Rhenium Multihydride Heterobimetallic Complexes containing Bridging and Chelating Diphosphine Ligands

Xavier L. R. Fontaine, Timothy P. Layzell and Bernard L. Shaw*
School of Chemistry, Leeds University, Leeds LS2 9JT, UK

Treatment of the rhenium pentahydride complex [ReH_5(dppen-*PP'*)(dppm-*P*)] (dppen = $Ph_2PCH{=}CHPPh_2$, dppm = $Ph_2PCH_2PPh_2$) with 0.5 mol equivalents of [$Rh_2Cl_2(cod)_2$] (cod = cycloocta-1,5-diene) gave the fluxional bimetallic complex [(dppen-*PP'*)$H_3Re(\mu\text{-}H)_2(\mu$-dppm)Rh(cod)]Cl **1a**, which was characterised as the corresponding PF_6 salt **1b**. Analogous complexes (**1c** and **1d**) were prepared from [$Rh_2Cl_2(nbd)_2$] [nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)]. The fluxionality of **1b** and **1d** was studied by $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectroscopies over a range of temperatures. Treatment of [ReH_5(dppen-*PP'*)(dppm-*P*)] with silver iodide gave a fluxional rhenium–silver bimetallic complex formulated as [(dppen-*PP'*)$H_3Re(\mu\text{-}H)_2(\mu$-dppm)AgI] which was studied by variable-temperature NMR spectroscopy.

Heterobimetallic complexes have been investigated in the hope that the close approach of two different metal centres would lead to unusual reactions.[1] Bimetallic complexes containing a multihydride moiety are of particular interest since mononuclear multihydrides, being co-ordinatively saturated, are often rather inert and the presence of a second metal might increase reactivity. Most of the complexes of this type contain hydrides as the only bridging ligands and one method of preparing complexes of this type has been to treat transition-metal multihydride anions with organometallic halides.[2] Complexes prepared by this method include [$(cp)_2YZrReH_6(PMePh_2)_2$] (Y = OPr^i or H, cp = cyclopentadienyl),[3] [$(cp)_2ClZr(\mu\text{-}H)_3Os(PMe_2Ph)_3$][3] {prepared by treating K[*fac*-$OsH_3(PMe_2Ph)_3$] with [$Zr(cp)_2Cl_2$]}, the rhenium–uranium bimetallics [$L_2ReH_6U(cp)_3$] [L = PPh_3 or $P(C_6H_4F\text{-}4)_3$],[4] and [$(cod)Ir(\mu\text{-}H)_3Ru(PPh_3)_3$] (cod = cycloocta-1,5-diene) which was shown to isomerise to [$(cod)Ir(\mu\text{-}H)_2RuH(PPh_3)_3$] as the thermodynamic product.[5] Heterobimetallic complexes containing an η^2-dihydrogen ligand are also known; protonation of the complex [$(Ph_3P)_2HRe(\mu\text{-}H)_3(\mu\text{-}CO)RuH(PPh_3)_2$] with a stoichiometric quantity of $HBF_4{\cdot}Et_2O$ gave the η^2-dihydrogen complex [$(Ph_3P)_2HRe(\mu\text{-}H)_3(\mu\text{-}CO)Ru(\eta^2\text{-}H_2)(PPh_3)_2$]$BF_4$.[6] However none of these complexes has a bridging diphosphine ligand between the two metals. Previous work from this laboratory has shown that the pentahydride complexes [$ReH_5\{P(C_6H_{11})_3\}_2$(L–L-*P*)] {L–L = dppm ($Ph_2PCH_2PPh_2$) or vdpp [$Ph_2PC({=}CH_2)PPh_2$]}[7] are useful complexes in the preparation of heterobimetallic complexes containing both bridging hydrides and also a bridging diphosphine ligand.[8–10] Rhenium–silver,[8] rhenium–copper[8] and rhenium–rhodium[9,10] complexes have been prepared and characterised. For example the complex [$\{(C_6H_{11})_3P\}_2H_4Re(\mu\text{-}H)(\mu$-vdpp)Rh(nbd)]$PF_6$ was prepared by treatment of the pentahydride [$ReH_5\{(C_6H_{11})_3P\}_2$(vdpp-*P*)] with [$Rh_2Cl_2(nbd)_2$] [nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)]. It was shown to contain one bridging hydride, a bridging diphosphine ligand and was formulated with a metal–metal bond.[10] In these systems the very bulky and monodentate tricyclohexylphosphine ligands would influence the nature of the bimetallic complexes formed and their fluxional behaviour. In a recent paper[11] we have described and studied some rhenium hydrides of the type [ReH_7(chelating diphosphine)], including low-temperature protonation studies, and also shown that [ReH_7(dppen-*PP'*)] (dppen = *cis*-$Ph_2PCH{=}CHPPh_2$) reacts with dppm to give [ReH_5(dppen-*PP'*)(dppm-*P*)]. It was of interest to see if the monodentate dppm in such a multihydride could be used to bridge to a second metal to give a bimetallic multihydride and what sort of fluxionality such a bimetallic complex would have. The compound [ReH_5(dppen-*PP'*)(dppm-*P*)] seemed a good choice to use since the presence of the protons in the PCH=CHP and the PCH_2P moieties would probably make the analysis of fluxional behaviour easier. For the second metal we chose to study two very different systems, namely (*i*) rhodium(I)–cycloocta-1,5-diene or –norbornadiene systems and (*ii*) a silver(I) system. Both of these have the metals with $I = \frac{1}{2}$, which again would help with the interpretation of the fluxional behaviour at different temperatures. We therefore describe herein our results on the bimetallic complexes formed by treating the pentahydride complex [ReH_5(dppen-*PP'*)(dppm-*P*)][11] with labile complexes of rhodium, or with silver iodide.

