New Multihydride Complexes of Rhenium containing Diphosphine Ligands: Low-temperature Protonation of $[ReH_7(Ph_2PCH{=}CHPPh_2\text{-}PP')]$

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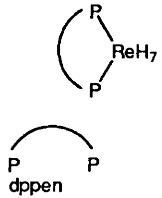
Treatment of oxochloro complexes of the type $[ReOCl_3(L\text{–}L)]$ (L–L = diphosphine) with sodium tetrahydroborate gave complexes of the type $[ReH_7(L\text{–}L)]$. Treatment of [ReH$_7$(dppen-*PP'*)] **1a** [dppen = *cis*-1,2-bis(diphenylphosphino)ethylene = *cis*-$Ph_2PCH{=}CHPPh_2$] with triphenylphosphine gave a mixture of the pentahydride [ReH$_5$(dppen-*PP'*)(PPh$_3$)] and the trihydride [ReH$_3$(dppen-*PP'*)(PPh$_3$)$_2$]. However, treatment of **1a** with dppm [bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$] in refluxing toluene, followed by slow crystallisation, gave [ReH$_5$(dppen-*PP'*)(dppm-*P*)] which was isolated and characterised by variable-temperature NMR spectroscopy. Prolonged heating of **1a** with dppm gave the trihydride [ReH$_3$(dppen-*PP'*)(dppm-*PP'*)], the fluxionality of which was studied by NMR spectroscopy between +90 and −70 °C. Protonation of **1a** with $HBF_4{\cdot}Et_2O$, at −80 °C, gave a complex formulated as [ReH$_6$(η^2-H$_2$)(dppen-*PP'*)]$^+$ which, on warming to ambient temperature, was cleanly converted to a dirhenium multihydride species tentatively formulated as [(dppen-*PP'*)H$_3$Re(μ-H)$_2$-ReH$_3$(dppen-*PP'*)] on the basis of IR and NMR evidence.

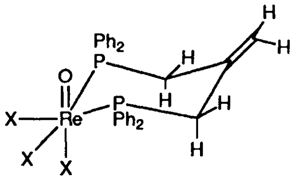
Transition-metal multihydride complexes, particularly those containing tertiary phosphine ligands, have been studied with renewed interest since the discovery of the first isolable dihydrogen complex by Kubas *et al.*[1] Rhenium has a large and diverse hydride chemistry[2–5] and interest in rhenium multihydrides stems from both their ability to activate hydrocarbons[6–8] and the relationship between multihydrides and dihydrogen complexes.[9–11] In this paper we will discuss multihydride complexes containing tertiary diphosphine ligands including the protonation of a heptahydride to give a mixed dihydrogen–hydride complex and its subsequent conversion to a dicationic dirhenium complex.

Results and Discussion

In the course of our work we have prepared some new heptahydrides of rhenium involving the chelating diphosphine ligands *cis*-1,2-bis(diphenylphosphino)ethylene (*cis*-dppen, $Ph_2PCH{=}CHPPh_2$), bis(diphenylphosphino)methane (dppm, $Ph_2PCH_2PPh_2$), 1,1′-bis(diphenylphosphino)ethane [1,1′-dppe, $Ph_2PCH(Me)PPh_2$] or $Ph_2PCH_2C({=}CH_2)CH_2PPh_2$.[12] Treatment of the oxochloro complex [ReOCl$_3$(dppen-*PP'*)][13] with sodium tetrahydroborate in absolute ethanol gave a 63% yield of the heptahydride [ReH$_7$(dppen-*PP'*)] **1a**; it was necessary to purify the product by passing a benzene solution of the complex through a column of florisil. This heptahydride **1a** was obtained as an off-white solid which was pure enough for the reactions described later. Further purification (for microanalysis) was achieved either by passage of its benzene solution through a second column of florisil or by recrystallisation from benzene–ethanol.



1a dppen
1b dppm
1c 1,1′-dppe
1d $Ph_2PCH_2C({=}CH_2)CH_2PPh_2$



	X
2a	Cl
2b	Br

The corresponding heptahydrides containing the chelating diphosphines dppm **1b**, 1,1′-dppe **1c** or $Ph_2PCH_2C({=}CH_2)CH_2PPh_2$ **1d** were similarly prepared from the corresponding oxochloro complexes, albeit in lower yields. These products were obtained as off-white or tan solids (see Experimental section). The preparations of the new oxochloro complex **2a**, and the corresponding oxobromo complex **2b**, used as the precursor to **1d**, are described in the Experimental section (data in Tables 1 and 2). [ReH$_7$(1,1′-dppe-*PP'*)] **1c** was prepared either by tetrahydroborate reduction of [ReOCl$_3$(1,1′-dppe-*PP'*)] or by the tetrahydroborate reduction of the vinylidenediphosphine complex [ReOCl$_3$(vdpp-*PP'*)][13] [vdpp = vinylidenebis(diphenylphosphine)] in which the activated vinylidene C=C double bond was also reduced by the tetrahydroborate. Complexes containing co-ordinated vdpp ligands have been shown previously to be susceptible to nucleophilic attack or Michael type additions at $C{=}CH_2$.[14,15] Recently, [ReH$_7$(dppen-*PP'*)] has been prepared by reducing [ReOCl$_3$(dppen-*PP'*)] with lithium aluminium hydride in diethyl ether,[16] but the yield was lower than by our methods. Satisfactory microanalytical data (C and H) were obtained for all four heptahydride complexes and all showed similar IR spectra in the region 2000–1850 cm^{-1}, due to Re–H stretching vibrations (Table 1), typical of rhenium heptahydrides of the type [ReH$_7$(PR$_3$)$_2$].[6,17]

The complex [ReH$_7$(dppen-*PP'*)] **1a** was further characterised by a ^{31}P-{^{1}H(selective)} NMR experiment, *i.e.* by observing the ^{31}P resonance (at δ 52.3) and decoupling all the organic protons only. The expected eight ($n + 1$) lines were observed in the intensity ratios 1.0:7.1:21.4:35.0:34.6:21.4:7.1:0.9, which compared very well with the theoretical ratios of 1:7:21:35:35:21:7:1, thus confirming that the ^{31}P nuclei were coupled to seven equivalent hydrides. Similarly, the heptahydrides **1b**–**1d** each showed only one ^{31}P resonance (a singlet) in the fully proton decoupled spectra (data in Table 3).

