General Strategy for inducing C–H Bond Fission (Cycloiridation) in Some Aryl, Heterocyclic, Alkenyl or Alkyl Groups in Azines derived from Aldehydes or Methyl Ketones†

Sarath D. Perera, Bernard L. Shaw* and Mark Thornton-Pett
School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

The phosphino hydrazone Z-PPh$_2$CH$_2$C(Bu^t)=NNH$_2$ **I** has been shown to be a convenient 'reagent' for converting aldehydes or ketones into azines which can then be cycloiridated rapidly with C–H bond fission to give iridium(III) hydrides. Condensation of **I** with a series of substituted benzaldehydes (RCHO) gave mixed azines of type Z,E-PPh$_2$CH$_2$C(Bu^t)=N–N=CHR [R = C$_6$H$_2$(OMe)$_3$-3,4,5 **IIa**, Ph **IIb**, C$_6$H$_4$OMe-4 **IIc**, C$_6$H$_4$NO$_2$-4 **IId**, C$_6$H$_4$Br-2 **IIe**, C$_6$H$_4$Cl-2 **IIf**, C$_6$H$_4$F-2 **IIg**, C$_6$H$_4$OH-2 **IIh** or C$_6$H$_2$(OH-2)(OMe)$_2$-4,6, **IIi**]. The Z,E configuration is necessary for the subsequent cyclometallation and when the azine **IIa** was treated with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-p)] in benzene at 75 °C for 5 min it underwent an aryl C–H bond fission to give the cyclometallated chlorocarbonyliridium(III) hydride [IrH(Cl)(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=CH[C$_6$H(OMe)$_3$-3,4,5]}] **1a**. The crystal structure of **1a** showed that (*i*) oxidative addition of the aryl C–H bond to iridium was *cis* with the hydride ligand *trans* to chloride, and (*ii*) the cyclometallated azine ligand was in the terdentate *mer* arrangement. Azines **IIb**–**IIg** reacted similarly. Treatment of **IIh** with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-p)] in dichloromethane at 20 °C effected O–H bond fission to give the O-cyclometallated iridium(III) hydride [IrH(Cl)(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_6$H$_4$O)}], which isomerised in benzene at 75 °C to the C-metallated isomer. Similar treatment of **IIi** also gave an O-cyclometallated iridium(III) hydride. The phosphino hydrazone **I** condensed with ferrocenecarbaldehyde to give an azine, which with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-p)] gave a cyclometallated iridium(III) hydride. Treatment of **I** with the 2-carbaldehydes of pyrrole, N-methylpyrrole or thiophene or with indole-3-carbaldehyde gave the corresponding azine phosphines with the required Z,E configuration. When the pyrrole azine was treated with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-p)] the N-cyclometallated chlorocarbonyliridium(III) hydride [IrH(Cl)(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_4$H$_3$N)}] was formed *via* a N–H bond fission. The azine phosphines of N-methylpyrrole, thiophene and indole gave C-cyclometallated chlorocarbonyliridium(III) hydrides. Condensation of **I** with cinnamaldehyde or 3-methylpent-3-en-2-one gave azines which underwent oxidative addition of the olefinic C–H bonds readily to give corresponding C-cyclometallated iridium(III) hydrides. Phosphino hydrazone **I** also condensed with *tert*-butyl methyl ketone to give an azine which with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-p)] gave the C-cyclometallated chlorocarbonyliridium(III) hydride, *i.e.* metallation in this case occurred on the single methyl group. Proton, ^{31}P-{^{1}H} and some ^{13}C-{^{1}H} NMR data are given.

