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A new method of creating co-ordinative unsaturation: synthesis and reactions of a reactive iridium(I) complex $[Ir(CO)\{PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2\}]PF_6$: crystal structures of $[Ir(CO)(\eta^2\text{-}L)\{PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2\}]PF_6$ (L = $MeO_2CC{\equiv}CCO_2Me$ or COCH=CHCONMe)

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Treatment of $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ with the azine diphosphine $PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2$ **1** in benzene gave the co-ordinatively saturated (18e) octahedral iridium(III) hydride $[IrH(Cl)(CO)(PPh_2CH=C(Bu^t)-N-N=C(Bu^t)CH_2PPh_2\}]$ **3** in which the P,N,P-terdentate diphosphine ligand had lost a hydrogen to give an ene–hydrazone backbone. On dissolution in methanol or ethanol, complex **3** immediately dissolved to give the isomeric but co-ordinatively unsaturated (16e) iridium(I) complex $[Ir(CO)\{PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2\}]Cl$ **4a** in which the P,N,P-terdentate ligand backbone contained an azine moiety. Complex **4a** was readily converted to the corresponding PF_6 salt **4b**. On dissolution in dichloromethane or benzene **4a** rapidly gave back **3**. Treatment of **4b** with acetylenes or olefins gave adducts $[Ir(CO)\{PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2\}L]PF_6$ in which L = $MeO_2CC{\equiv}CCO_2Me$ **5a**, $HC{\equiv}CCO_2Me$ **5b**, MeN(O=C)CH=CHCO **8a**, *trans*-$MeO_2CCH{=}CHCO_2Me$ **8b**, *trans*-$EtO_2CCH{=}CHCO_2Et$ **8c**, C_2H_4 **8d** or $CH_2{=}C{=}CH_2$ **8e**,**8f**. Proton NMR studies on the ethene adduct showed that the ethene ligand was rotating at *ca.* 20 °C but at −40 °C rotation had stopped. Allene gives a mixture of two isomeric adducts **8e** and **8f**. Complex **4b** reacted with $PhC{\equiv}CH$ in a different fashion to give the phenylacetylide hydride *fac*-$[IrH(C{\equiv}CPh)(CO)\{PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2\}]PF_6$ **6** which isomerised on heating to *mer*-$[IrH(C{\equiv}CPh)(CO)\{PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2\}]PF_6$ **7**. Treatment of **4b** with $EtO_2CN{=}NCO_2Et$ gave an adduct $[Ir(CO)\{PPh_2CH{=}C(Bu^t)-N-N=C(Bu^t)CH_2PPh_2\}(EtO_2CNHNCO_2Et)]PF_6$ **9** in which the diphosphine backbone had been deprotonated and the diethyl azocarboxylate protonated. Treatment of **4b** with carbon monoxide gave the dicarbonyliridium complex $[Ir(CO)_2\{PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)\text{-}CH_2PPh_2\}]PF_6$ **10**. Treatment of **4b** with dihydrogen gave a dihydridoiridium(III) adduct **11** in which the terdentate P,N,P diphosphine was in the *fac* arrangement. In solution **11** slowly isomerised over several hours to give a dihydride in which the terdentate P,N,P diphosphine was in the *mer* arrangement, *i.e.* the structure of the dihydride was **12**. Complex **4b** underwent other types of oxidative-addition reactions, *i.e.* with formic acid it gave the hydride *mer*-$[IrH(O_2CH)(CO)\{PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2\}]PF_6$ **13**, with methyl iodide the *mer*-methyliridium(III) adduct **14** and with bromine the *mer*-iridium(III) dibromide **15**. The crystal structures of **5a** and **8a** were determined.

Co-ordinative unsaturation is extremely important in transition-metal chemistry and in associated areas of catalysis.[1–4] Transition-metal hydrides are good illustrative examples: a hydride with a vacant co-ordination site can often take up an olefin (or acetylene) and, if this is followed by migration of hydride from metal to carbon giving an alkyl group, then subsequent chemistry can lead to a synthesis which might be catalytic. Examples of this include Wilkinson's catalyst $[RhCl(PPh_3)_3]$, which on reaction with dihydrogen loses a PPh_3 ligand to give $[RhH_2(Cl)(PPh_3)_2]$; this co-ordinatively unsaturated hydride can take up an olefin and rapid catalytic hydrogenation follows.[4] A similar situation arises with the chiral hydrogenation of olefins using rhodium or ruthenium chiral tertiary phosphine complexes as catalysts.[1–5] A good example of the importance of co-ordinative unsaturation is with the hydroformylation of olefins using $[CoH(CO)_4]$ as catalyst. This co-ordinatively saturated hydride needs to lose CO to create a vacant site so that the cobalt can co-ordinate to the substrate olefin; catalysis can then proceed. There are many other examples of co-ordinatively saturated complexes either being unreactive or reacting only very slowly compared to related co-ordinatively unsaturated species which are sometimes extremely reactive. A classic example illustrating the enormous differences in substitution rates between co-ordinatively saturated (18e) and co-ordinatively unsaturated (16e) complexes is $[Rh(C_2H_4)_2(acac)]$ (acac = acetylacetonate) which exchanges complexed ethylene with free ethylene at 10^{14} times the rate at which the co-ordinatively saturated (18e) complex $[Rh(C_2H_4)_2(\eta^5\text{-}C_5H_5)]$ exchanges.[6,7] In the present paper we describe a new method of generating a labile, co-ordinatively unsaturated iridium(I) complex by the rapid and reversible isomerisation of a co-ordinatively saturated iridium(III) hydride complex. The isomerisation involves using an ene–hydrazone backbone of a diphosphine as the sink for a hydrogen atom, thereby giving an azine backbone. We have found that azines or ene–hydrazones form very good backbones for diphosphines. Azines are relatively easy to prepare and are often very resistant to hydrolysis or other types of decomposition[8] but prior to our work[9] they have not been used in this way. In the present paper we describe results with iridium complexes, complexes which have in the past proved to be excellent model systems for predicting the behaviour of many other tertiary phosphine metal complexes including their use in catalysis.

Results and Discussion

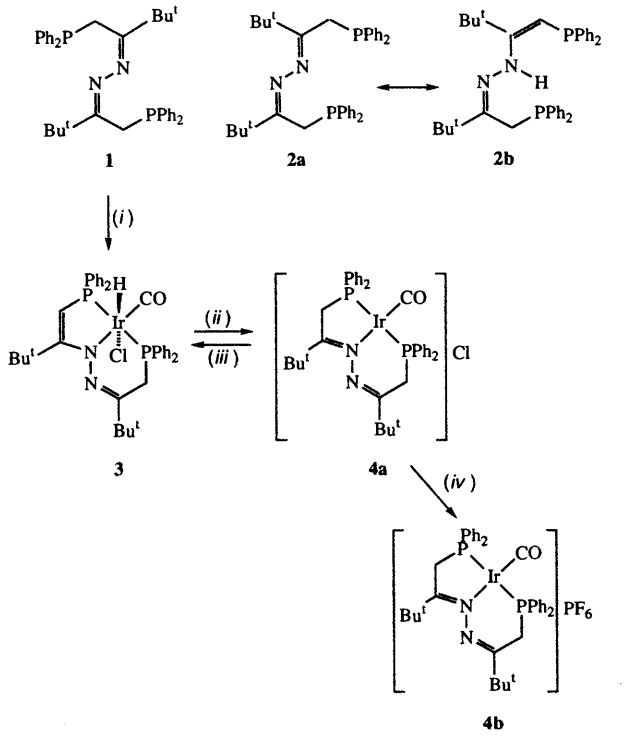
The azine diphosphine $PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2$ has the *Z,Z* configuration **1** but the energy barrier to rotation around the C=N bond is quite low[8,9] and it often co-ordinates

in the *E,Z* configuration **2a** to a metal either as nine-membered chelate ring with two P donors or as a terdentate chelate with P,N and P donors.[9–13] A convenient reagent for generating iridium(I) carbonyl derivatives is $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$[14] which, for example, readily gives complexes of the type *trans*-$[IrCl(CO)(PR_3)_2]$ when treated with PR_3. However, we find that on treating $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ with the azine diphosphine **1** in hot benzene an excellent yield (87%) of the octahedral hydrido(carbonyl)iridium(III) complex **3** is obtained. This and other complexes described in this paper were usually characterised by elemental analysis and infrared spectroscopy (see Experimental section) and by $^{31}P\text{-}\{^1H\}$, ^1H, $^1H\text{-}\{^{31}P\}$ and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy (Tables 1–3).

