Complexes of the Bidentate Ligands Z-$PPh_2CH_2C(Bu^t){=}NNR_2$ (R = Me or H) with Rhodium and Iridium

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Treatment of 0.5 equivalent of $[\{RhCl(CO)_2\}_2]$ with the phosphino dimethylhydrazone Z-$PPh_2CH_2C(Bu^t){=}NNMe_2$ (L^1) or the phosphino hydrazone Z-$PPh_2CH_2C(Bu^t){=}NNH_2$ (L^2) gave the chelate complexes $[RhCl(CO)\{PPh_2CH_2C(Bu^t){=}NNR_2\}]$ (R = Me **1a** or H **1b**). Complex **1a** reacts with another mole of L^1 to give the bis(phosphine)rhodium(I) complex *trans*-$[RhCl(CO)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}_2]$ **2a**. The analogous iridium(I) complex **2b** was prepared by treating $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ with 2 mol equivalents of L^1. Complex **2a** reacts with $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) to give a 1:1 mixture of the chelate **1a** and $[PtCl_2\{PPh_2CH_2C(Bu^t){=}NNMe_2\}]$. Treatment of $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ with 2 equivalents of L^2 gave the hydridoiridium(III) complex *cis*-$[IrH(Cl)\{PPh_2CH_2C(Bu^t){=}NNH_2\}_2]Cl$ **3a**. Treatment of $[\{MCl(cod)\}_2]$ (M = Rh or Ir) with two equivalents of L^1 in methanol in the presence of NH_4PF_6 gave the cationic complexes $[M(cod)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}]PF_6$ (M = Rh **4a** or Ir **4b**) in which L^1 is bidentate. When $[\{MCl(cod)\}_2]$ was treated with 2 equivalents of L^1 in benzene it yielded the neutral complexes $[MCl(cod)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}]$ (M = Rh **5a** or Ir **5b**) in which L^1 is monodentate through phosphorus. Treatment of $[\{MCl(cod)\}_2]$ with 2 equivalents of L^2 in CD_2Cl_2 gave the cationic chelate complexes $[M(cod)\{PPh_2CH_2C(Bu^t){=}NNH_2\}]Cl$ (M = Rh **4c** or Ir **4d**). Treatment of $[\{RhCl(cod)\}_2]$ or $[\{RhCl(C_8H_{14})_2\}_2]$ (C_8H_{14} = cyclooctene) with 2 equivalents of L^2 per rhodium atom gave the cationic bis(phosphine)rhodium(I) complex $[Rh\{PPh_2CH_2C(Bu^t){=}NNH_2\}_2]Cl$ **6**. Treatment of $[RhCl(PPh_3)_3]$ with 1 equivalent of L^1 in C_6D_6 gave the Wilkinson-type complex $[RhCl(PPh_3)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}]$ **7**, which readily reacts with dioxygen to give the adduct *cis*-$[RhCl(O_2)(PPh_3)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}]$ **8**. The rhodium(III) complex **8** reacts with sulfur dioxide to give the rhodium(III) sulfate *cis*-$[RhCl(SO_4)(PPh_3)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}]$ **9**. Treatment of $[\{MCl(C_8H_{14})_2\}_2]$ with 2 equivalents of L^1 per rhodium atom gave the bis(phosphine) complexes *cis*-$[MCl\{PPh_2CH_2C(Bu^t){=}NNMe_2\}\{PPh_2CH_2C(Bu^t){=}NNMe_2\}]$ (M = Rh **10a** or Ir **10b**), containing one chelate and one monodentate phosphine ligand. These complexes reacted rapidly with dioxygen to give corresponding dioxygen adducts *cis*-$[MCl(O_2)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}\{PPh_2CH_2C(Bu^t){=}NNMe_2\}]$ (M = Rh **11a** or Ir **11b**). Proton, $^{31}P\text{-}\{^1H\}$ and some $^{13}C\text{-}\{^1H\}$ NMR data are given.

In a previous paper[1] we reported the synthesis of Z-*tert*-butyl diphenylphosphinomethyl ketone dimethylhydrazone, Z-$PPh_2CH_2C(Bu^t){=}NNMe_2$ (L^1) and Z-*tert*-butyl diphenylphosphinomethyl ketone hydrazone, Z-$PPh_2CH_2C(Bu^t){=}NNH_2$ (L^2). We have described the complexes and subsequent chemistry of these bidentate (P,N) ligands L^1 and L^2 with Cr^0, Mo^0 and W^0,[1] and more recently with Pd^{II} and Pt^{II}.[2] We have also used L^2 as a 'reagent' for derivatising aldehydes and ketones, $R'C({=}O)R''$ (R' = H or Me, R'' = aryl, alkyl, alkenyl or heterocyclic radical), as azines of type $PPh_2CH_2C(Bu^t){=}N{-}N{=}CR'R''$. By complexing the azines to metals, one of the R groups becomes compressed against the metal which promoted agostic C–H interaction,[3] C–F co-ordination,[4] C–H bond fission[5] or C–X bond fission (X = I, Br, Cl[6] or F[7]). In the present paper we describe the synthesis and characterisation of some rhodium and iridium complexes containing L^1 or L^2 and other ligands such as carbon monoxide, cycloocta-1,5-diene, triphenylphosphine or dioxygen. There is increasing interest in the use of bidentate (P,N) compounds to generate new co-ordination, organometallic or catalytic chemistry.[8–21] Some examples with rhodium or iridium include o-$PPh_2C_6H_4(CH_2)_nNMe_2$ (n = 0 or 1),[14,15] $PPh_2(CH_2)_nNMe_2$ (n = 2 or 3),[15] o-$PPh_2C_6H_4NH_2$,[16] o-$PPh_2C_6H_4NHR$ (R = Et or CH_2Ph),[17] $PPh_2(CH_2)_2(2\text{-}C_5H_4N)$[18] and o-$PPh_2C_6H_4CH{=}NR$ (R = Et, Pr^n, Pr^i or Bu^t).[19,20]

Results and Discussion

For the convenience of the reader the phosphine ligands L^1 and L^2, and the complexes prepared from them, are shown in Schemes 1–4. Elemental analyses, and some mass spectral and infrared data are in the Experimental section, $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ NMR data in Table 1, and ^1H NMR data in Table 2. Some of the complexes are very air-sensitive[16,17,22] and were characterised by ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, only.

Treatment of L^1 with 0.5 mol equivalent of the binuclear rhodium(I) complex $[\{RhCl(CO)_2\}_2]$ gave a single product **1a** with a six-membered chelate ring and phosphorus *trans* to chlorine. There are several pieces of evidence, indicative of the formation of a six-membered chelate ring, *i.e.* with NMe_2 co-ordinated. The shifts to low field of the methyl protons of the NMe_2 group on co-ordination ($\Delta\delta_H \approx +0.9$ ppm) and also the carbon-13 shifts of the NMe_2 methyls ($\Delta\delta_C \approx +5.5$ ppm) suggest that the NMe_2 nitrogen is co-ordinated to rhodium. Similar co-ordination shifts have been found for o-(diphenylphosphino)-*N*,*N*-dimethylaniline, (o-$PPh_2C_6H_4NMe_2$) on chelation to rhodium.[14] Additionally, the carbon-13 chemical shift (δ_C) for the CH_2 group is 21.2, typical of a six-membered chelate ring.[2,6,23,24] The $^{31}P\text{-}\{^1H\}$ NMR data, δ_P = 54.4 with $^1J(RhP)$ = 178 Hz, are typical of phosphorus *trans* to chlorine[15,18,22,25,26] and the value of $^2J(PC)$ of 18 Hz for the

Table 1 ^{31}P-{^{1}H}[a] and ^{13}C-{^{1}H} NMR data[b]

