Chelate Ring-opening of Rhenium–Diphosphine Complexes by Diazonium Salts

Stuart W. Carr, Xavier L. R. Fontaine, and Bernard L. Shaw *
School of Chemistry, The University, Leeds LS2 9JT

Treatment of [ReCl(CO)$_5$] with Ph$_2$PC(=CH$_2$)PPh$_2$ (vdpp) gave *trans*-[ReCl(CO)(vdpp-*PP'*)$_2$] (**1a**); similar treatment with Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe) gave *trans*-[ReCl(CO)(dppe-*PP'*)$_2$] (**1b**) but Ph$_2$PCH$_2$PPh$_2$ (dppm) gave *trans*-[ReCl(CO)(dppm-*PP'*)$_2$] (**1c**) as a minor product, the main product being *mer,cis*-[ReCl(CO)$_2$(dppm-*PP'*)(dppm-*P*)]. Treatment of [ReCl(CO)$_5$] with Ph$_2$PCHMePPh$_2$ (mdppm) gave *trans*-[ReCl(CO)(mdppm-*PP'*)$_2$] as a mixture of two geometrical isomers; reduction of (**1a**) with sodium tetrahydroborate gave these same isomers but in different proportions. Treatment of (**1a**) with a solution of [4-FC$_6$H$_4$N$_2$][PF$_6$], even at −70 °C, caused immediate chelate ring-opening to give *mer*-[ReCl(CO)(N$_2$C$_6$H$_4$F-4)(vdpp-*PP'*)(vdpp-*P*)][PF$_6$], (**5a**), which was isolated in 90% yield; other diazonium salts, [4-MeC$_6$H$_4$N$_2$][BF$_4$], [4-MeOC$_6$H$_4$N$_2$][PF$_6$], or [2,6-Me$_2$-C$_6$H$_3$N$_2$][BF$_4$], similarly effected chelate ring-opening to give analogous complexes. In the case of *mer*-[ReCl(CO)(N$_2$C$_6$H$_3$Me$_2$-2,6)(vdpp-*PP'*)(vdpp-*P*)][BF$_4$] a mixture of two isomers was obtained; these were possibly due to restricted rotation around the Re–N$_2$ bond caused by the bulky aryl group. Treatment of *trans*-[ReCl(CO)(mdppm-*PP'*)$_2$] (mixture of isomers) with [4-FC$_6$H$_4$N$_2$][PF$_6$] caused chelate ring-opening to give [ReCl(CO)(N$_2$C$_6$H$_4$F-4)(mdppm-*PP'*)(mdppm-*P*)][PF$_6$] as a mixture of two isomers. The uncomplexed phosphorus of (**5a**) was methylated, on treatment with Me$_3$O·BF$_4$, to give [ReCl(CO)(N$_2$C$_6$H$_4$F-4)(vdpp-*PP'*){Ph$_2$PC(=CH$_2$)PMePh$_2$}][BF$_4$][PF$_6$]. Treatment of (**1b**) with [4-FC$_6$H$_4$N$_2$][PF$_6$] caused oxidation to the Re^{II} complex *trans*-[ReCl(CO)(dppe-*PP'*)$_2$][PF$_6$] and no ring-opening; treatment of the dinitrogen complex *trans*-[ReCl(N$_2$)(dppm-*PP'*)$_2$] with [4-FC$_6$H$_4$N$_2$][PF$_6$] gave *trans*-[ReCl(N$_2$C$_6$H$_4$-4)(dppm-*PP'*)$_2$][PF$_6$], also with no ring-opening. Phosphorus-31 and ^{1}H n.m.r. and i.r. data are given.