The ^{1}H NMR spectra showed that for **1a**–**1d** these heptahydrides are fluxional. All showed one 1:2:1 triplet hydride resonances (around δ −5) due to coupling to the two equivalent phosphorus nuclei. For these heptahydrides containing chelating diphosphines, values of ^2J(PH) of 12–15.4 Hz were observed (Table 3), slightly smaller than those observed for heptahydrides containing monodentate phosphines.[6,18] Even at −90 °C (in CD_2Cl_2) the hydride resonance pattern showed no evidence for any 'freezing out' of a static structure for $[ReH_7(dppen\text{-}PP')]$ **1a**, the hydride resonances being only slightly broader than in the room-temperature spectrum. Similarly, Shaw and co-workers[19] prepared a complex of stoichiometry $[ReH_7\{Bu^t_2P(CH_2)_5PBu^t_2\}]$ in the hope that the bulky diphosphine ligand would prevent the intramolecular exchange (fluxionality), but at −90 °C the hydride triplet was again only slightly broader than in the room-temperature spectrum. A similar rationale was used by Luo and Crabtree[16] who have recently prepared a series of rhenium heptahydrides containing bulky chelate diphosphines, including *cis*-dppen, with a view to 'freezing out' the fluxionality. It was found that for $[ReH_7(dppf\text{-}PP')]$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene], $[ReH_7(dppb\text{-}PP')]$ [dppb = 1,4-bis(diphenylphosphino)butane] and $[ReH_7\{(+)diop\text{-}PP'\}]$ [(+)-diop = (4*S*,5*S*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane] decoalescence of the hydride resonances at −120 °C was observed. These low-temperature spectra suggested that these heptahydrides adopted classical tricapped trigonal-prismatic geometries. For $[ReH_7(dppen\text{-}PP')]$, however, no low-temperature limiting spectrum was observed, consistent with our work.

Table 1 Microanalytical[a] and infrared[b] data

Complex	Analysis (%) C	H	ν(Re–H)/cm^{-1}
1a	53.55 (52.95)	4.95 (4.95)	1967, 1953, 1891
1b·$0.3C_6H_6$	53.85 (53.55)	5.05 (5.15)	1967, 1945, 1882
1c	52.65 (52.75)	5.2 (5.25)	1955, 1891
1d·$0.2C_6H_6$	55.4 (55.35)	5.45 (5.45)	1959, 1910
2a[c]	45.65 (45.9)	3.6 (3.6)	
2b[d]	37.75 (38.8)	3.0 (3.0)	
3b	63.0 (63.0)	5.05 (5.1)	1930, 1892
4a·$0.8CH_2Cl_2$	64.05 (64.0)	4.85 (4.85)	
4c	63.8 (63.15)	4.95 (4.9)	
4d	62.85 (63.6)	4.75 (4.8)	
6	45.95 (46.35)	3.7 (3.9)	1890, 1815, 1625

[a] Calculated values in parentheses. [b] Recorded as KBr discs. [c] Cl 14.5 (14.5)%, ν(Re=O) 992 cm^{-1}. [d] Br 26.6 (27.65)%, ν(Re=O) 985 cm^{-1}.

Table 2 ^{31}P-{^{1}H} and ^{1}H NMR data[a] for the rhenium(v) diphosphine complexes **2a** and **2b**

Complex	δ(P)	δ(H)	^2J(HH)	J(PH)
2a	−23.9	3.98[b] (PCH)		16[c]
		4.98 (=CH_2)		6[d]
2b	−33.7	4.18 (PCH)	14	12[c]
		4.06 (PCH)		n.r.[e]
		4.98 (=CH_2)		6[d]

[a] ^{31}P-{^{1}H} NMR spectra recorded at 40.3 MHz and ^{1}H at 100 MHz, in dichlorodeuteriomethane, unless otherwise stated; chemical shifts in ppm and coupling constants in Hz. [b] Two coincident resonances. [c] $N = {}^2J(PH) + {}^4J(PH)$. [d] $N = {}^4J(PH) + {}^4J(PH)$. [e] Not resolved.

Rhenium heptahydrides of the type $[ReH_7(PR_3)_2]$ are thermally unstable to loss of dihydrogen and when heated with σ donors form complexes of the type $[ReH_5(PR_3)_2L]$ (L = σ donors):[6,20] examples of such behaviour are given in equations (1) and (2) (thf = tetrahydrofuran, pyz = 1,4-pyrazine).

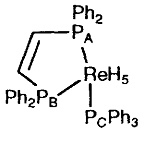
$$[ReH_7(PPh_3)_2] + PEt_2Ph \xrightarrow[10\ min]{thf/reflux} [ReH_5(PEt_2Ph)(PPh_3)_2] \quad (1)$$

$$[ReH_7(PPh_3)_2] + pyz \xrightarrow[10\ min]{thf/reflux} [ReH_5(PPh_3)_2pyz] \quad (2)$$

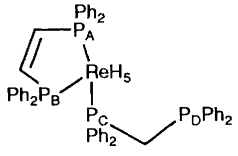
Similar reactions with potentially bidentate diphosphines, *e.g.* dppm or vdpp, gave monodentate diphosphine complexes of the type $[ReH_5(PR_3)_2(L\text{–}L\text{-}P)]$ (L–L = diphosphine).[19] These reactions worked particularly well for $[ReH_7\{P(C_6H_{11})_3\}_2]$ since the competing reaction to produce dirhenium complexes of the type $[Re_2H_4(\mu\text{-}H)_4(PR_3)_4]$ was avoided. The large cone angle of $P(C_6H_{11})_3$ (179°) was thought to prevent the close approach of the two rhenium centres.[21] In the preparation of these monodentate diphosphine complexes there was no evidence for the formation of chelates, except in the related reaction of $[OsH_6\{P(C_6H_{11})_3\}_2]$ with dppm.[19]

In contrast, complexes of the type $[ReH_7L_2]$ where L_2 is a chelating diphosphine (*e.g.* dppe), have been shown previously[6,22] to be resistant to hydrogen loss and when $[ReH_7(dppe\text{-}PP')]$ was heated with donor ligands such as PPh_3[6], pyridine[6] or silanes[22] in refluxing thf, no reaction apparently occurred. Other rhenium heptahydride diphosphine complexes have been found to be similarly unreactive, including $[ReH_7(dppen\text{-}PP')]$.[16] However we have found that the heptahydride $[ReH_7(dppen\text{-}PP')]$ **1a** does undergo substitution of dihydrogen by phosphine ligands thermally to give pentahydride complexes of the type $[ReH_5(dppen\text{-}PP')L]$ and also trihydride complexes of the type $[ReH_3(dppen\text{-}PP')L_2]$.

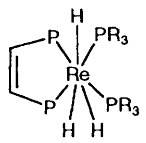
Prolonged treatment of $[ReH_7(dppen\text{-}PP')]$ with 1 mole equivalent of triphenylphosphine in refluxing benzene led to the formation of both $[ReH_5(dppen\text{-}PP')(PPh_3)]$ **3a** and $[ReH_3(dppen\text{-}PP')(PPh_3)_2]$ **4a**. The progress of the reaction was monitored by ^{31}P NMR spectroscopy and after *ca.* 8 h, $[ReH_5(dppen\text{-}PP')(PPh_3)]$ was the predominant product although the trihydride **4a** (see below) had started to form and there was still much unreacted heptahydride present. The pentahydride was found to be very difficult to isolate in a pure state without one or other of the other hydrides contaminating it. Thus it did not give satisfactory microanalytical data and the ^{1}H NMR spectrum was not analysed. The complex $[ReH_5(dppen\text{-}PP')(PPh_3)]$ **3a** was identified only from the ^{31}P-{^{1}H}



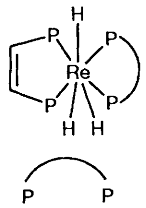
3a



3b



R
4a Ph
4b *p*-C_6H_4Me



4c dppm
4d dppen
4e vdpp

Table 3 ^{31}P-{^{1}H} and ^{1}H NMR data[a] for rhenium heptahydride diphosphine complexes