Compound	
L^1	δ_P: −9.7 δ_C: 28.3 (3C, s, C*Me*$_3$), 29.0 [1C, d, ^1J(PC) 21.6, CH$_2$], 38.4 (1C, s, *C*Me$_3$), 45.8 (2C, s, NMe$_2$), 128.1 (2C, s, C$_p$), 128.1 [4C, d, ^3J(PC) 7.0, C$_m$], 132.4 [4C, d, ^2J(PC) 20.1, C$_o$], 141.6 [2C, d, ^1J(PC) 16.9, C$_i$] and 177.1 (1C, s, C=N)
L^2	δ_P: −22.6 δ_C: 26.2 [1C, d, ^1J(PC) 22.7, CH$_2$], 28.6 (3C, s, C*Me*$_3$), 38.1 [1C, d, ^3J(PC) 1.4, *C*Me$_3$], 128.5 [4C, d, ^3J(PC) 7.0, C$_m$], 129.0 (2C, s, C$_p$), 132.8 [4C, d, ^2J(PC) 19.7, C$_o$], 137.6 [2C, d, ^1J(PC) 14.9, C$_i$] and 156.6 (1C, s, C=N)
1a	δ_P: 54.4 [^1J(RhP) 178] δ_C: 21.2 [1C, d, ^1J(PC) 22.5, CH$_2$], 27.1 (3C, s, C*Me*$_3$), 40.5 [1C, d, ^3J(PC) 2.2, *C*Me$_3$], 51.3 (2C, s, NMe$_2$), 128.6 [4C, d, ^3J(PC) 10.8, C$_m$], 131.2 [2C, d, ^4J(PC) 2.3, C$_p$], 132.4 [2C, dd, ^1J(PC) 52.3, ^2J(RhC) 2.0, C$_i$], 133.0 [4C, d, ^2J(PC) 12.1, C$_o$], 169.3 (1C, s, C=N) and 187.1 [1C, dd, ^2J(PC) 18.0, ^1J(RhC) 73.2, C≡O]
1b	δ_P: 73.7 [^1J(RhP) 189] δ_C: 24.9 [1C, d, ^1J(PC) 20.1, CH$_2$], 27.2 (3C, s, C*Me*$_3$), 39.2 (1C, s, *C*Me$_3$), 128.5 [4C, d, ^3J(PC) 10.8, C$_m$], 131.0 (2C, s, C$_p$), 132.6 [2C, d, ^1J(PC) 49.2, C$_i$], 133.0 [4C, d, ^2J(PC) 11.7, C$_o$], 172.2 (1C, s, C=N) and 187.8 [1C, dd, ^2J(PC), 18.2, ^1J(RhC) 73.3, C≡O]
2a	δ_P: 22.8 [^1J(RhP) 130] δ_C: 26.2 [2C, t, $\lvert {}^1J(\mathrm{PC}) + {}^3J(\mathrm{PC}) \rvert$ 20.7, CH$_2$], 28.9 (6C, s, C*Me*$_3$), 38.9 (2C, s, *C*Me$_3$), 46.4 (4C, s, NMe$_2$), 127.6 [8C, t, $\lvert {}^3J(\mathrm{PC}) + {}^5J(\mathrm{PC}) \rvert$ 9.7, C$_m$], 129.4 (4C, s, C$_p$), 133.7 [8C, t, $\lvert {}^2J(\mathrm{PC}) + {}^4J(\mathrm{PC}) \rvert$ 12.7, C$_o$], 135.3 [4C, t, $\lvert {}^1J(\mathrm{PC}) + {}^3J(\mathrm{PC}) \rvert$ 42.7, C$_i$], 172.1 [2C, t, $\lvert {}^2J(\mathrm{PC}) + {}^4J(\mathrm{PC}) \rvert$ 7.4, C=N] and 187.5 [1C, dt, ^2J(PC) 15.1, ^1J(RhC) 76.3, C≡O]
2b	δ_P(C$_6$D$_6$): 17.2 δ_C: 25.9 [2C, t, $\lvert {}^1J(\mathrm{PC}) + {}^3J(\mathrm{PC}) \rvert$ 25.0, CH$_2$], 29.2 (6C, s, C*Me*$_3$), 39.0 (2C, s, *C*Me$_3$), 46.0 (4C, s, NMe$_2$), 127.6 [8C, t, $\lvert {}^3J(\mathrm{PC}) + {}^5J(\mathrm{PC}) \rvert$ 10.2, C$_m$], 129.9 (4C, s, C$_p$), 134.2 [8C, t, $\lvert {}^2J(\mathrm{PC}) + {}^4J(\mathrm{PC}) \rvert$ 12.5, C$_o$], 135.3 [4C, t, $\lvert {}^1J(\mathrm{PC}) + {}^3J(\mathrm{PC}) \rvert$ 45.5, C$_i$], 171.1 [1 C, t, ^2J(PC) 11.0, C≡O] and 172.5 [2C, t, $\lvert {}^2J(\mathrm{PC}) + {}^4J(\mathrm{PC}) \rvert$ 16.1, C=N]
3a	δ_P(CD$_2$Cl$_2$): 24.9 δ_C(MeOH–C$_6$D$_6$): 25.9 [2C, d, ^1J(PC) 28.3, CH$_2$], 27.0 (6C, s, C*Me*$_3$), 39.6 [2C, d, ^3J(PC) 1.3, *C*Me$_3$], 128.2 [4C, d, ^3J(PC) 8.4, C$_m$], 128.6 [4C, d, ^3J(PC) 11.0, C$_m$], 130.2 [4C, d, ^1J(PC) 63.3, C$_i$], 131.5 (2C, s, C$_p$), 131.6 (2C, s, C$_p$), 133.2 [4C, d, ^2J(PC) 10.3, C$_o$], 134.8 [4C, d, ^2J(PC) 9.9, C$_o$] and 174.3 [2C, d, ^2J(PC) 1.3, C=N]
3b	δ_P(CD$_2$Cl$_2$): 22.3
4a	δ_P: 47.5, ^1J(RhP) 167 δ_C: 20.1, [1C, d, ^1J(PC) 20.5, CH$_2$], 27.1 (3C, s, C*Me*$_3$), 28.3 (2C, s, CH$_2$ of cod), 31.3 [2C, d, ^3J(PC) 2.4, CH$_2$ of cod], 40.9 [1C, d, ^3J(PC) 2.2, *C*Me$_3$], 52.8 (2C, s, NMe$_2$), 75.7 [2C, d, ^1J(RhC) 12.6, CH of cod], 109.1 [2C, dd, ^2J(PC) 6.6, ^1J(RhC) 9.6, CH of cod *trans* to P], 128.3 [2C, d, ^1J(PC) 46.4, C$_i$], 129.3 [4C, d, ^3J(PC) 10.3, C$_m$], 132.0 [2C, d, ^4J(PC) 2.2, C$_p$], 133.3 [4C, d, ^2J(PC) 11.0, C$_o$] and 169.6 (1C, s, C=N)
4b	δ_P: 35.9 δ_C: 18.8 [1C, d, ^1J(PC) 26.5, CH$_2$], 27.1 (3C, s, C*Me*$_3$), 29.2 [2C, d, ^3J(PC) 1.7, CH$_2$ of cod], 31.5 [2C, d, ^3J(PC) 3.0, CH$_2$ of cod], 41.5 [1C, d, ^3J(PC) 2.5, *C*Me$_3$], 53.6 [2C, d, ^3J(PC) 1.0, NMe$_2$], 60.9 (2C, s, CH of cod), 97.2 [2C, d, ^2J(PC) 12.0, CH of cod], 127.9 [2C, d, ^1J(PC) 54.3, C$_i$], 129.4 [4C, d, ^3J(PC) 10.6, C$_m$], 132.3 [2C, d, ^4J(PC) 2.3, C$_p$], 133.7 [4C, d, ^2J(PC) 10.8, C$_o$] and 171.4 (1C, s, C=N)
4c	δ_P(CD$_2$Cl$_2$): 53.6 [^1J(RhP) 169]
4d	δ_P(CD$_2$Cl$_2$): 35.9
5a	δ_P: 21.4 [^1J(RhP) 152] δ_C: 27.7 [1C, d, ^1J(PC) 16.0, CH$_2$], 28.6 (3C, s, C*Me*$_3$), 28.8 (2C, br s, CH$_2$ of cod), 32.8 (2C, br s, CH$_2$ of cod), 39.3 [2C, d, ^3J(PC) 1.3, *C*Me$_3$], 46.6 (2C, s, NMe$_2$), 70.2 (2C, br s, CH of cod), 101.9 (2C, br s, CH of cod), 127.8 [4C, d, ^3J(PC) 9.6, C$_m$], 130.0 [2C, d, ^4J(PC) 2.0, C$_p$], 132.5 [2C, d, ^1J(PC) 37.4, C$_i$], 134.4 [4C, d, ^2J(PC) 11.1, C$_o$] and 172.6 [1C, d, ^2J(PC) 7.7, C=N]
5b	δ_P(CD$_2$Cl$_2$): 11.7
6	δ_P(CD$_2$Cl$_2$): 74.2 [^1J(RhP) 191]
7	δ_P(C$_6$D$_6$): 60.3 (P$_A$), 49.9 (P$_B$) [^1J(RhP$_A$) 211, ^1J(RhP$_B$) 178 and ^2J(PP) 46]
8	δ_P: 41.8 (P$_A$), 36.3 (P$_B$) [^1J(RhP$_A$) 162, ^1J(RhP$_B$) 129 and ^2J(PP) 21] δ_C: 27.2 [1C, d, ^1J(PC) 20.3, CH$_2$], 27.4 (3C, s, C*Me*$_3$), 40.6 [1C, d, ^3J(PC) 2.5, *C*Me$_3$], 45.6 [1C, t, ^3J(PC) = ^2J(RhC) 2.0, NMe$_2$], 57.0 [1C, d, ^3J(PC) 1.4, NMe$_2$], 127.5 [6C, d, ^3J(PC) 10.6, C$_m$], 128.5 [2C, d, ^3J(PC) 9.9, C$_m$], 129.0 [2C, d, ^3J(PC) 9.4, C$_m$], 130.3 [3C, d, ^4J(PC) 2.5, C$_p$], 130.6 [1C, d, ^4J(PC) 2.0, C$_p$], 131.3 [1C, d, ^4J(PC) 2.5, C$_p$], 132.6 [2C, d, ^1J(PC) 60.4, C$_i$], 132.8 [2C, d, ^2J(PC) 9.4, C$_o$], 133.9 [3C, d, ^1J(PC) 54.0, C$_i$], 135.1 [6C, d, ^2J(PC) 9.2, C$_o$], 135.6 [2C, d, ^2J(PC) 9.8, C$_o$] and 170.0 [1C, d, ^2J(PC) 1.9, C=N]
9	δ_P(CD$_2$Cl$_2$): 40.7 (P$_A$), 22.6 (P$_B$) [^1J(RhP$_A$) 142, ^1J(RhP$_B$) 113 and ^2J(PP) 29]
10a	δ_P(CD$_2$Cl$_2$): 56.2 (P$_A$), 46.9 (P$_B$) [^1J(RhP$_A$) 218, ^1J(RhP$_B$) 179 and ^2J(PP) 44]
10b	δ_P(CD$_2$Cl$_2$): 25.3 (P$_A$), 7.9 (P$_B$) [^2J(PP) 22]
11a	δ_P(CD$_2$Cl$_2$): 43.0 (P$_A$), 33.5 (P$_B$) [^1J(RhP$_A$) 159, ^1J(RhP$_B$) 122 and ^2J(PP) 22]
11b	δ_P(CD$_2$Cl$_2$): 6.5 (P$_A$), −16.5 (P$_B$) [^2J(PP) 9]