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

Complex	$\delta(P_A)$	$\delta(P_B)$	$^2J(PP)$
1[b]	−14.4		
3[c]	44.3	20.3	312
4a[d]	60.6	56.0	303
4b[b]	61.7	54.4	308
5a	42.5	9.6	35
5b	42.2	10.1	45
6	29.4	7.9	11
7	34.3	15.3	323
8a	34.9	8.4	32
8b	36.6	8.4	35
8c	36.7	8.8	37
8d	38.4	10.4	57
8e, 8f	32.5[e]	14.5[e]	42[e]
	41.2[f]	6.7[f]	39[f]
9	3.7	−17.5	13
10	48.4	22.8	179
11	27.5	11.0	11
12	37.5	20.5	301
13	44.3	31.2	315
14[g]	24.7	20.7	342
15	25.4	20.1	364

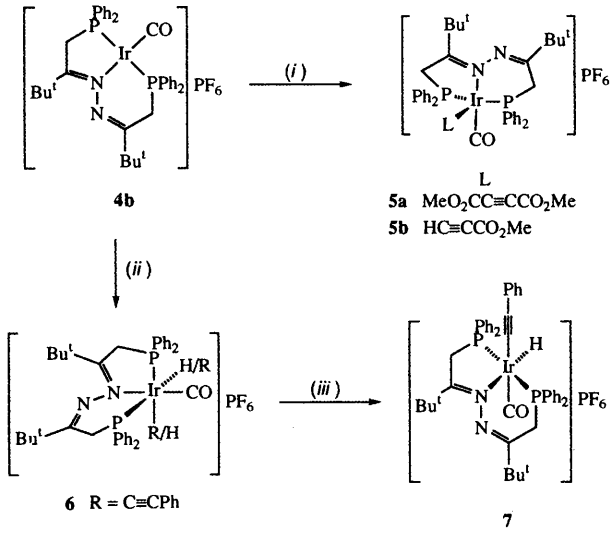
[a] Recorded at 36.2 MHz, chemical shifts (δ) in ppm relative to 85% H_3PO_4, solvent CD_2Cl_2 unless otherwise stated; *J* values are in Hz. [b] In $CDCl_3$. [c] In C_6D_6. [d] In MeOH–C_6D_6. [e] Major isomer. [f] Minor isomer. [g] At 161.9 MHz.



Scheme 1 (*i*) $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$; (*ii*) EtOH or MeOH; (*iii*) CH_2Cl_2 or C_6H_6; (*iv*) NH_4PF_6

Various complexes and their reactions are summarised in Schemes 1–4. In particular, for complex **3** $^2J(PP)$ is large (312 Hz) indicating mutually *trans*-co-ordinated P donors, and the value of $\delta(H)$ for the hydride (−15.4) is close to those of similar hydride ligands *trans* to chloride for a range of iridium(III) hydrides.[15–18] We suggest that in effect the diphosphine in its ene–hydrazone form **2b** has oxidatively added to the iridium. It is known that oxidative addition of X–H (X = H, B, C, N, O, S or Si) to iridium(I) is usually *cis* orientated.[15–28] The ^1H and $^1H\text{-}\{^{31}P\}$ NMR data (Table 2) show the presence of an alkene hydrogen and the two non-equivalent methylene hydrogens [δ = 3.03 and 3.99, $^2J(HH)$ = 11.7 Hz]. There are many examples of octahedral iridium(III) hydrides or hydridocarbonyls, *e.g.* of types $[IrH(Cl_2)(CO)(PR_3)_2]$, $[IrH_2(Cl)(CO)(PR_3)_2]$, $[IrH(Cl_2)(PR_3)_3]$, *etc.*[1–3,15] which show very poor reactivity towards alkenes or alkynes. However, we find that complex **3** dissolves readily in methanol or ethanol to give an isomeric but co-ordinatively unsaturated iridium(I) complex **4a** (Scheme 1) in which a hydrogen has moved back to the methine carbon of the ene–hydrazone regenerating the azine moiety **2a** and the hydride ligand has been lost from the iridium. The reverse process might be by deprotonation of iridium and protonation of carbon; or it might be by the reverse of the oxidative-addition reaction followed by a 1,3-prototropic shift **2b** ⟶ **2a**, *i.e.* overall an intramolecular process; in each case chloride is lost from iridium as chloride ion. The cation $[Ir(CO)\{PPh_2CH_2C(Bu^t)=N\text{–}N=C(Bu^t)CH_2PPh_2\}]^+$ was readily isolated as the PF_6^- salt **4b**, which was fully characterised. The $^{31}P\text{-}\{^1H\}$ and other NMR spectra showed that the cations of the chloride salt **4a** and the PF_6^- salt **4b** were identical. The iridium(I) chloride salt **4a** on dissolution in CH_2Cl_2 or C_6H_6 gave back the neutral iridium(III) hydride **3a** rapidly.

We anticipated that the co-ordinatively unsaturated cation in the salt $[Ir(CO)\{PPh_2CH_2C(Bu^t)=N\text{–}N=C(Bu^t)CH_2PPh_2\}]PF_6$ **4b** would take up unsaturated molecules, *e.g.* olefins, acetylenes or carbon monoxide, and also dihydrogen. This we have found to be the case. Thus treatment of the yellow solution of **4b** in dichloromethane with an excess of $MeO_2CC{\equiv}CCO_2Me$ at *ca.* 20 °C rapidly gave a colourless solution for which $^{31}P\text{-}\{^1H\}$ NMR spectroscopy indicated that essentially only one product was formed and this was characterised by an AX pattern, $\delta(P_A)$ 42.5, $\delta(P_B)$ 9.6, $^2J(P_AP_B)$ 35 Hz. The product $[Ir(CO)\{PPh_2CH_2C(Bu^t)=N\text{–}N=C(Bu^t)CH_2PPh_2\}(MeO_2CC{\equiv}CCO_2Me)]PF_6$ **5a** (Scheme 2) was isolated in 85% yield, its crystal structure was determined and is discussed below. An important feature of the structure is that it is based on a trigonal-bipyramidal cation with the two phosphorus atoms of



Scheme 2 (*i*) L; (*ii*) PhC≡CH; (*iii*) heat

Table 2 Proton NMR data[a]

