Bimetallic Complexes of Rhenium Multihydrides with Silver, Copper or Mercury containing Diphosphine Ligands

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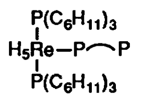
Treatment of the rhenium pentahydride complex [$ReH_5\{P(C_6H_{11})_3\}_2$(vdpp-*P*)] [vdpp = $Ph_2PC(=CH_2)PPh_2$], with silver iodide gives the fluxional complex [$\{(C_6H_{11})_3P\}_2H_3Re(\mu$-vdpp)$(\mu$-$H)_2AgI$]; the $Ph_2PCH_2PPh_2$ (dppm) complex [$ReH_5\{P(C_6H_{11})_3\}_2$(dppm-*P*)] behaves analogously. Analogous complexes were prepared with CuCl or CuCN, *e.g.* [$\{(C_6H_{11})_3P\}_2H_3Re(\mu$-dppm$)(\mu$-$H)_2Cu(CN)$]. The fluxionalities of these complexes were studied by ^{31}P-$\{^1H\}$ and ^1H-$\{^{31}P\}$ NMR spectroscopy over a range of temperatures. In contrast to the behaviour of silver iodide, copper(I) chloride or copper(I) cyanide, mercury(II) chloride reacts with [$ReH_5\{P(C_6H_{11})_3\}_2$(dppm-*P*)] to give an adduct, apparently [$HgCl_2\{ReH_5[P(C_6H_{11})_3]_2$(dppm-*P*)\}], in which the mercury is not complexed to the dppm but shows nuclear spin–spin coupling to the phosphorus atoms complexed to rhenium. The ^{31}P-$\{^1H\}$ and ^1H-$\{^{31}P\}$ NMR data are presented and discussed.

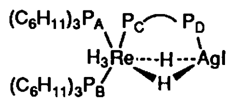
There has been much interest in the Lewis basicity of transition-metal multihydrides and the synthesis of complexes of multihydrides binding to a second metal. Complexes of rhenium, ruthenium, osmium and iridium polyhydrides have been reported with silver, copper, mercury, rhodium or zirconium. Thus, treatment of *fac*- or *mer*-[$IrH_3(PMe_2Ph)_3$] with [$Cu(NCMe)_4$]PF_6 or $AgBF_4$ gave near quantitative yields of *fac*- or *mer*-[$(PhMe_2P)_3HIr(\mu$-$H)_2Cu]PF_6$ or *fac*-[$(PMe_2Ph)_3HIr(\mu$-$H)_2Ag]BF_4$.[1] More complex species were formed by varying the iridium to copper stoichiometry.[2] Similarly, treatment of [$ReH_5(PMe_2Ph)_3$] or [$Re_2H_8(PMe_2Ph)_4$] with [$Cu(NCMe)_4$]PF_6 gave [$\{ReH_2(PMe_2Ph)_3(\mu$-$H)_3\}_2Cu]PF_6$, or the hexanuclear product [$Re_4Cu_2H_{16}(PMe_2Ph)_6][PF_6]_2$.[3] The rhenium heptahydride [$ReH_7(PPhPr^i{}_2)_2$] was found to react with $AgPF_6$, AgI, CuI or $HgCl_2$ to give 2:1 adducts. The osmium hexahydride [$OsH_6(PPhPr^i)_2$] was also reported to give a 2:1 adduct with $HgCl_2$.[4] Treatment of K[$ReH_6(PMe_2Ph)_2$] or K[$OsH_3(PMe_2Ph)_2$] with [$Zr(\eta$-$C_5H_5)(X)Cl$] gave [$Zr(\eta$-$C_5H_5)_2(X)\{ReH_6(PMe_2Ph)_2\}$] (X = OPr^i, H or Me) or [$Zr(\eta$-$C_5H_5)_2(X)\{OsH_3(PMe_2Ph)_2\}$] (X = halogen or H).[5] The zirconium–osmium complex has three bridging hydrides between the two metals. The complex [$ReH_7(PPh_3)_2$] reacts with KH to give [$K(thf)_2][ReH_6(PPh_3)_2$][6] and [$LiRuH_3(PPh_3)_3$] reacts with [$\{Rh(cod)Cl\}_2$] to give [$(cod)Rh(\mu$-$H)_3Ru(PPh_3)_3$] and then [$(cod)HRh(\mu$-$H)RuH(PPh_3)_3$] (cod = cycloocta-1,5-diene).