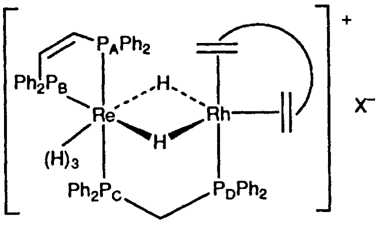
Results and Discussion

Treatment of a benzene solution of [ReH_5(dppen-*PP'*)(dppm-*P*)] with 0.5 mol equivalents of the labile dinuclear rhodium complex [$Rh_2Cl_2(cod)_2$] (cod = cycloocta-1,5-diene) at 20 °C gave a deep red solution after *ca.* 2 min. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of this solution at 20 °C consisted of three resonances of relative intensities 2 : 1 : 1. A doublet of intensity two, at δ 51.2, was assigned to the equivalent (due to rapid exchange) dppen phosphorus nuclei (P_A and P_B), with $^2J(P_AP_C)$ = 15 Hz. (NB. In the fast-exchange limiting spectra P_A refers to both P_A and P_B; in the low-temperature limiting spectra P_A and P_B become inequivalent, hence the use of different subscripts.) A doublet of triplets of intensity one, at δ 13.3, was due to the dppm phosphorus nuclei co-ordinated to rhenium (P_C), with $^2J(P_CP_D)$ = 64 Hz. The formerly unco-ordinated dppm phosphorus was now co-ordinated to rhodium and observed as a doublet of doublets of intensity one, at δ 44.1, with $^1J(RhP_D)$ = 139 Hz). These data were attributed to the presence in solution of the rhenium–rhodium bimetallic complex [(dppen-*PP'*)$H_3Re(\mu\text{-}H)_2(\mu$-dppm)Rh(cod)]Cl **1a**, due to the similarity of these data to those obtained for the corresponding PF_6 salt. The complex [(dppen-*PP'*)$H_3Re(\mu\text{-}H)_2(\mu$-dppm)Rh(cod)]$PF_6$ **1b** was isolated as a yellow microcrystalline solid in 72% yield on addition of NH_4PF_6 to an acetone solution of **1a**.

Similarly, addition of 0.5 mol equivalents of the labile complex [$Rh_2Cl_2(nbd)_2$] (nbd = norbornadiene) to a benzene solution of [ReH_5(dppen-*PP'*)(dppm-*P*)] at 20 °C gave a deep red solution, the $^{31}P-\{^1H\}$ NMR spectrum of which was consistent with the presence in solution of the heterobimetallic complex [(dppen-*PP'*)$H_3Re(\mu-H)_2(\mu$-dppm)Rh(nbd)]Cl **1c** ($^{31}P-\{^1H\}$ NMR data in Table 2). The PF_6 salt **1d** was isolated in 67% yield, as a yellow microcrystalline solid, in a similar manner to the corresponding cod complex **1b**. Both **1b** and **1d** were characterised by microanalysis (Table 1), and by $^{31}P-\{^1H\}$ (Table 2) and ^1H (Table 3) NMR spectroscopies.

The $^{31}P-\{^1H\}$ NMR spectra of **1b** and **1d** were similar and showed that both complexes were highly fluxional. The 162 MHz $^{31}P-\{^1H\}$ NMR spectrum of [(dppen-*PP'*)$H_3Re(\mu-H)_2(\mu$-dppm)Rh(nbd)] PF_6 **1d** at 20 °C was similar to the spectrum of the corresponding chloride salt **1c**. It showed a poorly resolved doublet at δ 55.2 due to the equivalent dppen phosphorus nuclei (P_A and P_B), a doublet of triplets at δ 14.9 due to P_C and a doublet of doublets, due to P_D at δ 45.4 (coupling constants in Table 2).

