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TRANSITION-METAL POLYHYDRIDE COMPLEXES

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DEDICATION

To the memory of E.L. Muetterties (1927–1984), whose early work in polyhydride chemistry led to a much clearer understanding of the stereochemistry of nonrigid species.

CONTENTS

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LIST OF ABBREVIATIONS

cod	1,5-cyclooctadiene
Cy	C_6H_{11}
dbp	5-phenyl-5*H*-dibenzophosphole
dmpe	$Me_2PCH_2CH_2PMe_2$
dmtpe	$(m\text{-}CH_3C_6H_4)_2PCH_2CH_2P(m\text{-}CH_3C_6H_4)_2$
dppb	$Ph_2PCH_2CH_2CH_2CH_2PPh_2$
dppe	$Ph_2PCH_2CH_2PPh_2$
dppp	$Ph_2PCH_2CH_2CH_2PPh_2$
dptpe	$(p\text{-}CH_3C_6H_4)_2PCH_2CH_2P(p\text{-}CH_3C_6H_4)_2$
p-tol	$p\text{-}CH_3C_6H_4$
py	C_5H_5N

A. INTRODUCTION

Since the preparation in 1955 of $(C_5H_5)_2ReH$ [1], the first non-carbonyl compound with a recognized transition metal–hydrogen bond, molecular transition-metal hydrides have been intensively studied and have been the subject of several reviews and monographs [2–21]. Of particular interest to chemists has been the role hydride complexes play in many homogeneous catalytic cycles, where they have either been used as catalysts or invoked as key intermediates in catalytic cycles [22–23].

This review examines one class of transition metal hydride compounds, the polyhydrides. For our purpose, we define these as discrete mononuclear or polynuclear complexes containing from four to nine hydride ligands covalently bound to each metal *. Only a few homoleptic polyhydrides, such

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* Covalent metal borohydride complexes (e.g. $Zr(BH_4)_4$) have been reviewed elsewhere [24] and will not be discussed here.

as ReH_9^{2-} and FeH_6^{4-} are known at present; all others contain stabilizing ligands. These are usually tertiary phosphines, but arsines, phosphites, secondary phosphines, various nitrogen donors, and cyclopentadienyl groups may also function as ligands.

Apart from their structural features and fluxional behaviour, much of the current interest in polyhydrides stems from their ability to lose H_2 by a variety of means. The coordinatively unsaturated intermediates generated may react with donor molecules to give new complexes, or function as homogeneous catalysts in reactions with various organic molecules, or activate notoriously stubborn substrates, such as N_2 or alkanes.

Although an excellent review of polyhydrides has been published [18], advances in the five years since it was written make a fresh survey of the area important. Accordingly, we cover comprehensively the literature on polyhydrides to the end of 1983.

B. RANGE OF COMPLEXES KNOWN

As can be seen in Table 1, polyhydrides are formed generally by transition metals from the second and third rows of the periodic table and from the elements of Group Vb (Nb and Ta) to the iron triad and iridium. Certain hydride-rich intermetallic compounds are also known for rhodium, iridium palladium, and nickel.

With its uniquely small steric requirement, the hydride ligand is ideal for higher-coordinate transition-metal complexes (C.N. = 7–9) [25]. The effect of the phosphine ligands on the coordination number should also be noted. It is well known [26] that bulky phosphines (PCy_3, PBu^t_3) stabilize low coordination numbers, for example in $Pt(PCy_3)_2$. Paradoxically, in the case of polyhydrides, these same phosphines stabilize high coordination numbers by steric protection of the metal (e.g. $MoH_6(PPr^i_3)_3$, $RuH_6(PCy_3)_2$). The steric bulk of these ligands allows only two or three of them to bind, leaving space close to the metal for the hydride ligands in the final 18-electron polyhydride.

It is notable that the general majority of polyhydrides contain phosphorus donors as stabilizing ligands. Clearly, any firmly bound ligand of comparable electronic character might be expected to act in the same way. Very recently, it has become apparent that polyalkylated cyclopentadienyl groups can be used as ligands and a new class of organometallic polyhydrides is currently emerging. These may also contain phosphorus donors, as in $(C_5Me_5)TaH_4(PMe_3)_2$, oxygen donors, as in $(C_5Me_5)_2Ta_2H_6(OCMe_3)_2$, or no other ligands at all, as in $(C_5Me_5)IrH_4$.

TABLE 1

Transition metal polyhydride complexes

Metal	Compound	Reference [a]
Nb	$NbH_5(dmpe)_2$	27,28
	$NbH_5(PMe_3)_4$	29
Ta	$TaH_5(dmpe)_2$	28,30
	$(C_5Me_5)TaH_4(dmpe)$	31
	$(C_5Me_5)TaH_4(PMe_3)_2$	31
	$(C_5Me_5)TaH_4(PMe_2Ph)_2$	31
	$(C_5Me_5)TaH_4(P(OMe)_3)_2$	31
	$[TaCl_2(PMe_3)_2](\mu\text{-}H)_4$	32
	$(C_5Me_5)_2Ta_2H_6(OCMe_3)_2$	33
Cr	$CrH_4(dmpe)_2$	34
Mo	$MoH_6(PCy_3)_3$	35
	$MoH_6(PCy_2Ph)_3$	35
	$MoH_6(PPr^i_3)_3$	35
	$MoH_6(PPr^i_2Ph)_3$	35
	$MoH_4(dmpe)_2$	36
	$MoH_4(dppe)_2$	37–48
	$MoH_4(dmtpe)_2$	45
	$MoH_4(dptpe)_2$	45
	$MoH_4(PMe_2Ph)_4$	37,49
	$MoH_4(PMePh_2)_4$	37,44,47,48 50,51
	$MoH_4(PEt_3)_4$	41
	$MoH_4(PEt_2Ph)_4$	38,44,48,51
	$MoH_4(PEtPh_2)_4$	37,41
	$MoH_4(PBuPh_2)_4$	48
	$MoH_4(P(OMe)_3)_4$	52
	$MoH_4(P(OEt_2)Ph)_4$	41
	$MoH_4(P(OPr^i)_3)_4$	53
W	$WH_6(PMe_3)_3$	54
	$WH_6(PMe_2Ph)_3$	35,41,55,57
	$WH_6(PEt_2Ph)_3$	55,56
	$WH_6(PPr^i_3)_3$	58
	$WH_6(PPr^i_2Ph)_3$	58
	$[WH_5(dppe)_2]^+$	59
	$[WH_5(PHPh_2)_4]^+$	59
	$[WH_5(PMe_2Ph)_4]^+$	59,60
	$[WH_5(PMePh_2)_4]^+$	60,61
	$[WH_5(PEt_2Ph)_4]^+$	60
	$[WH_5(PEtPh_2)_4]^+$	60
	$[WH_5(PBuPh_2)_4]^+$	60
	$[WH_5(P(OPr^i)_3)_4]^+$	60
	$WH_4(dppe)_2$	41,51,62,63
	$WH_4(PHPh_2)_4$	51

TABLE 1 (continued)

Metal	Compound	Reference [a]
	$WH_4(PMe_3)_4$	64
	$WH_4(PMe_2Ph)_4$	53,58,62
	$WH_4(PMePh_2)_4$	41,47,48,51 62,65
	$WH_4(PEt_2Ph)_4$	48,65
	$WH_4(PEtPh_2)_4$	41,47,51,65
	$WH_4(PPrPh_2)_4$	66
	$WH_4(PBuPh_2)_4$	51
	$WH_4(P(OMe)_3)_4$	52
	$WH_4(P(OEt)_3)_4$	51,65
	$WH_4(P(OEt)_2Ph)_4$	41
	$WH_4(P(OPr^n)_3)_4$	51,65
	$WH_4(P(OPr^i)_3)_4$	51,65
	$WH_4(P(OPr^i)_2Ph)_4$	51
	$\{(C_5Me_4Bu^t)WH_4\}_2$	67
	$\{(C_5Me_4Bu^t)WH_3\}_3$	67
Tc	K_2TcH_9	68
	$TcH_7(PEt_2Ph)_2$	69
Re	K_2ReH_9	70,71
	$(Et_4N)ReH_8(PEt_3)$	72
	$(Et_4N)ReH_8(PBu_3)$	72
	$(Et_4N)ReH_8(PPh_3)$	72
	$(Et_4N)ReH_8(AsPh_3)$	72
	$ReH_7(dppe)$	73
	$ReH_7(PMe_3)_2$	54
	$ReH_7(PMe_2Ph)_2$	74
	$ReH_7(PMePh_2)_2$	74
	$ReH_7(PEt_2Ph)_2$	73
	$ReH_7(AsEt_2Ph)_2$	73
	$ReH_7(PPr^i_2Ph)_2$	75
	$ReH_7(PPh_3)_2$	73,76–78
	$ReH_7(P(p\text{-tol})_3)_2$	79
	$ReH_7(P(p\text{-F-}C_6H_4)_3)_2$	80
	$ReH_5(dppe)_2$	73
	$ReH_5(PMe_2Ph)_3$	81
	$ReH_5(PMePh_2)_3$	74
	$ReH_5(PEt_2Ph)_3$	73
	$ReH_5(PEtPh_2)_3$	73
	$ReH_5(PPh_3)_3$	73,77
	$ReH_5(P(p\text{-tol})_3)_3$	79
	$ReH_5(PPh_3)_2(PEt_2Ph)_2$	73
	$ReH_5(PPh_3)_2(AsPh_3)$	73
	$ReH_5(PPh_3)_2(C_6H_{11}NH_2)$	73
	$ReH_5(PPh_3)_2(C_5H_{10}NH)$	73
	$ReH_5(PPh_3)_2(py)$	73

TABLE 1 (continued)

Metal	Compound	Reference [a]
	$ReH_5(PPh_3)_2(dppe)$	73
	$ReH_5(P(OMe)_3)_3$	82
	$ReH_4(PPh_3)_3Br$	83
	$ReH_4(PPh_3)_3I$	83
	$ReH_4(PPh_3)_3SnCl_3$	83
	$ReH_4(P(p\text{-tol})_3)_3I$	83
	$ReH_4(P(p\text{-tol})_3)_3SnCl_3$	83
	$[ReH_4(dppe)_2]^+$	84
	$[ReH_4(dppe)(PPh_3)_2]^+$	84
	$[ReH_4(PMe_3)_4]^+$	85
	$[ReH_4(PPh_3)_2(P(OPh)_3)_2]^+$	86
	$[ReH_4(PPh_3)(P(OPh)_3)_3]^+$	86
	$Re_2H_4(PMe_2Ph)_4(P(OCH_2)_3CMe)_2$	87
	$[Re_2H_5(PMe_2Ph)_4(P(OCH_2)_3CMe)_2]^+$	87
	$[Re_2H_5(PPh_3)_4(CNBu^t)_2]^+$	88
	$[Re_2H_5(PPh_3)_4(CNBu^t)_2]^{2+}$	88
	$Re_2H_6(PMe_2Ph)_5$	74,89
	$Re_2H_6(PMePh_2)_5$	74
	$[Re_2H_7(PPh_3)_4(NCMe)]^+$	88
	$[Re_2H_7(PPh_3)_4(NCMe)]^{2+}$	88
	$[Re_2H_7(PPh_3)_4(NCEt)]^+$	88
	$[Re_2H_7(PPh_3)_4(NCEt)]^{2+}$	88
	$[Re_2H_7(PPh_3)_4(NCPh)]^+$	88
	$[Re_2H_7(PPh_3)_4(NCPh)]^{2+}$	88
	$[Re_2H_7(PPh_3)_4(CNBu^t)]^+$	88
	$[Re_2H_7(PPh_3)_4(CNBu^t)]^{2+}$	88
	$[ReH_2(PMe_2Ph)_2]_2(\mu\text{-H})_4$	74
	$[ReH_2(PMePh_2)_2]_2(\mu\text{-H})_4$	74
	$[ReH_2(PEt_2Ph)_2]_2(\mu\text{-H})_4$	73
	$[ReH_2(PEtPh_2)_2]_2(\mu\text{-H})_4$	90
	$[ReH_2(PPh_3)_2]_2(\mu\text{-H})_4$	73,90
	$[\{ReH_2(PPh_3)_2\}_2(\mu\text{-H})_4]^+$	88
	$[ReH_2(AsPh_3)_2]_2(\mu\text{-H})_4$	88
	$[ReH_2(P(p\text{-tol})_3)_2]_2(\mu\text{-H})_4$	79
	$[\{ReH_2(PMe_2Ph)_3\}_2(\mu\text{-H})_6Cu]^+$	91
	$[\{ReH_2(PMePh_2)_3\}_2(\mu\text{-H})_6Cu]^+$	91
	$[Re_4Cu_2H_{16}(PMe_2Ph)_8]^{2+}$	91
	$[Re_4Cu_2H_{16}(PMePh_2)_8]^{2+}$	91
	$(C_5H_5)ReH_4(PMe_2Ph)$	92
	$(C_5H_5)ReH_4(PPh_3)$	92
Fe	$FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$	93
	$FeH_4(PEtPh_2)_3$	94
	$FeH_4(PBuPh_2)_3$	94
	$FeH_4(P(OMe)_3)_3$	95

TABLE 1 (continued)

