_2 + Zn + H_2\,(100\text{ atm}) + PF_3\,(300\text{ atm}) \xrightarrow{250°} H_2Fe(PF_3)_4 \quad (2)$$

Other examples of these reactions may be found for $HRe(PF_3)_5$ and the congeners of Fe and Co of analogous formulas (see Tables V and VI).

The synthesis of $H_2Os(CO)_4$ has been reported by L'Eplattenier and Calderazzo[8,9] from several materials (eq 3–5)

$$\begin{tikzcd}
OsO_4 + CO + H_2 \arrow[drr, "180\text{ atm}, 160°", "\text{heptane}, 6\text{ hr}"'] & & & (3) \\
Os(CO)_5 + H_2 \arrow[rr, "180\text{ atm}, 170°", "\text{heptane}, 10\text{ hr}"'] & & H_2Os(CO)_4 & (4) \\
Os_3(CO)_{12} + H_2 \arrow[urr, "80\text{ atm}, 100°", "6\text{ hr}"'] & & & (5)
\end{tikzcd}$$

Thus several of the reaction pathways mentioned under section A lead to the same product, namely, direct synthesis from the oxide, H_2, and CO as in eq 3, displacement of coordinated CO by H_2 (eq 4), and hydrogenolysis of metal–metal bonds (eq 5). The analogous $H_2Ru(CO)_4$ is thermally unstable (see footnote 2 of ref 9) and cannot be obtained by these routes; its synthesis is described in section II.D.1.

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(5) Yu. E. Bronshtein, V. Yu. Gankin, D. P. Krinkin, and D. M. Rudkovskii, *Russ. J. Phys. Chem.*, **40**, 802 (1966); *cf. Zh. Fiz. Khim.*, **40**, 1475 (1966).

(6) Th. Kruck, *Angew. Chem. Int. Ed. Engl.*, **6**, 53 (1967).

(7) Th. Kruck and A. Prasch, *Z. Anorg. Chem.*, **371**, 1 (1969).

(8) F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, **6**, 2092 (1967).

(9) F. L'Eplattenier and F. Calderazzo, *ibid.*, **7**, 1290 (1968).

Further investigations into eq 3 and eq 4 have led to other polynuclear hydrides in lower yield (see section III.K).

A simple and direct route to metal carbonyl hydrides has been found starting with metal carbonyls and hydrogen at atmospheric pressure.[10] In this manner the carbonyls $Re_2(CO)_{10}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ have yielded the carbonyl hydrides $H_3Re_3(CO)_{12}$ and $H_4Re_4(CO)_{12}$ (see also ref 11), $H_4Ru_4(CO)_{12}$, and $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$, respectively, in high yields and purity.

2. *Replacement by H_2 of Coordinated Ligands*

In mixed carbonyl–phosphine derivatives, H_2 is seen to displace CO.[9]

$$Os(CO)_4PPh_3 + H_2 \xrightarrow[\text{THF, 3 hr}]{\text{120 atm, 130°}} H_2Os(CO)_3PPh_3 \quad (6)$$

$$Os(CO)_3(PPh_3)_2 + H_2 \xrightarrow[\text{THF, 12 hr}]{\text{120 atm, 130°}} H_2Os(CO)_2(PPh_3)_2 \quad (7)$$

The analogous $H_2Ru(CO)_3PPh_3$ could not be obtained from $Ru(CO)_4PPh_3$ in a reaction similar to eq 6 owing, most likely, to the thermal instability of that product. However, treatment of the analogous Ru starting materials (eq 7) gives $H_2Ru(CO)_2(PPh_3)_2$.[9] Displacement by H_2 of coordinated N_2, on the other hand, occurs with greater ease and is reversible, as reported for the Co complexes in eq 8 (L = PPh_3,[12] and L = PPh_3, $PEtPh_2$[13]) and for Ru complexes in eq 9 (L = PPh_3[14]). The interconversion of hydrido derivatives by the displacement of H_2 by ligands has also been observed. Thus reaction of the pentahydrides of iridium with ligands leads to the formation of the trihydrides (L = L′ = PEt_2Ph,[15] and L = PEt_2Ph, L′ = PPh_3, $AsMe_2Ph$, $SbPh_3$, SMe_2, $P(OMe)_3$, $P(OMe)_2Ph$, MeNC, and CO[16]).

$$HCo(N_2)L_3 + H_2 \rightleftharpoons H_3CoL_3 + N_2 \quad (8)$$

$$H_2Ru(N_2)L_3 + H_2 \rightleftharpoons H_4RuL_3 + N_2 \quad (9)$$

$$H_5IrL_2 + L' \longrightarrow mer\text{-}H_3IrL_2L' + H_2 \quad (10)$$

With L′ = CO, the reaction will proceed to the monohydride product, $HIr(CO)_2L_2$.[16] Similarly, heptahydridorhenium diligand derivatives, H_7ReL_2, will give the pentahydrido triligand products.[17]

3. *Oxidative Addition of H_2 to Coordinatively Unsaturated Species*

The displacement of ligands or H_2 may proceed first through the formation of a coordinatively unsaturated derivative which then either undergoes oxidative addition of H_2 or addition of L. The separate steps have been demonstrated by Ito, *et al.*, for derivatives of ruthenium (L = PPh_3).[18]

$$H_2RuL_4 \xrightleftharpoons[+L]{-L} H_2RuL_3 \xrightleftharpoons[-H_2]{+H_2} H_4RuL_3 \quad (11)$$

Oxidative addition of H_2 to coordinatively unsaturated (d^8 square-planar) complexes of Ir was first demonstrated by Vaska and Rhodes (L = PPh_3, eq 12)[19] and by Malatesta, *et al.* (L = PPh_3, eq 13).[20]

$$trans\text{-}IrCl(CO)L_2 + H_2 \overset{\text{1 atm}}{\rightleftharpoons} cis\text{-}H_2IrCl(CO)\text{-}trans\text{-}L_2 \quad (12)$$

$$HIr(CO)L_2 + H_2 \overset{\text{1 atm}}{\rightleftharpoons} H_3Ir(CO)L_2 \quad (13)$$

Osborn, Jardine, Young, and Wilkinson[21] report the reversible oxidative addition of H_2 to rhodium derivatives (X = Cl, Br, I; S = solvent; L = PPh_3).

$$RhXL_2\cdot S + H_2 \rightleftharpoons cis\text{-}HRhXL_2\cdot S \quad (14)$$

The catalytic activity of this complex in olefin hydrogenation is believed to derive from the presence of loosely coordinated solvent which can be displaced by olefins. The mechanism of hydrogenation is discussed in section III.F.3. Similar, but lesser catalytic activity is observed for the $AsPh_3$ and $SbPh_3$ complexes whose addition of H_2 is not reversible.[22]

Reversible oxidative addition was demonstrated for a series of cobalt complexes by Rossi and Sacco (eq 15, L = PPh_3, $PMePh_2$, $PEtPh_2$, $PBuPh_2$, PEt_2Ph, PBu_2Ph, PBu_3, and $AsPh_3$);[23] the equilibrium is shifted to the right with greater π-acid strength of L.

$$HCoL_3 + H_2 \rightleftharpoons H_3CoL_3 \quad (15)$$

The kinetics of the addition of hydrogen to square-planar iridium(I) complexes have been studied by Chock and Halpern[24] and also reviewed by Halpern.[25] The addition obeys second-order rate law and the activation energy is found to be, for $IrX(CO)(PPh_3)_2$, ΔH^*, 10.8 (X = Cl) and 12.0 (X = Br) kcal/mol. Strohmeier and Müller[26a] have determined the equilibrium constants and kinetics of the addition of molecular hydrogen to $IrX(CO)L_2$ (X = Cl, Br, I and L = various tertiary phosphines and phosphites). They observed in toluene and for L = PPh_3 ΔH = 15.8 (X = Cl), 8.3 (X = Br), and 5.2 (X = I) kcal/mol. Vaska and Werneke[26b] recently report kinetics for the forward and reverse reactions from which they obtain the following thermodynamic data for the addition of hydrogen to $IrX(CO)(PPh_3)_2$: $\Delta H°$ = −14 (X = Cl), −17 (X = Br), and −19 (X = I) kcal/mol.

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(10) H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *J. Chem. Soc. D*, 477 (1971).

(11) R. Saillant, G. Barcelo, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **92**, 5739 (1970).

(12) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *ibid.*, **93**, 371 (1971).

(13) A. Sacco and M. Rossi, *Inorg. Chim. Acta*, **2**, 127 (1968); *Chem. Commun.*, 316 (1967).

(14) W. H. Knoth, *J. Amer. Chem. Soc.*, **90**, 7172 (1968).

(15) B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc. D*, 703 (1970).

(16) B. E. Mann, C. Masters, and B. L. Shaw, *ibid.*, 846 (1970).

(17) J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1963 (1969); *Chem. Commun.*, 545 (1966).

(18) T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **92**, 3011 (1970).

(19) L. Vaska and R. E. Rhodes, *ibid.*, **87**, 4970 (1965).

(20) (a) L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 6974 (1965); (b) L. Malatesta, *Helv. Chim. Acta* (Alfred Werner Commemorative Volume), 147 (1967).

(21) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966); *cf.* J. F. Young, *et al.*, *Chem. Commun.*, 131 (1965).

(22) J. T. Mague and G. Wilkinson, *J. Chem. Soc. A*, 1736 (1966).

(23) M. Rossi and A. Sacco, *Chem. Commun.*, 471 (1967).

(24) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

(25) J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970).

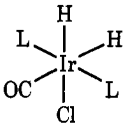
(26) (a) W. Strohmeier and F. J. Müller, *Z. Naturforsch. B*, **24**, 931 (1969); (b) L. Vaska and M. F. Werneke, *Trans. N. Y. Acad. Sci.*, **33**, 70 (1971).

For the complex $IrCl(PPh_3)_3$ some important differences were noted by Bennett and Milner (eq 16).[27] In contrast to the analogous Rh complex (see eq 14 above), L is not readily lost in solution and the oxidative addition of H_2 is irreversible; thus $IrClL_3$ does not function as a homogeneous hydrogenation catalyst.

$$IrClL_3 + H_2 \longrightarrow H_2IrClL_3 \qquad (16)$$

Deeming and Shaw[28] report cis addition of H_2 to $IrCl(CO)L_2$ ($L = PPh_3$).

trans-$IrCl(CO)L_2$ + H_2 ⟶



(17)

Oxidative addition of H_2 to cationic complexes, giving the equivalent of protonation of a neutral hydrido complex, is discussed in section II.E.2.

Coordinatively unsaturated species may also be involved as intermediates in the following two syntheses employing elemental hydrogen: eq 18, Bell, Chatt, and Leigh[29] (L = tertiary phosphine or arsine), and eq 19, Rose, *et al.*[30] ($L = PPh_3$).

$$trans\text{-}WCl_4L_2 + Na/Hg + H_2 + L \longrightarrow H_6WL_3 \qquad (18)$$

$$RuCl_2L_3 + H_2 + 2RCO_2Na \longrightarrow HRu(O_2CR)L_2 \qquad (19)$$

Protonation of the coordinatively saturated (18-electron) $H_3Ir(PPh_3)_3$ is accompanied by loss of H_2 to give a 16-electron cationic complex, eq 20;[20] the same is also true in the protonation of $H_3Ir(CO)L_2$ (eq 21, $L = PPh_3$).[20]

$$H_3IrL_3 + H^+ \longrightarrow H_2IrL_3^+ + H_2 \qquad (20)$$

$$H_3Ir(CO)L_2 + H^+ \longrightarrow H_2Ir(CO)L_2^+ + H_2 \qquad (21)$$

The heating of bis(π-cyclopentadienyl)tantalum trihydride at 80° causes loss of H_2 and the formation of the intermediate 16-electron species $(C_5H_5)TaH$ (see also section III.H); in the presence of D_2 gas, exchange is observed.[31] The 16-electron species will also catalyze the exchange of D_2 with C_6H_6, as will the species formed by loss of hydrogen from H_5IrL_2[31] or H_7ReL_1[17] ($L = PPh_3$).

4. *Hydrogenolysis of Transition Metal–Group IV Derivatives*

Addition of H_2 to coordinatively unsaturated species followed by reductive elimination of the group IV metal hydride has been suggested as the pathway involved in the formation of transition metal hydrides from the hydrogenolysis of group IV metal alkyl derivatives of platinum (eq 22[32] ($L = PEt_3$) and eq 23[33] (M = Si, Ge; $L = PEt_3$)). The activation energy for eq 23 has been estimated to be about 9 kcal[32] which proceeds to completion in the time indicated.

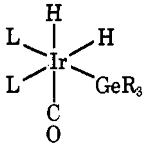
$$trans\text{-}Pt(GePh_3)_2L_2 + H_2 \xrightarrow[2\text{-}3\text{ hr}]{1\text{ atm }20°} HPt(GePh_3)L_2 + Ph_3GeH \qquad (22)$$

$$trans\text{-}PtCl(MMe_3)L_2 + H_2 \xrightarrow[24\text{ hr}]{1\text{ atm }20°} HPtClL_2 + Me_3MH \qquad (23)$$

Keim[34] has reported hydrogenolysis of alkylrhodium derivatives (R = Me, Ph; $L = PPh_3$).

$$RhRL_3 + H_2 \longrightarrow HRhL_3 + RH \qquad (24)$$

Hydrogenolysis of a coordinatively saturated derivative has been observed by Glockling and Wilbey[35] ($L = PPh_3$; R = Me, Et or Cl).



+ H_2 ⟶ $H_3Ir(CO)L_2$ + $HGeR_3$ (25)

Since other coordinatively saturated derivatives such as $Mo(Cp)(GeR_3)(CO)_3$ are resistant to hydrogenolysis even under drastic conditions, eq 25 is believed to proceed through a coordinatively unsaturated derivative formed by the loss of a phosphine ligand. Both of the phosphines in eq 25 are opposite ligands of high trans effect and in fact may be readily interchanged with other ligands. Hydrogenolysis of intermediate alkyl derivatives to give hydrocarbon and regenerated metal hydride has been proposed as one of the steps in the much discussed homogeneous hydrogenation of olefins by transition metal complexes; see discussion by James[36] and others.

B. REACTIONS OF METAL COMPLEXES WITH SALINE AND COMPLEX HYDRIDES

We depart slightly from the organization of Green and Jones[2] who discussed in their second category a variety of reducing agents but restricted it to the reactions of metal halides. We prefer instead to restrict the present section to a particular type of reagent to emphasize similarities which may exist in its reaction pathways. Thus, for instance, while it is possible to obtain successive replacement of halogen with hydride by the action of boiling alcohol in the presence of base, we have placed this route in section II.C.1 in which this and other examples of hydrogen transfer from coordinated solvent or ligand are discussed together.

Chatt, Coffey, and Shaw[37] have used the complex hydrides $LiAlH_4$ or $LiBH_4$ for the synthesis of trihydride derivatives of iridium.

$$mer\text{-}IrCl_3(AsEt_2Ph)_3 + LiAlH_4 \xrightarrow{THF} fac\text{-}H_3Ir(AsEt_2Ph)_3 \qquad (26)$$

$$HIrCl_2(PPh_3)_3 + LiAlH_4 \xrightarrow{THF} mer\text{-}H_3Ir(PPh_3)_3 \qquad (27)$$

The choice of solvent is important; a similar reduction in diethyl ether yields a mixture of products from which the monohydride complex was isolated in greatest amount.

The reader may have some question as to the usage of the term "reduction" as applied to reactions resulting in the

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(27) M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969); *Chem. Commun.*, 581 (1967).

(28) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969).

(29) B. Bell, J. Chatt, and G. J. Leigh, *J. Chem. Soc. D*, 842 (1970).

(30) D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc. A*, 2610 (1969).

(31) E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5234 (1970).

(32) R. J. Cross and F. Glockling, *J. Chem. Soc.*, 5422 (1965).

(33) F. Glockling and K. A. Hooton, *J. Chem. Soc. A*, 1066 (1967).

(34) W. Keim, *J. Organometal. Chem.*, **14**, 179 (1968); **8**, P25 (1967).

(35) F. Glockling and M. D. Wilbey, *J. Chem. Soc. A*, 1675 (1970); *J. Chem. Soc. D*, 286 (1969).

(36) "Homogeneous Catalysis with Special Reference to Hydrogenation and Oxidation," *Discuss. Faraday Soc.*, No. **46** (1968).

(37) J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965).

production of transition metal hydrides, and a brief comment may be appropriate. There is no doubt that, when hydrides replace halides bound to a metal, the metal acquires additional electron density. However, when electron tallies are made after this "reduction" or substitution as, for example, in eq 29, it is difficult to determine if the metal has formally undergone a reduction. We therefore use the terms "reduction" and "substitution" interchangeably without prejudice as to whether or not reduction has formally occurred.

Angoletta and Caglio[38] have used $LiAlH_4$ to obtain dihydride and trihydride reduction products from complexes of the type $HIrX_2L_3$. The alumino-hydride reduction is not always straightforward; Chatt, Coffey, and Shaw[37] observed loss of PPh_3 from transition metal (with formation of aluminum phosphides) in the reduction of IrX_3L_3 by $LiAlH_4$. They reported as product a five-coordinate complex of the type "H_3IrL_2" which was later shown by Mann, Masters, and Shaw[15] in the case of $L = PEt_2Ph$ to be a pentahydride derivative, and it may prove that more such "five-coordinate" complexes should thus be formulated

$$\textit{mer}\text{-IrCl}_3(\text{PEt}_2\text{Ph})_3 + \text{LiAlH}_4 \xrightarrow{\text{THF}} \text{H}_5\text{Ir}(\text{PEt}_2\text{Ph})_2 + \textit{fac}\text{-H}_3\text{Ir}(\text{PEt}_2\text{Ph})_3 \tag{28}$$

In the reduction of various halides or oxyhalides of rhenium, Chatt and Coffey[17] report the formation of the penta- or heptahydrides as major products (L = various tertiary phosphines).[39]

$$\text{ReCl}_3\text{L}_3 + \text{LiAlH}_4 \longrightarrow \text{H}_5\text{ReL}_3 \tag{29}$$

$$\text{ReOCl}_3\text{L}_2 \text{ or ReCl}_4\text{L}_2 \text{ or ReO(OR)Cl}_2\text{L}_2 + \text{LiAlH}_4 \longrightarrow \text{H}_7\text{ReL}_2 \tag{30}$$

In eq 29 no ligands are lost from the metal in contrast to the observations on similar iridium complexes mentioned above, although minor amounts of redistribution product, H_5ReL_3, and polymeric lower hydride $[H_xReL_2]_n$, $x < 7$, were also reported.

For complexes of the types ReX_2L_2diphos and ReX_2(diphos)$_2$, prolonged treatment with complex hydrides is required for reduction, which does not proceed to completion.[40]

$$\text{ReI}_2(\text{diphos})_2 + \text{LiAlH}_4 \longrightarrow \text{H}_2\text{ReI}(\text{diphos})_2 \tag{31}$$

The corresponding trihydrides must be obtained by substitution of the appropriate ligands on the pentahydrides (see section III.J).

Hydride ion is *eliminated* in the subsitution of tertiary phosphines or arsines on the ReH_9^{2-} ion resulting in octahydrido complex anions, H_8ReL^-.[41]

Douglas and Shaw[42] have obtained the tetrahydrido derivatives H_4OsL_3 (L = tertiary phosphine or arsine, or mixed derivatives) in the reduction of *mer*-$OsCl_3L_3$ with either $NaBH_4$ or $LiAlH_4$. Similarly, the hexahydrido derivatives H_6OsL_2 have been obtained from *trans*-$OsCl_4L_2$.[42]

Tetrahydrido complexes of molybdenum have been prepared by the reduction of *cis*-$MoCl_4L_2$ ($L = PMePh_2$ and $PEtPh_2$) with ethanolic $NaBH_4$ and excess ligand.[43]

$$\textit{cis}\text{-MoCl}_4\text{L}_2 + \text{L} + \text{NaBH}_4 \xrightarrow{\text{EtOH}} \text{H}_4\text{MoL}_4 \tag{32}$$

There is the possibility that at least part of the reduction is occurring by hydrogen transfer from the solvent, similar to that observed in other reductions employing alcohol and base (see below). Alcoholic sodium borohydride has also been used to obtain hydrido complexes of cobalt ($L = PPh_3, P(C_6D_5)_3$, $PEtPh_2$, and PEt_2Ph)[13] and of iron ($L = PEtPh_2$, $PBuPh_2$).[44]

$$\text{CoCl}_2\cdot6\text{H}_2\text{O} + \text{L} + \text{NaBH}_4 \xrightarrow{\text{EtOH}} \text{H}_3\text{CoL}_3 \tag{33}$$

$$\text{FeCl}_2\cdot2\text{H}_2\text{O} + \text{L} + \text{NaBH}_4 \xrightarrow{\text{EtOH}} \text{H}_4\text{FeL}_3 \tag{34}$$

The product in eq 34 was originally reported as H_2FeL_3;[45] this can be obtained from H_4FeL_3 by heating.

Similar conditions have been used by Kruse and Atalla[46] in the synthesis of $HCoL_4$ and H_2FeL_4 ($L = P(OEt)_3$) from the metal chlorides.

Hydrido carbonyl anions are obtained in the reduction of metal carbonyls $M(CO)_6$ (M = Cr, Mo, and W) with the complex hydrides.[47, 48]

$$\text{NaBH}_4 + \text{M(CO)}_6 \xrightarrow[\text{diglyme}]{60\text{–}150^\circ} \text{Na}^+\text{HM}_2(\text{CO})_{10}^- \tag{35}$$

In a similar reduction of $Re_2(CO)_{10}$, the hydrido anions $HRe_3(CO)_{12}^{2-}$[49] and $H_6Re_4(CO)_{12}^{2-}$[50] have been isolated (among other nonhydrogen containing anions). The metalate solution obtained in the reduction of $Re_2(CO)_{10}$ with hydrides shows at least ten different high-field signals due to hydrogen bonded to transition metal, testifying to the complexity of the mixtures.[49] Acidification yields $H_3Re_3(CO)_{12}$[51] or $HRe_3(CO)_{14}$[52] optimized in various preparations of the metalate solution.

Reduction of $Ru_3(CO)_{12}$ with complex hydride was studied among other of its reactions;[53] this has yielded, after acidification, the polynuclear hydrides $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$. There is evidence, however, that other species are also contained in the products, and at least for the former, the more direct route, that of H_2 and $Ru_3(CO)_{12}$[10] discussed earlier in this section, affords it in greater yield and purity.

Various reaction pathways are available to the entering hydride ion as demonstrated by Treichel and Shubkin[54] in studies of the reduction of cationic carbonyls (M = Mo, W).

$$[\text{M}(\text{C}_5\text{H}_5)(\text{CO})_4]^+ + \text{NaBH}_4 \longrightarrow \text{HM}(\text{C}_5\text{H}_5)(\text{CO})_3 + \text{CO} \tag{36}$$

$$[\text{M}(\text{C}_5\text{H}_5)(\text{CO})_3(\text{PPh}_3)]^+ + \text{NaBH}_4 \longrightarrow \text{M}(\text{CH}_3)(\text{C}_5\text{H}_5)(\text{CO})_2(\text{PPh}_3) \tag{37}$$

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(38) M. Angoletta and G. Caglio, *Gazz. Chim. Ital.*, **99**, 46 (1969).

(39) The interconversions of these penta and hepta hydrides is described in ref 17.

(40) M. Freni, R. Demichelis, and D. Giusto, *J. Inorg. Nucl. Chem.*, **29**, 1433 (1967).

(41) A. P. Ginsberg, *Chem. Commun.*, 857 (1968).

(42) P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 334 (1970).

(43) F. Pennella, *J. Chem. Soc. D*, 158 (1971).

(44) M. Aresta, P. Giannoccaro, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **5**, 115 (1971).

(45) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968).

(46) W. Kruse and R. H. Atalla, *ibid.*, 921 (1968).

(47) R. G. Hayter, *J. Amer. Chem. Soc.*, **88**, 4376 (1966).

(48) U. Anders and W. A. G. Graham, *Chem. Commun.*, 499 (1965).

(49) B. Fontal, Dissertation, University of California at Los Angeles, 1969.

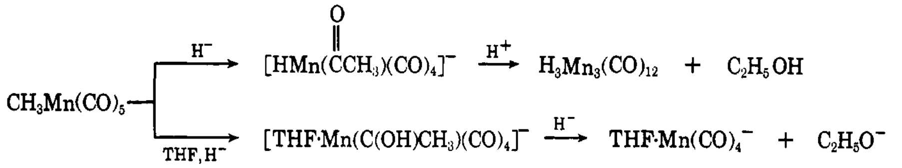
(50) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Amer. Chem. Soc.*, **91**, 1021 (1969).

(51) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *ibid.*, **86**, 4841 (1964).

(52) W. Fellman and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **2**, 63 (1966).

(53) (a) B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc. A*, 2856 (1968); (b) B. F. G. Johnson, J. Lewis, and I. G. Williams, *ibid.*, 901 (1970).

(54) P. M. Treichel and R. L. Shubkin, *Inorg. Chem.*, **6**, 1328 (1967).



$$CH_3Mn(CO)_5 \xrightarrow{H^-} [HMn(\overset{O}{\overset{\|}{C}}CH_3)(CO)_4]^- \xrightarrow{H^+} H_3Mn_3(CO)_{12} + C_2H_5OH \quad (38a)$$

$$CH_3Mn(CO)_5 \xrightarrow[THF,H^-]{} [THF{\cdot}Mn(C(OH)CH_3)(CO)_4]^- \xrightarrow{H^-} THF{\cdot}Mn(CO)_4^- + C_2H_5O^- \quad (38b)$$

We see in eq 36 a displacement of CO on the metal by H^-. In eq 37 there has been a reduction of metal carbonyl group to a methyl group originating no doubt from attack by H^- on C of the CO group. The reactivity of the carbon atom of coordinated carbon monoxide toward nucleophilic attack has been discussed by Caulton and Fenske;[55] through a Mulliken population analysis the carbon has been shown to be slightly positive in the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$. In yet other systems, H^- has been observed to become attached to the C_5H_5 ring giving rise to products with *tetrahapto*cyclopentadiene rings (see discussion in ref 4 and references cited therein).

The reduction of $CH_3Mn(CO)_5$ with $NaBH_4$ followed by acidification yields the trimer $H_3Mn_3(CO)_{12}$ in about 20% yield,[56] in contrast to the similar treatment of $Mn_2(CO)_{10}$ which produces $HMn_3(CO)_{10}B_2H_6$[57] as the major product, with only traces of the tetracarbonyl trimer. In the former reaction, ethanol is observed as a by-product in the acidification and Fischer and Aumann have proposed[56] two possible reaction paths (eq 38a,b) to account for this observation. In the first it is suggested that hydride may attack on the metal producing an intermediate hydridometal acyl anion from which acetaldehyde is eliminated (and further reduced). In the second the attack of hydride is postulated to occur on the acyl group of an intermediate solvated metal–acyl complex. A third possibility, the attack on carbon of CO in $CH_3Mn(CO)_5$ to give an intermediate anionic carbene complex, was considered less likely. These serve further to illustrate the multiplicity of pathways available in such reductions.

Trialkylborohydrides have found specific application in the synthesis of hydrido derivatives not isolable through other means, eq 39 (L–L = $(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2$, n = 2, 3, 4)[58] and eq 40 (L = PPh_3).[59]

$$2NiCl_2(L\text{–}L) + 4NaHBMe_3 \longrightarrow [HNi(L\text{–}L)]_2 + 4NaCl + 4BMe_3 + H_2 \quad (39)$$

$$Ni(C_3H_5)(Br)L + 2NaHBMe_3 \xrightarrow{-135°} HNi(C_3H_5)L + NaBr + BMe_3 \quad (40)$$

Finally, reduction with borohydride can lead to incorporation of this anion or groups derived therefrom into the final product as for instance in the formation of $HMn_3(CO)_{10}B_2H_6$ mentioned above and in the reduction of $(C_5H_5)_2MCl_2$ (M = Zr, Hf) with $LiBH_4$ which yields $(C_5H_5)_2M(BH_4)_2$; treatment of these with trialkylamines produce the hydrides as shown in eq 41.[60] On the other hand, the borohydride derivatives $Ti(BH_4)Cp_2$ and $Cu(BH_4)L$ do not yield hydride complexes in the treatment with NMe_3.[60]

$$\begin{tikzcd}(C_5H_5)M(BH_4)_2 + NMe_3 \arrow[r] & (C_5H_5)_2Zr(H)BH_4 + Me_3NBH_3 \arrow[d, "NMe_3"] \\ & H_2Zr(C_5H_5)_2\end{tikzcd} \quad (41)$$

C. HYDROGEN TRANSFER FROM SOLVENT OR METAL-COORDINATED GROUP

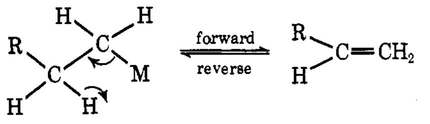
We examine a variety of methods in this section, greatly expanded since 1965, leading to the formation of transition metal hydrides. We have grouped these in the same section to emphasize similarities which we believe exist between them.

1. *Reactions with Alcohols, Hydrazine, and Metal Alkyls*

Some time ago, coordination chemists seeking complexes with transition metals in a low valent state discovered a variety of reducing agents such as hydroxylamine, or hydrazine, or alcohol in the presence of ligands and/or basic medium. The latter method (ROH + L + KOH) was developed principally by Malatesta and his coworkers and applied by several others, although it was Chatt, Duncanson, and Shaw in 1957 who first discovered that hydride derivatives of platinum, iridium, rhodium, osmium, and ruthenium are produced in the reduction of the corresponding halides by this route.

With isotopic techniques, Chatt and Shaw, and also Vaska, during the period 1960–1965 established that a primary alcohol is oxidized to an aldehyde (or a secondary alcohol to a ketone) with the transfer to the metal of the α-hydrogen of the coordinated alkoxide (β shift, eq 42 forward). It may be instructive to point out that the reverse of this reaction is the first step in the reduction by complex hydrides of aldehydes or ketones (eq 42 reverse) and that eq 42 must also be closely related to the shift of β-hydrogen in a metal alkyl which is followed by elimination of olefin (eq 43 forward; see discussion below). The latter of course is the microscopic reverse of the known addition of olefin to metal hydrides (eq 43, reverse).

(42)



(43)

A more extensive rearrangement is also observed to occur in the reductions, involving transfer to the metal of both *hydrogen* and *carbonyl group* of the alkoxide to form a hydridometal carbonyl and a hydrocarbon of one less carbon

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(55) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).

(56) E. O. Fischer and R. Aumann, *J. Organometal. Chem.*, **8**, P1 (1967).

(57) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2853 (1965).

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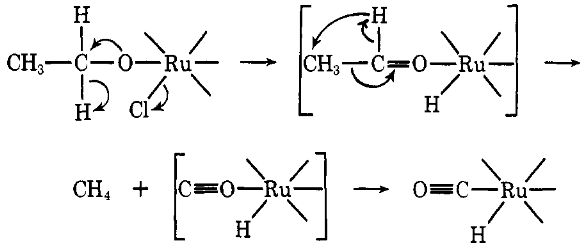
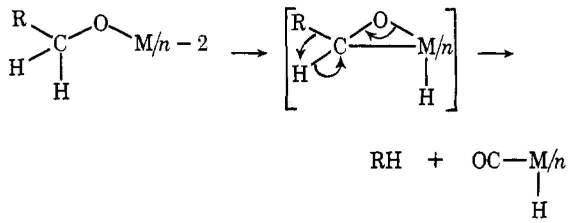
(59) H. Bönnemann, *ibid.*, **9**, 736 (1970).

(60) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *Inorg. Chem.*, **6**, 1979 (1967); *Chem. Commun.*, 849 (1966).

than the original alcohol. Chatt, Shaw, and Field[61] have proposed a possible pathway (eq 44a) for this interesting transformation although kinetic data at the present are lacking. To account for the difference in transfer of hydrogen and CO and elimination of hydrocarbon to that for transfer of hydrogen and elimination of aldehyde, we would like to elaborate somewhat on the proposed transformation by invoking for the *second type of* transfer, an *internal oxidative addition* (eq 44b). This type of rearrangement would occur when alkoxide is bound to a metal which is *coordinatively unsaturated* (M/*n* − 2); through intramolecular oxidative addition, transfer both of hydrogen and CO would be facilitated as the metal develops bonding *both to the α-carbon of the alkoxide as well as to shifting hydrogen.* This type of intramolecular oxidative-addition may also be extended to alkyl derivatives, in which an intermediate hydridometal–olefin complex would be obtained (see eq 107). The belief that lower coordination may play a key role in this transformation is reinforced in the observation that the formation of hydridometal carbonyls is observed for just those metals (Pt, Ir, Os, Rh, Ru) whose complexes have been shown to participate in oxidative addition including intramolecular oxidative addition through isolable lower coordinate species or otherwise (see below).



(44a)



(44b)

Thus we can identify two important routes in the reduction of metal complexes with alcohol and base. Both are very likely initiated by substitution of metal halide by alkoxide. In the first route, metal hydride is formed by elimination of aldehyde or ketone. This can lead to successive replacement of halogen by hydrogen even up to the formation of trihydrides, although, as mentioned above, the use of the saline and complex metal hydrides is usually more convenient for extensive reduction. A hydridometal carbonyl is most likely formed when the metal alkoxide complex becomes coordinatively unsaturated either through loss of L, or through reductive elimination either of HX in the basic medium, or X_2 through oxidation of L. This is summarized in Figure 1.

The effect of various phosphines on the ability of rhodium complexes to abstract hydrogen from alkoxide has been studied by Gregorio, Pregaglia, and Ugo.[62a] Transfer is facilitated through the more basic phosphines. In these reactions, phosphines employed as ligands may serve as reducing agents in the formation of R_3PX_2 or R_3PO. Indeed Sacco, Ugo, and Moles[62b] have reported the formation of rhodium hydrides by boiling rhodium trihalide with ligand in water in the absence of organic solvent (L = PPh_3 or $PEtPh_2$).

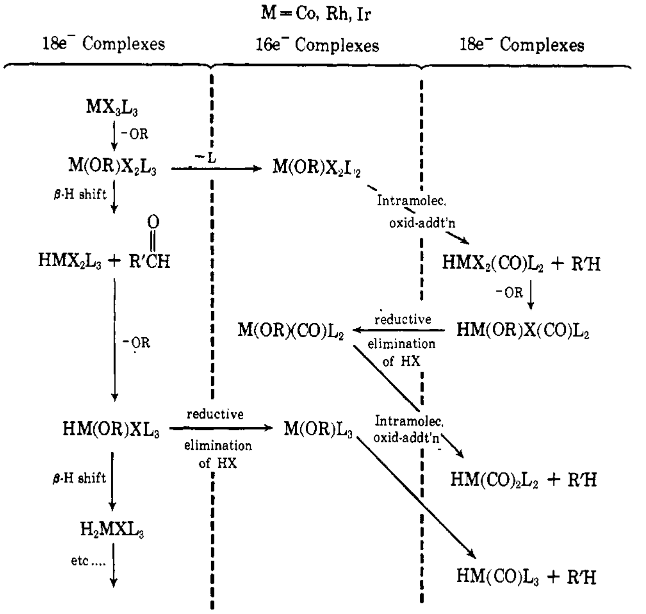


Figure 1. Illustration of probable successive and/or competing pathways in the reduction of metal halides by alkoxide.

$$RhX_3 \cdot 3H_2O + 4L \longrightarrow HRhX_2L_3 + R_3PO + HX + 2H_2O \quad (45)$$

The reaction of metal complexes with alcohol and base continues to find use in the synthesis of metal hydrides and hydridometal carbonyls. Reactions of this type may be found in several places in the tables as well as in discussions under the chemistry of individual metals in section III. To relate systems which undergo this type of β-transfer reaction to those which do not, Cross[63] has proposed an explanation based on the hard–soft acid–base theory. In this category is also included the decarboxylation of formate complexes produced either by direct substitution of the formate ion on the metal or through the hydrolysis of cationic metal carbonyls, as is discussed in some detail in section II.D.3.

The reduction of metal salts with the alkyl derivatives of lithium, magnesium, or aluminum must be regarded in close relation to the action of alcohol and base. As shown in eq 43, metal hydride is formed from metal alkyl through elimination of olefin. Thus while a stable alkyl or aryl derivative is formed in the treatment of $RhClL_3$ (L = PPh_3) with either the methyl or phenyl Grignard reagent,[34] reduction of the rhodium complex with aluminum triisopropyl yields a hydrido derivative and olefin.

$$RhClL_3 + Al(Pr^i)_3 \xrightarrow{\text{hexane}} HRhL_3 + CH_3CH{=}CH_2 \quad (46)$$

Chatt, *et al.*,[64] similarly obtained *n*-alkyl derivatives $Pt(R)XL_2$ (L = PEt_3; X = Cl) in the treatment of PtX_2L_2 with

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(61) J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1964).

(62) (a) G. Gregorio, G. Pregaglia, and R. Ugo, *Inorg. Chim. Acta*, 3, 89 (1969); (b) A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc. A*, 1670 (1966).

(63) R. J. Cross, *Inorg. Chim. Acta, Rev.*, 75 (1969).

(64) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. A*, 190 (1968).

ethyl- or *n*-propyl Grignard reagent but obtained instead the hydrido derivative $HPtXL_2$ from isopropylmagnesium chloride.

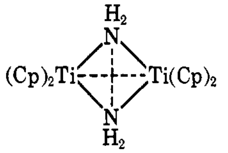
Similarly, metal hydrides have been obtained by reduction of metal complexes with dialkylaluminum alkoxides[12] (L = Ph_3, eq 47) or with hydridoalkyls of aluminum in the presence either of Ar or H_2[65] (eq 48, L = $(p\text{-}RC_6H_4)_3P$; R = H, CH_3, F, Cl).

$$\mathrm{Co(acac)_3 + Et_2AlOEt + L + N_2 \longrightarrow HCo(N_2)L_3} \tag{47}$$

$$\mathrm{Co(acac)_{\mathit{n}} + \mathit{n}Bu_2AlH + Ar\ (or\ H_2) \longrightarrow H_3CoL_3} \tag{48}$$

Brintzinger[66] has employed the Grignard reagent to bring about reduction of bis(cyclopentadienyl)titanium dichloride. Whereas the mono- and dimethyl complexes of bis(π-cyclopentadienyl)titanium(III) are stable, the ethyl and isopropyl derivatives eliminate olefin leading to mono- and dihydridometal derivatives. The hydridometal intermediates are capable of reducing nitrogen.[67,68]

$$\mathrm{(Cp)_2TiCl_2 \ + \ EtMgX(excess) \longrightarrow [(Cp)_2TiH]_2 \xrightarrow{N_2/H_2}}$$


(49)

The reduction of N_2 may be considered the reverse of the reaction in which metal hydrides are produced by atom transfer from hydrazine (reported by Chatt and Shaw in 1957 in their first synthesis of $HPtClL_2$, L = PPh_3).

$$\mathrm{PtCl_2L_2 + N_2H_4 \cdot H_2O \longrightarrow \mathit{trans}\text{-}HPtClL_2 + N_2} \tag{50}$$

A bis-μ-amino complex $[Pt(NH_2)L_2]_2^+\ Cl^-$ mixed with a bis-μ-dehydrodiimide species $[Pt(N_2H)L_2]_2^+\ Cl^-$ was isolated in the hydrazine reduction when carried out by Dobinson, *et al.*[69] These intermediates decompose to the product shown in eq 50.

Chatt, Leigh, and Paske[70] have used hydrazine hydrate in boiling alcohol to reduce halide complexes of osmium, and incidentally, have obtained a paramagnetic hydride (L = PBu^{n}_2Ph).

$$\mathrm{OsCl_3L_3 + N_2H_4 \cdot H_2O + EtOH \longrightarrow HOsCl_2L_3} \tag{51}$$

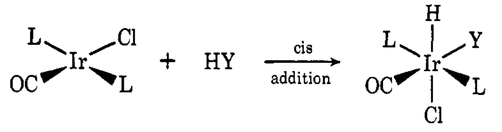
It is not established whether the metal hydrogen is derived from the alcohol or from the hydrazine which alternately could function as the base in the system. Other workers have included hydrazine in reduction mixtures such as eq 52[71] (L = PMe_2Ph) although in the presence of molecular H_2 and alcohol the function of the hydrazine may well be restricted to that of a base.

$$\mathrm{Ru_2Cl_3L_6^+ + N_2H_4 + EtOH + H_2 \longrightarrow H_2RuL_4} \tag{52}$$

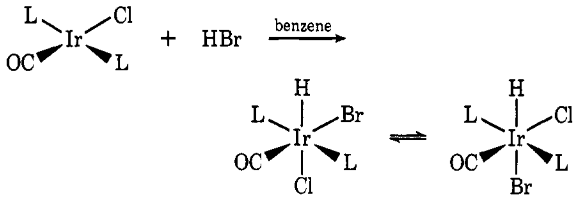
2. Oxidative Addition of Hydrogen Compounds

The oxidative-addition reaction covering a wide variety of substances has been recently reviewed by Halpern[25] and Collman and Roper.[72] The most extensive studies of this type of reaction have been carried out for square-planar iridium complexes, and it is with these that we begin our discussion. The oxidative addition of H_2 and the reduction of metal complexes by H_2 has been discussed in section II.A.2. These reactions were early extended to the compounds of hydrogen, namely, the oxidative addition of hydrogen halides, H_2S, HCN, and silicon hydrides including the reduction of metal halides by the latter (discussed later). An important question concerning these adducts is the stereochemistry of the products.

