Bimetallic Complexes of Platinum, Rhodium, or Copper bridged by $Ph_2PCH_2PPh_2$ or $Ph_2PC(=CH_2)PPh_2$ to Diazenidorhenium Groups; Crystal Structure of $[(4\text{-}MeC_6H_4N_2)ClRe(\mu\text{-}dppm)_2(\mu\text{-}CO)PtCl]\cdot 2Me_2CO$ †

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Treatment of $[ReCl(CO)(N_2C_6H_4Me\text{-}4)(dppm\text{-}PP')(dppm\text{-}P)][PF_6]$ (dppm = $Ph_2PCH_2PPh_2$) with *trans*-$[PtH(Cl)(PPh_3)_2]$ gave the neutral, rhenium–platinum complex $[(4\text{-}MeC_6H_4N_2)ClRe(\mu\text{-}dppm)_2(\mu\text{-}CO)PtCl]$ (**2a**); the analogous vdpp complex (**2b**) was made similarly [vdpp = $Ph_2PC(=CH_2)PPh_2$]. Complex (**2b**) was methylated on treatment with trimethyloxonium tetrafluoroborate to give the hydrazidorhenium complex $[\{(4\text{-}MeC_6H_4)MeNN\}ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl][BF_4]$ (**3**). Treatment of complex (**2b**) with $HBF_4\cdot Et_2O$ gave $[\{(4\text{-}MeC_6H_4)HNN\}ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl][BF_4]$ (**4**). The complex $[ReCl(CO)(N_2C_6H_4Me\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][BF_4]$ reacted with $[Rh_2Cl_2(CO)_4]$ to give $[(4\text{-}MeC_6H_4N_2)(OC)ClRe(\mu\text{-}vdpp)_2(\mu\text{-}Cl)Rh(CO)][BF_4]$ (**5a**); the analogous 4-fluorophenyldiazenido-(**5b**) and 4-methoxyphenyldiazenido-(**5c**) complexes were prepared similarly. Treatment of *trans*-$[ReCl(CO)(vdpp\text{-}PP')_2]$ with $[Rh_2Cl_2(CO)_4]$ gave a mixture of two complexes, which when treated with toluene-*p*-diazonium tetrafluoroborate gave, eventually, (**5a**) in essentially quantitative yield *via* a mixture of three complexes, one of which was (**5a**). Treatment of $[ReCl(CO)(N_2C_6H_4Me\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][PF_6]$ with CuCl gave a rhenium–copper complex $[(4\text{-}MeC_6H_4N_2)(OC)Re(\mu\text{-}vdpp)_2(\mu\text{-}Cl)CuCl][PF_6]$ (**6a**). Corresponding complexes were made containing the 4-fluoro- and the 4-methoxy-phenyldiazenido groups, and $[(4\text{-}FC_6H_4N_2)(OC)Re(\mu\text{-}vdpp)_2(\mu\text{-}Cl)Cu(CN)][PF_6]$ was made using CuCN. $^{31}P\text{-}\{^1H\}$, $^1H\text{-}\{^{31}P\}$, and ^1H n.m.r. and i.r. data are given; some of the AA′XX′ $^{31}P\text{-}\{^1H\}$ n.m.r. spectra showed 18—20 peaks (or 9—10 for the half pattern) and were analysed fully. Crystals of complex (**2a**) were orthorhombic, space group $P2_12_12_1$, a = 1 187.5(1), b = 1 898.2(2), c = 2 664.2(4) pm, and Z = 4; final R factor 0.0353 for 3 972 observed reflections.

We have recently reported convenient syntheses of diazenidorhenium complexes of the types $[ReCl(CO)(N_2C_6H_4Y\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][X]$ and $[ReCl(CO)(N_2C_6H_4Y\text{-}4)(dppm\text{-}PP')(dppm\text{-}P)][X]$, with Y = CH_3, F, or CH_3O, vdpp = $Ph_2PC(=CH_2)PPh_2$, dppm = $Ph_2PCH_2PPh_2$, and X = PF_6 or BF_4.[1] These complexes were prepared by treating bis chelates of the type *trans*-$[ReCl(CO)(diphosphine\text{-}PP')_2]$ with an arenediazonium salt, upon which one of the chelate rings opened up and became monodentate. Compounds of the type *fac*- or *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Cr, Mo, or W) or of type *cis*-,*mer*-$[MnX(CO)_2(dppm\text{-}PP')(dppm\text{-}P)]$ (X = Cl or Br) react with many metal complexes to give heterobimetallics containing the moiety $M^1(\mu\text{-}dppm)_2M^2$ (M^1 = Cr, Mo, W, or Mn; M^2 = a metal such as Pt, Pd, Rh, Ir, Cu, Ag, *etc.*).[2–4] We now report attempts to effect similar ring-opening reactions of the second chelate ring in diazenidorhenium complexes of type $[ReCl(CO)(N_2C_6H_4Y\text{-}4)(diphosphine\text{-}PP')(diphosphine\text{-}P)][X]$ (above) by treatment with substitution-labile complexes of Pt, Pd, Rh, Ir, Cu, or Ag.