		Hydrides		Diphosphine		
Complex	δ(P)	δ(H)	^2J(PH)	δ(H)	J(HH)	J(PH)
1a[b]	52.3	−5.63	13.4	7.26		57.6 [^2J(PH) + ^3J(PH)]
1b	−28.9	−4.48	12.7	4.61		9.3 [^2J(PH)]
1c	−7.6	−4.61	12.0	5.11 (CH)	7.8 [^3J(CH$_3$CH)]	< 2 [^2J(PH)
				0.87 (CH$_3$)		15.1 [^3J(PH)]
1d	8.5	−5.32	15.4	4.48 (=CH$_2$)		7.8 [^4J(PH) + ^4J(PH)]
				3.20 (CH$_2$)		13.2 [^2J(PH) + ^4J(PH)]

[a] Recorded at 100 MHz (^{1}H) or 40.3 MHz (^{31}P) at 22 °C in deuteriobenzene unless otherwise stated; chemical shifts in ppm and coupling constants in Hz. [b] ^{1}H recorded at 400 MHz.

Table 4 ^{31}P-{^{1}H}[a] and ^{1}H[b] NMR for rhenium pentahydride diphosphine complexes

Complex	δ(P$_A$)	δ(P$_C$)	δ(P$_D$)	^2J(P$_A$P$_C$)	^2J(P$_C$P$_D$)
3a	56.3	39.1		33	
3b[c]	55.6	26.5	−22.5	34	95
3b[d]	58.1 (P$_A$)[e]	28.0	−22.0	81 (P$_A$P$_C$)	105
	54.8 (P$_B$)			9 (P$_B$P$_C$)	

[a] Recorded at 40.3 MHz at 22 °C in deuteriobenzene; chemical shifts in ppm and coupling constants in Hz. [b] Recorded at 400 MHz at 22 °C in deuteriotoluene. [c] δ(H) −6.07 [Re–H, ^2J(P$_A$H) = 14.9, ^2J(P$_C$H) = 19.7], 3.20 [dppm, ^2J(P$_C$H) = 9.0, ^2J(P$_D$H) = 3.5] and 7.26 (Ph$_2$PCH=CHPPh$_2$; N = 53.7 Hz). [d] Recorded at −90 °C in deuteriotoluene. [e] ^2J(P$_A$P$_B$) = 22 Hz.

NMR spectrum (Table 4), which consisted of a doublet at δ 56.3 assigned to the dppen phosphorus atoms and a triplet at δ 39.1, assigned to the triphenylphosphine [^2J(PP) = 33 Hz]. After 15 h, unreacted heptahydride was still present, as well as both the tri- and the penta-hydrides. No attempt was made to separate the products at this stage, but when a similar reaction was carried out in refluxing toluene for 1.5 h (see below), the trihydride formed and was isolated. Encouraged by this we heated [ReH$_7$(dppen-*PP*′)] with dppm in the hope of preparing the monodentate diphosphine complex [ReH$_5$(dppen-*PP*′)(dppm-*P*)]. In refluxing benzene, again following the reaction by ^{31}P NMR spectroscopy, the required complex **3b** was formed but the trihydride [ReH$_3$(dppen-*PP*′)(dppm-*PP*′)] **4c** was also formed. However, when the reaction was repeated in refluxing toluene for 17 min., followed by very slow fractional crystallisation at −20 °C, we obtained a pure sample of the required product **3b** as a yellow microcrystalline solid, in 21% yield. The difficulty encountered in preparing this complex was possibly due to the fact that chelate formation, to give the trihydride **4c**, was sterically favourable. In comparison, with the complexes [ReH$_5${P(C$_6$H$_{11}$)$_3$}$_2$(L–L-*P*)][19] co-ordination of the unco-ordinated phosphorus atom of the diphosphines was hindered by the large cone angle of the tricyclohexylphosphine and so no trihydrides were formed, but with [ReH$_5$(dppen-*PP*′)(dppm-*P*′)] there is no such steric hindrance to chelation. The formulation of the complex as [ReH$_5$(dppen-*PP*′)(dppm-*P*)] **3b** was confirmed by microanalytical (Table 1) and spectroscopic data (Table 4).

The ^{31}P-{^{1}H} NMR spectrum at 22 °C consisted of three resonances of relative intensity 2 : 1 : 1, whereas in the spectrum recorded at −90 °C, four resonances were observed, *i.e.* the dppen phosphorus nuclei (P$_A$ and P$_B$) became inequivalent. From the difference in the coupling constants of P$_A$ and P$_B$ to P$_C$ (81 and 9 Hz respectively), P$_A$ was assigned as being transoid and P$_B$ cisoid to P$_C$. Assuming that the net fluxional process (at the fast exchange limit) simply results in the interchange of the positions of P$_A$ and P$_B$ with respect to P$_C$, then these individual couplings resolved at low temperature [^2J(P$_A$P$_C$) and ^2J(P$_B$P$_C$)] must be opposite in sign in order to give the average coupling [^2J(P$_A$P$_C$) = 34 Hz] observed in the high temperature (+22 °C) limiting spectrum.

The ^{1}H NMR spectrum of **3b** showed a single hydride resonance at 22 °C (δ −6.07), which, at −90 °C, became two distinct resonances at δ *ca.* −4.5 and *ca.* −6.4, showing that some 'freezing out' of the static structure was occuring, *i.e.* there were two distinct hydride sites. However the peaks were both very broad ($w_{\frac{1}{2}}$ > 100 Hz) and it was difficult to determine accurately the ratio of intensities of the two signals, although a 1 : 4 ratio seemed most likely. No such hydride inequivalence was observed for the complexes of the type [ReH$_5$(PR$_3$)$_2$(L–L)] prepared previously by Shaw and co-workers[19] or those prepared by Walton and co-workers.[23] Both groups reported only slight broadening of the hydride resonances at low temperatures. In **3b** the higher barrier to intramolecular exchange must be in part due to the rigid *cis* stereochemistry of the chelating ligand. The methylene protons of the dppm ligand also became inequivalent at −90 °C and two broad peaks were observed at δ *ca.* 2.8 and *ca.* 3.5.

Resonances due to non-equivalent hydrides have been observed previously[24–26] in low-temperature ^{1}H NMR studies of pentahydride complexes, *e.g.* [ReH$_5$(AsPh$_2$Et)$_3$], but required very low temperatures (below −130 °C) to freeze out fluxionality and, coupled with X-ray or neutron diffraction studies,[25–27] the geometries of the pentahydrides studied were found to be distorted dodecahedra.

Using a similar procedure to that used to prepare [ReH$_5$(dppen-*PP*′)(dppm-*P*)] we attempted to prepare the corresponding vdpp {Ph$_2$PC(=CH$_2$)PPh$_2$} complex *i.e.* [ReH$_5$(dppen-*PP*′)(vdpp-*P*)]. However, ^{31}P NMR evidence suggested that when [ReH$_7$(dppen-*PP*′)] was treated with vdpp, this complex was only a very minor component of a mixture of several other products and no product of this formulation could be isolated. The complex **3b** has potential for the co-ordination of a second metal centre to the 'free end' of the monodentate dppm, to give heterobimetallic complexes containing a multihydride moiety. Complexes of this type will be discussed in a future publication.