	δ(Bu^t)	δ(CH_2P)	Others
1[b]	0.90 (18 H, s)	3.26 [4 H, d, ^2J(PH) 3.9]	
3[c]	0.77 (9 H, s)	3.03 (1 H, m, ^2J(HH) 11.7][d]	−15.40 [1 H, dd, ^2J(PH) 11.4, 10.6, IrH]
	1.66 (9 H, s)	3.99 [1 H, dd, ^2J(HH) 11.7, ^2J(PH) 12.5]	4.80 [1 H, t, ^2J(PH) = ^4J(PH) 4.9, CH=]
4b	0.78 (9 H, s)	3.48 [2 H, d, ^2J(PH) 10.0]	
	1.22 (9 H, s)	4.17 [2 H, dd, ^2J(PH) 7.8, ^4J(PH) 2.5]	
5a[e]	0.80 (9 H, s)	2.47 [1 H, t, ^2J(HH) 12.9, ^2J(PH) 12.7]	3.59 (3 H, s, OMe)
	1.32 (9 H, s)	3.86 [1 H, t, ^2J(HH) 12.9, ^2J(PH) 13.3]	3.78 (3 H, s, OMe)
		4.12 [1 H, ddd, ^2J(HH) 19.0, ^2J(PH) 10.5, ^4J(PH) 2.5]	
		4.41 [1 H, dd, ^2J(HH) 19.0, ^2J(PH) 11.5]	
5b[e]	0.82 (9 H, s)	2.40 [1 H, dd, ^2J(HH) 12.8, ^2J(PH) 12.5]	3.40 (3 H, s, OMe)
	1.30 (9 H, s)	3.86 [1 H, dd, ^2J(HH) 12.8, ^2J(PH) 13.0]	6.99 [1 H, dd, ^3J(PH) 11.4, 8.8, HC≡]
		4.10 [1 H, ddd, ^2J(HH) 18.9, ^2J(PH) 8.3, ^4J(PH) 2.9]	
		4.34 [1 H, dd, ^2J(HH) 18.9, ^2J(PH) 11.5]	
6	0.86 (9 H, s)	2.57 [1 H, t, ^2J(HH) 13.2, ^2J(PH) 12.9]	−8.54 [1 H, dd, ^2J(PH) 155.0, 12.8, IrH]
	1.50 (9 H, s)	3.79 [1 H, t, ^2J(HH) 13.2, ^2J(PH) 13.5]	
		4.39 [2 H, d, ^2J(PH) 9.5]	
7	0.86 (9 H, s)	3.23 [1 H, t, ^2J(HH) = ^2J(PH) 12.5]	−16.77 [1 H, dd, ^2J(PH) 12.5, 8.8, IrH]
	1.50 (9 H, s)	3.96 [1 H, m, ^2J(HH) 12.5][d]	
		4.18 [1 H, m, ^2J(HH) 18.3][d]	
		4.64 [1 H, m, ^2J(HH) 18.3][d]	
8a[e]	0.86 (9 H, s)	2.40 [1 H, dd, ^2J(HH) 13.0, ^2J((PH) 12.5]	3.02 (3 H, s, NMe)
	1.42 (9 H, s)	3.75 [1 H, t, ^2J(HH) 13.0, ^2J(PH) 13.2]	3.10 [1 H, dt, ^3J(HH) 5.1, ^3J(PH) 6.0, 5.1, =CH]
		3.91 [1 H, ddd, ^2J(HH) 19.2, ^2J(PH) 7.0, ^4J(PH) 2.4]	3.98 [1 H, m, ^3J(HH) 5.1, ^3J(PH) 7.4, 2.3, =CH]
		4.54 [1 H, dd, ^2J(HH) 19.2, ^2J(PH) 12.0]	
8b[e]	0.97 (9 H, s)	2.58 [1 H, dd, ^2J(HH) 13.2, ^2J(PH) 12.7]	3.23 (3 H, s, OMe)
	1.39 (9 H, s)	3.08 [1 H, ddd, ^2J(HH) 19.1, ^2J(PH) 8.0, ^4J(PH) 3.0]	3.56 [1 H, ddd, ^3J(HH) 10.0, ^3J(PH) 6.0, 1.0, =CH]
		4.01 [1 H, t, ^2J(HH) 13.2, ^2J(PH) 13.2]	3.76 (3 H, s, OMe)
		4.23 [1 H, dd, ^2J(HH) 19.1, ^2J(PH) 12.1]	4.11 [1 H, m, ^3J(HH) 10.0, ^3J(PH) 7.9, 1.8, =CH]
8c[e]	0.98 (9 H, s)	2.54 [1 H, dd, ^2J(HH) 13.2, ^2J(PH) 12.7]	0.72 [3 H, t, ^3J(HH) 7.2, CH_2*Me*]
	1.38 (9 H, s)	3.05 [1 H, ddd, ^2J(HH) 19.2, ^2J(PH) 8.0, ^4J(PH) 3.0]	1.16 [3 H, t, ^3J(HH) 7.1, CH_2*Me*]
		4.00 [1 H, t, ^2J(HH) 13.2, ^2J(PH) 13.2]	3.14 [1 H, ddd, ^3J(HH) 10.1, ^3J(PH) 7.8, 1.8, =CH]
		4.22 [1 H, dd, ^2J(HH) 19.2, ^2J(PH) 12.1]	3.47 [1 H, dq, ^3J(HH) 7.1, C*H*$_2$Me]
			3.51 [1 H, ddd, ^3J(HH) 10.1, ^3J(PH) 6.4, 1.0, =CH]
			3.92 [1 H, dq, ^3J(HH) 7.1, C*H*$_2$Me]
			4.11 [1 H, dq, ^3J(HH) 7.2, C*H*$_2$Me]
			4.31 [1 H, dq, ^3J(HH) 7.1, C*H*$_2$Me]
8d[e]	0.78 (9 H, s)	2.22 [1 H, dd, ^2J(HH) 12.8, ^2J(PH) 12.2]	1.50 (1 H, m, CH_2=CH_2)
	1.33 (9 H, s)	3.59 [1 H, ddd, ^2J(HH) 19.4, ^2J(PH) 7.0, ^4J(PH) 2.6]	2.41 (1 H, m, CH_2=CH_2)
		3.71 [1 H, dd, ^2J(HH) 12.8, ^2J(PH) 12.6]	2.83 (2 H, m, CH_2=CH_2)
		4.38 [1 H, dd, ^2J(HH) 19.4, ^2J(PH) 11.0]	
8e, 8f	0.82 (9 H, s)	2.30 [1 H, dd, ^2J(HH) 12.8, ^2J(PH) 12.0]	2.45 [1 H, m, ^2J(HH) 7.8, ^4J(HH) 2.8, =CH_2
Major	1.33 (9 H, s)	3.59 [1 H, ddd, ^2J(HH) 18.9, ^2J(PH) 7.0, ^4J(PH) 2.8]	(co-ordinated)][d]
isomer[e,f]		3.72 [1 H, dd, ^2J(HH) 12.8, ^2J(PH) 12.7]	2.75 [1 H, m, ^2J(HH) 7.7, ^4J(HH) 2.8, =CH_2
		4.40 [1 H, dd, ^2J(HH) 18.9, ^2J(PH) 11.3]	(co-ordinated)][d]
			5.25 (1 H, m, =CH_2)[d]
			6.52 (1 H, m, =CH_2)[d]
9[e]	1.17 (9 H, s)	2.60 [1 H, dd, ^2J(HH) 17.5, ^2J(PH) 12.0]	0.62 [3 H, t, ^3J(HH) 7.0, CH_2*Me*]
	1.52 (9 H, s)	3.20 [1 H, dd, ^2J(HH) 17.5, ^2J(PH) 13.5]	0.91 [3 H, t, ^3J(HH) 7.0, CH_2*Me*]
			3.14 (1 H, m, C*H*$_2$Me), 3.26 (1 H, m, C*H*$_2$Me)
			3.83 (1 H, m, C*H*$_2$Me), 3.95 (1 H, m, C*H*$_2$Me)
			4.06 [1 H, d, ^2J(PH) 7.0, PCH=]
			10.61 (1 H, br s, NH)
10	0.82 (9 H, s)	3.20 [2 H, d, ^2J(PH) 11.7]	
	1.31 (9 H, s)	4.09 [2 H, dd, ^2J(PH) 10.3, ^4J(PH) 3.2]	
11[e]	0.82 (9 H, s)	2.42 [1 H, dd, ^2J(HH) 13.0, ^2J(PH) 11.8]	−8.76 [1 H, ddd, ^2J(PH) 138.0, 13.9, ^2J(HH) 2.1, IrH]
	1.44 (9 H, s)	3.48 [1 H, ddd, ^2J(HH) 18.6, ^2J(PH) 7.4, ^4J(PH) 2.6]	−7.56 [1 H, ddd, ^2J(PH) 132.6, 19.4, ^2J(HH) 2.1, IrH]
		3.61 [1 H, dt, ^2J(HH) = ^2J(PH) 13.0, ^4J(PH) 2.4]	
		4.52 [1 H, ddd, ^2J(HH) 18.6, ^2J(PH) 11.2, ^4J(PH) 1.9]	
12[e]	0.98 (9 H, s)	2.66 [1 H, t, ^2J(HH) = ^2J(PH) 13.1]	−17.32 [1 H, m, ^2J(PH) 9.6, ^2J(HH) 3.7, IrH]
	1.45 (9 H, s)	3.55 [1 H, ddd, ^2J(HH) 18.3, ^2J(PH) 9.9, ^4J(PH) 2.3]	−8.87 [1 H, m, ^2J(PH) 20.1, ^2J(HH) 3.7, ^4J(HH) 1.5,
		4.16 [1 H, dt, ^2J(HH) = ^2J(PH) 13.0, ^4J(PH) 4.8]	IrH]
		4.71 [1 H, m, ^2J(HH) 18.3, ^2J(PH) 7.7, ^4J(HH) 1.5]	
13	0.78 (9 H, s)	3.38 [1 H, m, ^2J(HH) 12.8][d]	−18.59 [1 H, dt, ^2J(PH) 11.0, ^4J(HH) 4.4, IrH]
	1.31 (9 H, s)	3.61 [1 H, m, ^2J(HH) 12.8][d]	7.17 [1 H, d, ^4J(HH) 4.4, HCO_2]
		4.14 [1 H, m, ^2J(HH) 17.6][d]	
		4.43 [1 H, m, ^2J(HH) 17.6][d]	
14	1.04 (9 H, s)	3.49 [1 H, ddd, ^2J(HH) 12.7, ^2J(PH) 9.5, ^4J(PH) 2.7]	0.62 [3 H, t, ^3J(PH) 5.0, IrMe]
	1.51 (9 H, s)	4.07 [1 H, dd, ^2J(HH) 12.7, ^2J(PH) 8.7]	
		4.83 [2 H, d, ^2J(PH) 6.1]	
15	1.03 (9 H, s)	3.61 [2 H, d, ^2J(PH) 10.8]	
	1.52 (9 H, s)	4.66 [2 H, dd, ^2J(PH) 6.6]	

[a] Recorded at 100 MHz, chemical shifts (δ) are in ppm relative to $SiMe_4$, J values are in Hz, solvent CD_2Cl_2 unless otherwise stated, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = double doublet of doublets, m = multiplet. [b] In $CDCl_3$. [c] In C_6D_6. [d] Coupling to phosphorus nuclei not resolved. [e] At 400 Mz. [f] Minor isomer: δ 0.84 (s, Bu^t) and 1.35 (s, Bu^t), methylene protons appeared as multiplets at δ 2.34, 3.65, 3.83 and 4.40.