In an effort to maintain kinetic control of product, Vaska in 1966[73] carried out the oxidative addition of the gaseous substances HF, HCl, HBr, HI, and H_2S with crystals of *trans*-$IrX(CO)L_2$ (eq 53, X = Cl, L = PPh_3). The stereochemistry of the adducts, as deduced from spectroscopic evidence (see discussion in section IV) showed cis addition as found in earlier work under the presence of solvent. Similarly, Chatt, Johnson, and Shaw[74] observed cis addition products in ethanolic medium for reactions of the type shown in eq 53 (L = PEt_2Ph; X = Cl, Br; HY = HCl, HBr).


(53)

In benzene solution, however, Collman and Sears[75] obtained a mixture of cis and trans adducts (eq 54, L = $PMePh_2$) which seemed to be in equilibrium.


(54)

It was therefore not possible to determine under these conditions which isomer was favored by kinetic control. Blake and Kubota[76] have found that under strictly anhydrous conditions, only cis product is obtained in the oxidative addition of HCl to $IrCl(CO)L_2$ in $CHCl_3$ solution. However, in the presence of *moisture* in these systems, *they find an equilibrium mixture of cis and trans adducts*, as they did in ionizing solvents such as CH_2Cl_2, dimethylformamide, benzene–acetonitrile, and benzene–methanol.

Oxidative additions in general can display either cis or trans stereochemistry, depending on the addend (see Halpern[25]), and presumably, if thermodynamic equilibrium can be achieved, depend also on thermodynamic control of the

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[65] J. Lorberth, H. Nöth, and P. V. Rinze, *J. Organometal. Chem.*, **16**, 1 (1969).

[66] H. Brintzinger, *J. Amer. Chem. Soc.*, **89**, 6871 (1967).

[67] H. Brintzinger, *ibid.*, **88**, 4307 (1966).

[68] H. Brintzinger, *ibid.*, **88**, 4305 (1966).

[69] G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini, and F. Bonati, *Chem. Commun.*, 739 (1967).

[70] J. Chatt, G. J. Leigh, and J. Paske, *ibid.*, 671 (1967).

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

[72] J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

[73] L. Vaska, *J. Amer. Chem. Soc.*, **88**, 5325 (1966).

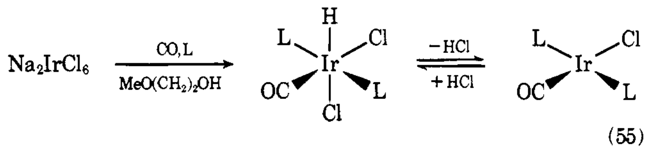
[74] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc. A*, 604 (1967).

[75] J. P. Collman and C. T. Sears, Jr., *Inorg. Chem.*, **7**, 27 (1968).

[76] D. M. Blake and M. Kubota, *ibid.*, **9**, 989 (1970).

system. Pearson and Muir[77] have pointed out that both cis and trans kinetic pathways are permitted by symmetry rules.

Oxidative additions of HCl to cationic complexes, giving the equivalent of protonation of neutral hydrido complexes, are discussed in section II.E. Under suitable conditions, the oxidative addition can be reversed; *i.e.*, adducts can be dehydrohalogenated (reductive elimination of HX). Deeming and Shaw[78] have demonstrated that the adduct with stereochemistry *trans*-L_2, *cis*-X_2 (see eq 55) is rapidly dehydrohalogenated by base (methanolic sodium methoxide, KOH, or triethylamine) while its isomer *trans*-L_2, *trans*-X_2 (eq 56) can be recovered unchanged after exposure to base for a short time in refluxing alcohol.



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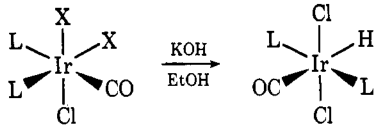
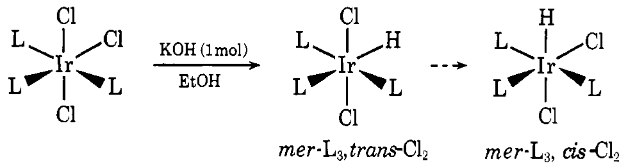


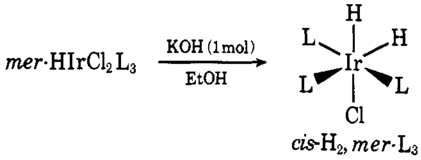
(stable to base) (56)

Harrod, Gilson, and Charles[79] report similar dehydrochlorination of $H_2IrCl(CO)L_2$ (L = PPh_3); however, they obtained about 50% $HIr(CO)L_3$ and an uncharacterized mixture of carbonyl-phosphine iridium complexes. Dehydrochlorination by KOH–ethanol in the presence of excess PPh_3 led to exclusive formation of $HIr(CO)L_3$. Since the isomer *trans*-L_2, *cis*-X_2 is the one which is obtained by cis addition of HCl to *trans*-$IrCl(CO)L_2$ (see eq 53 above), it is tempting to believe, according to the principle of microscopic reversibility, that it would be the isomer most easily dehydrohalogenated. This could provide some insight into why it is that certain hydridometal complexes, and not necessarily their more thermodynamically stable isomers, are obtained in the alcoholic base reduction of metal complexes. Thus, Chatt, Johnson, and Shaw[80] report that complex of the configuration *mer*-L_3, *trans*-Cl_2 is obtained in the treatment of *mer*-$IrCl_3L_3$ with alcoholic base (eq 57) rather than the complex *mer*-L_3, *cis*-Cl_2, which is thermodynamically more stable and is slowly formed in the isomerization of the former on standing.

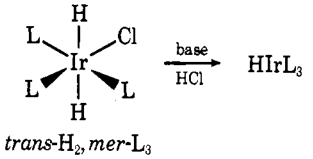


(57)

Similarly, treatment of *mer*-$HIrCl_2L_3$ with KOH (1 mol) in EtOH provides the dihydride *cis*-H_2IrCl-*mer*-L_3 (eq 58)[37] and not the dihydride *trans*-H_2IrCl-*mer*-L_3 (eq 59). The latter possesses the stereochemistry expected from cis addition



(stable to base) (58)



(59)

of HCl to $HIrL_3$ and would probably be dehydrohalogenated in the basic medium. The product described in eq 58, *cis*-H_2, *mer*-L_3, is related to $IrClL_3$ through cis-reductive elimination of H_2. Thus the two isomers can most likely be obtained independently using these chemical relations, namely, *cis*-H_2IrCl-*mer*-L_3 by cis addition of H_2 to $IrClL_3$ and *trans*-H_2IrCl-*mer*-L_3 by cis addition of HCl to $HIrL_3$.

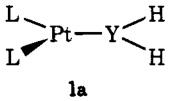
Adducts of HCl to complexes of rhodium are much less stable than the corresponding iridium derivatives. Mague and Wilkinson (for L = $AsPh_3$ and $SbPh_3$)[22] and Baird, *et al.* (for L = PPh_3),[81] have studied the addition of HCl among other species to $RhClL_3$. Five-coordinated complexes of formula $HRhCl_2L_2$ have been isolated which tend to lose HCl on standing. The sixth coordination position is most likely occupied by solvent, and the substances crystallize as the solvates, $HRhCl_2L_2\cdot {}^1/_2CH_2Cl_2$. It is postulated[21] that these substances participate in insertion reactions through initial coordination of olefin by the displacement of solvent in the coordination sphere.

Cariati, Ugo, and Bonati[82] have studied the addition of small molecules, in particular HCl and HCN and a variety of other acids to zerovalent complexes of platinum (L = PPh_3, ${}^1/_2$diphos). The complexes of the mineral acids H_2SO_4, HNO_3, and $HClO_4$ are all of the ionic form $[HPtL_3]^+A^-$.

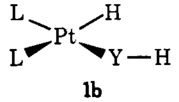
$$PtL_4 \underset{+L}{\overset{-L}{\rightleftarrows}} [PtL_3] \underset{KOH}{\overset{HCl}{\rightleftarrows}} [HPtL_3]^+Cl^- \underset{+L}{\overset{-L}{\rightleftarrows}} HPtClL_2 \underset{-HCl}{\overset{+HCl}{\rightleftarrows}} H_2PtCl_2L_2 \quad (60)$$

Formation of the zerovalent compounds in the alcoholic base reduction of $PtCl_2L_2$ in the presence of excess L may be understood as the reverse of the HCl addition reactions shown above.[83]

The coordination of H_2S, H_2Se, and H_2Te with bistriphenylphosphineplatinum(0) was studied by Morelli, *et al.*[84] Two types of adducts were isolated, which were isomers of each other: one, **1a**, in which the small molecule as a whole served as ligand, and the other, **1b**, in which hydrogen and the remaining fragment of the small molecule have oxidatively added to the lower coordinate platinum (L = PPh_3). These are mentioned again in section III.M.



1a



1b

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[77] R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5518 (1970); *cf.* also, R. G. Pearson, *Accounts Chem. Res.*, **4**, 152 (1971).

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

[79] J. F. Harrod, D. F. R. Gilson, and R. Charles, *Can. J. Chem.*, **47**, 1431 (1969).

[80] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1625 (1964).

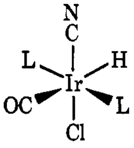
[81] M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1347 (1967); *Chem. Commun.*, 129 (1966).

[82] F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

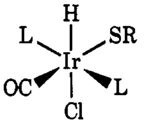
[83] R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

[84] D. Morelli, A. Segre, R. Ugo, G. La Monica, S. Cenini, F. Conti, and F. Bonati, *Chem. Commun.*, 524 (1967).

Cis addition of a number of acids, HCl, HCN, HSR, and $HClO_4$, to complexes of rhodium and iridium have been reported by Singer and Wilkinson,[85] L = PPh_3; in **2b**, R = H, C_6H_4Me, $C_6H_3(SH)Me$. No hydride species was isolated

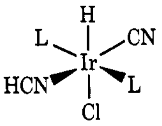


2a

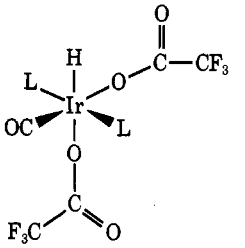


2b

with HNO_3; instead the compound $IrCl(NO_3)_2(CO)L_2$ was obtained. A second mole of HCN was found coordinated as ligand in the rhodium complex **3a** which was easily displaced by CO, while for the adduct of trifluoroacetic acid the halide was displaced by a second trifluoroacetate anion **3b**.[85]



3a



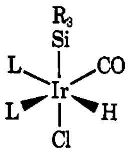
3b

3. *Reduction by and Oxidative Addition of Group IV Hydrides*

Chalk and Harrod in 1965[86] demonstrated that platinum(II)- and rhodium(I)-olefin complexes catalyzed the hydrosilation of olefins. Although they found no derivatives containing a Pt-Si or Rh-Si bond, reduction of the platinum halide by silane was observed (eq 61, L = PPh_3 and PBu^n_3). For complexes of iridium, adducts of a variety of organosilanes were obtained (eq 62, L = PPh_3, R_3Si = Cl_3Si, $EtCl_2Si$).

$$PtCl_2L_2 + R_3SiH \longrightarrow HPtClL_2 + R_3SiCl \qquad (61)$$

$$cis\text{-}IrCl(CO)L_2 + R_3SiH \xrightleftharpoons[150°]{} \qquad (62)$$



By analogy to other reactions of platinum, and in view of the behavior of the iridium complexes, Chalk and Harrod[86] postulated for eq 61 an initial oxidative addition of silane followed by reductive elimination of a chlorosilane. Different reactivities were observed for the silanes in these two reactions; those with electronegative substituents which participated in the oxidative addition to Ir(I) were not found to reduce platinum halides while the trialkyl- or triarylsilanes which were found to reduce the platinum complexes did not give isolable adducts of iridium. A further reaction of iridium(I) halide complexes involving 2 mol of silane and leading to derivatives of the type $H_2Ir(SiR_3)(CO)L_2$ was discovered later and is discussed below.

Brooks and Glockling[87a] obtained a reduction analogous to the one shown in eq 61, between trialkylgermane and chloropalladium derivatives (R = Me, Ph; L = PEt_3).

$$R_3GeH + PdCl_2L_2 \longrightarrow HPdClL_2 + R_3GeCl \qquad (63)$$

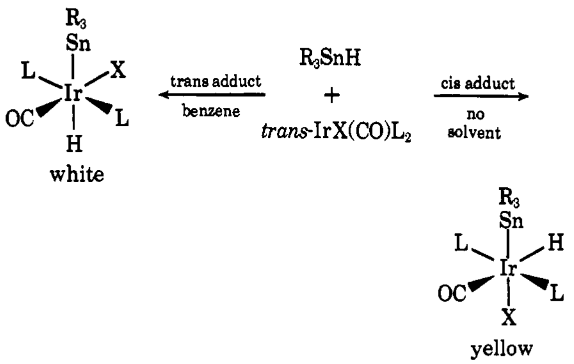
This method is ideally suited to the synthesis of hydridopalladium derivatives which are normally not stable either in strongly basic or strongly acidic media which characterize other routes to metal hydrides. The presence of Me_6Ge_2, H_2, and Pd as side products in eq 63, among other things, indicated to Brooks and Glockling a radical pathway. This reaction also proved to be quite specific. The treatment with trimethylgermane of the complexes $PdCl_2L_2$ (L = PPr^n_3, PPh_3) and $[PdCl_2PEt_3]_2$ gave no isolable palladium hydride species although addition of some palladium black to the reaction with L = PPr^n_3 produced some of the desired hydrido complex. The complex $NiBr_2(PEt_3)_2$ reacted with trimethylgermane, but no isolable Ni-H containing species were obtained. Similar reductions were attempted with trialkylstannanes but only decomposition was observed.

The reactions between silicon hydride derivatives and complexes of rhodium were investigated by two groups. These adducts are in general less stable than the corresponding ones of iridium, and isolable complexes were obtained only for silanes bearing electronegative groups: L = PPh_3, $AsPh_3$, $SbPh_3$; X = Cl, Br, I; R_3Si = Cl_3Si, Cl_2MeSi, Cl_2EtSi, $ClEt_2Si$, $(EtO)_3Si$ (see ref 278); and L = PPh_3; X = Cl; R_3Si = Cl_3Si.[87b] The first group of workers report five-

$$RhXL_3 + R_3SiH \longrightarrow HRh(SiR_3)XL_2 \cdot S \qquad (64)$$

coordinate complexes while the second group found solvates of the type isolated for other Rh(III) derivatives, S = $^1/_2$-CH_2Cl_2, $^1/_3SiHCl_3$ (a second mole of reagent), and $^1/_3C_6H_{13}$-$SiCl_3$ (after hydrosilation of hex-1-ene).

Lappert and Travers[88] have reported hydrostannation of *trans*-$IrX(CO)L_2$ (X = Cl, Br, I; L = PPh_3, $PMePh_2$, PEt_2Ph) by R_3SnH (R = Me, Et, Ph) to give white trans adducts in the presence of benzene and yellow cis adducts in absence of solvent (eq 65). Further dependence of solvent was reported in the reaction of Ph_3SnH which does not hydrostannate the iridium complex in the presence of tetrahydrofuran but does give adducts in solutions of benzene and diethyl ether and also in the absence of any solvent except excess Ph_3SnH. Although attempted, no hydrostannation of rhodium complexes was achieved.



(65)

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[85] H. Singer and G. Wilkinson, *J. Chem. Soc. A*, 2516 (1968).

[86] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965).

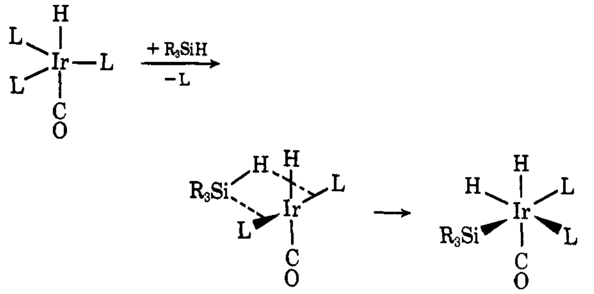
[87] (a) E. H. Brooks and F. Glockling, *J. Chem. Soc. A*, 1030 (1967); *Chem. Commun.*, 510 (1965); (b) F. de Charentenay, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 787 (1968).

[88] M. F. Lappert and N. F. Travers, *ibid.*, 3303 (1970); *Chem. Commun.*, 1569 (1968).

In 1969, Harrod, Gilson, and Charles[89] reported the addition of silicon hydrides to hydridocarbonyl derivatives of iridium (L = PPh_3; R_3Si = Cl_3Si, $MeCl_2Si$, $(EtO)_3Si$, Ph_3Si, Me_2PhSi, Me_3Si).

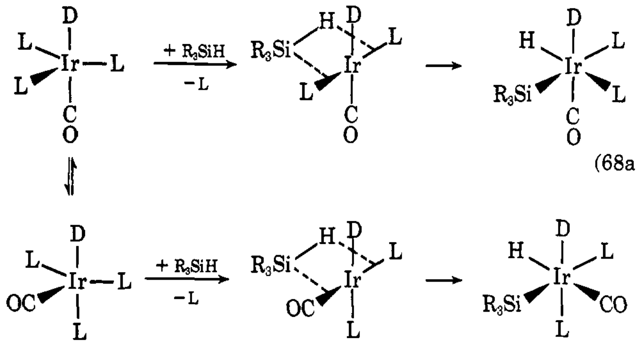
$$HIr(CO)L_3 + R_3SiH \longrightarrow H_2Ir(SiR_3)(CO)L_2 + L \qquad (66)$$

Adducts of the hydridorhodium complexes were obtained with trialkyl- and triarylsilanes, which were not stable for the chloroiridium complexes, attributed to the greater electron-releasing properties of hydrogen in stabilizing the oxidative addition compound. The adducts were also stable toward loss of hydrogen. The stereochemistry, deduced from spectroscopic data, indicated cis addition of R_3SiH to an intermediate square-planar complex formed by the loss of a ligand (eq 67). Starting with a deuterioiridium derivative,



(67)

hydrogen was found evenly distributed in the two positions (trans to L and trans to CO) which these authors regarded as a serious objection to their proposed mechanistic scheme, but which we feel can be accommodated assuming geometrical isomerization either in the starting five-coordinate complex or in the square-planar intermediate undergoing cis addition (or, as they are likely related, both (eq 68a,b)).

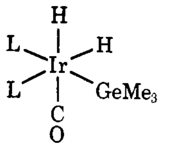


(68a)

(68b)

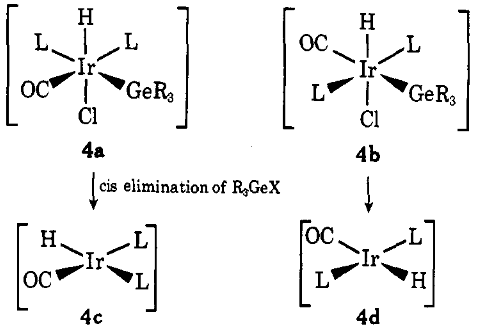
The same type of dihydridoiridium(III) adducts were obtained by Glockling and Wilbey[35] in the reduction of *trans*-$IrCl(CO)L_2$ with 2 mol of trialkylgermanes (L = PPh_3).

$2Me_3GeH$ + *trans*-$IrCl(CO)L_2$ $\longrightarrow$



$+ \; Me_3GeCl$ (69)

The stereochemistry of the product was determined by spectroscopic studies and a single crystal structure determination of one of the derivatives ($H_2Ir(GeMe_3)(CO)(PPh_3)_2$). Starting with only 1 mol of germane in eq 69, the same product is obtained while half of the haloiridium(I) complex is recovered unchanged. Believing the first step in this reaction to be oxidative addition of the germyl hydride to the chloroiridium(I) complex, the authors carried out the reaction in the presence of triethylamine and found no effect. They took this to indicate that in the intermediate adduct, H and Cl were in mutually trans positions **4a** or **b**, which would permit cis elimination of a germyl chloride and avoid a dehydrohalogenation reaction. Neither **4a** nor **4b** has the stereochemistry of the adducts reported by Lappert and Travers[88] in the hydrostannation of the same chloroiridium(I) complexes (eq 65). These would, however, lead to the square-planar hydrido complexes **4c** or **4d** through cis elimination of R_3GeX. Either of these could lead to observed product through cis addition of 1 mol of germyl hydride, similar to what is illustrated for the hydrosilation of hydridoiridium complexes (eq 67). In view of the many possibilities (see also comments by Lappert and Travers[88]), additional work will be needed to determine the true reaction path.



Glockling and Wilbey[35] observed two different types of reaction with chloroiridium(I) complexes and triphenyl- or triethylgermane. Addition of only 1 mol was observed for the former, accompanied by loss of ligand to give a five-coordinate intermediate not subject to further reduction; this product cyrstallized with 1 mol of solvent. The reduction with triethylgermane (eq 71) is reminiscent of eq 63 in which the appearance of the hexaalkyldigermane (among other things) was taken to indicate a radical mechanism.

$$Ph_3GeH + IrCl(CO)(PPh_3)_2 \longrightarrow HIrCl(GePh_3)(CO)PPh_3 + PPh_3 \qquad (70)$$

$$2Et_3GeH + IrCl(CO)(PPh_3)_2 \longrightarrow H_2IrCl(CO)(PPh_3)_2 + Et_6Ge_2 \qquad (71)$$

Following these developments, Chalk reexamined[90] the reaction between halogenoiridium(I) complexes and silanes and found, with longer reaction time and an excess of the latter, a dihydrido derivative.

$$HIrX(SiR_3)(CO)L_2 + HSiR_3 \longrightarrow H_2Ir(SiR_3)(CO)L_2 + R_3SiX \qquad (72)$$

With $HSi(OEt)_3$, formation of the hydridochloride of iridium(III) was followed by nmr and the position of H is assigned as trans to the $Si(OEt)_3$ group (*i.e.*, trans adduct) similar to observations in the hydrostannation of chloroiridium(I) complexes (eq 65). Further addition of silane led to dihydrido product as shown in eq 72. This product can also be obtained by hydrosilation of five-coordinate monohydrido-

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[89] J. F. Harrod, D. F. R. Gilson, and R. Charles, *Can. J. Chem.*, 47, 2205 (1969).

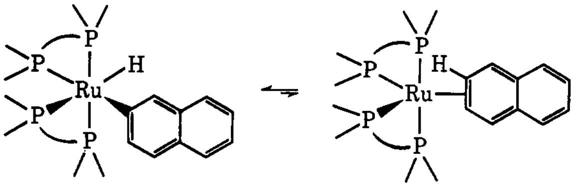
[90] A. J. Chalk, *J. Chem. Soc. D*, 1207 (1969).

iridium(I) species (eq 66), but, since that reaction is reversible, the present route is favored because the presence of free ligand can be avoided.

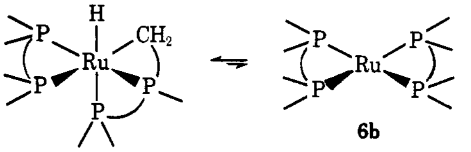
The trichlorosilane derivatives *cis*-$HFe(SiCl_3)(CO)_4$, $HCr(SiCl_3)(C_6H_6)(CO)_2$, $HMn(SiCl_3)Cp(CO)_2$, $HFe(SiCl_3)_2Cp(CO)$, and $HCo(SiCl_3)Cp(CO)$ have been formed by irradiation of $HSiCl_3$ and the corresponding carbonyl derivative.[91] It is suggested that the silane adds to the coordinatively unsaturated metal intermediates formed in the loss of one CO during irradiation. Similar additions with trichlorosilane and various ring-substituted triarylsilanes have been carried out on PtL_4 (L = PPh_3) to give a series of derivatives $HPt(SiR_3)L_2$ with the release of 2 mol of L.[92]

4. Intramolecular Oxidative Addition of C–H Bonds

In 1965, Chatt and Davidson reported[93] a series of complexes of ruthenium containing an aromatic hydrocarbon and chelating diphosphines whose spectroscopic properties indicated a hydridometal aryl derivative **5a** but whose reactions such as pyrolysis or treatment with ligand led to displacement of the arene, as from an olefin-π complex, **5b**. The authors proposed a tautomeric mixture with equilibrium favoring the hydridometal form. The bischelating complexes **6a,b** resulting from the loss of arene in the pyrolysis of **5a** could similarly be postulated as a tautomeric species involving a hydrido derivative of Ru(II), **6a**, and a lower coordinate species of Ru(0), **6b**, with equilibrium favoring the former.

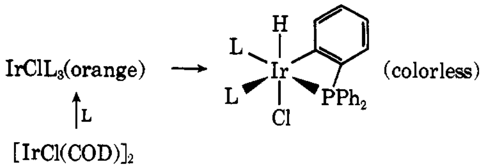


5a **5b** (73)



6a **6b** (74)

Subsequently, Bennett and Milner[27] isolated a series of orange and orange-red lower coordinate species $IrClL_3$ (L = PPh_3, $P(C_6D_5)_3$, $P(o\text{-}DC_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}CH_3C_6H_4)_3$, $P(p\text{-}CH_3OC_6H_4)_3$, $AsPh_3$, and $SbPh_3$) which were observed slowly to isomerize on standing (and more rapidly on heating in solvents) to colorless internal oxidative addition products of Ir(III) (eq 75). The same type of intramolecular oxidative addition was reported by Hata, Kondo, and Miyake[94] for olefin-bis(diphos)iron complexes (eq 76).



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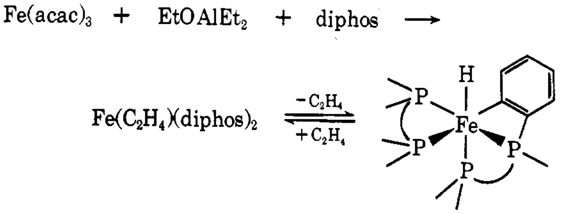
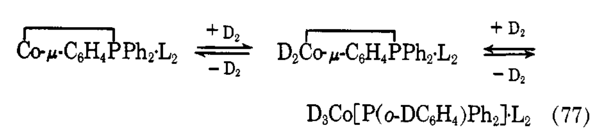


(76)

The participation of intramolecular insertion in coordinatively unsaturated intermediates was postulated by Parshall[95] in the deuteration of the ortho position of aryl groups on ligands in $HCo(N_2)L_3$ (L = PPh_3) and by Knoth and Schunn[96] in the similar reaction for $H_2Ru(N_2)L_2$ (L = PPh_3, $P(OPh)_3$) (see also Parshall, Knoth, and Schunn[97]).



$$HCo(N_2)L_3 \underset{+N_2}{\overset{-N_2}{\rightleftharpoons}} H_2\overline{Co\text{-}\mu\text{-}C_6H_4P}Ph_2\cdot L_2 \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}}$$

$$\overline{Co\text{-}\mu\text{-}C_6H_4P}Ph_2\cdot L_2 \underset{-D_2}{\overset{+D_2}{\rightleftharpoons}} D_2\overline{Co\text{-}\mu\text{-}C_6H_4P}Ph_2\cdot L_2 \underset{-D_2}{\overset{+D_2}{\rightleftharpoons}}$$

$$D_3Co[P(o\text{-}DC_6H_4)Ph_2]\cdot L_2 \quad (77)$$

Keim[34] has reported that $\overline{Rh\text{-}\mu\text{-}C_6H_4P}Ph_2(PPh_3)_2$ is formed by evolution of CH_4 from derivatives of the type $Rh(R)L_3$ (R = Me, Ph; L = PPh_3); the hydrogen attached to the ortho carbon of the phenyl of ligand is eliminated together with the methyl (or phenyl) group presumably either after or simultaneously with transfer of hydrogen to metal in an intramolecular substitution.

Intramolecular aromatic substitution has also been observed by Ainscough and Robinson[98] for a number of triphenyl phosphite complexes involving hydrido or hydridochloro complexes of rhodium and iridium; these reactions were accompanied either by elimination of H_2 or of HCl.

Intramolecular substitution is most likely also the source of anomalous hydrogen or metal hydrides reported by a number of workers for substituted manganese carbonyl derivatives; see section III.J.

X-Ray structures of $RuCl_2(PPh_3)_3$ (La Placa and Ibers[99]), $PdI_2(PMe_2Ph)_2$ (Bailey and Mason[100]), $HRuCl(PPh_3)_3$ (Skapski and Troughton[101]), and $HRhCl(SiCl_3)(PPh_3)_2$ (Muir and Ibers[102a]) reveal a short (less than 3.00 Å) separation between metal and ortho hydrogen in a phenyl ring of ligand; this provides further understanding of the facile internal substitution observed for these and related derivatives.

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(91) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 3375 (1969); *Inorg. Chem.*, **10**, 1159 (1971).

(92) J. Chatt, C. Eaborn, and P. N. Kapoor, *J. Chem. Soc. A*, 881 (1970); *J. Organometal. Chem.*, **13**, P21 (1968).

(93) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

(94) G. Hata, H. Kondo, and A. Miyake, *J. Amer. Chem. Soc.*, **90**, 2278 (1968).

(95) G. W. Parshall, *ibid.*, **90**, 1669 (1968).

(96) W. H. Knoth and R. A. Schunn, *ibid.*, **91**, 2400 (1969).

(97) G. W. Parshall, W. H. Knoth, and R. A. Schunn, *ibid.*, **91**, 4990 (1969).

(98) E. W. Ainscough and S. D. Robinson, *J. Chem. Soc. D*, 863 (1970).

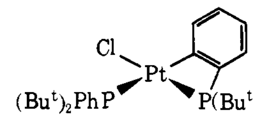
(99) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

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

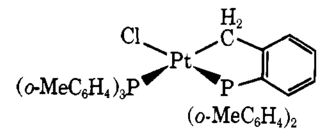
(101) A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 1230 (1968).

(102) (a) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **9**, 440 (1970); (b) L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *ibid.*, **9**, 447 (1970).

Cheney, *et al.*,[103] report that bulky substituents on the ligand (L = P(Bu^t)$_2$Ph, P(Bu^t)$_2$Pr^n, and P(*o*-MeC$_6$H$_4$)$_3$) promote intramolecular substitution, **7a–c**, which is accompanied by elimination of HCl in complexes PtCl$_2$L$_2$; no such elimination is observed when L = PMePh$_2$.



7a



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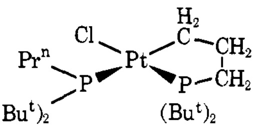
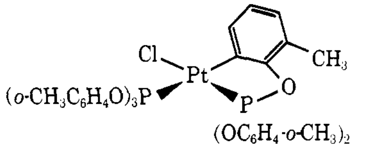


7c

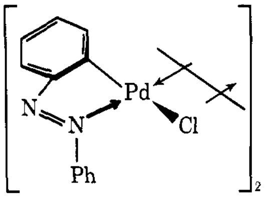
Ainscough and Robinson[104] find that for complexes of *o*-tolyl phosphite, hydrogen on the aromatic ring is involved in substitution, giving the five-membered ring complex **8** rather than the *o*-methyl group which would have given a six-membered ring.



8

Parshall has reviewed[105] the intramolecular substitution reaction summarizing the various reports in which hydrogen bound to metal is either retained in the product or is eliminated either as H$_2$, hydrocarbon, or HCl as discussed above. The relation of this reaction to intramolecular substitution products derived from azobenzene, eq 78 (and related benzylamine derivatives), as well as to the metal-catalyzed H–D exchange in aromatic hydrocarbons (see Hodges and Garnett[106] and references cited therein) has also been developed.[105] In the latter, equilibria on active metal sites such as that written in eq 73 are most likely involved.

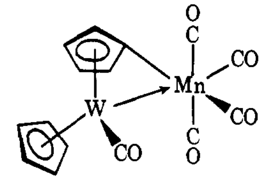
$K_2PdCl_4 + PhN{=}NPh \longrightarrow$



$+\ HCl$ (78)

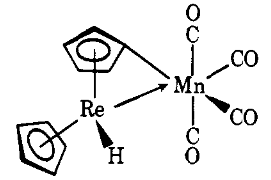
A novel intramolecular substitution product involving a cyclopentadienyl ring has been reported by Hoxmeier, Deubzer, and Kaesz[107] whose formation is accompanied by the loss of H$_2$ and CH$_4$ (eq 79) or of CO and CH$_4$ (eq 80). It is very likely that a similar intramolecular ring substitution may be present in Ti(C$_5$H$_5$)$_2$ in which a dimeric formula involving (C$_5$H$_4$) rings and Ti–H bonds has been indicated by spectroscopic data,[108] discussed further in section III.G.

$H_2W(C_5H_5)_2 + CH_3Mn(CO)_5 \xrightarrow{-CH_4,\ -H_2}$



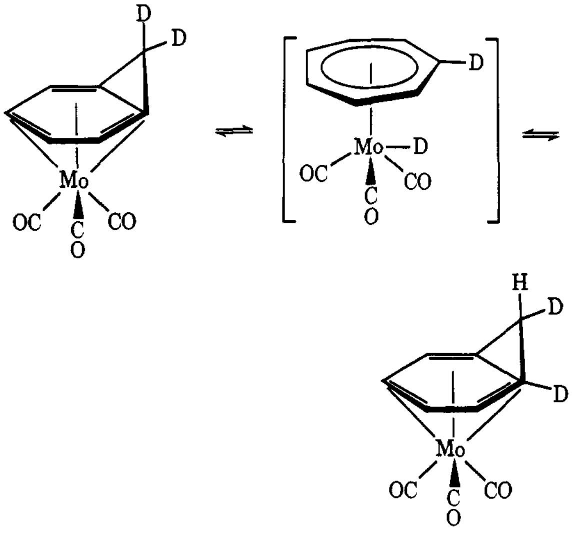
(79)

$HRe(C_5H_5)_2 + CH_3Mn(CO)_5 \xrightarrow{-CO,\ -CH_4}$



(80)

A number of olefin isomerization reactions are catalyzed by transition metals, and, especially where these involve hydride shift, the participation of metal has often been postulated (see reviews by Davies,[109] Rooney,[110] and Cramer[111]). Roth and Grimme[112] observed a statistical distribution of deuterium in the thermal rearrangement of cycloheptatriene-7-*d*$_1$-molybdenum tricarbonyl, which is in marked contrast to the 1,5 hydrogen shift products observed in the rearrangement of the deuterated hydrocarbon alone. They have postulated participation of metal hydride in this rearrangement (eq 81). This transfer is similar to those postulated between metal and cyclopentadiene discussed by Green and Jones.[2]



(81)

D. HYDROLYSES AND DEHYDROHALOGENATION

The protonation of metal complex anions in water (or acid, since many transition metal hydrides are themselves weak acids) is a well-established method for the formation of hydridometal complexes. In this section we include a reaction

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[103] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. D*, 1176 (1970).

[104] E. W. Ainscough and S. D. Robinson, *ibid.*, 130 (1971).

[105] G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

[106] R. J. Hodges and J. Garnett, *J. Phys. Chem.*, 73, 1525 (1969).

[107] R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 93, 536 (1971).

[108] H. Brintzinger and J. E. Bercaw, *ibid.*, 92, 6182 (1970).

[109] N. R. Davies, *Rev. Pure Appl. Chem.*, 17, 83 (1967).

[110] J. J. Rooney, *Chem. Brit.*, 2, 242 (1966).

[111] R. Cramer, *Accounts Chem. Res.*, 1, 186 (1968).

[112] W. R. Roth and W. Grimme, *Tetrahedron Lett.*, 2347 (1966).

derived from the base properties of anions, namely the dehydrohalogenation of alkyl halides and also the hydrolysis of metal carbonyl cations. In the latter, metal hydrides are formed accompanied by evolution of CO_2.

1. *Hydrolysis of Alkali Metal Salts of Transition Metal Complexes*

The metal complex anions are nucleophiles and abstract protons from water or other Brønsted acids. The nucleophilicity and base strength of metal anions can vary by large values as recently summarized by King[113] and, in reviews of the general base properties of transition metal complexes, by Shriver[114] and by Kotz and Pedrotty.[115]

The reduction by sodium amalgam of metal halogen complexes provides a clean and straightforward reaction from which hydrides are obtained in high yield, eq 82 ($L = PPh_3$, $P(OPh)_3$; $X = Cl$, Br, I)[116] and eq 83 ($L = PPh_3$, $P(OPh)_3$, $P(C_6H_{11})_3$; $X = Cl$, Br, I).[117] The presence of phosphine in these complexes greatly increases the base strength of the intermediate anion so that hydrides are obtained by treatment of the alkali metal salt with water as contrasted to acid required for the unsubstituted carbonyls. For cyclopentadienyl derivatives of molybdenum or tungsten, either halogen derivatives ($Mo(X)(Cp)(CO)_2L$, $L = CO$, PPh_3, $P(OPh)_3$, $P(OMe)_3$, PBu_3 and $SbPh_3$; $X = I$)[118] or mercury complexes, eq 84 ($M = Mo$, W; $L = P(OMe)_3$, $P(OPh)_3$; $x = 1$,[119] $x = 2$[120]) can be used for the same purpose.

$$Co(X)(CO)_2L_2 \xrightarrow[\text{ii. }H_2O]{\text{i. Na/Hg}} HCo(CO)_2L_2 \qquad (82)$$

$$Mn(X)(CO)_3L_2 \xrightarrow[\text{ii. }H_2O]{\text{i. Na/Hg}} HMn(CO)_3L_2 \qquad (83)$$

$$Hg[Mo(Cp)(CO)_{3-x}L_x]_2 \xrightarrow[\text{ii. acid}]{\text{i. Na/Hg}} HMo(Cp)(CO)_{3-x}L_x \qquad (84)$$

The reduction of triruthenium dodecacarbonyl with sodium in liquid ammonia with subsequent acidification has provided the unstable $H_2Ru(CO)_4$.[121] By contrast to these reactions in which metal–metal bonds have been cleaved, new metal cluster derivatives can also be formed during the reduction and acidification cycles. This is observed in the reduction of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ with complex hydrides in which higher cluster metalates and hydrides are found (see section II.B). Churchill, *et al.*,[122] have obtained the polynuclear hydride $H_2Ru_6(CO)_{18}$ in the treatment of $Ru_3(CO)_{12}$ with the salts of either $Mn(CO)_5^-$ or $Fe(Cp)(CO)_2^-$ followed by acidification and extraction.

Other bases also provide conditions for the reduction of metal carbonyls as in eq 85 ($M = Ru$,[53] Os,[123]) and eq 86.[124]

$$M_3(CO)_{12} \xrightarrow{OH^-/MeOH} \text{unspecified anions} \xrightarrow{H^+} \begin{matrix} H_2M_3(CO)_{10},\ HM_3(CO)_{10}OH\ (M = Os) \\ H_2M_4(CO)_{13},\ H_4M_4(CO)_{12}\ (M = Ru, Os) \end{matrix} \qquad (85)$$

$$Ir_4(CO)_{12} \xrightarrow[CO]{K_2CO_3\text{–}MeOH} HIr_4(CO)_{11}^- \xrightarrow[N_2]{H^+} H_2Ir_4(CO)_{11} \qquad (86)$$

In the latter, the same carbonyl metalate can be obtained by sodium amalgam reduction of the starting material in tetrahydrofuran. The source of hydrogen in that reaction is not specified and in the absence of other agents it seems reasonable to assume that an intermediate metalate of sufficient high base strength could be converted to metal hydride even by deprotonation of tetrahydrofuran.

Carbonyl metalates may also be formed in the disproportionation of metal carbonyls which, with various subsequent treatments, can lead to metal hydrides, eq 87 (Chini[125]) and eq 88 (Chini, Colli, and Peraldo[126]).

$$Co_2(CO)_8 \xrightarrow{EtOH} [Co(EtOH)]_x{}^{2+}[Co(CO)_4]_2^- \xrightarrow{\Delta} Co_6(CO)_{15}{}^{2-} \xrightarrow[-70°]{HCl} HCo_6(CO)_{15}^- \qquad (87)$$

$$Co_2(CO)_8 + Fe(CO)_5 \xrightarrow{\text{acetone}} [Co(C_2H_2)_6]^{2+}[FeCo_3(CO)_{12}]_2^- \xrightarrow{HCl} HFeCo_3(CO)_{12} \qquad (88)$$

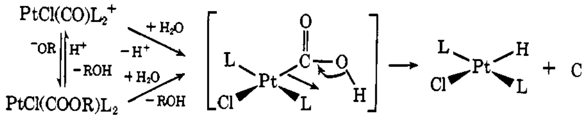
2. *Dehydrohalogenation of Alkyl Halides by Metal Anions*

Metal hydrides are obtained in the dehydrohalogenation of secondary or tertiary alkyl halides by anionic metal complexes.[127] Thus, while stable *n*-alkyl derivatives $Mo(R)(Cp)(CO)_2L$ ($L = P(OPh)_3$) are obtained for the halides of the Me, Et, allyl, and benzyl groups, isopropyl halide (eq 89) and *tert*-butyl halide give the metal hydride and the corresponding olefin. It is very likely that olefin is eliminated from an intermee diate (unstable) secondary or tertiary metal alkyl derivative (see eq 43 above).

$$Mo(Cp)(CO)_2L^- + Pr^iCl \longrightarrow HMo(Cp)(CO)_2L + NaCl + C_3H_6 \qquad (89)$$

3. *Hydrolysis of Metal Carbonyl Cations*

Hydridometal complexes have been obtained in the hydrolysis of cationic metal carbonyls as first demonstrated by Fischer, Fichtel, and Öfele[128] who isolated $HMn(CO)_5$ in the hydrolysis of $Mn(CO)_6^+$. More recently, Clark, Dixon, and Jacobs[129a] and Clark and Jacobs[130] have obtained metal hydrides in the hydrolysis of a cationic carbonyl (eq 90) or alkoxycarbonyl (eq 91) of platinum. The two types of starting complexes are



(90)

(91)

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(113) R. B. King, *Accounts Chem. Res.*, 3, 417 (1970).

(114) D. F. Shriver, *ibid.*, 3, 231 (1970).