Metal	Compound	Reference [a]
Ru	$M_2RuH_6(M = Ca,Sr,Eu,Yb)$	96–98
	$RuH_6(PCy_3)_2$	99
	$[RuH_5(PPh_3)_2]^-$	100
	$RuH_4(PPh_3)_3$	101–104
	$RuH_4(P(p\text{-tol})_3)_3$	102
	$RuH_4(P(p\text{-F-}C_6H_4)_3)_3$	105
	$RuH_4(dbp)_3$	106
	$Ru_2H_6(N_2)(PPh_3)_4$	107
	$[RuH_2(PPr^i_3)_2]_2(\mu\text{-H})_4$	99
	$[RuH_2(PBu^t_3)_2]_2(\mu\text{-H})_4$	99
	$[RuH_2(PPh_3)_2]_2(\mu\text{-H})_4$	107
Os	$OsH_6(PMe_2Ph)_2$	108
	$OsH_6(AsMe_2Ph)_2$	109
	$OsH_6(PCy_3)_2$	110
	$OsH_4(PMe_2Ph)_3$	108,111
	$OsH_4(PMe_2Ph)_2(AsMe_2Ph)$	108
	$OsH_4(PMe_2Ph)_2(PEt_2Ph)$	108
	$OsH_4(PMe_2Ph)_2(PPh_3)$	108
	$OsH_4(PMe_2Ph)_2(P(OMe)_2Ph)$	108
	$OsH_4(PMe_2Ph)_2(P(OEt)_3)$	108
	$OsH_4(AsMe_2Ph)_3$	108
	$OsH_4(PMePh_2)_3$	112
	$OsH_4(PEt_2Ph)_3$	108,111
	$OsH_4(PEtPh_2)_3$	112
	$OsH_4(AsEtPh_2)_3$	112
	$OsH_4(PBu^n_3)_3$	108
	$OsH_4(PPh_3)_3$	101,111,113
	$OsH_4(AsPh_3)_3$	114
	$OsH_4(P(p\text{-F-}C_6H_4)_3)_3$	110
	$OsH_4(P(OEt)_2Ph)_3$	115
Co	$ThCoH_4$	115a
Rh	Li_4RhH_5	116
	Li_4RhH_4	116
Ir	Li_3IrH_6	117
	Li_4IrH_6	117a
	$M_2IrH_5(M = Ca,Sr)$	96
	$IrH_5(PMe_3)_2$	118
	$IrH_5(PEt_3)_2$	119–120
	$IrH_5(PEt_2Ph)_2$	119–121
	$IrH_5(PPr^n_3)_2$	122
	$IrH_5(PPr^i_3)_2$	123,124
	$IrH_5(PBu^t_2Me)_2$	125
	$IrH_5(PBu^t_2Pr^n)_2$	126
	$IrH_5(AsBu^t_2Pr^n)_2$	127
	$IrH_5(PBu^t_3)_2$	125

TABLE 1 (continued)

Metal	Compound	Reference [a]
	$IrH_5(PBu^t_2Ph)_2$	125
	$IrH_5(PPh_3)_2$	121,123 124,128
	$IrH_5(P(p\text{-}F\text{-}C_6H_4)_3)_2$	105
	$IrH_5(PCy_3)_2$	123,124
	$IrH_4(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)$	129
	$(C_5Me_5)IrH_4$	130
	$[\{(dppp)IrH_2\}_2(\mu\text{-}H)_3]^+$	131
	$[\{(dppb)IrH_2\}_2(\mu\text{-}H)_3]^+$	131
	$[\{(PPh_3)_2IrH_2\}_2(\mu\text{-}H)_3]^+$	124
Ni	Mg_2NiH_4	132
Pd	Th_2PdH_6	132a
	Sr_2PdH_4	133
Cu	Li_3CuH_4	133a
	Li_4CuH_5	133a
	Li_5CuH_6	133a

[a] Different synthetic method used in each reference cited.

C. PREPARATIONS OF POLYHYDRIDES

Generally, polyhydrides are prepared from metal halides, their phosphine derivatives, or from organometallic complexes, either by the action of a hydridometallate or of hydrogen. A few preparations involving hydrogen transfer will also be mentioned.

(i) Action of hydridometallates

Hydrides of boron or aluminum are widely used in synthesizing polyhydrides (Table 2, eqns. 1–11). $NaBH_4$ in alcohols or $LiAlH_4$ in THF are commonly employed in reducing metal halides or their phosphine complexes, although other hydride ligand sources have been used successfully (eqns. 6, 11).

The reactions are carried out under anaerobic conditions, but the type of atmosphere used is sometimes important: a nitrogen atmosphere interferes with the preparation of some molybdenum and tungsten tetrahydrides [41] and $FeH_2(N_2)(PEtPh_2)_3$ is obtained instead of $FeH_4(PEtPh_2)_3$ when $FeCl_2$, $PEtPh_2$, and $NaBH_4$ react under N_2 [134]. Atmospheres of argon, helium, and H_2 have been used to circumvent this problem.

TABLE 2

Some preparations of polyhydrides using hydridometallates

Reaction	Reference	Eqn. No.
$\mathrm{RuCl_2(PPh_3)_2 \xrightarrow[MeOH/C_6H_6]{NaBH_4} RuH_4(PPh_3)_3}$	103	(1)
$\mathrm{[IrCl_4(PMe_3)_2]^- \xrightarrow[THF]{LiAlH_4} IrH_5(PMe_3)_2}$	118	(2)
$\mathrm{ReO(OEt)X_2(PPh_3)_2 \xrightarrow[EtOH]{NaBH_4} ReH_7(PPh_3)_2}$	77	(3)
$\mathrm{ReOCl_3(PPh_3)_2 \xrightarrow[THF]{LiAlH_4} ReH_7(PPh_3)_2}$	73	(4)
$\mathrm{ReH_3(PPh_3)_4 \xrightarrow[EtOH]{NaBH_4} ReH_5(PPh_3)_3}$	77	(5)
$\mathrm{WCl_4(PMe_2Ph)_3 \xrightarrow[THF]{NaH_2Al(OCH_2CH_2OCH_3)_2} WH_6(PMe_2Ph)_3}$	35	(6)
$\mathrm{MoCl_5 \xrightarrow[PMePh_2]{Ca(BH_4)_2} MoH_4(PMePh_2)_4}$	51	(7)
$\mathrm{Na_2OsCl_6 \xrightarrow[PPh_3]{NaBH_4,EtOH} OsH_4(PPh_3)_3}$	113	(8)
$\mathrm{Re_2Cl_8^{2-} \xrightarrow[PEtPh_2]{NaBH_4,EtOH} Re_2H_8(PEtPh_2)_4}$	90	(9)
$\mathrm{Mo_2Cl_4(dppe)_2 \xrightarrow[dppe]{NaBH_4,EtOH} MoH_4(dppe)_2}$	40	(10)
$\mathrm{WCl_6 \xrightarrow[PMePh_2]{LiEt_3BH,THF} WH_4(PMePh_2)_4}$	47	(11)

Occasionally, tetrahydroborato intermediates have been observed in $NaBH_4$ reductions. For example, $RuH(BH_4)(PPh_3)_3$ has been isolated from the reaction of $RuCl_2(PPh_3)_3$ and $NaBH_4$ in EtOH [106]. This decomposes with time to give either $RuH_4(PPh_3)_3$ or $RuH_2(N_2)(PPh_3)_3$ according to circumstances. The borane or alane liberated sometimes complexes with a phosphine to give a polyhydride with one less phosphine group than possessed by the starting complex (eqns. 5, 12) [77,103,121].

$$\mathrm{IrCl_3L_3 \xrightarrow[M=B,Al]{LiMH_4} IrH_5L_2 + L \cdot MH_3} \tag{12}$$

Reaction of $OsCl_4(PMe_2Ph)_2$ with $NaBH_4$ gives not only $OsH_6(PMe_2Ph)_2$ but also $[OsCl_4(PMe_2Ph)_2]^-$ (isolated as the Ph_4As^+ salt), an unusual example of reduction without concomitant hydride formation. $LiAlH_4$, a more active hydride donor, gives only the hexahydride [108].

(ii) Action of hydrogen

Preparation of polyhydrides by the action of H_2 on metal complexes (Table 3, eqns. 13–24) fall mainly into four categories: (1) alkali metal reductions in the presence of H_2; (2) hydrogenolysis of metal–carbon σ bonds; (3) displacement of π-bound olefins; (4) displacement of donor ligands.

Alkali metal reductions have been used to prepare polyhydride complexes of the Group V–VII metals. Potassium, sodium, sodium amalgam, and magnesium have been used as the reducing agents. Most reductions involve metal halides or their phosphine derivatives in THF or benzene. Presumably, the alkali metal reduces the halide complex, followed by oxidative addition of hydrogen (eqn. 25). When TcO_4^- or ReO_4^- are reduced by sodium or

$$L_nM{-}Cl \xrightarrow{Na} L_nM \xrightarrow{H_2} L_nMH_2 \tag{25}$$

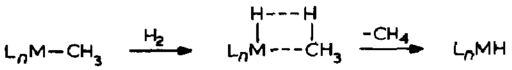
TABLE 3

Some preparations of polyhydrides using dihydrogen

Reaction	Reference	Eqn. No.
$MoCl_4(PEt_2Ph)_2 \xrightarrow[PEt_2Ph]{Na,H_2,THF} MoH_4(PEt_2Ph)_4$	38	(13)
$TaCl_5 \xrightarrow[dmpe,C_6H_6]{K,H_2(100atm.)} TaH_5(dmpe)_2$	30	(14)
$NaReO_4 \xrightarrow{Na,EtOH} Na_2ReH_9$	71	(15)
$WMe_6 \xrightarrow{PR_3,H_2,THF} WH_6(PR_3)_3$	58	(16)
$[(cod)Ir(PPh_3)_2]^+ \xrightarrow[CH_2Cl_2]{H_2,NEt_3} IrH_5(PPh_3)_2$	124	(17)
$(styrene)_2Ru(PPh_3)_2 \xrightarrow[hexane]{H_2} Ru_2H_8(PPh_3)_2$	107	(18)
$[(\eta^4\text{-anthracene})Ru(PPh_3)_2]^- \xrightarrow[THF]{H_2} [RuH_5(PPh_3)_2]^-$	100	(19)
$RuH_2(N_2)(PPh_3)_3 \xrightarrow{H_2,C_6H_6} RuH_4(PPh_3)_3$	103	(20)
$IrH_3(PPh_3)_3 \xrightarrow{h\nu,H_2} IrH_5(PPh_3)_2$	135	(21)
$Mo(acac)_3 \xrightarrow[H_2]{Et_3Al,dppe} MoH_4(dppe)_2$	39	(22)
$FeCl_3 \xrightarrow{PhMgBr,H_2,THF} FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$	93	(23)
$Ir \xrightarrow{SrH_2,H_2} Sr_2IrH_5$	96	(24)

potassium (eqn. 15) in an ethylenediamine/water or an ethanol medium, the source of hydrogen is the solvent.

Hydrogenolysis of methyl or phenyl σ-bonded complexes is limited at present to preparations of niobium, tantalum, and tungsten polyhydrides (eqn. 16). Yields of the polyhydrides can be very good (70–90%), but the organometallic precursors are usually highly air-sensitive. These organometallic complexes are usually formally d^0 systems and the addition of H_2 cannot proceed via a classical oxidative addition. More likely, addition of H_2 occurs by means of a four-center mechanism (eqn. 26).



$$L_nM{-}CH_3 \xrightarrow{H_2} \begin{array}{c} H{-}{-}{-}H \\ |\qquad | \\ L_nM{-}{-}{-}CH_3 \end{array} \xrightarrow{-CH_4} L_nMH \qquad (26)$$

Cleavage of π-bond olefins from metals by H_2 can be used to prepare polyhydrides from cationic (eqn. 17), neutral (eqn. 18), or anionic (eqn. 19) olefin complexes. When the starting complex is coordinatively unsaturated, oxidative addition of H_2 is the first step (eqn. 27) [136].

$$\begin{array}{ccc} [(\mathrm{cod})\mathrm{IrL_2}]^+ & \xrightarrow{H_2} & [(\mathrm{cod})\mathrm{IrH_2L_2}]^+ \\ & & \downarrow -\mathrm{coe} \\ \mathrm{IrH_5L_2} & \xleftarrow{\mathrm{NEt_3}} & \mathrm{IrH_6L_2^+}(?) \end{array} \qquad (27)$$

Sufficiently labile donor ligands, in particular N_2, can be displaced by H_2 (eqns. 20, 21), probably by dissociation of the ligand to give a 16-electron intermediate (eqn. 28). Ligand dissociation may be photoassisted in some

$$MH_2(N_2)L_3 \xrightarrow{-N_2} MH_2L_3 \xrightarrow{H_2} MH_4L_3 \qquad (28)$$

cases (e.g. eqn. 21).

Organoaluminum reagents in the presence of H_2 have been used to convert $Mo(acac)_3$ [39] and $RuHCl(PPh_3)_3$ [104] to $MoH_4(dppe)_2$ and $RuH_4(PPh_3)_3$ respectively. The yields are low and since better methods exist for preparing polyhydrides, this synthetic route is rarely used now.

The reaction of $FeCl_3$ with PhMgBr and H_2 was first reported to give FeH_3 [137], but the actual product of the reaction has recently been found to be $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$. which contains an FeH_6^{4-} unit (eqn. 23) [93]. Similar reactions were originally tried with chromium, tungsten, nickel, and cobalt chlorides; the products of these reactions await full characterization, but may also contain polyhydride units.

While most intermetallic metal hydrides, formed when hydrogen dissolves into a metal lattice, have a low hydride: metal ratio or are non-stoichiometric, some ternary metal hydrides with higher hydride: metal ratios (≥ 4) are known. These have been synthesized by reaction of a binary hydride of an alkali, alkaline-earth, or rare-earth metal, a transition metal, and hydrogen (eqn. 24) [138]. This method has been used to prepare anionic polyhydrides of some of the platinum group metals.