Table 3 ^{13}C-{^1H} NMR data[a]

	δ(CMe_3)	δ(CMe_3)	δ(CH_2)	δ(C=N)	δ(C≡O)	Others
3[b]	28.8 (s) 31.7 (s)	39.4 [d, *J*(PC) 15.2] 39.5 [d, *J*(PC) 3.6]	20.5 [d, *J*(PC) 26.2]	190.6 [dd, *J*(PC) 17.2, 1.8]	169.9 [t, *J*(PC) 7.9]	74.4 [d, *J*(PC) 66.5, PCH=] 149.6 [d, *J*(PC) 3.7, =CN]
4b[c]	26.5 (s) 27.3 (s)	40.0 [d, *J*(PC) 2.0] 40.4 [d, *J*(PC) 4.8]	22.7 [d, *J*(PC) 23.9] 40.5 [d, *J*(PC) 29.3]	172.8 [d, *J*(PC) 1.7] 191.8 [t, *J*(PC) 4.0]	177.2 [t, *J*(PC) 9.3]	
5a	26.6 (s) 28.2 (s)	40.3 [d, *J*(PC) 1.9] 40.8 [d, *J*(PC) 6.2]	26.9 [d, *J*(PC) 23.4] 47.6 [d, *J*(PC) 36.0]	176.6 [d, *J*(PC) 3.3] 188.0 [t, *J*(PC) 2.7]	164.1 [dd, *J*(PC) 8.5, 5.3]	52.9 (s, OMe), 53.1 (s, OMe) 93.2 [dd, *J*(PC) 55.9, 7.4, C≡] 93.6 [dd, *J*(PC) 51.0, 6.8, C≡] 161.8 [dd, *J*(PC) 8.9, 6.4, C=O] 162.7 [dd, *J*(PC) 9.4, 7.3, C=O]
6	26.9 (s) 28.6 (s)	40.2 [d, *J*(PC) 2.2] 41.5 [d, *J*(PC) 5.0]	24.7 [d, *J*(PC) 27.0] 46.2 [d, *J*(PC) 37.4]	175.5 [d, *J*(PC) 4.5] 188.8 [d, *J*(PC) 3.7]	163.1 [dd, *J*(PC) 7.6, 4.0]	73.2 [dd, *J*(PC) 104.5, 14.1, IrC≡] 108.2 [dd, *J*(PC) 25.8, 2.5, PhC≡]
8a	26.9 (s) 28.4 (s)	40.5 [d, *J*(PC) 1.9] 41.1 [d, *J*(PC) 5.7]	26.2 [d, *J*(PC) 23.1] 47.3 [d, *J*(PC) 35.7]	178.0 [d, *J*(PC) 3.0] 190.2 [t, *J*(PC) 2.7]	165.3 [dd, *J*(PC) 8.6, 5.3]	23.2 (s, NMe) 35.0 [dd, *J*(PC) 30.5, 5.0, CH=] 37.2 [dd, *J*(PC) 31.5, 5.4, CH=] 177.2 (br s, C=O) 177.8 [dd, *J*(PC) 3.9, 1.5, C=O]
8b	27.2 (s) 28.7 (s)	40.3 [d, *J*(PC) 1.9] 41.3 [d, *J*(PC) 6.0]	25.2 [d, *J*(PC) 22.4] 46.7 [d, *J*(PC) 34.7]	176.0 [d, *J*(PC) 2.8] 186.7 [t, *J*(PC) 3.5]	164.2 [dd, *J*(PC) 7.7, 6.1]	35.7 [dd, *J*(PC) 26.2, 5.3, CH=] 39.2 [dd, *J*(PC) 26.5, 5.6, CH=] 51.5 (s, OMe), 52.0 (s, OMe) 172.4 [dd, *J*(PC) 3.7, 2.5, C=O] 175.4 [t, *J*(PC) 3.6, C=O]
11	27.0 (s) 28.5 (s)	40.3 [d, *J*(PC) 2.1] 41.1 [d, *J*(PC) 6.9]	24.1 [d, *J*(PC) 21.6] 48.9 [d, *J*(PC) 36.1]	174.7 [d, *J*(PC) 3.3] 186.3 [t, *J*(PC) 5.7]	166.1 [t, *J*(PC) 5.3]	
12	27.8 (s) 28.3 (s)	40.6 [d, *J*(PC) 1.9] 41.0 [d, *J*(PC) 5.0]	25.3 [d, *J*(PC) 24.8] 47.7 [d, *J*(PC) 38.3]	173.7 [d, *J*(PC) 2.3] 185.3 [d, *J*(PC) 3.1]	176.1 [t, *J*(PC) 6.4]	
15	27.8 (s) 28.3 (s)	41.4 [d, *J*(PC) 1.7] 42.1 [d, *J*(PC) 5.4]	23.0 [d, *J*(PC) 23.5] 43.5 [d, *J*(PC) 38.6]	175.8 [d, *J*(PC) 1.8] 193.8 [dd, *J*(PC) 3.3, 2.0]	157.4 [dd, *J*(PC) 8.0, 6.3]	

[a] Recorded at 100.6 MHz, chemical shifts (δ) are in ppm relative to $SiMe_4$, solvent CD_2Cl_2 unless otherwise stated. [b] In C_6D_6. [c] In $CDCl_3$.

the terdentate $PPh_2CH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$ ligand occupying equatorial sites and a nitrogen and apical site. The C≡C occupies the third equatorial site with the C≡C and the P–P vectors approximately parallel. Complex **5a** was also characterised by elemental analytical and IR data (see Experimental section) and by phosphorus (Table 1), proton (Table 2) and carbon-13 (Table 3) NMR data.

Treatment of **4a** with $HC{\equiv}CCO_2Me$ similarly gave an adduct $[Ir(CO)\{PPh_2CH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2\}(HC{\equiv}CCO_2Me)]PF_6$ as a single isomer **5b**; presumably, the C≡C is co-ordinated approximately parallel to the P–P vector as found from the crystal structures of **5a** and other complexes, see below. Five-co-ordinate alkene iridium(I) complexes are trigonal bipyramidal with the alkene in the equatorial plane[29] and this is believed to be the preferred orientation of such complexes on theoretical grounds.[30] The $HC{\equiv}CCO_2Me$ proton is coupled to both phosphorus atoms, $^3J(PCH)$ = 11.4 and 8.8 Hz.

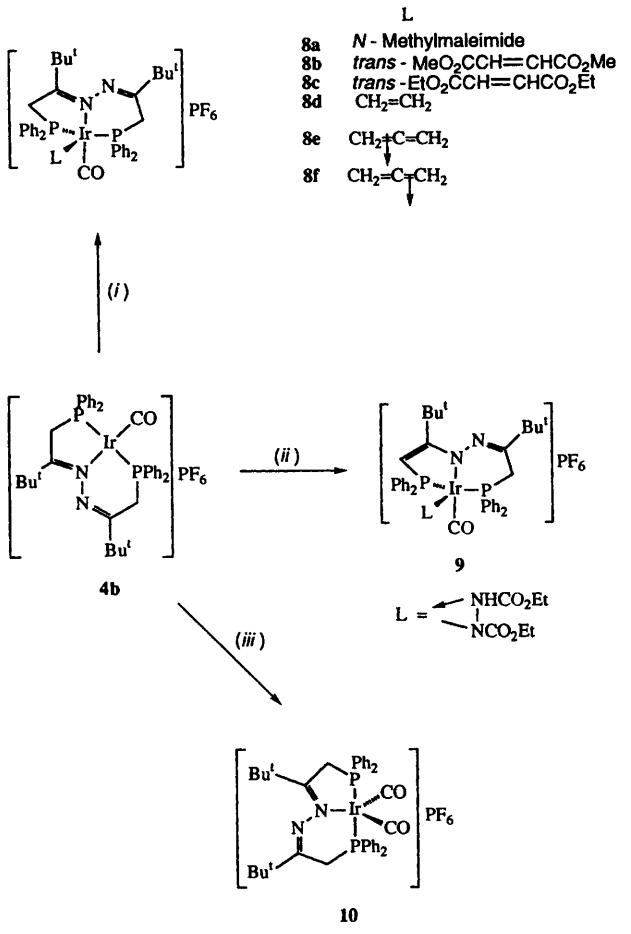
The alkyne PhC≡CH reacted with **4b** in a different fashion from $MeO_2CC{\equiv}CH$ in that C–H fission occurred to give an iridium phenylacetylide hydride. Thus treatment of **4b** in dichloromethane at *ca.* 20 °C with an excess of PhC≡CH rapidly gave a colourless adduct which the IR [ν(IrH) = 2120 cm^{-1}] and ^1H NMR data (Table 2) established to be the iridium hydride **6** with a *fac*-co-ordinated diphosphine ligand and with the hydride ligand *trans* to one phosphorus, $^2J(PH)$ = 155 Hz and *cis* to the other $^2J(PH)$ = 12.8 Hz (Table 2). When a solution of complex **6** in C_6D_6 was heated for 4 h at 75 °C, it isomerised to a phenylacetylide hydride with a *mer*-co-ordinated diphosphine ligand, $^2J(PP)$ = 323 Hz and a hydride resonance at δ −16.77; this hydride ligand was coupled to both phosphorus atoms, $^2J(PH)$ = 12.5 and 8.8 Hz, *i.e.* the phosphorus atoms were now both *cis* to the hydride. We formulate this isomeric complex as **7** with H in the *trans* position to nitrogen. We have found similar chemical shifts (δ ≈ −18) for other hydrides with the hydride *trans* to a nitrogen, see below. With much less electronegative donor atoms such as carbon or phosphorus *trans* to hydride, shifts of δ −8 to −9 would be expected.[15,17,24,27,28]

We have also made adducts of **4b** with electronegative olefins, with ethene and with allene (Scheme 3). Treatment of a dichloromethane solution of **4b** with *N*-methylmaleimide gave essentially a single adduct in 87% isolated yield. The structure of this adduct was determined by X-ray diffraction which showed it to be **8a**, with the C=C of the maleimide moiety co-ordinated to the iridium at an equatorial site and the C=C vector approximately parallel to the P–P vector (see below).