The arenediazo group, RN$_2$–, has been used extensively as a ligand.[1–3] Some of the reasons for this include the close relationship with co-ordinated N$_2$ or NO and also the variable geometry of co-ordinated RN$_2$, *i.e.* singly bent as a three-electron donor or doubly bent, as a one-electron donor.[1,3–5] Methods of introducing the RN$_2$ ligand include (*i*) displacement of another ligand, such as CO, by RN$_2^+$, (*ii*) oxidative addition of RN$_2^+$, and (*iii*) apparent insertion of RN$_2^+$ into a metal–ligand bond.[1–3,6–8] We now describe another method, namely a rapid chelate ring-opening reaction of rhenium(I) diphosphine complexes on treatment with RN$_2^+$, even at −70 °C. In order to study these ring-opening reactions we made some new chelate complexes of rhenium with the diphosphines Ph$_2$PC(=CH$_2$)PPh$_2$ (vdpp), Ph$_2$PCH$_2$PPh$_2$ (dppm), Ph$_2$PCHMePPh$_2$ (mdppm), and Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe); we describe these syntheses first.

Results and Discussion

The complex [ReCl(CO)$_5$] is quite slow to undergo substitution reactions but when heated with vdpp in boiling mesitylene for 36 h it produced *trans*-[ReCl(CO)(vdpp-*PP'*)$_2$] (**1a**) in >90% yield. Characterizing elemental analytical and i.r. data for this compound are given in Table 1 and ^{31}P-{^{1}H} and

Table 1. Microanalytical (%) and i.r. data

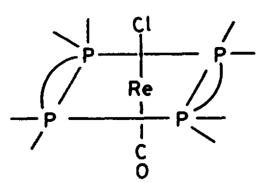
	Analysis[a] (%)				I.r.[b] (cm^{-1})	
Complex	C	H	N	Cl	ν(C=O)	ν(N=N)
(**1a**)	60.9 (60.9)	4.45 (4.45)		3.5 (2.4)	1 844s	
(**1b**)	61.2 (60.8)	4.55 (4.6)		3.2 (3.4)	1 790s, 1 831s 1 820s[c]	
(**1c**)	60.0 (60.15)	4.15 (4.35)		3.5 (3.5)	1 831s, 1 848s 1 839s[c]	
(**2**) or (**3**) + (**4**)·0.75CH$_2$Cl$_2$	58.2 (58.4)	4.3 (4.5)		6.95 (7.4)	1 825s	
(**5a**)	54.05 (54.05)	3.8 (3.7)	2.2 (2.15)	3.15 (2.7)	1 981s,br	1 715s,br
(**5b**)	57.5 (57.7)	4.3 (4.15)	2.15 (2.25)	3.1 (2.8)	1 961s,br	1 724s,br
(**5c**)	53.95 (54.5)	3.65 (3.9)	1.95 (2.1)	3.1 (2.7)	1 980s,br	1 725s,br
(**5d**)	54.0 (54.3)	4.05 (4.0)	1.8 (2.2)	3.15 (2.75)	1 982s	1 704s,br
(**5e**)	52.75 (53.0)	3.95 (3.9)	2.2 (2.1)	2.85 (2.65)	2 000s,br	1 700s,br
(**6**)	50.95 (51.0)	3.7 (3.65)	1.9 (2.0)	2.6 (2.5)	1 992s,br	1 740s,br
(**7**)/(**8**)	58.25 (58.05)	4.35 (4.25)	1.85 (2.2)	3.15 (2.8)	1 961s,br	1 745s,br
[ReCl(N$_2$C$_6$H$_4$F-4)(dppm-*PP'*)$_2$][PF$_6$]	55.65 (55.45)	4.0 (3.95)	2.35 (2.15)	2.8 (2.7)	1 961s,br	1 724s,br
[ReCl(CO)(dppe-*PP'*)$_2$][PF$_6$]	53.7 (53.4)	4.1 (4.1)		3.3 (3.0)	1 855s	

[a] Calculated values in parentheses. [b] As Nujol mulls unless stated otherwise; s = strong, br = broad. [c] In CH$_2$Cl$_2$ solution.