None of these complexes containing two or more different metals has a bridging diphosphine ligand between the two metals. However, in a previous paper[7] we have described that treatment of the rhenium heptahydride [$ReH_7\{P(C_6H_{11})_3\}_2$] with the diphosphines $Ph_2PC(=CH_2)PPh_2$ (vdpp) or $Ph_2PCH_2PPh_2$ (dppm) gives fluxional pentahydrides of the type [$ReH_5\{P(C_6H_{11})_3\}_2$(L-L-*P*)] (L-L = vdpp, **1a** or dppm, **1b**) in good yield. It seemed possible that we should be able to bond the uncomplexed phosphorus in these complexes to a second metal and thereby synthesize systematically new types of heterobimetallic complexes containing a rhenium multihydride moiety. In this paper we report some new heterobimetallic complexes formed by treating a complex of the type [$ReH_5\{P(C_6H_{11})_3\}_2$(L-L-*P*)] with silver, copper or mercury compounds.

Results and Discussion



1a P⌒P = vdpp
1b P⌒P = dppm



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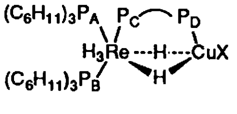

	P⌒P	X
3a	ydpp	Cl
3b	dppm	CN
3c	vdpp	Cl
3d	dppm	CN

Treatment of the rhenium pentahydride complex [$ReH_5\{P(C_6H_{11})_3\}_2$(vdpp-*P*)] with silver iodide in dichloromethane solution gave a hoped for rhenium-silver complex, which we formulate as [$\{(C_6H_{11})_3P\}_2H_3Re(\mu$-vdpp$)(\mu$-$H)_2AgI$] **2a**. Microanalytical data (C and H only) are given in Table 1. The ^{31}P-$\{^1H\}$ NMR spectrum at 21 °C consisted of one singlet and two multiplets [Fig. 1(*b*)]. The singlet is assigned to the two equivalent $P(C_6H_{11})_3$ groups, the doublet of triplets to the vdpp phosphorus bound to rhenium and the broad resonance at δ − 8.1 ppm to the vdpp phosphorus bound to silver; we attribute the broadness of this signal to rapid exchange of phosphorus (P_D) at silver, which is common for silver–phosphine complexes.[8] At −90 °C, P_D gave rise to a well-resolved doublet of doublets with additional coupling to the two silver isotopes [^{107}Ag, $I = \frac{1}{2}$, 52%; ^{109}Ag, $I = \frac{1}{2}$, 48%; $^1J(^{107}AgP)$ = 309, $^1J(^{109}AgP_A)$ = 346 Hz, Fig. 1(*a*)]. In addition P_C and P_D are mutually coupled, [$^2J(P_AP_B)$ = 145 Hz] and they show coupling to the inequivalent $P(C_6H_{11})_3$ ligands P_A and P_B. The resonances due to P_A and P_B were still poorly resolved at −90 °C. The NMR data (Table 2) showed the molecule to be fluxional at room temperature and also to be undergoing rapid phosphine exchange at silver. The ^1H-$\{^{31}P\}$ NMR spectrum at 21 °C showed resonances due to inequivalent $PC(=CH_2)P$ protons and a broad resonance at δ −6.50 of relative intensity five assigned to the hydrides, indicating that no hydride ligands

Table 1 Microanalytical and IR data

	Analysis[a] (%)				
Complex	C	H	N	X	ν(Re–H)[b]/cm^{-1}
2a	53.4 (53.85)	6.6 (6.8)		8.8 (9.1)	1962vw, br
2b	53.3 (53.4)	6.75 (6.85)		8.9 (9.25)	1986w, br
3a·0.33CH_2Cl_2	58.65 (58.65)	7.3 (7.4)		4.25 (4.6)	1975w, br
3b·CH_2Cl_2	58.5 (58.1)	7.4 (7.25)	0.9 (1.05)	5.2 (5.35)	1973w, br[c]
3c·0.5CH_2Cl_2	57.4 (57.8)	7.2 (7.4)		5.35 (5.5)	1960w, br
3d·0.75CH_2Cl_2	58.9 (58.5)	7.45 (7.4)	0.95 (1.1)	4.0 (4.1)	1970w, br[d]

[a] Calculated values in parentheses. [b] As KBr discs, w = weak, vw = very weak, br = broad and m = medium. [c] ν(C≡N) at 2137m cm^{-1}. [d] ν(C≡N) at 2123m cm^{-1}.