(115) (a) J. C. Kotz and D. G. Pedrotty, *Organometal. Chem. Rev., Sect. A*, 4, 479 (1969); (b) *J. Organometal. Chem.*, 22, 425 (1970).

(116) W. Hieber and H. Duchatsch, *Chem. Ber.*, 98, 2933 (1965).

(117) W. Hieber, M. Höfler, and J. Muschi, *ibid.*, 98, 311 (1965).

(118) A. R. Manning, *J. Chem. Soc. A*, 651 (1968).

(119) M. J. Mays and S. M. Pearson, *ibid.*, 2291 (1968).

(120) M. J. Mays and S. M. Pearson, *J. Organometal. Chem.*, 15, 257 (1968).

(121) J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 2162 (1968).

(122) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Chem. Soc. D*, 458 (1970).

(123) B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc. A*, 2859 (1968); *Chem. Commun.*, 180 (1968).

(124) L. Malatesta and G. Caglio, *ibid.*, 420 (1967).

(125) P. Chini, *ibid.*, 29 (1967).

(126) P. Chini, L. Colli, and M. Peraldo, *Gaz. Chim. Ital.*, 90, 1005 (1960).

(127) R. B. King and K. H. Pannell, *Inorg. Chem.*, 7, 2356 (1968).

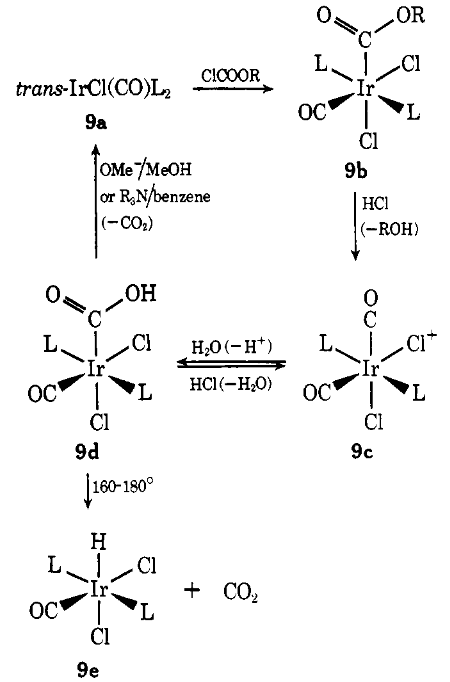
(128) E. O. Fischer, K. Fichtel, and K. Öfele, *Chem. Ber.*, 95, 249 (1962); see also, E. O. Fischer and K. Öfele, *Angew. Chem.*, 73, 581 (1961).

(129) (a) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, 91, 1346 (1969); *Chem. Commun.*, 548 (1968); (b) *J. Amer. Chem. Soc.*, 90, 2259 (1968).

(130) H. C. Clark and W. J. Jacobs, *Inorg. Chem.*, 9, 1229 (1970).

related by the well-known reversible treatment of the cationic carbonyl with alkoxide. In both of these hydrolyses, authors assume a common carboxy intermediate from which the hydride is obtained with evolution of CO_2.

A carboxy derivative of iridium **9d** has been obtained by Deeming and Shaw[131] in the sequence in eq 92 (L = PMe_2Ph); treatment of this derivative with acid restores the cationic complex **9c**, or treatment with base gives the starting material **9a**. Pyrolysis gives the hydridometal complex **9c** with evolution of CO_2. It should be pointed out that the carboxy derivatives shown in eq 90–91 or 92 contain the COOH group bonded through carbon, which is *isomeric* with the formate complex, $Co(OC(O)H)L_3$, obtained by Pu, Yamamoto, and Ikeda[132a] from the addition of CO_2 (with loss of N_2) to $HCo(N_2)L_3$ (L = PPh_3) or from the reaction of formic acid (with loss of H_2 and N_2) with the same starting material. The reverse of this reaction has been carried out by Laing and Roper[132b] in the decarboxylation of the diformate complex $Os[OC(O)H]_2(CO)_2(PPh_3)_2$ to give $H_2Os(CO)_2(PPh_3)_2$.



(92)

E. PROTONATION

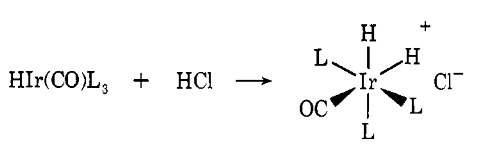
The protonation of metal complexes was first observed by Wilkinson and Birmingham in 1955 for $HReCp_2$. This derivative displayed base strength about that of ammonia and, when treated with HCl, afforded salts of $H_2ReCp_2^+$. A number of protonation reactions and their equivalent (such as the addition of H_2 of compounds of hydrogen to cationic metal complexes) are discussed in the next section.

The *donor* property of transition metals usually appears in complexes in which all the low-lying empty orbitals have become filled through interactions with various donor ligands (this has also been discussed in section II.D.1; see references cited there). In the event that there are fewer than 18 electrons in the bonding and/or nonbonding orbitals of a transition metal complex, treatment with acid usually leads to oxidative addition, with the exception of the derivatives of $HPtL_2^+ A^-$ which were ionic; these were discussed in section II.C.2.

Kotz and Pedrotty[115b] have reported that the triphenylphosphonium (tricarbonylchromium, -molybdenum, or -tungsten) cyclopentadienylides dissolve readily in CF_3COOH to give highly colored solutions and nmr spectra exhibiting a high-field line (τ 15–18) indicating metal protonation: $[HM(Cpylid)(CO)_3]^+$.

The protonation of $Ni(P(OEt)_3)_4$ has been reported by Drinkard, *et al.*,[133] and, in contrast to previous negative reports, Schunn[134] was able to isolate protonated derivatives from the addition of strong *nonaqueous* acids to solutions of $Ni(diphos)_2$.

Vaska[135] has reported protonation for the 18-electron complexes $HIr(CO)L_3$ (L = PPh_3) giving dihydrido cations of stereochemistry indicated in eq 93. Collman, Vastine, and Roper[136] report protonation for $HIr(CO)_2L_2$ but did not establish stereochemistry in the product. By contrast the trihydrido derivatives of iridium lose H_2 on treatment with acid as discussed in section II.A.2, as is the case in the treatment of H_3IrL_2 (L = PPh_3, $AsPh_3$) with dithiophosphoric and dithiophosphinic acids (Araneo, Bonati, and Minghetti[137]) or β-diketonates (Araneo[138]). In these reactions the dihydrido species $H_2Ir(chel)L_2$ are obtained, where chel is a chelating anion such as acac or the anions of the acids mentioned.



(93)

Freni, Demichelis, and Giusto[40] report protonation of $H_3Re(diphos)_2$ to give stable tetrahydrido cations, $H_4Re(diphos)_2^+$. Douglas and Shaw[42] observed exchange of protons in H_4OsL_3 (L = tertiary phosphine or arsine) with deuterio acid and have obtained evidence for the pentahydrido cationic species, $H_5OsL_3^+$, in solution although no stable salts could be isolated. The protonated species undergoes slow decomposition with the evolution of H_2. The treatment of H_4OsL_3 with HCl afforded only halogen derivatives and no hydrido complexes.

The protonation of many olefin complexes occurs on the hydrocarbon. Such products as well as the products resulting from the protonation of other metal-coordinated groups shall be considered outside the scope of this work. Cationic derivatives resulting from protonation of (or hydride abstraction from) hydrocarbon ligand have been reviewed by Haas.[139] *Metal* protonation has been observed for the dicycloheptadiene complex $C_7H_8Fe(CO)_3$ by Falkowski, *et al.*[140] (eq 94). In strong acid (HSO_3F) and at low temperatures (−78°),

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(131) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 443 (1969).

(132) (a) L. S. Pu, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **90**, 3896 (1968); (b) K. R. Laing and W. R. Roper, *J. Chem. Soc. A*, 1889 (1969).

(133) W. C. Drinkard, D. R. Eaton, J. P. Jesson, and R. V. Lindsey, Jr., *Inorg. Chem.*, **9**, 392 (1970).

(134) R. A. Schunn, *ibid.*, **9**, 394 (1970).

(135) L. Vaska, *Chem. Commun.*, 614 (1966).

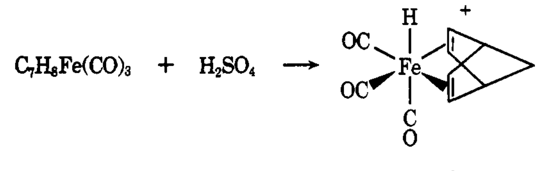
(136) J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, **90**, 2282 (1968).

(137) A. Araneo, F. Bonati, and G. Minghetti, *Inorg. Chim. Acta*, **4**, 61 (1970).

(138) A. Araneo, *J. Inorg. Nucl. Chem.*, **32**, 2925 (1970).

(139) M. A. Haas, *Organometal. Chem. Rev., Sect. A*, **4**, 307 (1969).

(140) D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, **89**, 6387 (1967).



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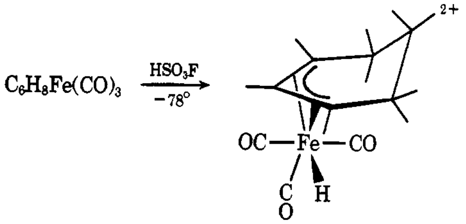
Young, Holmes, and Kaesz[141] have observed diprotonation of tricarbonyliron complexes of cyclohexadiene and cycloheptadiene, to give hydridometal–cyclohexadienyl (eq 95) and hydridometal–cycloheptadienyl complexes. At about −20°, an intramolecular exchange of metal hydrogen with selected olefin protons was observed. Metal-bonded proton was also observed for low-temperature solutions of a number of butadieneiron tricarbonyl complexes previously reported to give only methallyl derivatives. The metal-bonded proton participates in a rapid exchange with two terminal protons and less rapid exchange with all terminal protons of the coordinated butadiene.



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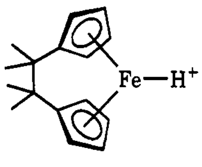
Lentzner and Watts[142] have found that ferrocene derivatives with rings tilted by intramolecular carbocyclic bridging have greater basicity than ferrocene (**10**). This is in accord with the theory proposed by Ballhausen and Dahl in 1961 in which tilting of the rings is expected to increase base strength through rehybridization of nonbonding electron pairs.



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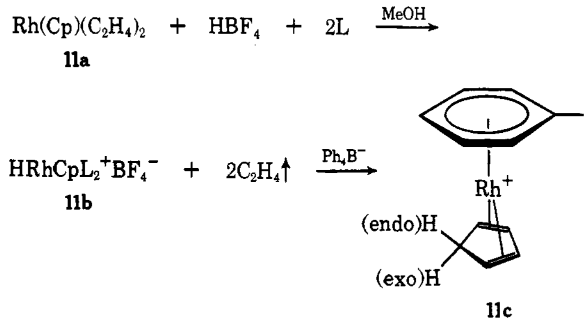
Metal protonation is observed in the treatment of the complex **11a** with HBF_4 (or $HClO_4$) in methanol in the presence of 2 mol of L (L = PPh_3).[149] In the presence of BPh_4^- ion, ligands on rhodium are displaced by phenyl ring and accompanied by a corresponding shift of proton from metal to Cp ring to give a cyclopentadiene derivative **11c**. The shift of hydrogen is stereospecific to the endo position, demonstrated with deuterium labeling.

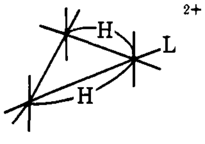


(96)

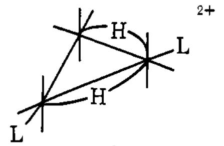
11c

Knight and Mays[143] report the protonation of the trimetal dodecacarbonyls of ruthenium and osmium to give salts of the type $[HM_3(CO)_{12}][PF_6]$ (M = Ru, Os). A high kinetic isotope effect was observed (11 ± 2), but no information concerning the structure of the derivatives other than to assume some type of bridging position for hydrogen could be ascertained (see section III.K).

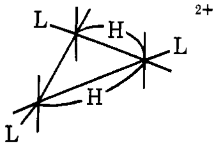
Protonation of trimeric osmium complexes $HOs_3(CO)_{10}$-SPh, $HOs_3(CO)_{10-x}L_x(SPh)$ (x = 0, 1, 2; L = PEt_3, $PMePh_2$) was reported by Deeming, Johnson, and Lewis.[144] For the derivative (x = 2) evidence for a doubly protonated species was obtained, in accord with the greater base strength of phosphine substituted carbonyls. These same workers observed[144] diprotonation for phosphine-substituted derivatives $Os_3(CO)_{12-x}L_x$ (L = PEt_3; x = 1, 2, 3) although monoprotonated derivatives could also be obtained. Both in monoprotonated and diprotonated species, **12a–c**, edge-bridging for hydrogen and radial position for ligand were proposed based on the observed nmr patterns (carbonyls omitted for clarity).



12a



12b



12c

When $Ir_4(CO)_{12}$ is dissolved in concentrated sulfuric acid, Knight and Mays[143] observed a high-field singlet at τ 28.4 in the nmr spectrum. By careful integration of this peak compared to a standard they concluded that they had prepared the dicationic species $H_2Ir_4(CO)_{12}^{2+}$. The equivalence of the protons must arise either through a rapid scrambling mechanism or positioning of the protons on one of the C_2 axes of the tetrahedral carbonyl. Both $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ decompose when subjected to strong acid media.

F. OXIDATIVE ADDITION OF H_2 AND HX TO CATIONIC METAL COMPLEXES

The equivalent of a protonated complex is obtained when H_2 or a compound of hydrogen is oxidatively added to a cationic metal complex. Vaska and Catone[145] and Sacco, Rossi, and Nobile[146] have observed addition of H_2 and HX (X = Cl, Br, I) to the cationic complexes $M(diphos)_2^+$ (M = Co, Ir) to give the hydrido species $H_2M(diphos)_2^+Y^-$ and $HMX(diphos)_2^+Y^-$ (Y = Cl, Br, I, ClO_4, and BPh_4). The corresponding rhodium complexes did not show, under ambient conditions, evidence of adding H_2 (or CO as did the other complexes). Butter and Chatt[147] report cis addition with H_2 (or Cl_2) to the cationic de-

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[141] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **91**, 6968 (1969).

[142] H. L. Lentzner and W. E. Watts, *J. Chem. Soc. D*, 26 (1970).

[143] J. Knight and M. J. Mays, *J. Chem. Soc. A*, 711 (1970); *J. Chem. Soc. D*, 384 (1969).

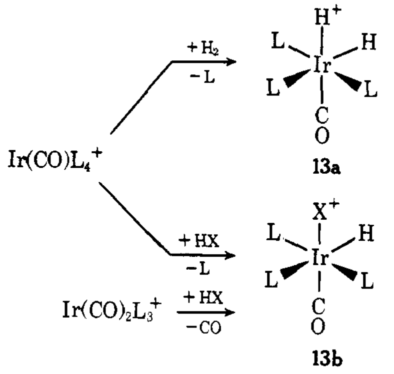
[144] (a) A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 2517 (1970); (b) *ibid.*, 2967 (1970).

[145] L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, **88**, 5324 (1966).

[146] A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Commun.*, 589 (1966).

[147] S. A. Butter and J. Chatt, *J. Chem. Soc. A*, 1411 (1970).

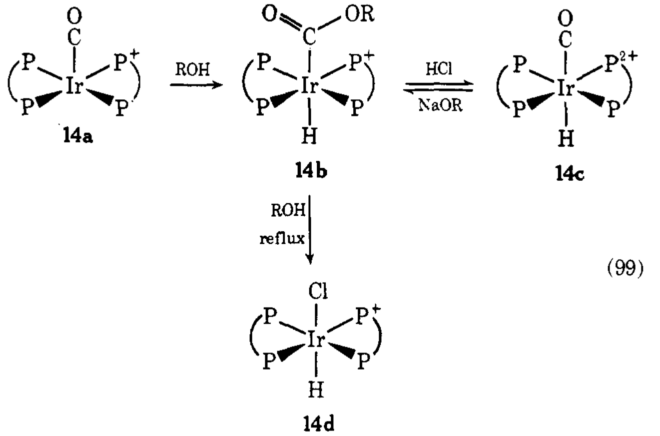
rivative $Rh(dmpe)_2^+$ but observed trans addition with HCl and HBr (and Br_2). Deeming and Shaw[148] obtained oxidative addition for five-coordinate cationic complexes of iridium (eq 97) which, as required by the 18-electron rule, must be accompanied by replacement of a ligand (L = PMe_2Ph) as observed. In the mixed complex $Ir(CO)(PMe_2Ph)(AsMe_2Ph)_2^+$, the displaced ligand is the arsine with the remaining arsine in position trans to hydrogen.



Shapley, Schrock, and Osborn[149] observe similar displacement of ligand (olefin) from cationic complex (eq 98, S = solvent) for salts of perchlorate and hexafluorophosphate. In the presence of the tetraphenylboron anion, an interesting substitution and shift of hydrogen from the metal is observed (see eq 96)

$$Rh(C_7H_8)L_2^+ + H_2 \xrightarrow{S} H_2RhL_2S_2^+ + C_7H_8 \qquad (98)$$

The five-coordinate cationic complex **14a** adds a mole of ROH (R = Me, Et) with attachment of alkoxide to carbon of metal carbonyl and proton to metal (P–P = dmpe, Ibekwe and Taylor[150]). Treatment of the hydridometal alkoxycarbonyl cation **14b** with aqueous acid produces a hydridometal carbonyl dication **14c**; this reaction can be reversed with alkoxide. Heating of **14b** causes substitution of the alkoxycarbonyl group by halide **14d**, to give a derivative analogous to that obtained by the addition of HCl to $Rh(dmpe)_2^+$.[147] Other cationic hydrides obtained from addition of hydrogen are discussed for Rh and Ir in section III.L.



III. Chemical Properties and Chemical Reactions of Transition Metal Hydrides, Survey by Metal Triads

The chemical properties and chemical reactions of hydrido complexes of the transition metals are summarized in this section. It was inevitable that discussion of a number of these has been encountered in the previous section as a consequence of the obvious close relation between synthesis and chemical properties; cross-references are noted as necessary. First we present summaries organized around a particular chemical property or reaction which are followed by a survey organized on the metal triads for reports of chemistry not accommodated elsewhere.

A. STABILITY

Previous reviewers[1,2] have presented some generalizations on the stability of metal hydride derivatives derived from two factors, namely the presence of suitable ligands (stable hydrides usually contain ligands which stabilize the low oxidation states of the metals) and atomic number of the metal (within series of congeners, the thermal stability of metal hydride usually increases with increasing atomic number). We find that subsequent observations have added further support. Witness the report that $H_2Os(CO)_4$ is stable in contrast to $H_2Ru(CO)_4$ and $H_2Fe(CO)_4$ which are increasingly less so (see section II.A.1). There have been few thermodynamic studies to provide information of a more quantitative kind with the notable exception of Bronshtein, *et al.*[5] (section II.A.1), and Vaska and Werneke[26] who have estimated the bond dissociation energy in $H_2IrX(CO)L_2$ derivatives to be 57–61 kcal (see also section II.A.3). There have also been attempts to estimate metal–hydrogen bond energies from mass spectral studies; see section IV.C.

B. TRANS EFFECT OF HYDRIDE

Hydrogen bonded to transition metals has been shown to be a very effective trans-directing ligand in the substitution of metal complexes (see Ginsberg[1] or Green and Jones[2]). As a kinetic phenomenon, the trans effect can arise from the destabilization of the ground state of the complex or from stabilization of the transition state in the reaction (or both). In order to separate phenomena such as spectroscopic observations which deal with the ground state of the complex, Pidcock, Richards, and Venanzi[151] have introduced the term *trans-influence*. This is defined as the tendency of a ligand to weaken the bond in position trans to itself in the ground state of the complex. Hydrogen is a ligand of high trans-influence arising from its inductive effect in directing toward itself a large component of s character in the σ bonds and thus weakening the σ bonds toward all ligands but in particular in the position trans to itself. The trans effect of hydrogen follows mainly from its trans-influence. Spectroscopic data from which the high trans-influence of hydrogen is deduced is discussed in section IV.B. The trans-influence of hydrogen (among other ligands) was investigated through extended Hückel molecular orbital calculations by Zumdahl and Drago[152] whose results largely support the conclusions mentioned above.

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(148) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A.*, 3356 (1970).

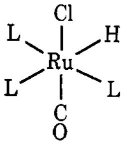
(149) J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, 91, 2816 (1969).

(150) S. D. Ibekwe and K. A. Taylor, *J. Chem. Soc. A*, 1 (1970).

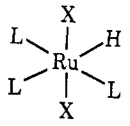
(151) A. Pidcock, R. E. Richards, and L. M. Venanzi, *ibid.*, 1707 (1966).

(152) S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 90, 6669 (1968).

In the series of complexes $HRuCl(CO)L_3$ (**15a**, L = PEt_2Ph, $PPr^n{}_2Ph$, $PBu^n{}_2Ph$), Douglas and Shaw[153] observed that equilibration of the ligand bonded trans to hydrogen is rapidly established and the relative affinities of L for the metal in that position have been obtained: $AsEt_2OPh < AsMe_2Ph < PBu^n{}_2Ph \sim PPr^n{}_2Ph \sim PEt_2Ph < PEt_3 < P(OEt)_3 \sim PMe_2Ph < P(OMe)_2Ph$. Ligands which are better π acceptors are more favorably accommodated trans to H than those which are better σ donors owing to competition of these for metal σ-bonding orbitals with H.



15a



15b

Similarly, Powell and Shaw[154] find the ligand trans to hydride in the complexes **15b** (X = Cl or Br; L = PMe_2Ph) exchanges rapidly with other ligands in solution. The relative rates of substitution studied by nmr are found to be in the order $AsEt_3 > PEt_3 > PBu^n{}_3 > PEt_2Ph > PBu_2Ph$, and substitution in the complex X = Br is faster than for X = Cl.

C. ELIMINATION OF H_2

Elimination of H_2 from monohydride derivatives is usually accompanied by the formation of metal–metal bonded species (reverse of hydrogenation of metal–metal bonds). Such a reaction is the decomposition of $HCo(CO)_4$ to give H_2 and $Co_2(CO)_8$, whose kinetics have been studied by Ungvary and Markó;[155] the rate-determining step was found to involve the reaction between $HCo(CO)_4$ and $HCo(CO)_3$ *without* participation of Co–H bonds. It is postulated that H_2 must therefore be rapidly eliminated from the dimeric species, $H_2Co_2(CO)_7$. The coordinatively unsaturated species $HCo(CO)_3$ has often been postulated as the active agent in many of the reactions of $HCo(CO)_4$, and the present study, in which its concentration in equilibrium with $HCo(CO)_4$ could be calculated, provides the first experimental evidence for its existence.

The reversible formation of $[Rh(CO)_2L_2]_2$ with loss of H_2 has been reported for $HRh(CO)_2L_2$ (L = PPh_3);[156] see further discussion section III.L.

From hydrido derivatives containing two (or more) metal-bonded hydrogen atoms, H_2 may be displaced with ligands (see section II.A.1) or by reductive elimination (section II.A.3).

Hydrogen is also eliminated in the treatment of a number of metal hydrides with acids, a number of which reactions were discussed in section II.A.3. To this may be added the reaction of HBF_4 with $HPtClL_2$ (in the presence of CO at 5 atm) to give the cationic carbonyls, $PtCl(CO)L_2{}^+$, with the evolution of H_2.[129b] This is often taken as a diagnostic test for H_2 although on account of the base properties of many hydridometal complexes (simply to add a proton) this is of limited usefulness. Ginsberg[41] reports evolution of H_2 in the acid treatment of $H_8Re(PPh_3)^-$; compared to the expected value of 6.0, 5.84 mol of H_2 was collected.

$$H_8Re(PPh_3)^- + 4H^+ \longrightarrow Re^{3+} + 6H_2 + PPh_3 \quad (100)$$

D. ACID–BASE CHARACTERISTICS

A number of hydrido complexes of transition metals (as do most zerovalent transition metal complexes) possess base properties (see section II.E). Others, in the presence of ionizing solvents, may show properties as Brønsted acids. The presence of phosphine on transition metal greatly reduces the acid strength of metal hydrogen bond; see eq 82 and eq 83 and discussion above.

The derivative $HFeCp(SiCl_3)(CO)$, obtained in the photochemical decomposition of $HFeCp(CO)_2$ and $HSiCl_3$, is reported by Jetz and Graham[91] to be a very strong acid, slightly less strong than perchloric acid in acetonitrile.

A reaction believed to derive from the protic properties of transition metal hydrides is the quantitative elimination of amine in eq 101 (M = Cr, Mo, W; M′ = Si, Ge, Sn).[157]

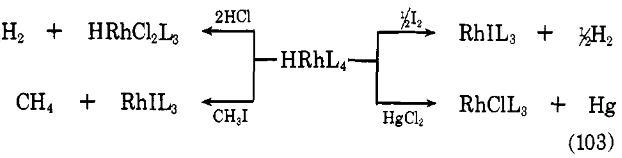
$$HMCp(CO)_3 + Me_3M'NMe_2 \longrightarrow M(M'Me_3)Cp(CO)_3 + HNMe_2 \quad (101)$$

Simple proton transfer was reported for the reaction of an aminosilicon derivative and $HCo(PF_3)_4$.[158]

$$HCo(PF_3)_4 + Me_3SiNMe_2 \longrightarrow Me_3SiNMe_2H^+Co(PF_3)_4{}^- \quad (102)$$

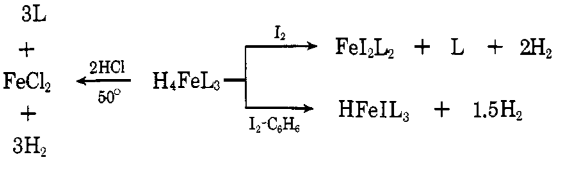
E. REACTION OF METAL HYDRIDES WITH HALOGENS, MERCURIC HALIDES, AND HALOCARBONS

The various reactions of hydrides with a variety of halogen compounds are illustrated in the chemical characterization of $HRhL_4$ (L = PPh_3),[159] eq 103. The HX molecule resulting



(103)

from the reaction of metal hydride with X_2 may itself react with starting material. Thus in the reaction with I_2, Ilmaier and Nyholm report that HI initially formed reacts with a mole of metal hydride to give H_2 and the metal halide. The resulting HX may simply protonate unreacted metal hydride complex, as in eq 121. Aresta, *et al.*,[44] report reactions of hydridometal derivatives with I_2 both directly and in benzene solution (which give different results) and with HCl.



(104)

Yamamoto, *et al.*,[12] observe the release of N_2 and H_2 in the reaction of $HCo(N_2)L_3$ (L = PPh_3) with either HCl or I_2; in both cases the metal complex was converted to the derivative CoX_2L_3.

By contrast to the reaction of $HRhL_4$ with $HgCl_2$ (eq 103), treatment of $HRhCl_2L_3$ (L = $PEtPh_2$) with $HgCl_2$ gave the

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(153) P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 1556 (1970); *J. Chem. Soc. D*, 632 (1969).

(154) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 617 (1968).

(155) F. Ungvary and L. Markó, *J. Organometal. Chem.*, 20, 205 (1969).

(156) D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 2660 (1968).

(157) D. J. Cardin, S. A. Keppie, and M. F. Lappert, *ibid.*, 2594 (1970); *cf.* D. J. Cardin and M. F. Lappert, *Chem. Commun.*, 506 (1966).

(158) A. D. Berry, J. R. Bergerund, R. E. Highsmith, A. G. MacDiarmid, and M. A. Nasta, Abstracts of Papers, presented at the 4th International Conference on Organometallic Chemistry, Bristol, England, 1969, Paper A4.

(159) B. Ilmaier and R. S. Nyholm, *Naturwissenschaften*, **56**, 415 (1969).

derivative $Rh(HgCl)Cl_2L_3$.[63] The hydrido complex is regenerated upon reduction of the mercuri chloride complex with ethanol and base.

The reaction of metal hydrides with CCl_4 is often employed to establish the presence of metal hydride; Kruse and Atalla[46] report this method in characterizing the derivatives H_2FeL_4 and $HCoL_4$ ($L = P(OEt)_3$). With CCl_4, $HMCp(CO)_2L$ (M = Mo or W; $L = PPh_3$) gives the halogen compounds $MClCp(CO)_2L$ with retention of configuration around M.[160]

The reaction of $HCo(N_2)L_3$ (L = a variety of tertiary phosphines) with CCl_4 gave two halocarbon products[13]

$$HCo(N_2)L_3 + CCl_4 \longrightarrow CoCl_2L_3 + CHCl_3 + CCl_2{=}CCl_2 \quad (105)$$

The unsaturated chloro olefin was separately shown to be produced in the reaction with CCl_4 of $CoClL_3$, which is no doubt an intermediate in reaction 105. Wilford, Forster, and Stone[161] report reduction products such as $CCl_2{=}CClH$, $CCl_2{=}CH_2$, and $CHCl{=}CHCl$ (among other reactions; see section III.D) in the treatment of $CCl_2{=}CCl_2$ with metal hydrides.

F. REACTION OF METAL HYDRIDES WITH UNSATURATED DERIVATIVES

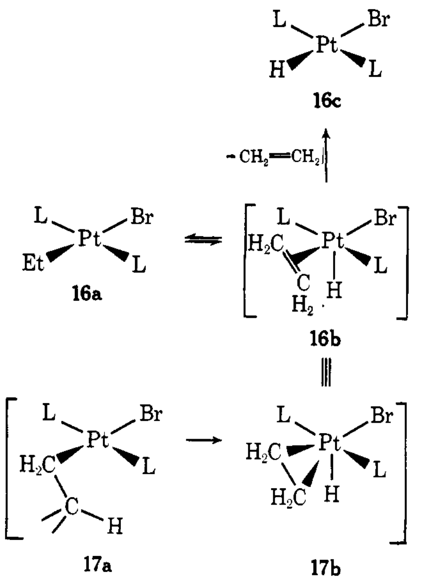
With unsaturated derivatives, transition metal hydrides enter into several types of reactions. The first is the addition of M–H across the unsaturated center. Very often this is followed (but not necessarily so) by elimination with isomerization, or hydrogenation, and (in the presence of CO) hydroformylation. Olefins are also hydrosilated in the presence of transition metal catalysts which is believed to occur through hydridometal derivatives.

1. Addition of Metal Hydrides to Unsaturated Compounds

The reversible addition of olefins and platinum hydrides has been studied by Chatt, *et al.*[64] The action of heat upon *trans*-$Pt(C_2H_5)BrL_2$ ($L = PEt_3$) gives *trans*-$HPtBrL_2$; deuterium labeling shows that the hydridic hydrogen may originate from both the α and β carbon atoms of the ethyl group. It is assumed that the alkyl complex participates in a reversible equilibrium (eq 106) whose position is determined both by the nature of the olefin and the group trans to the hydride. **16a** → **16b** (eq 106) may be regarded as an internal oxidative addition of CH to coordinatively unsaturated metal in the alkyl derivative. In the formation of the intermediate olefin complex, this reaction bears resemblance to the internal oxidative addition in coordinatively unsaturated alkoxide derivatives (eq 44b) which yield the analogous coordinatively saturated hydridometal carbonyl derivatives.

Cramer and Lindsey[162] have observed acceleration by 1% $SnCl_2$ of the addition of ethylene to *trans*-$HPtCl(PEt_3)_2$ which otherwise requires elevated temperatures and pressures. This is attributed to the high trans effect of the SnX_3^- group which labilizes hydride in the trans position.

Baird, *et al.*,[81] have studied the addition of $HRhCl_2(PPh_3)_2$ to ethylene, tetrafluoroethylene, and acetylene. The ethyl and vinyl complexes undergo ready insertion reactions with CO



(106)

(107)

to give the corresponding acyl derivatives. Mays and Wilkinson[163] have obtained addition reactions of $HCo(CN)_5^{3-}$ with C_2F_4 to give $Co(C_2F_4H)(CN)_5^{3-}$, a very stable complex. With $CF_3C{\equiv}CCF_3$, no reaction was observed while with $CF_2{=}CFCl$ an unstable complex was obtained which decomposed giving $CoCl(CN)_5^{3-}$. Kinetics of the addition of $HCo(CN)_5^{3-}$ to various unsaturated derivatives have been studied by Halpern and Wong.[164] Their results indicate that addition, although following a bimolecular rate law, does not involve coordination of the unsaturated molecule to the metal prior to insertion, because of the absence of CN^- dependence of the rates. This is thus distinguishable from other insertions in which prior coordination is believed to occur (see eq 106) or the addition of $HCo(CO)_4$ to olefins, in which the coordinatively unsaturated $HCo(CO)_3$ is believed to be the reaction intermediate.[165] Lawson, Mays, and Wilkinson[166] have obtained the insertion product $Rh(C_2F_4H)(CN)_5^{3-}$ from the hydridopentacyanorhodate(III) ion and tetrafluoroethylene.

The reaction of metal hydrides with fluoroolefins has been subject to much attention. Wilford and Stone[167] observed stable adducts of $HRe(CO)_5$ with $CF_2{=}CF_2$, $CF_2{=}CFCl$, and $CF_2{=}CCl_2$; the metal becomes bonded to the most highly fluorinated carbon. With hexafluorobut-2-yne, the derivative *trans*-$CF_3C(H){=}C(CF_3)Re(CO)_5$ was obtained. The stable adduct $HCF_2CF_2Co(CO)_4$ was obtained from $HCo(CO)_4$ and $CF_2{=}CF_2$; however, other fluoroolefins such as $CFCl{=}CF_2$ and $CF_3C{=}CCF_3$ gave hydrogenation products.[161] A number of chloroolefins also gave products in which the C–Cl bond(s) had been reduced (see section III.E).

Trans addition of metal hydride is observed in the reaction of $HMn(CO)_5$ with a number of acetylenes: $HC{\equiv}CCO_2Me$, $HC{\equiv}CCHO$, or $RO_2CC{\equiv}CCO_2R$ (R = H or Me).[168]

M–H additions followed by various fluorine or hydride shifts have been observed by Tattershall, *et al.*,[169] in the reac-

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[160] A. Bainbridge, P. J. Craig, and M. Green, *J. Chem. Soc. A*, 2715 (1968).

[161] J. B. Wilford, A. Forster, and F. G. A. Stone, *J. Chem. Soc.*, 6519 (1965).

[162] R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **88**, 3534 (1966).

[163] M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, 6629 (1965).

[164] J. Halpern and L. Wong, *J. Amer. Chem. Soc.*, **90**, 6665 (1968).

[165] R. F. Heck, *Advan. Chem. Ser.*, No. **49**, 181 (1964).

[166] D. N. Lawson, M. J. Mays, and G. Wilkinson, *J. Chem. Soc. A*, 52 (1966).

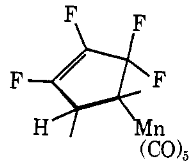
[167] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 93 (1965).

[168] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. A*, 2766 (1969).

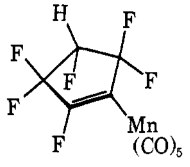
[169] B. W. Tattershall, A. J. Rest, M. Green, and F. G. A. Stone, *ibid.*, 899 (1968).

tion of $HMn(CO)_5$ or $HRe(CO)_5$ with hexafluorobuta-1,3-diene. With $HRe(CO)_5$ the complex $CHF_2CF_2CF{=}CFRe(CO)_5$ was isolated, produced from 1,4 addition of hydride to olefin followed by a 1,3 fluorine shift. The same type of product was obtained with $HMn(CO)_5$ among three others: the complex $CF_3CF{=}C(CHF_2)Mn(CO)_5$ resulting from a 1,2 addition followed by a 2,4 fluorine shift; $CF_2{=}CFCH(CF_3)Mn(CO)_5$ formed from 1,2 addition followed by a hydride shift; and an acyl derivative, $CHF_2CF{=}CFC(O)Mn(CO)_5$.

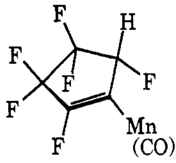
The reaction of $HMn(CO)_5$ with perfluorocyclopentadiene has been studied by Fields, *et al.*[170] Three major 1:1 adducts were obtained, **18a–c**, involving respectively 1,2 M–H addition, 1,4 M–H addition followed by 1,3 fluorine shift, and 1,2 M–H addition followed by 1,3 fluorine shift. A ketonic complex **18d** was obtained in low yield, while at −78° the major product was the 1,4 M–H adduct without rearrangement.



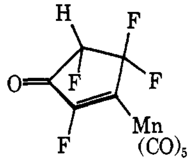
18a



18b



18c



18d

An anomalous reaction is observed by Clark and Tsang[171] in the treatment of fluoroolefins with platinum hydrides; HF is eliminated and fluorovinyl derivatives obtained (eq 108,

$$HPtClL_2 + C_2F_4 \longrightarrow Pt(CF{=}CF_2)ClL_2 + HF \qquad (108)$$

L = PPh_3). An intermediate adduct with C_2F_4 has been isolated which is believed to be the cationic complex $HPt(\pi\text{-}C_2F_4)L_2^+$ through conductivity measurements and Pt–H vibration at 2100 cm^{-1}.

The addition of tetracyanoethylene (TCNE) to the hydridoplatinum complexes *trans*-$HPtXL_2$ (L = PEt_3, X = Cl, Br, I, NO_2, CN, NCO; L = PPh_3; X = Cl, Br, I, CN) has been studied by Uguagliati and Baddeley.[172] For X = Cl and Br, the adduct $PtL_2\cdot$TCNE was formed together with elimination of HX. For other X groups, little or no such adduct was isolated owing to side reactions. A 1:1 adduct, $HPt(CN)L_2\cdot$TCNE, has been isolated and characterized as the hydrido olefinic complex, as written.

Pu, Yamamoto, and Ikeda[132] report addition of $HCo(N_2)L_3$ to CO_2, to yield the formate complex $Co(OCOH)L_3$. The platinum hydride $HPtCl(PEt_3)_2$ reacts with a diazonium salt to give the adduct $Pt(NH{=}NPh)ClL_2^+$ which can be further reduced and cleaved to give $PhNH_2$ and NH_4^+.[173]

The Mn–H bond in $HMn(CO)_5$ readily undergoes an insertion reaction with bis(trifluoromethyl)diazomethane forming $CH(CF_3)_2Mn(CO)_5$; the platinum hydride *trans*-$HPtCl(PEt_3)_2$ undergoes a similar insertion only at elevated temperatures.[174]

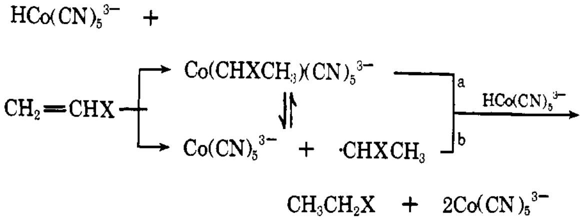
2. Isomerization of Olefins

Reversible addition of olefins by transition metal hydrides proceeding through an intermediate olefin coordinated metal hydride complex has been postulated by Cramer and Lindsey[162] as the mechanism for the isomerization of olefins by a number of transition metal catalysts of rhodium, palladium, platinum, nickel, or iron, with a variety of cocatalysts (HCl, H_2, $SnCl_2$). This and other papers have been reviewed by Cramer.[111] A variety of ways in which metal hydrides are either postulated or observed to participate in olefin isomerizations or hydrogen rearrangements reactions have also been discussed in section II.C.3.

Although reversible addition and elimination of $HCo(CO)_4$ was thought to be involved in the catalytic isomerization of allylbenzene to propenylbenzene, studies with $DCo(CO)_4$ by Roos and Orchin[175] show very little incorporation of deuterium in the hydrocarbon product. Thus, the metal–hydrogen may not participate in the observed 1,3 hydride shift of the olefin.

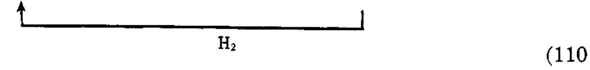
3. Hydrogenation

The addition reaction may also be involved in hydrogenation. Addition of Co–H to α,β-unsaturated carboxylic acids lacking an α substituent has been demonstrated by Jackman, Hamilton, and Lawlor[176] in the well-known catalytic hydrogenation by pentacyanocobaltate (eq 109a; *cf.* Kwiatek[177]). Hydrogenation is completed with a second mole of reagent. The addition of Co–H to olefin is one of two possible mechanisms, the other being hydrogen transfer (eq 109b) which may be in equilibrium with it, the position of which being determined by the substrate (see Halpern[25] and references cited therein).



$$\begin{array}{l} HCo(CN)_5^{3-} + \\ CH_2{=}CHX \begin{cases} \longrightarrow Co(CHXCH_3)(CN)_5^{3-} \quad (a) \\ \qquad\qquad \Updownarrow \\ \longrightarrow Co(CN)_5^{3-} + \cdot CHXCH_3 \quad (b) \end{cases} \xrightarrow{HCo(CN)_5^{3-}} \\ \qquad\qquad CH_3CH_2X + 2Co(CN)_5^{3-} \end{array} \qquad (109)$$

Hydrogenation of olefins by $HMCp(CO)_3$ (M = Cr, Mo, and W) has been reported by Miyake and Kondo.[178] For M = Mo or W, stoichiometric amounts (2 mol) of hydride were required for each mole of olefin; however, for M = Cr (eq 110) the reaction is catalytic owing to the ready re-formation of the hydride from the metal–metal bonded dimer in the presence of H_2.



$$2HCrCp(CO)_3 + RCH{=}CH_2 \longrightarrow [CrCp(CO)_3]_2 + RCH_2CH_3 \qquad \text{(}[CrCp(CO)_3]_2 \xrightarrow{H_2} 2HCrCp(CO)_3\text{)} \qquad (110)$$

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[170] R. Fields, M. Green, T. Harrison, R. N. Haszeldine, A. Jones, and A. B. P. Lever, *J. Chem. Soc. A*, 49 (1970).