Similar adducts were prepared from *trans*-MeO_2CCH=CH-CO_2Me (dimethyl fumarate) and *trans*-EtO_2CCH=$CHCO_2Et$ (diethyl fumarate) in 74 and 89% yields, respectively. Both complexes were fully characterised. In both cases essentially one adduct was detected in solution by NMR spectroscopy.

When ethene was bubbled into a solution of complex **4b** in dichloromethane the solution rapidly became colourless. The uptake was reversible and on bubbling dinitrogen through the solution **4b** was reformed (^{31}P-{^1H} NMR evidence). However, when an ethanol–dichloromethane solution of this ethene adduct was evaporated in a stream of ethene, a colourless ethene adduct **8d** was obtained as white crystals. The ^{31}P-{^1H} NMR pattern of this adduct indicated that the P nuclei were mutually *cis*, *i.e.* the diphosphine was in the *fac* arrangement as in the other adducts such as **5a**, **5b** and **8a**–**8c**, above. In the ^1H and ^1H-{^{31}P} NMR spectra (Table 2), the C_2H_4 hydrogens gave a broad resonance at 25 °C; this was very probably due to ethene rotation since at −40 °C (and at 600 MHz) a sharp resonance was observed for each of the four ethene non-equivalent hydrogens and at this temperature rotation had effectively ceased.

When allene was bubbled through a solution of complex **4b** a mixture of two colourless adducts was formed and isolated. We formulate these as **8e** and **8f**, *i.e.* with co-ordination of the allene through each of the double bonds, on the left **8e** or on the right **8f**. The ^{31}P-{^1H} NMR evidence is that one allene adduct is formed in a much larger amount than the other and we refer to these as major and minor adducts, although we cannot say which is **8e** and which is **8f**. In the ^1H and ^1H-{^{31}P} spectrum we can see all the resonances due to the major adduct (see Table 2),



Scheme 3 (*i*) L; (*ii*) $EtO_2CN{=}NCO_2Et$; (*iii*) C≡O

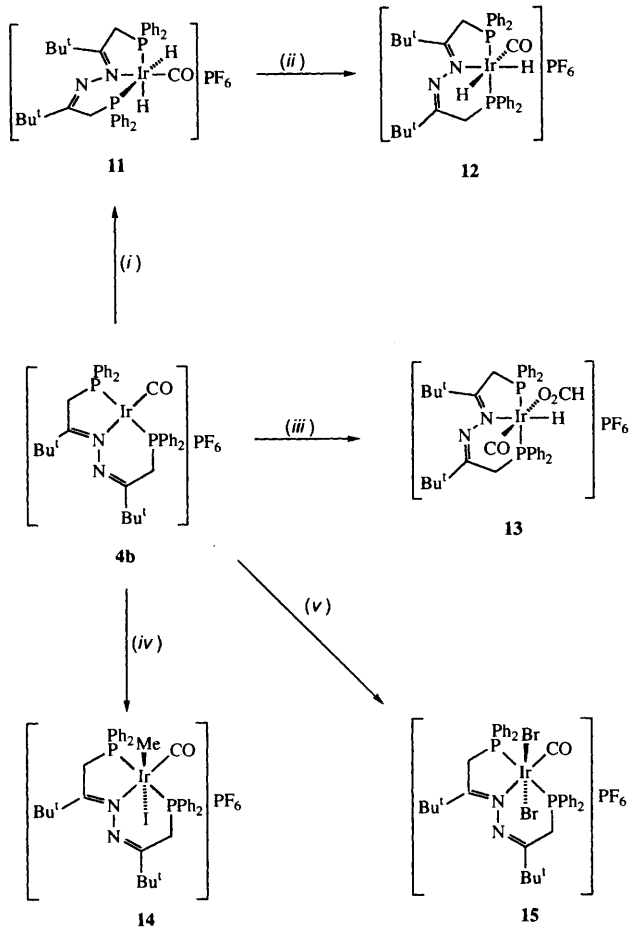
but can only identify some of the resonances for the minor adduct (see footnote to Table 2).

Treatment of **4b** with an excess of azoethyl formate gave a pale red solution from which an adduct was isolated as white crystals in 67% yield. The $^{31}P\text{-}\{^1H\}$ NMR spectrum (Table 1) showed that the P nuclei were mutually *cis*-co-ordinated. The ^1H and $^1H\text{-}\{^{31}P\}$ NMR spectra (Table 2), however, showed that only one CH_2 remained on the diphosphine backbone and that a proton had been removed from the other CH_2, leaving a PCH= group with δ(H) 4.06 and that the azoethyl formate moiety had been monoprotonated on one of the co-ordinated nitrogens δ(NH) 10.61, *i.e.* as depicted in complex **9**.

When carbon monoxide was bubbled through a CD_2Cl_2 solution of complex **4b** a dicarbonyliridium complex **10** was formed; this was characterised only in solution and not isolated. It showed carbonyl absorptions at 2015 and 1985 cm^{-1} in the IR spectrum; $^{31}P\text{-}\{^1H\}$, ^1H and $^1H\text{-}\{^{31}P\}$ NMR data are given in the Tables.

The iridium(I) salt **4b** in CD_2Cl_2 solution reacted rapidly with dihydrogen to give an iridium dihydride with a *fac* arrangement for the diphosphine and *cis*-dihydride ligands, each of which was co-ordinated *trans* to P as shown by the large values of $^2J(PH)$ *trans* 138.0 and 132.6 Hz (Table 2). In solution this *fac* hydride **11** gradually isomerised over several hours to give **12** in which the diphosphine was now co-ordinated in the *mer* configuration [$^2J(P_AP_B)$ = 301 Hz] and the two hydride ligands *trans* to CO and N (Scheme 4). In Fig. 1 we show the proton NMR spectra of the reaction solution in the hydride region (*a*) 45 min after the hydrogen was bubbled into **4b**; **11** is the major species but some of the *mer* isomer **12** is present and (*b*) after 24 h when the major species is **12** and very little of **11** remains.

We have also investigated some of the oxidative-addition reactions of complex **4b**. Treatment with formic acid in CH_2Cl_2 solution gave a colourless adduct **13** (Scheme 4) which was isolated as white crystals in good yield. This adduct gave a good C, H, N analysis and its $^{31}P\text{-}\{^1H\}$ NMR pattern showed that the diphosphine ligand was in the *mer* configuration with $^2J(P_AP_B)$ = 315 Hz. The ^1H and $^1H\text{-}\{^{31}P\}$ NMR data show the presence of a hydride δ(H) −18.59 and a formate ligand δ(H) 7.17 with mutual coupling $^4J(HH)$ 4.4 Hz (Table 2). Treatment of **4b** with methyl iodide gave an adduct, with the diphosphine in the *mer* configuration. This adduct was identified by $^{31}P\text{-}\{^1H\}$, ^1H and $^1H\text{-}\{^{31}P\}$ NMR spectroscopy, see Tables 1 and 2, and we tentatively formulate it as **14** with the methyl and iodide mutually *trans*. Similarly Br_2 added to **4b** to give a single adduct **15** with the diphosphine in the *mer* configuration [$^2J(P_AP_B)$ = 364 Hz] and the two Br atoms mutually *trans*, since both sets of CH_2 hydrogens were



Scheme 4 (*i*) H_2; (*ii*) 20 °C; (*iii*) HCO_2H; (*iv*) MeI; (*v*) Br_2

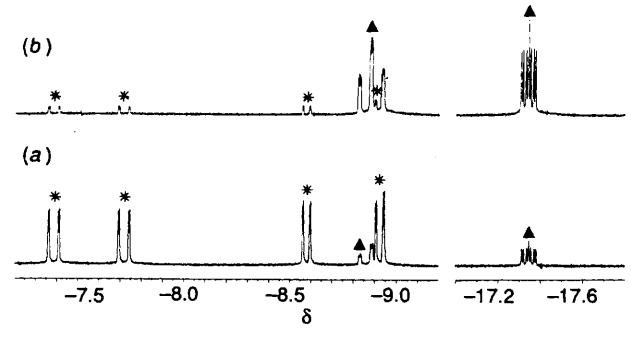


Fig. 1 Portions (in the hydride region) of the ^1H NMR spectrum of the dihydride mixture of **11** and **12**, formed by bubbling dihydrogen through a solution of **4b** in CD_2Cl_2 for *ca.* 2 min, (*a*) 45 min and (*b*) 24 h after the dihydrogen was introduced. The hydride resonances due to **11** are marked with an asterisk, those due to **12** are marked with ▲

chemically equivalent indicating a plane of symmetry and mutually *trans* bromine ligands. Compound **15** was also characterised by NMR data (Table 3). Compounds **14** and **15** were prepared on a small scale and were not characterised by elemental analysis.