[a] Recorded at 36.2 MHz, chemical shifts in ppm relative to 85% H$_3$PO$_4$, ^1J(RhP) values in Hz, solvent CDCl$_3$ unless otherwise stated. [b] Recorded at 100.6 MHz, chemical shifts in ppm relative to SiMe$_4$, J values in Hz, solvent CDCl$_3$ unless otherwise stated; C$_i$, C$_o$, C$_m$ and C$_p$ refer to *ipso*-, *ortho*-, *meta*- and *para*-carbons of the PPh$_2$ group.

C≡O ligand suggests that C≡O is *cis* to phosphorus.[26,27] The ν(C≡O) value of 1995 cm^{-1} is similar to values reported for carbonylrhodium(I) complexes.[15,18,28]

Similar treatment of the rhodium(I) complex [{RhCl(CO)$_2$}$_2$] with 2 equivalents of L^2 gave the corresponding chelate complex **1b** in excellent (89%) yield. This was characterised in a similar fashion to **1a**. A proton NMR study in which a CDCl$_3$ solution of **1b** was shaken with D$_2$O caused rapid exchange of the NH$_2$ protons for deuterons.

Treatment of [{RhCl(CO)$_2$}$_2$] with 2 equivalents of L^1 per rhodium atom gave the *trans*-chloro(carbonyl)rhodium(I) complex **2a**, which was also prepared by treating the chelate complex **1a** with 1 mol equivalent of L^1 *via* a ring-opening reaction. For **2a** the ^1J(RhP) value of 130 Hz is typical for complexes of type *trans*-[RhCl(CO)(PR$_3$)$_2$].[29–31] In the proton NMR spectrum the value of δ_H(NMe$_2$) 1.93 is similar to that of the free hydrazone (2.10) and quite different to the value when NMe$_2$ is co-ordinated, *i.e.* δ 3.03 for the chelate complex **1a**. In the ^{13}C-{^{1}H} NMR spectrum of **2a** the resonances for CH$_2$, C=N and C$_o$, C$_m$ and C$_p$ carbons of the phenyl rings are virtual 1:2:1 triplets,[31] whilst C≡O appears as a doublet of triplets (Table 1). The bis(phosphine) complex **2a** when treated with 1 equivalent of [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene) reacted rapidly to give a 1:1 mixture of the chelate complexes **1a** and [PtCl$_2${PPh$_2$CH$_2$C(Bu^t)=NNMe$_2$}][2] (Scheme 1).

Treatment of [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)] with 2 mol

Table 2 Proton NMR data[a]

	δ(Bu^t)	δ(CH_2P)	δ(NMe_2), δ(NH_2)
L^1	1.12 (9 H, s)	3.05 [2 H, d, ^2J(PH) 2.9]	2.10 (6 H, s, NMe_2)
L^2	0.98 (9 H, s)	3.10 [2 H, d, ^2J(PH) 2.2]	4.75 (2 H, br s, NH_2)
1a	0.70 (9 H, s)	3.14 [2 H, dd, ^2J(PH) 12.7, ^3J(RhH) 1.4]	3.03 (6 H, s, NMe_2)
1b	0.65 (9 H, s)	3.42 [2 H, d, ^2J(PH) 12.7]	6.58 (2 H, br s, NH_2)[b]
2a	1.14 (18 H, s)	3.97 (4 H, vt, N = 8.8)[c]	1.93 (12 H, s, NMe_2)
2b[d]	1.34 (18 H, s)	4.31 (4 H, vt, N = 9.3)[c]	1.91 (12 H, s, NMe_2)
3a[e]	0.59 (18 H, s)	3.33 [2 H, t, ^2J(PH) = ^2J(HH) 13.2]	−21.31 [1 H, t, ^2J(PH) 16.5, IrH]
		3.78 [2 H, t, ^2J(PH) = ^2J(HH) 13.2]	7.69 [2 H, br d, ^3J(HH) 11.0, NH_2][b]
			9.94 [2 H, br d, ^3J(HH) 11.0, NH_2][b]
3b[e]	0.59 (18 H, s)	2.92 [2 H, t, ^2J(PH) = ^2J(HH) 13.2]	−21.81 [1 H, t, ^2J(PH) 16.6, IrH]
		3.18 [2 H, t, ^2J(PH) = ^2J(HH) 13.2]	5.49 [2 H, br d, ^3J(HH) 11.7, NH_2][b]
			5.78 [2 H, br d, ^3J(HH) 11.7, NH_2][b]
4a[f,g]	0.63 (9 H, s)	3.13 [2 H, d, ^2J(PH) 11.5]	3.06 (6 H, s, NMe_2)
4b[f,h]	0.64 (9 H, s)	3.45 [2 H, d, ^2J(PH) 11.6]	3.21 (6 H, s, NMe_2)
4c[e,i]	0.61 (9 H, s)	3.64 [2 H, dd, ^2J(PH) 12.0, ^3J(RhH) 1.5]	8.19 (2 H, br s, NH_2)[b]
4d[e,j]	0.63 (9 H, s)	3.52 [2 H, d, ^2J(PH) 11.5]	[k]
5a[f,l]	1.22 (9 H, s)	3.89 [2 H, d, ^2J(PH) 12.6]	2.12 (6 H, s, NMe_2)
5b[e,m]	1.12 (9 H, s)	3.97 [2 H, d, ^2J(PH) 12.7]	2.06 (6 H, s, NMe_2)
6[e]	0.58 (18 H, s)	3.13 (4 H, fd, N = 9.3)[c]	8.07 (4 H, br s, NH_2)[b]
7[d]	0.45 (9 H, s)	2.61 [2 H, d, ^2J(PH) 11.2]	3.49 (6 H, s, NMe_2)
8[d]	0.69 (9 H, s)	2.66 [1 H, dd, ^2J(HH) 13.9, $^2J(P_AH)$ 10.1]	2.46 [3 H, d, $^4J(P_BH)$ 2.4, NMe_2]
		3.14 [1 H, t, ^2J(HH) = $^2J(P_AH)$ 14.0]	3.94 [3 H, d, $^4J(P_BH)$ 2.2, NMe_2]
9[e]	0.62 (9 H, s)	3.07 [1 H, m, ^2J(HH) 13.9][n]	3.01 [3 H, d, $^4J(P_BH)$ 3.7, NMe_2]
		3.38 [1 H, m, ^2J(HH) 13.9][n]	3.53 [3 H, d, $^4J(P_BH)$ 2.7, NMe_2]
10a[e]	0.49 (9 H, s)	2.80 [2 H, d, $^2J(P_BH)$ 11.3, CH_2P_B]	1.56 (6 H, s, NMe_2)
	1.48 (9 H, s)	3.95 [2 H, d, $^2J(P_AH)$ 12.5 CH_2P_A]	3.24 (6 H, s, Me_2NRh)
10b[e]	0.50 (9 H, s)	2.97 [2 H, d, $^2J(P_BH)$ 11.7, CH_2P_B]	1.51 (6 H, s, NMe_2)
	1.43 (9 H, s)	3.98 [2 H, d, $^2J(P_AH)$ 12.7, CH_2P_A]	3.35 [6 H, d, $^4J(P_BH)$ 1.2, Me_2NIr]
11a	0.48 (9 H, s)	2.38 [1 H, m, ^2J(HH) 15.5, CH_2P_A][n]	1.67 (6 H, s, NMe_2)
	0.97 (9 H, s)	2.76 (2 H, m, CH_2P_B)[n]	2.39 [3 H, d, $^4J(P_BH)$ 2.9, Me_2NRh]
		3.57 [1 H, dd, ^2J(HH) 15.5, $^2J(P_AH)$ 13.4, CH_2P_A]	3.48 [3 H, d, $^4J(P_BH)$ 2.4, Me_2NRh]
11b[e]	0.49 (9 H, s)	2.70 [1 H, dd, ^2J(HH) 15.4, $^2J(P_AH)$ 11.7, CH_2P_A]	1.69 (6 H, s, NMe_2)
	0.86 (9 H, s)	3.19 [1 H, t, ^2J(HH) = $^2J(P_BH)$ 14.1, CH_2P_B]	2.49 [3 H, d, $^4J(P_BH)$ 2.4, Me_2NIr]
		3.34 [1 H, t, ^2J(HH) = $^2J(P_BH)$ 14.1, CH_2P_B]	3.57 [3 H, d, $^4J(P_BH)$ 2.0, Me_2NIr]
		3.65 [1 H, dd, ^2J(HH) 15.4, $^2J(P_AH)$ 13.4, CH_2P_A]	