[171] H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, **89**, 529 (1967); *Chem. Commun.*, 123 (1966).

[172] P. Uguagliati and W. H. Baddeley, *J. Amer. Chem. Soc.*, **90**, 5446 (1968).

[173] G. W. Parshall, *ibid.*, **89**, 1822 (1967).

[174] J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 1872 (1969); *Chem. Commun.*, 170 (1968).

[175] L. Roos and M. Orchin, *J. Amer. Chem. Soc.*, **87**, 5502 (1965).

[176] L. M. Jackman, J. A. Hamilton, and J. M. Lawlor, *ibid.*, **90**, 1914 (1968).

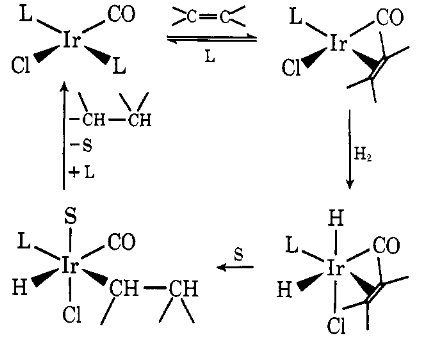
[177] J. Kwiatek, *Catal. Rev.*, **1**, 37 (1967).

[178] (a) A. Miyake and H. Kondo, *Angew. Chem., Int. Ed. Engl.*, **7**, 880 (1968); (b) *ibid.*, **7**, 631 (1968).

The complex $HRh(CO)L_3$ ($L = PPh_3$) has been shown to be an effective hydrogenation catalyst for unsaturated compounds of the formula $RCH{=}CH_2$,[179a] and to hydrogenate these alkenes more rapidly than the iridium complex.[179b] Hydrogenation is initiated by addition of Rh–H to the olefinic double bond by the active species, coordinatively unsaturated $HRh(CO)L_2$; the hydrogenation is completed by the addition of 1 mol of H_2 to the intermediate alkyl complex followed by reductive elimination of R'H (see also section II.A.4, hydrogenolysis by H_2).

Hydrogenation of methyl linoleate (Bailar and Itatani[180]) and nonaromatic polyolefins (Tayim and Bailar[181]) by complexes of Ni, Pd, or Pt proceeds to the monoene stage and is preceded by isomerization and olefin migration to conjugated system. As also observed in the addition reaction (see section II.F.1), these reactions are greatly enhanced by divalent group IV (Si, Ge, Sn, or Pb) derivatives although $SnCl_2 \cdot 2H_2O$ was found to be the most effective. Either hydrogen gas *or solvent* (CH_3OH) in the absence of H_2 gas can be the source of hydrogen.

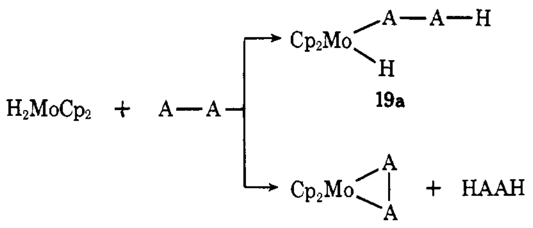
Hydrogenation is also observed with polyhydrido species, $H_2MX(CO)L_2$ (M = Rh, Ir;[183] M = Ir, X = H;[182] see also Vaska,[183] and references cited therein). The complex $RhClL_3$ ($L = PPh_3$) is a very effective catalyst for the hydrogenation of olefins;[21] the active form is a solvated dihydrido species, $H_2RhXL_2 \cdot S$, in which solvent is readily displaced by olefin substrate. These workers postulate simultaneous transfer of both hydrogen atoms in the rate-determining step. In studies of the analogous iridium complex, James and Memon[184] postulate a separate addition step (eq 111, $L = PPh_3$).



(111)

Similar mechanisms may also apply in the reduction of olefins with H_3IrL_3 ($L = PPh_3$); after hydrogenation of olefin a green intermediate is observed, formulated as $HIrL_2 \cdot S$, from which the active form of trihydride is regenerated with H_2.[185] Glockling and Wilbey[35] report hydrogenation of ethylene with $H_2Ir(GeR_3)(CO)L_2$ to give $Ir(GeR_3)(CO)L_2$; the dihydride is regenerated with H_2.

Otsuka, Nakamura, and Minamida[186] observed both addition and hydrogenation with H_2MoCp_2 and acetylenes or azo derivatives. Acetylenedicarboxylic esters and hexafluorobut-2-yne give addition compounds of the type **19a**,



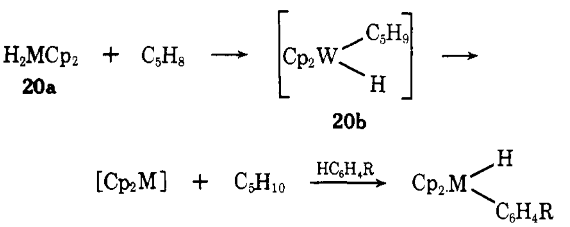
19a

19b

(112)

while diphenylacetylene and azobenzene give hydrogenated product and substituted metal complex **19b**.

Green and Knowles[187] observed formation of a phenyltungsten derivative **20c** (R = H or Me) from H_2MCp_2 (M = Mo or W) in benzene or toluene solvent and in the presence of propene which is hydrogenated in the process. Initial addition of M–H to propene giving **20b** is postulated which



20a

20b

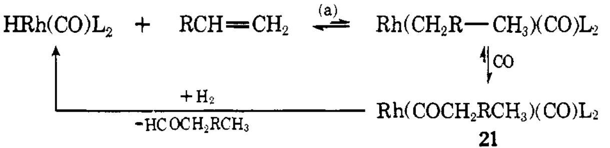
20c

(113)

produces coordinatively unsaturated MCp_2 by elimination of propane from **20b**. The final product results from the insertion of MCp_2 into C–H of the solvent.

4. Hydroformylation

The hydroformylation reaction is the catalyzed addition of the elements of H_2 and CO to olefins. In an attempt to obtain further insight into the hydroformylation reaction, Yagupsky, Brown, and Wilkinson[188] (see also references cited therein) have studied stable analogs such as $Rh(C_2F_4H)(CO)_{3-x}L_x$ or $Ir(COEt)(CO)_2L_2$ of otherwise unisolable reaction intermediates of rhodium catalyst. Except for the fluoroalkyl derivatives (also see below), adducts of M–H to olefins are usually unstable and the equilibrium eq 114a favors starting materials. In the presence of CO, alkyl derivative is stabilized as the acyl complex **21**. This may undergo dissociation of ligand and, in the presence of H_2, proceed rapidly (presumably through oxidative addition of H_2) to aldehyde and hy-



21

(114)

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(179) (a) C. O'Connor and G. Wilkinson, *J. Chem. Soc. A*, 2665 (1968); (b) W. Strohmeier and S. Hohmann, *Z. Naturforsch. B*, **25**, 1309 (1970).

(180) J. C. Bailar, Jr., and H. Itatani, *J. Amer. Chem. Soc.*, **89**, 1592 (1967).

(181) H. A. Tayim and J. C. Bailar, Jr., *ibid.*, **89**, 4330 (1967).

(182) (a) L. Vaska, *Inorg. Nucl. Chem. Lett.*, **1**, 89 (1965); (b) W. Strohmeier and T. Onoda, *Z. Naturforsch. B*, **24**, 1493 (1969); (c) *ibid.*, 461 (1969).

(183) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

(184) B. R. James and N. A. Memon, *Can. J. Chem.*, **46**, 217 (1968).

(185) M. Giustiniani, G. Dolcetti, M. Nicolini, and U. Belluco, *J. Chem. Soc. A*, 1961 (1969).

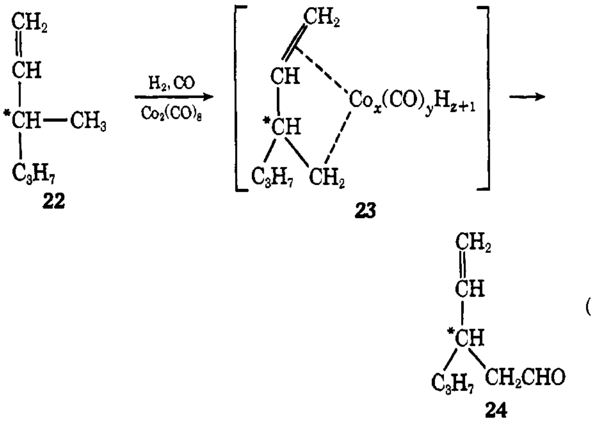
(186) S. Otsuka, A. Nakamura, and A. Minamida, *J. Chem. Soc. D*, 1148 (1969).

(187) M. L. H. Green and P. J. Knowles, *ibid.*, 1677 (1970).

(188) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

dride complex. The intermediate H_2 adduct of the acyl complex is not isolable although an HCl adduct could be obtained. The activation energy for the elementary steps is believed to be very low. It was also observed that $HIr(CO)_2L_2$ effected isomerization of olefins, while $HIr(CO)L_3$ did not. This suggests a possible effect of ligands on the mechanistic pathways and is a parallel to the earlier observation by Evans, Osborn, and Wilkinson[189] that $HRh(CO)L_3$ afforded a higher ratio of straight to branched chain aldehydes in hydroformylation of alkenes as compared to $HRh(CO)_2L_2$.

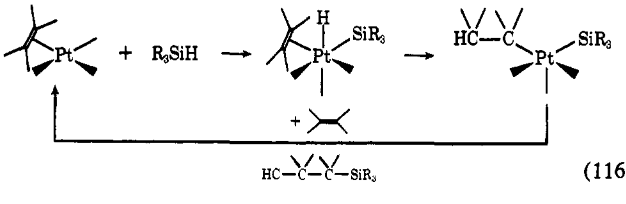
Using optically active substrate, (+)-(*S*)-3-methyl-1-hexene (**22**), Piacenti, *et al.*,[190] have shown that at least 70% of the hydroformylation occurs directly on the methyl group giving (*R*)-3-ethylhexanal (**24**), involving neither racemization nor inversion. This requires that, perhaps through some olefin coordinated intermediate **23**, a CH bond of the methyl group is oxidatively added to Co at which site it is subsequently hydroformylated.



(115)

5. *Hydrosilation*

Addition of M–H to olefins is involved in the hydrosilation reaction; two types of mechanisms are known: eq 116 (Chalk and Harrod,[86] and references cited therein) and eq 117 (Chalk and Harrod[191]).



(116)

$$R'CH{=}CH_2 + HCo(CO)_4 \longrightarrow R'CH_2CH_2Co(CO)_4 \xrightarrow{R_3SiH} R'CH_2CH_2SiR_3 + HCo(CO)_4 \quad (117)$$

In the second of these, considerable olefin isomerization and H–D exchange is observed. The oxidative addition of silanes to transition metal complexes, which is postulated in eq 116 (and which may also take place in eq 117 prior to elimination of alkylsilane) has been discussed in section II.C.2. Transition metal hydrides ($HCo(CO)_4$) are observed to react with silanes to give transition metal silyl derivatives ($Co(SiMe_3)(CO)_4$) together with the elimination of H_2 (Baay and MacDiarmid[192]). However, these are not hydrosilation catalysts, and this reaction may be responsible for deactivation of the catalyst (Chalk and Harrod[191]).

Sommer, Lyons, and Fujimoto[193] have recently demonstrated that the hydrosilation of olefins with a variety of transition metal catalysts proceeds with *retention* of configuration.

Survey by Metal Triads

Information concerning the methods of preparation and some additional pertinent data are presented for each listing in tables for the metal subgroups. We hope these tables will provide much of the information of interest in an easily accessible manner and also serve as a reference where more detailed information is required.

Within each table, the complexes are arranged first according to the atomic number of the metal in the subgroup beginning with the lowest. Mixed metal derivatives are placed in the table for the metal in most abundance in the complex, or if in equal numbers, by the lightest metal. The mixed metal derivatives are placed at the end of each table.

Within the listings of complexes for each metal, the sequence is determined by three parameters. First the number of metal-bonded hydrogen atoms in the complex is given, which, for convenience, is listed *before* the symbol of the metal. Within these groups, first are listed coordinatively saturated complexes (18 electron) and then others in decreasing number of electrons around the metal. Polynuclear complexes appear after the mononuclear complexes and before the mixed metal complexes. Following the symbol of the metal are listed the anionic or σ-bonded groups followed by neutral electron pair donors.

Abbreviations used in the tables are the following.

br = brown
bf = buff
bl = black
c = colorless
cr = cream
d = decomposition
D = deuterium
g = green
gy = gray
o = orange
p = pink
R = Raman
r = red
v = violet
w = white
y = yellow

G. TITANIUM, ZIRCONIUM, AND HAFNIUM

There are only a few reports of complex hydrides for members of the titanium triad. Recently Brintzinger[108] has reformulated "titanocene" as a bridged hydride containing one cyclopentadienylidene (C_5H_4) per metal. Reaction of "$(C_{10}H_{10}Ti)_2$" with HCl produces the dimeric chloride $(C_{10}H_9TiCl)_2$ and 1 mol of hydrogen gas per mole of titanium. The dichloride was characterized from its mass spectrum. That of the parent hydride contains doubly ionized peaks instead of the ion $C_{10}H_{10}M^+$ which is the most abundant for other metallocenes. In addition, peaks which correspond to the loss of one or more molecules of H_2 are found next to the parent ion. The infrared spectrum of the dihydride contains a strong absorption at 1230 cm^{-1}, the region attributed to the antisymmetric stretching mode of bridged hydrides, which is absent in the spectrum of the dichloride.

Based on the novel intramolecular substitution of a C_6H_4 ring observed in the structure of **25**, Hoxmeier, Deubzer,

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(189) D. Evans, J. A. Osborn, and G. Wilkinson, *J. Amer. Chem. Soc. A*, 3133 (1968).

(190) F. Piacenti, S. Pucci, M. Bianchi, R. Lazzaroni, and P. Pino, *J. Amer. Chem. Soc.*, **90**, 6847 (1968).

(191) A. J. Chalk and J. F. Harrod, *ibid.*, **89**, 1640 (1967).

(192) Y. L. Baay and A. G. MacDiarmid, *Inorg. Nucl. Chem. Lett.*, **3**, 159 (1967).

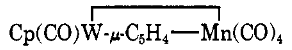
(193) L. H. Sommer, J. E. Lyons, and H. Fujimoto, *J. Amer. Chem. Soc.*, **91**, 7051 (1969); **90**, 4198 (1968).

Table I

Survey of Hydride Complexes: Ti, Zr, Hf

Complex	*Preparation*	*Color*	*Mp, °C*	*^1H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$[HTiCp_2]_2$	H_2 + 0.25 atm + $TiCp_2Me_2$	v	70 d				1450/1260, 1050	195
$[HTiC_{10}H_9]_2$	Na + $TiCp_2(CH_3)_2$						1230	108
$HZrCp_2BH_4$	$(CH_3)_3N + ZrCp_2(BH_4)_2$	w	60^a	5.47	1		1945	60
$[H_2ZrCp_2]_n$	$(CH_3)_3N + ZrCp_2(BH_4)_2$	w					1540	60

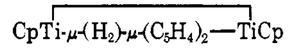
^{a} Sublimes.



$Cp(CO)W\text{-}\mu\text{-}C_5H_4\text{—}Mn(CO)_4$

25

and Kaesz[107] proposed similar arrangement in the bridged titanocene **26**. A structure containing just this type of intramolecular bridging C_5H_4 group has been found for nio-

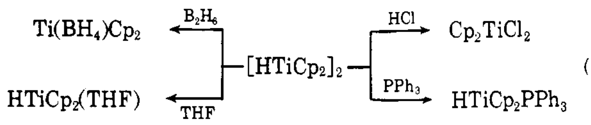


$CpTi\text{-}\mu\text{-}(H_2)\text{-}\mu\text{-}(C_5H_4)_2\text{—}TiCp$

26

bocene and tantalocene[194] (see **27**).

Bercaw and Brintzinger[195] have isolated $[HTiCp_2]_2$, which contains double hydride bridges, and have studied its chemistry. This diamagnetic, pyrophoric, violet solid reacts with HCl, B_2H_6, THF, and PPh_3 as shown in eq 118.



(118)

Earlier a titanium(III) complex, active in nitrogen fixation reactions, was postulated by Brintzinger[67,68] to be a dimeric hydride from electron paramagnetic studies. However, in a subsequent more highly resolved spectrum he observed[66] each component of the previously reported triplet to be split into a number of hyperfine lines. The triplet was due to coupling of the electron to two equivalent hydrides and the hyperfine splitting arose from coupling to the ten equivalent protons on the cyclopentadienyl rings. Since the spectrum could not be explained by coupling to 20 equivalent protons, the dimer was ruled out. The proposed monomeric bis(π-cyclopentadienyl)titanium(III) dihydride complex bears a structural resemblance to the well-known complexes $H_2Mo(\pi\text{-}C_5H_5)_2$ and $H_2W(\pi\text{-}C_5H_5)_2$ except that the titanium complex is immediately decomposed by weak acids instead of undergoing protonation. A similar titanium complex is observed by Henrici-Olivé and Olivé[196] when Cp_2TiCl_2 is reduced with alkali naphthalide in tetrahydrofuran solution; in this instance, the hyperfine pattern is due to coupling to a closely associated alkali metal ion. Although the arguments for the monomeric titanium complex are strong, the intriguing observation persists that under nitrogen a molar ratio of $NH_3/Ti = 1$ (*i.e.*, $N_2/Ti = 0.5$) could not be exceeded, which points strongly to a complex containing two titanium atoms.[196] The role of a titanium hydride in this nitrogen fixation process is still under debate.[197,198]

Evidence for a monohydrido monoisopropyl complex Cp_2TiPr^i has been obtained by epr but not characterized further.[66]

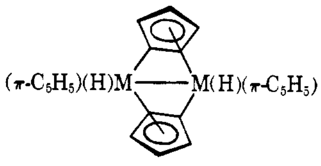
Two hydride complexes of zirconium have been reported by James, Nanda, and Wallbridge.[60] Both are products of the reaction of trialkylamines and bis(π-cyclopentadienyl)-zirconium bistetrahydroborate, $(C_5H_5)_2Zr(BH_4)_2$, as shown in eq 41. The derivative H_2ZrCp_2 was insoluble and nonvolatile and difficult to characterize; the metal hydride resonance was assigned at τ 5.47 which is unusually low for transition metal derivatives.[60]

H. VANADIUM, NIOBIUM, AND TANTALUM

There are known vanadium hydride complexes, but none have been the objects of recent investigations.

An unusual niobium hydride, HNb_6I_{11}, has been reported by Simon.[199] This may be the first example of a hydrogen atom fully enclosed in a cage of metals. It is formed when the lower iodide Nb_6I_{11} is heated under 1 atm of hydrogen above 300° absorbing one hydrogen atom per niobium octahedron. Other metal halide clusters did not seem to react similarly. It is believed from neutron diffraction studies on both the hydride and deuteride that the hydrogen atom occupies the center of the niobium cluster. The interaction of the hydrogen atom electron with the unpaired electron of the cluster is sufficient to substantially reduce the paramagnetism at room temperature and quench it entirely at 200°K.

The tantalum hydride $HTaCp_2PEt_3$ is obtained by heating H_3TaCp_2 in the presence of PEt_3.[31] Its exchange with D_2 has been discussed in section II.A.3. Niobocene and tantalocene have been shown to exist as binuclear dihydrido complexes containing bridging C_5H_4 groups, structure **27**;[194] see also discussions in section III.G.



M = Nb, Ta

27

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(194) (a) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971); (b) L. J. Guggenberger and F. N. Tebbe, *ibid.*, **93**, 5924 (1971).

(195) J. E. Bercaw and H. H. Brintzinger, *ibid.*, **91**, 7301 (1969).

(196) G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, 7, 386 (1968).

(197) E. E. Van Tamelen and H. Rudler, *J. Amer. Chem. Soc.*, **92**, 5253 (1970).

(198) E. E. Van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *ibid.*, **92**, 5251 (1970).

(199) A. Simon, *Z. Anorg. Allg. Chem.*, **355**, 311 (1967).

Table II

Survey of Hydride Complexes: V, Nb, Ta

Complex	*Preparation*	*Color*	*Mp*	*^{1}H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir*	*Ref*
HNb_6I_{11}	H_2 + 430° + Nb_6I_{11}							199
$HTaCp_2PEt_3$	$PEt_3 + H_3TaCp_2$	r		19.48	2	21		31

Table III

Survey of Hydride Complexes: Cr, Mo, W

Complex	*Preparation*	*Color*	*Mp, °C*	*^{1}H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$HCrSiCl_3(CO)_2C_6H_6$	$h\nu + SiCl_3 + Cr(\pi\text{-}C_6H_6)(CO)_3$		114	20.5	1			91
$HCr_2(CO)_{10}^-$	$NaBH_4 + Cr(CO)_6$	y		29.47	1			47, 48, 200
$HMoCp(CO)_2P(OPh)_3$	$H^+ + Na/Hg + Hg[MoCp(CO)_2L]_2$							119
	$(CH_3)_3CCl + [Mo(CO)_2CpL]^-$	p	106	16.63	2	72		127
$HMoCp(CO)_2P(OMe)_3$[a]	$H^+ + Na/Hg + Hg[MoCp(CO)_2L]_2$							120
	$L + HMoCp(CO)_3$		42	16.74	2	61.8		160
	$H^+ + Na/Hg + MoICp(CO)_2L$	y	181	16.71	2	62.3		119
$HMoCp(CO)[P(OMe)_3]_2$	$H^+ + Na/Hg + [MoCpCOL]^-$	c	Oil	17.46	3	64.5		118
$HMo(Cp)(CO)(C_4Ph_4)$	$(CH_3)_3CMgCl + Mo(CO)(C_4Ph_4)(Cp)X$	y	174	16.83	1		1818	201
$HMo_2(CO)_{10}^-$	$NaBH_4 + Mo(CO)_6$	y		22.15	1			47
$HWCp(CO)_2PPh_3$	$L + HWCp(CO)_3$		172	18.00	2	18		160
$HWCp(CO)_2P(OMe)_3$	$H^+ + Na/Hg + Hg[WCp(CO)_2L]_2$	y		17.85	2 × 3	66, 46[b]		119
$HW(Cp)_2(C_6H_5)$	C_6H_5/120°/3 days + $H_2W(Cp)_2$	y		21.1	2	0.7		187
	$Na/Hg/H_2 + t\text{-}WCl_4(PMe_2Ph)_2$	y		21.1	2	0.7		29
$HW_2(CO)_{10}^-$	$NaBH_4 + W(CO)_6$			22.52	1			47
$H_2W(Cp)_2 \cdot AlMe_3$	$Al_2Me_6 + H_2WCp_2$	y		23	11	0.7	1898	202
$H_2W(Cp)_2W(CO)_5$	$W(CO)_5THF + H_2WCp_2$			25.18[b]				203
$H_6W(PMe_2Ph)_3$	$Na/Hg + H_2/THF + t\text{-}WCl_4L_2$							29
	$NaBH_4 + t\text{-}[WCl_4(PMe_2Ph)_2]$	w	110 d	11.94	4	36.9	1834, 1792, 1755, 1731	204
$HCrMo(CO)_{10}^-$	$NaBH_4 + Cr(CO)_6/Mo(CO)_6$			25.31	1			47
$HCrW(CO)_{10}^-$	$NaBH_4 + Cr(CO)_6/W(CO)_6$			25.43	1			47
$HMoW(CO)_{10}^-$	$NaBH_4 + Mo(CO)_6/W(CO)_6$			22.37	1			47

[a] See also, L = PPh_3, $P(OCH_2)_3CEt$, $P(OPh_3)_3$, $P(Bu^n)_3$, $SbPh_3$. [b] ^{183}W satellites observed.

I. CHROMIUM, MOLYBDENUM, AND TUNGSTEN

The carbonyl hydride anions $[HM_2(CO)_{10}]^-$ (M = Cr, Mo, W) have been fully characterized.[47,48,200] The synthesis of these was discussed in section II.B. The anions are typically yellow and the tungsten complex may be briefly exposed to air without decomposition. Hetero bimetallic hydrides can be obtained either by reduction of equimolar mixtures of the hexacarbonyls of any two of these metals or by scrambling reactions of pairs of anions. Although never isolated as pure compounds, the appearance of the mixed metal derivatives were observed *via* new proton resonances in the metal hydride region. The proton chemical shifts of the various hydride anions are further discussed in section IV.B and the X-ray crystalllgraphic data in section V.

A stable chromium hydride has been reported as the product of a photochemical reaction of $HSiCl_3$ and $(\pi\text{-}C_6H_6)Cr(CO)_3$; see section II.C.2. Similarly the dimeric tungsten complex $[HW(CO)_4SiEt_2]_2$ results from the irradiation of tungsten hexacarbonyl in the presence of diethylsilane; it is believed to contain two Si–H–W bridges.[205]

The series of derivatives $Cp_2MH_2 \cdot M'(CO)_5$ (M = Mo, M′ = Cr, Mo, W; M = W, M′ = Cr, Mo, W) have been prepared by Deubzer and Kaesz.[203] These are believed to be best represented by the donor–acceptor formulation **42a** by interpretation of the metal–proton splittings in the nmr; see section IV.B. The hydrides H_2MCp_2 (M = Mo, W) participate in a novel intramolecular aromatic substitution derived from their reactions with $CH_3Mn(CO)_5$; see eq 79.

The molybdenum hydride $HMoCp(CO)_2P(OPh)_3$ is believed to result from a dehydrohalogenation of either *tert*-butyl chloride or isopropyl bromide (see eq 89). The same compound reported by Manning[118] is obtained by borohydride reduction of $CpMoI(CO)_2P(OPh)_3$. He assigns hydride trans to the phosphite ligand on the basis of infrared and nmr evidence.

Bainbridge, Craig, and Green[160] have measured the kinetics of substitution of L into $HMoCp(CO)_3$ to give derivatives

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(201) R. B. King and A. Efraty, *J. Chem. Soc. D*, 1370 (1970).

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(203) B. Deubzer and H. D. Kaesz, *J. Amer. Chem. Soc.*, **90**, 3276 (1968).

(204) J. R. Moss and B. L. Shaw, *Chem. Commun.*, 632 (1968).

(205) M. J. Bennett, W. L. Brooks, M. Cowie, W. A. G. Graham, T. E. Haas, J. Hoyano, and K. A. Simpson, Joint Conference of the Chemical Institute of Canada and the American Chemical Society, Toronto, May 24–29, 1970.

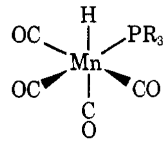
such as $HMoCp(CO)_2L$. The kinetics show dependence of substitution on ligand which rules out dissociation or intermediate acyl derivatives as in the case of methyl migration in the substitution of $MeMn(CO)_5$. The absence of a kinetic isotope effect also rules out migration of hydrogen in the rate-determining step.

The tetraphenylcyclobutadiene derivative $MoCp(CO)C_4Ph_4Cl$ is reported to react with Me_3CMgCl in diethyl ether to give the hydride derivative $HMoCp(CO)C_4Ph_4$.[201] This is very likely another example of a β elimination of olefin from an (intermediate) alkyl derivative; see section II.C.1.

The hexahydridotungsten complex $H_6W(PMe_2Ph)_3$ has been prepared by two independent synthetic routes. Moss and Shaw[204] first made hexahydridotris(dimethylphenylphosphine)tungsten(VI) by the borohydride reduction of *trans*-$[WCl_4(PMe_2Ph)_2]$. Later this white, air-stable complex was believed more conveniently prepared by the sodium amalgam reduction under hydrogen gas of the same starting material[29] (see eq 18). This represents the first of the series of hydridophosphinetungsten complexes $H_{6-2n}WL_{3+n}$, where $n = 0, 1, 2$, which are analogous to the known rhenium compounds $H_{7-2n}ReL_{2+n}$, $n = 0, 1, 2$.

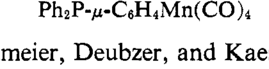
J. MANGANESE, TECHNETIUM, AND RHENIUM

The ^1H spectra for $HMn(CO)_4PR_3$ have now been reported by Hieber and Duchatsch,[116] and also Booth and Haszeldine.[206] These consist of doublets; R = Ph, τ 16.94, $J_{PH} = 34$ Hz; and R = (OPh), τ 17.95, $J_{PH} = 55$ Hz. The coupling constants support cis structural assignments as concluded from earlier arguments based on infrared studies. Whitesides and Maglio[207] have analyzed the proton magnetic resonance spectrum for hydrogen–carbon-13 spin–spin couplings, discussed in section IV.B.

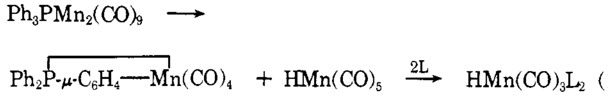


28

Booth and Haszeldine[206] have also obtained disubstituted $HMn(CO)_3L_2$ from the reaction of $HMn(CO)_5$ with L. They report evolution of H_2 in the heating of $HMn(CO)_2(P(OMe)_3)_2$ to give an unidentified compound. It seems likely that this will prove to be an intramolecular substitution product such as


$$Ph_2P\text{-}\mu\text{-}C_6H_4Mn(CO)_4$$

obtained by Hoxmeier, Deubzer, and Kaesz[107] in the heating of $Mn(CH_3)(CO)_4PPh_3$ (see section II.C.3). Ugo and Bonati[209] report isolation of a number of $HMn(CO)_3L_2$ derivatives in the treatment of $Mn_2(CO)_{10}$ with L = PPh_3 or $P(OPh)_3$ in refluxing xylene. The authors were not able to specify the origin of hydride, and it seems to us that a likely source would be the ortho hydrogen of the ligands.


$$Ph_3PMn_2(CO)_9 \longrightarrow$$
$$Ph_2P\text{-}\mu\text{-}C_6H_4\text{—}Mn(CO)_4 + HMn(CO)_5 \xrightarrow{2L} HMn(CO)_3L_2 \quad (119)$$

Hieber, Höfler, and Muschi[117] have prepared a series of disubstituted derivatives, $HMn(CO)_3L_2$, by reduction of the disubstituted halides followed by hydrolysis (see section II. D.1); they obtain both *fac*-$(CO)_3$ and *mer*-$(CO)_3$ derivatives and report their characteristic infrared patterns. Nmr data are discussed in section IV.B.

The mono- and disubstituted triphenylphosphine complexes of $HRe(CO)_5$ have also been prepared by different routes. Freni, Giusto, and Valenti[215] have prepared the disubstituted complex by the reaction of carbon monoxide and $H_5Re(PPh_3)_3$ at elevated temperatures and pressures. These derivatives are also obtained in the reaction of excess phosphine with $HRe(CO)_5$[214a] or with $H_3Re_3(CO)_{12}$ at 173°.[214b] The ^1H–^{31}P coupling pattern is a symmetric triplet and this, combined with the single broad infrared line in the carbonyl region, suggests a *mer*-$(CO)_3$ structure.

Miles and Clark[208] have reacted PF_3 with $HMn(CO)_5$ and report species of all possible compositions $HMn(PF_3)_x(CO)_{5-x}$. Both $HMn(PF_3)_5$ and $HRe(PF_3)_5$ had previously been prepared by Kruck and Englemann;[213] see also Kruck.[6] Miles and Clark[208] had expected to isolate a number of geometric isomers for the various derivatives $HMn(PF_3)_x(CO)_{5-x}$. Instead chromatographic separation repeatedly yielded only one band for each group of isomers of the same ligand to metal ratio, although infrared showed more bands in the carbonyl region than is predicted by group theory for any one isomer. By contrast they were able to isolate various geometric isomers for the PF_3-substituted alkylmanganese compounds. Therefore, they concluded that the geometric isomers were undergoing rapid intramolecular rearrangements precluding physical separation. The alkyl groups evidently hindered these rearrangements. Nmr studies by Whitesides and Maglio[207] on $HMn(CO)_5$ indicate that the barrier to rearrangement is probably greater than 16 kcal/mol, greater than would permit rapid rearrangement as indicated for the PF_3-substituted derivatives.

Osborne and Stone[221] have studied the reaction of pentacarbonyl hydrides of manganese and rhenium with pentafluorobenzenethiol and benzenethiol. Only the perfluoro ligands stabilized the monomeric complexes $C_6F_5S \cdot M(CO)_5$ sufficiently to allow isolation. The other products were dimeric with the stoichiometry $[PhS\text{–}M(CO)_4]_2$, Ph = C_6H_5 or C_6F_5.

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Table IV

Survey of Hydride Complexes: Mn, Tc, Re

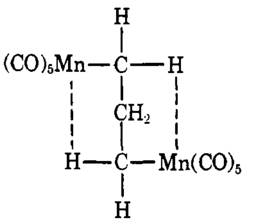
Complex	*Preparation*	*Color*	*Mp, °C*	*^1H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$HMn(PF_3)_5$	Uv + L + $HMn(CO)_5$	c	18.5				1845/1290	208
$HMn(CO)(PF_3)_4$	Uv + L + $HMn(CO)_5$	c	−56				1835/1290	208
$HMn(CO)_2(PF_3)_3$	Uv + L + $HMn(CO)_5$	c	−108				1823/1290	208
$HMn(CO)_3(PF_3)_2$	Uv + L + $HMn(CO)_5$	c	−73				1806/1290	208
$HMn(CO)_4PF_3$	Uv + L + $HMn(CO)_5$	c	−56				1790/1290	208
$HMn(CO)_4PPh_3$	L + $HMn(CO)_5$		137	16.94	2	34		116, 206
$HMn(CO)_4P(OPh)_3$	L + $HMn(CO)_5$			17.95	2	55		116
t-$HMn(CO)_3[PPh_3]_2$	L + $HMn(CO)_5$	y	210 d	17.4	3	29		117, 206, 209
t-$HMn(CO)_3[P(OPh)_3]_2$	L + $HMn(CO)_5$	y	84	18.00	3	50		206
	$H^+ + \{Mn(CO)_3[P(OPh)_3]_2\}^-$	y	84					117
	L + $Mn_2(CO)_{10}$	w	87 d	18.13	3	50		209
c-$HMn(CO)_3[P(OPh)_3]_2$	L + $HMn(CO)_5$	y	d					206
t-$HMn(CO)_3[PMe_2(OPh)]_2$	L + $HMn(CO)_5$	y		18.0	3	45		206
$HMn(CO)_3$diphos	L + $HMn(CO)_5$	y		17.8	3	45		206
$HMnSiCl_3Cp(CO)_2$	Uv + $HSiCl_3$ + $CpMn(CO)_3$		82	19.7	1			91
$HMn_3(BH_3)_2(CO)_{10}$	$NaBH_4$ + $Mn_2(CO)_{10}$	r		29.0				57
$H_3Mn_3(CO)_{12}$	H^+ + KOH + $Mn_2(CO)_{10}$	r	60[b]	34.0	1			210, 211
$HTc(Cp)_2$	$NaBH_4$ + NaCp + $TcCl_4$	g	150	17.8	Br		1923	212
$H_2Tc(Cp)_2^+$	H^+ + $HTc(Cp)_2$	w		17.7	Br		1984	212
$HRe(PF_3)_5$	H^+ + $Re(PF_3)_5^-$	c	42	18.2	1		1882	213
$HRe(CO)_4PPh_3$[a]	L + $HRe(CO)_5$	w		14.33	2	22	1828	214a
	L + $H_3Re_3(CO)_{12}$	w	100[b]	15.07	2	23		214b
$HRe(CO)_3(PPh_3)_2$	L + $H_3Re_3(CO)_{12}$	w	246	14.45	3	18.5		214b
	L + $H_5Re(PPh_3)_3$	w	207 d	15.35	3	17.5		215
$HRe(CO)_3(diphos)$[c]	diphos + $HRe(CO)_5$	w		15.20	3	26.0	1784	214a
$HReCp_2 \cdot AlMe_3$	$HReCp_2$ + Al_2Me_6	y		22.7	11	0.8		202
$HReCl(acac)(PPh_3)_3$[d]	HX + $H_2Re(acac)L_3$	y	176	11.8	4	58.9	2140	225a
$HRe_2Cl(CO)_8$	Ph_3SiCl + $NaRe(CO)_5$							216
$HReI_2(acac)(PPh_3)_2$[e]	X_2 + $H_2Re(acac)L_3$	v	181	*e*			1980, 1960	225a
$HRe_3(CO)_{14}$	$NaBH_4$ + $Re_2(CO)_{10}$	y		26.25	1			52
$H_2ReCl(diphos)_2$	$^1/_2Cl_2$ + $H_3Re(diphos)_2$	y	172 d	17.9	5	14.4	2040, 2020	40
$H_2ReBr(diphos)_2$	$^1/_2Br_2$ + $H_3Re(diphos)_2$	y	178	20.0	5	16	2030, 2010	40
$H_2ReI(diphos)_2$	$^1/_2I_2$ + $H_3Re(diphos)_2$	y	185 d	21.6	5	24	2050	40
$H_2ReBrCO(PPh_3)_3$[f]	EtOH + L + H_4ReXL_3	b	163	11.85	4	25	1950, 1910, 1880	215b
$H_2ReI(PPh_3)_2(diphos)$	$^1/_2I_2$ + $H_3Re(PPh_3)_2(diphos)$	y	135	15.0	5	26	2040, 2000	40
$H_2Re(acac)(PPh_3)_3$	Na(acac) + H_4ReXL_3	o	114				2115	225a
$H_2Re_2Si(CH_3)_2(CO)_8$	Uv + $(CH_3)_2SiH_2$ + $Re_2(CO)_{10}$	y	115 d	20.56	7	4.2		217
$H_2ReSiPh_2(CO)_8$	Uv + Ph_2SiH_2 + $Re_2(CO)_{10}$	c	168	19.56	1			217
$H_2Re_3(CO)_{12}^-$	$NaBH_4$ + $Re_2(CO)_{10}$	y		27.2	1		1100 R	218
$H_3Re(diphos)_2$	L + $H_5Re(PPh_3)_2$	y	202	16.75	5	24	1860	40
				17.97	5	17		
$H_3Re(PPh_3)_2(diphos)$	L + $H_5Re(PPh_3)_2$	y	164	16.27	1		1960, 1900, 1820	40
$H_3Re_2(CO)_6^-$	L + ReH_9^{2-}	y	190 d	27.49	1			219
$H_3Re_3(CO)_{12}$	$NaBH_4$ + $Re_2(CO)_{10}$	w	60[b]	27.1	1	1100 R		51, 220
$H_4ReBr(PPh_3)_3$[f]	X_2 + H_5ReL_3	g	163	11.82	4	24.5	2015, 1930, 1895	215b
$H_4Re(diphos)_2$	H^+ + $H_3Re(diphos)_2$	w	158	15.34	5	19.9	1950	40
$H_4Re(PPh_3)_2(diphos)^+$	H^+ + $H_3Re(PPh_3)_2(diphos)$	w	140	13.88	5	22.1	1970	40
$H_4Re_4(CO)_{12}$	Δ + $H_3Re_3(CO)_{12}$	r		15.08	1			11
$H_5Re(PPh_3)_3$	$LiAlH_4$ + $ReCl_3(PPh_3)_3$	y	164 d	14.64	4	19.0	2000, 1961, 1934, 1912, 1890	17
$H_5Re(AsPh_3)_3$	L + ReH_9^{2-}	y						41
$H_5Re(PEt_2Ph)_3$	$LiAlH_4$ + $ReCl_3(PEt_2Ph)_3$	w	62	16.90	4	18.0	1950, 1947, 1902, 1850, 1830	17
$H_5Re(PEtPh_2)_3$	$LiAlH_4$ + $ReCl_3(PEtPh_2)_3$	w	120	16.0	4	18.0	2006, 1984, 1951, 1905	17
$H_5Re(PPh_3)_2(AsPh_3)$	L + $H_7Re(PPh_3)_2$	y	175 d	15.5	3	19.55	1960, 1938, 1898 1862	17
$H_5Re(PEt_2Ph)(PPh_3)_2$	L + $H_7Re(PPh_3)_2$	w	136 d	15.50	4	18.1	1969, 1936, 1894, 1880	17
$H_5Re(diphos)_2$	L + $H_7Re(diphos)$	w	196 d	16.76	4	17.2	1972, 1934, 1890	17

Table IV (Continued)

Complex	*Preparation*	*Color*	*Mp, °C*	*^1H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$H_5Re(PPh_3)(diphos)$	$L + H_7Re(diphos)$	w	187 d	15.73	4	16.0	1943, 1926, 1888	17
$H_5Re(PPh_3)_2NHC_5H_{11}$	$L + H_7Re(PPh_3)_2$	y	145 d	14.49	3	19.55	2018, 1947, 1916, 1869	17
$H_5Re(PPh_3)_2NC_5H_5$	$L + H_7Re(PPh_3)_2$	y	154 d	14.56	3	19.36	2011, 1953, 1923, 1859	17
$H_5Re(PPh_3)_2NH_2C_6H_{11}$	$L + H_7Re(PPh_3)_2$	y	147 d	14.88	3	19.45	2041, 2014, 1946, 1894, 1838	17
$H_6Re_4(CO)_{12}^{2-}$	$NaBH_4 + Re_2(CO)_{10}$	y		27.4	1			50
$H_7Re(PPh_3)_2$	$LiAlH_4 + ReCl_4(PPh_3)_2$	w	135 d	14.90	3	19.40	1961, 1891/1388	17
$H_7Re(PEt_2Ph)_2$	$LiAlH_4 + ReCl_4(PEt_2Ph)_2$	w	53	15.82	3	19.50	1974, 1922, 1874/1351	17
$H_7Re(PEtPh_2)_2$	$LiAlH_4 + ReCl_4(PEtPh_2)_2$	w	84 d	15.10	3	18.90	1897, 1870	17
$H_7Re(diphos)$	$LiAlH_4 + ReCl_4(diphos)$	w	160	15.71	3	13.5	1967, 1916	17
$H_7Re(AsEt_2Ph)_2$	$LiAlH_4 + ReCl_4(AsEt_2Ph)_2$			16.0	1			17
H_8RePPh_3	$L + ReH_9^{2-}$	w		17.3	2	17.7	1860, 1940, 1980	91
$H_8RePBu^n{}_3^-$	$L + ReH_9^{2-}$	w		18.1	2	18.4	1850, 1920, 1980	41
$H_8RePEt_3^-$	$L + ReH_9^{2-}$	w		18.2	2	17.3	1850, 1920, 1980	41
$H_8ReAsPh_3^-$	$L + ReH_9^{2-}$	w		17.4	1		1850, 1940, 1980	41
$HRe_2Mn(CO)_{14}$	$NaBH_4 + Re_2(CO)_{10} + Mn_2(CO)_{10}$							52

[a] See also L = $P(OEt)_3$, $P(OPh)_3$: ref 214a. [b] Sublimes. [c] See also L–L = 1,2-bis(diphenylphosphinomethane). [d] See also X = Br, I. [e] Compound is paramagnetic; see also X = Cl, Br. [f] See also X = I.