Crystal structure of the adduct 5a

The crystal structure of complex **5a** is shown in Fig. 2, with crystallographic data in Table 4 and selected bond lengths and angles in Table 5. Some features are: (*i*) the azine diphosphine ligand is in the *fac* arrangement with P(2)–Ir–P(1) 109.97(4)° with the nitrogen donor occupying an axial site *trans* to C≡O; (*ii*) the acetylene bond length, C(8)–C(9) 1.285(7) Å, is longer than in free acetylenes (*ca.* 1.2 Å), as expected; (*iii*) the C–C≡C–C moiety has become bent to a considerable extent on co-ordination, *e.g.* C(8)–C(9)–C(91) 145.5(5) and C(9)–C(8)–C(81) 141.2(5)°; (*iv*) C(8)–C(9) is approximately parallel to P(1)–P(2), as might be expected.[29,30]

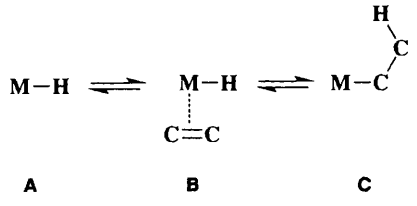
Crystal structure of the adduct 8a

The crystal structure of complex **8a** is shown in Fig. 3, with selected bond lengths and angles in Table 6. Some features are: (*i*) as with compound **5a**, the azine diphosphine ligand is in the *fac* arrangement with P(2)–Ir–P(1) 107.80(4)° with the nitrogen donor occupying an axial site *trans* to C≡O; (*ii*) the olefinic bond length C(9)–C(10) is 1.446(7) Å, much longer than C=C bond lengths in free olefins (*ca.* 1.35 Å) and approximately halfway towards that of a single C–C bond (1.54 Å); (*iii*) the C(9)–C(10) vector of the *N*-methylmaleimide ligand is approximately parallel to the P(1)–P(2) vector; (*iv*) C(13)–C(9)–Ir and C(11)–C(10)–Ir are 114.8(4) and 114.1(3)°, respectively.

A New Method of Creating Co-ordinative Unsaturation

The importance of creating co-ordinative unsaturation has been discussed briefly above. The results we have presented in this paper suggest a new method of creating co-ordinative unsaturation which might be useful in synthesis and catalysis. A key step in many organometallic and catalytic reactions is the migration of a hydride ligand from a metal to a co-ordinated olefin (**A** ⟶ **B** ⟶ **C**). Examples where this occurs include hydrogenation, hydroformylation, hydrosilylation, hydroboration, hydrocyanation and olefin oligomerisation; the reverse process (**C** ⟶ **B** ⟶ **A** β-hydrogen elimination) is also important.[1–4] The step **B** ⟶ **C** controls the regioselectivity and stereoselectivity of the overall catalytic process. For a hydride complex **A** to react with an olefin in this way it must be co-ordinatively unsaturated so that the olefin can become co-ordinated. Hydrides which are not co-ordinatively unsaturated such as for example complexes of the types $[IrH(Cl_2)(CO)L_2]$, $[IrH_2(Cl)(CO)L_2]$ or $[IrH_2ClL_3]$ (L = tertiary phosphine) react with olefins extremely slowly, if at all.[1–3,15]

Our work suggests the possibility of a hydride ligand in 18-electron complexes migrating on to the diphosphine backbone and this, coupled with loss of a chloride ion, as in the conversion of **3** into **4a**, frees co-ordination sites and the complex could then take up a substrate such as an olefin or acetylene. The migration might be temporary in that the α-hydrogen atom from the azine diphosphine ligand backbone could then migrate to the co-ordinated olefin or acetylene, possibly by an ene–hydrazone oxidative-addition path or by deprotonation/protonation. In effect the azine/ene–hydrazone backbone acts as a source or sink for a hydrogen atom. The work we have described in this paper shows that for iridium such interconversions are possible, *e.g.* the migration of a hydrogen atom from the iridium to the ene–hydrazone backbone and then to the $EtO_2CN{=}NCO_2Et$ substrate in the conversion of **3** to **4a** and then to **9**. In order to generate systems in which such transformations are involved in catalytic cycles it may be necessary to use metals more labile than iridium, such as rhodium, ruthenium or palladium, or to use more vigorous conditions. The substituents on the diphosphine backbone would also influence these transformations. We have published a preliminary note on some of this work.[32]



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, values of ν(C=O) were determined in CH_2Cl_2 solution, unless stated otherwise. The NMR spectra were recorded using a JEOL FX-90Q spectrometer (operating frequencies for ^1H and ^{31}P of 89.5 and 36.2 MHz, respectively), a JEOL FX-100 spectrometer (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz respectively), a Bruker ARX-250 spectrometer (operating

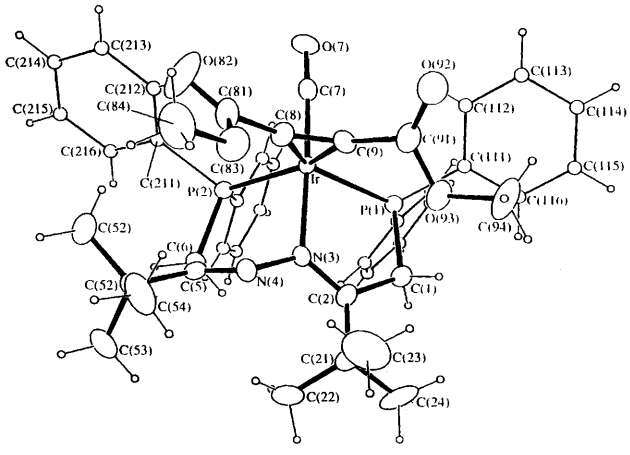


Fig. 2 An ORTEP[31] diagram of the crystal structure of complex **5a**. Ellipses are drawn at the 50% probability level. In the interests of clarity, phenyl carbons and hydrogen atoms are drawn as circles of arbitrary radius

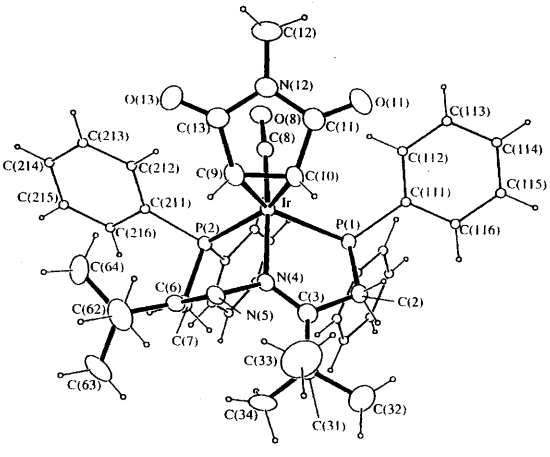


Fig. 3 An ORTEP[31] diagram of the crystal structure of complex **8a**. Details as in Fig. 2

Table 4 Crystallographic data for compounds **5a** and **8a**[a]

	5a	**8a**
Formula	$C_{43}H_{48}F_6IrN_2O_5P_3$	$C_{42}H_{47}F_6IrN_3O_3P_3$
M	1071.94	1040.9
Space group	$P2_1/n$	$P2_1/c$
Crystal dimensions/mm	0.65 × 0.27 × 0.12	0.72 × 0.30 × 0.30
a/Å	10.9282(11)	11.2268(12)
b/Å	33.729(3)	12.7431(11)
c/Å	12.1256(11)	29.878(2)
β/°	97.326(10)	91.126(8)
U/Å^3	4433.0(7)(5)	4273.6(7)
D_c/g cm^{-3}	1.61	1.62
$F(000)$	2144	2080
μ/mm^{-1}	3.191	3.305
Scan widths/° + a-doublet splitting	1.05	*b*
No. of data collected	8751	7349
No. of unique data, n	7793	7349
No. of data observed $\|F_o\| > 4.0\sigma(\|F_o\|)$	5777	6462
R_{int}[c]	0.0374	
R_{sig}[d]	0.0471	0.0240
Maximum, minimum transmission factors	0.3837, 0.5209	0.5465, 0.6415
T/K	200	140
ρ_{max},ρ_{min}/e Å^{-3}	0.94, −0.86	1.48, −1.58
Δ/σ_{max}	0.59	0.006
R_1[e]	0.0606	0.0375
wR_2[f]	0.0759	0.0891
Weighting parameters x,y[g]	0.0376, 5.8768	0.0296, 25.4324
No. of parameters, p	569	518
Goodness of fit[h]	1.028	1.019

[a] Common to both compounds: orthorhombic, $Z = 4$, $4.0 < 2\theta < 50.0°$, maximum and minimum scan speeds 1.5 and 8.0° min^{-1}. [b] Each scan divided into 30 steps, scan widths and step sizes from a learnt profile. [c] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. [d] $R_{sig} = \Sigma[\sigma(F_o^2)]/\Sigma[F_o]^2$. [e] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [f] $wR_2 = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$. [g] Weighting scheme used $w = [\sigma^2(F_o^2) + xP^2 + yP]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. [h] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{\frac{1}{2}}$.