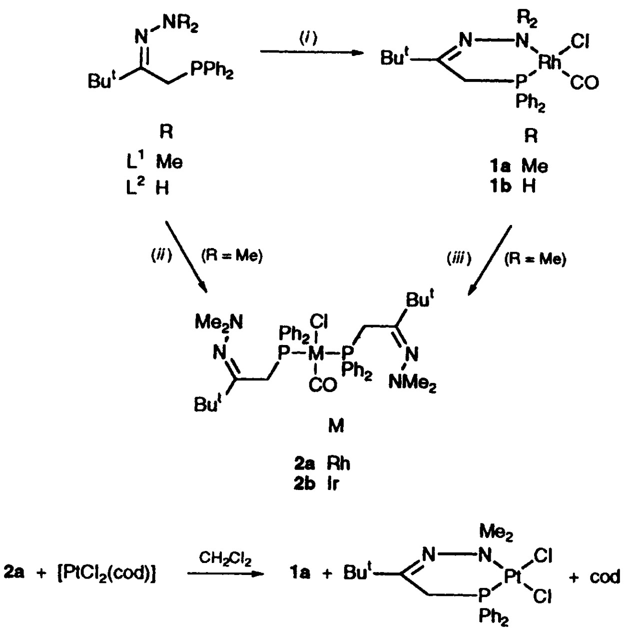
[a] Recorded at 100 MHz, chemical shifts (δ) in ppm relative to $SiMe_4$, solvent $CDCl_3$ unless otherwise stated, coupling constants J in Hz; s = singlet, d = doublet, dd = doublet of doublets, fd = apparent filled-in doublet, t = triplet, vt = virtual triplet and br = broad. [b] Observed weak coupling to phosphorus and exchange with D_2O. [c] $N = |^2J(PH) + {}^4J(PH)|$. [d] In C_6D_6. [e] In CD_2Cl_2. [f] Recorded at 400 MHz. [g] Resonances due to cod appeared as multiplets at δ 2.03 (2 H), 2.20 (2 H), 2.30 (2 H), 2.56 (2 H), 3.22 (2 H) and 5.55 (2 H). [h] Resonances due to cod appeared as multiplets at δ 1.78 (2 H), 2.00 (2 H), 2.08 (2 H), 2.38 (2 H), 3.00 (2 H) and 5.21 (2 H). [i] Resonances due to cod appeared as broad peaks at δ 1.95–2.50 (8 H), 4.22 (2 H) and 4.52 (2 H). [j] Resonances due to cod appeared as broad peaks at δ 1.68 (4 H), 2.19 (4 H) and 3.62 (4 H). [k] Resonances due to NH_2 were not observed. [l] Resonances due to cod appeared as broad peaks at δ 1.85 (2 H), 2.00 (2 H), 2.34 (4 H), 2.91 (2 H) and 5.46 (2 H). [m] Resonances due to cod appeared as broad peaks at δ 1.63 (4 H), 2.13 (4 H) and 3.67 (4 H). [n] Obscured by other peaks.

equivalents of L^1 gave the bis(phosphine) complex **2b** in good (78%) yield. The characterising data show that this Vaska-type iridium(I) complex is analogous to the rhodium(I) complex **2a**, *i.e.* the phosphine ligands are monodentate through phosphorus and mutually *trans*. The ν(C≡O) value of 1955 cm^{-1} is similar to literature values for carbonyliridium(I) complexes of the type *trans*-$[IrCl(CO)(PR_3)_2]$.[18,32]

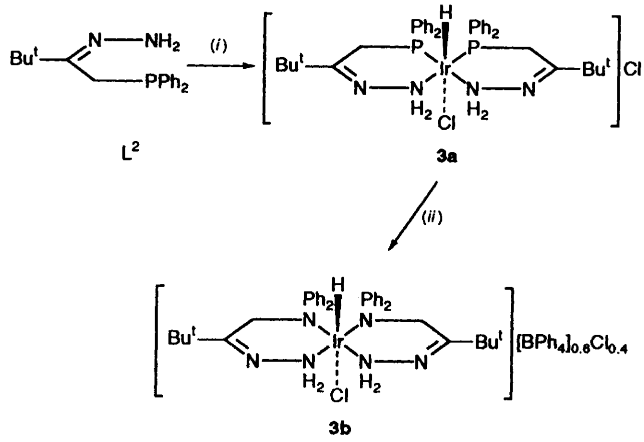
Treatment of $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ with 2 mol equivalents of L^2 gave the hydridoiridium(III) salt **3a** (Scheme 2), *i.e.* the carbonyl ligand was displaced. The mother-liquors from this reaction were very dark brown and we were unable to isolate any other product from them. We suggest that the source of hydride is an NH hydrogen from *p*-toluidine or from the hydrazone L^2. This chloride salt **3a** was converted into the corresponding mixed chloride–tetraphenylborate salt **3b**, when treated with $NaBPh_4$. The $^{31}P\text{-}\{^1H\}$ NMR data for **3a** or **3b** show a singlet resonance (*i.e.* the two phosphorus nuclei are chemically equivalent) whilst the hydride resonance is a triplet at δ ≈ −21.5 with a ^2J(PH) value of 16.5 Hz, and ν(Ir–H) at 2210 cm^{-1}.[17] The hydride must therefore be *trans* to chloride. As would be expected the CH_2 resonance in the $^1H\text{-}\{^{31}P\}$ NMR spectrum is an AB pattern with ^2J(HH) = 13.2 Hz. The NH_2 protons also showed an AB pattern with ^2J(HH) = 13.2 Hz. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the carbon-13 resonances for CH_2, C=N, and C_o, C_m and C_p carbons of the phenyl rings are doublets suggesting that the two phosphorus donor atoms are not strongly coupled and are therefore mutually *cis*. We have reported that palladium(II) or platinum(II) centres react with 2 mol of L^2 to give bis(chelate) complexes of type *cis*-$[M\{PPh_2CH_2C(Bu^t)\!=\!NNH_2\}_2]^{2+}$ (M = Pd or Pt).[2]