The manganese complex **29**, included by Ginsberg[1] in his review because it was believed to have an unusual metal–hydrogen interaction, has recently been shown by Casey[222] to be a totally different type of derivative. The product contains a metal–carbon bond with a cyclic lactone, **30**. This derivative is formed in the nucleophilic attack of $Mn(CO)_5^-$ on a carbonyl group of the intermediate $Mn(CH_2CH_2CH_2Br)(CO)_5$, followed by elimination of Br^- and cyclization.



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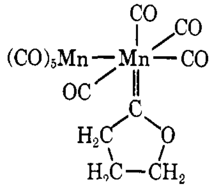

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Photolysis of $MnCp(CO)_3$ in the presence of $HSiCl_3$ produces the adduct $HMnCp(SiCl_3)(CO)_2$ with evolution of CO.[91] This is similar to other oxidative additions reported by these workers (see section II.C.2). This compound displayed a broad hydride resonance in the nmr due to either presence of a mixture of isomers or weak coupling to the cyclopentadienyl protons.

A bridged silicon–manganese hydride bond is known to occur in $HMnCp(SiPh_3)(CO)_2$ also prepared from the photolytic reaction of $HSiPh_3$ and π-$C_5H_5Mn(CO)_3$.[205] The hydride has been unambiguously located in the X-ray structure determination. It occupies an asymmetric bridging position displaced 1.55 Å from manganese and 1.76 Å from silicon and is displaced from the internuclear axis.

Similar products containing hydride-bridged rhenium–silicon bonds are believed to result from the photolysis of $Re_2(CO)_{10}$ and various disubstituted silanes.[205, 217] The products include $R_2SiH_2Re_2(CO)_8$, $(R_2SiH_2)_2Re_2(CO)_6$, $(R_2SiH)_2Re_2(CO)_7$, and $(Ph_2SiH)Re_2(CO)_8$; the structure of the latter has been determined.[217] Although the hydrogen atoms were not located, their positions were inferred from spectroscopic evidence on the bis(dimethyl)silyl derivative. The methyl resonances appeared as a symmetric triplet at τ 8.87 with $J = 1.5$ Hz, whereas the metal hydride resonance was broad consistent with an unresolved septuplet at τ 20.56. When the compound is irradiated at the broad high-field region, the methyl triplet collapses to a singlet. The moderate coupling of 1.5 Hz (compared to 4.5 Hz in free $H_2Si(CH_3)_2$) suggests a bridging hydride with the methyl groups symmetrically disposed about the Re_2Si plane. The conclusion that the hydride is near the silicon in preference to the rhenium is at variance to the known structure $HMnCp(SiPh_3)(CO)_2$ where the hydride was located closer to the manganese atom, as noted above.

Curtis[216] has isolated metal carbonyl cluster complexes in the reaction of Ph_3SiCl with $Re(CO)_5^-$. Among the products, he has isolated $HRe_2Cl(CO)_8$ which was also obtained in the treatment of $H_2Re_2(CO)_8$[217] with CCl_4.[205] Curtis also obtained evidence for the abstraction of oxygen of metal carbonyl groups in the observation of metal carbonyl carbides and hexamethyldisiloxane.[216]

Fischer and Schmidt[212] have prepared dicyclopentadienyltechnetium hydride and its protonated derivative. The hydride is obtained from a sodium cyclopentadienide–sodium borohydride mixture of technetium tetrachloride in THF. It is believed to possess a bent structure similar to that of $HReCp_2$.

Ginsberg and Sprinkle[223] have reported details of the synthesis of various salts of ReH_9^{2-} from sodium perrhenate.

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(222) C. P. Casey, *J. Chem. Soc. D*, 1220 (1970); *J. Amer. Chem. Soc.*, **93**, 3554 (1971).

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Derivative chemistry of this anion has also been investigated;[41,219] several phosphine and carbonyl complexes such as ReH_8L^- (L = PR_3, AsR_3) have been obtained and studied by nmr. The signal for eight rhenium-bonded hydrogen atoms appears as a doublet denoting dynamic isomerization (see section IV.B.1) as also postulated in the parent hydride ReH_9^{2-}.

When ReH_9^{2-} is treated with carbon monoxide in alkaline alcoholic media, the carbonyl hydride anion $H_3Re_2(CO)_6^-$ is obtained.[219] This anion is formulated, on the basis of conductance (1:1 electrolyte), nmr spectrum (typical hydride shift τ 27.49), and infrared spectrum (two ir bands in the CO region expected for D_{3h} symmetry) as a binuclear complex possessing three bridging hydrides. $H_3Re_2(CO)_6^-$ is formally related to the tetranuclear derivative $H_6Re_4(CO)_{12}^{2-}$ (Kaesz, *et al.*)[50] in the same sense that P_2 is related to P_4. The binuclear hydrides were shown by Hawkes and Ginsberg[224] to undergo further reaction with hydrohalic acids to produce the dianionic rhenium carbonyl halides $Re(CO)_3X_3^{2-}$ and $Re_2(CO)_6X_4^{2-}$ where X = Cl, Br.

Chatt and Coffey[17] have prepared and characterized a number of hydridorhenium complexes containing tertiary phosphines. The hydrides were obtained by lithium aluminum hydride reduction of various phosphine-substituted chlorides, oxychlorides, and alkoxy oxychlorides of rhenium (see eq 29 and 30). They observed that the complex $H_7Re(PEt_2Ph)_2$ is converted to the deuteride when heated in deuteriobenzene at 100°. This catalytic exchange may be similar to that observed by Barefield, Parshall, and Tebbe[31] in the system containing H_3TaCp_2 (see sections II.A.3 and III.H).

Freni, Demichelis, and Giusto[40] have reported the hydrogen displacement reaction on H_5ReL_3 (L = PPh_3) with diphos to give the series of complexes H_3ReL_2(diphos) and $H_3Re(diphos)_2$. These can be readily and reversibly protonated to give the corresponding tetrahydrido cationic complexes.

$$H_5ReL_3 + \text{diphos} \longrightarrow H_2ReL_2\text{diphos} \quad (120)$$

$$H_3ReL_2\text{diphos} + H^+ \longrightarrow H_4ReL_2\text{diphos}^+ \quad (121)$$

$$H_3ReL_2\text{diphos} + Cl_2 \longrightarrow H_4ReL_2\text{diphos}^+Cl^- + H_2ReL_2\text{diphosCl} \quad (122)$$

Reaction of trihydrides with halogens yield mixtures of dihydride and cationic tetrahydrido species, which result from the protonation of a molecule of starting material by the HCl produced in the reaction.

The reaction of H_5ReL_3 with halogen or $SnCl_2$ produces the derivatives H_4ReXL_3 (X = Br, I, $SnCl_3$; L = PPh_3, $P(C_6H_4CH_3)_3$);[215b] further reaction of these derivatives with ethanol and excess ligand yields the carbonyl containing complexes $H_2ReX(CO)L_3$ (X = Br, I; L = PPh_3). The reaction of H_4ReXL_3 (X = Cl, Br, I; L = PPh_3) with acetylacetone and excess L gives the derivatives $HRe(acac)XL_3$;[225a] with the sodium salt of acac the dihydride is obtained, $H_2Re(acac)L_3$. Reaction of the dihydride with either HCl or I_2 gives the *paramagnetic* monohydrides, $HRe(acac)X_2L_2$.[225a]

The tertiary phosphine substituted trihydrides of rhenium, H_3ReL_4 and H_3ReL_2 (L = PPh_3), react with nitric acid to give the compound $Re(NO)_2L_2(NO_3)_2$, a nonelectrolyte and paramagnetic substance.[225b]

The derivative $HRe_3(CO)_{14}$ is one of many which can be isolated in the reduction of $Re_2(CO)_{10}$ with $NaBH_4$[52] (see also section II.B). This complex reacts at room temperature with CO to give $HRe(CO)_5$ and $Re_2(CO)_{10}$;[226] experiments with ^{13}CO have shown that in the $Re_2(^{13}CO)(^{12}CO)_9$ thus produced, the label is stereospecifically incorporated in the *radial* position. Similar facile CO cleavage is observed for $H_4Re_4(CO)_{12}$;[11] the products observed in this reaction are $HRe(CO)_5$ and $H_3Re_3(CO)_{12}$. The derivative $H_4Re_4(CO)_{12}$ can be considered unsaturated in the sense that it lacks four electrons from a closed valence shell of 60 electrons as found in $H_4M_4(CO)_{12}$ (M = Ru, Os).[10,53] Thus, $H_4Re_4(CO)_{12}$ may be treated with $NaBH_4$ in a heterogeneous reaction using cyclohexane solvent to give the known $H_6Re_4(CO)_{12}^{2-}$ salt.[11]

K. IRON, RUTHENIUM, AND OSMIUM

The complex $H_2Os(CO)_4$ and its less stable ruthenium analog have been prepared by various routes (see eq 3–5 and section II.D.1). These derivatives have cis H_2 configuration (see also discussion of M–H, CO resonance interaction, section IV.A). With PPh_3, $H_2Os(CO)_4$ gives the substituted derivatives *fac*-$H_2Os(CO)_3L$.[8] Such derivatives may also be obtained by treatment of $Os(CO)_4L$ with hydrogen (see eq 6). Reaction of the hydride $H_2Os(CO)_4$ with CCl_4 or CBr_4 gives the corresponding halides, *cis*-$OsX_2(CO)_4$, while $H_2Ru(CO)_4$ gives $[Ru(CO)_3Cl_2]_2$. Reaction of $H_2Ru(CO)_4$ with iodine yields *cis*-$RuI_2(CO)_4$ which transforms to $[Ru(CO)_3I_2]_2$ on standing.[8,9] Reaction with triphenylphosphine forming $H_2Ru(CO)_2(Ph_3P)_2$ is also reported.

A recent review by Bruce and Stone[227] covering the chemistry of $Ru_3(CO)_{12}$ includes a section on the chemistry of $H_2Ru(CO)_4$ and its dianion $Ru(CO)_4^{2-}$.

The proton resonance of $H_2Ru(CO)_4$ occurs at τ 17.62 in pentane compared to τ 18.73 in heptane for the osmium compound and τ 20.8 for $H_2Fe(CO)_4$.[1] The stability increases with increasing atomic number, and the changes in chemical shifts satisfy the qualitative observation of Ginsberg,[1] showing a decrease from Fe to Ru and then an increase going further down in a column of the periodic table.

Iqbal and Waddington[228] report the isolation of the yellow-orange salt $[HFe(CO)_5]^+PF_6^-$ from $Fe(CO)_5$ in liquid hydrogen chloride; this is an improvement over earlier preparations.

Stable protonated species have been produced in the treatment of $Os(CO)_3L_2$ (L = PPh_3) with various strong acids, HCl, HBr, $HClO_4$, HBF_4, and HPF_6.[130b] Infrared spectra in the CO stretching region indicate trans arrangement of L_2; carbonyl groups are not displaced from cation in the presence of an excess of $PMePh_2$ even under vigorous conditions. The hydrido cations are also inert to phosphine exchange.

$Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have been protonated in 98% H_2SO_4 producing stable solutions and yielding the solid salts, $[HRu_3(CO)_{12}^+]PF_6^-$ and $[HOs_3(CO)_{12}^+]PF_6^-$.[143] The structures of these salts and the isoelectronic anion HRe_3-

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[224] M. J. Hawkes and A. P. Ginsberg, *Inorg. Chem.*, **8**, 2189 (1969).

[225] (a) M. Freni, P. Romiti, and D. Giusto, *J. Inorg. Nucl. Chem.*, **32**, 145 (1970); (b) M. Freni, D. Giusto, and V. Valenti, *Gazz. Chim. Ital.*, **94**, 797 (1964).

[226] R. W. Harrill and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **2**, 69 (1966).

[227] M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, **80**, 460 (1968); *cf. Angew. Chem. Int. Ed. Engl.*, **7**, 427 (1968).

[228] Z. Iqbal and T. C. Waddington, *J. Chem. Soc. A*, 2958 (1968).

$(CO)_{12}^{2-}$ (Kirtley, *et al.*[229]) are presumed to be similar on the basis of similar carbonyl absorption patterns in the infrared. The hydrogen atom in the latter has been located (by indirect means) in a position bridging one edge of the triangle of metal atoms. Protonation of other iron compounds is discussed in section II.E.1.

Ultraviolet irradiation of $Fe(CO)_5$–$HSiCl_3$ mixtures has produced *cis*-$HFe(SiCl_3)(CO)_4$.[91] This volatile air-sensitive liquid is also believed to be the intermediate in the thermal reaction leading to *cis*-$Fe(SiCl_3)_2(CO)_4$. The complex $HFeCp(SiCl_3)_2CO$ can be obtained either photochemically from $CpFe(SiCl_3)(CO)_2$ and $HSiCl_3$ or thermally by the action of Cl_3SiH on $[CpFe(CO)_2]_2$.

The reaction of iodosilane and $Na_2Fe(CO)_4$ *in vacuo* produces the iron hydrides $HFe(SiH_3)(CO)_4$ and $H_2Fe(CO)_4$ in 5 and 2% yields, respectively.[249] The principal product $Fe(SiH_3)_2(CO)_4$ (70%) is easily cleaved by hydrogen chloride gas to the hydrides $HFe(SiH_3)(CO)_4$ and $H_2Fe(CO)_4$. The presence of amines seemed to facilitate these reactions.

Sacco and Aresta[45] report nitrogen complexes $H_2Fe(N_2)L_3$ (L = PEt_2Ph, $PBuPh_2$). Later work[44] has shown that the original complexes isolated in the reduction of iron(II) halide with $NaBH_4$ are the tetrahydrido species which can be heated to give coordinatively unsaturated complexes or can be treated with nitrogen to give the nitrogen complex

$$\mathrm{FeCl_2{\cdot}H_2O} + \mathrm{L} + \mathrm{NaBH_4/EtOH} \longrightarrow$$

$$\begin{tikzcd} & \mathrm{H_2FeL_3} + \mathrm{H_2}\ \ \mathbf{31a} \arrow[d, "N_2"] \\ \mathrm{H_4FeL_3} \arrow[ur, "\Delta"] \arrow[r, "N_2"] & \mathrm{H_2Fe(N_2)L_3}\ \ \mathbf{31b} \end{tikzcd} \qquad (123)$$

(eq 123). The hydridoiron nitrogen complex **31b**, in the presence of sunlight, is observed to evolve H_2 (reversibly) forming an intramolecular substitution compound involving the ortho position of the phenyl group of the ligand. The nitrogen molecule in **31b** can be replaced by CO under mild conditions.[45]

When either $RuCl_3$ or $Ru(acac)_3$ is treated with $AlEt_3$ in the presence of PPh_3, the light yellow dihydride is obtained, H_2RuL_4 (see Ito, *et al.*,[18] and references cited therein). Through loss of L, this complex may either coordinate a molecule of nitrogen or hydrogen, which derivatives may be converted into each other (see eq 11). This compound is also observed to participate in intramolecular substitution of phenyl ring on ligand, which will give ortho deuteration in the presence of D_2 (see section II.C.3).

$H_2Ru(PPh_3)_4$ has also been obtained in the reaction of triphenylphosphine and $H_4Ru(PPh_3)_3$. The latter complex results from the treatment of $HRuCl(PPh_3)_3$ with triethylaluminum followed by hydrogenation with molecular hydrogen.[14] A mixture of $H_2RuN_2(PPh_3)_3$ and $H_2RuNH_3(PPh_3)_3$ in THF loses hydrogen forming a complex believed to be the tetraruthenium cluster $Ru_4(NH_3)_3(PPh_3)_5$.[14] $H_2RuN_2(PPh_3)_3$ readily exchanges hydrogen with the ortho hydrogens of the ligand phenyl groups.

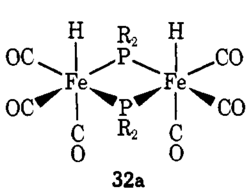
The complex $HRuCl(PPh_3)_3$ is a very active catalyst for hydrogen of alk-1-enes in benzene or toluene solutions.[236, 239] This complex catalyzes olefin isomerization, and with deuterium slow substitution into the ortho positions of the phenyl rings of ligand is observed (*cf.* section II.C.3).

Chloride ion can be replaced by dinitrogen in the cationic hydride *trans*-$HFeCl(depe)_2^+$.[231] Nitrogen is in turn displaced by carbon monoxide in this compound.

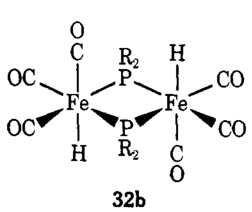
The tetrahydrides of osmium, H_4OsL_3 (L = tertiary phosphines or arsine), were inert toward N_2 up to 150 atm. They did, however, react with toluene-*p*-sulfonyl azide forming $H_2OsN_2L_3$ (L = $PEtPh_2$) which decomposes at 20°.[244] Thus, there is evidence that the order of stability of the hydride dinitrogen complexes of the iron triad is Fe > Ru > Os.

The complex *trans*-$H_2Fe[P(OEt)_3]_4$ precipitates in 40% yield from iron halide solutions treated with sodium borohydride.[46] The proton nmr data indicate rapid tautomerism (see section IV.D).

The binuclear dihydride $H_2Fe_2(CO)_6[P(CF_3)_2]_2$, prepared by the reaction of $(CF_3)_2PH$ with either $Fe(CO)_5$ or $Fe_3(CO)_{12}$, exists as cis and trans isomers in solution (**32** and **32b**, R = CF_3).[235] The ratio of isomers was shown through nmr integration studies to be 5:9 cis:trans. An ^{57}Fe Mössbauer spectrum supports the gross bioctahedral structure without detailing the hydride positions since each Fe nucleus is bound to the same atoms.



32a



32b

Chatt, Leigh, and Paske[70] have characterized the paramagnetic hydride $HOsCl_2(PBu^n{}_2Ph)_3$, which they isolated from the reaction of hydrazine with $OsCl_3(PBu^n{}_2Ph)_3$. The red solid melts at 139–142° and has a magnetic moment at room temperature of 1.9 BM. Boiling carbon tetrachloride converted this trans complex into another unspecified para-

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Table V

Survey of Hydride Complexes: Fe, Ru, Os

Complex	*Preparation*	*Color*	*Mp, °C*	*^1H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$HFe(CO)_5^+$	$H^+ + Fe(CO)_5$						1900	228
c-$HFe(SiCl_3)_2(CO)_4$	$HSiCl_3 + h\nu + Fe(CO)_5$		<25	19.0	1			230
$HFe(CO)_3C_7H_8$	$H^+ + Fe(CO)_3C_7H_8$	g		17.3	3	13		140
t-$HFe(CO)(depe)_2^+$	$NaBPh_4/CO$ + *t*-$HFeCl(depe)_2$		170	20.9	5	47	1875	231
$HFeCp(SiCl_3)_2CO$	$HSiCl_3 + h\nu + FeCpSiCl_3(CO)_2$		131	21.6	1			91
t-$HFe(N_2)(depe)_2^+$	$NaBPh_4/N_2$ + *t*-$HFeCl(depe)_2$	o	135	28.2	5	49	1870	231
t-$HFeCl(diphos)_2$	$HCl + HFe(\mu\text{-}C_6H_4\text{-}PhPCH_2CH_2PPh_2)(diphos)$	v	209 d	39.2	3	47		232
$HFe(\mu\text{-}C_6H_4\text{-}PhPCH_2CH_2PPh_2)\text{-}(diphos)$	$h\nu + Fe(diphos)_2 \cdot C_2H_4$	b	179	24.2	Cplx		1893	232
$HFe_3CN(Me)_2(CO)_{10}$	$(CH_3)_2NCOH + Fe_3(CO)_{12}$	r	162 d	27.80	1			233
$HFe_3SBu^t(CO)_9$[a]	$HSBu^t + Fe_3(CO)_{12}$			32.8				234
c-$H_2Fe(PF_3)_4$	$H_2/Pt + h\nu + Fe(PF_3)_5$	c	−80	20.8	Cplx		1935/1396	7
t-$H_2Fe(P(OEt)_3)_4$	$NaBH_4/CH_3OH$ + L + iron halide			26.0	5	40	1912	46
$H_2FeN_2(PEt_2Ph)_3$	L + $H_2Fe(PEt_2Ph)_3$	y	80 d				1855	45
$H_2Fe(diphos)_2C_6H_6$	L + $Fe(diphos)_2C_2H_4$	y	219				1840	232
c-$H_2Fe_2[P(CF_3)_2]_2(CO)_6$	$(CF_3)_2PH + Fe(CO)_5$	y	50[b]	15.60	3	41.8		235
t-$H_2Fe_2[P(CF_3)_2]_2(CO)_6$	$(CF_3)_2PH + Fe(CO)_5$	y	50[b]	15.82	3	44.7		235
$HRu(CO)_5^+$	$H^+ + Ru(CO)_5$			18.0	1			145
$HRuCl[P(OPh)_3]_4$	L + H_2 (pressure) + $HRuCl(PPh_3)_3$	w	166	16.8	2 × 2 × 3	174, 28, 24	1930	96
c-$HRu(C_6H_5)(dmpe)_2$	$K^0/THF/C_6H_6$ + *t*-$RuCl_2(dmpe)_2$		136				1806	93
c-$HRu(2\text{-}C_{10}H_7)(dmpe)_2$	$Na^+C_{10}H_8^-$ + *t*-$RuCl_2(dmpe)_2$		182	17.6, 19.8	Cplx		1802	93
c-$HRu(C_{14}H_9)(dmpe)_2$	$Na_2C_{14}H_8$ + *t*-$RuCl_2(dmpe)_2$		185				1802	93
$HRuCl(C_7H_8)(PPh_3)_2$	L + $HRuCl(PPh_3)_3$	b	136	18.92	3	24	2080	236
$HRuCl(bipy)(PPh_3)_2$	L + $HRuCl(PPh_3)_2$	r	160	22.25	3	25	1930	236
$HRuCl(CO)(PEt_2Ph)_3$	$EtOH/OH^-$ + $[Ru_2Cl_3(PEt_2Ph)_6]Cl$	w	99	17.1	3 × 2	107, 24		61
$HRuI(CO)(PEt_2Ph)_3$	$EtOH/OH^-$ + $[Ru_2I_3(PEt_2Ph)_6]I$	w	141 d					61
$HRuBr(CO)(PEt_2Ph)_3$	$EtOH/OH^-$ + $[Ru_2Br_3(PEt_2Ph)_6]Br$	w	110	17.65	3 × 2	106, 25		61
$HRuClCO(PPhPr^n{}_2)_3$	$KOH/H_2O + RuCl_2CO(PPhPr^n{}_2)_3$	c	131	17.5	2 × 3	109, 25	1869	237
$HRuBrCO(PPhPr^n{}_2)_3$[c]	$LiBr/HOCH_2CH_2N(CH_3CH_2)_2$ + $[Ru_2Cl_3(PPhPr^n{}_2)_6]Cl$	c	126	17.8	2 × 3	108, 26	1880	237
$HRuClCO(PMe_2Ph)_3$	$KOH/H_2O + RuCl_2CO(PMe_2Ph)_3$	cr	91	18.2	1			237
$HRuClCO(PPhPr^n{}_2)_2\text{-}(PMe_2Ph)$[d]	L + $HRuClCO(PPhPr^n{}_2)_3$		110	16.80	2 × 3	25, 115	1874	153
$H_2Ru(CO)_4$	$2H^+ + Ru(CO)_4^{2-}$	w	−63	17.62	1		1980	121
c-$H_2Ru(PF_3)_4$	$PF_3 + H_2Cu$ (400 atm) + $RuCl_3$	c	−76	18.5	Cplx		1996/1436	7
$H_2Ru(PPh_3)_4$	Et_3Al + L + $RuCl_3$	y					2080/1560	238, 18
c-$H_2Ru(PMePh_2)_4$	$H_4N_2 + H_2$ (600 psi) + $[Ru_2Cl_3(PMePh_2)_6]Cl$	w	188	19.54	Cplx		1940, 1885/1390, 1340	71
c-$H_2Ru(dmpe)_2$	$Na^+C_{10}H_8^-$ + *t*-$HRuBr(dmpe)_2$		82	18.6			1806	93
$H_2RuCO(PPh_3)_3$	$NaBH_4/EtOH + N_2$ + $RuCl_2(Ph_3)_3$	o	147				2020	236
c-$H_2RuCO(PPh_3)_3$	$NaBH_4/EtOH + H_2$ + $RuCl_2(PPh_3)_3$	w	147	16.69 18.67	Cplx Cplx	30, 16 29, 74, 6	1900, 1960	236
$H_2Ru(N_2)(PPh_3)_3$	Et_3Al + L + $HRuCl(PPh_3)_3$	w	185				1947, 1917	13
$H_2Ru(CO)_2(PEt_3)_2$[e]	$LiAlH_4 + RuCl_2(CO)_2(PEt_3)_2$	w		18.48	3	24		121
	H_2 + 120 atm/130° + $Ru(CO)_3(PEt_3)_2$							9
$H_2Ru(CO)_2(PPh_3)_2$	L + $H_2Ru(CO)_4$	w		16.90	3	23	1878, 1823	9, 121
c-$H_2RuCO(PMePh_2)_3$	CO (13 atm) + *c*-$H_2Ru(PMePh_2)_4$	w	170	18.02	Cplx			71
$H_4Ru(PPh_3)_3$	L + $H_2RuN_2(PPh_3)_3$						1910	13, 18
$HRuBr(PPh_3)_3$	$H_2/Et_3N + RuBr_2(PPh_3)_3$	v	238	27.11	4	26	2025	236
$HRuCl(PPh_3)_3$	$H_2/Et_3N + RuCl_2(PPh_3)_3$	v	95	27.44	4	26	2020	236, 239
$HRuClP(OPh)_3$	L + $HRuCl(PPh_3)_3$	w		16.8	Cplx × 2	176		96
$HRu(MeCO_2)(PPh_3)_3$[f]	$MeCO_2^- + H_2/CH_3OH$ + $RuCl_2(PPh_3)_3$	y		29.89	2	27	2012	30

Table V (Continued)

Complex	*Preparation*	*Color*	*Mp, °C*	*^{1}H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$HRu_3(CO)_{12}^+$	$H^+ + Ru_3(CO)_{12}$	y		28.6	1			143
$HRu_3(CO)_9(C_{13}H_9)$	$LiPh + Ru_3(CO)_{12} + H^+$	r	139	30.2	1			240
$HRu_3SC_2H_5(CO)_{10}$	$HSC_2H_5 + Ru_3(CO)_{12}$	o	110	25.40	1			241
$HRu_3SC_4H_9(CO)_{10}$	$HSC_4H_9 + Ru_3(CO)_{12}$	o	69	25.42	1			241
β-$H_2Ru_4(CO)_{13}$	$KOH/MeOH/H_2O + Ru_3(CO)_{12}$	r		19.1				53a
α-$H_2Ru_4(CO)_{13}$	$Bu^n{}_2O + Ru_3(CO)_{12}$	r		28.6				53b
$H_2Ru_6(CO)_{18}$	$Mn(CO)_5^- + Ru_3(CO)_{12}$	v						122
α-$H_4Ru_4(CO)_{12}$	$Na/Hg + H^+ + Ru_3(CO)_{12}$	y		27.6			1248/902	53a
	$H_2 + Ru_3(CO)_{12}$			28.0				10
β-$H_4Ru_4(CO)_{12}{}^{l}$	$KOH/MeOH/H_2O + Ru_3(CO)_{12}$							53
$HOs(CO)_5^+$	$NH_4PF_6 + H_2SO_4 + Os_3(CO)_{12}$	w		18.2	1			242
$HOs(CO)_3(PPh_3)_2^+$	$HA + Os(CO)_3L_2$; $A^- = HCl_2^-$, Br^-, ClO_4^-, BF_4^-, PF_6^-	c					2015–2005	132b
$HOsCl(CO)_2(PPh_3)_2$	$CO + HOsCl(CO)_2L_2$	c					1920	132b
$HOsCl_2(PBu^n{}_2Ph)_3{}^{g}$	$H_2N_2H_2 + OsCl_3(PBu^n{}_2PhP)_3$	r	139				2064	70
$HOsCl_2(PBu^n{}_2Ph)_3{}^{h}$	Heat in CCl_4 + $HOsCl_2(PBu^n{}_2Ph)_3$	r	145				1915	70
$H_2Os(CO)_4$	H_2/CO (high temp-press.) + OsO_4	c		18.73	1		1845/1427	8
c-$H_2Os(PF_3)_4$	PF_3 (400 atm) + $H_2/Cu + OsCl_3$	c	−72	20.4	Cplx		1922, 1915/1379	7
$HOs(SiMe_3)(CO)_4{}^{i}$	$HSiMe_3 + Os_3(CO)_{12}/h\nu$	c	−55	19.03	1		1948	243
c-$H_2Os(PEtPh_2)_4{}^{j}$	$L + H_4OsL_3$	w						244
$H_2Os(CO)_3(PBu^n{}_3)$	$H_2Os(CO)_4$			18.97	2	25		121
$H_2Os(CO)_3(PPh_3)_1$	$L + H_2Os(CO)_4$	c	148	18.00	2	24	1955, 1923/1434	8, 121
$H_2Os(CO)_2(PBu^n{}_3)_2$	$L + H_2Os(CO)_3(PPh_3)$			19.42	3			8, 121
				18.97	2	25		
$H_2Os(CO)_2(PPh_3)_2$	H_2 (high press.-temp) + $Os(CO)_3(PPh_3)_2$			17.65	3	23	1928, 1873	9
	C_6H_6 reflux/$Os(OC(O)H)_2(CO)_2L_2$	c					1930, 1875	132b
c-$H_2OsCO(PEtPh_2)_3$	$CO + c$-$H_2Os(PEtPh_2)_3$	w					1940, 1840	244
$H_2OsN_2(PEtPh_2)_3$	p-$CH_3C_6H_4OsO_2$-N_3 + $H_4Os(PEtPh_2)_3$	w					1925	244
$H_4Os(PMe_2Ph)_3$	$LiAlH_4 + OsCl_3(PMe_2Ph)_3$	w	80	18.81	5	9.8	2051, 1988, 1864	41
$H_4Os(PEt_2Ph)_3{}^{k}$	$L + NaBH_4 + OsCl_3L_3$			18.9	4	9	2050, 2030, 1982, 1760	245
$H_4Os(PMe_2PhP)_2(PEt_2Ph)$	$LiAlH_4 + OsCl_3(PMe_2Ph)_2(PEt_2Ph)$	w	92	19.13		8.1, 12.9	2053, 1984, 1874	41
$H_4Os(PMe_2Ph)_2$-$(AsMe_2Ph)$	$LiAlH_4 + OsCl_3(PMe_2Ph)_2$-$(AsMe_2Ph)$	w	135 d	19.07		12.6	2037, 1962, 1862, 1843	41
$H_2Os_2(CO)_8$	CO + pressure + OsO_4	c		20.11	1			246
$H_2Os_2(CO)_6(PPh_3)_2$	$L + H_2Os_2(CO)_8$	c	207	19.46	2	18.5		246
$HOs_3(CO)_{12}^+$	$NH_4PF_6 + H_2SO_4 + Os_3(CO)_{12}$	cr		29.1	1			143
$HOs_3(OH)(CO)_{10}$	$CO/MeOH + OsO_4$	o						123
$HOs_3(OMe)(CO)_{10}$	$CO/MeOH + OsO_4$	y						123
$HOs_3SC_4H_9(CO)_{10}$	$HSC_4H_9 + Os_3(CO)_{12}$	y	75	27.4	1			241
$HOs_3SC_2H_5(CO)_{10}$	$HSC_2H_5 + Os_3(CO)_{12}$	y	141	27.5	1			241
$HOs_3(CO)_9(PMePh_2)_3^+$ "A"	$NH_4PF_6 + H_2SO_4 + Os_3(CO)_9$-$(PMePh_2)_3$	y	146	27.58	5	8.3, 11.3		143
				28.33	5	10.6, 18.9		242
$HOs_3(CO)_9(PMePh_2)_3^+$ "B"	$MeOH/\Delta + HOs_3(CO)_9$-$(PMePh_2)_3^+$ A	o	146	28.85	3	9.5		143, 242
$HOs_3(CO)_9(PEt_3)_3^+$ "A"	$NH_4PF_6 + H_2SO_4 + Os_3(CO)_9$-$(PEt_3)_3$	y	119 d					143, 242
$HOs_3(CO)_9(PEt_3)_3^+$ "B"	$MeOH/\Delta/KCl + HOs_3(CO)_9$-$(PEt_3)_3^+$ A	o	151					143, 242
$HOs_3(SPh)(CO)_9(PEt_3)$	$L + HOs_3(SPh)(CO)_{10}$	y	128	26.72	2	26.1		144a
$HOs_3(SPh)(CO)_9$-$(PMePh_2)$	$L + HOs_3(SPh)(CO)_{10}$	y	113	26.88	2	28.5		144a
$HOs_3(SPh)(CO)_8(PEt_3)_2$ "A"	$L + HOs_3(SPh)(CO)_{10}$	y	128	26.46	3	30.2		144a
$HOs_3(SPh)(CO)_8(PEt_3)_2$ "B"	$L + HOs_3(SPh)(CO)_{10}$	r	142	26.66	2	26.0		144a
$H_2Os_3(CO)_{12}$	$H_2 + CO + OsO_4$	c	95	19.85	1			247
$H_2Os_3(CO)_{11}(PMe_2Ph)^{2+}$	$H_2SO_4 + Os_3(CO)_{11}(PMePh_2)$			29.58	2	12.6		144b
				30.00	2	13.5		
$H_2Os_3(CO)_{10}$	$NaBH_4 + Os_3(CO)_{12}$	r						123

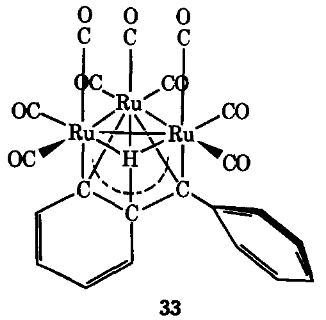
Table V (Continued)

Complex	*Preparation*	*Color*	*Mp, °C*	*^1H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
α-$H_2Os_3(SPh)^+(CO)_{10}$	H_2SO_4 + $HOs_3(SPh)(CO)_{10}$	y		26.88 29.55	1 1			144a
β-$H_2Os_3(SPh)(CO)_{10}^+$	Δ + α-$H_2Os_3(SPh)(CO)_{10}^+$	y		29.43 26.98	1 1			144a
$H_2Os_3(SEt)(CO)_{10}^+$	H_2SO_4 + $HOs_3(SEt)(CO)_{10}$			29.84 27.12	1 1			144a
$H_2Os_3(CO)_{10}(PMePh_2)_2^{2+}$ "A"	H_2SO_4 + $Os_3(CO)_{10}(PMePh_2)_2$			29.30 29.98	3 3	9.8 7.0		144b
$H_2Os_3(CO)_{10}(PMePh_2)_2^{2+}$ "B"	H_2SO_4 + $H_2Os_3(CO)_{10}(PMePh_2)_2^{2+}$ A			29.14 29.77	2 5	14.0 8.7, 18.8		144b
$H_2Os_3(CO)_9(PEt_3)_3^{2+}$	NH_4PF_6 + H_2SO_4 + $Os_3(CO)_9(PEt_3)_3$	y						143, 242
$H_2Os_3(CO)_9(PMePh_2)_3^{2+}$	H_2SO_4 + $Os_3(CO)_9(PMePh_2)_3$			28.97 29.38	5 5	6.2, 13.0 8.9, 18.8		144b
$H_2Os_3(SPh)(CO)_9(PEt_3)^+$	H^+ + NH_4PF_6 + HOs_3-$(SPh)(CO)_9(PEt_3)$	w		25.88 29.01	2 2	23.8 12.4		144a
$H_2Os_3(SPh)(CO)_9$-$(PMePh_2)^+$	H^+ + NH_4PF_6 + $HOs_3(SPh)(CO)_9(PMePh_2)$	y		26.22 28.34	2 2	27.0 13.0		144a
$H_3Os_3(SPh)(CO)_8$-$(PEt_3)_2^{2+}$	H^+ + NH_4PF_6 + $H_2Os_3(SPh)(CO)_8(PEt_3)_2$	y		29.44 24.97 30.73	5 2 2	18.0, 10.2 16.0 11.2		144a
$H_2Os_4(CO)_{13}$	OH^-/MeOH + H^+ + $Os_3(CO)_{12}$	o						123
$H_4Os_4(CO)_{12}$	100° + $H_2Os(CO)_4$ H_2 + $H_2Os_3(CO)_{10}$	y						247 10
$HOsRe(CO)_9$	$HRe(CO)_5$ + $H_2Os_3(CO)_{12}$ + Δ			20.37				247
$H_2FeRu_3(CO)_{13}$	$Fe(CO)_5$ + $[Ru(CO)_3Cl_2]_2$ or $Ru_3(CO)_{12}$	o	112 d	28.7	1			248

[a] See also, *sec*-butyl and isopropyl derivatives. [b] Sublimes. [c] See also $HRuXCOL_3$; X = I and L = $PPhPr^n_2$ and X = Br, I and L = PBu^n_2Ph. [d] See also $HRuClCOL_2L_1$; L_2 = $PPhPr^n_2$ and L_1 = PEt_3, $P(OEt)_3$, PEt_2Ph, $P(OMe)_2Ph$, $AsMe_2Ph$; L_2 = PEt_2Ph and L_1 = PMe_2Ph; L_2 = PBu^n_3 and L_1 = $AsMe_2Ph$; L_2 = PBu^n_2Ph and L_1 = PMe_2Ph. [e] *cis*-H_2, *trans*-$(PEt_3)_2$. [f] See also $ClCH_2CO_2^-$, $F_3CCO_2^-$, $EtCO_2^-$, $Pr^nCO_2^-$, $Pr^iCO_2^-$, $MeBu^tCO_2^-$, *o*-$(OH)C_6H_4CO_2^{2-}$, $PhCO_2^-$. [g] H trans to Cl. [h] H trans to P. [i] See also $SiEt_3$, $GeEt_3$, $SnMe_3$. [j] See also L = PMe_2Ph, PEt_2Ph, $PMePh_2$, $AsEt_2Ph$, $AsEtPh_2$. [k] See also L = PMe_2Ph, PPh_3, $AsPh_3$. [l] Unconfirmed; see ref 10.

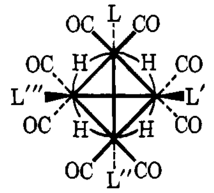
magnetic isomer. This stereochemical conversion required both moisture and oxygen.

Treatment of triruthenium dodecacarbonyl with 1 equiv of phenyllithium in THF at low temperatures gives the cluster $HRu_3(CO)_9(C_6H_5CC_6H_4)$, which contains a bridging hydride.[240] An X-ray study revealed an Ru_3 triangle with one edge expanded to accommodate the hydride. The organic ligand system occupies one side of the plane formed by the ruthenium atoms and the bridging hydride(**33**).



33

The derivative $H_4Ru_4(CO)_{12}$ has been obtained in improved yield and purity.[10] Its spectrum contains five strong carbonyl stretching modes in the infrared in agreement with the D_{2d} structure **34** (L = L′ = L″ = L‴ = CO). A rapid intramolecular rearrangement of hydrogen has been detected in the nmr of the various phosphine-substituted derivatives (see section IV.B).



34

Greatrex, *et al.*,[233] report the characterization of HFe_3-$(CNMe_2)(CO)_{10}$ which was first obtained by Rhee, Ryang, and Tsutsumi[250] in the reaction of benzoyl chloride with $Fe_3(CO)_{12}$ in dimethylformamide. This is believed to possess a structure **35a** containing bridging hydride and $CNMe_2$ groups resembling the structure of $HFe_3(CO)_{11}^-$, **35**.[251, 252]

The structurally related derivatives of ruthenium and osmium, $HM_3(OR)(CO)_{10}$[123] and $HM_3(SR)(CO)_{10}$, [241] have

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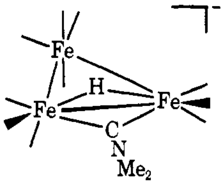
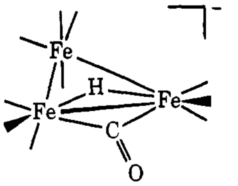


35a



35b

been prepared by reaction of the corresponding trimetal dodecacarbonyl with alcohol or thiol. These have been characterized by nmr, ir, and mass spectra. The iron analogs are unknown; these derivatives contain two electrons less than the compounds **35a** and **35b**. With $Fe_3(CO)_{12}$ and secondary and tertiary alkyl thiols, the derivative $HFe_3(SR)(CO)_9$, among others, is obtained.[253]

L. COBALT, RHODIUM, AND IRIDIUM

Perhaps more than for any other subgroup the chemistry of these metals has been extensively cited in the various portions of section II. It will therefore not be practical to cross-reference these citations here or to attempt complete coverage in this section.