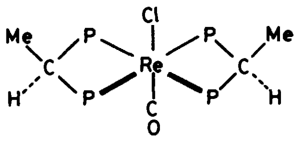
Table 2. Phosphorus-31[a] and ^{1}H[b] n.m.r. data

	^{31}P			^{1}H				
		J[d]		Arenediazo[e]		$P_2C{=}CH_2$		
Complex	δ[c]			δ	J	δ	J(PH)	
(5a)	−23.9 A	209 BD	4 BC	6.63	N = 9.0	6.86	22.2, 8.9	
	−11.3 B	70 AB		5.91	^{3}J(FH) = 8.2	6.16	44.6, 6.3	
	−11.0 C	80 CD			^{4}J(FH) = 4.7	6.66	32.0, 21.8	
	+14.7 D	21 AD				6.41	34.1, 20.7 ^{2}J(HH) = 1.7	
(5b)	−23.2 A	204 BD	4 BC	6.82	N = 8.3	6.83	22.3, 9.1	
	−11.0 B	69 AB		5.91		6.14	44.7, 6.4	
	−10.8 C	78 CD				6.61	32.0, 21.9 ^{2}J(HH) = 1.7	
	+15.6 D	21 AD				6.38	34.1, 20.6	
(5c)	−23.6 A	204 BD	4 BC	6.43	N = 9.2	6.85	22.3, 9.2	
	−10.7 B	71 AB		5.86		6.15	44.0, 6.3	
	−11.7 C	79 CD		δ(Me) = 3.72		6.60	31.8, 21.8	
	+15.9 D	21 AD				6.34	44.0, 26.3 ^{2}J(HH) = 1.7	
(7)/**(8)**, major isomer	−22.5 A	205 BD	7 BC	δ(Me) = 2.0		6.04	46.1, 6.2	
	−12.4 B	68 AB		*f*		*f*		
	−12.0 C	62 CD				6.57	43.1, 21.9	
	+11.0 D	23 AD				6.25	33.6, 21.0 ^{2}J(HH) = 1.4	
(7)/**(8)**, minor isomer	−21.3 A	184 BD	4 BC	δ(Me) = 2.2		5.99	46.1, 6.1	
	−11.4 B	66 AB		*f*		*f*		
	−11.6 C	73 CD				6.59	33.6, 20.7 ^{2}J(HH) = 1.7	
	+16.7 D	23 AD				6.45	32.1, 21.8	
(6)	−22.1 A	213 BD		6.59	N = 9.0	6.59	21.1, 1.9	
	−10.2 B	64 AB		5.66		6.45	*f*	
	+25.5 C	19 AD			^{3}J(FH) = 8.3		δ(CH_3) = 2.04	
	+14.3 D	7 CD			^{4}J(FH) = 3.6		$^{2}J(PCH_2)$ = 13.2	
						P_2CHCH_3		
						δ(CH)	δ(CH_3)	$^{3}J(CHCH_3)$
(5e), minor isomer	−29.4 A	193 BD	~3 BC	*f*		5.42	1.28, 7.6	
	−10.4 B	10 AB				3.77	0.97, 7.6	
	−6.3 C	105 CD						
	+13.7 D	21 AD						
(5e), major isomer	−29.1 A	196 BD	~4 BC	*f*		5.53	1.31	7.4
	−11.3 B	7 AB				3.96	1.15	7.4
	−7.4 C	108 CD						
	+12.6 D	22 AD						
						PCH_2P		
(5d)	−50.5 A	189 BD	6 BC	6.15	N = 10.7	6.20 } CH_2	^{2}J(HH) = 15.7	
	−28.6 B	~3 AB		*f*		5.77 } CH_2	^{2}J(PH) = 5.6, 4.5	
	−28.5 C	54 CD						
	−3.3 D	23 AD						
						δ	J	
(1a)[g]	1.2					5.67 (=CH_2)		
(1b)[g]	30.4					2.4—2.7 (m) (CH_2CH_2)		
(1c)[g]	−28.1					5.81 (PCH_2P)	^{2}J(PH) = 3.2	
						5.50	^{2}J(PH) = 4.7	
							^{2}J(HH) = 14.9	
(2) or **(3)**	−7.4					5.8 (CH)	^{3}J(HH) = 7.7	
						1.28 (CH_3)		
(4)	−11.3, −4.7					5.59 (CH)	^{3}J(HH) = 7.5	
						1.32 (CH_3)		
						5.13 (CH)	^{3}J(HH) = 7.6	
						1.48 (CH_3)		