(iii) Hydrogen transfer

While hydrogen transfer from alcohols via β abstraction has long been used to make hydride compounds (eqn. 29), it is uncommon in the synthesis

$$L_nM{-}X \xrightarrow{(CH_3)_2CHO^-} L_nMOCH(CH_3)_2 \rightarrow L_nMH + (CH_3)_2CO \qquad (29)$$

of polyhydrides. However, some examples are known. $IrH_5(PBu^t_2Ph)_2$ and $IrH_5(PBu^t_2Pr^n)_2$ have been prepared from $IrH_2Cl(PBu^t_2Ph)_2$ and $IrHCl_2(PBu^t_2Pr^n)_2$ by reaction with sodium isopropoxide [125,126]. $Mo(N_2)_2(dppe)_2$ also reacts with isopropanol to form $MoH_4(dppe)_2$ and acetone [43]. Hydrogen transfer also takes place from THF, pyrrolidine, and indoline.

D. CHARACTERIZATION

The problem of characterizing polyhydrides is perhaps best illustrated by the story of the "rhenide" ion. In the early 1950's, investigators characterized the product of the reaction of $KReO_4$ and lithium [139] or potassium [140,141] as $M[Re(H_2O)_4]$ on the basis of elemental analysis [141,142]. In 1959, ^1H NMR studies [143] showed the presence of a high-field signal, indicating an Re–H bond. Hydrogen evolution studies suggested the formulation $K[ReH_4]\cdot 2\text{–}4\ H_2O$ [144], while integration of the NMR signal pointed to $K_6[Re_2H_{14}]\cdot 6H_2O$ as another possibility [145]. The same criteria applied to the carefully purified product led to the formulation K_2ReH_8 [70], the lack of a magnetic moment in this putative d^1 species notwithstanding [146]. At last, in 1964 a joint X-ray [147] and neutron [148] diffraction study conclusively showed the formula to be K_2ReH_9.

(i) "Classical" methods

This protracted saga shows that "classical" methods of analysis are inadequate for the total characterization of polyhydrides. An important factor is the very small amount which the hydride ligands contribute to the total molecular weight (ca. 0.5–1%). While chemical analysis and molecular weight measurements may be useful for determining the purity of a polyhydride or its gross formulation, the uncertainties inherent in these techniques are too great to determine reliably the number of hydrides bound to the metal.

Gas evolution studies (mostly by acidolysis) have also been used in attempts to determine hydride ligand multiplicities. Knoth [149] characterized $RuH_4(PPh_3)_3$ by measurement of stepwise gas evolution (eqn. 30).

$$RuH_4(PPh_3)_3 \xrightarrow[-H_2]{PPh_3} RuH_2(PPh_3)_4 \xrightarrow[-2H_2]{HCl} RuCl_2(PPh_3)_4 \tag{30}$$

However, the acidolysis of polyhydrides sometimes yields products which still contain hydride ligands (see Section F.(iv)), giving a spuriously low figure for the total number of hydrides. (We might add parenthetically that the misformulations of polyhydrides which have occurred always underestimated the number of hydrides.) Spectroscopic and crystallographic methods are needed to characterize polyhydrides completely, but the 18-electron rule is a useful method for arriving at the correct formula.

(ii) Infra-red spectroscopy

Terminal M–H stretching bands are often observed in the IR spectra of polyhydrides. The frequencies tend to be lower in the early transition metals: ca. 1500–1800 cm^{-1} for the Group V metals, 1700–1900 cm^{-1} for Group VI, and 1800–2100 cm^{-1} for the other metals. This may be the result of the metal–hydrogen bonding in the early transition metals being more "hydridic" and hence weaker. The one later polyhydride having a low ν(MH), $[RuH_5(PPh_3)_2]^-$ (1750 cm^{-1}) [100], also has relatively strong hydridic character.

These frequencies tend to increase by 20–60 cm^{-1} on moving from the second to the third row of a group. For example, $MoH_4(P(OEt)_2Ph)_4$ has ν(MH) at 1818 and 1751 cm^{-1} while the analogous bands appear at 1886 and 1808 cm^{-1} in $WH_4(P(OEt)_2Ph)_4$ [41]. This phenomenon reflects an increase in the M–H bond strength on going to heavier metals within a group.

Terminal M–H bending modes are occasionally detected around 850 cm^{-1}: e.g. $IrH_5(PPr^i_3)_2$ (875 cm^{-1}), $RuH_4(PPh_3)_3$ (805 cm^{-1}), ReH_9^{2-} (735 cm^{-1}), $WH_4(PEt_2Ph)_4$ (843 cm^{-1}). However, these bands are often obscured by other ligand vibrations [108,105]. A full assignment of the IR bands for a series of $MH_4(PR_3)_4$ complexes (M = Mo, W) has been carried out [151].

Bridging hydride ligands commonly absorb at lower frequencies than do terminal hydride ligands. $Ru_2H_8(PPh_3)_4$ and $Ru_2H_6(N_2)(PPh_3)_4$ absorb in the 1550–1650 cm^{-1} range [107] and $Ta_2Cl_4(\mu\text{-}H)_4(PMe_3)_4$ has a particularly low ν(MH) of 1225 cm^{-1} [32].

It should be pointed out that the intensities of these M–H bands are often weak and the absence of observable vibrations need not mean the absence of M–H bonds. Deuterium substitution is used to assign M–H bands in doubtful cases ($\nu(\mathrm{MH})/\nu(\mathrm{MD}) \cong \sqrt{2}$).

(iii) NMR spectroscopy

NMR spectroscopy is a powerful tool in determining the stoichiometry of polyhydrides. Since most polyhydrides contain phosphorus donors, both ^{1}H and ^{31}P NMR techniques are useful.

Metal–hydride resonances in the ^{1}H NMR spectrum are almost always in a distinctive area, to high field of TMS (0 to -50 δ). This has been attributed to the strong shielding of the ^{1}H nuclei by the *d* electrons of the metal [152,153]. In polyhydrides, the hydride resonances usually appear between $+1$ and -15 δ, though $\mathrm{Ta_2Cl_4(\mu\text{-}H)_4(PMe_3)_4}$ shows a complex multiplet at $+8.79$ δ [32]. As expected, the shift to higher field becomes more pronounced in compounds with more *d* electrons: $\mathrm{WH_6(PMe_2Ph)_3}$ (d^0, -1.94 δ), $\mathrm{ReH_5(PMe_2Ph)_3}$ (d^2, -6.1 δ), $\mathrm{OsH_4(PMe_2Ph)_3}$ (d^4, -8.81 δ).

Most polyhydrides contain phosphorus donors, so the ^{1}H signal is spin–spin coupled to ^{31}P. Since these compounds are non-rigid in solution at or just above room temperature (see Section Vc), a binomial multiplet of $n + 1$ lines is seen in a compound with n phosphorus donors bound to the metal. Thus the quartet appearing at -6.76 δ in the spectrum of $\mathrm{ReH_5(dppe)_2}$ indicates that one dppe ligand is bidentate and the other monodentate [73]. In $\mathrm{RuH_4(PR_3)_3}$ complexes, only a broad feature is observed for the Ru–H resonance. This may be due to the reversible dissociation of $\mathrm{H_2}$ from the complex in solution (eqn. 31) [102].

$$\mathrm{RuH_4(PR_3)_3 \rightleftarrows RuH_2(PR_3)_3 + H_2} \qquad (31)$$

The coupling constant, $^2J_{\mathrm{MH}}$, is between 10 and 40 Hz for terminal M–H groups in polyhydrides. In certain cases with bridging hydride ligands, this is reduced: in $\mathrm{[ReH_2(PMe_2Ph)_2]_2(\mu\text{-}H)_4}$, $^2J_{\mathrm{MH}}$ is 9.5 Hz vs. 20.4 Hz in $\mathrm{ReH_7(PMe_2Ph)_2}$ [74]. This has been explained in terms in terms of a reduced bond order in bridging hydrides [136]. Coupling to isotopes with $I = 1/2$, notably ^{183}W (14.4% abundance) and ^{187}Os (1.64% abundance), can give rise to satellites with $^1J_{\mathrm{MH}}$ between 25 and 35 Hz.

NMR spectroscopy also makes it possible to determine the hydride ligand multiplicity in a polyhydride complex. Two methods have been used. It is occasionally possible to integrate the area of the hydride resonances and compare it to that of the ligand protons. A series of iridium polyhydrides previously characterized as $\mathrm{IrH_3L_2}$ were reformulated as $\mathrm{IrH_5L_2}$ complexes when the ratio of the integral intensity of the PEt_2Ph alkyl proton resonances to that of the hydrides was found to be 20.1 : 4.8 [120]. Unfortunately, this method suffers from two drawbacks: (1) the relaxation times of the hydride ligands may differ from those of the other ligand protons; (2) the compound may decompose in solution and lose H_2, as in eqn. 31, giving an incorrect figure for the number of hydride ligands. The first problem can be circumvented by integrating against another, well-characterized polyhydride used as an internal standard [154] or by using high-field FT spectrometers using short pulses and long delay times to integrate hydride ligand and other ligand proton signals [155].

When phosphorus donors are present, ^{31}P NMR spectroscopy is often a more reliable method of determining hydride ligand multiplicity. In the absence of a noise-band modulation, the decoupling field can be positioned so that only the protons downfield of TMS (0 to 10 δ) are decoupled ("selective" decoupling). Only the interaction of the MH_n protons with phosphorus remains and a binomial multiplet of $n + 1$ lines results. Even though the apparent $^2J_{PMH}$ is lower than in the ^1H NMR spectrum, the alkyl and aryl protons are sufficiently decoupled without the off-resonance effects affecting the hydride ligand region too severely, even in $WH_5(PMePh_2)_4^+$, where the hydride resonances are at $+0.37\ \delta$ [61]. Selective-decoupling techniques have been used to characterize many polyhydrides and clarify several misformulations. For example, $MoH_2(dppe)_2$ [38,39,156] was later proved to be $MoH_4(dppe)_2$ on the basis of the $^{31}P\{selective\text{-}^1H\}$ NMR spectrum [45].

(iv) ESR spectroscopy

Virtually all polyhydrides are 18-electron, diamagnetic compounds; therefore ESR spectroscopy is of no use in characterizing them. However, there are some examples of paramagnetic polyhydrides, the ESR spectra of which have been recorded. The ESR spectrum of $TaH_4(dmpe)_2$ (generated from $TaH_5(dmpe)_2$ and t-butyl peroxide) shows hyperfine coupling to ^{181}Ta ($I = 7/2$, $\langle a_M \rangle = 106.3$ G) and ^{31}P ($I = 1/2$, $\langle a_P \rangle = 32.9$ G) [157]. Oxidation of $Re_2H_8L_4$ complexes gives $[Re_2H_8L_4]^+$ ions, which have slightly asymmetrical 11-line spectra [88]. These have been interpreted to mean that the unpaired electron occupies an orbital in the Re–Re bond with coupling to two rhenium nuclei ($I = 5/2$).

E. STRUCTURES

(i) Crystallographic methods [158]

The peculiar nature of the hydride ligand has caused difficulties in determining not only the stoichiometry of hydride complexes but also their structures [159]. The X-ray crystallographic characterization of metal hydrides is complicated by the small X-ray scattering factor for hydrogen. This makes it difficult to detect hydrides crystallographically in the presence of heavier metal atoms. In mono-or dihydrides, the approximate positions of the hydrogens, even when not directly detected, can often be deduced from the positions of the other ligands, but in polyhydrides this is less feasible. Occasionally direct location and refinement of metal hydride positions is possible by use of difference-Fourier techniques and collection of data at low temperatures, which limits the thermal motion of the hydride ligands. For example, all six hydride ligands in $WH_6(PPr^i_2Ph)_3$ were located using data collected at 200 K [58].

Neutron-diffraction analysis, which gives both accurate hydride ligand positions and metal–hydrogen distances, has played an important part in characterizing hydrides in general and polyhydrides in particular. The neutron method relies on scattering from the nucleus rather than from the electron cloud of an atom and the neutron scattering factor for hydrogen is substantial. Unfortunately, neutron diffraction facilities are far less common than are X-ray laboratories. Since the neutron beam flux is low compared to an X-ray beam, the size of the crystal required for neutron work must be much larger (1–20 mm^3 vs. 10^{-3} mm^3 for an X-ray sample).

The structural parameters obtained by the two methods differ slightly. The neutron bond length is the true internuclear distance, while the X-ray bond length tends to be up to 0.1 Å shorter, since the electrons in the M–H bond are displaced from the H nucleus toward the metal.

Typical M–H internuclear separations are 1.6–1.7 Å for the second and third row elements that tend to form polyhydrides. In those polyhydrides containing M–H–M bridges, M–H distances nearer to 1.8 Å are expected.

Both X-ray and neutron diffraction methods have been widely used in attempts to determine the molecular structures of polyhydrides. The geometries which these compounds adopt can sometimes be compared with their dynamic behavior in solution, as studied by variable-temperature NMR.

(ii) Coordination polyhedra adopted

No ligand offers a wider array of higher-coordinate complexes than does the hydride, but only certain geometries have been found so far for each coordination number (e.g. dodecahedral for C.N. = 8). We examine these here.

(1) Four-coordinate polyhydrides. The structure of Li_4RhH_4, determined by single-crystal X-ray methods, shows a square-planar RhH_4^{4-} unit [116]. The Rh–H distances were found to be 1.90 Å, considerably longer than the 1.60

Å seen in $RhH(CO)(PPh_3)_3$ [160]. The bonding here is believed to have a greater degree of ionic character.