Treatment of the binuclear complex $[\{RhCl(cod)\}_2]$ with 2 mol equivalents of L^1 in methanol in the presence of NH_4PF_6 gave the hoped for cationic cycloocta-1,5-diene complex **4a** (Scheme 3). The ^1H and $^{13}C\text{-}\{^1H\}$ NMR data [*e.g.* $\delta_H(NMe_2)$ = 3.06 and $\delta_C(NMe_2)$ = 52.8] clearly indicate the co-ordination of the NMe_2 nitrogen to rhodium. The P,N chelation is also supported by the observation of a downfield ring shift[17] ($\Delta\delta_P$ ≈ 26 ppm) in the phosphorus-31 resonance (δ_P 47.5) of **4a** when compared to the phosphorus-31 chemical shift of complex **5a** (δ_P 21.4, see below) in which the phosphine ligand L^1 is monodentate. The analogous cationic iridium(I) complex **4b** was similarly prepared and fully characterised.

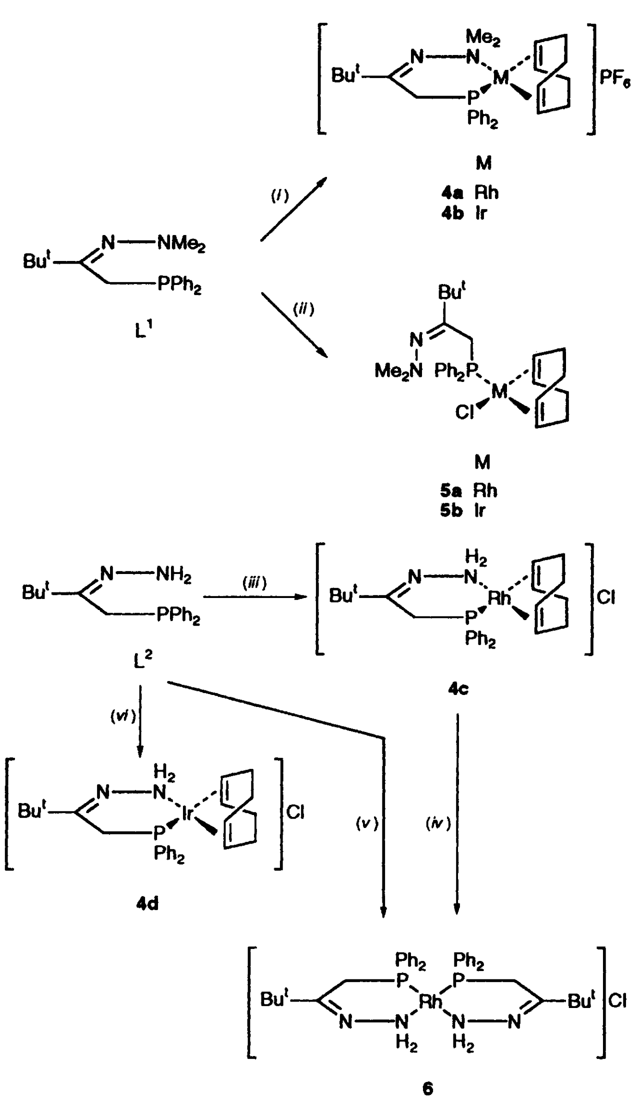
Treatment of $[\{MCl(cod)\}_2]$ (M = Rh or Ir) with L^1 in benzene gave the neutral cycloocta-1,5-diene complex **5a** (Rh) or **5b** (Ir), respectively in which L^1 is monodentate. The complexes were characterised by $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectroscopy (Tables 1 and 2) and **5a** additionally by $^{13}C\text{-}\{^1H\}$ NMR spectroscopy. The proton, $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ NMR spectra clearly show that the NMe_2 is not co-ordinated in these



Scheme 1 (*i*) 0.5 equivalent [$\{RhCl(CO)_2\}_2$]; (*ii*) 0.25 equivalent [$\{RhCl(CO)_2\}_2$] or 0.5 equivalent [$IrCl(CO)_2(H_2NC_6H_4Me$-*p*)]; (*iii*) 1.0 equivalent L^1



Scheme 2 (*i*) 0.5 equivalent [$IrCl(CO)_2(H_2NC_6H_4Me$-*p*)]; (*ii*) $NaBPh_4$

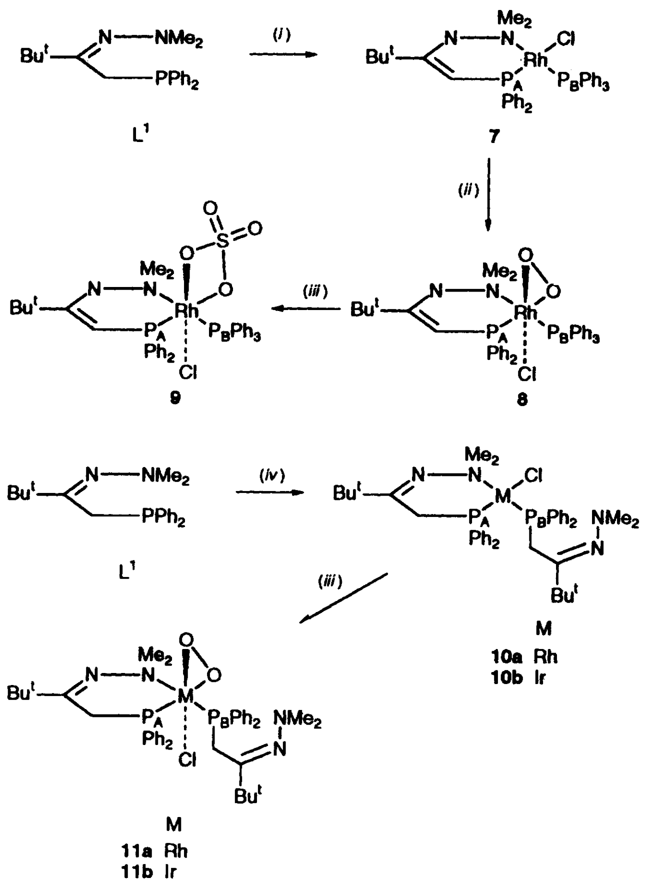


Scheme 3 (*i*) 0.5 equivalent [$\{MCl(cod)\}_2$] and NH_4PF_6 in MeOH; (*ii*) 0.5 equivalent [$\{MCl(cod)\}_2$]–C_6H_6; (*iii*) 0.5 equivalent [$\{RhCl(cod)\}_2$]–CD_2Cl_2; (*iv*) L^2; (*v*) 0.25 equivalent [$\{RhCl(cod)\}_2$]–CD_2Cl_2; (*vi*) 0.5 equivalent [$\{IrCl(cod)\}_2$]–CD_2Cl_2

complexes. The value of $^1J(RhP)$ of 152 Hz is typical for a complex of type [$RhCl(diene)(PR_3)$].[17,22,25,33]

The chelating phosphine cycloocta-1,5-diene salts **4c** (Rh) or **4d** (Ir) from L^2 were prepared *in situ* by treating the appropriate complex [$\{MCl(cod)\}_2$] (M = Rh or Ir) with L^2 in CD_2Cl_2 solution. These chelate complexes **4c** and **4d** are extremely air-sensitive. Treatment of [$\{RhCl(cod)\}_2$] with 1 mol equivalent of L^2 per rhodium atom gave salt **4c** which when treated with a second mol of L^2 gave the bis(chelate) salt *cis*-[$\overline{Rh\{PPh_2CH_2C(Bu^t)=N}NH_2\}_2$]Cl **6**. We assign a *cis* geometry to the bis(chelate) ligands from the value of $^1J(RhP)$ of 191 Hz, typical of phosphorus *trans* to nitrogen, and in the ^1H NMR spectrum the CH_2 resonance is of a 'filled in' doublet type with $N = 9.3$ Hz suggesting that $^2J(PP)$ is not large and that the phosphorus donor atoms are not mutually *trans*.[2,31] We also made the bis(chelate) salt **6** by treating L^2 with 0.25 equivalent of the complex [$\{RhCl(C_8H_{14})_2\}_2$] (C_8H_{14} = cyclooctene).