Results and Discussion

Treatment of $[ReCl(CO)(N_2C_6H_4Me\text{-}4)(dppm\text{-}PP')(dppm\text{-}P)][PF_6]$ (**1a**) with *trans*-$[PtH(Cl)(PPh_3)_2]$ in refluxing acetone gave the mixed, neutral, rhenium–platinum complex $[(4\text{-}MeC_6H_4N_2)ClRe(\mu\text{-}dppm)_2(\mu\text{-}CO)PtCl]$. The structure of this compound (**2a**) was determined by *X*-ray diffraction and is discussed in detail below. The elemental analytical data and i.r. data are given in Table 1. The $^{31}P\text{-}\{^1H\}$ n.m.r. pattern is of the AA′XX′ + AA′MXX′ (M = Pt) type (Table 2). The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum showed a methyl resonance for the $4\text{-}CH_3C_6H_4$ protons and an AA′XX′ pattern for the four aromatic protons of the 4-methylphenyldiazenido ligand. Somewhat surprisingly, the resonance of the PCH_2P protons at 20 °C consisted of a singlet but the complex was too insoluble for low-temperature studies. We suggest that the two CH_2 protons happen to have the same chemical shift. The i.r. spectrum (Nujol mull) showed a total of three bands due to carbonyl and diazenido ligands (Table 1) instead of the two bands expected. The complex was too insoluble to obtain a suitable i.r. spectrum in solution and we suggest that the extra band was due to a solid-state effect.

Treatment of *mer*-$[ReCl(CO)(N_2C_6H_4Me\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][PF_6]$ (**1b**) with *trans*-$[PtH(Cl)(PPh_3)_2]$ in refluxing acetone similarly gave $[(4\text{-}MeC_6H_4N_2)ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl]$ (**2b**), analogous to (**2a**). This structure follows from the microanalytical and i.r. data (Table 1) and from the n.m.r. data (Table 2). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed an AA′XX′ + AA′MXX′ (M = ^{195}Pt) pattern, with the phosphorus atoms bonded to rhenium giving a broader pattern than those bonded to platinum: this broadening was in part due to coupling to ^{195}Pt but also probably due to quadrupolar relaxation (^{185}Re, $I = \frac{5}{2}$, 37% abundant; ^{187}Re, $I = \frac{5}{2}$, 63% abundant). The observation of the outer (very weak) lines of the high-frequency (Pt-bonded) part of the AA′XX′ pattern enabled $K = |J(AA') + J(XX')|$, $L = |J(AX) - J(AX')|$, $M = |J(AA') - J(XX')|$, and $N = |J(AX) + J(AX')|$ to be measured.[5] Since couplings ^2J(P–M–P) (*trans*) (M = metal) are normally large and positive we were able to calculate $J(AA')$ and $J(XX')$ and also, since $^2J[PC(=CH_2)P]$ is positive,[6] we could calculate $J(AX)$ and $J(AX')$ (Table 2). In the $^1H\text{-}\{^{31}P\}$ n.m.r. pattern the vinylidene $[PC(=CH_2)P]$ protons showed two singlets, one

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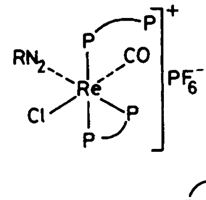
† Bis-μ-[1,2-bis(diphenylphosphino)methane]-μ-carbonyl-1,2-dichloro-2-*p*-tolyldiazenidoplatinumrhenium (*Pt–Re*)-acetone (1/2).

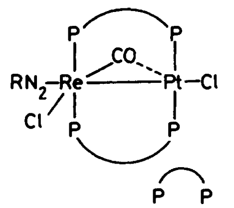
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Infrared (cm^{-1})[a] and microanalytical data[b]

Complex	I.r. ν(CO)	I.r. ν(NN)	Analysis/% C	H	N	Cl
(2a)[c]	1 784m, 1 748m, 1 709s		50.4(50.9)	4.1(3.75)	1.8(2.05)	5.45(5.2)
(2b)[c]	1 752s, 1 747(sh)		51.75(51.75)	3.85(3.7)	1.8(2.0)	4.85(5.1)
(2c)[c]	1 765(sh), 1 745s		50.5(50.5)	3.75(4.0)	1.65(2.0)	5.15(5.05)
(3)	1 765s	*d*	48.95(49.05)	3.55(3.65)	1.8(1.85)	4.45(4.75)
(4)[e]	1 785m	*d*	48.45(47.9)	3.45(3.45)	1.85(1.85)	6.55(6.95)
(5a)	[f] 2 080w, 1 962s	1 715s	51.9(51.6)	3.7(3.6)	1.9(1.95)	5.15(4.9)
	[g] 2 080w, 2 065w, 1 982s, 1 963s, 1 936m,	1 715s	51.7(51.6)	3.5(3.6)	1.8(1.95)	5.05(4.9)
(5b)	2 082w, 1 970s	1 722s	48.4(48.7)	3.25(3.25)	1.65(1.9)	4.85(4.8)
(5c)	2 082w, 1 968s	1 719s	48.7(48.7)	3.35(3.4)	1.8(1.85)	4.85(4.7)
(6a)	1 980s	1 715s	53.7(53.5)	3.9(3.8)	2.2(2.1)	5.35(5.25)
(6b)	1 980s	1 720s	50.9(50.3)	3.45(3.45)	2.0(2.0)	4.8(5.0)
(6c)·$0.25CH_2Cl_2$[h]	1 997s	1 710s	50.5(50.9)	3.3(3.45)	3.1(3.0)	3.2(3.7)
(6d)	1 968s	1 719s	49.9(50.7)	3.55(3.6)	2.05(1.95)	5.45(5.0)

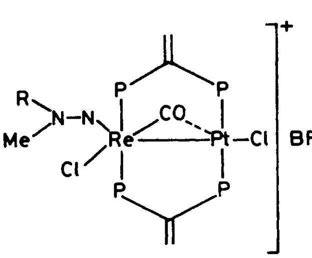
[a] As Nujol mulls; s = strong, m = medium, w = weak, and sh = shoulder. [b] Calculated values in parentheses. [c] We could not assign which band is due to ν(CO) and which to ν(NN). [d] Not observed. [e] ν(NH) at 2 620w cm^{-1}. [f] Product formed from complexes **(1b)** and $[Rh_2Cl_2(CO)_4]$, see Discussion section. [g] Product mixture formed from *trans*-[ReCl(CO)(vdpp-*PP′*)$_2$], $[Rh_2Cl_2(CO)_4]$, and $[4\text{-}MeC_6H_4N_2][BF_4]$, see Discussion section. [h] The presence of CH_2Cl_2 of crystallization was confirmed by ^1H n.m.r. spectroscopy; ν(CN) at 2 135w cm^{-1}.