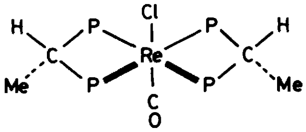
[a] Spectra measured at 162 MHz at *ca.* 21 °C, unless stated otherwise. Chemical shifts (δ) in p.p.m. (±0.1) to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz (±1). [b] Spectra measured at 400 MHz and at *ca.* 21 °C, unless stated otherwise. Chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$, and couplings constants (J) in Hz (±0.1). [c] A = δ(P_A), B = δ(P_B), *etc.* as labelled in (**5**)—(**8**). [d] BD = $J(P_BP_D)$, AB = $J(P_AP_B)$, *etc.* [e] The arenediazo aromatic protons formed an AA′XX′ spin system [in the case of (**5a**) and (**6**) there was further coupling to fluorine]. N = J(AX) + J(AX′). [f] Resonance(s) obscured or partly obscured by overlap with other resonances. [g] At 40.25 MHz (^{31}P) and 100 MHz (^{1}H).



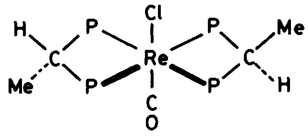
(1a), P⌒P = vdpp
(1b), P⌒P = dppe
(1c), P⌒P = dppm



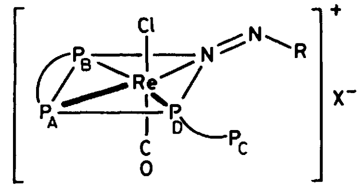
(2)



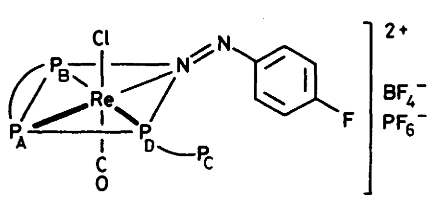
(3)



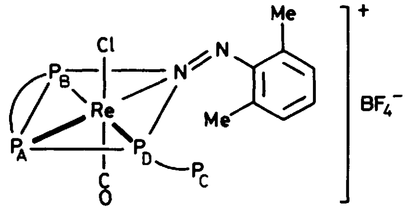
(4)



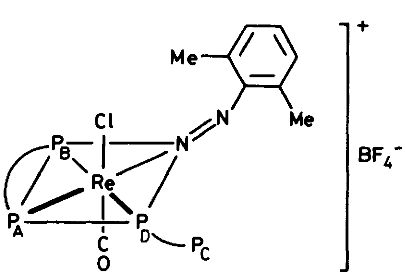
(5a), P⌒P = vdpp, R = C_6H_4F-4, X = PF_6
(5b), P⌒P = vdpp, R = C_6H_4Me-4, X = BF_4
(5c), P⌒P = vdpp, R = C_6H_4OMe-4, X = PF_6
(5d), P⌒P = dppm, R = C_6H_4Me-4, X = PF_6
(5e), P⌒P = mdppm, R = C_6H_4F-4, X = PF_6



(6), P_A⌒P_B = vdpp, P_D⌒P_C = $Ph_2PC(=CH_2)PMePh_2$



(7), P⌒P = vdpp



(8), P⌒P = vdpp

^{1}H n.m.r. data in Table 2. Similar treatment of [ReCl(CO)$_5$] with dppe gave *trans*-[ReCl(CO)(dppe-*PP*′)$_2$] (**1b**) in 74% yield; characterizing data are in Tables 1 and 2. However, treatment of [ReCl(CO)$_5$] with dppm gave only 5—16% of *trans*-[ReCl(CO)(dppm-*PP*′)$_2$], the main product being *mer,cis*-[ReCl(CO)$_2$(dppm-*PP*′)(dppm-*P*)] (61% yield), a compound which has been described previously;[9] characterizing data for these two compounds are given in Tables 1 and 2. We also wished to study the effect of a central substituent (Me) on dppm, such as with mdppm, on the tendency for a chelate ring to open upon treatment with RN_2^+ (see below). We therefore treated [ReCl(CO)$_5$] with mdppm in boiling mesitylene. This gave in high yield a mixture of two isomers, both of type *trans*-[ReCl(CO)(diphosphine-*PP*′)$_2$]. One of these showed a singlet ^{31}P resonance and a well defined AX$_3$ pattern for C*H*C*H*$_3$ in the ^{1}H-{^{31}P} n.m.r. spectrum; this isomer was therefore assigned either structure (**2**) or (**3**). The other component showed two equally intense AX$_3$ C*H*C*H*$_3$ patterns in the ^{1}H-{^{31}P} n.m.r. spectrum and a complex pattern in the ^{31}P-{^{1}H} n.m.r. spectrum, consistent with an AA′BB′ spin system but these were not analysed; we assign structure (**4**) to this product. The approximate ratio of (**2**) or (**3**) to (**4**) was 1 : 4. We also reduced the vdpp complex (**1a**) with sodium tetrahydroborate. This gave a high (87%) total yield of the same mixture, *viz.* (**2**) or (**3**) and (**4**), but this time in a ratio of 1 : 1.