At −90 °C, the exchange of P_A and P_B was halted and these inequivalent phosphorus nuclei were observed as broad apparent triplets at δ 59.4 (P_A) and 56.2 (P_B). The phosphorus P_A showed a larger coupling (35 Hz) to P_C than P_B to P_C (17 Hz) which suggested that P_A was transoid to P_C and P_B was cisoid to P_C, although no other conclusions about the geometry at the rhenium could be made at this stage. We also suggest that these coupling constants were opposite in sign; if we assume that the fluxionality of the phosphorus nuclei simply involved P_A and P_B exchanging positions, at the fast-exchange limit, one of $^2J(P_AP_C)$ or $^2J(P_BP_C)$ must be negative to give the average $^2J(P_AP_C)$ coupling of 10 Hz observed in the spectrum recorded at 20 °C. Both P_A and P_B were also mutually coupled with $^2J(P_AP_B)$ = 27 Hz. The resonance due to P_C in the low-temperature spectrum was a doublet of doublet of doublets, coupled to P_A, P_B and P_D and as in the high-temperature spectrum, the resonance due to P_D was a doublet of doublets [$^2J(P_CP_D)$ = 74 and $^1J(RhP_D)$ = 154 Hz]. The $^{31}P-\{^1H\}$ NMR spectra of the cod complex **1b** at 20 and −90 °C showed analogous temperature dependence (data in Table 2).



		X
1a	cod	Cl
1b	cod	PF_6
1c	nbd	Cl
1d	nbd	PF_6

Table 1 Microanalytical[a] data for rhenium multihydride bimetallic complexes

Complex	Analysis (%)		
	C	H	X[b]
1b	53.15 (53.35)	4.8 (4.65)	8.4 (8.6)
1d·$2H_2O$	51.2 (51.65)	4.1 (4.45)	7.9 (8.45)
2·CH_2Cl_2	49.1 (48.35)	3.9 (4.0)	9.2 (9.8)

[a] Calculated values in parentheses. [b] X = F or I, as appropriate.

Related studies[9,10] of the low-temperature $^{31}P-\{^1H\}$ NMR spectra of complexes of the type [$\{(C_6H_{11})_3P\}_2H_4Re(\mu-H)(\mu$-L–L)RhCl(CO)] (L–L = dppm or vdpp) or [$\{(C_6H_{11})_3P\}_2H_4Re(\mu-H)(\mu$-L–L)Rh(L'–L')]X (L–L = dppm or vdpp; L'–L' = cod or nbd; X = ReO_4, PF_6, BF_4 or Cl) showed that for all these complexes, with the exception of [$\{(C_6H_{11})_3P\}_2H_4Re(\mu-H)(\mu$-vdpp)Rh(cod)][$ReO_4$], resonances due to two or more isomers were present in the spectra. We found no evidence for the presence of other isomers at low temperature for **1b** or **1d** and this could be due, in part, to the stereochemical rigidity of the chelating dppen ligand compared to the monodentate $P(C_6H_{11})_3$ ligands.

The 400 MHz ^1H NMR spectrum of [(dppen-*PP'*)$H_3Re(\mu-H)_2(\mu$-dppm)Rh(nbd)]PF_6 **1d** at 50 °C showed a broad resonance (*ca.* 50 Hz) at δ −6.78 assigned to the five equivalent (due to fluxionality) hydrides. In the $^1H-\{^{31}P\}$ NMR spectrum this resonance was still broad (*ca.* 25 Hz) and so neither Rh–H nor P–H couplings were resolved. This was not the fast-exchange limit, *i.e.* the hydride fluxionality was in an intermediate stage. However, the fast-exchange limiting spectrum was observed in the 100 MHz ^1H and $^1H-\{^{31}P\}$ NMR spectra recorded at 50 °C. In the $^1H-\{^{31}P\}$ NMR spectrum the five equivalent hydrides appeared as a sharp doublet and showed an average coupling to rhodium of 8.1 Hz. The hydride resonance was an apparent doublet of quartets in the ^1H NMR spectrum and showed an average coupling to phosphorus ($P_{A/B}$, P_C) of *ca.* 17 Hz; no coupling to P_D was resolved. In the 400 MHz spectrum, the overlapping doublet of doublets, of relative intensity two, at δ 4.12 was assigned to the equivalent methylene protons of the bridging dppm ligand [$^2J(P_CH) + {}^2J(P_DH)$ = 22.5 Hz]. The AA'XX' pattern at δ 7.87 was assigned to the olefinic protons of the chelating dppen, with *N* = 58.0 Hz. Two broad singlets, both of intensity two, at δ 4.31 and 3.05, were assigned to the two sets of CH=CH protons (presumably one set *cis* and the other *trans* to P_D) of the co-ordinated norbornadiene {*cf.* δ 3.92 for all four CH=CH protons in [Rh_2Cl_2(nbd)][12]}, although no couplings to phosphorus were resolved for either set. The two, much sharper, singlets at δ 3.47 and 1.28 were assigned to the two bridgehead protons and the methylene group of the norbornadiene, respectively.