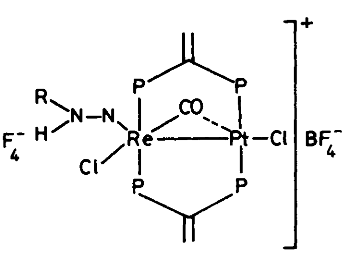


	R	P⌒P
(1a)	C_6H_4Me-4	dppm
(1b)	C_6H_4Me-4	vdpp
(1c)	C_6H_4F-4	vdpp
(1d)	C_6H_4OMe-4	vdpp

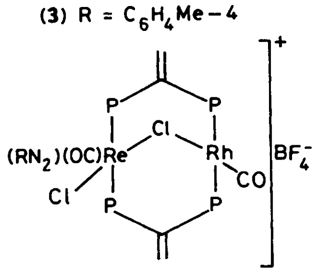
	R	P⌒P
(2a)	C_6H_4Me-4	dppm
(2b)	C_6H_4Me-4	vdpp
(2c)	C_6H_4F-4	vdpp

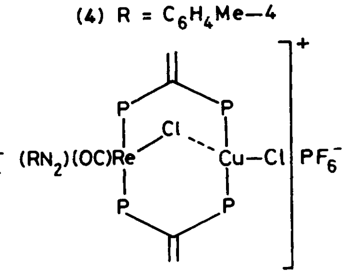


(3) R = C_6H_4Me-4



(4) R = C_6H_4Me-4





	R
(5a)	C_6H_4Me-4
(5b)	C_6H_4F-4
(5c)	C_6H_4OMe-4

	R	X
(6a)	C_6H_4Me-4	Cl
(6b)	C_6H_4F-4	Cl
(6c)	C_6H_4F-4	CN
(6d)	C_6H_4OMe-4	Cl

for each of the non-equivalent hydrogens, and the aromatic hydrogens of the 4-methylphenyldiazenido group gave two chemical shifts and *N* was readily measured (Table 2). In the ^1H n.m.r. spectrum, the vinylidene (=CH_2) protons gave a complex second-order pattern, whilst the aromatic methylphenyldiazenido hydrogens were not coupled to phosphorus. In the i.r. spectrum (Nujol mull) a strong band at 1 752 cm^{-1} and a shoulder at 1 747 cm^{-1} were assigned to ν(N=N) and ν(C=O). The closely related 4-fluorophenyldiazenido complex $[(4\text{-}FC_6H_4N_2)ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl]$ was prepared similarly and assigned an analogous structure **(2c)**. Preparative details are in the Experimental section and characterizing data in Tables 1 and 2. This complex gave a well defined AA′XX′ + AA′MXX′ $^{31}P\text{-}\{^1H\}$ n.m.r. pattern at 162 MHz, shown in Figure 1.

Singly bent diazenido complexes of the type discussed above might be expected to undergo electrophilic attack at N_β (*viz.* $RN_\beta N_\alpha M$), to give hydrazido complexes.[7] Accordingly, we tried to methylate the aryldiazenido complex **(2a)** with trimethyloxonium tetrafluoroborate and found that the hoped for methylation occurred. The product was formulated as the hydrazidorhenium complex $[\{(4\text{-}MeC_6H_4)MeNN\}ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl][BF_4]$ **(3)** on the basis of microanalytical and spectroscopic data (Tables 1 and 2). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum was of the AA′XX′ type with satellites due to ^{195}Pt, whilst in the $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum there were resonances due to $CH_3C_6H_4$ and $CH_3(R)N_2$ and P(=CH_2)P. A band at 1 765 cm^{-1} (Nujol) in the i.r. spectrum was assigned to the semi-bridging carbonyl ligand.

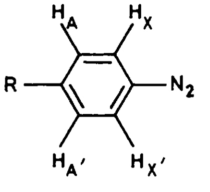
We also found that we could protonate the nitrogen of the diazenido ligand in **(2b)**. Treatment of $[(4\text{-}MeC_6H_4N_2)ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl]$ **(2b)** with $HBF_4 \cdot Et_2O$ gave $[\{(4\text{-}MeC_6H_4)HNN\}ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl][BF_4]$ **(4)**. This structure is supported by the presence of a broad, weak band at 2 620 cm^{-1}, in the i.r. spectrum, assigned to ν(NH).