We also studied the action of L^1 on the Wilkinson catalyst [$RhCl(PPh_3)_3$] (Scheme 4). Treatment with 1 mol of L^1 displaced two triphenylphosphine ligands and gave the hoped for chelate triphenylphosphine complex **7**. This was very air-sensitive and only characterised by NMR spectroscopy in C_6D_6 solution. The ^{31}P-$\{^1H\}$ NMR data [$^2J(PP) = 46$ Hz] indicated that the two phosphorus nuclei were mutually *cis*. The resonances were assigned to P_A (the chelate) and P_B (PPh_3) on the basis of selective decoupling which established that the CH_2 protons were coupled to P_A only [$^2J(P_AH) = 11.2$ Hz]. The ^1H NMR spectrum suggested from the value of $\delta(NMe_2)$ 3.49 that the NMe_2 nitrogen is co-ordinated to rhodium. A benzene solution of this Wilkinson-type complex **7**, prepared *in situ*, reacted with dioxygen (or air) to give the pale yellow dioxygen adduct **8** in 95% isolated yield. This dioxygen adduct was fully characterised, by C, H, N and Cl analysis, ^1H, ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR and mass spectroscopy. In the mass spectrum the parent molecular ion ($M + 1$) was readily observed as were the other ions corresponding to loss of dioxygen, and dioxygen and chlorine. In the infrared spectrum (KBr) there is a band at 870 cm^{-1}, assigned to ν(O–O).[34–37] As would be expected in the ^1H NMR spectrum the CH_2 protons are non-equivalent and mutually coupled [$^2J(HH) = 13.9$ Hz], and they are coupled only to P_A. In contrast, the NMe_2 hydrogens are coupled only to P_B suggesting that the NMe_2 group is *trans* to P_B,[4,28] the methyls being non-equivalent with $^4J(P_BMe) = 2.2$ and 2.4 Hz, respectively. The dioxygenrhodium(III) complex **8** reacted rapidly with sulfur dioxide to give the rhodium(III) sulfate **9** in 76% isolated yield. Complex **9** was fully characterised. In the



Scheme 4 (*i*) $[\mathrm{RhCl(PPh_3)_3}]$; (*ii*) $\mathrm{O_2}$; (*iii*) $\mathrm{SO_2}$; (*iv*) 0.25 equivalent $[\{\mathrm{MCl(C_8H_{14})_2}\}_2]$

infrared spectrum the bands due to $\nu(\mathrm{SO_4})$ at 1260, 1160 and 655 $\mathrm{cm^{-1}}$ are at similar frequencies to those found for other bidentate sulfur complexes.[19,37]

Treatment of $[\{\mathrm{RhCl(C_8H_{14})_2}\}_2]$ with 2 mol equivalents of $\mathrm{L^1}$ per rhodium atom gave the bis(phosphine)rhodium(I) complex **10a**, containing one chelate and one monodentate *Z*-$\mathrm{PPh_2CH_2C(Bu^t){=}NNMe_2}$ ligand. This complex was characterised by elemental analysis and mass spectrometry and by $^{31}\mathrm{P}$-$\{^1\mathrm{H}\}$ and $^1\mathrm{H}$ NMR spectroscopy. In particular, in the $^{31}\mathrm{P}$-$\{^1\mathrm{H}\}$ NMR spectrum the value of $^2J(\mathrm{PP})$ of 44 Hz indicates mutually *cis*-phosphine ligands, and the $^1J(\mathrm{RhP})$ values of 218 and 179 Hz are similar to those of **7**. In the $^1\mathrm{H}$ NMR spectrum there are two sets of $\mathrm{Bu^t}$, $\mathrm{CH_2}$ and $\mathrm{NMe_2}$ protons, corresponding to chelating and monodentate *Z*-$\mathrm{PPh_2CH_2C(Bu^t){=}NNMe_2}$ ligands, respectively. The singlet at δ 1.56 is assigned to the un-co-ordinated $\mathrm{NMe_2}$ group. Treatment of complex **10a** with a one-third mol of $\mathrm{L^1}$ did not result in a ring-opening reaction to give a complex of type $[\mathrm{RhCl(L^1)_3}]$ at 20 °C in benzene solution.

An analogous bis(phosphine)iridium(I) complex **10b** was prepared *in situ* and characterised in solution. From the NMR data it is clearly analogous to the bis(phosphine)rhodium(I) complex **10a**. Complex **10a** or **10b** in dichloromethane solution reacted rapidly with dioxygen to give the corresponding dioxygen adduct **11a** or **11b**, respectively, both of which were isolated and characterised.

Experimental

All the reactions were carried out in an inert atmosphere of dry nitrogen or dry argon. Infrared spectra were recorded using a Perkin-Elmer model 457 grating spectrometer, NMR spectra using a JEOL FX-90Q (operating frequencies for $^1\mathrm{H}$ and $^{31}\mathrm{P}$ of 89.5 and 36.2 MHz), FX-100 (operating frequencies for $^1\mathrm{H}$ and $^{31}\mathrm{P}$ of 99.5 and 40.25 MHz) or a Bruker AM-400 spectrometer (operating frequencies for $^1\mathrm{H}$, $^{31}\mathrm{P}$ and $^{13}\mathrm{C}$ of 400.13, 161.9 and 100.6 MHz), respectively. The $^1\mathrm{H}$ and $^{13}\mathrm{C}$ chemical shifts are relative to tetramethylsilane and $^{31}\mathrm{P}$ shifts to 85% phosphoric acid. Fast atom bombardment (FAB) mass spectra were recorded on a VG Autospec spectrometer using 8 kV acceleration. For metal complexes *m*/*z* values are quoted for $^{35}\mathrm{Cl}$, $^{103}\mathrm{Rh}$ and $^{193}\mathrm{Ir}$.

The compounds *Z*-$\mathrm{PPh_2CH_2C(Bu^t){=}NNMe_2}$ $\mathrm{L^1}$ and *Z*-$\mathrm{PPh_2CH_2C(Bu^t){=}NNH_2}$ $\mathrm{L^2}$ were prepared according to our published procedure;[1] $[\{\mathrm{RhCl(CO)_2}\}_2]$,[38] $[\mathrm{IrCl(CO)_2(H_2NC_6H_4Me}$-*p*$)]$,[39] $[\{\mathrm{RhCl(cod)}\}_2]$,[40] $[\mathrm{RhCl(PPh_3)_3}]$,[41] $[\{\mathrm{IrCl(cod)}\}_2]$,[42] $[\{\mathrm{IrCl(C_8H_{14})_2}\}_2]$[42] and $[\{\mathrm{RhCl(C_8H_{14})_2}\}_2]$[43] were prepared according to literature procedures.

$[\mathrm{RhCl(CO)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}}]$ **1a**.—The complex $[\{\mathrm{RhCl(CO)_2}\}_2]$ (75 mg, 0.19 mmol) was added to a solution of the phosphino dimethylhydrazone $\mathrm{L^1}$ (126 mg, 0.38 mmol) in benzene (3 $\mathrm{cm^3}$). After 10 min the resulting yellow solution was concentrated to a low volume (*ca.* 0.5 $\mathrm{cm^3}$) under reduced pressure and the residue triturated with methanol to give the required product **1a** as yellow microcrystals (144 mg, 76%) (Found: C, 51.15; H, 5.5; Cl, 7.4; N, 5.7. $\mathrm{C_{21}H_{27}ClN_2OPRh}$ requires C, 51.2; H, 5.2; Cl, 7.2; N, 5.7%); *m*/*z* (FAB) 466 (*M* − CO) and 457 (*M* − Cl); $\mathrm{IR(CH_2Cl_2)}$: $\nu(\mathrm{C{\equiv}O})$ 1995 $\mathrm{cm^{-1}}$.