In a previous paper[1] we described the synthesis of a new phosphino hydrazone Z-PPh$_2$CH$_2$C(Bu^t)=NNH$_2$ I from the corresponding phosphino dimethylhydrazone Z-PPh$_2$CH$_2$C(Bu^t)=NNMe$_2$ by a hydrazine-exchange reaction. The very reactive functionalised phosphine I condenses with aldehydes or ketones QC(=O)R (Q = H or Me, and R more sterically demanding than Q) to give mixed-azine phosphines of type PPh$_2$CH$_2$C(Bu^t)=N–N=C(Q)R[1–11] having the Z,E configuration. Under mild conditions one would expect an azine of this type to chelate to a metal through phosphorus and the N=C(Q)R nitrogen to give a six-membered chelate ring thus forcing the sterically demanding R group against the metal (M) but in the co-ordination plane defined by the N–M–P chelate system. We have used this strategy to promote agostic interaction (C–H→Ru)[3] or aryl fluoride co-ordination (RF→Ru)[4] with ruthenium(II), and also to promote cyclometallation involving C–H,[5,6] C–I,[6,7] C–Br,[6,7] C–Cl,[7] C–F,[8] N–H[5,6] or O–H[5,6] bond fission with tungsten(0)[7] or platinum(II)[6] and with iridium(I)[5] in a preliminary publication. We have now extended this work with iridium and report on it more fully. Cyclometallation processes involving C–H bond fission in ligands containing nitrogen, phosphorus or sulfur donors have been reviewed.[12–16] Some examples of cyclometallated iridium hydrides (X–Ir–H), formed by oxidative addition of an X–H (X = C, N, O, S or Si) bond, are with phosphine ligands such as P(C$_6$H$_4$X-p)$_3$ (X = H, F, OMe or Me),[17] PBu$^t_2$R (R = allyl, Pr^n, Pr^i, Bu^n or Bu^t),[18,19] PPr$^i_3$,[19] P(C$_6$H$_{11}$)$_3$,[20] Bu$^t_2$P(CH$_2$)$_5$PBu$^t_2$,[21] m-Bu$^t_2$PC$_6$H$_4$PBu$^t_2$,[22] o-Ph$_2$PC$_6$H$_4$CHO,[23] o-Ph$_2$PC$_6$H$_4$OH,[23] o-Ph$_2$PC$_6$H$_4$CO$_2$H,[23] o-Ph$_2$PC$_6$H$_4$NHR (R = H, Et or CH$_2$Ph),[24,25] Ph$_2$PCH$_2$CH$_2$SH[26] and Ph$_2$PCH$_2$CH$_2$SiHR$_2$ (R = Me or Ph).[27] In all these cases the oxidative addition of an X–H bond to iridium is *cis*.

Results and Discussion

The mixed azines and the complexes prepared from them are shown in Schemes 1–3. Elemental analytical, mass spectral and some carbon-13 NMR data are in the Experimental section and

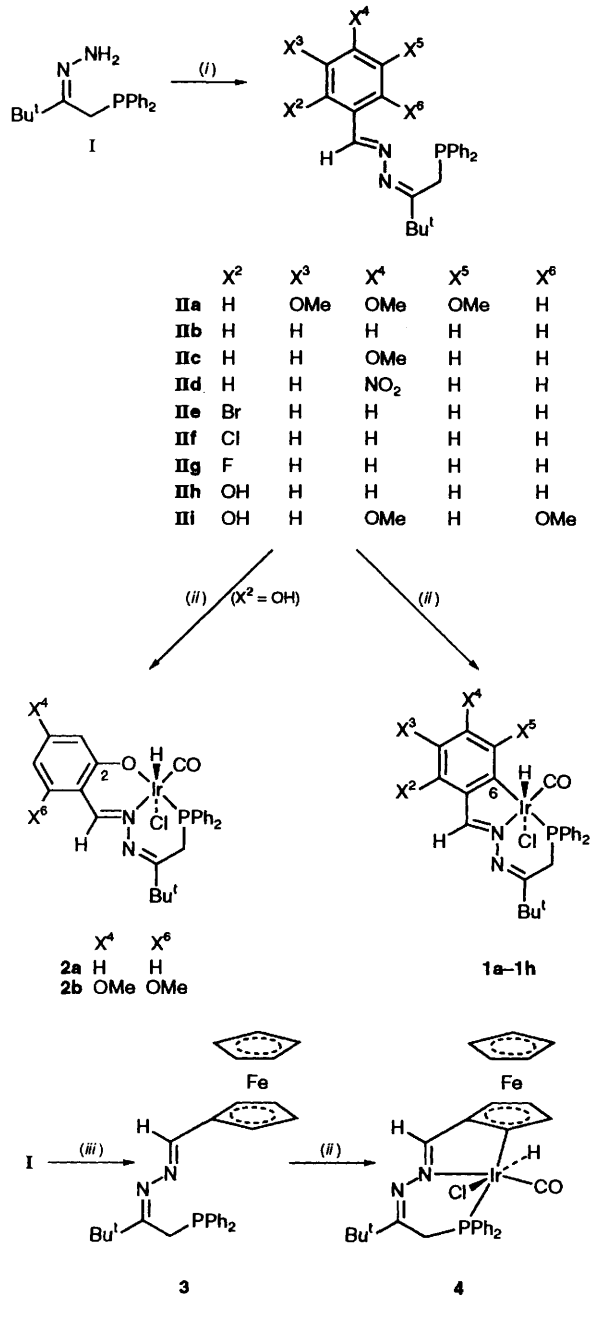
---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