Treatment of (**1a**), in dichloromethane solution at −70 °C, with an acetone solution of [4-FC$_6$H$_4$N$_2$][PF$_6$] caused an immediate colour change to brown and the arenediazo complex, *mer*-[ReCl(CO)(N$_2$C$_6$H$_4$F-4)(vdpp-*PP*′) (vdpp-*P*)][PF$_6$] (**5a**), in which one of the chelate vdpp rings had ring-opened to become monodentate, was formed immediately (^{31}P-{^{1}H} n.m.r. evidence). On a preparative scale, carried out at room temperature, (**5a**), was isolated in 90% yield. The microanalytical and i.r. data for this compound are given in Table 1. The i.r. spectrum shows a strong band at 1 981 cm^{-1} due to ν(CO) and a very strong band at 1 715 cm^{-1}, typical of a singly bent, *i.e.* three-electron donor, RN$_2$ group.[1—3] The ^{31}P-{^{1}H} n.m.r. data for this compound are given in Table 2. Four multiplets each showing phosphorus–phosphorus couplings were observed: δ(P$_A$) −23.9, δ(P$_B$) −11.3, δ(P$_C$) −11.0, and δ(P$_D$) +14.7 p.p.m. Of note is the large coupling of 209 Hz, *J*(P$_B$P$_D$), typical of *trans* coupling across a metal such as rhenium(I) and showing that the three-co-ordinated phosphorus atoms are *mer*.[9] When complex (**5a**) was treated with Me$_3$O·BF$_4$ the uncomplexed phosphorus was quaternized to give (**6**), a mixed PF$_6$/BF$_4$ salt. As a result of this quaternization the chemical shift of P$_C$ changed from −11.0 to +25.5 p.p.m. whilst the chemical shifts of the other three P atoms hardly changed. The couplings between P atoms in the same vdpp ligand are ^2J(P$_A$P$_B$) = 70 and ^2J(P$_C$P$_D$) = 80 Hz, values which we have found typical of this ligand. Thus the assignments of *J* and δ values given in Table 2 are consistent with the designated P atom bonding for (**5a**). Although another arrangement cannot be ruled out we suggest the Cl and CO ligands remain mutually *trans*, as shown in (**5a**): consistent with this, the completely analogous complex (**5b**) reacts with *trans*-[Pt(H)Cl(PPh$_3$)$_2$] to give the heterobimetallic [Cl(RN$_2$)Re(μ-dppm)$_2$(μ-CO)PtCl], in which the Cl and CO ligands on the Re are mutually *trans*, as shown by the crystal structure.[10]

We have also studied the action of other diazonium salts on (**1a**) to see if electronic and/or steric effects were significant in controlling the chelate ring-opening process. Treatment of (**1a**) with [4-MeC$_6$H$_4$N$_2$][PF$_6$] or [4-MeOC$_6$H$_4$N$_2$][PF$_6$] induced rapid ring opening to give (**5b**) or (**5c**), respectively, in good yield (see Experimental section, Tables 1 and 2). We did not observe any significant difference in the ring-opening process by 4-YC$_6$H$_4$N$_2^+$ with Y = F, Me, or OMe. We also studied the ring-opening process by the sterically hindered diazonium salt