At −90 °C, five distinct hydride resonances were observed, in the ^1H NMR spectrum, at δ −5.17, −5.96, −7.13, −7.48 and −9.62 indicating that the static structure had been 'frozen out'. In the $^1H-\{^{31}P\}$ NMR spectrum the resonances at δ −5.17, −5.96 and −7.13 were singlets and were assigned to three terminal hydrides, whereas the resonances at δ −7.48 and −9.62 were doublets and showed coupling to rhodium (19 and 22 Hz, respectively). Thus these were assigned to two bridging hydrides. Averaging these Rh–H couplings over five hydride sites gave an average $^1J(RhH)$ value of 8.2 Hz, in excellent

Table 2 $^{31}P-\{^1H\}$ NMR data[a] for the complexes [(dppen-*PP'*)$H_3Re(\mu-H)_2(\mu$-dppm)Rh(L'–L')]X(L'–L' = cod or nbd; X = Cl or PF_6)

Complex	δ(P_A)	δ(P_B)	δ(P_C)	δ(P_D)	$^2J(P_AP_B)$	$^2J(P_AP_C)$	$^2J(P_BP_C)$	$^2J(P_CP_D)$	$^1J(RhP_D)$
1a[b]	51.2		13.3	44.1		15		64	139
1b	51.4		13.0	39.4		9		70	141
1b[c]	55.9	53.7	12.7	40.9	24	37	17	68	139
1c[b]	54.4		15.9	47.6		13		71	156
1d[d]	55.2		14.9	45.4		10		74	156
1d[c,d]	59.4	56.2	15.0	46.2	27	35	17	74	154

[a] Recorded at 40.3 MHz in deuterioacetone at 20 °C, unless otherwise stated; chemical shifts (δ) in ppm and coupling constants in Hz. [b] Recorded in deuteriobenzene. [c] Recorded at −90 °C. [d] Recorded at 162 MHz.

agreement with the value of 8.1 Hz observed in the high-temperature limiting spectrum. Thus it would appear that the fluxionality of the hydrides was restricted to 'hydride sites', *i.e.* the hydrides did not exchange with phosphorus sites, which supported the assumption made about the fluxionality of the dppen ligand (see above). In the related complex $[\{(C_6H_{11})_3P\}_2H_4Re(\mu\text{-}H)(\mu\text{-vdpp})Rh(nbd)]PF_6$,[10] a similar value of $^1J(RhH)$ was observed, 20.9 Hz, for the one bridging hydride. In the low-temperature limiting spectrum of this complex all five hydrides were similarly inequivalent, but two isomers were present.[10] Thus **1d** appeared to be the first dppm-bridged rhenium–rhodium heterobimetallic multihydride in which all five hydrides were distinguishable at low temperature. In none of the related dppm-bridged complexes was a low-temperature limit reached.[10] This higher barrier to intramolecular exchange in **1d** must again be due to the rigid stereochemistry of the chelating dppen. All five hydrides were found to be inequivalent in both isomers of the rhenium–silver dppm-bridged bimetallic complex $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-}H)_2(\mu\text{-dppm})AgI]$ at −90 °C.[8] In **1d**, the three terminal hydrides showed coupling to phosphorus in the ^1H NMR spectrum. The resonance at δ −5.17 was an apparent triplet [$^2J(PH)$ = 30 Hz], the resonance at δ −7.13 an apparent quartet [$^2J(PH)$ = 35 Hz] and the resonance at δ −5.96 a complex multiplet, presumably coupled to all three rhenium-bound phosphorus nuclei. No hydride–hydride couplings were resolved. This appeared to be the only example, in complexes of this type, in which all three terminal hydrides showed resolvable coupling to phosphorus. In the related complex $[\{(C_6H_{11})_3P\}_2H_4Re(\mu\text{-}H)(\mu\text{-vdpp})Rh(nbd)]PF_6$, only one of the four terminal hydrides showed resolvable coupling to phosphorus (coupling to two phosphorus nuclei *ca.* 30 Hz).[10]

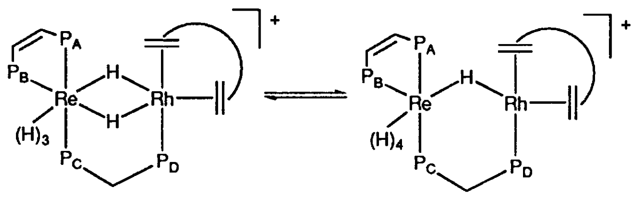
The ^1H NMR resonance due to the methylene protons of the dppm ligand broadened as the temperature was lowered and at −90 °C the two protons were inequivalent. An AX pattern was observed in the $^1H\text{-}\{^{31}P\}$ NMR spectrum of **1d**; the A part, at δ 4.74, was broader than the X part, at δ 3.92, presumably due to unresolved coupling to rhodium [$^2J(HH)$ = 12 Hz]. In the ^1H NMR spectrum the proton absorbing at δ 4.74 was an apparent quartet [$^2J(P_CH) + {}^2J(P_DH)$ = 23 Hz, *cf.* 22.5 Hz in the high-temperature limiting spectrum] whereas the proton absorbing at δ 3.92 was still a sharp doublet (very small coupling to phosphorus). The olefinic protons of the norbornadiene became inequivalent in the low-temperature limiting spectrum and thus four resonances were observed, all of which showed coupling to rhodium [only resolved for the resonances at δ 3.30 and 3.27, $^2J(RhH)$ *ca.* 2 Hz]. The resonances at 3.30 and 3.27 also appeared to be phosphorus-coupled (not resolved) and were tentatively assigned as being *trans* to P_D, in a trigonal-bipyramidal arrangement around rhodium. The two bridgehead protons were also inequivalent at −90 °C and appeared as two broad peaks at δ 3.83 and 2.96, but the resonance due to the methylene protons was still a singlet, at δ 1.10.