$[\mathrm{RhCl(CO)\{PPh_2CH_2C(Bu^t){=}NNH_2\}}]$ **1b**.—The complex $[\{\mathrm{RhCl(CO)_2}\}_2]$ (75 mg, 0.19 mmol) was added to a solution of the phosphino hydrazone $\mathrm{L^2}$ (111 mg, 0.37 mmol) in benzene (3 $\mathrm{cm^3}$). After 10 min the resulting yellow solution was concentrated to a low volume (*ca.* 0.5 $\mathrm{cm^3}$) under reduced pressure. Addition of hexane to the residue gave the required product **1b** as yellow microcrystals (155 mg, 89%) (Found: C, 49.05; H, 5.05; Cl, 7.65; N, 5.65. $\mathrm{C_{19}H_{23}ClN_2OPRh}$ requires C, 49.1; H, 5.0; Cl, 7.65; N, 6.0%); *m*/*z* (FAB) 437 (*M* + 1 − CO); $\mathrm{IR(CH_2Cl_2)}$: $\nu(\mathrm{C{\equiv}O})$ 1995 $\mathrm{cm^{-1}}$.

trans-$[\mathrm{RhCl(CO)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}_2}]$ **2a**.—The complex $[\{\mathrm{RhCl(CO)_2}\}_2]$ (50 mg, 0.13 mmol) was added to a solution of $\mathrm{L^1}$ (168 mg, 0.51 mmol) in benzene (3 $\mathrm{cm^3}$). After 10 min the resulting yellow solution was filtered and concentrated to a low volume (*ca.* 0.5 $\mathrm{cm^3}$) under reduced pressure. Addition of hexane (2 $\mathrm{cm^3}$) to the residue gave the required product **2a** as pale yellow microcrystals (170 mg, 80%) (Found: C, 60.95; H, 6.75; Cl, 4.25; N, 6.6. $\mathrm{C_{41}H_{54}ClN_4OP_2Rh{\cdot}0.25C_6H_6}$ requires C, 60.85; H, 6.65; Cl, 4.25; N, 6.7%); *m*/*z* (FAB) 819 (*M* + 1), 783 (*M* − Cl) and 755 (*M* − Cl − CO); $\mathrm{IR(CH_2Cl_2)}$: $\nu(\mathrm{C{\equiv}O})$ 1960 $\mathrm{cm^{-1}}$.

trans-$[\mathrm{IrCl(CO)\{PPh_2CH_2C(Bu^t){=}NNMe_2\}_2}]$ **2b**.—The complex $[\mathrm{IrCl(CO)_2(H_2NC_6H_4Me}$-*p*$)]$ (75 mg, 0.19 mmol) was added to a solution of $\mathrm{L^1}$ (126 mg, 0.39 mmol) in benzene (4 $\mathrm{cm^3}$) and the solution was warmed to *ca.* 70 °C for 1 min. The solution was then filtered and concentrated to a low volume (*ca.* 0.5 $\mathrm{cm^3}$) under reduced pressure. Addition of hexane (2 $\mathrm{cm^3}$) to the residue gave the required product **2b** as yellow microcrystals (135 mg, 78%) (Found: C, 54.4; H, 6.0; Cl, 4.0; N, 6.0. $\mathrm{C_{41}H_{54}ClIrN_4OP_2}$ requires C, 54.2; H, 6.0; Cl, 3.9; N, 6.15%); *m*/*z* (FAB) 909 (*M* + 1) and 873 (*M* − Cl); $\mathrm{IR(CH_2Cl_2)}$: $\nu(\mathrm{C{\equiv}O})$ 1955 $\mathrm{cm^{-1}}$.

cis-$[\mathrm{IrH(Cl)\{PPh_2CH_2C(Bu^t){=}NNH_2\}_2]Cl}$ **3a**.—The complex $[\mathrm{IrCl(CO)_2(H_2NC_6H_4Me}$-*p*$)]$ (100 mg, 0.25 mmol) and $\mathrm{L^2}$ (150 mg, 0.50 mmol) in benzene (4 $\mathrm{cm^3}$) were heated under reflux for 15 min. The resulting white precipitate of **3a** was filtered off, washed with hexane and dried. Yield 105 mg, 97% with respect to chlorine (Found: C, 50.0; H, 5.5; Cl, 7.95; N, 6.65. $\mathrm{C_{36}H_{47}Cl_2IrN_4P_2}$ requires C, 50.2; H, 5.5; Cl, 8.25; N, 6.5%); *m*/*z* (FAB) 825 (*M* − Cl) and 789 (*M* − Cl − HCl); IR(KBr): $\nu(\mathrm{Ir{-}H})$ 2210 $\mathrm{cm^{-1}}$.

cis-$\mathrm{[IrH(Cl)\{PPh_2CH_2C(Bu^t)=NNH_2\}_2][BPh_4]_{0.6}Cl_{0.4}}$ **3b**.—An excess of $\mathrm{NaBPh_4}$ (100 mg, 0.29 mmol) in ethanol (1 cm^3) was added to a solution of the chloride salt **3a** (50 mg, 0.058 mmol) in ethanol (1.5 cm^3). The required product **3b** was obtained as a white solid (42 mg, 64%) (Found: C, 60.3; H, 5.65; Cl, 4.05; N, 4.85. $\mathrm{C_{36}H_{47}IrN_4P_2{\cdot}0.6C_{24}H_{20}B{\cdot}0.4Cl}$ requires C, 60.1; H, 5.65; Cl, 4.05; N, 4.85%). *m*/*z* (FAB) 825 ($M - \mathrm{BPh_4/Cl}$) and 789 ($M - \mathrm{BPh_4/Cl} - \mathrm{HCl}$); IR(KBr): ν(Ir–H) 2210 cm^{-1}.

$\mathrm{[Rh(cod)\{PPh_2CH_2C(Bu^t)=NNMe_2\}]PF_6}$ **4a**.—An excess of $\mathrm{NH_4PF_6}$ (0.2 g, 1.2 mmol) in methanol (*ca.* 1 cm^3) was added to a solution containing $\mathrm{[\{RhCl(cod)\}_2]}$ (125 mg, 0.25 mmol) and $\mathrm{L^1}$ (165 mg, 0.50 mmol) in methanol (3 cm^3). The resulting yellow crystals of complex **4a** were filtered off, washed with cold methanol and dried. Yield 0.31 g, 91% (Found: C, 49.6; H, 5.65; N, 4.1. $\mathrm{C_{28}H_{39}F_6N_2P_2Rh}$ requires C, 49.3; H, 5.75; N, 4.1%); *m*/*z* (FAB) 537 ($M - \mathrm{PF_6}$).

$\mathrm{[Ir(cod)\{PPh_2CH_2C(Bu^t)=NNMe_2\}]PF_6}$ **4b**.—Complex **4b** was prepared from $\mathrm{[\{IrCl(cod)\}_2]}$ and isolated in 35% yield as orange microcrystals in a similar manner to the analogous rhodium(I) complex **4a**. An analytical sample was recrystallised from benzene–methanol (Found: C, 44.75; H, 5.05; N, 3.5. $\mathrm{C_{28}H_{39}F_6IrN_2P_2{\cdot}0.25C_6H_6}$ requires C, 44.75; H, 5.15; N, 3.55%); *m*/*z* (FAB) 627 ($M - \mathrm{PF_6}$).

$\mathrm{[Rh(cod)\{PPh_2CH_2C(Bu^t)=NNH_2\}]Cl}$ **4c**.—Complex **4c** was prepared *in situ* by dissolving $\mathrm{[\{RhCl(cod)\}_2]}$ (15 mg, 0.03 mmol) and $\mathrm{L^2}$ (17 mg, 0.057 mmol) in $\mathrm{CD_2Cl_2}$ (*ca.* 0.4 cm^3).

$\mathrm{[Ir(cod)\{PPh_2CH_2C(Bu^t)=NNH_2\}]Cl}$ **4d**.—Complex **4d** was prepared *in situ* by dissolving $\mathrm{[\{IrCl(cod)\}_2]}$ (10 mg, 0.015 mmol) and $\mathrm{L^2}$ (8.9 mg, 0.03 mmol) in $\mathrm{CD_2Cl_2}$ (*ca.* 0.4 cm^3).

$\mathrm{[RhCl(cod)\{PPh_2CH_2C(Bu^t)=NNMe_2\}]}$ **5a**.—The complex $\mathrm{[\{RhCl(cod)\}_2]}$ (50 mg, 0.10 mmol) and $\mathrm{L^1}$ (66 mg, 0.20 mmol) were dissolved in benzene (3 cm^3). After 15 min the solution was concentrated to a low volume (*ca.* 0.3 cm^3) under reduced pressure. Addition of hexane (1 cm^3) to the residue gave the required product **5a** as bright yellow microcrystals (80 mg, 70%) (Found: C, 58.05; H, 6.45; Cl, 6.35; N, 4.5. $\mathrm{C_{28}H_{39}ClN_2PRh}$ requires C, 58.7; H, 6.85; Cl, 6.2; N, 4.9%); *m*/*z* (FAB) 573 ($M + 1$) and 537 ($M - \mathrm{Cl}$).