Table 5 Selected bond lengths (Å) and angles (°) for compound **5a** with estimated standard deviations (e.s.d.s) in parentheses

Ir–C(7)	1.854(5)	Ir–C(9)	2.113(5)
Ir–N(3)	2.129(4)	Ir–C(8)	2.132(5)
Ir–P(2)	2.3237(12)	Ir–P(1)	2.3263(12)
P(1)–C(121)	1.816(5)	P(2)–C(221)	1.819(5)
P(1)–C(111)	1.820(5)	P(2)–C(211)	1.832(5)
P(1)–C(1)	1.844(5)	P(2)–C(6)	1.854(5)
C(1)–C(2)	1.497(6)	C(5)–C(6)	1.508(7)
C(2)–N(3)	1.300(6)	N(4)–C(5)	1.276(6)
C(2)–C(21)	1.537(7)	C(5)–C(51)	1.528(7)
N(3)–N(4)	1.411(5)	C(7)–O(7)	1.137(6)
C(8)–C(9)	1.285(7)	C(8)–C(81)	1.476(7)
C(81)–O(82)	1.192(6)	C(81)–O(83)	1.325(7)
O(83)–C(84)	1.450(7)	C(9)–C(91)	1.462(7)
C(91)–O(92)	1.194(6)	C(91)–O(93)	1.337(6)
O(93)–C(94)	1.448(6)		
C(7)–Ir–C(9)	98.2(2)	C(81)–C(8)–Ir	147.3(4)
C(9)–Ir–N(3)	85.5(2)	C(7)–Ir–N(3)	176.1(2)
C(9)–Ir–C(8)	35.3(2)	C(7)–Ir–C(8)	96.0(2)
C(7)–Ir–P(2)	91.36(15)	N(3)–Ir–C(8)	86.2(2)
N(3)–Ir–P(2)	84.83(10)	C(9)–Ir–P(2)	147.54(13)
C(7)–Ir–P(1)	99.27(15)	C(8)–Ir–P(2)	113.12(13)
N(3)–Ir–P(1)	81.37(11)	C(9)–Ir–P(1)	99.04(13)
P(2)–Ir–P(1)	109.97(4)	C(8)–Ir–P(1)	133.65(13)
C(1)–P(1)–Ir	100.3(2)	C(6)–P(2)–Ir	106.6(2)
C(2)–C(1)–P(1)	115.0(3)	C(5)–C(6)–P(2)	113.1(3)
N(3)–C(2)–C(1)	116.8(4)	N(4)–C(5)–C(6)	123.5(4)
N(3)–C(2)–C(21)	124.6(4)	N(4)–C(5)–C(51)	117.0(4)
C(1)–C(2)–C(21)	118.4(4)	C(6)–C(5)–C(51)	119.4(4)
C(2)–N(3)–N(4)	119.4(4)	C(2)–N(3)–Ir	124.6(3)
N(4)–N(3)–Ir	115.2(3)	C(5)–N(4)–N(3)	115.1(4)
O(7)–C(7)–Ir	117.0(4)	C(8)–C(9)–C(91)	145.5(5)
C(9)–C(8)–C(81)	141.2(5)	C(8)–C(9)–Ir	73.2(3)
C(9)–C(8)–Ir	71.6(3)	C(91)–C(9)–Ir	141.3(4)

Table 6 Selected bond lengths (Å) and angles (°) for compound **8a** with e.s.d.s in parentheses

Ir–C(8)	1.859(5)	Ir–N(4)	2.118(4)
Ir–C(10)	2.165(5)	Ir–C(9)	2.186(5)
Ir–P(1)	2.3329(12)	Ir–P(2)	2.3382(12)
C(2)–C(3)	1.500(7)	C(3)–N(4)	1.289(6)
C(3)–C(31)	1.544(7)	N(4)–N(5)	1.411(5)
N(5)–C(6)	1.282(6)	C(6)–C(7)	1.508(7)
C(6)–C(61)	1.527(7)	C(8)–O(8)	1.141(6)
C(9)–C(10)	1.446(7)	C(9)–C(13)	1.466(8)
C(10)–C(11)	1.497(7)	C(11)–O(11)	1.214(6)
C(11)–N(12)	1.393(7)	N(12)–C(13)	1.402(7)
N(12)–C(12)	1.453(7)	C(13)–O(13)	1.209(7)
C(8)–Ir–N(4)	175.1(2)	C(8)–Ir–C(10)	98.5(2)
N(4)–Ir–C(10)	85.8(2)	C(8)–Ir–C(9)	96.4(2)
N(4)–Ir–C(9)	86.5(2)	C(10)–Ir–C(9)	38.8(2)
C(8)–Ir–P(1)	101.1(2)	N(4)–Ir–P(1)	80.51(11)
C(10)–Ir–P(1)	97.11(14)	C(9)–Ir–P(1)	135.09(14)
C(8)–Ir–P(2)	90.59(14)	N(4)–Ir–P(2)	84.54(10)
C(10)–Ir–P(2)	151.31(14)	C(9)–Ir–P(2)	113.53(14)
P(1)–Ir–P(2)	107.80(4)	C(3)–C(2)–P(1)	112.9(3)
N(4)–C(3)–C(2)	116.7(4)	N(4)–C(3)–C(31)	124.6(5)
C(2)–C(3)–C(31)	118.5(4)	C(3)–N(4)–N(5)	119.4(4)
C(3)–N(4)–Ir	124.5(3)	N(5)–N(4)–Ir	115.5(3)
C(6)–N(5)–N(4)	116.1(4)	N(5)–C(6)–C(7)	122.9(4)
N(5)–C(6)–C(61)	116.5(4)	C(7)–C(6)–C(61)	120.7(4)
C(6)–C(7)–P(2)	112.9(3)	O(8)–C(8)–Ir	175.5(4)
C(10)–C(9)–C(13)	107.9(5)	C(10)–C(9)–Ir	69.8(3)
C(13)–C(9)–Ir	114.8(4)	C(9)–C(10)–C(11)	106.1(5)
C(9)–C(10)–Ir	71.4(3)	C(11)–C(10)–Ir	114.1(3)
O(11)–C(11)–N(12)	124.2(5)	O(11)–C(11)–C(10)	128.8(5)
N(12)–C(11)–C(10)	107.0(4)	C(11)–N(12)–C(13)	111.7(4)
C(11)–N(12)–C(12)	124.7(5)	C(13)–N(12)–C(12)	123.6(5)
O(13)–C(13)–N(12)	123.2(5)	O(13)–C(13)–C(9)	129.8(5)
N(12)–C(13)–C(9)	107.1(5)		

frequencies for ^{1}H, ^{31}P and ^{13}C of 250.1, 101.3 and 62.9 MHz, respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^{1}H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively). The ^{1}H and ^{13}C chemical shifts are relative to tetramethylsilane and ^{31}P shifts are relative to 85% phosphoric acid, and all coupling constants are in Hz. Electron impact

(EI) and fast-atom bombardment (FAB) mass spectra were recorded using a VG Autospec spectrometer with 8 kV acceleration, and for the metal complexes the calculated *m/z* values are quoted for ^{35}Cl and ^{193}Ir.

Preparation of the iridium complexes

[IrH(Cl)(CO){$PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh_2$}] 3. A solution containing the diphosphine **1** (1.30 g, 2.3 mmol) and $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ (0.89 g, 2.3 mmol) in benzene (30 cm^3) was gently refluxed for 20 min. The resulting yellow-brown solution was filtered and then concentrated to low volume (*ca.* 10 cm^3) under reduced pressure. Addition of *n*-hexane (*ca.* 20 cm^3) to the residue gave the iridium(III) hydride **3** as yellow microcrystals (1.63 g, 87%) (Found: C, 54.95; H, 5.35; Cl, 4.45; N, 3.3. $C_{37}H_{42}ClIrN_2OP_2\cdot0.2C_6H_6$ requires C, 54.95; H, 5.2; Cl, 4.25; N, 3.35%). IR (CH_2Cl_2): ν(C≡C) 2030 cm^{-1}.

[Ir(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}]Cl 4a. The neutral complex **3** was dissolved in methanol (*ca.* 0.5 cm^3) containing C_6D_6 as an NMR lock (reference). The $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ NMR and the IR spectra were recorded and established that the salt **4a** had formed essentially quantitatively (see Discussion section).

[Ir(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}]$PF_6$ 4b. An excess of NH_4PF_6 (0.20 g, 1.2 mmol) in ethanol (2 cm^3) was added to a solution of **3** (0.20 g, 0.24 mmol) in ethanol (8 cm^3). The required iridium(I) complex **4b** deposited as yellow microcrystals (0.15 g, 66%) (Found: C, 47.6; H, 4.55; N, 3.0. $C_{37}H_{42}F_6IrN_2OP_3$ requires C, 47.8; H, 4.55; N, 3.0%). IR (CH_2Cl_2): ν(C≡O) 2000 cm^{-1}.