(2) Five-coordinate polyhydrides. Room-temperature [96,161] and low-temperature [161] powder neutron diffraction studies have been carried out on Sr_2IrD_5. At 4.2 K, the IrD_5^{4-} unit has a square-based pyramidal structure (Fig. 1) with basal Ir–D distances of 1.693 Å and an apical Ir–D distance of 1.82 Å.

(3) Six-coordinate polyhydrides. An X-ray diffraction study [162] of $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$ revealed an octahedral FeH_6^{4-} unit with four magnesium atoms tetrahedrally arrayed on the faces (Fig. 2). All six hydrides were located and the Fe–H distances average 1.69 Å, indicative of covalent metal–hydrogen bonds. A powder neutron diffraction study of Sr_2RuD_6 [96] shows the RuD_6^{4-} ion is similar. Impure Li_3IrH_6 has also been reported [117], but its structure has not yet been determined.

(4) Seven-coordinate polyhydrides. The structure of $OsH_4(PMe_2Ph)_3$ was determined by X-ray and neutron methods [163]. The compound has a distorted pentagonal biprismatic structure (Fig. 3). The four hydrides lie in

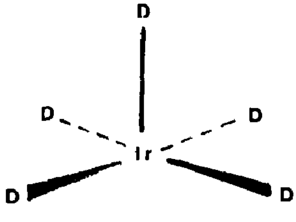


Fig. 1. Structure of IrD_5^{4-}.

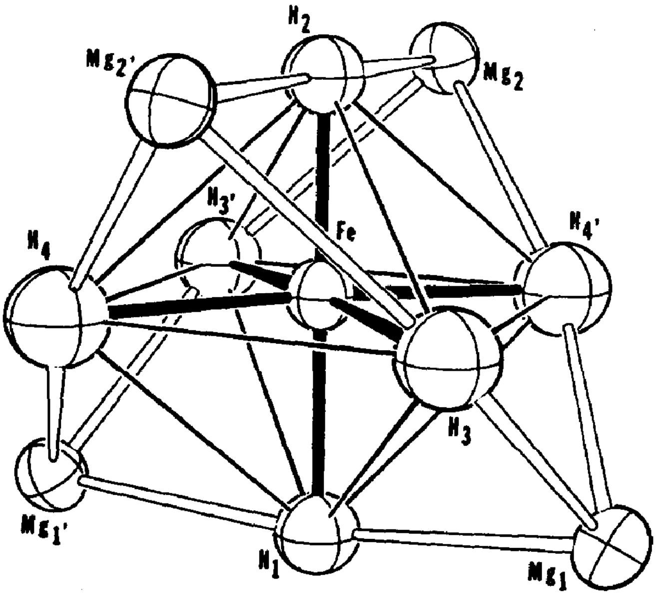


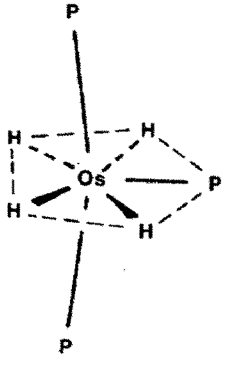
Fig. 2. Structure of the FeH_6^{4-} ion with surrounding Mg atoms. Reprinted from Reference 162 by permission.

the pentagonal plane with Os–H distances averaging 1.66 Å. One phosphine is in this plane while the other two are axially aligned and bent slightly away from the equatorial phosphine (P(ax)–Os–P(ax) = 166°). Preliminary studies of $IrH_5(PEt_2Ph)_2$ [163] and $OsH_4(PEtPh_2)_3$ [164] show similar structures; in the former compound, the phosphine ligands are *trans*.

While the hydride ligands were not located in the crystal structure determinations of two dimeric iridium polyhydrides $[Ir_2H_5(PPh_3)_4][PF_6]$ [165] and $[Ir_2H_5(dppp)_2][BF_4]$ [131] (their positions were located by ^1H NMR), they were located in the study of the related rhodium complex $[((Fe(C_5H_4PPhBu^t)_2)RhH)_2(\mu\text{-}H)_3][ClO_4]$ [165a]. All these compounds have the structure shown in Fig. 4. Metal–metal distances are 2.51 Å for the iridium compounds and 2.59 Å for the rhodium complex, indicating a substantial degree of M–M interaction in the three M–H–M 3-center, 2-electron bonds. The bridging Rh–H distances (1.79 Å (av.)) are longer than the terminal distances (1.64 Å (av.)). The disposition of ligands about each metal is roughly octahedral.

All four hydrides were located in the X-ray diffraction study of $MoH_4(PMePh_2)_4$ [166]. The structure (Fig. 5) is derived from the dodecahedron with the hydrides occupying an elongated tetrahedron (the *A* sites, with four nearest neighbors by the Hoard–Silverton rules [166a]) and the phosphines occupying a flattened tetrahedron (the *B* sites, with five nearest neighbors). The Mo–H distances average 1.70 Å. Studies on $WH_4(PEtPh_2)_4$ [167] and $WH_4(P(OPr^i)_3)_4$ [168] show no significant deviation from this geometry. The structures of $ReH_5(PPh_3)_3$ [169] and $OsH_6(PPr^i_2Ph)_2$ [169a] are believed to be derived from the dodecahedron with hydrides occupying respectively one and two of the *B* sites.

Two dimeric rhenium polyhydrides of the type $[(ReHL_2L')_2(\mu\text{-}H)_3]^+$ (L = PMe_2Ph, L′ = $P(OCH_2)_3CMe$ [87]; L = PPh_3, L′ = Bu^tNC [170]) have



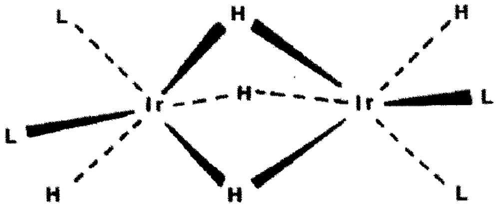


Fig. 3. Representation of the inner OsH_4P_3 core of $OsH_4(PMe_2Ph)_3$.

Fig. 4. Structure of the $Ir_2H_5L_4^+$ complexes.

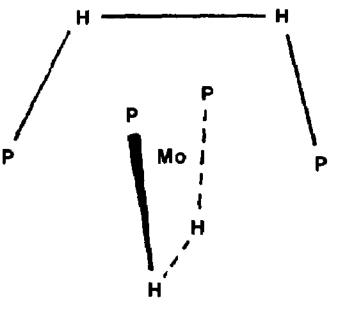
remarkably similar structures (Fig. 6). The Re–Re distances are rather short (2.60 Å) and, as expected, the terminal Re–H bond lengths (1.60 Å (av.)) are shorter than the bridging ones (1.83 Å (av.)). The coordination geometry around each metal has been described as a distorted pentagonal biprism with two triangular faces fused to form the dimer.

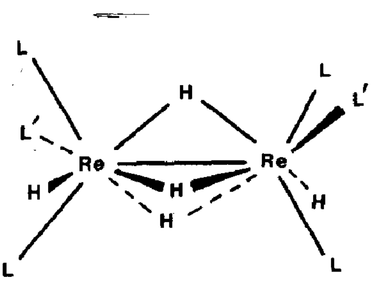
(5) Nine-coordinate polyhydrides The classic example of a nine-coordinate polyhydride is the $\mathrm{ReH_9^{2-}}$ ion, the structure of which was determined by a neutron diffraction study of $\mathrm{K_2ReH_9}$ [148]. The structure (Fig. 7) is a tricapped trigonal prism of D_{3h} symmetry, with Re–H distances averaging 1.68 Å. The powder diffraction patterns of $\mathrm{K_2ReH_9}$ and $\mathrm{K_2TcH_9}$ are similar and the technetium compound is probably isostructural [68].

Nine-coordinate polyhydrides containing phosphine ligands also have structures based on the $\mathrm{ReH_9^{2-}}$ geometry. The solid-state structure of the $\mathrm{ReH_8L^-}$ complexes [72] have not yet been determined, but the phosphine could occupy either a prismatic or an equatorial site (Fig. 8(a), 8(b)).

X-ray crystallographic studies of several $\mathrm{ReH_7L_2}$ complexes ($\mathrm{L = PMe_2Ph}$ [171], $\mathrm{PPr^i_2Ph}$ [75], and $\mathrm{PPh_3}$ [75]) did not locate the hydride ligands. The P–Re–P angles, ranging from 138.9° to 147°, are wider than the 120° expected for a structure with two equatorial phosphines (Fig. 8(c)). This can be attributed either to steric interactions between two equatorial phosphines or to a structure in which one phosphine is equatorial and the other prismatic (Fig. 8(d)).

The latter supposition gains credence when the structure of $\mathrm{WH_6(PPr^i_2Ph)_3}$ is considered (Fig. 8(e)). X-ray [58] and neutron [172] diffraction studies revealed a structure in which two phosphines occupy eclipsed prismatic sites





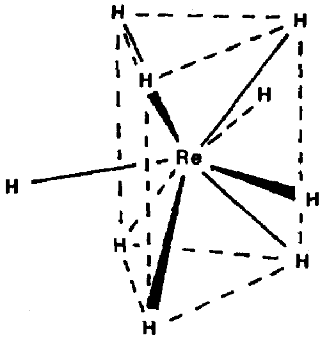


Fig. 5. Representation of the inner $\mathrm{MoH_4P_4}$ core of $\mathrm{MoH_4(PMePH_2)_4}$.

Fig. 6. Structure of the $[\{\mathrm{ReHL_2L'}\}_2(\mu\text{-H})_3]^+$ cations.

Fig. 7. Structure of the $\mathrm{ReH_9^{2-}}$ ion.

(∠PWP = 107.8°) and the third an equatorial site. W–H distances average 1.73 Å. No study has yet been done on the structures of $NbH_5(dmpe)_2$ or $TaH_5(dmpe)_2$, but a disposition similar to that in Fig. 8(f) seems most likely, with the chelating phosphines occupying adjacent equatorial and prismatic sites.

If we consider a C_5Me_5 ring as occupying three coordination sites, the $(\eta^5\text{-}C_5Me_5)TaH_4(PR_3)_2$ complexes are nine-coordinate. In the structure of the PMe_3 compound (Fig. 9) [32], the ring center, metal, and phosphorus atoms are not coplanar: the angle defined by the P–P midpoint, metal, and ring center is 153°. The hydrides were not located crystallographically, but their probable positions were determined by variable-temperature ^1H NMR (see Section E.(iii)).

Among dinuclear polyhydrides, the $[MH_2(PR_3)_2]_2(\mu\text{-}H)_4$ complexes (M = Re, Ru) and $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$ are nine-coordinate. The structure of $Re_2H_8(PEt_2Ph)_4$ was determined by neutron diffraction methods (Fig.

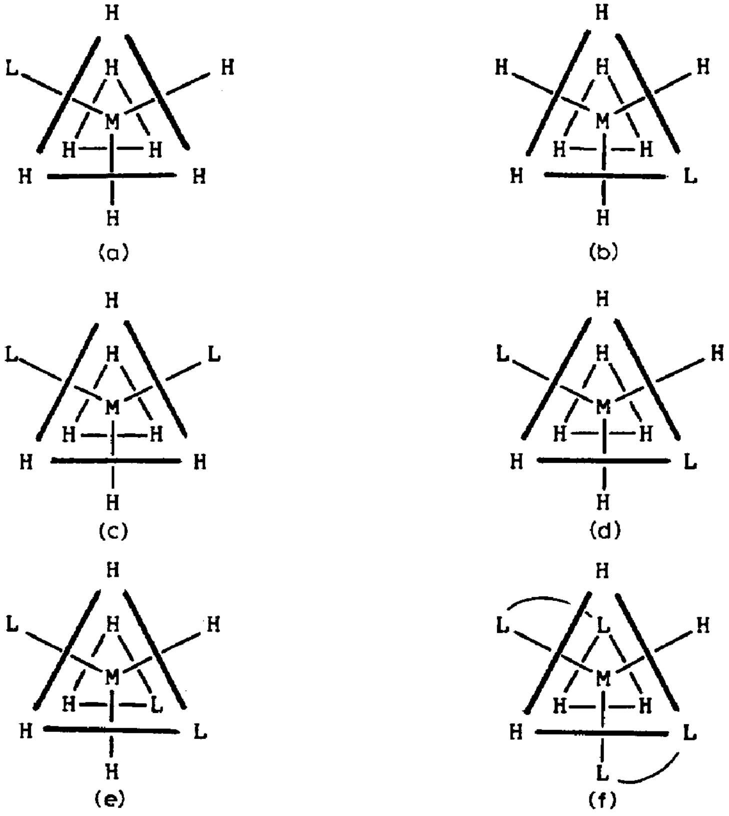


Fig. 8. Ligand distribution in $MH_{9-n}L_n$ polyhydrides (n = 1–4). (a) MH_8L, L in equatorial site; (b) MH_8L, L in prismatic site; (c) MH_7L_2, L in equatorial sites; (d) MH_7L_2, L in prismatic and equatorial sites; (e) MH_6L_3; (f) $MH_5(L_2)_2$ with chelating ligands. The view shown in these diagrams is along the threefold axis of the prism.

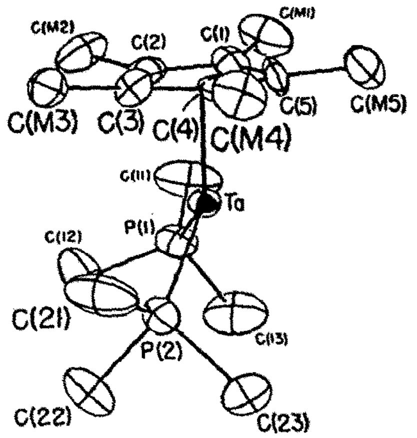


Fig. 9. Structure of the $(C_5Me_5)Ta(PMe_3)_2$ core of $(C_5Me_5)TaH_4(PMe_3)_2$. Reprinted from ref. 33 by permission.