Table 2 $^{31}P-\{^1H\}$ NMR data[a,b]

		δ			Coupling constants/Hz				
Complex	T/°C	P_A/P_B	P_C	P_D	$^2J(P_AP_C)$	$^2J(P_CP_D)$	$^2J(P_BP_C)$	$^4J(P_AP_D)$	Other
2a	21	32.8	41.2	−8.1[c]	12	122			
	−90	31.2	38.4	−5.6	16	145	43	23	$^1J(^{109}AgP_D)$ 346
		33.0							$^1J(^{107}AgP_D)$ 309
2b	21	33.9	21.8	−8.3	10	86			$^1J(AgP_D) \approx 260$[d]
2b[e]	−90	38.9	18.7	−12.9		126			$^1J(AgP_D)$ 289
		24.5							
2b[f]	−90	38.2	19.4	−5.7		86			$^1J(AgP_D)$ 314
		28.2							
3a	21	33.9	40.8	−15.7	<2	156			
	−90	33.5	35.7	−14.8	≈40	154			
		31.8							
3b	21	34.4	37.3	−11.1	<2	149			
3b	−90	~32	~37	−11.8					
3c	21	34.1	16.5	−13.6[c]	<2				
3d	21	35.8	24.6	−9.4[c]	≈5				
4	22	33.7	14.0	−19.2	≈12				$^2J(HgP_A)$ 205 $^2J(HgP_C)$ 302

[a] Chemical shifts (δ) in ppm (±0.1 ppm) relative to 85% H_3PO_4 (positive to high frequency). Recorded at 162 MHz. [b] In CD_2Cl_2. [c] Very broad, couplings not resolved. [d] Separate couplings to ^{109}Ag and ^{107}Ag not resolved. [e] Major isomer. [f] Minor isomer.

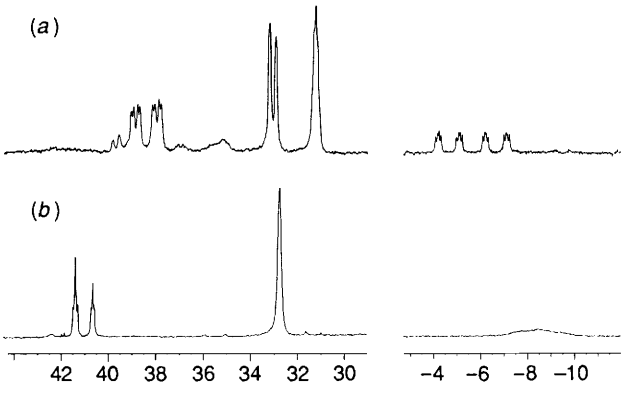

Fig. 1 The $^{31}P-\{^1H\}$ NMR spectrum of $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-vdpp})(\mu\text{-}H)_2AgI]$ **2a** in CD_2Cl_2 at (*a*) −90 and (*b*) −21 °C

were lost on treatment with silver iodide. At −90 °C there were five distinct but broad hydride resonances, two of which showed coupling to silver, although the separate couplings to silver-109 and silver-107 were not resolved (Fig. 2). We assign these two resonances to bridging hydrides; the values of J(AgH) are similar to those reported previously for bridging hydrides.[1] In the ^1H NMR spectrum at −90 °C the hydride resonances were broadened further, presumably by ^{31}P coupling, although no J(P–H) coupling constants could be resolved (Table 3). At intermediate temperatures, between 21 and −90 °C, the hydrides all broadened at approximately the same rate