Trihydride complexes of rhenium have been prepared either by treating a pentahydride complex with a diphosphine[28] or by reducing complexes of the type [ReOX$_3$L$_2$] or [ReX$_3$L$_3$] (X = halide) with NaBH$_4$ or LiAlH$_4$ in the presence of an excess of the phosphine L.[29,30] The most widely studied of these complexes have been [ReH$_3$(dppe-*PP*′)(PPh$_3$)$_2$] and [ReH$_3$(dppe-*PP*′)$_2$]. Both were shown to be fluxional in solution when studied by ^{1}H NMR spectroscopy;[31] [ReH$_3$(dppe-*PP*′)$_2$] gave a high-field quintet in the ^{1}H NMR spectrum whereas [ReH$_3$(dppe-*PP*′)(PPh$_3$)$_2$] showed three equivalent hydrides coupled to two non-equivalent pairs of phosphorus nuclei. The temperature dependance of the spectra was studied between +30 and −90 °C and it was shown that, for [ReH$_3$(dppe-*PP*′)$_2$], at *ca.* −50 °C two of the three hydrides were equivalent and the other was unique, the decoupled spectrum showing an AB$_2$ pattern [J(H$_A$H$_B$) = 9.5 Hz]. For [ReH$_3$(dppe-*PP*′)(PPh$_3$)$_2$] the barrier to hydride interchange was significantly lower and no such hydride inequivalence was observed. X-Ray crystal structure determinations[31,32] of these trihydrides (hydrides not located) suggested that the geometry of $[ReH_3(dppe\text{-}PP')_2]$ was a distorted pentagonal bipyramid, whereas that of $[ReH_3(dppe\text{-}PP')(PPh_3)_2]$ was a distorted monocapped *cis*-octahedron. A similar X-ray crystallographic study of $[ReH_3(PMePh_2)_4]$[33] located the hydrides and showed a distorted pentagonal-bipyramidal geometry. The ^1H NMR spectrum at −105 °C showed two resonances in the hydride region assigned to two different types of hydride ligand.

As previously mentioned, when discussing the formation of $[ReH_5(dppen\text{-}PP')(PPh_3)]$ **3a**, when $[ReH_7(dppen\text{-}PP')]$ was treated with triphenylphosphine in refluxing toluene for 1.5 h $[ReH_3(dppen\text{-}PP')(PPh_3)_2]$ **4a** was formed and was isolated as a yellow solid in 30% yield. $[ReH_3(dppen\text{-}PP')(dppm\text{-}PP')]$ **4c** and $[ReH_3(dppen\text{-}PP')_2]$ **4d** were prepared as yellow solids by treating $[ReH_7(dppen\text{-}PP')]$ with dppm or dppen respectively. Evidence from the preparation of the pentahydrides $[ReH_5(dppen\text{-}PP')(PPh_3)]$ **3a** and $[ReH_5(dppen\text{-}PP')(dppm\text{-}P)]$ **3b** suggested that these reactions go *via* the pentahydrides which then reacted further to give the trihydrides. It has been noted previously[34] that the pentahydrido complexes $[ReH_5(PR_3)_3]$ and $[ReH_5(PR_3)_2L]$ (L = phosphine, arsine or amine) were quite kinetically stable to further reaction with σ donors, *e.g.* phosphines, and vigorous reaction conditions were necessary to induce further reaction. In the case of $[ReH_7(dppen\text{-}PP')]$ vigorous conditions were required to form both the penta- and tri-hydrides.

The three new trihydride complexes were characterised by microanalysis (Table 1) and from NMR spectroscopic data (Table 5). The $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[ReH_3(dppen\text{-}PP')(PPh_3)_2]$ **4a** consisted of two triplets (due to the fluxionality of the complex), one at δ 62.6 assigned to the dppen phosphorus nuclei and the other at δ 34.3 assigned to the triphenylphosphines. The temperature dependence of the $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[ReH_3(dppen\text{-}PP')(dppm\text{-}PP')]$ **4c** was studied between +90 and −70 °C. At −70 °C, the spectrum showed an AA′XX′ spin system with the A part absorbing at δ 60.0, assigned to the dppen phosphorus nuclei, and the X part absorbing at δ −19.9 assigned to the dppm phosphorus nuclei. The *N* doublet coupling $^2J(P_AP_C) + {}^2J(P_AP_D)$ was 95 Hz. The spectrum was not well enough resolved to obtain any further coupling information. As the temperature was increased the spectrum broadened, but by +50 °C the broad resonances collapsed into two well-resolved triplets. These were assigned to the dppen phosphorus nuclei (δ +59.0) and the dppm phosphorus nuclei (δ −19.4). At this high-temperature limit, rapid exchange of the phosphorus nuclei was occurring giving rise to the simplification of the spectrum. Increasing the temperature further (to +90 °C) caused no change in the appearance of the spectrum. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[ReH_3(dppen\text{-}PP')_2]$ **4d** showed a singlet at δ 60.6 again due to rapid exchange making all the phosphorus nuclei equivalent.

In the ^1H NMR spectrum of $[ReH_3(dppen\text{-}PP')(PPh_3)_2]$ **4a** the expected triplet of triplets was observed for the hydrides, at δ −6.18. The separate couplings to the dppen phosphorus nuclei and the PPh_3 phosphorus nuclei were assigned using selective phosphorus decoupling (see Table 5). At lower temperatures (down to −90 °C) the triplet of triplets broadened into an unresolvable quartet (due to the slowing down of the fluxional processes), but no evidence for the 'freezing out' of any static structure was observed.

In the ^1H NMR spectrum of $[ReH_3(dppen\text{-}PP')(dppm\text{-}PP')]$ **4c** the hydride resonances were broader at ambient temperature than those for **4a**. A broad triplet of triplets was observed at δ −6.00 showing that all the hydrides were exchanging, but not at the fast-exchange limit. The temperature dependence of the resonances due to the methylene protons of the dppm ligand and the hydrides were studied between +85 and −60 °C. At the fast exchange limit (+85 °C), a single resonance was observed for the methylene protons, at δ 5.43, indicating that rapid exchange was occurring. As the temperature was lowered this resonance broadened and decoalesced into two distinct (but still broad) resonances (+28 °C) at δ 5.96 and 5.05, and at −40 °C became a sharp AB pattern (in the $^1H\text{-}\{^{31}P\}$ NMR spectrum) with $^2J(HH)$ = 14.8 Hz. The couplings to the dppm phosphorus nuclei were resolved in the ^1H NMR spectrum, in which two ABXY patterns were observed [$^2J(PH)$ = 8.3 and 10.1 Hz, respectively]. The resonance due to the hydrides was broad at room temperature. The couplings to phosphorus were resolved in the high-temperature limiting spectrum (+85 °C), the hydride resonance being a triplet of triplets due to coupling to the two equivalent dppm phosphorus nuclei and to the two equivalent dppen phosphorus nuclei. Selective phosphorus decoupling was again used to give the couplings to the dppen phosphorus nuclei [$^2J(PH)$ = 20.0 Hz] and to the dppm phosphorus nuclei [$^2J(PH)$ = 15.4 Hz]. As the temperature was lowered the hydride resonance broadened and decoalesced into two peaks (at *ca.* −40 °C), one of relative intensity two at δ −6.14 (H_a) and the other of relative intensity one at δ −5.75 (H_b). Hydride–hydride coupling between these two distinct types of hydride was not resolved in the $^1H\text{-}\{^{31}P\}$ NMR spectrum even at − 60 °C and the coupling to the two types of phosphorus nuclei was also difficult to resolve. The temperature dependence of the $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectra observed can be accounted for by a static structure based on a capped trigonal-prismatic geometry, with the four phosphorus nuclei in the same plane and two hydrides above (H_a) and one below (H_b)