10) [173]. The ligands around each metal define a distorted square antiprism. The Re–Re distance is short (2.538 Å). The mean terminal Re–H distance is 1.67 Å, while the bridging Re–H distance average 1.88 Å. The Re–H–Re angles are about 85°. The phosphines are eclipsed, giving the molecule formal D_{2h} symmetry.

The tantalum compound $Ta_2Cl_4H_4(PMe_3)_4$ has an M–M bond length (2.511 Å), M–$H_{(br)}$ distances (1.81 Å), and M–H–M angles (88°) similar to the rhenium complex [174]. The curious difference between the two is that the phosphines are staggered in the tantalum dimer, which has a formal D_{2d} symmetry (Fig. 11). The reasons for this are not clear, but extended-Hückel calculations [175] indicate that the two conformations are energetically similar.

(iii) Dynamic behavior

Polyhydrides provide some of the classic examples of fluxionality among transition metal complexes. Several alternative structures are available in

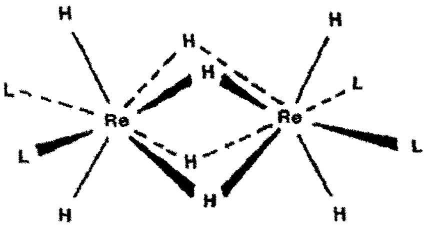


Fig. 10. Structure of $Re_2H_8(PEt_2Ph)_4$.

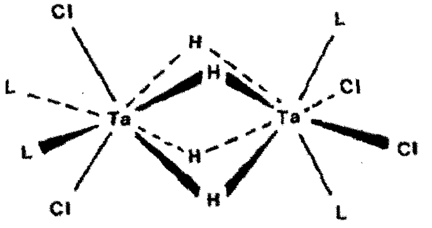


Fig. 11. Structure of $Ta_2H_4Cl_4(PMe_3)_4$.

seven-, eight-, and nine-coordination. Permutation of the hydride and other ligands in the ground-state structure is possible via these alternative geometries (which are often of similar energies) and relatively little movement of the ligands is needed for interconversion [176]. Isomers having different geometries have not yet been detected in this process. This contrasts with six-coordinate hydrides, which are usually rigid because the octahedral geometry is a deep minimum in the potential energy surface.

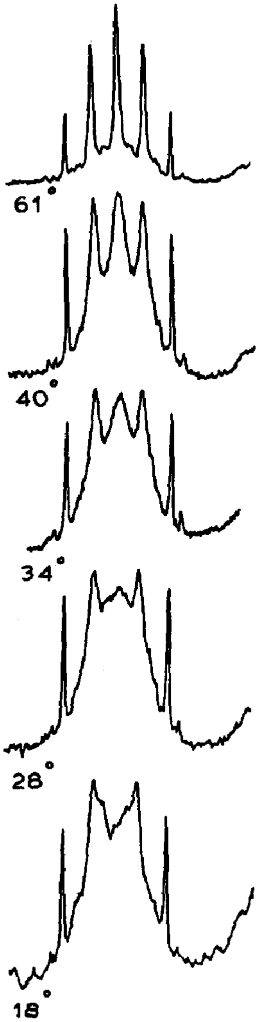
Fluxionality is detected by the variable-temperature NMR spectrum of the complex. Often at low temperatures the ^1H NMR spectrum of a phosphine polyhydride is observed which can be assigned to the "rigid" ground-state structure. As the temperature is raised, the lines eventually sharpen to a binomial multiplet. Clearly, stereochemical conclusions about the ground state structure cannot be drawn from the appearance of the spectrum at this elevated temperature.This represents a time-averaged structure and only gives information about the number of PR_3 ligands present. The rearrangement barriers can be obtained from the line-shape behavior with respect to temperature [177].

Seven-coordinate polyhydrides have several common accessible geometries derived from the D_{5h} pentagonal biprism (normally adopted in the ground state), the C_{2v} capped prism, and the C_{3v} capped octahedron [178]. The barrier to interconversion between these is low [179]. Accordingly, $OsH_4(P(OEt)_2Ph)_3$ shows a simple quartet at 25°C which broadens on cooling, but a spectrum corresponding to the rigid geometry was not observed even at −100° C [115]. Possible pathways for such rearrangements have been discussed [178,179]. The IrH_5L_2 complexes are also fluxional at all accessible temperatures.

Eight-coordinate polyhydrides have accessible geometries derived from the D_4 square antiprism and the D_{2d} dodecahedron [180]. Based on the MH_4L_4 structures [166–168], the ground state appears to be the dodecahedron.

The dynamic behavior of the $MoH_4(PR_3)_4$ and $WH_4(PR_3)_4$ complexes has been thoroughly studied [41]. The tungsten cases are unusual insofar as they are the only polyhydrides for which the "rigid" spectrum is observed at room temperature in the ^1H NMR (Fig. 12); the molybdenum analogues are fluxional at room temperature. The rearrangement barriers are surprisingly high, with activation energies of 12–13.5 kcal mol^{-1} for the $MoH_4(PR_3)_4$ complexes and 14–17 kcal mol^{-1} for the $WH_4(PR_3)_4$ complexes.

The variable-temperature ^1H NMR spectrum of $ReH_5(AsEtPh_2)_3$ shows a singlet at +30°C for the hydride resonances. At −130°, this splits into four resonances with relative intensities of 1 : 2 : 1 : 1 (Fig. 13) [169]. The "rigid" spectrum corresponds to a dodecahedral geometry, (among other possible ground-state structures).



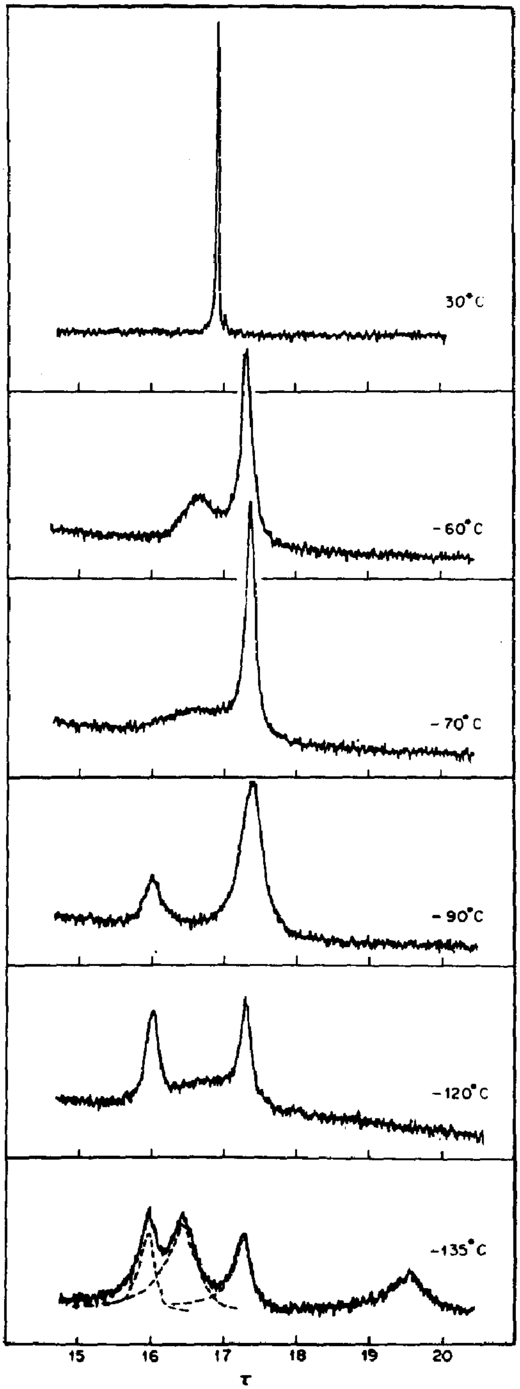


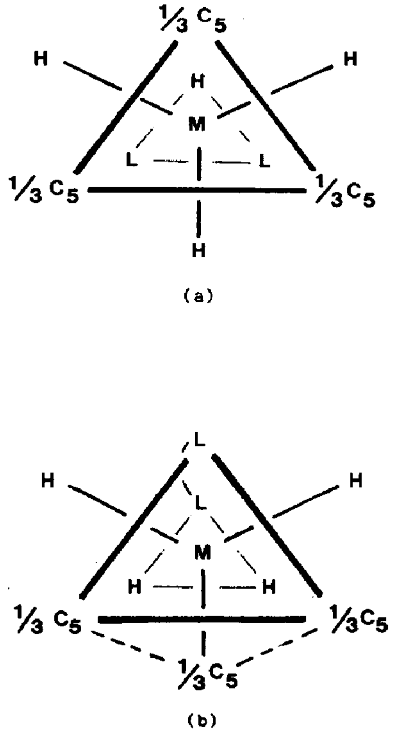
Fig. 12. Variable-temperature ^1H NMR spectrum of $WH_4(PMe_2Ph)_4$. Reprinted from Reference 41 by permission.

Fig. 13. Variable-temperature ^1H NMR spectrum of $ReH_5(AsEtPh_2)_3$. Reprinted from Reference 169 by permission.

Nine-coordinate polyhydrides adopt structures based on the D_{3h} tricapped trigonal prism, but the monocapped square antiprism is often relatively close in energy [181], allowing fluxionality. The polyhydrides ReH_9^{2-}, $ReH_8(PR_3)^-$, and $ReH_7(PR_3)_2$ are fluxional at all temperatures, as is $WH_6(PMe_2Ph)_3$ [41]. However, the dynamic process can be slowed by introducing bulky ligands. The quartet M–H resonance seen in the room temperature spectra of $WH_6(PPr^i_2Ph)_3$ [57] and $MoH_6(PPr^i_2Ph)_3$ [35] broaden on cooling and collapse to a single resonance at −75° to −80°C. The formally nine-coordinate $(C_5Me_5)TaH_4L_2$ complexes are non-rigid at room temperature, but the low temperature spectrum of the PMe_3 and $P(OMe)_3$ derivatives differ from that of the dmpe complex. The ground state structures are believed to be those shown in Figs. 14 (a) and 14 (b) [33].

The $Re_2H_8L_4$ dimers also show fluxionality in solution. This involves exchange of bridging and terminal hydride ligands, a process which cannot be resolved by lowering the temperature [173]. In contrast, $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$ is rigid; there is no exchange of chloride and hydride ligand positions (eqn. 32) [174].

$$[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4 \not\rightleftharpoons [TaH_2(PMe_3)_2]_2(\mu\text{-}Cl)_4 \tag{32}$$



(a)

(b)

Fig. 14. Probable structures of $(C_5Me_5)TaH_4L_2$: (a) L = PMe_3, $P(OMe)_3$; (b) L = 1/2 dmpe. 1/3 C_5 denotes each coordination site of the C_5Me_5 rings.

F. REACTIONS

The key feature of polyhydride chemistry is their ability to generate multiple sites of coordinative unsaturation by losing H_2 either thermally, photochemically, or on acidolysis. No other MX_nL_y species ($X = Cl$, Me, etc.) [182] is as effective in this respect because the central metal in these compounds is more positively charged than in a polyhydride due to the higher electronegativity of the X group. The metal *d* orbitals, sensitive to this bond polarization, contract and the characteristic *d*-orbital chemistry of the low oxidation states is lost.

In contrast, the M–H bond in polyhydrides is relatively unpolarized. Despite the high formal oxidation states of these compounds (4+ to 7+), the metal bears a charge closer to that of the free metal. XPS studies on various polyhydrides bear this out [66,183–185]. For instance, compared with $ReCl_3(PMe_2Ph)_3$, arbitrarily assigned an oxidation state of 3.0, $ReH_5(PMe_2Ph)_3$ has an oxidation state of 1.9 [184]. Theoretical studies on ReH_9^{2-} suggest the charge on the metal is -0.17, increasing to $+0.19$ in $ReH_8(PH_3)^-$ [186]. This lower true oxidation state leads to a chemistry resembling that of organometallic compounds and one in which *d* orbitals play a full role.

(i) Reactions with donor molecules

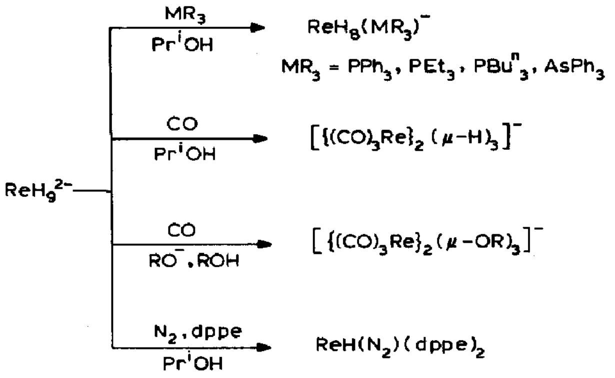
Polyhydrides often undergo reactions with donor molecules, which replace H_2 in the complex (eqns. 33–39). These reactions can sometimes be reversed by the action of H_2 (eqn. 40).

$$L_nMH_2 \underset{H_2}{\overset{L'}{\rightleftharpoons}} L_nM\text{–}L' \tag{40}$$

For a given metal, these reactions are more facile for compounds with higher hydride multiplicities (e.g. ReH_7L_2 vs. ReH_5L_3). Addition of two donor ligands is occasionally possible, but sometimes more vigorous conditions are required and loss of phosphine can result.