We have also been successful in synthesizing heterobimetallic complexes of rhenium with rhodium and copper by chelate ring-opening reactions of compounds of type **(1)**. Treatment of **(1b)** with $[Rh_2Cl_2(CO)_4]$ rapidly gave a mixed rhenium–rhodium complex as deep red microcrystals. This complex was formulated as $[(4\text{-}MeC_6H_4N_2)(OC)ClRe(\mu\text{-}vdpp)_2(\mu\text{-}Cl)Rh(CO)][BF_4]$ **(5a)**. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed the expected AA′MXX′ spin system and was sufficiently

Table 2. The $^{31}P-\{^1H\}$, $^1H-\{^{31}P\}$, and ^1H n.m.r. data

					$^1H-\{^{31}P\}^{b,c}$				
	$^{31}P-\{^1H\}^{a,b}$				RN_2 ^{g}				
Complex	$\delta(P_A)^d$	$\delta(P_X)^d$	$^1J(MP)^e$	'N' or J^f	$\delta(CH_3)$	$\delta(H_A)$	$\delta(H_X)$	'N'	$\delta[PCH_2P$ or $PC(CH_2)P]$
(2a)	−0.7	17.0	3 021	'N' 95	2.19	6.73	6.37	8.0	4.22
(2b)	10.4	27.5	3 167	AX 137, AX′ 13	2.17	6.62	6.10	8.5	6.10, 5.42
(2c)	9.8	27.7	3 161	AX 137, AX′ 13		6.49[h]	6.13[h]	9.1	6.10, 6.09
(3)	1.5	26.4	2 830	'N' 147	2.26[i]	6.92	6.24	8.7	6.52, 6.38
(4)	4.4	25.4	2 642	AX 132, AX′ 13 AA′ 340, XX′ 263	2.18	6.70	6.07	8.0	6.39, 6.32
(5a)	[j] 11.2	41.8	114	AX 43, AX′ −4 AA′ 340, XX′ 200	2.27	6.77	6.10	8.6	6.96,[k] 6.30[l]
	[m] 11.2	41.8	114	'N' 39	n	n	n	n	n
	8.7	31.7	112	'N' 70					
	11.7	29.8	105	'N' 105					
(5b)	11.0	41.8	112	'N' 39		6.68[o]	6.19[o]	9.2	6.97, 6.42
(5c)	11.2	42.0	112	'N' 39	3.66	6.49	6.15	9.1	6.96, 6.38
(6a)	14.0	8.4		'N' 63	2.29	6.81	6.22	8.5	6.84, 6.49
(6b)	13.5	8.2		AX 67, AX′ −2 AA′ 226, XX′ 73[p]		6.71[q]	6.29[q]	9.1	6.83, 6.50
(6c)	10.4	4.8		AX 82, AX′ −2 AA′ 199, XX′ 90		6.67[r]	6.20[r]	8.5	6.86, 6.37
(6d)	13.7	8.2		'N' 63	3.67	6.52	6.25	9.0	6.83, 6.48

[a] Measured at 162 MHz. Chemical shifts (δ) in p.p.m. (±0.1 p.p.m.) relative to 85% H_3PO_4 (positive to high frequency). [b] In CD_2Cl_2 solution at 21 °C, unless stated otherwise. [c] Measured at 400 MHz. Chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) relative to tetramethylsilane; coupling constants (J) in Hz (±0.2 Hz). [d] P_A is the phosphorus atom bonded to rhenium and P_X that bonded to platinum, rhodium, or copper, respectively; the two make up an AA′XX′ spin system with further coupling to Pt or Rh. [e] M = platinum-195 or rhodium-103. [f] 'N' = $^2J(AX) + {}^4J(AX')$; AX in the Table represents $^2J(AX)$, AX′ represents $^4J(AX')$, AA′ represents $^2J(AA')$, and XX′ represents $^2J(XX')$. [g] The diazenide protons make up an AA′XX′ system and 'N' = $^2J(AX) + {}^4J(AX')$ where H_A, $H_{A'}$, H_X, and $H_{X'}$ are as designated:



R = Me, F, or OMe

[h] $^3J(FH_A) = 8.8$, $^4J(FH_X) = 5.1$ Hz. [i] $\delta(NCH_3)$ 2.73 p.p.m. [j] Product from complexes (**1b**) and $[Rh_2Cl_2(CO)_4]$ (see text). [k] $^3J(P_AH)$ 17.4, $^3J(P_XH)$ 29.2 Hz. [l] $^3J(P_AH)$ 33.9, $^3J(P_XH)$ 17.7 Hz. [m] Product prepared from *trans*-$[ReCl(CO)(vdpp\text{-}PP')_2]$, $[Rh_2Cl_2(CO)_4]$, and $[4\text{-}MeC_6H_4N_2][BF_4]$ (see text). [n] Not assigned because of overlapping resonances. [o] $^3J(FH_A)$ 8.7, $^4J(FH_X)$ 4.8 Hz. [p] Coupling constants ±0.3 Hz. [q] $^3J(FH_A)$ 8.0, $^4J(FH_X)$ 4.7 Hz. [r] $^3J(FH_A)$ 8.4, $^4J(FH_X)$ 4.5 Hz.