Table 5 $^{31}P\text{-}\{^1H\}$[a] and ^1H[b] NMR data for rhenium trihydride complexes

				Hydrides		CH$_2$		
Complex	δ(P)[c]	δ(P)[d]	*J*(PP)	δ(H)	^2J(PH)	δ(H)	^2J(HH)	^2J(PH)
4a	62.6	34.3	61[e]	−6.18	24 (to PPh$_3$) 17 (to dppen)			
4b	62.2	32.0	61[e]					
4c[f]	59.0	−19.4	48[e]	−6.00	15.4 (to dppm) 20.0 (to dppen)	5.43		9.0
4c[g,h]	60.0	−19.9	95[i]	−6.14 (H$_a$) −5.75 (H$_b$)	n.r.[j] n.r.	5.96 5.05	14.8	8.3 10.1
4d	60.6			−7.32	17			
4e	59.3	14.1	107[i]					

[a] Recorded at 40.3 MHz at 22 °C in deuteriobenzene unless otherwise stated. [b] Recorded at 100 MHz at 22 °C in deuteriotoluene unless otherwise stated. [c] dppen. [d] Other phosphine. [e] ^2J(PP). [f] $^{31}P\text{-}\{^1H\}$ recorded at +50 °C; ^1H recorded at 400 MHz at +85 °C in deuteriotoluene. [g] $^{31}P\text{-}\{^1H\}$ recorded at −70 °C; ^1H recorded at 400 MHz at −40 °C in deuteriotoluene. [h] Also dppen CH at δ 7.10 (*N* = 58 Hz). [i] $^2J(P_AP_C) + {}^2J(P_AP_D)$. [j] n.r. = Not resolved.

this plane. The observed low-temperature $^{31}P\text{-}\{^1H\}$ NMR spectrum was not consistent with a geometry based on a pentagonal bipyramid and the low-temperature ^1H NMR spectrum rules out the monocapped octahedral structure unless the two hydrides H_a were still exchanging at −60 °C. Thus we suggest that the complex **4c** has a static structure based on a capped trigonal prismatic geometry, see Fig. 1(*a*)–(*c*).

The ^1H NMR spectrum of $[ReH_3(dppen\text{-}PP')_2]$ **4d** showed a quintet at δ −7.32 for the hydrides, coupled to the four equivalent phosphorus nuclei. However, this complex was not amenable to being studied at low temperatures due to poor solubility. Tri-*p*-tolylphosphine and vinylidenebis(diphenylphosphine) also gave trihydride complexes of the type $[ReH_3(dppen\text{-}PP')L_2]$ when heated with $[ReH_7(dppen\text{-}PP')]$. However the complexes formed, $[ReH_3(dppen\text{-}PP')\{P(C_6H_4Me\text{-}4)_3\}_2]$ **4b** and $[ReH_3(dppen\text{-}PP')(vdpp\text{-}PP')]$ **4e** were found to be difficult to isolate pure and were characterised only by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy (Table 5). The $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[ReH_3(dppen\text{-}PP')\{P(C_6H_4Me\text{-}4)_3\}_2]$ **4b** was very similar to that of **4a**, *i.e.* it consisted of two triplets at δ 62.2 (dppen) and 32.0 $[P(C_6H_4Me\text{-}4)_3]$ with phosphorus–phosphorus coupling of 61 Hz. The complex $[ReH_3(dppen\text{-}PP')(vdpp\text{-}PP')]$ **4e** showed an AA′XX′ pattern in its $^{31}P\text{-}\{^1H\}$ NMR spectrum (similar to **4c** with the A part at δ 59.3 (dppen) and the X part at δ 14.1 (vdpp) and an *N* doublet splitting of 107 Hz.

Since the preparation of the first examples of complexes containing an η^2-dihydrogen ligand by Kubas *et al.*,[1] many complexes of this type have been prepared and characterised, by a number of methods.[9–11] It has been suggested that one of the factors which determines whether complexes containing an η^2-dihydrogen ligand are stable is the degree of back-bonding from the metal d orbitals to the σ* orbitals of the $\eta^2\text{-}H_2$ and thus cationic complexes may favour the $\eta^2\text{-}H_2$ rather than the corresponding dihydride form.[10,11] A number of complexes formulated as containing an η^2-dihydrogen ligand have been prepared by protonation of the corresponding hydride complex, which contained only classical hydride ligands.[11,35]

It has been shown that, at or below −40 °C, on addition of $HBF_4{\cdot}Et_2O$, rhenium heptahydrides of the type $[ReH_7(PR_3)_2]$ $[PR_3 = P(C_6H_{11})_3$, PPh_3 or $PBu^t{}_2Me]$ reversibly form species of composition $[ReH_{8-2x}(\eta^2\text{-}H_2)_x(PR_3)_2]^+$ which must be η^2-dihydrogen complexes.[36] We have now attempted to make an η^2-dihydrogen complex by protonating the heptahydride $[ReH_7(dppen\text{-}PP')]$ **1a**.

On addition of 1 equivalent of $HBF_4{\cdot}Et_2O$ to the formally d^0 rhenium heptahydride complex $[ReH_7(dppen\text{-}PP')]$ **1a** at −80 °C in dichlorodeuteriomethane no gas was evolved and partial conversion to an η^2-dihydrogen complex, of possible formulation $[ReH_6(\eta^2\text{-}H_2)(dppen\text{-}PP')]^+$ **5** occurred. $^{31}P\text{-}\{^1H\}$ and selected ^1H NMR data for both **1a** and the protonated species **5** are given in Table 6. On the addition of $HBF_4{\cdot}Et_2O$ at −80 °C a new singlet at δ 49.6 was observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum and in the $^1H\text{-}\{^{31}P\}$ NMR spectrum, a new broad singlet was observed at δ −5.60. Both the $^{31}P\text{-}\{^1H\}$ and the $^1H\text{-}\{^{31}P\}$ NMR spectra also showed resonances due to the presence of the starting heptahydride. In the $^1H\text{-}\{^{31}P\}$ NMR spectrum, a broad resonance (linewidth *ca.* 50 Hz) at δ *ca.* 11.5 due to $HBF_4{\cdot}Et_2O$ was also observed. The relative intensities of the three resonances in the $^1H\text{-}\{^{31}P\}$ NMR spectrum suggested that only *ca.* 40% conversion to the protonated complex had occurred and it appeared that an equilibrium between **1a** and the η^2-dihydrogen complex had been set up, equation (3).

$$[ReH_7(dppen\text{-}PP')] + HBF_4{\cdot}Et_2O \rightleftharpoons [ReH_6(\eta^2\text{-}H_2)(dppen\text{-}PP')]BF_4 \quad (3)$$

This protonation was reversible and addition of 1 equivalent of triethylamine to the mixture gave back the heptahydride cleanly, as evidenced by the $^{31}P\text{-}\{^1H\}$ and $^1H\text{-}\{^{31}P\}$ NMR spectra.