Reflecting their higher M–H bond strength, polyhydrides of the third-row metals often require more forcing conditions to react with donors than do their second-row counterparts. For example, CO and N_2 react with $RuH_4(PPh_3)_3$ under mild conditions (1 atm., 25°C) [103], while $OsH_4(PEtPh_2)_3$ reacts with CO only after 18 hours in refluxing toluene and not at all with N_2, even at 150 atm. [191].

There are some exceptions to the general reactivity outlined in Table 4. The ReH_9^{2-} ion undergoes several reactions *sui generis* (eqns. 41–44). In the



[72] (41)

[194] (42)

[194] (43)

[195] (44)

absence of alkoxide, the reaction with CO gives several products, the one characterized being the triple-hydride-bridged ion (eqn. 42).

The action of triisopropylphosphite on the Group VI tetrahydrides results in substitution not of the hydride ligands but of the phosphines (eqn. 45)

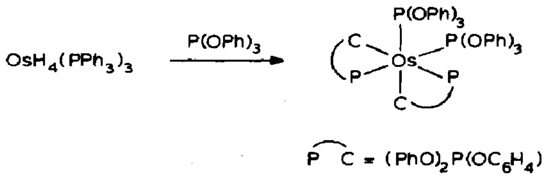
TABLE 4

Some reactions of polyhydrides with two-electron donors

Reaction	Eqn. No.
$NbH_5(dmpe)_2 \xrightarrow{L} NbHL_2(dmpe)_2$	(33)
L = CO,C_2H_4 [28]	
$MH_4(PR_3)_4 \xrightarrow{L} ML_3(PR_3)_3 + ML_4(PR_3)_2$	(34)
M = Mo,W; L = CO [187]	
$ReH_7(PR_3)_2 \xrightarrow{L} ReH_5(PR_3)_2L$	(35)
L = $C_6H_{11}NH_2$, $C_5H_{10}NH$, C_5H_5N, PR_3, $AsPh_3$ [73]	
$ReH_5(PR_3)_3 \xrightarrow{L} ReH_3(PR_3)_2L_2 + PR_3$	(36)
L = CO [188], 1/2 dppe [84]	
$RuH_4(PR_3)_3 \xrightarrow{L} RuH_2(PR_3)_3L$	(37)
L = CO, RCN [103], N_2 [103,149], PR_3, NH_3 [149], PF_3, $PF_2(NMe_2)$ [189]	
$RuH_4(PR_3)_3 \xrightarrow{L} RuH_2(PR_3)_2L_2 + PR_3$	(38)
L = PF_3, $PF_2(NMe_2)$ [189], 1/2 RN=CR′–CR′=NR [190]	
$IrH_5(PR_3)_2 \xrightarrow{L} IrH_3(PR_3)_2L$	(39)
L = CO [126,128,191], C_5H_5N [128], PR_3, $P(OR)_3$, $AsPh_3$, $SbPh_3$, SMe_2 [192], RNC [192,193]	

$$MH_4(PBuPh_2)_4 \xrightarrow[100^\circ]{P(OPr^i)_3} MH_4(P(OPr^i)_3)_4 \qquad (45)$$

[53]. Triphenylphosphite reacts with $ReH_5(PPh_3)_3$ under strenuous conditions to form $Re_2(P(OPh)_3)_{10}$ [86] and with $OsH_4(PPh_3)_3$ to give a cyclometalated product (eqn. 46) [196].

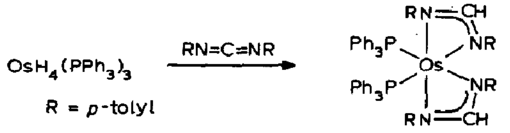


(46)

The reaction of isonitriles with $ReH_7(PPh_3)_2$ does not result in simple substitution. An intermediate abstracts a proton from the solvent and loses H_2 to give $Re(CNR)_4(PPh_3)_2^+$ salts [197]. $WH_6(PMe_2Ph)_3$ similarly gives $[W(CNBu^t)_5(PMe_2Ph)_2][PF_6]_2$ [198].

TABLE 5

Reactions of CO_2 and CO_2-like molecules with polyhydrides

Reaction	Reference	Eqn. No.
$RuH_4(PPh_3)_3 \underset{H_2}{\overset{CO_2}{\rightleftharpoons}} RuH(HCO_2)(PPh_3)_3$	103,199,200	(48)
$FeH_4(PEtPh_2)_3 \xrightarrow{CO_2} Fe(HCO_2)_2(PEtPh_2)_2$	202	(49)
$RuH_4(PPh_3)_3 \xrightarrow{CS_2} Ru(HCS_2)_2(PPh_3)_2$	103	(50)
$OsH_4(PPh_3)_3 \xrightarrow{CS_2} Os(HCS)_2(PPh_3)_2$	203	(51)
	204	(52)
	205	(53)
$MH_4(PR_3)_4 \xrightarrow{CO_2} M(CO)_3(PR_3)_3 + M(CO)_4(PR_3)_2$ M = Mo, W	207	(54)

The oxophilicity of tantalum leads to acetone inserting into the Ta–H bond of $(C_5Me_5)TaH_4(PMe_3)_2$ to give an isopropoxide complex (eqn. 47) [31].

$$(C_5Me_5)TaH_4(PMe_3)_2 \xrightarrow{Me_2CO} (C_5Me_5)Ta(OPr^i)_4 \qquad (47)$$

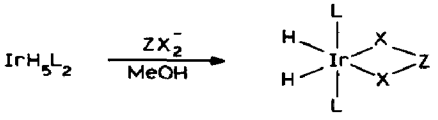
(ii) *Reactions with CO_2 and CO_2-like molecules*

Carbon dioxide and related molecules insert into the M–H bond of polyhydrides of the iron triad to form formato, dithioformato, or formamidinato complexes (Table 5, eqns. 48–53). The reaction of CO_2 with $RuH_4(PPh_3)_3$ is reversible by action of H_2 (eqn. (48). This and the ability of donors to replace CO_2 may imply a $RuH(\eta^2\text{-}CO_2)(PPh_3)_3$ intermediate. [201].

When CO_2 reacts with $WH_4(PR_3)_4$ at 20°C, a CO_2-containing adduct can be detected in the IR spectrum [206]. In refluxing toluene, however, these tetrahydrides give carbonyl-containing complexes and phosphine oxide (eqn. 54).

(iii) *Miscellaneous donors*

The reactions of IrH_5L_2 with dithiophosphate [208], dithiophosphinate [208], xanthate [209], dithiocarbamate [209,210], and diselenocarbamate [211] salts all give products with a *cis, cis, trans* configuration (eqn. 55).



(55)

where L = PPh_3, $AsPh_3$; $ZX_2^- = (RO)_2PS_2^-$, $R_2PS_2^-$, $EtOCS_2^-$, $R_2NCS_2^-$, $Et_2NCSe_2^-$. A dimeric phosphide-bridged complex $[Ir(CO)(PPh_2R)]_2(\mu\text{-}PPhR)_2$ (R = *p*-tolyl) is formed from the reaction of refluxing DMF and $IrH_5(PPh_2R)_2$ [212]. Aryldiazonium salts insert into the Ir–H bonds of $IrH_5(PPh_3)_2$ to give, at −10°C, $[IrH_2(NH{=}NC_6H_4R)(PPh_3)_2]^+$ and, at 40–50°C, a metalated product $[IrH(NH{=}NC_6H_3R)(PPh_3)_2]^+$ [213].

Nitric oxide acts as a three-electron donor in reactions with polyhydrides. Action of NO on $RuH_4(PPh_3)_3$ gives $Ru(NO)_2(PPh_3)_2$ [103] while $IrH_5(PPh_3)_2$ give a dimeric complex $[Ir(NO)_2(PPh_3)]_2$ [214]. Sulfur dioxide also reacts with $RuH_4(PPh_3)_3$ to give $Ru(SO_2)_2(PPh_3)_2$ [215].

(iv) Reactions with acids

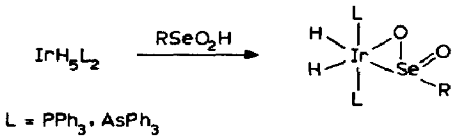
The action of protonic acids on polyhydrides usually results in loss of H_2. In d^{n+2} complexes, lone pairs of electrons are available and the first step is protonation at the metal (eqn. 56). While stable $WH_5L_4^+$ salts can be

$$L_nMH \xrightarrow{H^+} L_nMH_2^+ \xrightarrow{-H_2} L_nM^+ \tag{56}$$

obtained from WH_4L_4 complexes [59–61], similar adducts of other polyhydrides are more often unstable. Evidence has been put forward for the existence of $MoH_5(PMePh_2)_4^+$ [216], $ReH_6(PMe_2Ph)_3^+$ [81], $OsH_5(PMe_2Ph)_3^+$ [108,217], and $IrH_6(PPh_3)_2^+$ [218], but all these lose H_2 at room temperature. In d^0 complexes, no lone pairs are available and the first step of the acidolysis is probably M–H bond protonation [216].

Numerous reactions of polyhydrides with hydrohalic acids have been carried out, often to determine the number of hydrides present. These generally yield metal halides or their phosphine derivatives, but sometimes the product still contains hydrides. This is especially true of the iridium polyhydrides (e.g. eqn. 57) [121,124,125,212,219,220]. Other acids with coordinating anions, such as CF_3COOH or *p*-toluenesulfonic acid, have also been used in reactions with $OsH_4(PPh_3)_3$ [221,222] and $MoH_4(PMePh_2)_4$ [61]. Substituted arylselenic acids and IrH_5L_2 complexes give Se-bound products (eqn. 58) [223,224].

$$IrH_5(PBu^t_2Ph)_2 \xrightarrow{HCl} IrH_2Cl(PBu^t_2Ph)_2 \tag{57}$$



(58)

In reactions with acids having "non-coordinating" anions (ClO_4^-, BF_4^-, PF_6^-), the active sites generated in the complex are not filled by a non-labile anion. Instead these can be "masked" by coordinating, but labile solvent molecules.

Fluoroboric acid has been most commonly used in this class of acidolysis (Table 6) and acetonitrile is often used as the solvating molecule. Methanol and acetone, which are more weakly binding, also give stable ruthenium and iridium complexes. Acidolysis of $MoH_4(PMePh_2)_4$ by HBF_4 or HPF_6 in THF, a very weakly coordinating solvent, has been claimed to give salts of $[MoH_3(PMePh_2)_3]^+$ [61]. However, another study showed that with HBF_4 fluoride abstraction from BF_4^- occurs and a hydrido-fluoro complex $[\{MoH_2(PMePh_2)_3\}(\mu\text{-}F)_3][BF_4]$ is formed [227].

TABLE 6

Some reactions of polyhydrides with HBF_4

Reaction	Reference	Eqn. No.
$MoH_4(PMePh_2)_4 \xrightarrow[CH_3CN]{HBF_4} [MoH_2(CH_3CN)_3(PMePh_2)_3][BF_4]_2$	49	(59)
$WH_4(PMe_3)_4 \xrightarrow{HBF_4} [WH_3(PMe_3)_4][BF_4]$	64	(60)
$ReH_7(PPh_3)_2 \xrightarrow[CH_3CN]{HBF_4} [ReH(CH_3CN)_4(PPh_3)_2][BF_4]_2$	216, 225	(61)
$Re_2H_8(PPh_3)_4 \xrightarrow[CH_3CN]{HBF_4} [Re_2H_7(CH_3CN)(PPh_3)_4][BF_4]$	225	(62)
$RuH_4(PPh_3)_3 \xrightarrow[MeOH]{HBF_4} [RuH(H_2O)(MeOH)(PPh_3)_2][BF_4]$	226	(63)
$IrH_5(PPh_3)_2 \xrightarrow[S]{HBF_4} [IrH_2S_2(PPh_3)_2][BF_4]$ $S = Me_2CO, MeOH, CH_3CN$	216	(64)

Alcohols, thiols, and water can act as acids in some cases. Both ReH_9^{2-} and TcH_9^{2-} are unstable in non-alkaline aqueous solutions [68,71]. Polyhydrides of the Group V metals decompose in alcohols or water [28,30,31], and thiols react with $RuH_4(PPh_3)_3$ [228] and $MoH_4(dppe)_2$ [229] to give mercapto complexes.

Lewis acids can either abstract hydrides from the complex or act as oxidants. The action of Ph_3C^+ or $C_7H_7^+$ on $Re_2H_8(PPh_3)_4$ in dichloromethane results in formation of paramagnetic $[Re_2H_8(PPh_3)_4]^+$ salts [88]. These are much more reactive to Bu^tNC than the neutral complex (eqn. 65).

$$[Re_2H_8(PPh_3)_4]^+ \xrightarrow{Bu^tNC} [Re_2H_5(Bu^tNC)_2(PPh_3)_4]^+ \qquad (65)$$

The isonitrile complex can be further oxidized to $[Re_2H_5(Bu^tNC)_2(PPh_3)_4]^{2+}$ by NO^+.

The reactions of $MoH_4(dppe)_2$ with Lewis acids have also been studied. The product of the reaction with Ph_3C^+ in toluene has been characterized crystallographically as $[Mo(O)(OH)(dppe)_2]^+$, possibly formed from $[MoH(dppe)_2]^+$ and stray water or oxygen [230]. $MoH_4(dppe)_2$ also reacts with $[NO][PF_6]$ to give $MoF(NO)(dppe)_2$ and $[MoF(HNO)(dppe)_2][PF_6]$ [231].