$[2,6\text{-}Me_2C_6H_3N_2][BF_4]$. This opened the chelate ring of (**1a**) rapidly but gave a mixture of two products (isomers). These showed ^{31}P and ^{1}H n.m.r. data (Table 2) characteristic of a *mer*-Re(vdpp-*PP′*)(vdpp-*P*) moiety and could involve different arrangements of the Cl and CO ligands but we tentatively suggest that the two isomers are due to restricted rotation around the Re–N=N–R ligand; *i.e.* the two isomers are (**7**) and (**8**), although we do not know which is the major and which the minor isomer.

We have found that a chelate ring involving mdppm is much less likely to open to give a monodentate ligand complex than is dppm.[11–13] For example, $[PtMe_2(dppm\text{-}PP')]$[11] or $[CH_2CH_2CH_2CH_2Pt(dppm\text{-}PP')]$[12] are opened up rapidly and essentially completely on treatment with more dppm to give the bis-monodentate ligand complexes $[PtMe_2(dppm\text{-}P)_2]$ or $[CH_2CH_2CH_2CH_2Pt(dppm\text{-}P)_2]$, respectively (n.m.r. evidence). In contrast, on treatment of the corresponding complexes $[PtMe_2(mdppm\text{-}PP')]$ or $[CH_2CH_2CH_2CH_2Pt(mdppm\text{-}PP')]$ with more mdppm, none of the ring-opened monodentate complexes could be detected.[13] This remarkable result is another example of the Thorpe-Ingold effect or of 'stereopopulation control,' *i.e.* the effect of Me group(s) on the stability of rings. Thus it was by no means obvious that the chelate rings of mdppm in (**2**), (**3**), or (**4**) would ring-open when treated with an arenediazonium salt. However, we found that the mixture of (**4**) and (**2**) or (**3**), when treated with $[4\text{-}FC_6H_4N_2][PF_6]$, immediately gave the ring-opened product (**5e**), as a mixture of two isomers: the n.m.r. data (Table 2) are clearly analogous to those of the ring-opened complex (**5d**) from the dppm chelate.

We did not expect to be able to open up the five-membered chelate ring complex *trans*-$[ReCl(CO)(dppe\text{-}PP')_2]$ (**1b**) by treatment with a diazonium salt and indeed when we treated this complex with $[4\text{-}FC_6H_4N_2][PF_6]$ oxidation to the rhenium(II) complex *trans*-$[ReCl(CO)(dppe\text{-}PP')_2][PF_6]$ occurred in 87% yield (see Experimental section, Table 1).

The arenediazo complex $[Re(\eta\text{-}C_5H_5)(CO)_2(N_2C_6H_4CF_3\text{-}2)][BF_4]$ reacts with halide ions, such as iodide, to give the dinitrogen complex $[Re(\eta\text{-}C_5H_5)(CO)_2(N_2)]$.[14] However, we found that prolonged treatment (5 d at 20 °C) of our arenediazo complexes with a large excess of iodide ion caused no detectable conversion to a dinitrogen complex and the arenediazo complex was recovered largely unchanged.

We attempted to effect a ring-opening reaction on the dinitrogen complex analogous to (**1c**), *viz.* *trans*-$[ReCl(N_2)(dppm\text{-}PP')_2]$, but when we treated this dinitrogen complex with $[4\text{-}FC_6H_4N_2][PF_6]$ dinitrogen was lost and we obtained the bis-chelate *trans*-$[ReCl(N_2C_6H_4F\text{-}4)(dppm\text{-}PP')_2][PF_6]$ (see Experimental section, Tables 1 and 2).