well defined to calculate $J(AX)$, $J(AX')$, $J(XX')$, and $J(AA')$[5] (Table 2). The $^1H-\{^{31}P\}$ n.m.r. spectrum showed resonances for the diazenido and the vinylidene protons. In the ^1H n.m.r. spectrum the vinylidene protons gave second-order multiplets. Using selective $^1H-\{^{31}P\}$ decoupling experiments we were able to measure $^3J(PC{=}CH_2)$ values (Table 2); one value (presumably due to *trans* coupling) was larger than the other (*cis* coupling). The i.r. spectrum (Nujol mull) showed two bands assigned to carbonyl ligands; the more intense band (at 1 962 cm^{-1}) was assigned to terminal CO on rhenium and the band at 2 080 cm^{-1} was assigned to ν(CO) on rhodium. There was also a strong diazenido band at 1 715 cm^{-1}. The frequency of this band (Table 1) is similar to that for compound (**1b**) and thus we suggest the diazenido ligand is acting as a three-electron donor to rhenium. We tentatively suggest that (**5a**) may have a bridging chloride ligand. The analogous 4-fluorophenyldiazenido- (**5b**) and 4-methoxyphenyldiazenido- (**5c**) complexes were prepared and characterized similarly; preparative details are in the Experimental section and characterizing data are given in Tables 1 and 2. The 4-methylphenyldiazenidorhenium–rhodium complex (**5a**) was also prepared by a different route. Treatment of *trans*-$[ReCl(CO)(vdpp\text{-}PP')_2]$ with $[Rh_2Cl_2(CO)_4]$ gave an orange solution, which $^{31}P-\{^1H\}$ n.m.r. spectroscopy showed to contain a mixture of two complexes, each with a Re(μ-vdpp)$_2$Rh moiety, in the approximate ratio of 3:1. The major complex had $\delta_P = -0.4$ (Re), 21.6 (Rh) p.p.m., 'N' = 49 Hz, and $^1J(RhP) = 111$ Hz; and the minor complex $\delta_P = -3.9$ (Re), 19.1 (Rh) p.p.m., 'N' = 31 Hz, and $^1J(RhP) = 119$ Hz. Treatment of this orange solution with toluene-*p*-diazonium tetrafluoroborate gave a mixture of three closely related complexes in the ratio of 2:1:1, with the formulation $[(4\text{-}MeC_6H_4N_2)(OC)ClRe(\mu\text{-}vdpp)_2(\mu\text{-}Cl)Rh(CO)][BF_4]$, based on microanalytical, n.m.r., and i.r. data (Tables 1 and 2). The spectroscopic data showed that the predominant species was the same as that prepared by treating (**1a**) with $[Rh_2Cl_2(CO)_4]$ and, after 4 d in dichloromethane solution, this

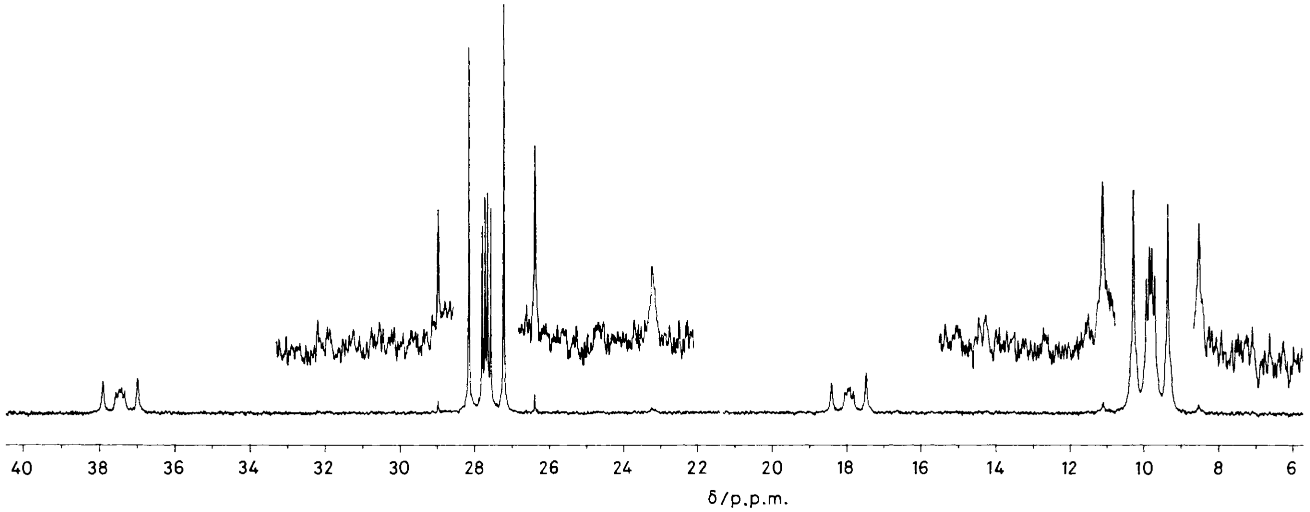


Figure 1. The $^{31}P-\{^1H\}$ n.m.r. spectrum of complex (**2c**) recorded at 162 MHz and 21 °C in CD_2Cl_2, showing the AA′XX′ + AA′MXX′ (M = ^{195}Pt) pattern. The Pt-bonded phosphorus, P_X, absorbs at 27.7 p.p.m. and the Re-bonded phosphorus, P_A, at 9.8 p.p.m.

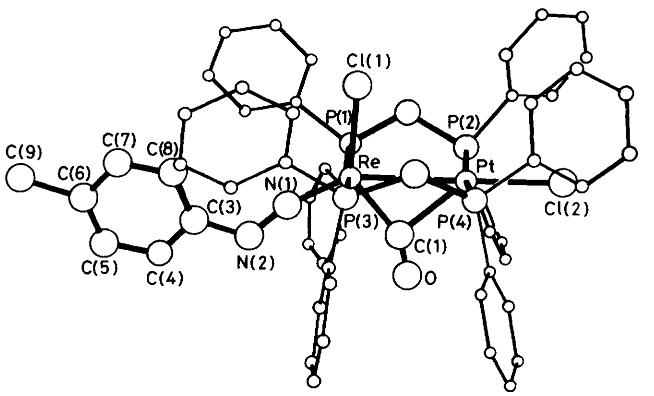


Figure 2. Molecular structure of $[(4-MeC_6H_4N_2)ClRe(\mu-dppm)_2(\mu-CO)PtCl]$ (**2a**) showing the principal atomic numbering

Table 3. Selected bond lengths (pm) and angles (°) for complex (**2a**)