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

Compound	δ(P)	δ(IrH)	δ(Bu^t)	δ(CH_2P)	δ(CH=N)
I	−22.6	—	0.98 (9 H, s)	3.10 (2 H, d, 2.2[c])	—
IIa[d]	−9.2	—	1.50 (9 H, s)	3.48 (2 H, d, 3.4[c])	8.02 (1 H, d, 1.0[e])
IIb	−10.0	—	1.22 (9 H, s)	3.52 (2 H, d, 3.2[c])	8.04 (1 H, s)
IIc[f]	−10.0	—	1.22 (9 H, s)	3.52 (2 H, d, 3.2[c])	8.04 (1 H, s)
IId[g]	−10.4	—	1.25 (9 H, s)	3.50 (2 H, d, 2.9[c])	8.14 (1 H, s)
IIe	−10.8	—	1.24 (9 H, s)	3.49 (2 H, d, 2.5[c])	8.33 (1 H, s)
IIf	−10.7	—	1.24 (9 H, s)	3.50 (2 H, d, 2.7[c])	8.39 (1 H, s)
IIg	−10.7	—	1.24 (9 H, s)	3.50 (2 H, d, 2.7[c])	8.24 (1 H, s)
IIh	−14.1	—	1.26 (9 H, s)	3.45 (2 H, d, 1.2[c])	7.95 (1 H, s)
IIi[h]	−14.2	—	1.21 (9 H, s)	3.41 (2 H, d, 1.2[c])	8.38 (1 H, s)
1a[i]	10.2	−17.44 (1 H, d, 10.3[c])	0.76 (9 H, s)	3.49 (1 H, dd, 13.2,[j] 12.5[c]) 4.03 (1 H, dd, 13.2,[j] 12.5[c])	8.91 (1 H, s)
1b	11.4	−16.89 (1 H, d, 10.3[c])	0.82 (9 H, s)	3.53 (1 H, dd, 12.9,[j] 13.6[c]) 4.03 (1 H, t, 12.9,[j] 12.9[c])	8.99 (1 H, s)
1c[k]	10.0	−16.98 (1 H, d, 10.1[c])	0.76 (9 H, s)	3.47 (1 H, dd, 12.9,[j] 13.6[c]) 3.96 (1 H, t, 12.9,[j] 12.9[c])	8.83 (1 H, s)
1d[l]	11.5	−16.74 (1 H, d, 10.3[c])	0.80 (9 H, s)	3.56 (1 H, dd, 12.9,[j] 13.6[c]) 4.05 (1 H, t, 12.9,[j] 13.2[c])	9.09 (1 H, s)
1e	12.1	−16.77 (1 H, d, 10.3[c])	0.79 (9 H, s)	3.50 (1 H, dd, 12.9,[j] 13.6[c]) 3.99 (1 H, t, 12.9,[j] 12.6[c])	9.36 (1 H, s)
1f	11.8	−16.81 (1 H, d, 10.3[c])	0.78 (9 H, s)	3.53 (1 H, dd, 12.9,[j] 13.5[c]) 4.02 (1 H, t, 12.9,[j] 12.8[c])	9.36 (1 H, s)
1g	11.5(d)[m]	−16.89 (1 H, d, 10.3[c])	0.79 (9 H, s)	3.51 (1 H, dd, 13.2,[j] 13.5[c]) 4.02 (1 H, dd, 13.2,[j] 12.8[c])	9.20 (1 H, s)
1h	10.7	−17.34 (1 H, d, 9.8[c])	0.79 (9 H, s)	3.51 (1 H, dd, 12.9,[j] 13.5[c]) 3.97 (1 H, t, 12.9,[j] 12.8[c])	9.19 (1 H, s)
2a[n]	13.9	−16.10 (1 H, d, 15.4[c])	0.73 (9 H, s)	3.41 (1 H, dd, 13.2,[j] 15.4[c]) 4.40 (1 H, dd, 13.2,[j] 15.4[c])	8.23 (1 H, s)
2b[o]	14.6	−16.20 (1 H, d, 15.4[c])	0.74 (9 H, s)	3.39 (1 H, dd, 13.2,[j] 15.4[c]) 4.10 (1 H, dd, 13.2,[j] 15.4[c])	8.55 (1 H, s)
3[p]	−8.1	—	1.11 (9 H, s)	3.43 (2 H, d, 3.9[c])	8.09 (1 H, s)
4[q]	13.3	−17.00 (1 H, d, 11.0[c])	0.77 (9 H, s)	3.53 (1 H, t, 12.4,[j] 13.1[c]) 3.81 (1 H, t, 12.4,[j] 13.2[c])	8.89 (1 H, s)
IIIa[r]	−9.0	—	1.23 (9 H, s)	3.50 (2 H, d, 2.9[c])	8.10 (1 H, s)
IIIb[s]	−10.9	—	1.15 (9 H, s)	3.49 (2 H, d, 3.4[c])	8.07 (1 H, s)
IIIc[t]	−9.5	—	1.20 (9 H, s)	3.54 (2 H, d, 2.7[c])	8.15 (1 H, s)
IV[u]	−10.0	—	1.18 (9 H, s)	3.66 (2 H, d, 3.4[c])	8.37 (1 H, s)
5[v]	5.3	−17.15 (1 H, d, 13.3[c])	0.77 (9 H, s)	3.43 (1 H, dd, 13.2,[j] 15.4[c]) 4.04 (1 H, dd, 13.2,[j] 14.7[c])	8.35 (1 H, s)
6a[w]	7.9	−17.65 (1 H, d, 11.0[c])	0.78 (9 H, s)	3.45 (1 H, t, 13.2,[j] 13.2[c]) 3.87 (1 H, t, 13.2,[j] 13.2[c])	8.58 (1 H, s)
6b	8.2	−17.40 (1 H, d, 11.0[c])	0.79 (9 H, s)	3.50 (1 H, dd, 12.5,[j] 13.2[c]) 3.95 (1 H, t, 12.5,[j] 12.5[c])	8.87 (1 H, s)
7[x]	6.1	−17.14 (1 H, d, 11.0[c])	0.76 (9 H, s)	3.44 (1 H, dd, 12.5,[j] 13.9[c]) 3.85 (1 H, dd, 12.5,[j] 13.2[c])	8.87 (1 H, s)
Va[y]	−9.3	—	1.22 (9 H, s)	3.41 (2 H, d, 2.9[c])	7.82 (1 H, dd, 9.3,[z] 0.6[e])
Vb*	−11.6	—	1.14 (9 H, s)	3.23 (2 H, d, 3.2[c])	—
8a	6.6	−17.13 (1 H, d, 11.0[c])	0.77 (9 H, s)	3.45 (1 H, dd, 12.8,[j] 13.9[c]) 3.90 (1 H, t, 12.8,[j] 12.8[c])	8.66 (1 H, d, 2.2[z])
8b†	12.6	−17.40 (1 H, d, 10.3[c])	0.73 (9 H, s)	3.39 (1 H, dd, 12.5,[j] 13.1[c]) 3.69 (1 H, dd, 12.5,[j] 12.1[c])	—
VI‡	−12.4	—	0.99 (9 H, s) 1.02 (9 H, s)	3.23 (2 H, d, 4.4[c])	—
9§	14.9	−17.77 (1 H, d, 9.8[c])	1.29 (9 H, s) 1.44 (9 H, s)	4.08 (1 H, dd, 18.3,[j] 9.2[c]) 4.49 (1 H, dd, 18.3,[j] 11.0[c])	—