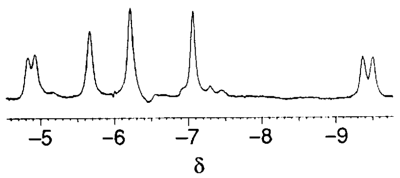

Fig. 2 The $^1H-\{^{31}P\}$ NMR spectrum of the hydride region of $[\{(C_6H_{11})_3P\}H_3Re(\mu\text{-vdpp})(\mu\text{-}H)_2AgI]$ **2a** in CD_2Cl_2 at −90 °C

indicating that hydride exchange occurs in a complicated manner. There was no evidence for a fluxional process involving distinct hydrides. The dppm analogue **2b** was prepared similarly to **2a**. In its $^{31}P-\{^1H\}$ and $^1H-\{^{31}P\}$ NMR spectra at 21 °C, phosphorus P_D showed coupling to silver and the hydride resonance was a doublet due to silver coupling. At −90 °C the $^{31}P-\{^1H\}$ and $^1H-\{^{31}P\}$ NMR spectra indicated the presence of two closely related species in a ratio of 5 : 1, presumably arising from isomers. The $^{31}P-\{^1H\}$ NMR spectrum of these two isomers both show three broad resonances, due to P_B, P_C and P_A, whilst P_D gave well-defined doublets of doublets with additional silver couplings (Table 2). We suggest that the major isomer has a similar structure to **2a**. For the minor isomer, only four hydride resonances, each of relative intensity one, were observed, one of which showed coupling to silver. The fifth one may be obscured by the hydride peaks of the major isomer. We suggest tentatively that it has a similar structure to **2a**, possibly with only one bridging hydride.

We have also prepared and characterised the corresponding adducts of the rhenium pentahydrides **1a** and **1b** with copper(I)

Table 3 ^1H-$\{^{31}P\}$ and selected ^1H NMR data[a,b]

		PCH$_2$P or PC(=CH$_2$)P		Hydrides	
Complex	T/°C	δ	J(PH)	δ	J(AgH)
2a	21	5.96	16.2, 19.0	−6.5[c]	
		5.58	11.6, 31.7		
	−90	6.0	15.7, 16.8	−4.88	39[d]
		5.74	11.0, 31.0	−5.67	
				−6.22	
				−7.07	
				−9.45	54[d]
2b	21	2.86	8.8	−6.89	18[d]
2b[e]	−90	[f]		−5.1	46[d]
				−6.86	
				−7.01	
				−7.12	
				−8.92	58
2b[g]	−90	[f]		−5.27	
				−5.87	45
				−6.62	
				−8.20	
3a	21	5.69		−6.57[c]	
		5.71			
	−90	5.87		−5.36	
		5.93		−5.55	
				−6.06	
				−6.68	
				−10.0	
3b	21	6.0		−6.66	
	−90	5.86		−5.51[h]	
		5.78		−6.58	
				−10.67	
3c	21	2.73		−7.33	
3d[i]	21	2.75	9.5	−7.13	
4	21	3.27	2.7	−6.0[c]	

[a] In CD_2Cl_2. [b] Chemical shifts (δ) (±0.01) relative to tetramethylsilane; coupling constants (J) in Hz (±0.2 Hz). Measured at 400 MHz. [c] Broad, couplings not resolved. [d] Separate couplings to ^{109}Ag and ^{107}Ag not resolved. [e] Major isomer. [f] PCH$_2$P proton resonances obscured by cyclohexyl resonances. [g] Minor isomer. [h] Very broad signal; integrates for three hydrogens. [i] $J(P_C$–$H) = 12$, $J(P_A$–$H) = 20$.

chloride and copper(I) cyanide. These adducts are formulated as $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-vdpp})(\mu\text{-}H)_2CuCl]$ **3a**, $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-vdpp})(\mu\text{-}H)_2Cu(CN)]$, **3b** $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-dppm})(\mu\text{-}H)_2CuCl]$ **3c**, and $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-dppm})(\mu\text{-}H)_2Cu(CN)]$ **3d** and are assigned a similar structure to **2a**. Preparative details for these four adducts are in the Experimental section and characterising data are given in Tables 1–3. In the ^{31}P-$\{^1H\}$ NMR spectrum of **3a** at 21 °C there is a singlet due to the $P(C_6H_{11})_3$ ligands, a doublet for P_C and a very broad resonance for P_D. Broadening of the resonance due to P_D could arise from chemical exchange at the copper or slow quadrupolar relaxation of the copper (^{63}Cu, $I = \frac{3}{2}$, 69%; ^{65}Cu, $I = \frac{3}{2}$, 31%). At −90 °C the ^1H-$\{^{31}P\}$ NMR spectrum of **3a** showed five broad ($w_{\frac{1}{2}} \approx 50$ Hz) hydride resonances with similar chemical shifts to those of **2a**, (Table 3). The cyanide complex **3b** gave broad resonances in its ^{31}P-$\{^1H\}$ and ^1H-$\{^{31}P\}$ NMR spectra at −90 °C. This complex showed a medium intensity ν(CN) band at 2137 cm^{-1}; this frequency is typical of a terminal cyanide stretching vibration.