$\mathrm{[IrCl(cod)\{PPh_2CH_2C(Bu^t)=NNMe_2\}]}$ **5b**.—The complex $\mathrm{[\{IrCl(cod)\}_2]}$ (67 mg, 0.10 mmol) and $\mathrm{L^1}$ (66 mg, 0.20 mmol) were heated under reflux in benzene (4 cm^3) for 20 min. The solution was then filtered and the filtrate concentrated to a low volume (*ca.* 0.3 cm^3) under reduced pressure. Addition of hexane (2 cm^3) to the residue gave the required product **5b** as bright yellow microcrystals (53 mg, 40%) (Found: C, 50.8; H, 5.85; Cl, 5.5; N, 4.35. $\mathrm{C_{28}H_{39}ClIrN_2P}$ requires C, 50.75; H, 5.95; Cl, 5.35; N, 4.2%); *m*/*z* (FAB) 663 ($M + 1$) and 627 ($M - \mathrm{Cl}$).

cis-$\mathrm{[Rh\{PPh_2CH_2C(Bu^t)=NNH_2\}_2]Cl}$ **6**.—(*i*) *From* $\mathrm{[\{RhCl(cod)\}_2]}$. Complex **6** was prepared *in situ* by dissolving $\mathrm{[\{RhCl(cod)\}_2]}$ (15 mg, 0.03 mmol) and $\mathrm{L^2}$ (37 mg, 0.057 mmol) in $\mathrm{CD_2Cl_2}$ (*ca.* 0.5 cm^3).

(*ii*) *From* $\mathrm{[\{RhCl(C_8H_{14})_2\}_2]}$. Complex **6** was prepared *in situ* by dissolving $\mathrm{[\{RhCl(C_8H_{14})_2\}_2]}$ (15 mg, 0.021 mmol) and $\mathrm{L^2}$ (25 mg, 0.084 mmol) in $\mathrm{CD_2Cl_2}$ (*ca.* 0.5 cm^3).

cis-$\mathrm{[RhCl(PPh_3)\{PPh_2CH_2C(Bu^t)=NNMe_2\}]}$ **7**.—Complex **7** was prepared *in situ* by dissolving $\mathrm{[RhCl(PPh_3)]}$ (15 mg, 0.016 mmol) and $\mathrm{L^1}$ (5.3 mg, 0.016 mmol) in $\mathrm{C_6D_6}$ (*ca.* 0.5 cm^3).

cis-$\mathrm{[RhCl(O_2)(PPh_3)\{PPh_2CH_2C(Bu^t)=NNMe_2\}]}$ **8**.—Dioxygen was bubbled for 2 min through a solution containing $\mathrm{[RhCl(PPh_3)_3]}$ (0.24 g, 0.26 mmol) and $\mathrm{L^1}$ (84 mg, 0.26 mmol) in benzene (5 cm^3), and the solution was then concentrated to a low volume (*ca.* 0.5 cm^3) under reduced pressure. Addition of cyclohexane (2 cm^3) to the residue gave the required product **8** as yellow microcrystals (0.19 g, 95%) (Found: C, 59.75; H, 5.45; Cl, 4.8; N, 3.45. $\mathrm{C_{38}H_{42}ClN_2O_2P_2Rh}$ requires C, 60.1; H, 5.5; Cl, 4.65; N, 3.7%); *m*/*z* (FAB) 759 ($M + 1$), 726 ($M - 2\mathrm{O}$) and 691 ($M - 2\mathrm{O} - \mathrm{Cl}$); IR(KBr): ν(O–O) 870 cm^{-1}.

cis-$\mathrm{[RhCl(SO_4)(PPh_3)\{PPh_2CH_2C(Bu^t)=NNMe_2\}]}$ **9**.—Sulfur dioxide was bubbled for 30 s through a solution containing complex **7** (50 mg, 0.065 mmol) in $\mathrm{CH_2Cl_2}$ (1.5 cm^3). After 30 min the solution was concentrated to a low volume (*ca.* 0.3 cm^3) under reduced pressure. Addition of hexane (1 cm^3) to the residue gave the required product **9** as yellow microcrystals (41 mg, 76%) (Found: C, 55.25; H, 5.05; Cl, 4.5; N, 3.4. $\mathrm{C_{38}H_{42}ClN_2O_4P_2RhS}$ requires C, 55.45; H, 5.15; Cl, 4.3; N, 3.4%); *m*/*z* (FAB) 823 ($M + 1$), 786 ($M - \mathrm{HCl}$) and 725 ($M - \mathrm{HSO_4}$); IR(KBr): ν($\mathrm{SO_4}$) 1260m, 1160s and 655s cm^{-1}.

cis-$\mathrm{[RhCl\{PPh_2CH_2C(Bu^t)=NNMe_2\}\{PPh_2CH_2C(Bu^t)=NNMe_2\}]}$ **10a**.—The complex $\mathrm{[\{RhCl(C_8H_{14})_2\}_2]}$ (30 mg, 0.042 mmol) and $\mathrm{L^1}$ (55 mg, 0.167 mmol) were warmed in acetone (2 cm^3) for 1 min. The resulting yellow solution was then cooled to −30 °C. The required product **10a** deposited as orange crystals (47 mg, 71%) (Found: C, 60.65; H, 7.35; Cl, 4.25; N, 6.25. $\mathrm{C_{40}H_{54}ClN_4P_2Rh{\cdot}C_3H_6O}$ requires C, 60.8; H, 7.1; Cl, 4.15; N, 6.6%); *m*/*z* (FAB) 790 (M^+) and 755 ($M - \mathrm{Cl}$).

cis-$\mathrm{[IrCl\{PPh_2CH_2C(Bu^t)=NNMe_2\}\{PPh_2CH_2C(Bu^t)=NNMe_2\}]}$ **10b**.—Complex **10a** was prepared *in situ* by dissolving $\mathrm{[\{IrCl(C_8H_{14})_2\}_2]}$ (15 mg, 0.016 mmol) and $\mathrm{L^1}$ (22 mg, 0.067 mmol) in $\mathrm{CD_2Cl_2}$ (*ca.* 0.5 cm^3).

cis-$\mathrm{[RhCl(O_2)\{PPh_2CH_2C(Bu^t)=NNMe_2\}\{PPh_2CH_2C(Bu^t)=NNMe_2\}]}$ **11a**.—Dioxygen was bubbled for 1 min through a solution containing $\mathrm{[\{RhCl(C_8H_{14})_2\}_2]}$ (90 mg, 0.125 mmol) and $\mathrm{L^1}$ (165 mg, 0.50 mmol) in $\mathrm{CH_2Cl_2}$ (4 cm^3). The solution was then concentrated to a low volume (*ca.* 0.5 cm^3) under reduced pressure. Addition of hexane (3 cm^3) to the residue gave the required product **11a** as brown microcrystals (0.16 g, 77%) (Found: C, 56.55; H, 6.7; Cl, 7.85; N, 6.45. $\mathrm{C_{40}H_{54}ClN_4O_2P_2Rh{\cdot}0.5CH_2Cl_2}$ requires C, 56.2; H, 6.4; Cl, 8.2; N, 6.45%); *m*/*z* (FAB) 823 ($M + 1$); IR(KBr): ν(O–O) 865 cm^{-1}.

cis-$\mathrm{[IrCl(O_2)\{PPh_2CH_2C(Bu^t)=NNMe_2\}\{PPh_2CH_2C(Bu^t)=NNMe_2\}]}$ **11b**.—Complex **11b** was prepared using $\mathrm{[\{IrCl(C_8H_{14})_2\}_2]}$ in a similar manner to that of **11a**, in 45% yield (Found: C, 52.65; H, 5.8; Cl, 3.8; N, 6.0. $\mathrm{C_{40}H_{54}ClIrN_4O_2P_2}$ requires C, 52.65; H, 5.95; Cl, 3.9; N, 6.15%); *m*/*z* (FAB) 913 ($M + 1$); IR(KBr): ν(O–O) 860 cm^{-1}.

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