[a] Recorded at 36.2 MHz, chemical shifts δ(P) are in ppm relative to 85% H_3PO_4. [b] Recorded at 100 MHz, chemical shifts are in ppm relative to $SiMe_4$, *J* values are in Hz; solvent for the phosphines **I**, **IIa–IIi**, **3**, **IIIa–IIIc**, **IV**, **Va**, **Vb** and **VI** is $CDCl_3$ whilst all the metal complexes are in CD_2Cl_2 or otherwise stated. [c] ^{2}J(PH). [d] δ 3.73 (6 H, s, 2 OMe) and 3.87 (3 H, s, OMe). [e] ^{6}J(PH). [f] δ 3.81 (3 H, s, OMe). [g] δ 8.03 [2 H, d, ^{3}J(HH) 8.6 Hz, H^3 and H^5]. [h] δ 3.79 (6 H, s, 2 × OMe), 5.90 [1 H, d, ^{4}J(HH) 2.2, H^3 or H^5] and 6.02 [1 H, d, ^{4}J(HH) 2.2 Hz, H^3 or H^5]. [i] δ 3.79 (3 H, s, OMe), 3.84 (3 H, s, OMe), 3.96 (3 H, s, OMe) and 7.13 [1 H, d, ^{5}J(PH) 2.2 Hz, H^2]. [j] ^{2}J(HH). [k] δ 3.87 (3 H, s, OMe). [l] δ 8.61 [1 H, dd, ^{4}J(HH) 2.2, ^{4}J(PH) 6.2 Hz, H^5]. [m] ^{5}J(PF) = 8.8 Hz. [n] For the minor isomer δ_P 34.5 and δ_H −19.64 [1 H, d, ^{2}J(PH) 16.1 Hz, IrH]. [o] δ 3.78 (6 H, s, 2 × OMe), 5.70 [1 H, d, ^{4}J(HH) 2.2, H^3 or H^5] and 6.02 [1 H, d, ^{4}J(HH) 2.2, H^3 or H^5]; for the minor isomer δ_P 35.5 and δ_H −19.76 [1 H, d, ^{2}J(PH) 16.1 Hz, IrH]. [p] δ 4.15 (5 H, s, C_5H_5), 4.30 (2 H, m, C_5H_4) and 4.82 (2 H, m, C_5H_4). [q] δ 4.22 (5 H, s, C_5H_5), 4.77 (2 H, m, C_5H_3) and 4.42 (1 H, m, C_5H_3). [r] δ 6.10 [1 H, dd, *J*(HH) 2.6, 5.5 Hz, pyrrole H] and 6.41 (2 H, m, pyrrole H). [s] δ 3.56 (3 H, s, NMe), 6.09 [1 H, dd, *J*(HH) 2.4, 3.9, pyrrole H], 6.41 [1 H, dd, *J*(HH) 1.8, 3.8 Hz, pyrrole H] and 6.62 (1 H, m, pyrrole H). [t] δ 6.69 (1 H, m, thiophene H) and 7.13 (1 H, m, thiophene H). [u] δ 8.46 (1 H, br s, NH). [v] δ 6.40 (1 H, m, pyrrole H), 7.03 (1 H, m, pyrrole H) and the other pyrrole hydrogen resonance was not resolved. [w] δ 3.81 (3 H, s, NMe), 6.43 [1 H, t, ^{3}J(HH) = ^{4}J(PH) 2.2, H^4] and 7.00 [1 H, d, ^{3}J(HH) 2.2 Hz, H^5]. [x] δ 9.50 (1 H, br s, NH). [y] δ 6.37 [1 H, dd, ^{3}J(HH) 16.1, 9.3, C*H*=CPh] and 6.77 [1 H, d, ^{3}J(HH) 16.1 Hz, =C*H*Ph]. [z] ^{3}J(HH). * δ 1.69 (Me), 1.76 [3 H, d, *J*(HH) 1.0 Hz, Me], 1.83 (Me) and 5.90 (1 H, m, CH=). † δ 1.95 (Me), 2.48 (Me) and 2.86 [3 H, d, *J*(PH) 6.6 Hz, Me]. ‡ δ 1.83 (3 H, s, MeC=). § δ 3.26 [1 H, dd, ^{2}J(HH) 17.6, ^{3}J(PH) 5.9, CH_2Ir] and 3.53 [1 H, dd, ^{2}J(HH) 17.6, ^{3}J(PH) 5.9 Hz, CH_2Ir].