Experimental

The apparatus used and the general techniques were the same as in other recent papers from this laboratory.[15] The complex $[ReCl(CO)_5]$,[16] arenediazonium salts, $[RN_2]BF_4$ and $[RN_2]PF_6$,[17,18] and *trans*-$[ReCl(N_2)(dppm\text{-}PP')_2]$[19] were prepared by literature methods.

trans-$[ReCl(CO)(vdpp\text{-}PP')_2]$ (**1a**).—A mixture of $[ReCl(CO)_5]$ (0.65 g, 1.8 mmol) and vdpp (1.60 g, 4.05 mmol) in mesitylene (40 cm^3) was heated under reflux for 36 h. The resultant solution was then cooled to ambient temperature giving the required product as red flakes. Yield 1.70 g, 90%. This was sufficiently pure for most purposes but could be recrystallized from dichloromethane–propan-2-ol.

trans-$[ReCl(CO)(dppe\text{-}PP')_2]$ (**1b**) was prepared similarly, with a reflux time of 96 h, and was isolated as large white prisms in 74% yield.

trans-$[ReCl(CO)(dppm\text{-}PP')_2]$ (**1c**).—A mixture of $[ReCl(CO)_5]$ (0.80 g, 2.2 mmol) and dppm (1.87 g, 4.88 mmol) in mesitylene (50 cm^3) was heated under reflux for 36 h. The hot mother-liquors were decanted from the precipitated yellow prisms, which were washed with ethanol then diethyl ether and dried, to give the required product (0.38 g, 16%). The known complex *mer,cis*-$[ReCl(CO)(dppm\text{-}PP')(dppm\text{-}P)]$ was isolated from the mother-liquor, in the manner previously described,[9] in 61% yield.

trans-$[ReCl(CO)(mdppm\text{-}PP')_2]$ *as a Mixture of Isomers* (**2**) *or* (**3**) *and* (**4**).—(*i*) *From trans*-$[ReCl(CO)(vdpp\text{-}PP')_2]$. Sodium tetrahydroborate (0.088 g, 2.35 mmol) was added to a stirred solution of *trans*-$[ReCl(CO)(vdpp\text{-}PP')_2]$ (0.50 g, 0.47 mmol) in wet tetrahydrofuran (20 cm^3). The resultant mixture was stirred for 1 h to give a yellow solution, which was then evaporated to dryness. The required product was isolated with dichloromethane and formed yellow prisms from dichloromethane–diethyl ether. Yield 0.435 g, 87%.

(*ii*) *From* $[ReCl(CO)_5]$. A mixture of $[ReCl(CO)_5]$ (0.20 g, 0.57 mmol) and mdppm (0.57 g, 1.42 mmol) in mesitylene (20 cm^3) was heated under reflux for 72 h. The resultant solution was then cooled to room temperature giving the required product as yellow prisms. Yield 0.42 g, 73%.

mer-$[ReCl(CO)(N_2C_6H_4F\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][PF_6]$ (**5a**).—A solution of $[4\text{-}FC_6H_4N_2][PF_6]$ (0.144 g, 0.58 mmol) in acetone (15 cm^3) was added dropwise over 10 min to a stirred solution of *trans*-$[ReCl(CO)(vdpp\text{-}PP')_2]$ (0.60 g, 0.58 mmol) in dichloromethane (25 cm^3). The resulting brown solution was stirred for 10 min and then evaporated to dryness under reduced pressure. The required product was isolated from the residue with dichloromethane and formed brown microcrystals from dichloromethane–diethyl ether. Yield 0.67 g, 89%.

The following five complexes were prepared similarly: *mer*-$[ReCl(CO)(N_2C_6H_4Me\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][BF_4]$ (**5b**) (71%), *mer*-$[ReCl(CO)(N_2C_6H_4OMe\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][PF_6]$ (**5c**) (76%), *mer*-$[ReCl(CO)(N_2C_6H_3Me_2\text{-}2,6)(vdpp\text{-}PP')(vdpp\text{-}P)][BF_4]$ (**7**)/(**8**) (86%), *mer*-$[ReCl(CO)(N_2C_6H_4Me\text{-}4)(dppm\text{-}PP')(dppm\text{-}P)][PF_6]$ (**5d**) (76%), *mer*-$[ReCl(CO)(N_2C_6H_4F\text{-}4)(mdppm\text{-}PP')(mdppm\text{-}P)][PF_6]$ (**5e**) (87%).