(v) Reactions with metal complexes

Some transition metal ions and complexes can act as oxidants or Lewis acids toward polyhydrides. The reaction of $MoH_4(PMe_2Ph)_4$ with $AgBF_4$

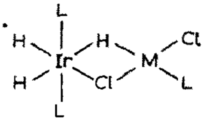
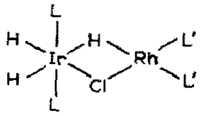
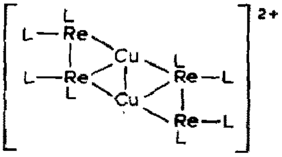
(an oxidizing agent) in CH_3CN gives a solvent complex and Ag metal (eqn. 66) [49].

$$MoH_4L_4 \xrightarrow[CH_3CN]{Ag^+} [MoH_2(CH_3CN)_2L_4]^{2+} + Ag^0 \qquad L = PMe_2Ph \tag{66}$$

Reactions with ligand-deficient metal complexes, acting as Lewis acids, can result in formation of di- or multinuclear species (Table 7). These may involve the polyhydride breaking a halide bridge or displacing a solvent molecule. While H_2 is frequently lost from the polyhydride in these reactions, all hydrides appear to be retained in the formation of the remarkable rhenium–copper complexes (eqns. 70–71). In the product of the reaction of ReH_5L_3 with $Cu(CH_3CN)_4^+$, the copper atom is octahedrally surrounded by six hydrides. This CuH_6 core is unprecedented and is essentially a homo-

TABLE 7

Reactions of polyhydrides with metal complexes

Reaction	Reference	Eqn. No.
$IrH_5L_2 + M_2Cl_4L_2 \longrightarrow$  $M = Pd, Pt; L = PPr^i_3$	232	(67)
$IrH_5L_2 + Rh_2Cl_4L'_2 \longrightarrow$  $L = PEt_3; L' = PEt_3$, 1/2 dppe	233	(68)
$IrH_5L_2 + [Pt(R)(CH_3OH)L'_2]^+ \rightarrow [(R)(L')Pt(\mu\text{-}H)_2Ir(H)L_3]^+$ $L = PEt_3, PPr^i_3; L' = PEt_3, PPr^i_3; R = Ph, Et$	234–236	(69)
$ReH_5L_3 + Cu(CH_3CN)_4^+ \rightarrow [\{ReH_2L_3\}_2(\mu\text{-}H)_6Cu]^+$ $L = PMe_2Ph, PMePh_2$	91	(70)
$Re_2H_8L_4 + Cu(CH_3CN)_4^+ \longrightarrow$  $[Re_4Cu_2H_{16}L_8]^{2+}$ $L = PMe_2Ph, PMePh_2$	91	(71)

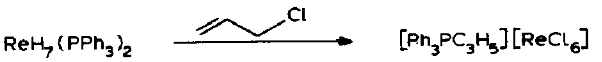
leptic copper hydride. With the dimeric $Re_2H_8L_4$ complexes, a planar, rhomboidal "raft-like" Re_4Cu_2 cluster is obtained (eqn. 71).

(vi) Reactions with halogens and organic halides

Halogens react like hydrohalic acids towards polyhydrides and have also been used as a means of determining the number of hydrides bound to the metal. They too have the drawback that the products may still contain hydrides. For example, an excess of I_2 totally decomposes $ReH_5(PPh_3)_3$ [77], but stoichiometric amounts of I_2, Br_2, or $SnCl_2$ give halide tetrahydride complexes [83] (eqn. 72).

$$ReO_2 \xleftarrow[-2.5H_2]{I_2,H_2O} ReH_5(PPh_3)_3 \xrightarrow[-1/2H_2]{1/2X_2} ReH_4X(PPh_3)_3 \qquad (72)$$

Organic halides can also act as halide sources. Many polyhydrides decompose in halogenated solvents over time, CCl_4 being the most oxidizing and CH_2Cl_2 less so. The molybdenum and tungsten tetrahydrides $MH_4(dppe)_2$ are converted to $MCl_2(dppe)_2$ by CCl_4 and light [237]. Allyl halides convert rhenium and molybdenum polyhydrides to phosphonium salts of the metal halides (e.g. eqn. 73) [238].



(73)

(vii) Electrochemistry

The electrochemistry of polyhydrides is a new area and studies are limited so far to rhenium complexes. The d^0 complex $ReH_7(PPh_3)_2$ shows no reversible electrochemistry, but the $ReH_5(PPh_3)_2L$ compounds undergo quasi-reversible one-electron oxidations between +0.11 and +0.37 V vs. SCE [239]. The ease of oxidation correlates with the basicity of the ligands: $L = C_5H_{10}NH > C_6H_{11}NH_2 > C_5H_5N > PEt_2Ph > PPh_3$.

The dinuclear complexes $Re_2H_8L_4$ exhibit one reversible oxidation wave between −0.16 and −0.40 V vs. SCE and a second, irreversible oxidation between +0.38 and +0.64 V [88]. Again, potentials correspond to ligand basicity, with the PEt_2Ph derivative being the most easily oxidized and the $AsPh_3$ compound the least so. The $[Re_2H_7(PPh_3)_4(NCR)]^+$ ions have two reversible oxidation waves; the analogous Bu^tNC complex is oxidized with more difficulty.

(viii) Photochemistry

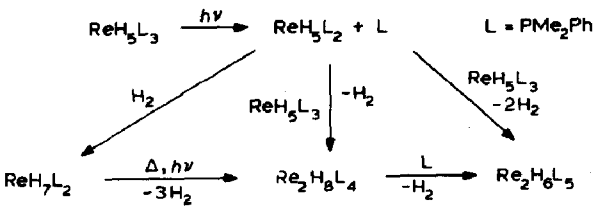
The photochemistry of polyhydrides has also been studied only recently, but has great potential in opening active sites in complexes which are otherwise thermally stable [240]. These reactions depend on the photoextrusion of H_2 from the complex, a reaction first discovered and developed in $(C_5H_5)_2WH_2$ [241].

Irradiation of the $MH_4(PR_3)_4$ complexes (M = Mo, W) at 366 nm results in evolution of two equivalents of H_2 and the generation of a 14-electron intermediate, which can react with various donors (e.g. eqn. 74) [242–248].

$$\mathrm{MoH_4(dppe)_2} \underset{-2H_2}{\overset{h\nu}{\rightarrow}} \text{“}\mathrm{Mo(dppe)_2}\text{”} \underset{L\,=\,CO,N_2,C_2H_4}{\overset{L}{\rightarrow}} \mathrm{Mo(L)_2(dppe)_2} \qquad (74)$$

Loss of H_2 appears to be concerted and does not involve radical or ionic intermediates [242]. The tungsten tetrahydrides are much less photoreactive than those of molybdenum [246,248]. Only one mole of H_2 is lost from $OsH_4(PMe_2Ph)_3$ on photolysis [249]. The $OsH_2(PMe_2Ph)_3$ intermediate generated can form $OsH_2(PMe_2Ph)_4$ when excess phosphine is present or otherwise can dimerize to give $[OsH(PMe_2Ph)_3]_2(\mu\text{-}H)_2$.

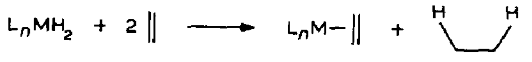
Sometimes, however, loss of phosphine is the primary photochemical event. Irradiation of the thermally stable complex $ReH_5(PMe_2Ph)_3$ results in dissociation of PMe_2Ph and the formation of a highly reactive $ReH_5(PMe_2Ph)_2$ phototransient [74,89,250]. In an H_2 atmosphere, $ReH_7(PMe_2Ph)_2$ is formed, but this too is photosensitive. The entire process, involving dimerization, loss of H_2, and addition or loss of phosphine, gives a variety of products, the major one being the dimeric hexahydride (eqn. 75).



(75)

(ix) Reactions with unsaturated hydrocarbons

In reactions of polyhydrides with olefins, hydride ligands are almost always transferred to a second olefin molecule (eqn. 76). Hydrogenation of the olefin complex can regenerate another hydride species and release a second alkane molecule (eqn. 77). Thus polyhydrides can function as homo-



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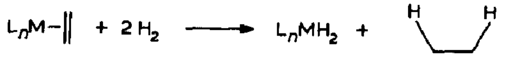


(77)

geneous catalysts for the hydrogenation or isomerization of olefins. Many studies of polyhydride reactions with unsaturated hydrocarbons have been directed to this end.

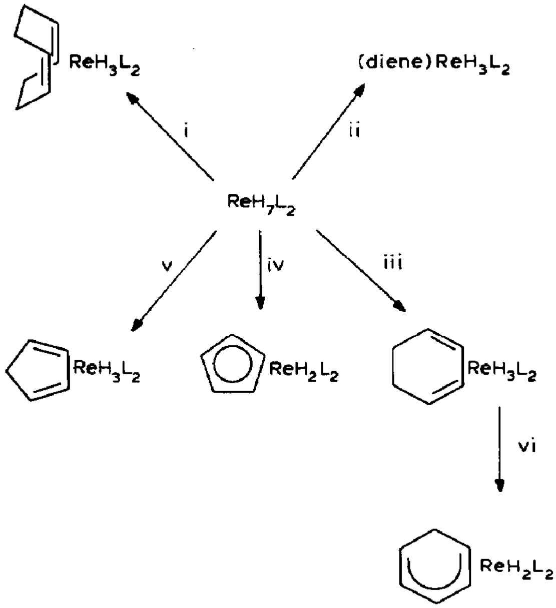
The reaction of $NbH_5(dmpe)_2$ with ethylene results in formation of $NbH(C_2H_4)_2(dmpe)_2$ with, exceptionally, the evolution of hydrogen [28]. The tantalum pentahydride is reported to catalyze the hydrogenation, dimerization, and polymerization of ethylene [27]. Photolysis of $(C_5Me_5)TaH_4(PMe_3)_2$ in the presence of ethylene gives $(C_5Me_5)TaH_2(C_2H_4)(PMe_3)_2$ and ethane [31]. Under thermal conditions, the tetrahydride functions as a catalyst for ethylene dimerization to 1-butene.

Photolysis of $MoH_4(dppe)_2$ with ethylene or propene affords $Mo(C_2H_4)_2(dppe)_2$ or $MoH(\eta^3\text{-}C_3H_5)(dppe)_2$ [248]. In an H_2 atmosphere, the photolyzed compound is also active for the catalytic hydrogenation of terminal olefins. Little or no isomerization is observed. However, certain functionalized olefins, such as allyl alcohol, are isomerized by $MoH_4(dppe)_2$ [251]. $MoH_4(dppe)_2$ and $WH_4(dppe)_2$ also act as electron donors toward TCNE and TCNQ [252] and the molybdenum tetrahydride catalyzes the addition of organic halides to 1-hexene [253].

An extensive chemistry of rhenium polyhydrides with olefins has been developed in recent years. The reaction of cyclic and acyclic dienes with

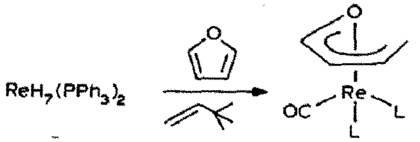
TABLE 8

Reactions of $ReH_7(PPh_3)_2$ with olefins and dienes [78,254]



(i) 1,5- or 1,3-cyclooctadiene; (ii) 1,4-butadiene, 1,4-pentadiene, 2-methyl-1,4-butadiene, 2,3-dimethyl-1,4-butadiene; (iii) 1,3- or 1,4-hexadiene; (iv) cyclopentene; (v) cyclopentadiene; (vi) heat.

$ReH_7(PPh_3)_2$ gives a wide range of hydrido-diene and -dienyl rhenium complexes (Table 8) [74,254]. Ethylene affords a cyclometalated compound $Re(C_2H_4)_2(Ph_2PC_6H_4)(PPh_3)$ [122] while furan is fragmented to give an oxapentadienyl carbonyl complex (eqn. 78) [255].



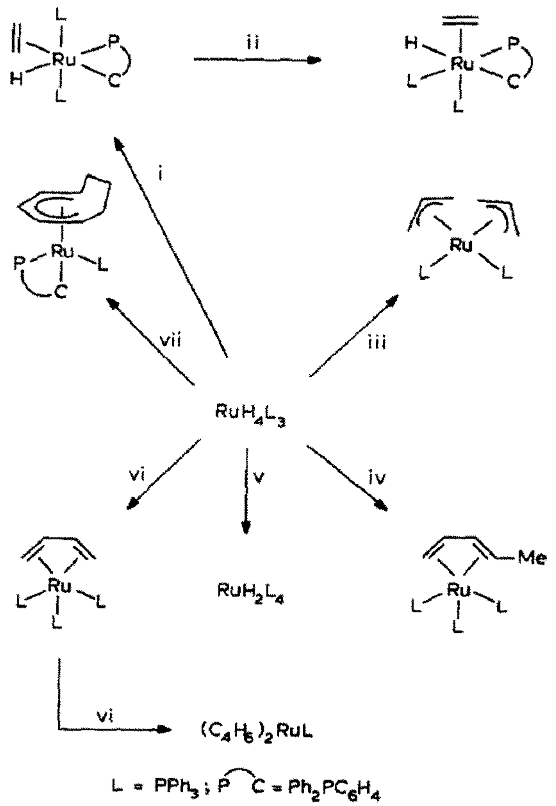
(78)

The coordinatively-unsaturated fragment $ReH_5(PMe_2Ph)_2$, photogenerated from $ReH_5(PMe_2Ph)_3$, also reacts with olefins, catalytically hydrogenating 1-hexene under H_2 and adding a variety of olefins [92,256]. For example, cycloheptatriene reacts with $ReH_5(PMe_2Ph)_3$ under photolytic conditions to form $(\eta^5\text{-}C_7H_9)ReH_2(PMe_2Ph)_2$ [256].