	X^2	X^3	X^4	X^5	X^6
IIa	H	OMe	OMe	OMe	H
IIb	H	H	H	H	H
IIc	H	H	OMe	H	H
IId	H	H	NO_2	H	H
IIe	Br	H	H	H	H
IIf	Cl	H	H	H	H
IIg	F	H	H	H	H
IIh	OH	H	H	H	H
IIi	OH	H	OMe	H	OMe

Scheme 1 (*i*) RCHO; (*ii*) $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$; (*iii*) ferrocenecarbaldehyde

proton and phosphorus-31 NMR data are in Table 1. Carbon-13 spectra were assigned using attached proton tests and by comparison with published data.[2,4,7,9,28–31]

The phosphino hydrazone *Z*-$PPh_2CH_2C(Bu^t){=}NNH_2$ **I** readily condensed with a range of benzaldehyde derivatives (RCHO) to give mixed azine phosphines of type *Z,E*-$PPh_2CH_2C(Bu^t){=}N{-}N{=}CHR$ [R = $C_6H_2(OMe)_3$-3,4,5 **IIa**, Ph **IIb**, C_6H_4OMe-4 **IIc**, $C_6H_4NO_2$-4 **IId**, C_6H_4Br-2 **IIe**, C_6H_4Cl-2 **IIf**, C_6H_4F-2 **IIg**, C_6H_4OH-2 **IIh** or $C_6H_2(OH\text{-}2)(OMe)_2$-4,6 **IIi**] (Scheme 1). The phosphorus-31 resonances for these azine phosphines **IIa**–**IIg** were singlets at $\delta \approx -10$ whereas the resonances for **IIh** and **IIi** were at $\delta \approx -14$. When **IIa**,[6] derived from 3,4,5-trimethoxybenzaldehyde, was treated with $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$[32] in benzene at 75 °C for 5 min it underwent an aryl C–H bond fission to give the cyclometallated chlorocarbonyliridium(III) hydride $[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH[C_6H(OMe)_3\text{-}3,4,5]\}]$ **1a** in 96% yield. Except when stated otherwise, these conditions were used with other azines and the progress of the reaction was followed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The iridium(III) hydride **1a** was characterised by microanalyses, IR and mass spectroscopy (Experimental section) and by proton, $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy and the molecular structure was confirmed by a crystal structure determination (Fig. 2, see below). The crystal structure shows that (*i*) the cyclometallated azine ligand is in the terdentate *mer* arrangement, (*ii*) the oxidative addition of the aryl C–H bond to iridium is *cis*, and we assume all our other oxidative-addition processes are *cis* as are most other X–H (X = H, B, C, N, O, S or Si)[17–27,33–36] bond-activation processes and (*iii*) the hydride ligand is *trans* to chloride. The microanalytical data were in agreement with the composition $C_{29}H_{33}ClIrN_2O_4P{\cdot}0.25C_6H_6$, and the presence of benzene was evidenced by proton NMR spectroscopy and also by X-ray crystallography. The IR bands due to ν(Ir–H) and ν(C≡O) occurred at 2195 and 2040 cm^{-1}, respectively.[17,26,33,35–37] In the $^{13}C\text{-}\{^1H\}$ NMR spectrum a doublet was observed at δ 151.9 with a large $^2J(PC)$ value of 92.6 Hz for the quaternary aryl carbon (*i.e.* C^6) directly bonded to iridium confirming that it was *trans* to the phosphorus atom. The low value of δ_C 21.6 observed for the CH_2 carbon agreed well with the values reported for methylene carbons in six-membered rings in similar complexes.[2,7,29] In the proton NMR spectrum, the resonance at δ −17.44 with $^2J(PH)$ = 10.3 Hz is typical of a hydride ligand *cis* to a tertiary phosphine ligand. Such a chemical shift is more likely for a hydride ligand *trans* to a chloride[17,26,35] than to a phosphine, carbonyl or aryl ligand.[23,26,27,33] Similar hydride chemical shifts and NMR data were obtained for the other iridium(III) hydrides discussed below suggesting that in all these cases the hydride ligand was *trans* to the chloride ligand. Treatment of the azine phosphines **Ib**, **Ic** or **Id**, derived from benzaldehyde, 4-methoxybenzaldehyde or 4-nitrobenzaldehyde, with $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ gave the corresponding iridium(III) hydrides, **1b**–**1d** which showed similar NMR and IR properties to those of **1a**.