mer-$[ReCl(CO)(N_2C_6H_4F\text{-}4)(vdpp\text{-}PP')\{Ph_2PC(=CH_2)PMePh_2][BF_4][PF_6]$, (**6**).—A solution of $[ReCl(CO)(N_2C_6H_4F\text{-}4)(vdpp\text{-}PP')(vdpp\text{-}P)][PF_6]$ (0.10 g, 0.075 mmol) in dichloromethane (2 cm^3) was stirred with $Me_3O{\cdot}BF_4$ (0.017 g, 0.11 mmol) for 2 h. The resulting brown solution was filtered and the filtrate evaporated to dryness under reduced pressure. The required product was isolated with dichloromethane and formed brown microcrystals on trituration with diethyl ether. Yield 0.086 g, 81%.

trans-$[ReCl(N_2C_6H_4F\text{-}4)(dppm\text{-}PP')_2][PF_6]$.—A solution of $[4\text{-}FC_6H_4N_2][PF_6]$ (0.023 g, 0.86 mmol) in acetone (5 cm^3) was added dropwise, with stirring, to a solution of *trans*-$[ReCl(N_2)(dppm\text{-}PP')_2]$ (0.090 g, 0.086 mmol) in dichloromethane (20 cm^3) at −70 °C. The resultant red solution was warmed to room temperature and then evaporated to dryness under reduced pressure. The required complex was isolated with dichloromethane and formed red prisms from dichloromethane–propan-2-ol. Yield 0.065 g, 60%.

trans-$[ReCl(CO)(dppe\text{-}PP')_2][PF_6]$.—A solution of $[4\text{-}FC_6H_4N_2][PF_6]$ (0.052 g, 0.20 mmol) in acetone (10 cm^3) was added to a stirred solution of *trans*-$[ReCl(CO)(dppe\text{-}PP')_2]$

(0.20 g, 0.20 mmol) in dichloromethane (15 cm^3) at −70 °C. The resultant mixture was warmed to room temperature during which N_2 was evolved and a green solution was formed. The mixture was evaporated to dryness under reduced pressure and the product isolated as green microcrystals by trituration with diethyl ether. Yield 0.20 g, 86%. A similar treatment of *trans*-[ReCl(CO)(dppe-*PP*′)$_2$] with [4-$MeC_6H_4N_2$][PF_6] gave *trans*-[ReCl(CO)(dppe-*PP*′)$_2$][PF_6] in 87% yield.

Acknowledgements

We thank the S.E.R.C. for financial support.

References

1 D. Sutton, *Chem. Soc. Rev.*, 1975, 443.
2 C. F. Barrientos-Penna, A. B. Gilchrist, A. H. Klahn-Oliva, A. J. Lee Hanlan, and D. Sutton, *Organometallics*, 1985, **4**, 478 and refs. therein.
3 R. A. Henderson, G. J. Leigh, and C. J. Pickett, *Adv. Inorg. Chem. Radiochem.*, 1983, **27**, 197 and refs. therein.
4 R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *J. Am. Chem. Soc.*, 1974, **96**, 260.
5 B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3060.
6 S. Cenini, F. Porta, and M. Pizzotti, *Inorg. Chem. Acta*, 1976, **20**, 119.
7 G. W. Parshall, *J. Am. Chem. Soc.*, 1967, **89**, 1822.
8 K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 1973, 176.
9 S. W. Carr, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 1763.
10 S. W. Carr, X. L. R. Fontaine, B. L. Shaw, and M. Thornton-Pett, unpublished work.
11 F. S. M. Hassan, D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 1501.
12 P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 849.
13 S. A. Al-Jibori, P. G. Pringle, and B. L. Shaw, unpublished work.
14 C. F. Barrientos-Penna and D. Sutton, *J. Chem. Soc., Chem. Commun.*, 1980, 11.
15 S. W. Carr and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 2131.
16 R. Colton and J. E. Knapp, *Aust. J. Chem.*, 1972, **25**, 9.
17 K. G. Rutherford, W. Redmond, and J. Rigamonti, *J. Org. Chem.*, 1961, **26**, 5149.
18 A. Roe, *Organic Reactions*, 1945, 205.
19 J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1973, 612.

Received 15*th December* 1986; *Paper* 6/2412