The reactions of iron tetrahydrides with olefins have been little studied.

TABLE 9

Reactions of $RuH_4(PPh_3)_3$ with olefins [258]



(i) Ethylene; (ii) heat; (iii) propene; (iv) 1-pentene; (v) 2-pentene; (vi) 1,3-butadiene; (vii) 1,5-cyclooctadiene

Cyclohexene and $FeH_4(PEtPh_2)_3$ form what is reported to be an alkyl hydride complex $FeH(C_6H_{11})(PEtPh_2)_3(THF)$, but this formulation is based only on IR evidence [257]. Hex-1-ene is catalytically isomerized and hydrogenated by $FeH_4(P(OMe)_3)_3$, while the reaction with benzene gives $(\eta^6\text{-}C_6H_6)Fe(P(OMe)_3)_2$ [95].

The ruthenium tetrahydride $RuH_4(PPh_3)_3$ reacts with a number of olefins to give a variety of complexes (Table 9) [258]. The product of the reaction with ethylene was first believed to be $(C_2H_4)Ru(PPh_3)_3$ [259], a re-examination showed it to be the cyclometalated complex.

The tetrahydride functions as a catalyst for the hydrogenation [103], isomerization [260–262], and hydroformylation [263] of olefins. Isomerization is preferred to hydrogenation. N_2 acts as a poison by competing for the active site [261]. The anionic polyhydride $[RuH_5(PPh_3)_2]^-$ also reacts with olefins and is active for the catalytic hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene [100].

Osmium tetrahydrides are far more reluctant to react with olefins. $OsH_4(PEtPh_2)_3$ hydrogenates and isomerizes 1-octene, but only in refluxing toluene, and require 65 h at 100°C to react with 1,5-cyclooctadiene [112].

The $IrH_5(PR_3)_2$ complexes have been found to be catalysts for the hydrogenation, isomerization, hydroformylation, and disproportionation of olefins [264–269]. When reacted with ethylene, these pentahydrides are converted to the cyclometalated complexes $(C_2H_4)_2\overline{Ir(R_2PX})(PR_3)$ [122,123], while propene and *cis*-2-butene yield $(\eta^3\text{-}C_3H_5)Ir(PR_3)_2$ [123,270] and $(\eta^4\text{-}C_4H_6)IrH(PR_3)_2$ [123].

Higher olefins do not give identifiable olefins complexes. Rather, disproportionation to alkane and diene occurs. Thus the reaction of $IrH_5(PR_3)_2$ with 1- or 2-hexene gives hexane and predominantly 2,4-hexadiene. The reactivity of the pentahydrides decreases in the order $PPr^i_3 > PPh_3 > PMe_3 \gg PCy_3$ [123].

A variety of olefins are catalytically hydrogenated by $IrH_5(PPh_3)_2$ in the presence of CF_3CO_2H [271,272]. This probably involves an $IrH_2(CF_3CO_2)(PPh_3)_2$ intermediate.

(x) Miscellaneous reactions

Several additional reactions involving the intermediacy of polyhydrides should also be mentioned. Ethylene glycol has been detected in CO/H_2 atmospheres when $WH_5(PMePh_2)_4^+$ and $Rh_{12}(CO)_{34}^{2-}$ or $Co(CO)_4^-$ are present [273]. The dimerization of propionaldehyde is catalyzed by $RuH_4(PPh_3)_3$ [274]. In the presence of CF_3CO_2H, $IrH_5(PPh_3)_2$ is reported to be active for the hydrogenation of triphenylcarbinol [272], azomethines [275], and ketones [276].

(xi) Isotopic exchange

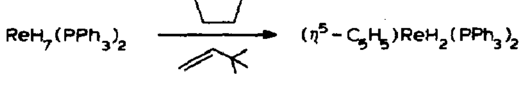
The relatively facile loss of H_2 from polyhydrides provides the opportunity for the replacement of protium by deuterium, whether it be on the metal, in the ligands, or in other substrates. $FeD_4(PR_3)_3$ is slowly formed from $FeH_4(PR_3)_3$ and D_2 under mild conditions [94]. Similar H–D exchange in $ReH_7(PPh_3)_2$ [73], $OsH_4(PMe_2Ph)_3$ [108], and $IrH_5(PEt_2Ph)_2$ [119] can take place in EtOD when catalyzed by acids, while ReH_9^{2-} is converted to ReD_9^{2-} in 15% KOD/D_2O [70].

Activation of arene C–H bonds and subsequent H–D substitution is possible with polyhydrides. Not only are all the metal hydrides in $IrH_5(PEt_2Ph)_2$ replaced by deuterium, but also the four *ortho* sites in the ligand arene rings by metalation of the PEt_2Ph group [119]. Intermolecular H–D exchange in arenes, particularly C_6H_6, is possible via η^2 precoordination of the aromatic ring before C–H bond cleavage occurs [277]. The incorporation of deuterium into arenes is catalyzed by $ReH_7(PPh_3)_2$ [73], $IrH_5(PR_3)_2$ [119], $TaH_5(dmpe)_2$ [27,30], and, under photolytic conditions, $OsH_4(PMe_2Ph)_3$ [249], $ReH_5(PMe_2Ph)_3$ [89], and $MH_4(PR_3)_4$ (M = Mo, W) [278].

(xii) Reaction with alkanes

While the cleavage of C–H bonds in arenes is well known, the activation of alkane C–H and C–C bonds by homogeneous metal complexes has proved to be far more difficult [279,280]. One approach used in solving this problem has been to generate metal species of high coordinative unsaturation in the presence of alkanes [281]. In favorable cases, this leads to alkane dehydrogenation products by multiple hydrogen abstraction from the substrate. This hydrogen is passed on to an acceptor, such as t-butylethylene, thereby reopening active sites on the metal. The first reports of homogeneous alkane activation employed $[IrH_2(Me_2CO)_2(PPh_3)_2][BF_4]$ (the product of the acidolysis of $IrH_5(PPh_3)_2$ in acetone) as the active metal complex in the dehydrogenation of cyclopentane [282]. A related complex, $[IrH_2(Me_2CO)_2(P(p\text{-}F\text{-}C_6H_5)_3)_2][SbF_6]$, can aromatize cyclohexane [283] and cleave C–C bonds in certain cycloalkanes [284] (Table 10).

Polyhydrides themselves have played an important part in the development of this area. Cyclopentane is dehydrogenated by $ReH_7(PPh_3)_2$ and t-butylethylene to give a cyclopentadienyl complex (eqn. 79) [285]. Photo-

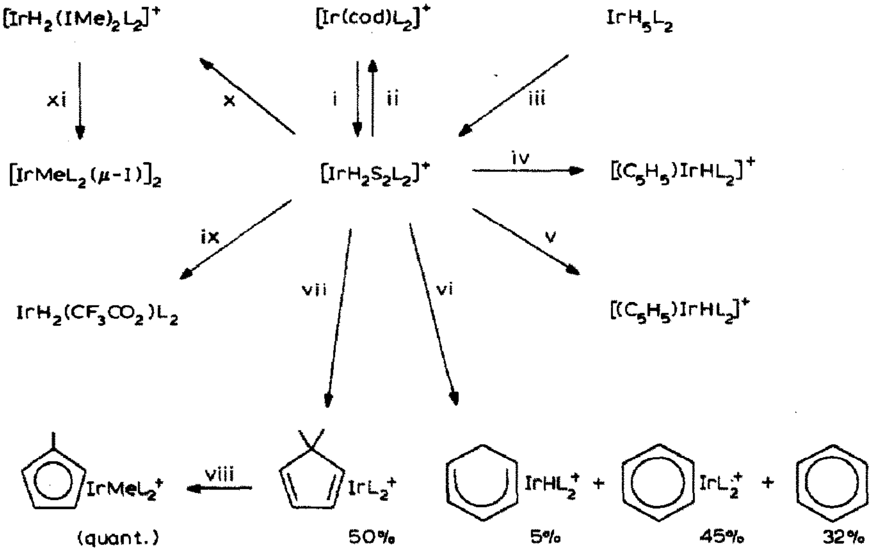


$$ReH_7(PPh_3)_2 \longrightarrow (\eta^5\text{-}C_5H_5)ReH_2(PPh_3)_2 \qquad (79)$$

generated fragments from $ReH_5(PMe_2Ph)_3$ [92] and $OsH_4(PPh_3)_3$ [110] are also active reagents for cyclopentane dehydrogenation.

TABLE 10

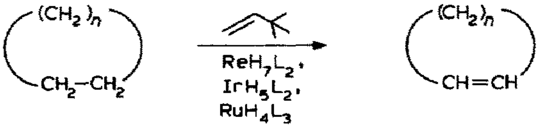
Some reactions of $[IrH_2S_2L_2][SbF_6]$



S = Me_2CO; L = PPh_3 or $P(p\text{-}C_6H_4F)_3$; tbe = $Bu^tCH{=}CH_2$

(i) H_2, S; (ii) 1,5-cyclooctadiene; (iii) H^+, S; (iv) cyclopentene; (v) cyclopentane, tbe; (vi) cyclohexane, tbe; (vii) 1,1-dimethylcyclopentane, tbe; (viii) heat; (ix) $CF_3CO_2^-$; (x) MeI; (xi) tbe.

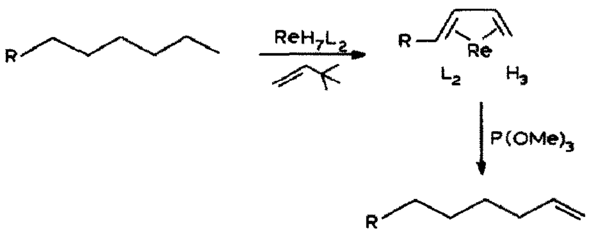
Higher cyclic alkanes are also dehydrogenated by ReH_7L_2, IrH_5L_2, and RuH_4L_3 complexes, most effectively when $L = P(p\text{-}F\text{-}C_6H_4)_3$ [80,105,286]. In these cases, the dehydrogenated hydrocarbons are not bound to the metal in the product, but are released as free cycloalkanes, in amounts ranging from stoichiometric to up to 70 catalytic cycles (eqn. 80).



(80)

n = 4,5,6

Linear C_6 to C_8 alkanes are dehydrogenated by $ReH_7(PPh_3)_2$ to form mixtures of diene complexes [287]. The metal fragment can be displaced by $P(OMe)_3$ to yield the free 1-alkene (eqn. 81).



(81)

G. SUMMARY

Several general conclusions can be drawn from the information now available on polyhydride complexes. Perhaps their most striking property is simply their existence in such great numbers. Their relative stability to loss of H_2 seems to be thermodynamic, not simply kinetic, because many synthetic routes involve H_2 addition, and H_2 addition/elimination rarely shows large activation energies. This implies that M–H bond energies do not fall much below their usual values (ca. 60 kcal/mol^{-1}) [288] even for polyhydrides, since only this can prevent H_2 (bond energy: 103 kcal mol^{-1}) loss from being thermodynamically favorable. The first-row elements do not form so extensive a series of polyhydrides, perhaps because the M–H bond strengths are lower. Similarly the general stability trends—Group VIII (but not Pd, Pt) $\simeq$ Group VII > Group VI > Group V and 3rd row > 2nd row—can probably also be understood in the same way.

The polyalkyls do not form an extensive analogous series, perhaps because M–C bonds are generally weaker than M–H bonds [288], and alkyl groups are also more bulky than hydride ligands. However, the recent preparation of $(C_5Me_5)IrMe_4$ [289], analogous to $(C_5Me_5)IrH_4$, may point the way toward the synthesis of further polyalkyls

It was once thought that the highly electronegative elements F and O are best able to stabilize the highest oxidation states of metals. We now know that other small anionic ligands such as Me and H are also effective. As the least electronegative of all the formally anionic ligands (H, Me, O, and the halides) capable of giving polyligated species, the polyhydrides are expected to be the most electron rich, and to have the most extensive chemistry with π-bonding co-ligands. This aspect also has been illustrated in this review.

Very few cluster polyhydrides have been prepared. The few known examples suggest that hydride ligands bond just as strongly to interstitial, bridging, and terminal sites in clusters as in classical polyhydrides. For example, $[(IrH_2LL')_3(\mu_3\text{-}H)]^{2+}$ [290] does not lose H_2 readily, even on heating. This in turn suggests that even "pure" or homoleptic cluster hydrides of the type $[M_xH_y]^{n-}$ should be capable of existence. The corresponding polyalkyls may also be stable; $[Re_3Me_9]_n$ is known [291].

Both cationic and anionic polyhydrides are relatively rare, but it is likely that this represents prejudices of synthetic chemists rather than any unusual instability of these species, which may well have interesting properties.

The upper limit for n in polyhydride complexes MH_nL_m has up to now been the maximum valency of the metal (e.g. Re, 7; W, 6; Ta, 5), but the recent isolation by Kubas and co-workers [292] of a complex of molecular hydrogen opens the way for the synthesis of polyhydrides of the type $M(H_2)_{n/2}L_m$ where $n >$ maximum valence.

One feature of the reaction chemistry of polyhydrides that is very promising but is only just beginning to be exploited is thermal, photochemical, or protolytic H_2 loss to give species containing multiple vacant coordination sites. Their importance to the newly-emerging field of alkane activation has led to the extensive application of polyhydrides. Both catalytic alkane dehydrogenation [80,105,283,286] and alkane C–C bond activation [284] also seem to require multiple sites.

The center of interest in transition metal polyhydrides is beginning to move from the more traditional areas of synthesis and structural studies to the newer areas of reaction chemistry and catalysis. We hope that this review reflects the recent developments and will stimulate further research in this area.

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