In contrast to the behaviour with silver or copper, treatment of complex **1b** with mercury(II) chloride gave a colourless oil, which from ^{31}P-$\{^1H\}$ NMR evidence, contained only one phosphorus containing species which we formulate tentatively as $[HgCl_2\{ReH_5[P(C_6H_{11})_3]_2(\text{dppm-}P)\}]$ **4**. The ^{31}P-$\{^1H\}$ NMR spectrum gave three multiplets in essentially the same positions as for **1b**; both the $P(C_6H_{11})_3$ resonance and the P_C resonance show ^{199}Hg satellites (^{199}Hg, $I = \frac{1}{2}$, 16%), whilst P_D showed no discernable coupling to mercury (Table 2). The hydride resonance consisted of a very broad singlet of relative intensity five, at δ −6.0 at 21 °C. At lower temperatures (down to −50 °C) the signal remained broad. We suggest that the mercury is bound indirectly to the rhenium but not *via* P_D. Perhaps the mercury is bound in a similar fashion to that found in the adduct $[HgCl_2\{ReH_7(PPhPr^i{}_2)_2\}]$ in which Hg is coupled to both H and ^{31}P at room temperature.[4]

Experimental

The experimental techniques were as described previously.[9]

Preparations.—$[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-vdpp})(\mu\text{-}H)_2AgI]$ **2a**. Silver iodide (0.045 g, 0.19 mmol) was added to a solution of $[ReH_5\{P(C_6H_{11})_3\}_2(\text{vdpp-}P)]$ (0.200 g, 0.17 mmol) in dichloromethane (5 cm^3) and the resultant mixture was then stirred for 2 h, to give a pale yellow solution. Addition of methanol to this solution gave the required product as pale yellow plates. Yield 0.12 g, 51%.

$[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-dppm})(\mu\text{-}H)_2AgI]$ **2b**. This was made in an analogous fashion to **2a** and formed white needles in 53% yield.

$[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-vdpp})(\mu\text{-}H)_2CuCl]$ **3a**. A mixture of CuCl (0.012 g, 0.13 mmol) and $[ReH_5\{P(C_6H_{11})_3\}_2(\text{vdpp-}P)]$ (0.15 g, 0.13 mmol) in dichloromethane (3 cm^3) was stirred for 2 h, by which time the CuCl had dissolved and a pale yellow solution was obtained. Methanol (10 cm^3) was then added and the volume of the solution was reduced to 5 cm^3, to give the required product as pale yellow microcrystals. Yield 0.75 g, 46%.

The complexes $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-vdpp})(\mu\text{-}H)_2Cu(CN)]$ **3b**, $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-dppm})(\mu\text{-}H)_2CuCl]$ **3c** and $[\{(C_6H_{11})_3P\}_2H_3Re(\mu\text{-dppm})(\mu\text{-}H)_2Cu(CN)]$ **3d** were prepared similarly, in yields of 28, 51 and 56% respectively.

$[HgCl_2\{ReH_5[P(C_6H_{11})_3]_2(\text{dppm-}P)\}]$ **4**. A mixture of mercury(II) chloride (0.048 g, 0.18 mmol) and $[ReH_5\{P(C_6H_{11})_3\}_2(\text{dppm-}P)]$ (0.20 g, 0.18 mmol) was heated in dry toluene (2 cm^3) to give a colourless solution. The mixture was evaporated to low volume *in vacuo*, to give a colourless oil, which did not crystallize but was investigated by NMR spectroscopy (see Results Discussion section). The formation of **4** appeared to be quantitative, from ^{31}P-$\{^1H\}$ NMR spectroscopy.

Acknowledgements

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