Several conflicting reports have been made on the formulations of some hydride and hydridonitrogen complexes of cobalt. The formulations H_3CoL_3 and $HCo(N_2)L_3$ appear to be correct based on X-ray analyses[254,255] and nmr.[256] Nevertheless, Speier and Marko[257] give convincing evidence that paramagnetic $H_2Co(PPh_3)_3$ and $CoN_2(PPh_3)_3$ do exist. This is based on gas evolution in thermal decompositions, the reaction of CCl_4 which gives $HCCl_3$ for the dihydride (and no $HCCl_3$ for the dinitrogen complex) and, of course, magnetic susceptibility.

The complex $HCoN_2L_3$ (L = PPh_3) exhibits remarkably versatile chemical properties which have recently been summarized by Yamamoto, *et al.*[12] Through reversible displacement of the coordinated N_2, it combines readily with H_2,[258,259] C_2H_4, and with NH_3.[258] It forms a carbonyl complex by reaction with CO[258,259] or by CO abstraction from aldehydes[259] and adds to CO_2 to give the formate complex $Co(OC(O)H)L_3$.[132] $HCo(N_2)L_3$ also catalyzes the hydrogenation of ethylene, the oxidation of Ph_3 to Ph_3PO, the reduction of N_2O, and the dimerization of ethylene and propylene.[258b]

Campbell and Stone[263] irradiated $HCo(PF_3)_4$ in the presence of PH_3 and obtained $HCo(PH_3)(PF_3)_3$. The nmr contained a doublet of quartets arising from a trigonal-bipyramidal structure in which the hydride is trans to PH_3.

Udovich and Clark[264] followed the substitution of PF_3 on $HCo(CO)_4$ (among other derivatives). Through gas-liquid partition chromatography, they were able to separate complexes of different composition, $HCo(PF_3)_{4-x}(CO)_x$. Infrared spectra indicated the presence of several isomers within each fraction, but these could not be separated further; see also the report of PF_3-substituted derivatives of $HMn(CO)_5$ (section III.J).

The complex $HRhL_3$ (L = PPh_3) has been prepared in what may be two separate modifications, first by Keim[34] and Dewhirst, Keim, and Reilly[71] in the reduction of $RhClL_3$ with $Al(Pr^i)_3$ and isolated as an orange solid. Ilmaier and Nyholm[276] report a yellow modification with Rh–H stretching vibration at 1885 cm^{-1} in contrast to the orange solid whose analogous absorption was observed at 2020 cm^{-1}. The nmr of this derivative, which is rapidly tautomerizing, is discussed in section IV.D. A complex of the formula $HRhL_4$ (L = PPh_3) is also obtained by the workers cited above[34,71] as well as by Ito, *et al.*,[18] who prepared this formulation in the reduction of the rhodium(III) chloride or acetylacetonate with $AlEt_3$ in THF. This complex participates only to a limited extent in exchange of D_2 with the ortho hydrogens in the phenyl group of ligand, by contrast to the ruthenium derivative H_2RuL_4 (see section III.K); the rhodium complex does not give an isolatable nitrogen adduct.[18]

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Table VI

Survey of Hydride Complexes: Co, Rh, Ir

Complex	*Preparation*	*Color*	*Mp, °C*	*^{1}H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$HCo(PF_3)_4$	$L + H_2/Cu + CoI_2$	c	−51	22.5	Cplx			260, 261
$HCo[P(OEt)_3]_4$	$NaBH_4/EtOH + L +$ cobalt chlorides		>180 d	25.8	5	12	1964	46
$HCo[P(OPh)_3]_4$	$NaBH_4/EtOH + L +$ Co(II) salt	y	160		5	17		96
$HCo(diphos)_2$	$(EtO)Et_2Al + L + Co(acac)_3$	r	268 d				1884	65, 232
$HCo(CO)_3PPh_3$	$Na/Hg + [Co(CO)_3PPh_3]_2 + H^+$			20.7	2	51		116
$HCo(CO)_3(PF_3)$	$L + HCo(CO)_4$						1929	264
$HCo(PF_3)_3PH_3$	$L + HCo(PF_3)_4$	y	25	24.4	Cplx		1967	263
$HCo(CO)_2(PF_3)_2$	$L + HCo(CO)_4$						1945	264
$HCo(CO)_2(PPh_3)_2$	$H^+ + Na/Hg + CoCl(CO)_2(PPh_3)_2$	y	150	20.35	3	41		116
	$CO + HCoN_2(PPh_3)_3$	y		20.00	3	41		265
$HCo(CO)_2[P(OPh)_3]_2$	$H^+ + Na/Hg + CoCl(CO)_2[P(OPh)_3]_2$	c	88	21.9	3	21		116
$HCoCO(PPh_3)_3$	$L + HCoN_2(PPh_3)_3$	o		22.0	4	48	1960	265
$HCoN_2(PPh_3)_3$	$L + H_3Co(PPh_3)_3$	o	80 d	29	4	50		13, 266
$HCoNCMe(PPh_3)_3$	$L + HCoN_2(PPh_3)_3$	r	120 d					265b
$HCoCpSiCl_3CO$	$HSiCl_3 + h\nu + CoCp(CO)_2$		31	23.3	1			91
$H_2Co(PPh_3)_3$	$(EtO)Et_2Al + L + Co(acac)_2 + H_2$	b		Paramagnetic				257
$H_3Co(PPh_3)_3$	$NaBH_4 + CoX_2L_3$[a]	y					1933, 1745	13
$H_3Co(PPh_3)_3$	$NaBH_4 + L + CoCl_2 \cdot 6H_2O$	y	80 d				1933, 1745/1395, 1263	13
	$Bu^n{}_2AlH/Et_2O + L + Co(acac)_3$			20.96		0.36	1934, 1887, 1754	65
$CoX_2(PEtPh_2)_3$	$NaBH_4 + CoX_2L_3$[a]	y					1745, 1933	13
$H_3Co(PEtPh_2)_3$	$NaBH_4 + L + CoCl_2 \cdot 6H_2O$	o					1958, 1736/1260	13
$H_3Co(PEt_2Ph)_3$	$NaBH_4 + L + CoCl_2 \cdot 6H_2O$						1940, 1720	13
$H_3Co[P(p\text{-}FC_6H_4)_3]_3$[b]	$Bu^n{}_2AlH/Et_2O + L + Co(acac)_3$			21.75		0.32	1946, 1895, 1767	65, 267
$HRh(PF_3)_4$	90 atm PF_3 + 30 atm $H_2 + RhCl_3$	c	−40					281
$HRh(PPh_3)_4$	$Et_3Al/L + RhCl_3$	y	168 d	20.6			2147, 2152/1548	18, 268, 71
	$H_2 + L + Rh(C_6H_5)(C_8H_{12})L$	y						238
$HRh[P(OPh)_3]_4$	$L + HRh(CO)(PPh_3)_3$	w			5	45		261
$HRh(PMePh_2)_4$	$H_2N_2H_2 + L + RhCl(PMePh_2)_3$	y	174	22.1			2005	34, 71
$HRh(PPh_3)_3(AsPh_3) \cdot {}^1/_2C_6H_6$	$L + HRh(PPh_3)_3$	o					2125, 2180	269
$HRh(AsPh_3)_3PPh_3$	$L + HRh(AsPh_3)_3$	y					2118, 2140	268
$HRh(CO)(PEt_3)_3$[c]	$L + CH_3CH_2CH_2O^- + RhCl(PEt_3)_2$			21.3		17	1952	62a
$t\text{-}HRhBr(dmpe)_2{}^+$	$HBr + Rh(dmpe)_2{}^+$						2030	147
$t\text{-}HRhCl(dmpe)_2{}^+$	$HCl + Rh(dmpe)_2{}^+$	w	183				2050	147
$HRhCp(PPh_3)_2{}^+$	$L + HBF_4 + RhCp(C_2H_4)_2$	y		20.4	2 × 3	16.5, 28	2045	270
$HRhCl_2(PBu^nPh_2)_3$	$L/EtOH + RhCl_3 \cdot 3H_2O$	y	140 d				2090	271
$HRhCl_2CO(phen)$	$L + Rh(CO)_2Cl_2{}^-$						2117	272
$HRhBr_2CO(phen)$	$L + Rh(CO)_2Br_2{}^-$						2110	272
$HRhCl_2CO(dipy)$	$L + Rh(CO)_2Cl_2{}^-$						2115	272
$HRhBr_2CO(dipy)$	$L + Rh(CO)_2Br_2{}^-$						2115	272
$HRhCl(CN)(HCN)(PPh_3)_2$	$HCN + RhCl(PPh_3)_3$	y		19.65	4	12.0	2163	85
$HRhCl_2(CO)(AsPh_3)_2$[d]	$HCl + Rh(CH_3OCO)(CO)(AsPh_3)_3$	y					2087	273
$HRhCl_2(CO)(SbPh_3)_2$[d]	$HCl + Rh(CH_3OCO)(CO)$ $(SbPh_3)_3$						2035	273
$HRhCl_2(PEtPh_2)_3$[e] (α)	$L/EtOH + RhCl_3 \cdot 3H_2O$	y	210 d				2120/1515	62b
(β)	$L/H_3PO_4 + RhCl_3 \cdot 3H_2O$	y					1982	62b
$HRhCl_2(PPh_3)_3$ (α)	$L/(CH_3)_2CO + RhCl_3 \cdot 3H_2O$	y	160 d				2220	62b
(β)	$RhCl(PPh_3)_3 + HCl/C_6H_6$	y	100 d				2120/1510	62b
$HRhCl(CF_2CF_2H)CO(PPh_3)_2$	$HCl + Rh(CF_2CF_2H)CO(PPh_3)_2$		25 d	22.6			2155	274
$c\text{-}H_2Rh(dmpe)_2{}^+$	$H_2/THF + Rh(dmpe)_2{}^+$	w					1900, 1870	147

Table VI (Continued)

Complex	*Preparation*	*Color*	*Mp, °C*	*^{1}H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$H_2RhCl(PEtPh_2)_3$	$H_2 + RhCl(PEtPh_2)_3$	y		27.7 19.4	1 2	155.5	2115 2059, 1915	62b, 275
$H_2RhCl(PPh_3)_3$	$H_2 + RhCl(PPh_3)_3$	y	110 d				2012, 2082	62b
$H_2RhCl(PPh_3)_2Py$	$H_2/Py + RhCl(PPh_3)_3$	w						21
$H_2Rh(PPh_3)_2(NCCH_3)_2{}^+$	$H_2/CH_3CN + Rh(PPh_3)_2C_7H_8$			27.4	2 × 3	13, 17		149
$HRh(PPh_3)_3$	$[(CH_3)_2CH]_3Al + RhCl(PPh_3)_3$	o		18.9			2020	71, 34, 156
	1% $KOH/EtOH + RhCl(PPh_3)_3$	o	120	17.8	2	14	1865, 1855	159, 276
$HRhCl_2(AsPh_3)_2\cdot{}^1/_2CH_2Cl_2$	$HCl/CH_2Cl_2 + RhCl(AsPh_3)_3$	y		25.9	2	6	2069	22
$HRhCl_2(SbPh_3)_2$	$HCl/CH_2Cl_2 + RhCl(SbPh_3)_3$	b		28.3	2	7	2014	22
$HRhClSiCl_3(PPh_3)_2$	$HSiCl_3 + RhCl(PPh_3)_3$	y		24.3	2 × 3	15, 21	2116	87b
$HRhCl(SiCl_3)(PPh_3)_2{}^f$	$HSiCl_3 + RhClL_3$	y	168 d	24.30	2 × 3	21, 14	2040	277, 278
$HRhCl(Si(OEt)_3)(AsPh_3)_2{}^g$	$HSi(OEt)_3 + RhClL_3$	y	142 d	26.3	2	22	2065	278
$HRhClSiMeCl_2(PPh_3)_2$	$HSiMeCl_2 + RhCl(PPh_3)_3$	y		24.4	2 × 3	13, 21	2048	87b
$HRhBrSi(OEt)_3(PPh_3)_2$	$HSi(OEt)_3 + RhCl(PPh_3)_3$			23.6 24.6	2 × 3	24.0 14.3		278
$HRhCl(SH)(PPh_3)_2$	$H_2S + RhCl(PPh_3)_3$						2160	85
$HRhCl(SC_6H_4Me)(PPh_3)_2$	$HSC_6H_4Me + HRhCl(PPh_3)_3$			26.5	4	190	2119	85
$H_2RhCl(PPh_3)_2$	$H_2 + RhCl(PPh_3)_3$	y		28.2 20.15	1 2	152.3	2078, 2013	21
$H_2RhCl(AsPh_3)_2$	$H_2/CH_2Cl_2 + RhCl(AsPh_3)_3$	y		22.1, 29.1			2030, 2051	22
$H_2RhCl(SbPh_3)_2$	$H_2/CHCl_3 + RhCl(SbPh_3)_3$			19.9, 27.9			2002, 2078	22
$[H_2RhCl(PPh_3)_2]_2$	$H_2 + [RhCl(PPh_3)_3]_2$	y		26.6	2 × 3	15, 20	2095/1507	21
$HRh_3(Cp)_4$	$C_5H_5MgBr/Et_2O + H_2O + RhCl_3$	bl		22.47	4	26.5		279
$HIrBrPPh_3(QP)^+$	$L + HIrBr_2(PPh_3)_3$ $L + H_2IrBr(PPh_3)_3$	y		17.2	2	120		280
$HIr(PF_3)_4$	PF_3 (160 atm)/H_2 (45 atm) + $IrCl_3/Cu$	c	−39	21.9	65			281
$HIr[P(OPh)_3]_4$	$P(OPh)_3 + H_3Ir[P(OPh)_3]_3$	w	127	23	5	25	2055	282
$HIrCO(PPh_3)_3$	$L + HIrCO(PPh_3)_2$ $KOH + H_2IrCO(PPh_3)_2{}^+$	y	145				2120–1920	20
$HIrCS(PPh_3)_3$	$NaBH_4/EtOH + IrClCS(PPh_3)_2$	o		23.0	4	25	2000	283
$HIr(CO)[P(OPh)_3]_3$	$L + HIrCO(PPh_3)_2$			21.0	4	14		262a
$HIrCl(QP)^+$				18.8	2	130		284
t-$HIrCO(dmpe)_2{}^+$	$HCl + t$-$HIr(CO_2Et)(dmpe)_2$	w	237	22.09	5	16	2135	150
t-$HIrCl(dmpe)_2{}^+$	$H_2O/EtOH + t$-$IrClCO(dmpe)_2$	w	225	32.2	5	17.5	2162	150
t-$HIr(CO_2Me)(dmpe)_2{}^+$	$NaBPh_4/EtOH + t$-$IrClCO(dmpe)_2$	w	180	25.50	5	18	1960	150
t-$HIr(CO_2Et)(dmpe)_2{}^+$	$NaBPh_4/EtOH + t$-$IrClCO(dmpe)_2$	w	184	25.56	5	17	1935/1396	150
$HIrCl_2[P(OEt)_3]_3$	$[IrCl(COD)]_2 + L$	w					2180	262b
$HIrCl_2(PEt_3)_3{}^{h,i}$	$KOH/EtOH + IrCl_3(PEt_3)_3$	y	83	22.55	3 × 2	19, 163	2090	37
$HIrCl_2(PEt_3)_3{}^{i,j}$	$KOH/EtOH/H_2O + IrCl_3(PEt_3)_3$	w	99.5	31.6	4	15	2194	37
$HIrCl_2(PMe_2Ph)_3{}^k$	$HCl + H_2IrCl(PMe_2Ph)_3$	c	178				2182	285
$HIrCl_2(PMePh_2)_3{}^l$	$KOH/EtOH + IrCl_3(PMePh_2)_3$	y	186	22.5	2 × 3	165, 15	2060	38
$HIrBr_2(PEt_2Ph)_3{}^m$	LiBr + 2-methoxyethanol + t-$IrCl_3(PEt_2Ph)_3$	o	121				2073, 2042	37
$HIrCl_2(PEt_3)_2(PMe_2Ph)^n$	$L + HIrCl_2(PEt_3)_3{}^o$			22.40		169, 19		154
$HIrCl_2(CO)(PPh_3)_2$	$HCl + IrClCO(PPh_3)_2$						2240/1608	73
$HIrBr_2CO(PPh_3)_2$	$HBr + IrBrCO(PPh_3)_2$						2231	73
$HIrI_2CO(PPh_3)_2$	$L/EtOH + IrI_5CO^{2-}$	y	155				2180, 2040	20
$HIrBrCl(CO)(PPh_3)_2$	$HBr + IrClCO(PPh_3)_2$	w					2240	73
$HIrClF(CO)(PPh_3)_2{}^p$	$HF + IrCl(CO)(PPh_3)_2$						2240	73
$HIrCl_2CO(PEt_2Ph)_2{}^q$	OH^-/alcohol + 77°/70 atm + $IrCl_3(CO)(PEt_2Ph)$	y	110	19.0	3	16	2008	80
$HIrCl_2CO(PEt_2Ph)_2{}^r$	OH^-/alcohol + 120°/78 atm + $IrCl_3(CO)(PEt_2Ph)$	c	123	26.05	3	12	2194	80
$HIrBr_2CO(PEt_2Ph)_2$	OH^-/alcohol + $IrBr_3(CO)(PEt_2Ph)$	c	140 d				2193	80
$HIrCl_2CO(PMe_2Ph)_2{}^s$	$CO/EtOH + L + H_3IrCl_6$	w	149 d	25.7		12.3	2191	78
$HIrCl_2CO(PMePh_2)_2$	$HCl + IrCOCl(PMePh_2)_2$	c					2225	75

Table VI (Continued)

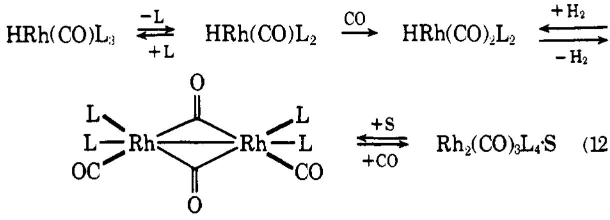
Complex	*Preparation*	*Color*	*Mp, °C*	*^1H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$HIrCl_2CO(SbPh_3)_2$	$HCl + Ir(OCOCH_3)CO(SbPh_3)_3$ $HCl + IrClCO(SbPh_3)_3$	y	163 d				2157/1552	273
$HIrCl_2NH_2NH_3(PPh_3)_2$[t]	NH_3 + "$H_2IrCl_2(PPh_3)_2$"		148					286
$HIrBrClCO(PMePh_2)_2$	$HBr + IrClCO(PMePh_2)_2$	w					2210	75
$HIrCl(SnCl_3)(PPh_3)_3$	$SnCl_2 + L/EtOH + Na_3IrCl_6$	y	132	24.7 30.2 31.4	2 5 3	14 13 10	2155	287
$HIrCl[\mu\text{-}C_6H_4\text{-}PPh_2\text{-}(PPh_3)_2]$	$Ir(PPh_3)_3Cl$	c					2190/1600, 1540	27
$HIrCl(SnCl_3)CO(PPh_3)_2$	$SnCl_2 + IrClCO(PPh_3)_2$	y	155	19.9	3	10	2148/1530	287
$HIrCl(SnMe_3)CO(PPh_3)_2$[u]	Me_3SnH/C_6H_6 + *t*-$IrClCO(PPh_3)_2$	y		20			2080/1508	88
$HIrCl(SnMe_3)CO(PPh_3)_2$[v]	Me_3SnH + *t*-$IrClCO(PPh_3)_2$	w					2093/1503	88
$H_2IrCl(PMe_2Ph)_3$[w]	$LiCl + Et_2NCH_2CH_2OH$ + *mer*-$IrCl_3(PMe_2Ph)$	c	122				2174, 2010	285
$H_2IrCl(PMePh_2)_3$[x]	$LiAlH_4 + HIrCl_2(PMePh_2)_3$	w	206	20.09 32.3	2 × cplx Cplx	126, 24, 6 20, 6	2100, 2075	38
$H_2IrCl(PEt_2Ph)_3$[y]	$KOH/EtOH/H_2O$ + *t*-$IrCl_3(PEt_2Ph)_3$	w	132.5	18.6 31.5	2 × 3 4 × 2 H_1–H_2	19.9, 125 14.3 8	2020, 2171	37
$H_2IrBr(PEt_2Ph)_3$[y]	$LiBr$ + 2-methoxyethanol + *t*-$IrCl_3(PEt_2Ph)_3$	w	132				2177, 2030	37
$H_2IrI(PEt_2Ph)_3$[y]	NaI + 2-diethylaminoethanol + *t*-$IrCl_3(PEt_2Ph)_3$	w	120.5				2167, 2036	37
$H_2IrCl(AsEt_2Ph)_3$[y]	$KOH/EtOH/H_2O$ + *t*-$IrCl_3(AsEt_2Ph)_3$	y	105	24.3 35.0	2 2	8	2168 2058	37
$H_2Ir(SnCl_3)(PPh_3)_3$	$SnCl_2 + L/MeOCH_2CH_2OH + Na_3IrCl_6$	w	206	21.3 23.0 24.7	3 3 5	10 10 20	2262 2205	287
$H_2IrClCO(PMe_2Ph)_2$[z]	$H_2 + IrClCO(PMe_2Ph)_2$	c	Oil	28.36 17.58		14.1, 8.4 20.2, 8.4	2169, 2067	28
$H_2IrBrCO(PEt_2Ph)_2$[z,aa]	$H_2 + IrClCO(PEt_2Ph)_2$	c	Oil	28.29 18.73		13.5, 5.1 18.9, 5.1	2196, 2100/1570	28
$H_2Ir(SnCl_3)CO(PPh_3)_2$	$SnCl_2$/acetone + $H_2IrClCO(PPh_3)_2$	y	191	19.9 22.5	3 3	10 10	2112, 2014/1563	287
$H_2Ir(GeMe_3)CO(PPh_3)_2$[bb]	Me_3GeH + *t*-$IrClCO(PPh_3)_2$	w	153	19.50 20.50	2 × 2 × 2 2 × 2 × 2	22, 16, 4 117, 18, 3.5	2114, 1076, 1969[ll]	35
$H_2Ir(CO)_2(PPh_3)_2^+$	$H^+ + HIr(CO)_2(PPh_3)_2$	y					2180, 2155	136
$H_2Ir(acac)(PPh_3)_2$[cc]	Hacac + $[H_3Ir(PPh_3)_2]^+$	w	198	34.7	3	17.2	2180, 2140	138, 288
$H_2Ir(CF_3COCHOCH_3)(PPh_3)_2$	$CF_3COCH_2OCH_3 + [H_3Ir(PPh_3)_2]^+$	y	198	35.2 35.7	Cplx	H–H = 8 P–H = 17.2	2220 2180	138 288
$H_2Ir[P(MeO)_2S_2](PPh_3)_2$[dd]	$[P(MeO)_2S_2]^- + H_3Ir(PPh_3)_3$	w	195 d	29.8	3 × 2	6, 18	2210, 2140	137
$H_2Ir(PPh_3)_2[(CH_3)_2CO]_2^+$	$H_2 + Ir(PPh_3)_2$(1,5-cyclooctadiene)$^+$						2230, 2260	149
mer-$H_3Ir(PPh_3)_3$	$LiAlH_4$ + *t*-$IrCl_3(PPh_3)_3$	w	225 d				2104, 1755	37
fac-$H_3Ir(PPh_3)_3$	$LiBH_4 + HIrCl_2(PPh_3)_3$	w	233 d	22.1	6 peaks		2090	37
mer-$H_3Ir(PEt_3)_3$[ee]	$L + H_5Ir(PEt_3)_2$			22.87 24.40	2 × 2 × 3 2 × 2 × 3	16.1, 15.2, 4.6 23.4, 115.3		16
mer-$H_3Ir(PEt_3Ph)_3$[ff]	$L + H_5Ir(PEt_2Ph)_2$			21.82 23.54	2 × 2 × 3 2 × 3 × 3	16.8, 14.2, 4.6 23.0, 114.6		16
fac-$H_3Ir(PEt_2Ph)_3$[gg]	$L + H_5Ir(PEt_2Ph)$			21.94	Cplx			16
fac-$H_3Ir(PEtPh_2)_3$[hh]	$LiAlH_4 + HIrCl_2(PEtPh_2)_3$ isomerization of *mer* deriv	w	131	21.75	4	15	2080, 2050	38
mer-$H_3Ir(PEtPh_2)_3$[hh]	$LiAlH_4 + HIrCl_2(PEtPh_2)_3$	w	117	21.17	6		2100, 1750	38
fac-$H_3Ir(AsEtPh)_3$	$LiAlH_4$ + *t*-$IrCl_3(AsEt_2Ph)_3$	w	75	24.9	1		2058	37
$H_3IrCO(PPh_3)_2$	$LiAlH_4 + IrClCO(PPh_3)_2$	w	135				2080, 1965, 1785/1510, 1278	20
$H_3IrPy(PPh_3)_2$	$L + H_3Ir(PPh_3)_2$		134				1700, 2120	20

Table VI (Continued)

Complex	*Preparation*	*Color*	*Mp, °C*	*^{1}H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$H_3Ir(NCEt)(AsPh_3)_2$	L + $H_3Ir(AsPh_3)_2$			21.6 22.6	3 2	~3 ~3	2090 2075	289
$H_3Ir[NC(p\text{-anisyl})]\text{-}(AsPh_3)_2$	L + $H_3Ir(AsPh_3)_2$			20.98 22.21	3 2	~3 ~3	2075 2060	289
$H_3Ir[NC\text{-}(p\text{-tolyl})]\text{-}(AsPh_3)_2$	L + $H_3Ir(AsPh_3)_2$			20.88 22.14	3 2	~3 ~3	2080 2060	289
$H_3Ir(NCC_6H_{11})(AsPh_3)_2$	L + $H_3Ir(AsPh_3)_2$			21.73 22.62	3 2	~3 ~3	2120 2080	289
$H_5Ir(PEt_3)_2$	$LiAlH_4$ + *t*-$IrCl_3(PEt_3)_3$	w	34	20.7	3	13.5	1932	15, 16, 37
$H_5Ir(PMe_3)_2$	$LiAlH_4$ + $Me_3PH^+[IrCl_4(PMe_3)_2]^-$			19.73	3	14		31
$H_5Ir(PPh_3)_2$	$LiAlH_4$ + *t*-$IrCl_3(PPh_3)_3$	w	184				1948	15, 16, 37
$H_5Ir(PPh_3)_2$	L + $NaBH_4$ + Na_3IrCl_6	w	127				1945	31
$H_5Ir(PEt_2Ph)_2$	$LiAlH_4$ + *t*-$IrCl_3(PEt_2Ph)_3$	w	78 d	19.4	3	13	1945/1404	15, 16, 37
$H_5Ir(PEt_2Ph)_2$	$LiAlH_4$ + *mer*-$IrCl_3(PEt_2Ph)_2$			34.07 34.23	3 3	19.8 19.4	2240	15
c-$H_5Ir(PEt_2Ph)_3$	$LiAlH_4$ + *t*-$IrCl_3(PEt_2Ph)_3$	w	105	23.0	6 peaks		2025	37
t-$H_5Ir(PEt_2Ph)_3$	$LiAlH_4$ + *t*-$IrCl_3(PEt_2Ph)_3$	w	62	21.73	4	15	2037, 1740	37
$HIrCO(PPh_3)_2$	L + $H_3Ir(PPh_3)$	y	132				2120, 2000, 1950,[ll] 1920	31
$HIrCl_2(PBu^t{}_2Me)_2$[ii]	L/Pr^iOH + $IrCl_6{}^{4-}$	v		60.5	3		2000	290
$HIr(OCOCF_3)_2(PPh_3)_2$	AgO_2CCF_3 + $HIrCl(OCOCF_3)\text{-}(PPh_3)_2$			28.1	3	10.6	2245	85
$HIrCl(CN)(PPh_3)_2$[jj]	HCN + $IrCl(CO)(PPh_3)_2$			19.4	3	15.2	2145	85
$HIrCl(Si(OEt)_3)(PPh_3)_2$	$HSi(OEt)_3$ + $IrClCO(PPh_3)_2$			16.1	3	14		90
$HIrCl(GePh_3)(PPh_3)_2\cdot{}^1/_2C_6H_{12}$	$HGePh_3$ + $IrClCO(PPh_3)_2$	bf	152	18.50	2	15.6	1970, 2088[ll]	35
$H_2IrI(PPh_3)_2$	NaI + $H_2Ir(PPh_3)_2{}^-$		167				2220	20
$H_2Ir(PMe_2Ph)_3{}^+$	H^+ + $H_3Ir(PMe_2Ph)_3$	w	149					110
$H_2IrCO(PPh_3)_2{}^+$	H^+ + $H_3IrCO(PPh_3)_2$ H^+ + $HIrCO(PPh_3)_2$						2165,[ll] 2085, 2050	20
$H_2IrSi(OEt)_3(PPh_3)_2$[z,kk]	$HSi(OEt)_3$ + $HIrCO(PPh_3)_3$	w	152	20.2 21.5	2 × 2 × 2 2 × 22	22, 17, 4 110.5, 18.5, 4	2090	89
$HIrCl(CN)C_8H_{12}$	HCN + $[IrCl(C_8H_{12})]_2$			24.1			2140	85
$H_2Ir(PPh_3)_2{}^+$	H^+ + $H_3Ir(PPh_3)_2$	w	152				2315–2280	20
$[HIrCl_2C_8H_{12}]_2$	Cycloocta-1,5-diene + H_3IrCl_6	w	>200 d				2261/1613	291
$[HIrCl_2CO(PEt_3)]_2$	HCl + $MeOCH_2CH_2OH$ + L + CO + H_3IrCl_6	c	170 d				2242	80
$HIr_4(CO)_{11}{}^-$	K_2CO_3 + $Ir_4(CO)_{12}$	y		5.5	1			124, 292
$H_2Ir_4(CO)_{11}$	H^+ + $HIr_4(CO)_{11}{}^-$	y		5.53	1		2130	124, 292
$HFeCo_3(CO)_{12}$	HCl + $[Co(H_2O)_6][FeCo_3(CO)_{12}]$	v	100 d				1118/817	126, 143
$HRuCo_3(CO)_{12}$	HCl + $[Co(H_2O)_6][RuCo_3(CO)_{12}]$ $[Ru(CO)_3Cl_2]_2$ + $Co_2(CO)_8$						1121/805	143, 293 248
$HOsCo_3(CO)_{12}$	HCl + $OsCo_3(CO)_{12}{}^-$	r					1109/809	143

[a] X = Cl, Br, I. [b] See also L = $P(p\text{-}ClPh)_3$, $P(p\text{-}CH_3Ph)_3$. [c] See also L = PPh_3, $PMePh_2$, PEt_2Ph, $PBu^n{}_3$. [d] Unstable except under HCl atmosphere. [e] See also *sec*-butyl and isopropyl sulfides. [f] For $HRh(SiR_3)X(PPh_3)_2$, see also X = Cl, SiR_3 = $SiCl_2Me$, $SiCl_2Et$, $SiClMe_2$, $SiClEt_2$, $SiEt_3$, $SiMe_3$, $SiPh_3$, $Si(OEt)_3$; X = Br, SiR_3 = $SiCl_3$, $SiCl_2Me$, $SiCl_2Et$, $SiClMe_2$, $SiClEt_2$, $SiEt_3$, $Si(OEt)_3$; X = I, SiR_3 = $SiCl_3$, $Si(OEt)_3$. [g] For $HRh(SiR_3)ClL_2$ see also L = $AsPh_3$, SiR_3 = $SiCl_3$; L = $SbPh_3$, SiR_3 = $Si(OEt)_3$, $SiCl_3$. [h] H cis to both halides. [i] See also $PPr^n{}_3$, PEt_2Ph, $PEt_2(p\text{-}MeOPh)$, $AsEt_3$, $AsEt_2Ph$, where $X_2 = Cl_2$; PEt_3, PEt_2Ph, where $X_2 = Br_2$; PEt_3, PEt_2Ph, where $X_2 = I_2$. [j] H trans to one halide. [k] *mer*-L_3, *cis*-Cl_2. [l] *mer*-L_3, *trans*-Cl_2; see also X = Br and L = $PEtPh_2$; *mer*-L_3, *cis*-Cl_2. [m] H trans to Cl. [n] *trans*-$(PEt_3)_2$, *trans*-Cl_2, *trans*-Br_2. [o] *mer*-PEt_3, *trans*-L_2. [p] $HIrX_1X_2CO(PPh_3)_2$, where X_1 = Br, X_2 = Cl, F, I; X_1 = F, X_2 = I; X_1 = Cl, X_2 = I. [q] *trans*-L_2, *trans*-X_2, CO cis to Cl. [r] *trans*-L_2, *cis*-X_2, CO trans to Cl. [s] $HIrX_2COL_2$, where X = Br, Cl, L = $AsMe_2Ph$, PEt_3, PMe_3; X = Cl, L = PMe_2Ph. [t] See also py, CH_3CN with Cl_2; NH_3, py, $SbPh_3$ with Br_2. [u] *trans*-L_2, H cis to $SnMe_3$; see also $HIrX(SnR_3)COL_2$: R = Me, X = Br, L = PPh_3; R = Me, X = Cl, L = $PMePh_2$; R = Ph, X = Cl, Br, I, L = PPh_3; R = Ph, X = Cl, L = $PMePh_2$. [v] *trans*-L_2, H trans to $SnMe_3$. [w] *mer*-L_3, *cis*-H_2. [x] *mer*-L_3, *cis*-H_2; see also X = Br, L = $PEtPh_2$. [y] H trans to halide and H trans to phosphorus. [z] *cis*-L_2, *cis*-H_2. [aa] See also HD derivative. [bb] See also $GeEt_3$, $GeCl_3$, and $H_2Ir(GeEt_3)CO(diphos)$, $H_2Ir(GeMe_3)CO(PMe_2Ph)_2$, $H_2Ir(GeMe_3)CO(PEt_3)_2$. [cc] See also PPh_3 with $CF_3COCH_2OCH_3$, $CF_3COCH_2OCF_3$; $AsPh_3$ with $CH_3COCH_2OCH_3$, $CF_3COCH_2OCH_3$, $CF_3COCH_2OCF_3$. [ee] See also $P(OEt)_2S_2{}^-$, $P(p\text{-}ClPhO)_2S_2{}^-$, $P(OEt)_2S_2{}^-$, $PEt_2S_2{}^-$, $PPh_2S_2{}^-$ with PPh_3; $PEt_2S_2{}^-$ with $AsPh_3$. [ee] See also L = $AsMe_2Ph$. [ff] See also L = PPh_3, $AsMe_2Ph$, $SbPh_3$, SMe_2, $P(OMe)_3$, $P(OMe)_2Ph$, CO, NCMe. [gg] See also L = $SbPh_3$, SMe_2. [hh] See also $PMePh_2$. [ii] See also L = $PBu^t{}_2Et$, $PBu^t{}_2Pr^n$. [jj] See also $IrClCO(PPh_3)_2$ with H_2S, MeC_6H_4SH, $Me(SH)C_6H_3SH$, CF_3COOH, C_2F_5COOH, $HClO_4$. [kk] See also $SiCl_3$, $SiCH_3Cl_2$, $SiPh_3$, $SiMe_2Ph$, $SiMe_3$. [ll] ν_{CO} mixed with ν_{MH}.

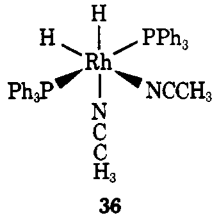
The complex $HRh(CO)L_3$ ($L = PPh_3$) can be obtained in 90% yield from the reaction of *trans*-$RhCl(CO)L_2$ with $NaBH_4$, or in 72% yield from the direct combination of L, $NaBH_4$, and $RhCl_3 \cdot 3H_2O$ in ethanol.[156] This complex is a catalyst for hydrogenation, isomerization, and hydroformylation reactions.[239] Its thermal equilibria and reaction with H_2 and CO have been studied in detail (eq 124).[156] Of these species only $HRh(CO)_2L_2$ reacts readily with ethylene. In a related study on the hydrogen transfer from alcohols to metals Gregorio, Pregaglia, and Ugo[62a] postulate $[Rh(CO)_2(PPh_3)_2]_2$ as an intermediate in the formation of $[Rh(CO)(PPh_3)_3]_2$ which activates molecular hydrogen. The known complex $HRh(CO)(PPh_3)_3$ could be obtained in two crystalline forms depending upon conditions, similar to the isolation of the α and β forms of $HIr(CO)(PPh_3)_3$ reported by Malatesta, Caglio, and Angoletta.[20] The tendency to abstract hydrogen from solvent with varying ligand as studied by this group has been discussed in section II.C.1.



(124)

Complexes of rhodium have been found to be active hydrogenation catalysts. Oxidative addition of H_2 to these complexes was discussed in section II.A.3 and the mechanism of hydrogenation in section III.D. Reactions and catalytic properties of rhodium complexes in solution, including a discussion of catalysis *via* hydride intermediates, has been reviewed by James.[294] Very recently, bridging hydride complexes $H[M(C_5Me_5)Cl]_2Cl$ of rhodium and iridium have been isolated which are good catalysts for the homogeneous hydrogenation of olefins.[295] These complexes had previously been postulated as likely intermediates in the catalytic cycle in which the starting material was $[MC_5Me_5Cl_2]_2$.

Treatment of the diene complexes of rhodium or iridium, $[M(diene)Cl]_2$, with PPh_3 in polar medium gives cationic derivatives of the formula $M(diene)L_2^+$. These add H_2 in cis geometry giving hydrido species containing L and solvent, **36**, which are good hydrogenation catalysts.[149]



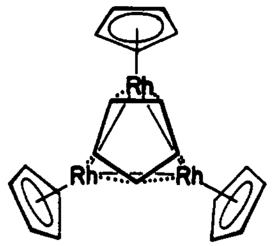
36

Hartwell and Clark[296] find that the complex $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ is dissociated in solution to Cl^- and the corresponding rhodium cation. The unsaturated group in the ligand can be hydrogenated, which reaction is believed to proceed through hydridorhodium intermediates.

The anion $Rh(CO)_4^-$ was obtained in the reduction of $Rh_2Cl_2(CO)_4$ with an alkali metal (Li, Na) in THF in the presence of CO. Attempts to isolate either $HRh(CO)_4$ or $Rh_2(CO)_8$ from this anion have yielded only polynuclear carbonyl derivatives.[297]

The cyanohydridorhodium complex $K_2[HRh(CN)_4(H_2O)]$ adds to olefins and fluoroolefins (see section III.F.1); its reactions with O_2, giving $K_4[(CN)_4(H_2O)RhO_2Rh(CN)_4(H_2O)]$, and with NO giving $K_2[Rh(CN)_4NO_2(H_2O)]$, have been reported by Lawson, Mays, and Wilkinson.[166]

Fischer and Wawersik[279] have obtained the diamagnetic hydrido cluster HRh_3Cp_4 in the treatment of $RhCl_3$ with CpMgBr followed by hydrolysis. The structure of this derivative has been reported by Mills, *et al.*,[298] and shown to be **37**. The authors postulate the presence of hydrogen in (or perhaps above) the plane of the Rh_3 triangle based on the slightly enlarged Rh–Rh distance of 2.72 ± 0.003 Å compared to the expected 2.62 Å observed in $[Rh(Cp)(CO)]_3$.



37

Hieber and Frey[273] obtain alkoxycarbonyl derivatives of rhodium and iridium, $M(CO(OR))(CO)_2L_2$ ($L = PPh_3$, $P(C_6H_{11})_3$) and $M(CO(OR))(CO)_2L_3$ ($L = SbPh_3$) by the treatment of the corresponding cationic complexes with alkoxide. With HCl, the hydrido complexes $HM(CO)L_3$ are obtained apparently through intermediates such as $M(CO)_2L_3^+HCl_2^-$ isolated at low temperature.

A number of reactions and interconversions of complexes of iridium, including acid-reversible formation of alkoxycarbonyl derivatives and various coordinatively unsaturated species, were reported by Malatesta, Caglio, and Angoletta;[20a] these are summarized in schematic form in Figure 2. These and related reactions have been reviewed by Malatesta.[20b]

Organotin derivatives of iridium may be obtained either by the addition of $SnCl_2$ to chloroiridium complexes or directly in the reduction of chloroiridate(III) species with alcohol, and ligand in the presence of $SnCl_2$.[287] A number of hydridoiridium–tin derivatives have thus been prepared and a large trans influence for the $SnCl_3^-$ group noted by its effect on the spectroscopic properties of the Ir–H bond (see section IV.A). The possibility that some of the hydridoiridium–tin derivatives are formed by oxidative addition of $HSnCl_3$, obtained in the hydrolysis of $SnCl_2/H_2O$, was also discussed.

The thiocarbonyl derivative $HIr(CS)L_3$ ($L = PPh_3$) is prepared by $NaBH_4$ reduction of the corresponding chloro complex, obtained in the reaction of CS_2 and *trans*-$IrCl(CO)L_2$.[288]

Iridium tetracarbonyl hydride claimed as early as 1940 has been observed by Whyman[299] in the reaction of $Ir_4(CO)_{12}$ in a high-pressure spectrophotometric cell. Using carbon monoxide and hydrogen pressures ranging from 315 (20°) to 430 atm

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(200°), he was able to identify three new carbonyl stretching frequencies (2054 m, 2031 s, and 1999 w) which are in the range and intensity ratios corresponding to the known $HCo(CO)_4$. The product, however, is not stable at ambient conditions.