Addition of a second equivalent of $HBF_4{\cdot}Et_2O$ at −80 °C (again no gas was evolved) led to complete conversion of the heptahydride to the η^2-dihydrogen complex **5**. This was confirmed by the $^{31}P\text{-}\{^1H\}$ NMR spectrum, which showed only one peak, at δ 49.6, whilst in the $^1H\text{-}\{^{31}P\}$ NMR spectrum the only peak in the hydride region was that at δ −5.59. This peak was broad and showed no resolvable coupling to phosphorus between −80 and 0 °C. The protonated complex was not isolated since above −20 °C it was unstable and evolved dihydrogen (^1H NMR evidence) to give another product (see below), but it was stable at −80 °C for several hours ($^{31}P\text{-}\{^1H\}$ NMR evidence). The fact that the protonation of **1a** required the addition of 2 equivalents of acid suggested that this heptahydride was less basic than those of the type $[ReH_7(PR_3)_2]$ $[PR_3 = P(C_6H_{11})_3$, PPh_3 or $PBu^t{}_2Me]$, the protonation of which were studied by Shaw and co-workers,[36] which were completely converted to complexes of the type $[ReH_6(\eta^2\text{-}H_2)(PR_3)_2]^+$ on addition of only 1 equivalent of acid. The protonation of **1a** was similarly found to be reversible after the addition of the second equivalent of acid, the heptahydride being regenerated on addition of 2 equivalents of triethylamine.

The protonation proceeded either *via* protonation of a Re–H bond, as suggested by Crabtree *et al.*[37] for the protonation of $[ReH_7(PPh_3)_2]$ in acetonitrile to give the complex $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$, or by protonation of the formally d^2 complex $[ReH_5(\eta^2\text{-}H_2)(dppen\text{-}PP')]$ which may be in equilibrium, in solution, with the heptahydride. In the protonation of $[MoH_4(dppe\text{-}PP')_2]$, to give the transient complex $[Mo(\eta^2\text{-}H_2)H_4(dppe\text{-}PP')_2]^{2+}$ (lifetime 0.75 s), the presence of an $\eta^2\text{-}H_2$ ligand was invoked since a classical formulation, *i.e.* $[MoH_6(dppe\text{-}PP')_2]^{2+}$, would exceed the maximum formal oxidation state of the metal and there are insufficient metal orbitals to form this classical hexahydride.[38] Complexes of the type $[WH_{7-2x}(\eta^2\text{-}H_2)L]^+$ $\{L = PPh(CH_2CH_2PPh_2)_2$, $PPh(C_6H_4\text{-}o\text{-}PPh_2)_2$ or $MeC(CH_2PPh_2)_3\}$ were formulated as containing at least one $\eta^2\text{-}H_2$ for the same reason.[39] Similar arguments apply to the formulation of $[ReH_6(\eta^2\text{-}H_2)(dppen\text{-}PP')]^+$ as containing an η^2-dihydrogen ligand since its formulation as a classical octahydride would exceed the maximum formal oxidation state of rhenium.

The significance and limitations of the assignment of very short values of T_1(min) to η^2-dihydrogen complexes has been

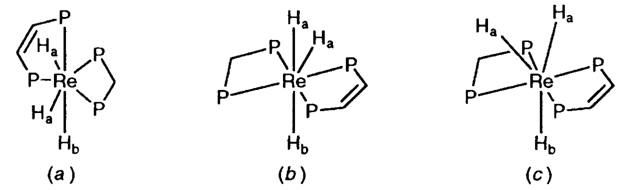


Fig. 1 Possible geometries of the complex $[ReH_3(dppen\text{-}PP')(dppm\text{-}PP')]$ (*a*) pentagonal bipyramidal, (*b*) monocapped octahedral or (*c*) capped trigonal prismatic

Table 6 Protonation experiments: $^{31}P\text{-}\{^1H\}$ and ^1H NMR data[a] for the complexes $[ReH_7(dppen\text{-}PP')]$ **1a**, $[ReH_6(\eta^2\text{-}H_2)(dppen\text{-}PP')]^+$ **5** and $[Re_2H_8(dppen\text{-}PP')_2][BF_4]_2$ **6**

		Hydrides		dppen	
Complex	δ(P)	δ(H)	^2J(PH)	δ(H)	N[b]
1a	50.8	−6.88	13.4	7.61	57.6
5	49.6	−5.59	n.r.[c]	7.79	63.5
6[d]	58.5	−4.93	8	7.64	62.0

[a] Recorded at 400 MHz (^1H) or 162 MHz (^{31}P) at −80 °C in dichlorodeuteriomethane unless otherwise stated; chemical shifts in ppm and coupling constants in Hz. [b] ^2J(PH) + ^3J(PH). [c] n.r. = Not resolved. [d] Recorded at 100 MHz (^1H) or 40.3 MHz (^{31}P) at 22 °C.

discussed widely in the literature.[10,11,35,40,41] However, no value higher than 35 ms (at 250 MHz) has been observed for a complex containing an η^2-dihydrogen ligand.[10] Hence we measured T_1 values at various temperatures in an attempt to find a T_1(min) value for the η^2-H_2 complex **5** (Table 7). For the *ca.* 60:40 mixture of **1a** and **5** at −80 °C the T_1 value for the heptahydride was 98 ± 10 ms (at 400 MHz), apparently indicative of a classical heptahydride structure for this complex. This value was comparable to the value of 68 ms (at 250 MHz) at −67 °C reported by Crabtree *et al.*[16] for **1a**. The T_1 value for the η^2-H_2 complex, at −80 °C, was 20 ± 2 ms in this mixture and 19 ± 2 ms for the solution which contained only the η^2-H_2 complex. At −60 °C, the value was 18 ± 2 ms, although it was not clear if this was the T_1(min) since it was comparable to the value at −80 °C. However, this correlates to a value of *ca.* 11 ms at 250 MHz, well within the range expected for η^2-dihydrogen complexes,[10] *e.g.* T_1(min) was 4 ms for the complex $[Ru(\eta\text{-}C_5H_5)(CO)(PR_3)(\eta^2\text{-}H_2)]^+$ (at −68 °C and 250 MHz) which had only one η^2-H_2 and no terminal M–H bonds.[42] For $[ReH_6(\eta^2\text{-}H_2)(\text{dppen-}PP')]^+$, the observed T_1 value was a weighted average (due to fluxionality) of the T_1 value for the η^2-H_2 ligand and the T_1 value for the classical hydrides, as was the case for $[ReH_6(\eta^2\text{-}H_2)\{P(C_6H_{11})_3\}_2]^+$ {T_1(min) = 30 ms at 400 MHz[36]}. For $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_2Ph)_3]^+$ this fluxionality was 'frozen out' and T_1(min) values measured for the classical hydrides (43 ms) and η^2-H_2 ligand (7 ms) at −75 °C (250 MHz).[43] It was not possible to obtain separate T_1 values for the classical hydrides and the η^2-H_2 ligand in $[ReH_6(\eta^2\text{-}H_2)(\text{dppen-}PP')]^+$ since it was fluxional at all accessible temperatures.