[Ir(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}(η²-$MeO_2CC{\equiv}CCO_2Me$)]$PF_6$ 5a. An excess of $MeO_2CC{\equiv}CCO_2Me$ (30 μl) was added to a solution of **4b** (48 mg, 0.052 mmol) in CH_2Cl_2 (*ca.* 1.5 cm^3). The resulting colourless solution was concentrated to low volume (*ca.* 0.25 cm^3) and MeOH (*ca.* 1 cm^3) added, to give the required product **5a** as white microcrystals (47 mg, 85%) (Found: C, 48.45; H, 4.65; N, 2.45. $C_{43}H_{48}F_6IrN_2O_5P_3$ requires C, 48.15; H, 4.5; N, 2.6%). IR (CH_2Cl_2): ν(C≡O) 2035, ν(C≡C) 1800 and ν(C=O) 1700 cm^{-1}.

[Ir(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}(η-HC≡C-$CO_2Me$)]$PF_6$ 5b. The complex **5b** was prepared in a similar fashion to **5a**, as white microcrystals, in 86% yield (Found: C, 48.3; H, 4.4; N, 2.75. $C_{41}H_{46}F_6IrN_2O_3P_3$ requires C, 48.55; H, 4.55; N, 2.75%). IR (CH_2Cl_2): ν(C≡O) 2030 cm^{-1}.

[IrH(C≡CPh)(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}]$PF_6$ 6. An excess of phenylacetylene (0.10 cm^3) was added to a solution of **4b** (100 mg, 0.10 mmol) in CH_2Cl_2 (*ca.* 2.5 cm^3). After 3 h the solution was concentrated to low volume (*ca.* 0.25 cm^3) and MeOH (1 cm^3) added. The complex **6** was deposited as off-white microcrystals (85 mg, 77%) (Found: C, 52.35; H, 4.7; N, 2.7. $C_{45}H_{48}F_6IrN_2OP_3$ requires C, 52.35; H, 4.7; N, 2.7%). IR (CH_2Cl_2): ν(C≡O) 2060 and ν(IrH) 2120 cm^{-1}.

[Ir(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}(η²-CO-CH=CHCONMe)]$PF_6$ 8a. The complex **8a** was prepared in 87% yield as white microcrystals in a similar manner to the method described for **5a**. An analytical sample was crystallised from CH_2Cl_2–MeOH (Found: C, 48.1; H, 4.45; N, 3.9. $C_{42}H_{47}F_6IrN_3O_3P_3\cdot0.25CH_2Cl_2$ requires C, 48.3; H, 4.55; N, 4.0%). IR (CH_2Cl_2): ν(C≡O) 2035 cm^{-1}.

[Ir(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}(η²-$MeO_2$-CCH=$CHCO_2Me$)]$PF_6$ 8b. This was prepared similarly in 74% yield as white microcrystals (Found: C, 47.65; H, 4.65; N, 2.45. $C_{43}H_{50}F_6IrN_2O_5P_3\cdot0.25CH_2Cl_2$ requires C, 48.1; H, 4.7; N, 2.6%). IR (CH_2Cl_2): ν(C≡O) 2040 cm^{-1}.

[Ir(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}(η²-$EtO_2C$-CH=$CHCO_2Et$)]$PF_6$ 8c. This was prepared similarly in 89% yield as white microcrystals (Found: C, 48.75; H, 4.85; N, 2.3. $C_{45}H_{54}F_6IrN_2O_5P_3\cdot0.25CH_2Cl_2$ requires C, 49.05; H, 4.95; N, 2.55%). IR (CH_2Cl_2): ν(C=O) 2040 cm^{-1}.

[Ir(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}(η²-$CH_2$=$CH_2$)]$PF_6$ 8d. Ethene was bubbled through a solution of **4b** (134 mg, 0.144 mmol) in CH_2Cl_2 (*ca.* 1.5 cm^3) for 2 min. EtOH was then added to the resulting colourless solution which was concentrated under a stream of ethene to give the ethene complex **8d** as white microcrystals (103 mg, 74%) (Found: C, 48.45; H, 4.7; N, 2.75. $C_{39}H_{46}F_6IrN_2O_3P_3$ requires C, 48.9; H, 4.85; N, 2.9%). IR: ν(C≡O) 2015 cm^{-1}.

[Ir(CO){$PPh_2CH{=}C(Bu^t){-}N{-}N{=}C(Bu^t)CH_2PPh_2$}(η²-$CH_2$=C-=$CH_2$)]$PF_6$ 8e, 8f. The mixture of the two complexes **8e**, **8f** was prepared in 53% yield as white microcrystals (Found: C, 49.25; H, 4.65; N, 2.9. $C_{40}H_{46}F_6IrN_2O_3P_3$ requires C, 49.55; H, 4.8; N, 2.9%). IR: ν(C≡O) 2030 cm^{-1}.

[Ir(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}(η²-$EtO_2$-$CNHNCO_2Et$)]$PF_6$ 9. An excess of azoethyl formate (30 μl) was added to a solution of complex **4b** (40 mg, 0.043 mmol) in CH_2Cl_2 (1.5 cm^3). After 1.5 h the resulting pale red solution was concentrated to low volume and EtOH was added to the residue to give the complex **9** as white microcrystals (32 mg, 67%) (Found: C, 44.95; H, 4.45; N, 4.8. $C_{43}H_{52}F_6IrN_4O_5P_3\cdot0.75CH_2Cl_2$ requires C, 45.0; H, 4.6; N, 4.8%). IR: ν(C≡O) 2065 cm^{-1}.

[Ir(CO)$_2${$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}]$PF_6$ 10. Carbon monoxide was bubbled through a solution of complex **4b** (20 mg, 0.022 mmol) in CD_2Cl_2 (*ca.* 0.5 cm^3) for 15 min. The $^{31}P\text{-}\{^1H\}$, ^1H, $^1H\text{-}\{^{31}P\}$ NMR spectra were recorded (see Discussion section). IR: ν(C≡O) 2015 and 1985 cm^{-1}.

***fac*-[IrH_2(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}]$PF_6$ 11 and *mer*-[IrH_2(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2$-$PPh_2$}]$PF_6$ 12.** Hydrogen was bubbled through a solution of complex **4b** (30 mg, 0.032 mmol) in CD_2Cl_2 (*ca.* 0.5 cm^3) for 3 min. This gave a solution of the *fac*-dihydride **11**, which over a period of *ca.* 15 h isomerised almost completely to the *mer*-dihydride **12** (see Discussion section). IR (CD_2Cl_2): complex **11**, ν(C≡O) 2045, ν(IrH) 2100 and 2170 cm^{-1}; complex **12**, ν(C≡O) 2015, ν(IrH) 2110 and 2160 cm^{-1}.

[IrH(O_2CH)(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}]-$PF_6$ 13. An excess of HCO_2H (50 μl) was added to a solution of complex **4b** (50 mg, 0.054 mmol) in CH_2Cl_2 (1.5 cm^3). The solvent was evaporated under reduced pressure and diethyl ether (2 cm^3) added to the residue, followed by formic acid (*ca.* 0.1 cm^3). This gave **13** as white microcrystals (40 mg, 76%) (Found: C, 46.0; H, 4.45; N, 2.75. $C_{38}H_{44}F_6IrN_2O_3P_3\cdot0.2CH_2Cl_2$ requires C, 46.2; H, 4.5; N, 2.8%).

[IrI(Me)(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}]$PF_6$ 14. An excess of MeI (50 μl) was added to a solution of complex **4b** (40 mg, 0.043 mmol) in CH_2Cl_2 (1.5 cm^3). After 24 h the solution was concentrated to low volume under reduced pressure and MeOH was added to give the required product as pale yellow microcrystals (21 mg, 42%).

[$IrBr_2$(CO){$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$}]$PF_6$ 15. A solution of bromine (0.045 mmol) in CCl_4 was added to a solution of complex **4b** (40 mg, 0.043 mmol) in CH_2Cl_2 (2 cm^3) at 0 °C. After 30 min, the solution was concentrated to low volume (0.25 cm^3) and methanol added. This gave the required product **15** as yellow microcrystals (20 mg, 43%).

X-Ray diffraction analysis

All diffraction measurements were made on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated X-radiation (λ = 0.710 69 Å) and, for compound **8a**, an on-line profile fitting method.[33] Crystal data are listed in Table 4 together with details of data collection and structure refinement. Both data sets were corrected for absorption using azimuthal ψ-scans.

Both structures were solved by standard heavy-atom techniques using SHELXS 86[34] and were refined by full-matrix least squares using SHELXL 93.[35] For both complexes all non-hydrogen atoms were refined with anisotropic thermal parameters. The PF_6^- anion of compound **5a** was disordered over two positions about the central phosphorus atom. Restraints were applied to all phenyl groups such that they remained flat with overall C_{2v} symmetry. All hydrogen atoms were constrained to calculated positions with fixed isotropic thermal parameters of nU_{eq} of the parent carbon atom, where n was 1.5 for methyl hydrogens and 1.2 for all others.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/46.

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