M. NICKEL, PALLADIUM, AND PLATINUM

Until recently only platinum of the metals in this triad has been known to form a well-defined series of hydrido complexes. The least stable hydrides of this family are those of nickel.

Nickel phosphine and phosphite hydrides have been obtained in protonation of the complexes NiL_4 in strong acid. The five-coordinate cationic complex $[HNi(diphos)]_2^+$ was isolated as high-melting orange salts with various anions.[134] These salts decompose slowly in air and possess an usually low P–H coupling constant, $J = 6$ Hz. This was in marked contrast to that reported for the analogous hydridometal phosphite $HNi[P(OEt)_3]_4^+$, for which $J_{PH} = 26$ Hz.[133] The latter cation was isolated as an air-sensitive yellow oil from a chilled (−50°) diethyl ether solution to which H_2SO_4 had been added.[300] The ^1H and ^{31}P nmr spectra led to the proposal of a square-pyramidal geometry with hydrogen at the apex. Although no broadening in the nmr spectrum on cooling to −60° occurred, the possibility of a rate process causing fast exchange between the nonequivalent phosphorus nuclei in a trigonal-bipyramidal structure cannot be ruled out.[133]

A study of the kinetics and thermodynamics of ligand exchange of this pentacoordinate salt revealed that protonation preceded ligand dissociation although there was also evidence for a species $HNi[P(OEt)_3]_3^+$ which would result from a dissociation in the cationic species.[300] Such a tetracoordinate cation was the typical product reported for the interaction of acid and $Pt[PPh_3]_4$ in which proton addition followed ligand dissociation.[82]

There have been several reports of nickel hydride complexes containing bulky phosphine ligands. Dichlorobis(tricyclohexylphosphine)nickel will undergo a reduction in a tetrahydrofuran–ethanol (4:1) mixture at room temperature in the presence of sodium borohydride.[301] On exposure to air the product, $HNiCl[P(C_6H_4)_3]_2$, is rapidly decomposed in solution and somewhat slower in the solid state. Its relative stability is believed to be partly due to the bulkiness of the cycloalkylphosphine ligands which prevent rearrangement of the square-planar complex to the tetrahedral form and which also shield the metal from attack by reactive substances. A trans configuration is assigned based on the high-field triplet at τ 34.6 and $J_{PH} = 73.5$ Hz in the nmr. Bis(tricyclohexylphosphine)nickel adds the elements of HCl or organic acids to yield four-coordinate hydrides.[302] Presumably these are also sterically shielded. A dimeric nickel hydride, $[HNi(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2]$, has been isolated by the same group.[58] The diamagnetism of the complex is believed due to the presence of a Ni–Ni bond. The hydrides occupy bridging positions above and below the phosphine nickel plane.

Munakata and Green[303] have observed nmr evidence for a species $HNi(BH_4)(PPr^i_3)_2$. The interaction of this hydridometal borohydride with *trans*-$PdCl_2(PR_3)_2$ (R = cyclohexyl or isopropyl) gives an equilibrium mixture of hydrides. These are separated by the addition of excess phosphine ligand and recrystallizations. A rapid intramolecular exchange is believed responsible for the nmr equivalence of the BH_4 hydrogens in its complexes.

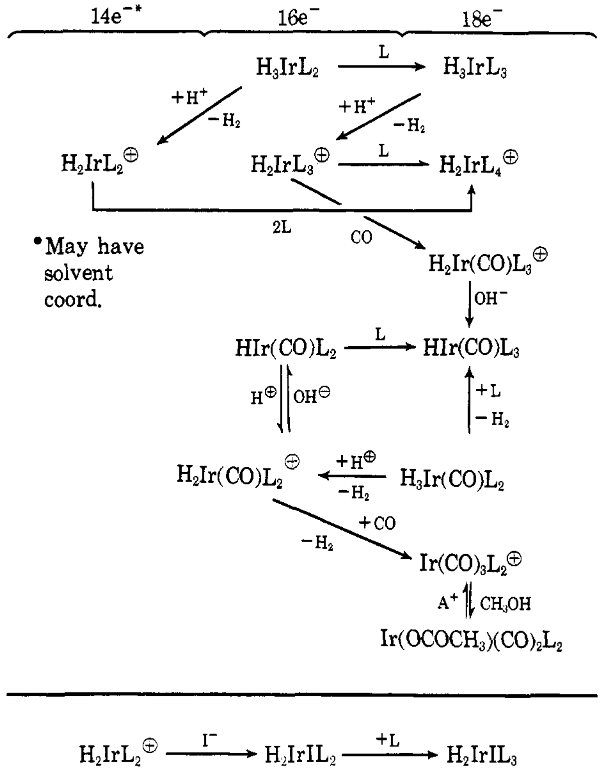

Figure 2. Interconversions of iridium complexes, after Malatesta, Caglio, Angoletta.[20a]

Trimethylgermane has been shown to react with *trans*-PdX_2L_2 (L = PEt_3) in the following fashion (X = Cl^-, Br^-).[87a]

$$trans\text{-}PdX_2L_2 + Me_3GeH \xrightarrow{40^\circ} Me_3GeX + trans\text{-}HPdXL_2 \quad (125)$$

The palladium product of eq 125 releases hydrogen upon treatment with HCl in contrast to the platinum complex which is believed to add HCl to form an octahedral complex.[87]

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Table VII

Survey of Hydride Complexes: Ni, Pd, Pt

Complex	*Preparation*	*Color*	*Mp, °C*	*^1H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$HNi[P(OEt)_3]_4^+$	$H_2SO_4 + Ni[P(OEt)_3]_4$	y		24.2	5	25	1970	300
$HNi(diphos)_2^+$	$HCl + Ni(diphos)_2$	o	198	23.00	5	6	1950	134
$\{HNi[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]_2\}_2$	$Na[HB(CH_3)_3] + NiCl_2[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]_2$	r		21.4	5	23.5		58
t-$HNiCl(PPh_3)_2$	$NaBH_4 + NiCl_2(PPh_3)_2$	y	150 d	34.6	3	73.5	1916	301
$HNiCpP(C_6H_{11})_3$	$C_5H_6 + Ni[P(C_6H_{11})_3]_2$						1920	302
$HNiCH_3[P(C_6H_{11})_3]_2$	$Al(CH_3)_3 + HNi(OAc)[P(C_6H_{11})_3]_2$						1800/1300	302
$HNi[P(C_6H_{11})_3]_2(OAc)$	$CH_3COOH + \{Ni[P(C_6H_{11})_3]_2\}_2N_2$						1920/1360	302
$HNiBH_4[P(Pr^i)_3]_2$	$NaBH_4 + [NiCl_2[P(Pr^i)_3]_2$			29.7	3 × 5	70.5		303
t-$HPdCl(PEt_3)_2$	$Me_3GeH + PdCl_2(PEt_3)_2$	c	84	23.6	1		2009	87b
$HPdCl(PPr^i{}_3)_2$	$NaBH_4 + PdCl_2(PPr^i{}_3)_2$	c		24.5	3	4.6	2010	303
$HPdCl(PCy_3)_2$	$NaBH_4 + PdCl_2(PCy_3)_2$	c		24.4	3	4.1	2002	303
t-$HPdBr(PEt_3)_2$	$Me_3GeH + PdCl_2(PEt_3)_2$	c	91	22.5	1		2002	87b
$HPdBr(PCy_3)_2$	$NaBH_4 + PdCl_2(PCy_3)_2$	c		23.3	3	6	1991	303
$HPdBH_4(PPr^i{}_3)_2$	$NaBH_4 + PdCl_2(PPr^i{}_3)_2$			23.2	7	9	2013	303
$HPdBH_4(PCy_3)_2$	$NaBH_4 + PdCl_2(PCy_3)_2$						2002	303
$HPd(GePh_3)(PEt_3)_2$	$H_2 + Pd(GePh_3)_2(PEt_3)_2$	g	Unstable					304
$HPt(SnCl_3)_4^{3-}$	$H_2/500\ atm + Pt(SnCl_3)_5^{3-}$	y					2072, 2052	305
$HPt(SnCl_3)_2(PEt_3)_2^-$	$SnCl_3^- + HPt(SnCl_3)(PEt_3)_2$ $SnCl_2 + H_2 + PtCl_2(PEt_3)_2$	y					2108	305
$HPt(GeCl_3)_5^-$	$HGeCl_3 + K_2PtCl_4$	cr	257 d				2080	306
t-$HPt(SnCl_3)(PEt_3)_2$	$SnCl_2 \cdot 2H_2O$ + *t*-$HPtCl(PEt_3)_2$	w	100	19.2	1		2105	171, 307
c-$HPt(Si(C_6H_4F\text{-}p)_3(PPh_3)_2$[a]	$HSi(C_6H_4F\text{-}p)_3 + Pt(PPh_3)_4$	y	131				2095	92
$HPt(SiPh_3)(PEt_3)_2$	$HSiPh_3 + CH_3OH + PtCl_2(PEt_3)_2$	y	130 d				2056	308
$HPt(SnCl_3)(PPh_3)_2$	$SnCl_2 \cdot 2H_2O + HPtCl(PPh_3)_2$	o	172				2100	309
$HPt(C{\equiv}CPh)(PEt_3)_2$	$PhC{\equiv}CH$ + *t*-$PtCl(SiMe_3)(PEt_3)_2$	c	34	16.12	3	18	2020	33
$HPt(GePh_3)(PPh_3)_2$	$H_2 + Pt(GeMe_3)(GePh_3)(PPh_3)_2$ $H_2 + Pt(SiMe_3)(GePh_3)(PPh_3)_2$	w	150 d				2024	33
$HPt(GePh_3)(PEt_3)_2$	$H_2 + Pt(GePh_3)_2(PEt_3)_2$	w	150 d				2051	32
$HPt(GePh_3)diphos$	$H_2 + Pt(GePh_3)_2diphos$		221				1998/1428	310, 311
$HPtSH(PPh_3)_2$	$H_2S + Pt(PPh_3)_2$	cr		19.187	Cplx 3+	11	2116	84
$HPtSeH(PPh_3)_2$	$H_2Se + Pt(PPh_3)_2$	cr		18.807	Cplx 3+		2140	84
$HPtSPh(PPh_3)_2$	$HSPh + Pt(PPh_3)_2$			19.926	1		2130	84
$HPtSCN(PPh_3)_2$	$NaSCN + HPt(PPh_3)_3^+$		195				2247	82
t-$HPtCl(PMe_2Ph)_2$	HCl + *t*-$PtCl(SiMePh_2)(PMe_2Ph)_2$		102				2205	312
t-$HPt(O_2CC_6H_4X)(PEt_3)_2$[b]	$XC_6H_4CO_2Ag$ + *t*-$HPtCl(PEt_3)_2$	w or y	−5–91	31.7–33.6	Pt–H P–H	1161–1298 15.3–158	2224–2263	313
c-$HPtCl(diphos)$	$H_2 + PtCl(SiMe_3)(diphos)$	y	142				2002	310
$HPtCN(PPh_3)_2$[c]	$KCN + HPtCl(PPh_3)_2$	w	185 d				2075	180
	$NaCN + HPt(PPh_3)_3^+$		224				2062	82
$HPt(PPh_3)_3^+$	HX[d] $+ EtOH/H_2O + Pt(PPh_3)_4$							82
	HX[d] $+ EtOH/H_2O + Pt(PPh_3)_3$		110				2102	82
$HPt(PEt_3)(diphos)^+$	$H_2 + Pt(GeMe_3)(PEt_3)diphos^+$	w		12.91	3 × 2 × 2 × 2		2043	314
t-$HPtCO(PEt_3)_2^+$	L + *t*-$HPtCl(PEt_3)_2$	w		14.76	3	13.5	2167	315
t-$HPtCO(AsEt_3)_2^+$[e]	L + *t*-$HPtCl(AsEt_3)_2$	w		15.65	1		2106	315
c-$HPt(PEt_3)(AsEt_3)_2^+$	L + *c*-$HPtCl(AsEt_3)_2$	w		19.05	2	11.5		315
c-$HPtP(OMe)_3(AsEt_3)_2^+$	L + *c*-$HPtCl(AsEt_3)_2$	w		17.81	2	<2.0	2089	315
c-$HPt(PPh_3)(AsEt_3)_2^+$	L + *c*-$HPtCl(AsEt_3)_2$	w		18.51	2	9.8	2069	315
c-$HPtP(OPh)_3(AsEt_3)_2^+$	L + *c*-$HPtCl(AsEt_3)_2$	w		18.31	2	4.0	2082	315
t-$HPt(C_2H_4)(PEt_3)_2^+$	$NaBPh_4 + C_2H_4$ + *t*-$HPtNO_3(PEt_3)_2$			17.2	3	12		317
t-$HPtNCCMe_3(PEt_3)_2^+$[f]	L + *t*-$HPtCl(PEt_3)_2$	w		17.13	3	14.4	2104	315

[a] See also $HPtSiCl_3(diphos)$, *cis*-$HPtSi(C_6H_4F\text{-}m)_3(PPh_3)_2$, *cis*-$HPt(SiC_6H_4CF_3\text{-}p)_3(PPh_3)_2$, *cis*-$HPt(SiC_6H_4CF_3\text{-}m)_3(PPh_3)_2$. [b] X = *p*-$NO_2$, *p*-NC, *p*-I, *p*-Br, *p*-Cl, *p*-Me, *p*-OMe, *p*-NMe_2, *m*-NO_2, *m*-I, *m*-Br, *m*-Cl, *m*-F, *m*-Me, *m*-NMe_2, *o*-NO_2, *o*-Br, *o*-Cl; *t*-$HPt(O_2CR)(PEt_3)_2$, R = 3,5-$C_6H_3(NO_2)_2$, 2,5-$C_6H_3(NO_2)_2$, 2,4,6-$C_6H_2(NO_2)_3$, CF_3, $CHCl_2$, CH_2Cl, $PhCH_2$. [c] See also NO_2, Br, SCN. [d] See also $X^- = NO_3^-$, ClO_4^-, BF_4^-, $CH_3OSO_3^-$, HSO_4^-, BF_4^- salts. [e] See also L = $AsEt_3$, $NCCMe_3$, PPh_3, $P(OPh)_3$, $P(OMe)_3$. [f] See also L = NCC_6H_4OMe, $P(OMe)_3$, $P(OPh)_3$, PPh_3, PEt_3, py.

Some platinum(II) complexes combine with substituted main group metal hydrides to form octahedral complexes but in only a few cases are the octahedral compounds stable enough to be isolated; see Clemmit and Glockling[318] and references therein. The cationic complex [Pt(GeMe$_3$)PEt$_3$diphos]$^+$ was believed[314] to oxidatively add HCl forming [HPtCl(GeMe$_3$)PEt$_3$diphos]$^+$; further investigation has shown this complex to contain the hydrogen dichloride anion, HCl$_2^-$, instead of an octahedral Pt(IV) complex.[319]

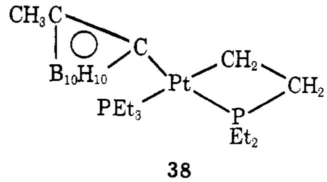
The product HPtCl(diphos) formed in the hydrogenolysis of PtCl(SiMe$_3$)diphos is required by ligand constraint to have cis geometry. Based on its spectroscopic properties a reinvestigation of the complexes reported[309] as *cis-* and *trans*-HPtCl(PEt$_3$)$_2$ was undertaken. Infrared and nmr spectra show that these are different crystallographic modifications of the trans isomer.[310] The same observations have also been reported by Collamati, Furlani, and Attioli[320] who observed three different crystallographic forms which are easily interconverted according to the method of purification.

Cationic hydride phosphine and arsine complexes of platinum have been prepared by displacement of coordinated halide with neutral ligand. The equilibrium in eq 126 can be

$$\mathrm{HPtCl(PEt_3)_2 + L \rightleftharpoons HPtL(PEt_3)_2^+ + Cl^-} \qquad (126)$$

shifted to the right by the addition of sodium salts to acetone solutions of complex with excess ligand (L = py, PEt$_3$, PPh$_3$, P(OMe)$_3$, P(OPh)$_3$, and others).[315] Falk and Halpern[316a] have found the isotopic exchange of *trans*-HPtCl(PEt$_3$)$_2$ with D$_2$O to be catalyzed by acid; an intermediate involving oxidative addition of DCl is postulated.

In a study of the mechanism of the poisoning of platinum catalysts by H$_2$S and H$_2$Se, Morelli, *et al.*,[84] have isolated two types of complexes, **1a** and **1b**. In the latter, two types of protons are found. The one bonded to sulfur is observed rapidly to exchange with D$_2$O but the metal hydride is unaffected; ^{195}Pt satellites have not been observed for either proton. Bresadola, *et al.*,[321] have treated *trans*-PtCl$_2$(PEt$_3$)$_2$ with lithium derivatives of alkyl and aryl monosubstituted 1,2- and 1,7-dicarba-*closo*-dodecaborane(12) and obtained stable complexes. Since the reaction occurs with both the 1,2 and 1,7 isomers and the B–H stretching region is unaffected by coordination, they propose that platinum achieves four-coordination by elimination of hydrogen of one of the ethyl groups of the phosphine ligand **38**; this is similar to other intramolecular oxidative addition reactions discussed in section II.C.3. A number of hydridoplatinum complexes are discussed in a review by Cross[316b] of the σ complexes of this metal.



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N. ZINC, CADMIUM, AND MERCURY

We have included the hydride chemistry of these elements because it is rather limited, although some may question whether this boundary subgroup should be included with the transition metals. The hydride resonances for derivatives in this subgroup occur below τ 10, in keeping with their closed subshell arrangement. Kubas and Shriver[322] observe a limiting resonance at τ 3.0 for the bridge hydrogen in the dialkylzinc dimer [R$_2$Zn–H–ZnR$_2$]$^-$ (R = C$_2$H$_5$) which participates in the mobile equilibrium

$$\mathrm{R_2Zn + HZnR_2^- \rightleftharpoons [R_2Zn\text{–}H\text{–}ZnR_2]^-} \qquad (127)$$

The resonance is concentration dependent and the value reported above is obtained when the ratio of dialkylzinc to hydride is 10/1. Equilibrium constants were calculated, molecular weight studies were made, and deuterium analogs were prepared. The evidence suggests a terminally bound metal hydride monomer with the structure H–ZnRR$^-$ or its etherate in equilibrium with the bridging hydride [R$_2$Zn–H–ZnR$_2$]$^-$ or its dietherate.

Since the phenyl analog of the 1:1 complex was too insoluble for characterization, a similar equilibrium was not observed. However, the perfluorophenyl derivative was considerably more soluble and provided strong infrared and molecular weight evidence for a dimer with dihydride bridges.[323]

When zinc hydride and trimethylethylenediamine are warmed together in toluene, hydrogen is evolved and a dimer of 2-dimethylaminoethyl(methyl)aminozinc is obtained as colorless crystals.[324] This compound exhibits a broad infrared absorption centered at 1825 cm^{-1} assigned to a terminal zinc–hydride stretch. A crystal structure of this complex has confirmed this assignment although proton resonance was not observed in the nmr spectrum.

IV. *Spectroscopic Characteristics of Transition Metal Hydrides*

A. INFRARED AND RAMAN

Data for the characteristic metal–hydrogen (and deuterium) stretching absorptions in the infrared are given in Tables I–VIII. The terminally bonded M–H stretching absorptions (ν_{MH}) occur in the region 1900 ± 300 cm^{-1}. They are of variable intensity and sometimes slightly broadened, $\Delta\nu_{1/2} \sim$ 10–30 cm^{-1}. They are usually stronger than the ν_{CH} modes at 3000 cm^{-1} but not as strong as the ν_{CO}, $\nu_{\mathrm{N_2}}$, or ν_{NC} modes in metal carbonyl, nitrogen, or isocyanide complexes, which absorptions occur approximately in the same region as ν_{MH}. In HCo(N$_2$)L$_3$ (L = a variety of tertiary phosphines) a strong band attributable to $\nu_{\mathrm{N_2}}$ is reported (for L = PPh$_3$: 2096 cm^{-1},[13] 2090 cm^{-1} [65]), but no absorption attributable to ν_{CoH} was observed. For H$_3$CoL$_3$, Sacco and Rossi[13] report two sharp bands of medium intensity, one in the region 1930–1950 cm^{-1} and the other in the region 1720–1760 cm^{-1}. Lorberth, Nöth, and Rinze[65] assign three hydride bands (as expected) for the derivatives H$_3$Co(*p*-RC$_6$H$_4$P)$_3$ (R = CH$_3$, H, F, Cl): $\nu_{\mathrm{CoH_2}}$ (asym) 1767–1801, $\nu_{\mathrm{CoH_2}}$ (sym) 1895–1908, and ν_{CoH} 1934–1955 cm^{-1}. The relative intensity of ν_{CoH} in H$_3$CoL$_3$ and $\nu_{\mathrm{N_2}}$ in HCo(N$_2$)L$_3$ may be compared in the published spectra[13] of these two derivatives, taking ligand bands common to both as a point of reference.

For the complexes [*trans*-HPtLL'$_2$]$^+$[ClO$_4$]$^-$ (L = Me$_3$CNC, *p*-MeOC$_6$H$_4$NC; L' = PEt$_3$; see Table XII), Church and

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(318) A. F. Clemmit and F. Glockling, *J. Chem. Soc. A*, 1164 (1971).

(319) K. A. Hooton, *ibid.*, 680 (1969).

(320) I. Collamati, A. Furlani, and G. Attioli, *ibid.*, 1694 (1970).

(321) D. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968).

(322) G. J. Kubas and D. F. Shriver, *J. Amer. Chem. Soc.*, **92**, 1949 (1970).

(323) G. J. Kubas and D. F. Shriver, *Inorg. Chem.*, **9**, 1951 (1970).

(324) N. A. Bell and G. E. Coates, *J. Chem. Soc. A*, 823 (1968).

Table VIII

Survey of Hydride Complexes: Zn, Cd, Hg

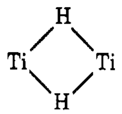
Complex	*Preparation*	*Color*	*Mp, °C*	*^1H nmr, τ, ppm*	*Mult*	*Sepn, Hz*	*Ir, ν_{MH}/ν_{MD}*	*Ref*
$HZn(CH_3)_2^-$	$NaH + Zn(CH_3)_2$	w		4.33	1			322
$HZn(C_6H_5)_2^-$	$NaH + Zn(C_6H_5)_2$	c		3.40	1		1200–900	322
$HZn(C_6F_5)_2^-$	$NaH + Zn(C_6F_5)_2$	w					1700–1300	323
$[HZnN(Me)C_2H_4N(Me)_2]_2$	$CH_3NHCH_2CH_2N(CH_3)_2 + ZnH_2$	c	128 d				1825	324

Mays report very weak ν_{M-H} absorptions[316a] and could not observe any absorptions[316b] for L = Me_3CNC, L′ = $AsEt_3$; see Table XIII. The MH and NC stretching frequencies appear to be mixed; see Tables XII and XIII.

A comparison between the ν_{MH} and ν_{CO} bands may be made from published spectra, such as for $HIr(CO)_2(PPh_3)_2$ (ν_{MH} 2029; ν_{CO} 1970, 1915 cm^{-1}),[325] $HMn(CO)_3(PF_3)_2$ (ν_{MH} 1806; ν_{CO} 2086–1969 cm^{-1}),[208] $H_2Os(CO)_3PPh_3$ (ν_{MH} 1959, 1922; ν_{CO} 2079–2018 cm^{-1}), and $H_2Os(CO)_4$ (ν_{MH} 1942; ν_{CO} 2141–2047 cm^{-1}).[8] In the hydridometal carbonyls, these modes may be mixed (see below).

When ν_{MH} is weak in the ir, it may be stronger in the Raman, following the complementary intensity relationships which are usually observed between these two spectroscopic methods. Thus, ν_{MH} (1780 cm^{-1}) is medium to strong compared to the carbonyl modes (2119–1993 cm^{-1}) in the Raman spectrum of $HMn(CO)_5$,[326] which should be contrasted to the difficulties which had been experienced in attempts to observe this mode in the infrared (1784 cm^{-1}); see Edgell, *et al.*,[327] and references cited therein.

For hydridometal derivatives in which hydrogen is in a position bridging two (or more) metals, the hydrogen mode is shifted to lower energy, *ca.* 1100 ± 300 cm^{-1}, and considerably broadened, $\Delta\nu_{1/2} \sim 100$ cm^{-1}. In some cases, it has proved difficult to see in the infrared; *cf.* $H_3Re_3(CO)_{12}$[51] or [HNi(P–P)]$_2$.[68] Bercaw and Brintzinger,[195] however, have identified an absorption at 1450 cm^{-1} in the spectrum of $[HTiCp]_2$ in the solid as the antisymmetric



bridging mode. Upon deuteration (believed only to be partially, *i.e.*, 75%, complete) two peaks were observed, at 1260 and 1050 cm^{-1}. In Cp_2Ti-μ-H_2–BH_2, a strong absorption was observed[195] at 1350 cm^{-1} which shifted to 1000 cm^{-1} upon deuteration. In $[HTiCp(C_5H_4)]_2$[108] the stretching mode of what is believed to be bridging hydrogen is assigned at 1230 cm^{-1}. Mays and Simpson[328] have observed a broad band centered at 1114 ($\Delta\nu_{1/2} \sim 110$) cm^{-1} in the infrared spectrum of $HFeCo_3(CO)_{12}$ in concentrated KBr disks; this is observed to shift and narrow to 813 ($\nu_{1/2} \sim 40$) cm^{-1} in the deuterated derivative. Johnson, Lewis, and Williams[58b] report a broad band centered around 1284 ($\Delta\nu_{1/2} \sim 40$) cm^{-1} for $H_4Ru_4(CO)_{12}$ which is observed to shift to 902 ($\Delta\nu_{1/2} \sim 20$) cm^{-1} in the deuterated derivative. In the Raman, it is in fact possible to identify two broad bands due to bridging hydrogen in these derivatives (see Figure 3 and Table IX), and a closer investigation reveals a pair of broad bands for each in the infrared spectra (cm^{-1}): 1605 and 1272 for $H_4Ru_4(CO)_{12}$ and 1095 and 895 for $D_4Ru_4(CO)_{12}$.[331b] In the derivative $H_2D_2Ru_4(CO)_{12}$, both sets of peaks are observed.[331b]

Raman spectroscopy will prove to be of great help in discerning bridging metal–hydrogen modes too weak and broad to be seen in the infrared. Smith, Fellman, and Jones[220] (see also Kirtley[329]) have assigned a broad absorption which contains three shallow maxima at 1100, 1076, and 1000 cm^{-1} as the bridging mode in $H_3Re_3(CO)_{12}$. This is observed to shift (and narrow) in the deuterated derivative to a band of medium intensity at 792 cm^{-1} with two weak components at 752 and 692 cm^{-1}. The anion $H_6Re_4(CO)_{12}^{2-}$ displays in the Raman a broad band centered at 1165 cm^{-1} ($\Delta\nu_{1/2} \sim 110$) which is not present in the spectrum of the deuterated derivative where a band at 832 cm^{-1} ($\Delta\nu_{1/2} \sim 37$) is observed.[50] This and data for some other polynuclear hydrido metal clusters and their deuterated derivatives are summarized in Table IX, and two representative (hitherto unpublished) spectra are shown in Figure 3. The bands may contain multiple maxima which complicate their assignment. Claydon and Sheppard[330] attribute multiple maxima in the infrared spectra of strongly hydrogen-bonded systems to Fermi resonance of the broad hydrogen modes with overtones of lower lying bands (with the minima corresponding to the overtone frequencies). Circumventing this complication for the metal-bridged hydrogen bands by taking the intensity weighted average for the various observed maxima, Kirtley[329] has shown that there is a correlation of ν_{M-H-M} with the M–H–M angle, known at this time for only a few derivatives in which the hydrogen has been located (see section V) and in some other derivatives in which it can be estimated by indirect methods.

As mentioned above, in hydridometal carbonyls it is observed that ν_{MH} and ν_{CO} are sometimes mixed. In the deuterated derivatives, ν_{MD} appears at lower energy and is therefore less mixed with ν_{CO}; thus the latter is observed to shift upon deuteration if the modes are appreciably mixed in the hydrido derivative. The energy relationships are illustrated in Figure 4, for $HRe(CO)_5$ and $DRe(CO)_5$, after Braterman, Harrill, and Kaesz.[332] In this derivative, ν_{MH} is at *lower* en-

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(325) G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, 725 (1969).

(326) A. Davison and J. W. Faller, *Inorg. Chem.*, **6**, 845 (1967).

(327) W. F. Edgell, J. W. Fisher, G. Asato, and W. M. Risen, Jr., *ibid.*, **8**, 1103 (1969).

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

(329) (a) S. W. Kirtley, Dissertation, University of California at Los Angeles, Aug 1971; (b) H. D. Kaesz and S. W. Kirtley, manuscript in preparation.

(330) M. F. Claydon and N. Sheppard, *J. Chem. Soc. D*, 1431 (1969).

(331) (a) S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, **93**, 4594 (1971); (b) manuscript in preparation.

(332) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **89**, 2851 (1967).

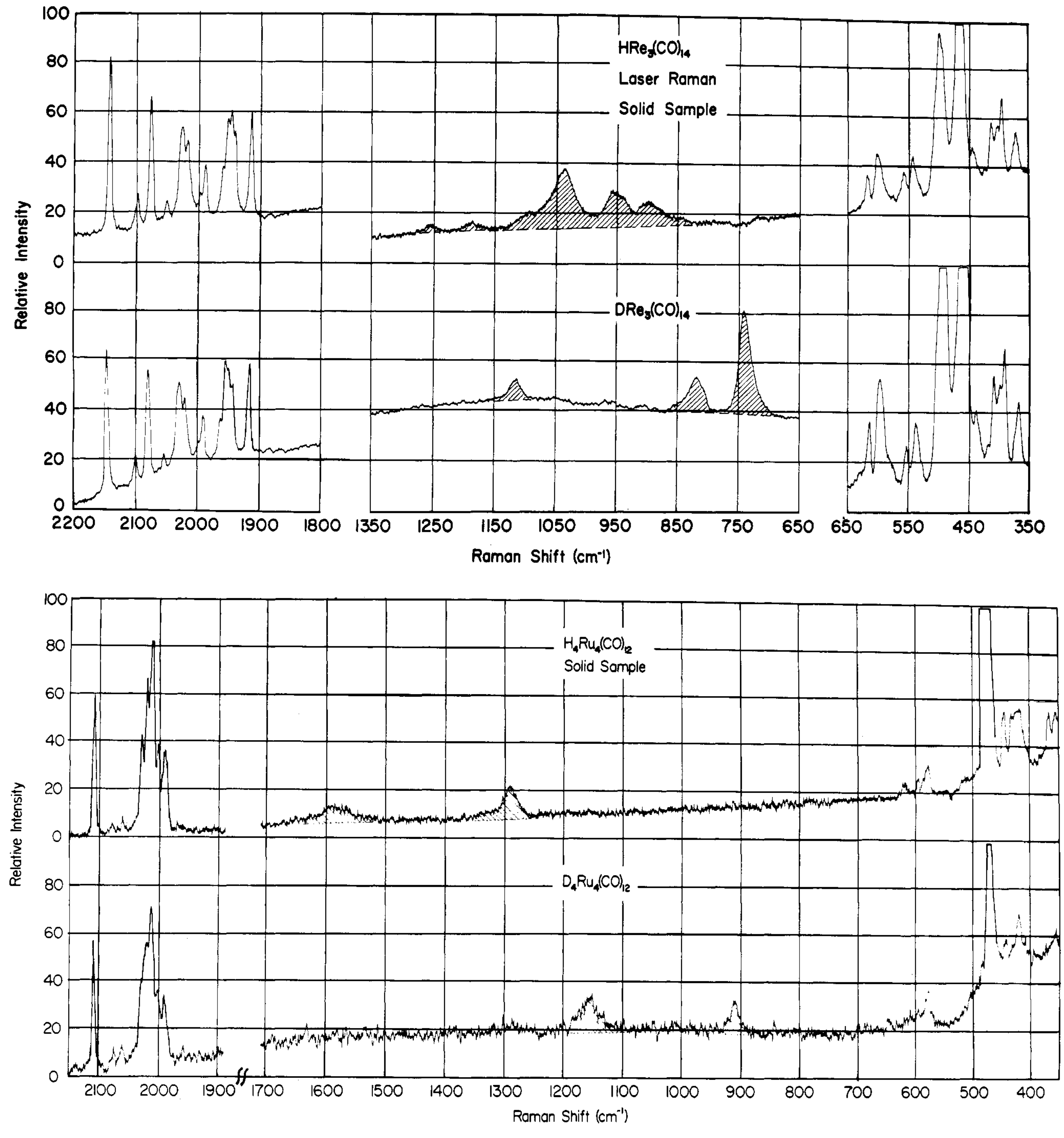

Figure 3. Raman spectra of polynuclear carbonyl hydrides.

ergy than ν_{CO} and an A_1 mode of the latter is observed to shift to *lower* energy by 5 cm^{-1} upon deuteration. By similar arguments, it can be shown that when ν_{MH} is *higher* than ν_{CO}, the latter will shift to *higher* energy upon deuteration. Observations of the resonance interaction in a number of hydridoosmium and hydridoiridium derivatives have been made by Vaska.[135, 333]

In $HRe(CO)_5$, symmetry permits mixing of ν_{MH} (of A_1 species) with the A_1 modes of both radial and axial carbonyl groups; however, the mixing is greatest for the A_1 principally axial mode, *i.e.*, for the carbonyl group in trans position to hydrogen. Also, the observed shift ν_{MH}/ν_{MD} may take on anomalous values.

Because the resonance interaction is observed principally for CO trans to H, this can assist in the assignment of stereochemistry. For instance, of three possible structures for $H_2Ir(CO)L_3^+$ (**39**, L = PPh_3), that containing *mer*-L_3, *cis*-H_2 (in which the CO is trans to MH) is assigned by Vaska[135] on the basis of the observation of shift in ν_{CO} of 35 cm^{-1} upon deuteration. A resonance interaction is observed in *cis*-$H_2Os(CO)_4$

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(333) L. Vaska, *J. Amer. Chem. Soc.*, **88**, 4100 (1966).

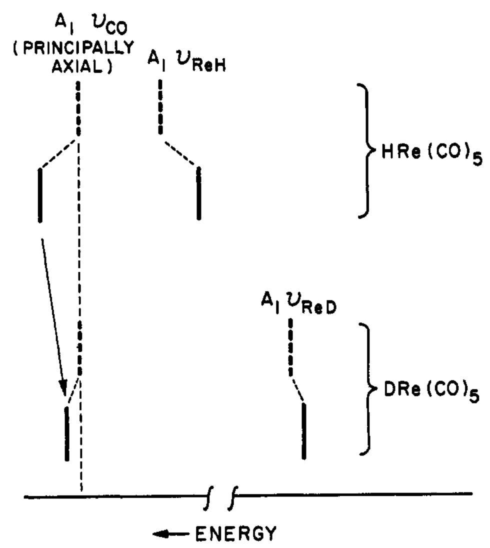


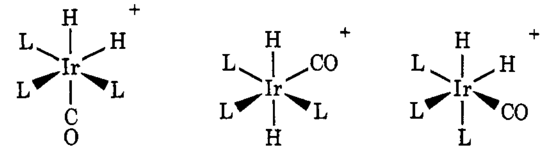
Figure 4. Representation of observed shift (diagonal arrow) of A_1 (principally axial) carbonyl stretching absorption when H is replaced by D in going from $HRe(CO)_5$ to $DRe(CO)_5$ The vertical dashed lines represent the symmetry coordinates before mixing of ν_{CO} with either ν_{ReH} or ν_{ReD}. The solid vertical lines represent the positions of the observed bands, after Braterman, Harrill, and Kaesz.[332]

Table IX

Bridging Hydrogen and Deuterium Modes[a] in Raman Spectra of Some Polynuclear Carbonyl Hydrides

Complex	ν_{MH}, *cm*$^{-1}$	ν_{MD}, *cm*$^{-1}$	*Ref*
$H_3Re_3(CO)_{12}$	1100 w	792 m	220, 329
	1076 vw	752 w	
	1000 vw	692 w	
$H_2Re_3(CO)_{12}^-$	1102 m	803 m	49, 329
	1052 w	740 w	
		632 w	
$HRe_3(CO)_{14}$	1258 vw	1122 w	49, 329
	1184 vw	825 w	
	1097 vw	742 m-s	
	1041 m		
	952 w		
	904 w		
	850 vw		
$H_6Re_4(CO)_{12}^{2-}$	1165 m	832 m	50, 329
	1125 w		
$H_2Re_2(CO)_8$	1382 w	973 w	329
	1275 m	922 m	
$H_4Ru_4(CO)_{12}$	1585 m	1153 m	331a
	1290 m	909 m	
$HCr_2(CO)_{10}^-$	1004 m	705 m	329
	850 m	560 m	
	640 m		

[a] m-s = medium strong, m = medium, w = weak, vw = very weak.


mer-L_3,*cis*-H_2 *mer*-L_3,*trans*-H_2 *fac*-L_3,*cis*-H_2

39

Table X

Summary of Frequency Positions for ν_{IrH}, ν_{CO_3}, and ν_{IrCl} in Iridium Complexes[a]

	Frequency, cm^{-1}	*Trans ligand*
ν_{IrH}	~1750	H
	2000–2100	R_3P, CO
	2180–2240	Halogen
ν_{CO}	1980	H
	2027	Cl
ν_{IrCl}[b]	246–249	H
	260–290	R_3P
	304–316	CO
	303–330	Halogen

[a] After Glockling and Wilbey.[35] [b] See also Jenkins and Shaw[285] and Bennett, Clark, and Milner.[334]

and $H_2Os(CO)_3PPh_3$ by L'Eplattenier and Calderazzo,[8] in which several of the carbonyl modes are observed to shift a total of 35–45 cm^{-1} in going from the hydrido to the deuterio derivatives. Similarly, Church and Mays report a shift of 43 cm^{-1} (to higher energy) in going from *trans*-$HPt(CO)L_2^+$ (L = $AsEt_3$) to the deuterated derivative[315b] and a shift of 38 cm^{-1} in the analogous derivatives for L = PEt_3.[315a]

An interesting manifestation of the resonance effect is observed for the derivative *cis*-$H_2IrBr(CO)$-*trans*-L_2 (L = PEt_2Ph; see product in eq 17) in which ν_{IrH} = 2196, 2100 and ν_{CO} = 1975 cm^{-1}. In the derivative partially deuterated in both positions, there is a shift in the ν_{IrH} (2188, 2090 cm^{-1}) owing to reduced interaction between the metal–hydrogen and metal–deuterium modes, and a peak for ν_{IrD} at 1570 cm^{-1}; there are also two carbonyl modes, one at 1980 cm^{-1} for the derivative in which H is trans to CO and one at 2014 cm^{-1} in which D is trans to CO. Finally, in the dideuterated derivative, ν_{IrD} = 1570 and ν_{CO} = 1998 cm^{-1}.[28] A resonance effect for ν_{MH} and ν_{NC} for isocyanide complexes of platinum hydrides has also been observed (see Tables XII and XIII).

The coupling of ν_{MH} and ν_{CO} is much weaker in first- and second-row derivatives. Braterman, Harrill, and Kaesz[332] did not observe any shift in ν_{CO} in $HMn(CO)_5$ and $DMn(CO)_5$ nor have any workers reported shifts in hydrido and deuterio carbonyls of the other first- or second-row transition metal complexes.

The MH stretching vibration is sensitive to other substituents in the metal complex, as it also affects other modes, particularly of ligands in position trans to hydrogen (see discussion of trans effect and definition of trans-influence in section III.B). A variety of such observations have recently been summarized by Glockling and Wilbey[35] and are presented in Table X. These generalizations, together with the resonance effect between ν_{MH} and ν_{CO} and observations from nmr data (see section IV.B) have been used extensively to arrive at assignments of stereochemistry in complexes. Additional correlations for ν_{MH} are discussed in the next section (see Tables XI, XII, and XIII) together with trends in nmr parameters.

B. NUCLEAR MAGNETIC RESONANCE

Developments in nuclear magnetic resonance of transition metal hydrido complexes have been surveyed in the annual

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(334) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 6, 1647 (1967).

specialist reports of the Chemical Society; see Greenwood, *et al.*[335] The data discussed in this section will in the main be for stereochemically rigid systems. Complexes in which the chemical shift and coupling constants of nonequivalent protons becomes averaged through various dynamic processes are discussed under Stereochemical Exchange (p 278).

The metal–hydrogen bond in transition metal hydrido complexes exhibits magnetic resonance at high fields, typically in the range τ 15–30. These high shifts are derived principally from two effects, a paramagnetic shielding term arising from the mixing into the ground state of excited electronic states and from diamagnetic shielding, which term becomes increasingly important with shorter metal–hydrogen bond lengths; see Atkins, Green, and Green,[318] and references cited therein. Basch and Ginsberg[336] have calculated the shielding for TcH_9^{2-} and find satisfactory agreement with the experimental value (τ 18.4).

A number of workers have suggested that, for derivatives of the same metal, the resonance of bridging hydrogen in hydridometal clusters appears at higher field than that of terminally bonded hydrogen. Ginsberg and Hawkes[219] observe the hydrogen resonance in $H_3Re_2(CO)_6^-$ at τ 27.49 and thus infer a bridging position for hydrogen, as in the cluster $HRe_3(CO)_{14}$, τ 26.25,[337] and $H_3Re_3(CO)_{12}$, τ 27.1.[49] Species known to contain terminally bonded hydrogen show resonance at lower field, *e.g.*, $HRe(CO)_5$, τ 15.7, ReH_9^{2-}, τ 18.5, and $H_8RePEt_3^-$, τ 18.2. In applying this rule to some hydridoruthenium complexes, Johnson, *et al.*,[53] cite further comparisons: $HCrCp(CO)_3$, τ 15.95, $HCr_2(CO)_{10}^-$, τ 29.17,[47] and $HMn(CO)_5$ τ 17.5, $H_3Mn_3(CO)_{12}$, τ 34.0.[56] In view of the wide variation possible for the metal–hydride resonance, including some exceptionally high values which have been lately observed for terminally bonded hydrogen (see below), we feel this correlation should be regarded with some caution.