No phosphorus coupling was resolved for the hydride/η^2-H_2 nuclei in the ^1H NMR spectrum of **5** at any of the temperatures studied. An H–P coupling was observed for the complex $[Ru(\eta\text{-}C_5H_5)(\eta^2\text{-}HD)(\text{dppe-}PP')]^+$ [^2J(PH) = 2 Hz], much lower than for the corresponding dihydride (28 Hz),[44] although this coupling is not normally observed since the linewidth of the hydride/η^2-H_2 resonance is usually too large. However, H–P coupling was resolved for the hydride/η^2-H_2 resonances in the complexes $[ReH_6(\eta^2\text{-}H_2)(PPh_3)_2]^+$ and $[ReH_6(\eta^2\text{-}H_2)(PBu^t{}_2Me)_2]^+$ [^2J(PH) = 4.2 and 6.1 Hz, respectively].[36]

Intramolecular exchange of the hydride and η^2-H_2 ligand in $[ReH_6(\eta^2\text{-}H_2)(\text{dppen-}PP')]^+$ **5** was fast on the NMR timescale, even at low temperature, and it was possible that two or more complexes of the type $[ReH_{8-2x}(\eta^2\text{-}H_2)_x(\text{dppen-}PP')]^+$, with x = 1, 2, 3 or even 4, were in dynamic equilibrium, as was suggested[36] for the complexes $[ReH_6(\eta^2\text{-}H_2)(PR_3)_2]^+$.

In solution, the complex formulated as $[ReH_6(\eta^2\text{-}H_2)(\text{dppen-}PP')]^+$ **5** was unstable above *ca.* −20 °C to loss of dihydrogen. The ^1H NMR spectrum at 0 °C showed the appearance of a new pattern of resonances assigned to a complex **6**. The complex giving rise to these resonances was prepared in good yield by treating a dichloromethane solution of **1a** with *ca.* 2.5 equivalents of $HBF_4{\cdot}Et_2O$ at −78 °C, to give **5**. The solution was then allowed to warm to room temperature and on addition of diethyl ether, a brown microcrystalline solid was obtained. The microanalytical data (Table 1) were consistent with the formulation $[Re_2H_8(\text{dppen-}PP')_2][BF_4]_2$ **6** and the IR spectrum showed very broad bands at 1890 and 1815 cm^{-1}, assigned to terminal Re–H bond stretches and also a broad band at 1625 cm^{-1} assigned to bridging hydrides. An electrical conductivity measurement of a *ca.* 10^{-3} mol dm^{-3} solution of **6** in acetone at 20 °C showed the molar conductivity (Λ_m) to be 163 Ω^{-1} mol^{-1} cm^2, consistent with it being a 2:1 electrolyte (expected range 160–200). The presence of BF_4^- was confirmed from the ^{19}F NMR spectrum, which showed a singlet at δ −30.0, very close to the value for $NaBF_4$ (δ −32.8). The ^{31}P-{^1H} NMR spectrum showed a singlet at δ +58.5, a value indicative of a five-membered chelate ring rather than of two dppen ligands bridging the two rhenium atoms. A ^{31}P-{^1H(selective)} NMR spectrum, to determine the number of hydrides, consisted of a broad featureless resonance. The ^1H NMR spectrum of **6** at 22 °C showed a quintet hydride resonance at δ −4.93 [^2J(PH) = 8 Hz] which became a singlet in the ^1H-{^{31}P} NMR spectrum (Table 6); this clearly indicated the presence of two dppen ligands in the complex. An accurate integration, against a known amount of hexamethylbenzene (as an integration marker), suggested that there were eight hydride protons in addition to the 44 expected from the two dppen ligands. The ^{13}C-{^1H} NMR spectrum showed five resonances attributed to the carbons in the dppen ligands at δ 150.2 (m, CH=CHP), 136.1 (m, C_{ipso}), 132.6 (m, C_{ortho}), 131.6 (s, C_{para}) and 129.3 (m, C_{meta}). The resonances that did exhibit coupling to ^{31}P could be simulated as AXY (AXX′) patterns indicating the presence of only one dppen ligand per rhenium atom. Therefore we were able to conclude that **6** must be binuclear with bridging hydride ligands (IR evidence).

Table 7 Measurements of T_1/ms[a] for the hydride–η^2-dihydrogen resonance for the complexes $[ReH_7(\text{dppen-}PP')]$ **1a**, $[ReH_6(\eta^2\text{-}H_2)(\text{dppen-}PP')]^+$ **5** and $[Re_2H_8(\text{dppen-}PP')_2]^{2+}$ **6**

T/°C	**1a**[b]	**5**[b]	**5**	**6**
−80	98	20	19	
−60			18	
−40			23	
−20			35	
0			49	170

[a] Calculated using the inversion–recovery method at 400 MHz in deuteriodichloromethane. Calculated standard deviations were *ca.* ± 10%. [b] Measured for the 60:40 mixture of **1a**:**5**.

The appearance of the ^1H-{^{31}P} NMR spectrum, *i.e.* a sharp singlet, indicated that rapid bridging hydride–terminal hydride exchange was occurring, as in the neutral complexes of the type $[Re_2H_8(PR_3)_4]$ (*e.g.* PR_3 = PPh_3[6], PEt_2Ph[45] or $PPr^n{}_3$[46]) for which single hydride resonances were observed, even at low temperatures. A T_1 relaxation time of 170 ms was found for **6** (Table 7) at 0 °C (400 MHz) and although this was not a T_1(min) value it would appear to indicate a classical formulation for **6**, *i.e.* that only classical Re–H bonds were present. Thus **6** was tentatively formulated as $[(\text{dppen-}PP')H_3Re(\mu\text{-}H)_2ReH_3(\text{dppen-}PP')]$, although other formulations cannot be ruled out. A related reaction has been shown to occur for the ruthenium multihydride complex $[RuH_2(\eta^2\text{-}H_2)_2\{P(C_6H_{11})_3\}_2]$, which loses hydrogen thermally or photochemically to give $[Ru_2H_4(\eta^2\text{-}H_2)\{P(C_6H_{11})_3\}_4]$.[47]

Experimental

General methods and instrumentation were as described in recent publications from this laboratory.[48]

Preparations.—$[ReH_7(\text{dppen-}PP')]$ **1a**. Sodium tetrahydroborate (3.4 g, 90 mmol) was added to a suspension of $[ReOCl_3(\text{dppen-}PP')]$ (3.78 g, 5.36 mmol) in absolute ethanol (200 cm^3). The resultant mixture was stirred vigorously with a mechanical stirrer under dinitrogen for 1 h during which time the colour changed from pale blue to orange. The ethanol was then removed under reduced pressure and the residue extracted with benzene (5 × 50 cm^3). The benzene solution was passed down a column of florisil, evaporated to dryness and the residue triturated with ethanol to give the required product as an off-white powder. This was filtered off, washed with ethanol and dried. Yield 2.0 g, 63%.