Pt–Re	285.9(4)		
Cl–Re	244.1(6)	Cl(2)–Pt	240.8(6)
P(1)–Re	243.0(6)	P(2)–Pt	230.3(6)
P(3)–Re	243.1(6)	P(4)–Pt	230.6(6)
C(1)–Re	191.8(17)	C(1)–Pt	220.8(17)
N(1)–Re	178.6(14)	C(3)–N(2)	141.6(16)
N(2)–N(1)	127.0(18)		
O–C(1)	117.0(18)		
Cl(1)–Re–Pt	87.8(2)	Cl(2)–Pt–Re	179.8(2)
P(3)–Re–P	170.0(1)	P(4)–Pt–P(2)	166.3(1)
C(1)–Re–Pt	50.5(6)	C(1)–Pt–Re(1)	42.1(4)
C(1)–Re–Cl(1)	138.3(5)	C(1)–Pt–Cl(2)	138.1(4)
N(1)–Re–Pt	151.5(4)	O–C(1)–Pt	114.2(12)
N(1)–Re–C(1)	101.0(7)	C(3)–N(2)–N(1)	119.2(14)
N(1)–Re–Cl(1)	120.7(5)		
Pt–C(1)–Re	87.4(7)		
O–C(1)–Re	158.4(13)		
N(2)–N(1)–Re	164.3(11)		

mixture was quantitatively converted into complex (**5a**). It seems likely that the other two complexes and (**5a**) are isomers produced by having the four ligands, RN_2, Cl, CO, and CO, in different positions around the $Re(\mu-vdpp)_2Rh$ moiety.

Treatment of $[ReCl(CO)(N_2C_6H_4Me-4)(vdpp-PP')(vdpp-P)][PF_6]$ with CuCl in dichloromethane for 24 h at 20 °C gave $[(4-MeC_6H_4N_2)(OC)Re(\mu-vdpp)_2(\mu-Cl)CuCl][PF_6]$ (**6a**) as red microprisms, in 80% yield. This formulation follows from the elemental analytical and i.r. data (Table 1) and the n.m.r. data (Table 2). The $^{31}P-\{^1H\}$ n.mr. spectrum showed an AA′-XX′ pattern with an '*N*' doublet separation of 63 Hz and there were well defined proton resonances for the vdpp and 4-methylphenyldiazenido ligands (Table 2). Similar treatment of $[ReCl(CO)(N_2C_6H_4F-4)(vdpp-PP')(vdpp-P)][PF_6]$ with CuCl gave $[(4-FC_6H_4N_2)(OC)Re(\mu-vdpp)_2(\mu-Cl)CuCl][PF_6]$ (**6b**) which showed a particularly well defined AA′XX′ $^{31}P-\{^1H\}$ n.m.r. pattern. At 21 °C the $^{31}P-\{^1H\}$ n.m.r. spectrum showed the AA′ part of an AA′XX′ pattern for the phosphorus atoms bound to rhenium, with all ten lines observed and hence the magnitudes of *J*(AX), *J*(AX′), *J*(AA′), and *J*(XX′) were calculated (Table 2). A much broader resonance pattern was observed for the phosphorus atoms bound to copper (the XX′ part); this pattern sharpened as the temperature was lowered and was quite sharp at −20 °C and we therefore attribute the broadening to quadrupolar effects (^{63}Cu, $I = \frac{3}{2}$, 69% abundant; ^{65}Cu, $I = \frac{3}{2}$, 31% abundant), since lowering the temperature would cause faster relaxation of the copper nuclei. The $^1H-\{^{31}P\}$ n.m.r. spectrum gave the expected resonance pattern for the diazenido protons and the $PC(=CH_2)P$ protons (Table 2). The i.r. spectrum showed bands at 1 980 and 1 720 cm^{-1}, which were assigned to terminally bound carbonyl and diazenido ligands on rhenium. The related 4-fluorophenyldiazenido-complex (**6c**) was prepared by treating $[ReCl(CO)(N_2C_6H_4F-4)(vdpp-PP')(vdpp-P)][PF_6]$ with CuCN; this complex showed an i.r. absorption band at 2 135w cm^{-1}, assigned to ν(CN), and well defined $^{31}P-\{^1H\}$ and ^1H n.m.r. spectra (data in Table 2). The 4-methoxyphenyldiazenido-complex (**6d**) was similarly made from $[ReCl(CO)(N_2C_6H_4OMe-4)(vdpp-PP')(vdpp-P)][PF_6]$ and CuCl and similarly characterized (data in Tables 1 and 2). The formulations (**6a**)—(**6d**), with bridging chloride ligands, are somewhat tentative.