The ^1H and $^1H\text{-}\{^{31}P\}$ NMR spectra of complex $[(dppen\text{-}PP')H_3Re(\mu\text{-}H)_2(\mu\text{-dppm})Rh(cod)]\ PF_6$ **1b** were similarly temperature dependent (see Table 3 for data), although only four hydride resonances, in the intensity ratio 1:2:1:1, were observed in the spectrum at −90 °C. The peaks at δ −7.09 and −10.09 were coupled to rhodium, but the coupling constants were not resolved, and the resonance of intensity two, at δ −6.59, was coupled to three phosphorus nuclei [$^2J(PH)$ *ca.* 30 Hz]. It was not clear whether this was the slow-exchange limiting spectrum or if the two equivalent hydrides would become inequivalent at lower temperatures.

Thus it appeared that the hydride scrambling in the rhenium–rhodium complexes **1b** and **1d**, which was localised to 'hydride sites', appeared to occur *via* bridging hydride–terminal hydride exchange (Scheme 1).

These two complexes **1b** and **1d** were less deeply coloured than the related tricyclohexylphosphine complexes[10] and were formulated without metal–metal bonds. The increased σ-donor effect of the tricyclohexylphosphine ligands, as compared to the dppen ligand in **1b** and **1d**, would increase the electron density at the rhenium thereby making metal–metal bond formation more favourable. From the variable-temperature NMR spectra for **1b** and **1d**, several structures (dodecahedral at rhenium and trigonal bipyramidal at rhodium, sharing an edge) can be postulated, containing five inequivalent hydrides and three inequivalent phosphorus nuclei, for the static structure.

It has been shown previously that when silver iodide was added to a solution of $[ReH_5\{(C_6H_{11})_3P\}_2(dppm\text{-}P)]$ or $[ReH_5\{(C_6H_{11})_3P\}_2(vdpp\text{-}P)]$, the complexes $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-}H)_2(\mu\text{-dppm})AgI]$ or $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-}H)_2(\mu\text{-vdpp})AgI]$ were formed.[8] Addition of silver iodide to a dichloromethane



Scheme 1

Table 3 ^1H NMR data^a for $[(dppen\text{-}PP')H_3Re(\mu\text{-}H)_2(\mu\text{-dppm})Rh(L'\text{–}L')]PF_6(L'\text{–}L'$ = cod **1b** or nbd **1d**)

		Hydrides			dppm		Diene			dppen	
Complex	T/°C	δ(H)^b	^1J(RhH)	^2J(PH)	δ(H)	J(PH)^c	δ(HC=CH)	δ(CH)	δ(CH$_2$)	δ(H)	N^d
1b	50	−6.84	7.0^e	n.r.	4.40	21.7	4.50, 3.20^f		2.20, 1.90, 1.78	8.02	56.6
	−90	−5.35 (1)		n.r.	4.85	22	5.18, 2.50^g		2.15, 1.95^h		
		−6.59 (2)		≈30^i	3.77	*j*	3.58, 2.97^k		1.48, 1.20^l		
		−7.09 (1)	*m*	n.r.							
		−10.09 (1)	*m*	n.r.							
1d	50	−6.78	8.1^e	≈$17^{e,i}$	4.12	22.5	4.31, 3.05^l	3.47	1.28	7.87	58.0
	−90	−5.17 (1)		30^n	4.74^o	23	4.90, 3.30^p	3.83	1.10		
		−5.96 (1)		n.r.^{q}	3.92^o	*j*	3.27, 2.25^p	2.96			
		−7.13 (1)		35^i							
		−7.48 (1)	19	n.r.							
		−9.62 (1)	22	n.r.							

n.r. = Not resolved. ^{a} Recorded at 400 MHz in deuterioacetone; chemical shifts (δ) in ppm and coupling constants in Hz. ^{b} Values in parentheses refer to relative intensities. ^{c} $^2J(P_CH) + {}^2J(P_DH)$. ^{d} $^2J(PH) + {}^3J(PH)$. ^{e} Only resolved in the 100 MHz spectrum at 50 °C. ^{f} Both showed coupling to rhodium; for δ 3.20 $^2J(RhH)$ = 3 Hz. ^{g} Very broad (> 100 Hz). ^{h} Both resonances partially obscured by acetone peak. ^{i} This resonance was coupled to three ^{31}P nuclei (P_A, P_B and P_C); $^2J(PH)$ is given. ^{j} Very small, unresolved coupling to ^{31}P. ^{k} Broad (*ca.* 20 Hz). ^{l} Broad (*ca.* 40 Hz). ^{m} Coupled to rhodium, but not resolved. ^{n} This resonance was coupled to two ^{31}P nuclei; $^2J(PH)$ is given. ^{o} $^2J(HH)$ = 12 Hz. ^{p} Coupled to rhodium; for δ 3.30 and 3.27 $^2J(RhH)$ *ca.* 2 Hz. ^{q} Complex multiplet, couplings unresolved.