We used the azine phosphines *Z,E*-$PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4X\text{-}2)$ (X = Br **IIe**, Cl **IIf** or F **IIg**), derived from 2-halogenobenzaldehydes, to investigate in particular the tendency (or the relative reactivity) of the C–H bond in the presence of the weaker C–X bond (X = Br or Cl). When the azine phosphine **IIe** was treated with $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ in benzene it underwent C–H bond fission to give the cyclometallated iridium(III) hydride **Ie** as the only product, isolated in excellent 97% yield (Scheme 1). In the proton NMR spectrum, the hydride resonance appeared as a doublet at δ −16.77 with $^2J(PH)$ = 10.3 Hz. It has been shown that the cationic iridium(I) complex $[Ir(cod)(o\text{-}PPh_2C_6H_4Br\text{-}P,Br)]^+$ (cod = cycloocta-1,5-diene) does not undergo C–Br bond fission even at 100 °C but reacts with H_2 at −80 °C to give hydridoiridium(III) complex $[IrH_2(cod)(o\text{-}PPh_2C_6H_4Br\text{-}P,Br)]^+$.[38] In contrast, treatment of the 2-bromo azine phosphine **IIe** with a dimethylplatinum(II) complex or $[W(CO)_3(NCEt)_3]$ effected the C–Br bond fission to give the cyclometallated platinum(IV) complex $[PtMe_2Br\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4)\}]$[6] or the tungsten(II) complex $[\{WBr(CO)_3\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4)\}]$.[7] Treatment of the 2-chloro azine phosphine **IIf** or the 2-fluoro azine phosphine **IIg** with $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ similarly gave the cyclometallated iridium(III) hydride **1f** or **1g**, respectively. The carbon-13 resonances (see Experimental section and Fig. 1) of the iridium(III) hydride **1g** were fully assigned with the aid of *J*(FC) values, and the $^{13}C\text{-}\{^1H\}$ NMR data for the C_6H_3F-2 moiety are as follows: C^1 at δ 129.2 (obscured by C_m of the PPh_2 group), C^2 as a doublet of doublets at δ 163.4 with $^1J(FC)$ = 262.6 and $^4J(PC)$ = 7.2 Hz, C^3 as a doublet at δ 110.2 with $^2J(FC)$ = 19.1 Hz, C^4 as a triplet at δ 136.2 with $^3J(FC)$ = $^4J(PC)$ = 7.6 Hz, C^5 as a doublet of doublets at δ 133.3 with $^4J(FC)$ = 1.2 and $^3J(PC)$ = 3.0 Hz