We have been unable to prepare heterobimetallic com-

Table 4. Fractional atom co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
Re	7 773(1)	4 870.9(3)	1 412.3(2)
Pt	6 135(1)	4 855.0(3)	626.1(2)
Cl(1)	9 001(4)	5 533(2)	849(2)
Cl(2)	4 759(4)	4 843(3)	−38(2)
P(1)	7 146(4)	6 023(2)	1 694(1)
P(2)	5 504(4)	5 970(2)	819(2)
P(3)	8 691(3)	3 826(2)	1 080(2)
P(4)	6 929(3)	3 870(2)	264(2)
C(1)	6 300(13)	4 456(8)	1 401(6)
O	5 514(10)	4 145(6)	1 546(4)
N(1)	8 220(10)	4 654(6)	2 033(5)
N(2)	8 266(12)	4 433(7)	2 483(5)
C(3)	9 269(7)	4 529(6)	2 762(4)
C(4)	9 173(7)	4 387(6)	3 274(4)
C(5)	10 108(7)	4 459(6)	3 586(4)
C(6)	11 140(7)	4 673(6)	3 387(4)
C(7)	11 236(7)	4 814(6)	2 875(4)
C(8)	10 300(7)	4 743(6)	2 562(4)
C(9)	12 202(20)	4 742(12)	3 707(8)
C(111)	8 283(8)	6 616(6)	1 892(4)
C(112)	8 988(8)	6 362(6)	2 270(4)
C(113)	9 841(8)	6 790(6)	2 462(4)
C(114)	9 989(8)	7 471(6)	2 276(4)
C(115)	9 283(8)	7 724(6)	1 898(4)
C(116)	8 430(8)	7 297(6)	1 706(4)
C(121)	6 202(10)	6 085(6)	2 227(4)
C(122)	5 681(10)	5 477(6)	2 409(4)
C(123)	5 026(10)	5 508(6)	2 843(4)
C(124)	4 892(10)	6 146(6)	3 096(4)
C(125)	5 413(10)	6 754(6)	2 914(4)
C(126)	6 067(10)	6 723(6)	2 480(4)
C(13)	6 515(13)	6 512(8)	1 169(6)
C(211)	5 419(11)	6 489(6)	244(4)
C(212)	6 407(11)	6 577(6)	−33(4)
C(213)	6 402(11)	6 992(6)	−465(4)
C(214)	5 410(11)	7 319(6)	−621(4)
C(215)	4 423(11)	7 232(6)	−344(4)
C(216)	4 427(11)	6 817(6)	88(4)
C(221)	4 173(8)	6 068(8)	1 145(4)
C(222)	3 792(8)	6 716(7)	1 323(4)
C(223)	2 732(8)	6 768(7)	1 546(4)
C(224)	2 053(8)	6 172(7)	1 591(4)
C(225)	2 434(8)	5 523(7)	1 413(4)
C(226)	3 494(8)	5 471(7)	1 190(4)
C(311)	10 227(7)	3 794(6)	1 136(4)
C(312)	10 957(7)	3 962(6)	744(4)
C(313)	12 119(7)	3 905(6)	811(4)
C(314)	12 550(7)	3 681(6)	1 271(4)
C(315)	11 820(7)	3 513(6)	1 663(4)
C(316)	10 659(7)	3 569(6)	1 596(4)
C(321)	8 334(9)	2 972(4)	1 351(4)
C(322)	7 608(9)	2 907(4)	1 760(4)
C(323)	7 370(9)	2 242(4)	1 957(4)
C(324)	7 859(9)	1 643(4)	1 746(4)
C(325)	8 585(9)	1 709(4)	1 337(4)
C(326)	8 823(9)	2 373(4)	1 140(4)
C(33)	8 421(12)	3 765(8)	400(5)
C(411)	6 221(9)	3 037(4)	394(4)
C(412)	5 113(9)	3 053(4)	568(4)
C(413)	4 559(9)	2 426(4)	684(4)
C(414)	5 112(9)	1 783(4)	627(4)
C(415)	6 220(9)	1 767(4)	453(4)
C(416)	6 774(9)	2 394(4)	336(4)
C(421)	7 022(10)	3 933(6)	−407(3)
C(422)	7 593(10)	4 511(6)	−606(3)
C(423)	7 731(10)	4 573(6)	−1 124(3)
C(424)	7 297(10)	4 058(6)	−1 443(3)
C(425)	6 726(10)	3 479(6)	−1 244(3)
C(426)	6 589(10)	3 417(6)	−726(3)
O(1S)	4 527(18)	5 019(13)	4 573(8)
C(1S)	4 329(34)	4 366(20)	4 697(14)
C(2S)	5 228(31)	3 836(19)	4 509(13)
C(3S)	3 387(31)	4 204(18)	5 012(13)
O(2S)	1 339(17)	1 360(10)	6 999(7)
C(4S)	−604(26)	1 836(15)	6 606(11)
C(5S)	92(29)	1 518(16)	7 003(12)
C(6S)	−938(26)	1 329(15)	7 385(11)

plexes by treating the diazenido complex (**1a**) with AgCl, $HgCl_2$, $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}4)]$, $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene), or $[Mo(CO)_3(C_7H_8)]$ (C_7H_8 = cyclohepta-1,3,5-triene). These reagents gave complicated mixtures, which we could not separate; presumably the diazenido group plays an important part in these reactions.

Crystal Structure of $[(4\text{-}MeC_6H_4N_2)ClRe(\mu\text{-}dppm)_2(\mu\text{-}CO)PtCl]$ (**2a**).—A suitable crystal was obtained from refluxing acetone. The structure is shown in Figure 2 and selected intramolecular bond lengths and angles are given in Table 3. The Re and Pt atoms are linked by two dppm bridges to give an eight-membered ReP_4C_2Pt ring in the boat conformation. The Re–Pt distance of 285.9(4) pm indicates that there is a metal–metal bond; this is slightly shorter than the only other complex, $[(ON)(\eta\text{-}C_5H_5)Re(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]$, reported to have a Re–Pt bond [286.7(1) pm].[8] The bond lengths and the angle N(1)–N(2)–C(3) are typical of a singly bent diazenido ligand; however, the Re–N(1)–N(2) angle [164.3(11)°] is significantly lower than previously reported for other diazenidorhenium complexes (typically greater than 170°).[9–11] This lowering of the bond angle may be caused by a small contribution from the doubly bent form or by packing forces in the crystal lattice. The semi-bridging carbonyl ligand has a strong interaction with the platinum.

Experimental

General methods and instrumentation were as described in recent publications from this laboratory.[4]

$[(4\text{-}MeC_6H_4N_2)ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl]$ (**2b**).—A mixture of $[ReCl(CO)(N_2C_6H_4Me\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][PF_6]$ (0.290 g, 0.22 mmol) and *trans*-$[PtH(Cl)(PPh_3)_2]$ (0.170 g, 0.22 mmol) in acetone (20 cm^3) was heated under reflux for 16 h and then allowed to cool to 20 °C. The required product separated from the reaction mixture and was collected. Yield 0.156 g (51%).