Table 4 ^{31}P-{^{1}H} NMR data^a for [(dppen-*PP'*)H$_3$Re(μ-H)$_2$(μ-dppm)AgI] **2**

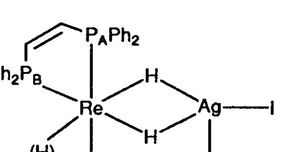
T/°C	δ(P$_A$)	δ(P$_B$)	δ(P$_C$)	δ(P$_D$)	^2J(P$_A$P$_B$)	^2J(P$_A$P$_C$)	^2J(P$_B$P$_C$)	^2J(P$_C$P$_D$)	^1J(AgP$_D$)
25	51.8		30.2	*ca.* −12^b		37		n.r.	n.r.
−50	52.1		31.0	−12.1		38		126	306^c 348^d
−80	50.1	54.2	31.0	*ca.* −12^b	n.r.	81	n.r.	125	n.r.

n.r. = Not resolved. ^{a}Recorded at 162 MHz in deuteriodichloromethane, unless otherwise stated; chemical shifts (δ) in ppm and coupling constants in Hz. ^{b} Broad resonance, couplings not resolved. ^{c} ^1J(^{107}AgP$_D$). ^{d} ^1J(^{109}AgP$_D$).

Table 5 ^{1}H NMR data^a for [(dppen-*PP'*)H$_3$Re(μ-H)$_2$(μ-dppm)AgI] **2**

	Hydrides			dppm		dppen	
T/°C	δ(H)^b	^2J(PH)^c	^2J(P$_D$H)	δ(H)	J(PH)^d	δ(H)	N^e
25	−6.10	15.8	6.9	3.38	18.3	7.43	56.2
−90	−5.35 (1) −5.79 (1) −6.95 (3)						

^{a} Recorded at 400 MHz in deuteriodichloromethane, unless otherwise stated; chemical shifts (δ) in ppm and coupling constants in Hz. ^{b} Values in parentheses refer to relative intensities. ^{c} ^2J(P$_A$H) ≈ ^2J(P$_C$H) = 15.8 Hz. ^{d} ^2J(P$_C$H) + ^2J(P$_D$H). ^{e} ^2J(PH) + ^3J(PH).



2

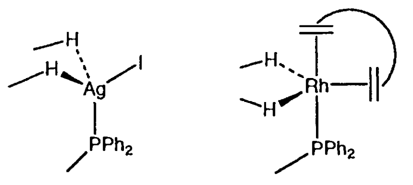
solution of the pentahydride complex [ReH$_5$(dppen-*PP'*)(dppm-*P*)] similarly gave a rhenium–silver bimetallic complex, tentatively formulated as [(dppen-*PP'*)H$_3$Re(μ-H)$_2$(μ-dppm)AgI] **2**, in 73% yield. The white microcrystalline solid was characterised by microanalysis (Table 1), and by ^{31}P-{^{1}H} and ^{1}H NMR spectroscopies (Tables 4 and 5). The fluxional behaviour of this complex was studied by variable-temperature ^{31}P-{^{1}H} NMR spectroscopy. At 25 °C, the 162 MHz ^{31}P-{^{1}H} NMR spectrum consisted of three resonances of relative intensities 2:1:1. A doublet of relative intensity two, at δ 51.8, was assigned to the two equivalent dppen phosphorus nuclei (P$_A$ and P$_B$), coupled to P$_C$ [^2J(P$_{A/B}$P$_C$) = 37 Hz]. Thus P$_A$ and P$_B$ were rapidly exchanging at this temperature (as in the rhenium–rhodium bimetallic complexes discussed above). The broad resonance at δ 30.2 was assigned to P$_C$, the dppm phosphorus nucleus co-ordinated to rhenium, and the broad resonance at δ *ca.* −12 to the dppm phosphorus nucleus co-ordinated to silver (P$_D$). The broadness of this resonance was attributed to the rapid exchange of the phosphorus (P$_D$) at silver which is common for silver–phosphine complexes.[8,13]

At −50 °C, the resonances due to P$_C$ and P$_D$ in the ^{31}P-{^{1}H} NMR spectrum were well resolved. The phosphorus P$_C$ gave rise to a sharp doublet of triplets, due to coupling to P$_{A/B}$ [^2J(P$_{A/B}$P$_C$) = 38 Hz] and to P$_D$ [^2J(P$_C$P$_D$) = 126 Hz]. The resonance assigned to P$_D$ was a doublet of doublet of doublets, at δ −12.1. It was split by coupling to P$_C$ and by additional coupling to the two isotopes of silver [^{107}Ag, $I = \frac{1}{2}$, 52%; ^{109}Ag, $I = \frac{1}{2}$, 48%; ^1J(^{107}AgP$_D$) = 306 Hz, ^1J(^{109}AgP$_D$) = 348 Hz]. These silver–phosphorus coupling constants were very similar to those found for the related complex [{(C$_6$H$_{11}$)$_3$P}$_2$H$_3$Re(μ-H)$_2$(μ-vdpp)AgI], whereas for the dppm-bridged rhenium–silver complex prepared by Shaw and co-workers,[8] the individual couplings of P$_D$ to ^{107}Ag and ^{109}Ag were not resolved. In the corresponding dppm-bridged complex, two isomers were present at low temperature (−90 °C), as in the related rhenium–rhodium bimetallics (see above),[9,10] whereas only a single isomer was found for **2**, as was the case for **1b** and **1d**. At −50 °C, the resonance (in **2**) due to P$_{A/B}$ was a broad singlet suggesting that the exchange of P$_A$ and P$_B$ had been slowed but not stopped, *i.e.* it was in an intermediate stage.