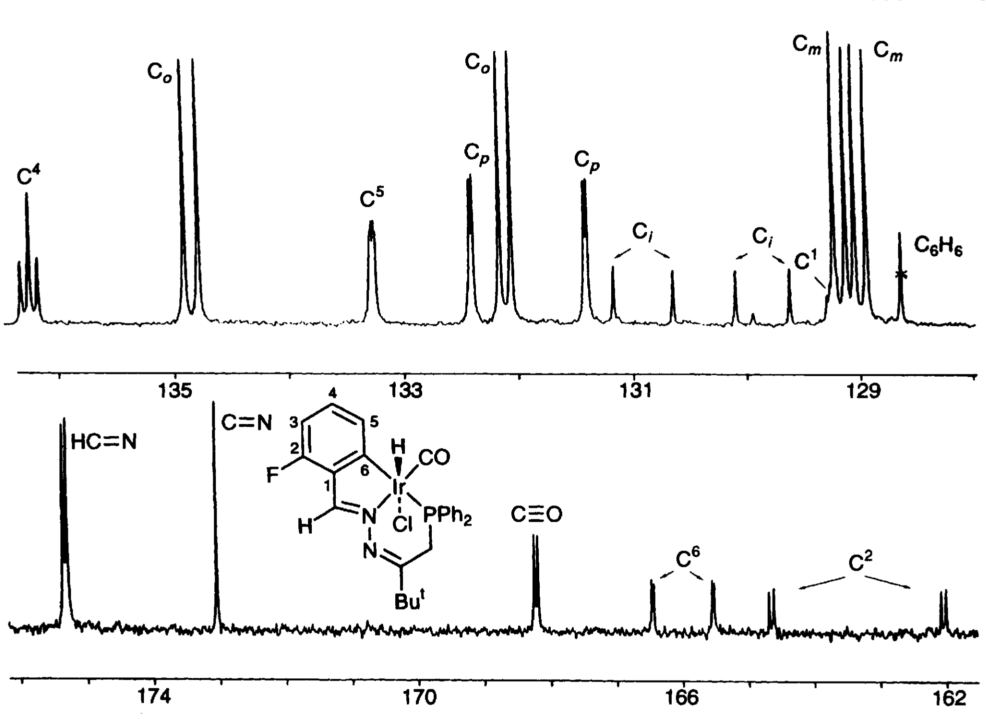
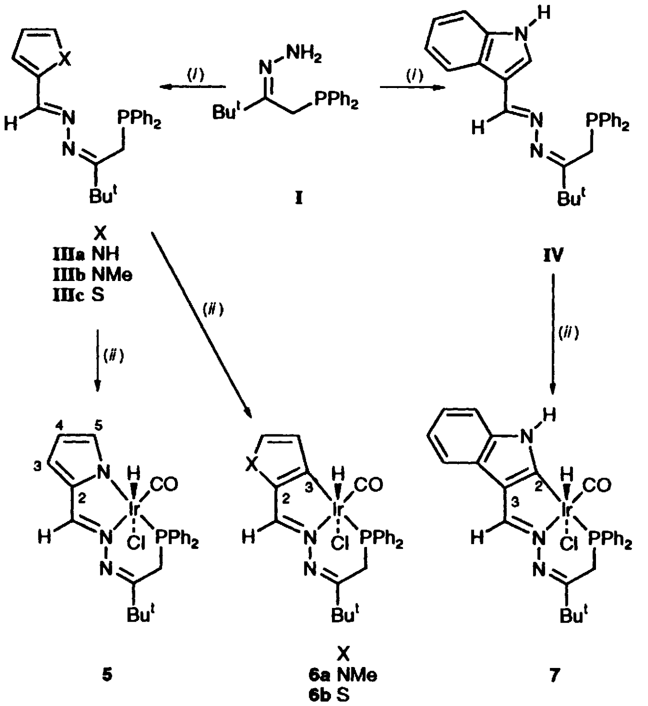


Fig. 1 Portions (between δ 128 and 176) of the ^{13}C-$\{^1H\}$ NMR spectrum of the complex [IrH(Cl)(CO){PPh$_2$CH$_2$C(Bu^t)=N-N=CH(C$_6$H$_3$F-2)}] **1g**, recorded in CD$_2$Cl$_2$ at 100.6 MHz; C$_i$, C$_m$, C$_o$ and C$_p$ refer to the *ipso-*, *meta-*, *ortho-* and *para*-carbons of the PPh$_2$ group

and C^6 as a doublet of doublets at δ 165.9 with ^3J(FC) = 3.3 and ^2J(PC) = 92.4 Hz.