Unusually high chemical shifts of τ 40 and 60 have been reported for the complexes $HRhCl_2(PBu^t_2Me)_2$ and $HIrCl_2(PBu^t_2R)_2$ (R = Me, Et, Pr^n), respectively, by Masters, *et al.*,[338] and Masters, Shaw, and Stainbank.[290] It is believed that five-coordinate complexes are obtained because of the bulky substitutents on the ligands; spectroscopic data indicate that the two chlorine atoms are trans to each other as are the two tertiary phosphines. The electronic absorptions for these complexes are observed at exceptionally low frequencies, and a decrease in the separation between ground and excited electronic states could thus contribute to the observed high shielding through the paramagnetic shielding term. The metal–hydrogen bond distance is also a contributing factor to shifts to high field and, because of the absence of a ligand trans to hydrogen, the metal–hydrogen distance could be unusually short in these complexes.[290]

Both the chemical shift of metal–hydrogen as well as its coupling with magnetically active nuclei in the complex are affected by stereochemistry. When hydrogen is trans to a ligand of low trans-influence (see section III.B), its chemical shift is at high field, τ 20 or above, while opposite a ligand of high trans-influence (like H or CO), its chemical shift is at the lower part (below τ 20) of the high-field region. The data in Tables I–VIII and that in Tables XI–XIII may be consulted for more specific information.

By their influence on the metal–hydrogen resonance in a variety of metal hydrido derivatives, a strong trans-influence is assigned to the methyl group (Tobias[339]), the trialkylgermanium group (Brooks, Cross, and Glockling[311] and Glockling and Hooton[33]), the trialkyltin group (Lappert and Travers[88]), and the $SnCl_3^-$ group (Taylor, Young, and Wilkinson[287] and Lindsey, Parshall, and Stolberg[340]).

Lorberth, Nöth, and Rinze[65] report an increase in ν_{CoH} and τ_{CoH} with increasing electron-withdrawing character of substituent R in the para position of the phenyl group on the ligand in the series $H_3Co[(p\text{-}RC_6H_4)_3P]_3$ (R = H, CH_3, F, Cl).

The coupling of hydrogen with other hydrogen atoms in the complex, with magnetically active nuclides in the ligands (^{31}P or ^{13}C) and with various isotopes of the metals, provides additional useful information. The couplings between protons in polyhydrido complexes are small, on the order of 10 Hz or less; *cf.* Deeming and Shaw[28] and Dewhirst, Keim, and Reilly.[71] A small long-range coupling for trans-substituted alkyl group IV metal hydrides, *trans-H*-Ir-Ge-C*H*$_3$ or *trans*-H-Ir-Ge-CH_2-C*H* may also be expected; *cf.* Glockling and Wilbey.[35]

The coupling of H with ^{31}P (nuclear spin of $^1/_2$ and 100% natural abundance) has provided extensive aid in stereochemical assignments in square-planar and octahedral complexes. For H cis to ^{31}P, coupling is observed in the range 5–30 Hz, while the coupling H trans to ^{31}P is in the range 60–180 Hz; couplings have been observed as high as 260–290 Hz in some cationic complexes of platinum (see Tables XII and XIII). For some H_2FeL_4 derivatives, the trans coupling appeared *smaller* than the cis coupling; however, a departure from the idealized octahedral structure is also noted (see discussion in section IV.B.1). Similarly, for $HMCp(CO)_2L$ (L = $P(OMe)_3$, PMe_3,[341] $P(OPh)_3$, PPh_3[342b]), $J_{^{31}P-H}$(trans) is in the range 21–26 Hz while $J_{^{31}P-H}$(cis) is in the range 64–73 Hz, reflecting departure from octahedral values, as is also true for five-coordinate complexes (see below).

Analysis of the second order resonance in *cis*-$H_2Ru(L)_4$ and *cis*-$H_2Ru(CO)L_3$ (L = $PMePh_2$) indicate J_{PH}(cis) values (−29, −25, and −19.5 Hz) are of *opposite* sign to J_{PH}(trans) (+74, +75 Hz).[71]

When a tertiary phosphine is replaced by a tertiary phosphite, the coupling constant $J_{^{31}P-H}$(trans) is increased by a factor of about 1.6.[315a] Since this ratio is similar to that observed for the coupling of ^{31}P to atoms directly bonded (*i.e.*, $^{31}P-^{195}Pt$[151] or $^{31}P-^{183}W$[343]), this implies that the Fermi contact term dominates $J_{^{31}P-M-H}$(trans) coupling.

Fewer observations and no correlations yet exist for complexes with stereochemistry other than square planar or octahedral; in some of these, intermolecular exchange of ligand obliterates the couplings.[81] In $HRh(PMe_2Ph)_4$, Dewhirst, Keim, and Reilly[71] were able to slow down this exchange sufficiently to see ^{31}P-H coupling (18 Hz) (as well as ^{103}Rh-H coupling; see below). Yagupsky and Wilkinson[325] were able to rule out intermolecular exchange of ligands in

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(335) N. N. Greenwood, *et al.*, *Spectrosc. Prop. Inorg. Organometal. Compds.:* (a) **1**, 11 (1968); (b) **2**, 17 (1969); (c) **3**, 14 (1970).

(336) H. Basch and A. P. Ginsberg, *J. Phys. Chem.*, **73**, 854 (1969).

(337) H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Amer. Chem. Soc.*, **89**, 2775 (1967).

(338) C. Masters, W. S. McDonald, G. Raper, and B. L. Shaw, *J. Chem. Soc. D*, 210 (1971).

(339) R. S. Tobias, *Inorg. Chem.*, **9**, 1296 (1970).

(340) R. V. Lindsey, Jr., G. W. Parshall, and V. G. Stolberg, *J. Amer. Chem. Soc.*, **87**, 658 (1965).

(341) P. Kalck and R. Boilblanc, *J. Organometal. Chem.*, **19**, 115 (1969).

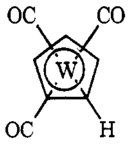
(342) (a) J. W. Faller, A. S. Anderson, and C. Chen, *J. Chem. Soc. D*, 719 (1969); (b) *J. Organometal. Chem.*, **17**, P7 (1969).

(343) S. O. Grimm, P. R. McAllister, and R. M. Singer, *J. Chem. Soc. D*, 38 (1969).

$HIr(CO)_2(PPh_3)_2$ but observed evidence for an intramolecular tautomerism. Infrared spectra and low-temperature nmr indicated two isomers in solution (at −70° $J_{^{31}P-H}$ = 19 and 35 Hz). At room temperature a time-averaged signal was observed whose separation due to ^{31}P–H coupling (*ca.* 2–9 Hz) was much smaller than either of the separations observed at low temperature. At some critical temperatures (*ca.* −45 to −25°), the splitting was obliterated; the authors were led to the conclusion that the coupling constants in the limiting structures must be of opposite sign. Haszeldine, Parish, and Parry[278] report $J_{^{31}P-H}$ for a number of five-coordinate silylrhodium and related complexes, which values fall in the range 13–17 Hz.

In derivatives containing two or more phosphine ligands, strong coupling between the phosphorus nuclei in ligands trans to each other will affect the multiplicity of the resonances of hydrogens of the groups on the phosphines. This is most readily observed for methyl or methoxy resonances where a virtual triplet is obtained for phosphines in positions trans to each other.[344] This has also proved to be an important aid in assigning the stereochemistry in square-planar and octahedral complexes and, because applied early and frequently by Jenkins and Shaw,[345] has become known as the rule bearing their name (see recent reviews, ref 335a, p 11, and 335b, p 19).

The coupling of metal–hydrogen with ^{13}C has received less attention, owing to the low natural abundance (1.1%) of the isotope. Whitesides and Maglio[207] have observed the spin-coupling satellites in a number of *ca.* 20% ^{13}C-enriched metal cyanides and carbonyls. For the complexes $HM(CN)_5^{3-}$ the $J_{^{13}C-H}$ cis and trans coupling were respectively (Hz): M = Ir, 5.7, 37.2; M = Rh, 5.7, 56.2; M = Co (not observed, owing most likely to intramolecular exchange of CN^-). In *trans*-$HPt(CN)(PEt_3)_2$, $J_{^{13}CH}$(trans) = 41.9 Hz. In metal carbonyls, the relative magnitudes of the cis and trans coupling constants were similar, thus limiting the usefulness of these as an absolute stereochemical probe: $J_{^{13}CH}$ for $HMn(CO)_5$ = 14.0 (cis), 7.0 Hz (trans); $J_{^{13}CH}$(cis) for *cis*-$HMn(CO)_4PPh_3$ = 15.7 (CO cis to ligand) and 12.1 (CO trans to ligand), and $J_{^{13}CH}$(trans) = 5.2 Hz. In the polynuclear anions $HM_2(CO)_{10}^-$, the ^{13}C–H coupling constants were (Hz): M = W, *J*(cis) = 3.5, *J*(trans) = 4.3; M = Mo, *J*(cis) = 4.3, *J*(trans) = either 4.3 or ≤ 3. Faller, Anderson, and Chen[342] report for $HWCp(CO)_3$ (**40**) $J(^{13}CO_{cis}\text{-}H)$ = 18.5 Hz and *J*(trans) = 5.5 Hz (not resolved from main resonance).



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A number of transition metals possess isotopes of spin $^1/_2$ of sufficient abundance to permit observation of spin-coupling satellites; for complexes of platinum, there is a convenient isotope, ^{195}Pt, 33.7% abundance. A number of studies correlating the considerably strong coupling of this isotope to H (as well as to other magnetically active nuclides) have been made.

Atkins, Green, and Green[313] have presented linear correlations between the chemical shift of hydride with the metal hydrogen coupling constant, the metal–hydrogen stretching frequency, and the pK_a of the parent carboxylic acid in a series of *trans*-$HPtX(PEt_3)_3$ complexes where X is a carboxylato ligand. The relationship between the chemical shift of the hydride and γ_{M-H} is interpreted as a reflection of the sensitivity of the M–H bond length to these measurements. It appears that the s character of the platinum–hydrogen bond most strongly influences the platinum–hydrogen coupling constant. Their results suggest that $J_{PtH} \propto \tau_{PtH} \propto \nu_{PtH} \propto R_{PtH}^{-3}$. The parameters p$K_a$, τ_{PtH}, J_{PtH}, ν_{PtH}, and J_{PH} for 26 different carboxylato complexes of platinum and effects of solvent on these are presented in their paper. For other complexes, summarized in Table XI, a relation with ΔE^* (first ligand-field band obtained from complexes $[Co(NH_3)_5L]^{2+}$) was explored, but no satisfactory correlation was obtained.

Using heteronuclear double resonance techniques, Dean and Green[346] studied the ^{195}Pt chemical shifts in the series *trans*-$HPtX(PEt_3)_2$ (X = a variety of anions and carboxylato groups). The platinum resonance was observed to shift to higher field according to the following order: X = $RCO_2 < NO_3 < NO_2 < Cl < SCN < Br < CN < I$. It was concluded that the platinum shifts were influenced primarily by the increased covalency of the metal–ligand bond since this order, with the exception of cyanide, parallels the nephelauxetic series.

Table XI

Nmr[a] and Ir[b] Data for *trans*-$HPtX(PEt_3)_2$

X =	τ_{Pt-H}, *ppm*	J_{Pt-H}, *Hz*	ν_{Pt-H}, cm^{-1}
I	22.65	1369	2156
Cl	26.8	1275	2183
Br	25.55	1346	2178
NO_3	33.6	1322	2242
NCO	27.7	1080	2229
OCN	27.0		
ONO	29.4	1003	2150
SCN	22.95	1233	2112
NCS	27.6	1086	
CN	17.6	778	2041

[a] After Powell and Shaw,[347] also a few of these with As are contained in the work. [b] After Atkins, Green, and Green.[313]

Two series of cationic complexes $HPtLL'_2{}^+$ (L'_2 = PEt_3, $AsEt_3$) were studied by Church and Mays,[315] and some of the data pertinent to this review are summarized in Tables XII and XIII. Combining results from the two studies in which it was observed that J_{Pt-H} increased as the σ donor strength of the ligand increased, the order for increasing values of *J* is L = $PEt_3 < P(OMe)_3 < P(OPh)_3 < ArNC \simeq RNC \simeq PPh_3 < CO < AsEt_3 <$ py. These results provide support for the idea that the trans-influence is largely due to a rehybridization of the metal orbitals which does not measurably affect the cis bonds.

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(344) R. K. Harris, *Can. J. Chem.*, 42, 2275 (1964).
(345) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 1407 (1966).
(346) R. R. Dean and J. C. Green, *ibid.*, 3048 (1968).
(347) J. Powell and B. L. Shaw, *J. Chem. Soc.*, 3879 (1965).

Table XII

Nmr and Ir Data for [*trans*-$HPtL(PEt_3)_2$]$^+$[ClO_4]$^-$ [a]

L =	τ_{Pt-H}, ppm	J_{Pt-H}, Hz	J_{P-H}, Hz Cis	J_{P-H}, Hz Trans	ν_{MH}, cm^{-1}
py	29.32	1106	14.4		2216
CO	14.76	967	13.5		2167[b,e]
Me_3CNC	17.13	895	14.4		2104[c,e]
p-$MeOC_6H_4NC$	16.56	890	14.0		2096[d,e]
$P(OPh)_3$	15.21	872	14.4	289	2090
$P(OMe)_3$	14.54	846	15.2	268	2067
PPh_3	16.51	890	14.4	165	2100
PEt_3	16.24	790	15.0	156	2090

[a] After Church and Mays;[315a] nmr spectra in $CDCl_3$ solution at 35°; ir spectra in Nujol. [b] ν_{CO} 2064; for $DPtCO(PEt_3)_2^+$, ν_{CO} 2102 cm^{-1}. [c] ν_{NC} 2209; for $DPt(Me_3CNC)(PEt_3)_2^+$, ν_{NC} 2199 cm^{-1}. [d] ν_{NC} 2191; for DPt (*p*-$MeOC_6H_4NC)(PEt_3)_2^+$, ν_{NC} 2181 cm^{-1}. [e] The M–H absorptions were weak in solution and M–D stretches were unobserved.

Table XIII

Nmr and Ir Data for $HPtL(AsEt_3)_2^+ClO_4^-$ [a]

L =	τ_{Pt-H}, ppm	J_{Pt-H}, Hz	J_{P-H}, Hz	ν_{Pt-H}, cm^{-1}
		Trans		
$P(OMe)_3$	15.28	699	270	2044
$P(OPh)_3$	15.92	716	290	2066
Me_3CNC	18.27	721		...[b]
PPh_3	17.34	739	168	2069[c]
CO	15.65	768		2149[d]
$AsEt_3$	19.73	846		2099
		Cis		
PPh_3	18.51	881	9.8	...[c]
$P(OPh)_3$	18.13	886	4.0	2082
$P(OMe)_3$	17.81	936	<2	2089
PEt_3	19.05	945	11.5	

[a] After Church and Mays;[315b] nmr spectra in $CDCl_3$ solution at 35°; ir spectra in $CHCl_3$ solution. [b] ν_{MH} not observed, ν_{NC} 2191; for $DPt(Me_3CNC)(AsEt_3)_2^+$, ν_{NC} 2185; ν_{M-D} 1500 cm^{-1}. [c] Cis–trans mixture; M–H band very broad. [d] ν_{CO} 2049; for $DPt(CO)(AsEt_3)_2^+$, ν_{CO} 2092 cm^{-1}.

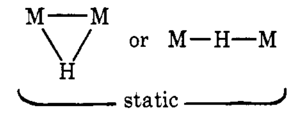
Table XIV

^{183}W–H Coupling Constants

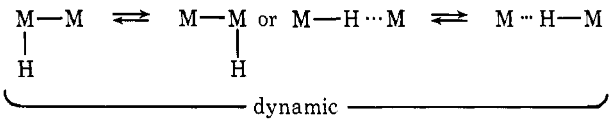
Complex	$J(^{183}W\text{-}H)$, Hz	Ref
$[HW_2Cp_2(CO)_6]^+$	38.6	348
$[HMoWCp_2(CO)_6]^+$	38.0	348
$[HW_2(CO)_{10}]^-$	41.9[a]	47
$[HMoW(CO)_{10}]^-$	42.3	47
$Cp_2WH_2 \cdot W(CO)_5$	63.0, 19.2	203
$Cp_2WH_2 \cdot Cr(CO)_5$	64.5, ...	203
$Cp_2WH_2 \cdot Mo(CO)_5$	65.8, ...	203
$Cp_2MoH_2 \cdot W(CO)_5$	..., 19.6	203
H_2WCp_2	73.2	348
$[H_3WCp_2]^+$	47.8[b]	348
$HWCp(CO)_3$	36.7 (37.7)	342 (348)
$HWCp(CO)_2P(OMe)_3$	46 (44)	119 (341)
$H_6W(PMe_2Ph)_2$	27.8	204

[a] Two different values were reported in this paper; the value shown is taken from Figure 2 and Table III of the cited reference, while in Figure 4, a value of 42.7 Hz is given for this coupling in this derivative. [b] For A_2 of A_2B set of metal protons.

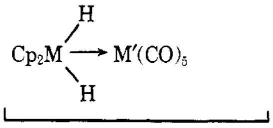
The coupling of ^{183}W (14% relative abundance) with hydrogen has been observed in a number of derivatives, and the data are summarized in Table XIV. An important question to be answered for the polynuclear derivatives is the location of hydrogen. Hayter[47] has concluded that the data do not distinguish between two possibilities for the anions $HM_2(CO)_{10}^-$, the static symmetrically bonded model **41a**, or the dynamic model **41b**. The same conclusion was reached earlier by Davison, *et al.*,[348] concerning the protonated dimers, $HM_2Cp_2(CO)_6^+$.



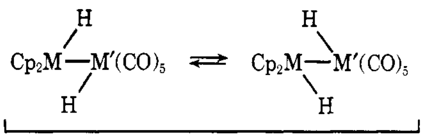
41a



41b



42a, static



42b, dynamic

Deubzer and Kaesz[203] have isolated the derivatives $Cp_2MH_2 \cdot M'(CO)_5$ (M = Mo, W; M′ = Cr, Mo, and W). In the compound M = M′ = W, two distinct ^{183}W spin-coupling satellites were observed, while in the derivatives M = W, M′ = Cr or Mo, only the strongly coupled satellites, and for M = Mo and M′ = W, only the weakly coupled satellite peaks were observed (see Table XIV). Because the strongly coupled peaks are close to the value observed in $H_2W(Cp)_2$ (see Table XIV), Deubzer and Kaesz[203] took their observations to favor a static structure **42a** rather than the tautomerizing species **42b**. If the values of approximately 60 and 20 Hz are then taken as limiting values for the near and far coupling of proton to ^{183}W in a static model, it is tempting to believe that the values close to 40 Hz observed for the protonated dimers $HM_2Cp_2(CO)_6^+$ or the hydrido anions $HM_2(CO)_{10}^-$ could represent *average* values for the tautomerizing models of these species. On the other hand, $J(^{183}W\text{-}H)$ is low in $HWCp(CO)_3$ as it also is in $H_3WCp_2^+$ (see Table XIV), which indicate that it may not be possible to transfer limiting values for (^{183}W–H) from one derivative to the next, unless these low values are due to as yet undiscerned intramolecular averaging between positions of lower and higher ^{183}W–H coupling.

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(348) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962); see also A. Davison, J. A. McCleverty, and G. Wilkinson, *ibid.*, 1133 (1963).

For complexes of rhodium, the isotope of nuclear spin $^1/_2$ (^{103}Rh) exists in 100% natural abundance; its coupling to directly bonded hydrogen is relatively low, in the range 5–40 Hz. A number of these constants are summarized by Haszeldine, Parish, and Parry[277] for five-coordinate silylrhodium and related derivatives. The ^{103}Rh–H coupling has been reported for $HRh(PPh_3)_3$ (13.7 Hz), $HRh(PMe_2Ph)_4$ (7.0 Hz), and $HRh(PPh_3)_4$ (~0 Hz);[71] a correlation between this coupling and structure of the complex is proposed. In HRh_3Cp_4 the metal hydride resonance appears as a quartet, $J_{^{103}Rh-H} = 26.5$ Hz.[279]

The coupling of ^{187}Os ($I = {}^1/_2$, natural abundance = 1.64%) with directly bonded hydrogen has been observed for the first time in the derivatives H_4OsL_3 (L = PEt_2Ph, $J = 30.8$ Hz and L = $AsEt_2Ph$, $J = 34.0$ Hz).[230] The reduced coupling constant $^1K(^{187}\mathrm{Os}\text{–H}) \simeq 455$ to 496×10^{-20} cm^{-3} [$^1K_{NN'} = J_{NN'}2\pi/\hbar(\gamma_N\gamma_{N'})$; see discussion by McFarlane[349]] is as expected intermediate between that of $^1K(^{183}\mathrm{W}\text{–H})$ (239×10^{-20} cm^{-3} for $H_6W(PEt_2Ph)_3$; see Table XIV) and $^1K(^{195}\mathrm{Pt}\text{–H})$ ~ 1220 to 2100 10^{-20} cm^{-3} (see compounds in Table XI).

Stereochemical Exchange

For those derivatives which are either known or expected to contain nonequivalent hydrogen atoms, the presence of a single chemical shift may indicate stereochemical equilibration, as was postulated for ReH_9^{2-} (see Ginsberg[1] or Green and Jones[2]). On the other hand, there is always the possibility of accidental degeneracy of the chemical shift; a molecular orbital calculation for TcH_9^{2-} by Basch and Ginsberg[336] indicates that the various hydrogen atoms may be in almost identical environments.

With other magnetically active nuclides in the complex, retention (and averaging) of coupling to hydrogen serves to indicate an intramolecular rearrangement ("stereochemical nonrigidity") best confirmed by low-temperature studies. Signal averaging has been reported for all of the known hydrides of rhenium derived from ReH_9^{2-}, namely $H^8{}_8ReL^-$,[41] H_7ReL_2,[17] H_5ReL_3,[1,2] H_4ReXL_3,[215b] and $H_3Re(L\text{–}L)_2$.[40] For the series $HMn(PF_3)_{5-x}(CO)_x$ ($x = 1$–4), the presence of geometrical isomers is indicated by ir, but these cannot be separated by gas chromatography, achieved for the derivatives $MnR_f(PF_3)_{5-x}(CO)_x$.[208] Nmr measurements were not reported, but these authors suspect on the basis of these observations that a rapid internal isomerization could be taking place in the hydridomanganese derivatives.

A single chemical shift and equivalent coupling to phosphines are also observed for the derivatives H_6WL_3,[204] H_4MoL_4,[43] and H_4OsL_3.[42,245] Douglas and Shaw[42] find that protonation of the tetrahydridoosmium complex gives $H_5OsL_3^+$ which shows only a singlet in the nmr indicating rapid intermolecular exchange; addition of excess acid gives the species H_6OsL_2 which shows a triplet for the metal–proton resonance, from rapid intramolecular exchange. Further examples of signal averaging are reported by Kruse and Atalla[46] for H_2FeL_4 and $HCoL_4$ (L = $P(PEt)_3$), by Levison and Robinson[262] for $HRh(P(OEt)_3)_4$, and by Yagupsky and Wilkinson[325] for $HIr(CO)_2L_2$ (L = PPh_3, $AsPh_3$, $PEtPh_2$ and $P(C_6H_4F)_3$ (see section IV.B). Tebbe, *et al.*,[350] have obtained limiting spectra at 220 MHz for *cis*-H_2FeL_4 (L = $P(PEt)_3$, $P(OEt)_2Ph$) at −50°; the complex $H_2Fe[P(OEt)_2Ph]_4$ is observed at the low temperature to exist in an equilibrium mixture of isomers, cis (triplet of doublets, $J_{^{31}P-H}(\mathrm{cis}) = 66.5$, $J_{^{31}P-H}(\mathrm{trans}) = 25$ Hz) and trans (quintet, $J_{^{31}P-H}(\mathrm{cis}) = 48$ Hz). The time-averaged signal at +50° (quintet, $J_{^{31}P-H}(\mathrm{av}) = 40.5$ Hz) is centered close to that of the low-temperature multiplet of the cis isomer. The coupling constants are not in the relation observed for the usual octahedral complexes (see section IV.B) in which the complex's signal averaging is also usually *not* observed (*cf.* H_2RuL_4, $H_2Ru(NCPh)L_3$, $H_2Os(CO)L_3$[351]) or in the complexes H_3IrL_3,[37] which exist as *mer* and *fac* isomers. Meakin, *et al.*,[351] have obtained the structure for *cis*-$H_2Fe(P(OEt)_2Ph)_4$; the ligands are bent toward the cis hydrogen atoms in positions intermediate between an idealized octahedron and a tetrahedral disposition of the phosphinite ligands around the metal. Thus stereochemical nonrigidity, which is common for coordination numbers 5, 7, 8 and 9, might be brought about in six-coordinate complexes (and facilitated for the other coordination complexes) when ligands are distorted toward what might be the transition state in the polytopal rearrangements.[35]

Intramolecular tautomerism has been demonstrated for the complexes $HWCp(CO)_3$[342a] and $HMCp(CO)_2L$ (M = Mo, L = PPh_3[342b] and M = W, L = PMe_3, $P(OMe)_3$[341]). For $HWCp(CO)_3$ at −70°, two discrete sets of ^{13}CO–H coupling satellites are observed for the metal–hydrogen resonance (see section IV.B) which coalesce to a single set with averaged separation of 14.1 Hz at room temperature, indicating rapid intramolecular rearrangement. For M = Mo, the compound is present almost entirely (99%) as the cis isomer when L = $P(OPh)_3$; enthalpy differences between isomers are extremely small and the activation energy for isomerization is of the order of 12 kcal/mol.[342b] For M = W and L = PMe_3, $P(OMe)_3$, the ratio of two isomers are close to 1:1.[341] The ^{31}P–M–H coupling constants, trans ~ 20–25 and cis ~ 65–75, show a departure for those observed for octahedral complexes.

An intramolecular tautomerism has been demonstrated for a hydridometal cluster. Knox and Kaesz[331] observe a single chemical shift (τ ~27.6–27.8) for the metal hydrogen atoms and equivalent coupling to the phosphorus nuclei in the series of derivatives $H_4Ru_4(CO)_{12-x}[P(OMe)_3]_x$, $J_{^{31}P-H}$, Hz: $x = 1$, doublet, $J_{^{31}PH} = 2.65$; $x = 2$, triplet, $J = 6.63$; $x = 3$, quartet, $J = 7.70$; $x = 4$, quintet, $J = 7.95$. In the parent derivative $H_4Ru_4(CO)_{12}$, evidence indicates that the bridging hydrogen atoms occupy positions on the four edges; see D_{2h} structure **34**. There is good reason to believe that the hydrogen atoms occupy similar positions in the substituted derivatives and that the tautomerism is occurring through a simultaneous edge-to-face-to-edge rearrangement of these atoms.

C. MISCELLANEOUS INSTRUMENTAL STUDIES

The metal–hydrogen bond lengths in $HMn(CO)_5$ (1.28 Å) and $HCo(CO)_4$ (1.42 Å) have been estimated from the sec-

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(349) W. McFarlane, *Quart. Rev., Chem. Soc.*, **23**, 187 (1969).

(350) F. N. Tebbe, P. Meakin, J. P. Jesson, and E. I. Muetterties, *J. Amer. Chem. Soc.*, **92**, 1068 (1970); *cf.* also, E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

(351) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 3482 (1970).

ond-moment analysis of their broadline nmr spectrum.[352,353] For $HMn(CO)_5$, a gas-phase electron diffraction analysis indicates that the Mn–H bond distance is 1.425 Å[354] (see also, Table XV); Sheldrick[355] has shown that neglect of quadrupole effects in the second-moment analysis of the broad-line spectrum leads to the erroneously low values of the metal–hydrogen bond length.

The mid-infrared metal hydride frequencies of $HCo(CO)_4$[356] and $H_3Mn_3(CO)_{12}$[357] have been obtained by White and Wright through the use of a combination of infrared and neutron scattering spectroscopy. This technique relies on the high scattering efficiency of hydrogen where the intensity of the scattering is proportional to the square of the amplitude of the hydrogen motion.

Electron spin resonance measurements have been reported by Henrici-Olivé and Olivé for HCoR(L-L) (L-L = diphos, depe)[358] and $[HTiCp_2]_2^-$.[196] In both of these, the coupling of the unpaired electron with metal–hydrogen provides the predominant hyperfine splitting. The paramagnetic hydride, $HOsCl_2(PBu^n{}_2Ph)_3$ has been reported by Chatt, Leigh, and Paske;[70] only a broad absorption at −196° could be observed. The paramagnetic hydrido complexes $HRe(acac)X_2L_2$ are also known[225a] (see section III.J), but no spin resonance is reported.

Mass spectra of a number of transition metal hydrides have been reported: $HMn(CO)_5$,[359,360] $HRe(CO)_5$,[360] $HCo(CO)_4$,[360] $H_3Mn_3(CO)_{12}$,[210,361] $H_3Re_3(CO)_{12}$,[210,361] $HRe_2Mn(CO)_{14}$,[361] $HRe_3(CO)_{14}$,[361] $HMn_3(CO)_{10}B_2H_6$[360,361] and $HMCo_3(CO)_{12}$ (M = Fe, Ru).[328] A number of these and additional derivatives $HMCp(CO)_3$ (M = Cr, Mo, W), $HPtX(PEt_3)_2$ (X = Cl, Br, CN, CNO), $H_2Ru_4(CO)_{13}$, $H_4M_4(CO)_{12}$, (M = Ru, Os), $H_2Os_3(CO)_{10}$, and $H_2FeRu_3(CO)_{13}$ have been studied by Johnson, Lewis, and Robinson.[360] It appears, in general, that for monomeric hydrido complexes, there is loss of H from the parent ion, and for hydridometal carbonyls, competitive loss of H and CO. For most polynuclear hydrido metal complexes (but not *all; cf.* $H_3Re_3(CO)_{12}$) hydrogen loss does not occur from the parent ion. The mass spectra of some polynuclear metal hydrides together with other complexes have been reviewed by Lewis and Johnson.[362a] The mass spectra of $HCo(CO)_{4-x}(PF_3)_x$, $x = 0$–4, have been reported by Saalfeld, *et al.*[362b] The heats of formation of these compounds, calculated from appearance potential data, show a substantial increase in the series as CO is replaced by PF_3; as $x = 0$–4, the values are (error limits ±9 through 14) −173, −381, −579, −783, and −978 kcal/mol. The H–Co bond energy is estimated as 4 ± 15 kcal/mol.

The Mössbauer and mass spectra of the complex previously reported as $HFe_3(CO)_{11}NMe_2$ have led to its reformulation as $HFe_3(CO)_{10}CNMe_2$.[233] The structure of $HFe_3(CO)_{11}^-$ as observed from X-ray[251] and Mössbauer spectra[252] has led to a new assignment of the structure of $Fe_3(CO)_{12}$. The complex $HFe_2(CO)_8^-$ is believed related to $Fe_2(CO)_9$ as determined from its Mössbauer spectrum.[363] A bridging carbonyl is replaced by the hydride ligand.

The photoelectron spectrum of $HMn(CO)_5$, among a number of other $MnX(CO)_5$ derivatives, has been determined by Evans, *et al.*[364] The low ionization potential region of the spectrum for $HMn(CO)_5$ is believed to be related to ionization from molecular orbitals composed principally of the metal 3d atomic orbitals. The proposed upper orbital configurations (mainly carbonyl σ and π followed by metal 3d) agree with those derived from an LCAO calculation by Fenske and DeKock.[365a] Based on previous computation for metal hexacarbonyls, these authors obtained levels in $HMn(CO)_5$ by substituting a CO group in $Mn(CO)_6^+$ with a hydride ligand. This substitution was shown to affect the redistribution of electrons in the π-bonding network without substantially altering the σ-bonding framework. The 2π occupation of the carbonyls cis and trans (0.437 and 0.496, respectively) to the hydride were observably increased over 0.372 for the cation. The cis and trans force constants (16.58 and 16.46 mdyn/Å)[332] obtained from an infrared analysis of $HMn(CO)_5$ compared to 18.33 mdyn/Å for $Mn(CO)_6^+$ support their interpretation.

Strohmeier and Müller[365b] have reported the ultraviolet absorption spectra for the complexes $H_2IrX(CO)L_2$ where X = Cl, Br, I and L = various tertiary phosphines and phosphites. They were unable to correlate the observed electronic transitions with variations in the π-acceptor strength of the ligand L, but they were able to determine the position of the equilibrium 128 by changes in the positions and intensities of the absorption maxima.

$$IrX(CO)L_2 + H_2 \rightleftarrows H_2IrX(CO)L_2 \qquad (128)$$

V. Structure Determinations of Transition Metal Hydride Complexes

This aspect was separately reviewed by Ibers[366] in 1965 when it became evident, contrary to earlier beliefs, that hydrogen could exert a significant influence on the stereochemistry of metal hydride complexes.

In structures containing either a heavy metal atom (atomic number 70 or above) or data of insufficient precision, indirect evidence such as the disposition of other ligands around the metal atom is used as an indication for the location of the metal-bonded hydrogen. This is true for $HPtBr(PPh_3)_2$,[367] $HPtCl(PEtPh_2)_2$,[368] or $HIr(NO)(PPh_3)_3^+ClO_4^-$.[369] In these, the ligands surrounding the metal-bonded hydrogen are usually bent slightly toward this coordination site, owing to the

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reduced steric requirements of the hydrogen atom. With only bulky ligands on the metal, this distortion reaches an extreme such that the geometry of the complex approaches that which would be taken by the ligands alone in the absence of a metal-bonded hydrogen. Thus, in the structures of $HRh(PPh_3)_2(AsPh_3)$,[269] $HRh(PPh_3)_4$,[370] and $H_2Fe[P(OEt)_3]_4$[351] (see section IV.B), the heavy atom ligands approach tetrahedral geometry around the metal, reflecting, albeit for different reasons, the earlier notion that hydrogen did not occupy a coordination position in metal hydrides owing to erroneous interpretation of the early (1939) electron diffraction data for $HCo(CO)_4$.

With high precision data collection and the advent of neutron diffraction, hydrogen has been located and its position refined in the data processing for a number of cases summarized in Table XV. Evidence to date indicates that the hydrogen does occupy a coordination site on the metal and is situated close to what might be calculated as the normal covalent bond distance, which data are also presented in Table XV. Contrary to an earlier report for H_2MoCp_2,[371] Abrahams and Ginsberg[372] were unable to locate the hydrogen atoms in a reexamination of the published data for this derivative.

Table XV

Terminal Metal-Hydride Distances

Complex	*M-H (Å) obsd*	*M-H (Å) covalent*[a]	*Ref*
β-$HMn(CO)_5$	1.601 (16)[b]	1.6_5	373
$HMn(CO)_5$	1.425[c]	1.6_5	354
H_9Re^{2-}	1.68 (5)[b,d]	1.7	374
$HRuCl(PPh_3)_3$	1.7 (2)	1.6_5	101
$HRuC_{10}H_7(dmpe)_2$	1.7	1.6_5	375
$HRu(O_2)CCH_3(PPh_3)_3$	1.7	1.6_5	376
$HCo(N_2)(PPh_3)_3$	1.65 (12)	*e*	254, 255
$HRh(CO)(PPh_3)_3$	1.60 (12)	1.5_5	99, 377
$HRhCl(SiCl_3)(PPh_3)_2$	1.48	1.5_5	102
$HIr(CO)_2(PPh_3)_2$	1.66 (20)	1.5_5	378
$\{HZnN(CH_3)C_2H_4N(CH_3)_2\}_2$	1.7	*e*	379
	1.60[b]		

[a] A method for obtaining approximate M-H distances has been described[380] and values are given[200] based on empirical covalent radii for hydrogen and selected transition metals. [b] Neutron diffraction. [c] Electron diffraction. [d] Average. [e] Not estimated.

Table XVI

Bridging Metal-Hydride Bond Distances

Complex	*M-H-M (Å) obsd/2*	*M-H (Å) covalent*[a]	*Ref*
$HCr_2(CO)_{10}^-$	1.70[b]	1.7	200
$Cr(B_3H_8)(CO)_4^-$	1.78 (6)	1.7	384
$HMnCpSiPh_3(CO)_2$[c]	1.55[d]	1.6_5	205
$HMn_2PPh_2(CO)_8$	1.86 (6)	1.6_5	386
$HMn_3(BH_3)_2(CO)_{10}$	1.65 (10)[e]	1.6_5	57
$H_2Re_2SiPh_2(CO)_8$	1.68[b]	1.7	217, 390
$HRe_3(CO)_{12}^{2-}$		1.7	229
$H_2Re_3(CO)_{12}^-$	1.7[b]	1.7	218
$HRe_3(CO)_{14}$	1.67[b]	1.7	389
$HRe_2Mn(CO)_{14}$	1.70[b]	1.7	391
$HRu_3(CO)_9(C_6H_5CC_6H_4)$	1.457[b]	1.6_5	240
$HMo_2Cp_2(PMe_2)(CO)_4$	1.8	1.8	380
$CuBH_4(PPh_3)_2$	2.02 (5)	*f*	392, 393
$CuB_3H_8(PPh_3)_2$	1.84 (5)	*f*	385

[a] See footnote *a*, Table XV. [b] Estimated, see ref 389. [c] An electron tally and the long 1.77-Å Si-H distance suggest that this hydride may be terminally bound; a similar structural problem may exist in the derivative $HFeCp(SiCl_3)(CO)$; see ref 102b. [d] Not available in abstract ref 205 but was presented at the meeting. [e] Average, see also discussion in ref 200. [f] Not estimated.

The structure of $HMn(CO)_5$ has attracted much attention. This complex crystallizes in both α and β forms. An X-ray investigation of the α form established the C_{4v} molecular symmetry,[381] but this study did not reveal the hydride. A neutron diffraction study[373] of the β form at low temperature unambiguously fixed the Mn-H bond length at 1.601 (16) Å. Although many theoretical models had been devised to predict this distance, only one based on Platt's united-atom model for diatomic hydrides gave the correct value.[382,383] The coordination geometry deviates slightly from a regular octahedron because the carbonyls cis to hydrogen undergo the characteristic displacement, which is 6° in this case, toward the hydride (see also section IV.C).

The structures of a number of polynuclear metal hydride complexes have been reported, and the data for the M-H-M bridge bonds are summarized in Table XVI. Hydrogen atoms have been located in bridging positions between the relatively light metal atoms Cr-B in $Cr(B_3H_8)(CO)_4^-$,[384] Mn-B and Mn-Mn in $HMn_3(BH_3)_2(CO)_{10}$,[57] Cu-B in $Cu(B_3H_8)(PPh_3)_2$,[385] Mn-Mn in $HMn_2(PPh_2)(CO)_8$,[386] and Mn-Si in $HMnCp(SiPh_3)(CO)_2$.[205] In the structure of $Zr(BH_4)_4$, Bird and Churchill[387] have located a single terminal hydrogen, indicating the other three hydrogen atoms on each BH_4 group to be bridging to the metal. More frequently, the location of hydrogen must be inferred from indirect evidence such as the increased intermetallic separations over normal covalent M-M bonds and the dispositions of ligands near the suspected position. In all cases thus far studied, the position of hydrogen is indicated as bridging between atoms in metal clusters. Thus, the separation observed within the anion $HCr_2(CO)_{10}^-$ is twice the normal covalent M-H separation of (1.70 Å for Cr-H).[200] This is clearly greater than the metal-metal

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bond of 2.97 Å in the deprotonated complex[200, 388] $Cr_2(CO)_{10}$.$^{2-}$ This is the only known bridging hydride complex which contains a linear three-center, two-electron bond which has been investigated crystallographically.

In cluster complexes which have nonlinear M–H–M bonds, a correlation has been proposed relating the intermetallic separation and the M–H–M angle.[389] The assumptions are that (1) the M–H distances are relatively incompressible, and (2) the metal atoms are in nearly octahedral-like environments as defined by the carbonyl ligands. Therefore compression along the metallic axis results in a displacement of the hydride away from this axis. The Mn–Mn distance in $HMn_2(PPh_2)(CO)_8$ is 2.937(5) Å,[386] which is nearly that of 2.92 Å found in $Mn_2(CO)_{10}$;[379] thus hydrogen is displaced from the Mn–Mn bond, and an Mn–H–Mn angle 104.1 (4.8)° is observed. Estimates of the M–H distances based on these assumptions have been presented for the following complexes: $HRe_3(CO)_{14}$,[389] $HRe_2Mn(CO)_{14}$,[391] $H_2Re_3(CO)_{12}^-$,[218] $HRe_3(CO)_{12}^{2-}$,[229] and $H_2Re_2SiPh_2(CO)_8$.[217, 390] Through similar reasoning, triply bridging hydrides have been postulated to occupy positions above the two enlarged trans faces in octahedral $H_2Ru_6(CO)_{18}$[122] and in the Rh_3 plane in HRh_3Cp_4; see section III.L for data. In $H_2FeRu_3(CO)_{13}$, Gilmore and Woodward[394] find two asymmetric CO bridges between adjacent Fe and Ru atoms in the tetrahedral cluster, the carbonyls associating more closely with the Fe atom; indirect evidence indicates that the two H atoms are probably bridging two of the Ru–Ru bonds. Chini[395] has recently reviewed the metal carbonyl cluster compounds.

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