As the temperature was lowered the resonance due to P$_{A/B}$ decoalesced into two distinct peaks and at −80 °C P$_A$ and P$_B$ became inequivalent. The broad doublet at δ 50.1 was assigned to P$_A$, coupled to P$_C$ [^2J(P$_A$P$_C$) = 81 Hz], and the broad singlet at δ 54.2, to P$_B$. No coupling was resolved between P$_A$ and P$_B$ and the coupling between P$_B$ and P$_C$ was very small (< 10 Hz). The resonance due to P$_C$ was now a doublet of doublets, due to coupling to P$_A$ and to P$_D$. Thus P$_A$ was assigned as being transoid to P$_C$ and P$_B$ cisoid to P$_C$. Averaging the P$_A$–P$_C$ coupling (81 Hz) between P$_A$ and P$_B$ gave a value of 40.5 Hz [*cf.* ^2J(P$_{A/B}$P$_C$) = 38 Hz in the high-temperature limiting spectrum (at +25 °C)] and since ^2J(P$_B$P$_C$) was very small, and probably negative, it appeared that P$_A$ and P$_B$ simply exchanged with each other at the high-temperature limit. At −80 °C, the resonance due to P$_D$ was very broad and at −90 °C all the resonances had started to broaden. Thus the two independent fluxional processes, *i.e.* the exchange of P$_A$ and P$_B$ around rhenium and the exchange of P$_D$ around silver, showed different temperature dependence and were 'frozen out' at different temperatures, −80 and −50 °C respectively.

The 400 MHz ^{1}H NMR spectrum of **2**, at 25 °C, showed as its main features an apparent triplet at δ 3.38 and a doublet of apparent quartets at δ −6.10. In the ^{1}H-{^{31}P} NMR spectrum both resonances became singlets. The doublet of doublets, of intensity two, was assigned to the equivalent methylene protons of the dppm ligand, coupled to P$_C$ and P$_D$ [^2J(P$_C$H) + ^2J(P$_D$H) = 18.3 Hz], although separate couplings to P$_C$ and P$_D$ were not resolved. The doublet of apparent quartets of relative intensity five (*i.e.* no hydrides were lost on treatment of the pentahydride with AgI) was due to the hydrides which were all equivalent due to fluxionality and no coupling of the hydrides to either ^{107}Ag or ^{109}Ag was resolved. The hydrides were coupled to P$_A$, P$_B$ and P$_C$ [^2J(P$_{A/B}$H) ≈ ^2J(P$_C$H) = 15.8 Hz] and also to P$_D$ [^2J(P$_D$H) = 6.9 Hz]. The olefinic protons of the dppen ligand were observed as half of an AA'XX' pattern at δ 7.43 [^2J(PH) + ^3J(PH) = 56.2 Hz].

The temperature dependence of the ^{1}H-{^{31}P} NMR spectrum of **2** in the hydride region was studied. As the temperature was lowered the hydride resonance broadened and at −50 °C, began to decoalesce. By −90 °C, three separate resonances were observed, at δ −5.35, −5.79 and −6.95 of relative intensities



Scheme 2

1:1:3, respectively. This did not appear to be the low-temperature limiting spectrum since the resonance at δ −6.95, which was initially separated out at −70 °C, had broadened by −90 °C suggesting that at lower temperatures this resonance would decoalesce further. Shaw and co-workers[8] observed five separate resonances for the complex $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-}H)_2(\mu\text{-vdpp})AgI]$ for five inequivalent hydrides, two of which showed coupling to silver and were thus assigned as being due to bridging hydrides. Thus the resonances at δ −5.35 and −5.79 were tentatively assigned as being due to two bridging hydrides (although no coupling to silver was resolved) and the resonance at δ −6.95 to three terminal hydrides on rhenium which were still exchanging, around the rhenium centre, at −90 °C. However, we have no direct evidence for bridging hydrides and the formation of this complex as $[Re(\text{dppen-}PP')H_3Re(\mu\text{-}H)_2(\mu\text{-dppm})AgI]$ was based on the structures assigned to the related complexes.

For **2**, the hydrides showed coupling to the dppm phosphorus co-ordinated to silver (P_D) [$^2J(P_DH)$ = 6.9 Hz], a coupling which was not resolved for $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-}H)_2(\mu\text{-dppm})AgI]$ or $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-}H)_2(\mu\text{-vdpp})AgI]$. This may be indirect evidence for the formulation and we suggest that the observed splitting was more likely to be a $^2J(H_{\text{bridging}}P_D)$ coupling constant averaged with a $^4J(H_{\text{terminal}}P_D)$ coupling than a $^4J(H_{\text{terminal}}P_D)$ coupling constant for a structure with no bridging hydrides. Such coupling was not observed for the rhenium–rhodium complexes **1b** and **1d**, due to the H_b–M–P_D angle being *ca.* 90° at rhodium (trigonal bipyramidal) whereas this angle was increased at tetrahedral silver (Scheme 2).