The following three multihydride complexes were prepared in a similar manner: $[ReH_7(\text{dppm-}PP')]$ **1b** from $[ReOCl_3(\text{dppm-}PP')]$ as a tan solid in 40% yield, $[ReH_7(1,1'\text{-dppe-}PP')]$ **1c** from either $[ReOCl_3(\text{vdpp-}PP')]$ or $[ReOCl_3(1,1'\text{-dppe-}PP')]$ as an off-white solid in 26% yield; $[ReH_7\{Ph_2PCH_2C(=CH_2)CH_2PPh_2\text{-}PP'\}]$ **1d** from $[ReOCl_3\{Ph_2PCH_2C(=CH_2)CH_2PPh_2\text{-}PP'\}]$ **2a** as a tan solid in 40% yield.

The complex $[ReOCl_3\{Ph_2PCH_2C(=CH_2)CH_2PPh_2\text{-}PP'\}]$ **2a** was prepared in an analogous manner to $[ReOCl_3(dppm\text{-}PP')]$[13] from $[ReOCl_3(AsPh_3)_2]$ and $Ph_2PCH_2C(=CH_2)CH_2PPh_2$,[12] as a blue-green powder in 80% yield; $[ReOBr_3\{Ph_2PCH_2C(=CH_2)CH_2PPh_2\text{-}PP'\}]$ **2b** was similarly prepared from $[ReOBr_3(AsPh_3)_2]$, as a green powder in 78% yield.

$[ReH_5(dppen\text{-}PP')(dppm\text{-}P)]$ **3b**. A mixture of $[ReH_7(dppen\text{-}PP')]$ (0.665 g, 1.12 mmol), dppm (0.480 g, 1.25 mmol) and toluene (25 cm^3) was heated at 110 °C under dinitrogen for 17 min. The cooled reaction mixture was filtered, ethanol (25 cm^3) was added, and the resultant solution reduced slowly in volume under reduced pressure. The crude product thus obtained was recrystallised from toluene–ethanol to give the required product as a cream microcrystalline solid. This was filtered off, washed with ethanol and dried. Yield 0.227 g, 21%.

$[ReH_3(dppen\text{-}PP')(PPh_3)_2]$ **4a**. A mixture of $[ReH_7(dppen\text{-}PP')]$ (0.219 g, 0.371 mmol), triphenylphosphine (0.210 g, 0.801 mmol) and toluene (8 cm^3) was heated at 110 °C under dinitrogen for 1.5 h. The cooled reaction mixture was evaporated to *ca.* 2 cm^3 under reduced pressure and methanol (10 cm^3) was added to give a yellow precipitate. Recrystallisation from dichloromethane–methanol gave the required product as a yellow microcrystalline solid. Yield 0.125 g, 30%.

$[ReH_3(dppen\text{-}PP')(dppm\text{-}PP')]$ **4c**. A mixture of $[ReH_7(dppen\text{-}PP')]$ (0.300 g, 0.509 mmol), dppm (0.220 g, 0.572 mmol) and toluene (10 cm^3) was heated at 110 °C for 3 h. The cooled reaction mixture was evaporated under reduced pressure to give a thick brown oil to which diethyl ether (10 cm^3) was added. The resultant mixture was vigorously scratched and then set aside at room temperature for 2 h. This gave a yellow microcrystalline solid which was filtered off, washed with diethyl ether and dried. Yield 0.176 g, 36%.

$[ReH_3(dppen\text{-}PP')_2]$ **4d**. A mixture of $[ReH_7(dppen\text{-}PP')]$ (0.174 g, 0.295 mmol), dppen (0.130 g, 0.328 mmol) and toluene (5 cm^3) was heated at 110 °C for 1 h. Ethanol (12 cm^3) was added to the cooled reaction mixture and the mixture set aside at -20 °C for 16 h. The resultant orange-yellow microcrystalline solid was filtered off, washed with ethanol and dried. Yield 0.103 g, 36%.

Protonation Experiments.—Preparation of a solution containing a ca. *60:40 mixture of* $[ReH_7(dppen\text{-}PP')]$ **1a**: $[ReH_6(\eta^2\text{-}H_2)(dppen\text{-}PP')]^+$ **5**.

A solution of $HBF_4{\cdot}Et_2O$ in dry dichlorodeuteriomethane (0.1 cm^3 of a 0.4 mol dm^{-3} solution, 0.040 mmol) was added to a solution of $[ReH_7(dppen\text{-}PP')]$ (0.023 g, 0.039 mmol) in dichlorodeuteriomethane (0.4 cm^3) in a 5 mm NMR tube at -80 °C. The resultant solution, which was pale brown, was degassed at -80 °C and the NMR tube was then sealed with a gas-tight cap. The NMR tube was then transferred to the spectrometer probe which had been previously cooled to -80 °C. The $^{31}P\text{-}\{^1H\}$ and $^1H\text{-}\{^{31}P\}$ NMR spectra of this mixture showed that it contained an approximately 60:40 mixture of **1a**:**5**, as well as some $HBF_4{\cdot}Et_2O$. The T_1 relaxation times at -80 °C of the two components of the mixture were estimated using the 180°–τ–90° inversion–recovery pulse sequence[40] using five different values of τ and a program (INVREC) supplied by Bruker for the AM400 spectrometer.

Preparation of a solution containing only $[ReH_6(\eta^2\text{-}H_2)(dppen\text{-}PP')]^+$ **5**. This solution was prepared by addition of 2 mole equivalents of $HBF_4{\cdot}Et_2O$ to a solution of $[ReH_7(dppen\text{-}PP')]$ in dichlorodeuteriomethane at -80 °C. The $^{31}P\text{-}\{^1H\}$ and $^1H\text{-}\{^{31}P\}$ NMR spectra of this solution showed that it contained only $[ReH_6(\eta^2\text{-}H_2)(dppen\text{-}PP')]^+$ **5** and $HBF_4{\cdot}Et_2O$. The T_1 relaxation times were estimated as above, using five different values of τ at each temperature (-80 to 0 °C).

$[Re_2H_8(dppen\text{-}PP')_2][BF_4]_2$ **6**. $HBF_4{\cdot}Et_2O$ (0.200 g, 1.05 mmol) was added to a solution of $[ReH_7(dppen\text{-}PP')]$ (0.250 g, 0.424 mmol) in dichloromethane (5 cm^3) at -80 °C. The resultant mixture was stirred for 15 min at -80 °C and then allowed to warm slowly to room temperature during *ca.* 45 min. Diethyl ether was added and the mixture set aside at room temperature for 16 h to give a brown precipitate. This was filtered off and recrystallised from dichloromethane–diethyl ether to give the required product as a brown microcrystalline solid. Yield 0.221 g, 77%.

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