The analogous complexes (**2a**) and (**2c**) were prepared in 51 and 48% yields, respectively.

$[\{(4\text{-}MeC_6H_4)MeNN\}ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl][BF_4]$ (**3**).—A mixture of $[OMe_3][BF_4]$ (0.011 g, 0.072 mmol) and complex (**2b**) (0.100 g, 0.072 mmol) in dichloromethane (5 cm^3) was stirred for 45 min. n-Hexane (3 cm^3) was then added to the resultant orange solution and the mixture set aside. This gave the required product as orange prisms. Yield 0.074 g (69%).

$[\{(4\text{-}MeC_6H_4)HNN\}ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl][BF_4]$ (**4**).—A mixture of $HBF_4\cdot Et_2O$ (0.014 g, 0.086 mmol) and $[(4\text{-}MeC_6H_4N_2)ClRe(\mu\text{-}vdpp)_2(\mu\text{-}CO)PtCl]$ (0.100 g, 0.072 mmol) in dichloromethane (5 cm^3) was stirred for 10 min, to give an orange solution. Diethyl ether (1 cm^3) was then added to give the required product as orange prisms. Yield 0.065 g (63%).

$[(4\text{-}MeC_6H_4N_2)(OC)ClRe(\mu\text{-}vdpp)_2(\mu\text{-}Cl)Rh(CO)][BF_4]$ (**5a**).—(*i*) *From* $[ReCl(CO)(N_2C_6H_4Me\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][BF_4]$. A solution containing $[Rh_2Cl_2(CO)_4]$ (0.031 g, 0.080 mmol) and $[ReCl(CO)(N_2C_6H_4Me\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][BF_4]$ (0.20 g, 0.16 mmol) in dichloromethane (5 cm^3) was stirred for 20 min. The resulting red solution was evaporated to dryness and the required product obtained by trituration with diethyl ether. Yield 207 mg, 92%.

(*ii*) *From trans*-$[ReCl(CO)(vdpp\text{-}PP')_2]$. To the orange solution formed by adding $[Rh_2Cl_2(CO)_4]$ (0.037 g, 0.095 mmol) to a solution of *trans*-$[ReCl(CO)(vdpp\text{-}PP')_2]$ (0.200 g, 0.19 mmol) in dichloromethane (10 cm^3) was added a solution of $[4\text{-}MeC_6H_4N_2][BF_4]$ (0.039 g, 0.19 mmol) in acetone (5 cm^3). The resulting mixture was stirred for 15 min and then evaporated to dryness under reduced pressure. The required product was obtained as deep red microprisms by trituration with diethyl ether. Yield 0.22 g, 78%. The product from this reaction was shown by n.m.r. spectroscopy to be a mixture which, over 4 d in dichloromethane solution, changed into a single product (**5a**) which was the same as that prepared by method (*i*) above (see Discussion section).

The analogous complexes (**5b**) and (**5c**) were prepared from (**1c**) and (**1d**), respectively and $[Rh_2Cl_2(CO)_4]$ in 76 and 86% yields.

$[(4\text{-}MeC_6H_4N_2)(OC)Re(\mu\text{-}vdpp)_2(\mu\text{-}Cl)CuCl][PF_6]$ (**6a**).—Copper(I) chloride (0.007 g, 0.076 mmol) and a solution of $[ReCl(CO)(N_2C_6H_4Me\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][PF_6]$ (0.100 g, 0.076 mmol) in dichloromethane (5 cm^3) were stirred for 24 h to give a deep red solution. The solution was then evaporated to dryness under reduced pressure and the required product isolated as deep red prisms by trituration with diethyl ether. Yield 0.086 g, 80%.

The complexes (**6b**) (81% yield), (**6c**) (82%), and (**6d**) (87%) were prepared in an analogous manner.

X-Ray Diffraction Analysis of Complex (**2a**).—All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω—2θ scan mode using graphite-monochromated Mo-K_α radiation following a procedure described elsewhere.[12] The data set was corrected for absorption empirically.[13]

Crystal data. $C_{58}H_{49}Cl_2N_2OP_4PtRe\cdot 2Me_2CO$, M = 1 482.3, orthorhombic, a = 1 187.5(1), b = 1 898.2(2), c = 2 664.2(4) pm, U = 6.9995 nm^3, Z = 4, space group $P2_12_12_1$, D_c = 1.64 g cm^{-3}, μ = 43.70 cm^{-1}, $F(000)$ = 2 672.

Data collection. Scans widths 1.8° + α-doublet splitting, scan speeds 2.0—29.3° min^{-1}, and $4.0 < 2\theta < 45.0°$. 4 231 Unique data, 3 972 $[I > 2.0\sigma(I)]$ observed; T = 290 K.

The structure was solved by standard heavy-atom methods and refined by full-matrix least squares using SHELX 76.[14] Only the Re, Pt, Cl, and P atoms were assigned anisotropic thermal parameters. All other atoms were assigned individual isotropic thermal parameters except two acetone molecules which were each refined with an overall isotropic thermal parameter. All phenyl rings were treated as rigid bodies with idealized hexagonal symmetry (C–C 139.5 pm). Unit weights were used throughout. The final R value was 0.0353 (235 parameters, 3 972 observed data). Fractional atomic coordinates are given in Table 4.

Acknowledgements

We thank the S.E.R.C. for support and Johnson Matthey Ltd. for the generous loan of platinum salts.

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Received 20*th May* 1987; *Paper* 7/906