Thus $[ReH_5(\text{dppen-}PP')(\text{dppm-}P)]$, like $[ReH_5\{P(C_6H_{11})_3\}_2(\text{L–L-}P)]$ (L–L = dppm or vdpp)[8–10] and $[ReH_5L_3]$ (L = PMe_2Ph or $PMePh_2$),[14] behaved as a tridentate ligand towards a second metal (rhodium or silver) to give stable bimetallic complexes. The compound $[ReH_5(\text{dppen-}PP')(\text{dppm-}P)]$ formed complexes with two bridging hydrides to rhodium, unlike $[ReH_5\{P(C_6H_{11})_3\}_2(\text{L–L-}P)]$ which formed complexes containing one bridging hydride and a metal–metal bond. Only one isomer was observed for the complexes derived from $[ReH_5(\text{dppen-}PP')(\text{dppm-}P)]$ due to the rigidity of the dppen backbone.

Experimental

General methods and instrumentation were as described in recent publications from this laboratory.[15]

$[(\text{dppen-}PP')H_3Re(\mu\text{-}H)_2(\mu\text{-dppm})Rh(\text{cod})]PF_6$ **1b**.—The compound $[Rh_2Cl_2(\text{cod})_2]$ (0.016 g, 0.032 mmol) was added to a solution of $[ReH_5(\text{dppen-}PP')(\text{dppm-}P)]$[11] (0.060 g, 0.062 mmol) in benzene (1.5 cm^3) and the resultant deep red solution was stirred for 1 h under dinitrogen. The solvent was then removed under reduced pressure and the residue dissolved in acetone (3 cm^3) and filtered. A solution of NH_4PF_6 (0.050 g, 3.0 mmol) in 1:1 water–ethanol (3 cm^3) was added slowly to the acetone solution until precipitation started and the mixture was then set aside at −20 °C for 24 h. The resultant precipitate was filtered off, washed with water and cold ethanol and dried. This gave the required product as a yellow microcrystalline solid. Yield: 0.060 g, 72%.

Complex $[(\text{dppen-}PP')H_3Re(\mu\text{-}H)_2(\mu\text{-dppm})Rh(\text{nbd})]PF_6$ **1d** was similarly prepared as a yellow microcrystalline solid from $[ReH_5(\text{dppen-}PP')(\text{dppm-}P)]$, $[Rh_2Cl_2(\text{nbd})_2]$ and NH_4PF_6 in 67% yield.

$[(\text{dppen-}PP')H_3Re(\mu\text{-}H)_2(\mu\text{-dppm})AgI]$ **2**.—Silver iodide (0.008 g, 0.034 mmol) was added to a solution of $[ReH_5(\text{dppen-}PP')(\text{dppm-}P)]$ (0.031 g, 0.032 mmol) in dichloromethane (1.2 cm^3) and the resultant mixture was stirred for 1 h under dinitrogen to give a pale yellow solution. Methanol (2 cm^3) was added and the mixture set aside at −20 °C for 24 h. The resultant precipitate was filtered off, washed with cold methanol and dried to give the required product as a white microcrystalline solid. Yield: 0.028 g, 73%.

Acknowledgements

We thank the SERC for a studentship (to T. P. L.) and for other support.

References

1 D. A. Roberts and G. L. Geoffrey, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, Ch. 40.
2 E. G. Lundquist and K. G. Caulton, *Inorg. Synth.*, 1990, **27**, 26.
3 J. W. Bruno, J. C. Huffman, M. A. Green and K. G. Caulton, *J. Am. Chem. Soc.*, 1984, **106**, 8310.
4 D. Baudry and M. Ephritikhine, *J. Organomet. Chem.*, 1986, **311**, 189.
5 J. T. Poulton, K. Folting and K. G. Caulton, *Organometallics*, 1992, **11**, 1364.
6 M. Cazanoue, Z. He, D. Neilbecker and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, 1991, 307.
7 S. W. Carr, E. H. Fowles, X. L. R. Fontaine and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1990, 573.
8 S. W. Carr, X. L. R. Fontaine and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1991, 1025.
9 S. W. Carr and B. L. Shaw, unpublished work.
10 E. H. Fowles and B. L. Shaw, unpublished work.
11 X. L. R. Fontaine, T. P. Layzell and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, in the press.
12 H. C. Volger, M. M. P. Gaasbeek, H. Hogeveen and K. Vrieze, *Inorg. Chim. Acta*, 1969, **3**, 145.
13 C. W. Alegranti and E. L. Muetterties, *J. Am. Chem. Soc.*, 1972, **94**, 6386.
14 L. F. Rhodes, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1983, **105**, 5137.
15 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1992, 1469.

Received 2nd September 1993; *Paper* 3/05266D