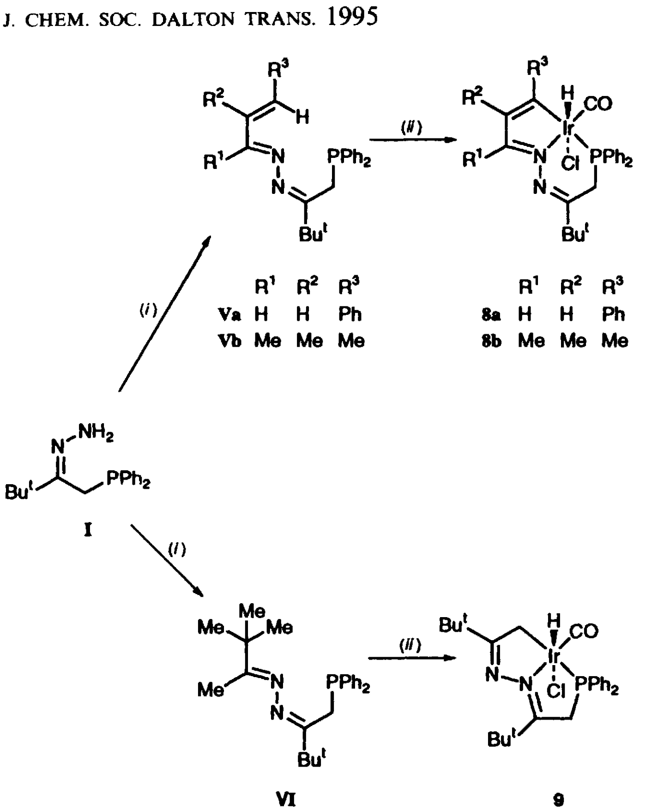
The azine phosphine **IIh**,[9] derived from 2-hydroxybenzaldehyde, underwent O–H bond fission very rapidly at 20 °C in dichloromethane solution to give the *O*-cyclometallated iridium(III) hydride **2a** (Scheme 1). The IR band due to ν(Ir–H) was at 2185 cm^{-1}, and in the proton NMR spectrum δ(IrH) occurred at −16.10 with ^2J(PH) = 15.4 Hz. The analogous *O*-cyclometallated iridium(III) hydride **2b** was prepared using the azine phosphine **IIi**,[9] derived from 4,6-dimethoxysalicylaldehyde. Dehydrochlorination of **2b** gave the corresponding iridium(I) complex [Ir(CO){PPh$_2$CH$_2$C(Bu^t)=N-N=CH[C$_6$H$_2$O(OMe)$_2$-4,6]}] which underwent oxidative-addition reactions with organic halides such as iodomethane, allyl chloride, acetyl chloride and propargyl (prop-2-ynyl) chloride.[9] On heating at 75 °C in benzene solution **2a** isomerised to the *C*-cyclometallated iridium(III) hydride **1h**, for which ν(O–H) occurred at 3225 cm^{-1}. This complex was prepared directly by treating the azine phosphine **IIh** with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)] in benzene at 75 °C for 3 h.

Condensation of the phosphino hydrazone **I** with ferrocenecarbaldehyde gave the azine phosphine **3** as reddish brown needles in 86% yield (Scheme 1). Treatment of it with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)] gave the cyclometallated iridium(III) hydride **4** as a purple solid. This showed a hydride resonance as a doublet at δ −17.00 with ^2J(PH) = 11.0 Hz, and ν(Ir–H) was at 2200 cm^{-1}.



Scheme 2 (*i*) Heterocyclic aldehyde; (*ii*) [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)]

We also investigated the C–H/N–H bond activation reactions of azine phosphines of type *Z*,*E*-PPh$_2$CH$_2$C(Bu^t)=N-N=CHR in which R is a heterocyclic group containing a pyrrole (**IIIa**), *N*-methylpyrrole (**IIIb**), thiophene (**IIIc**) or indole (**IV**) moiety (Scheme 2). When the pyrrole azine phosphine **IIIa**[6] was treated with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)] it underwent N–H bond activation to give the *N*-cyclometallated iridium(III) hydride **5** as a yellow solid in 85% yield. The hydride resonance was a doublet at δ −17.15 with ^2J(PH) = 13.3 Hz, and ν(Ir–H) occurred at 2190 cm^{-1}. The ^{13}C-$\{^1H\}$ NMR spectrum (see Experimental section) showed that three of the heterocyclic carbons of the pyrrole moiety were each attached to a single hydrogen (attached proton test), confirming that the N–H bond had been cleaved. Similar N–H bond fission occurred when **IIIa** was treated with [PtMe$_2$(cod)], giving the *N*-cyclometallated platinum(II) complex [PtMe{PPh$_2$CH$_2$C(Bu^t)=N-N=CH(C$_4$H$_3$N)}] and methane.[6] The azine phosphines **IIIb** and **IIIc** *C*-metallated exclusively in the 3 position to give the iridium(III) hydrides **6a** and **6b** respectively. The azine phosphine **IV**, derived from indole-3-carbaldehyde, *C*-metallated exclusively in the 2 position to give the iridium(III) hydride **7** in 83% yield. The IR bands



Scheme 3 (*i*) Aldehyde or ketone; (*ii*) $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$

due to ν(N–H) and ν(Ir–H) occurred at 3290 and 2195 cm^{-1}, respectively.

We have also studied cyclometallation processes involving an alkenyl or alkyl bond fission by iridium(I) (Scheme 3). When the azine phosphine **Va**, derived from cinnamaldehyde, was treated with $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ it underwent an olefinic C–H bond activation reaction to give the cyclometallated iridium(III) hydride **8a** as a yellow solid in 92% yield. The hydride resonance was a doublet at δ −17.13 with $^2J(PH) = 11.0$ Hz, and ν(Ir–H) occurred at 2180 cm^{-1}. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum, a doublet was observed at δ 205.6 with a large $^2J(PC)$ value of 89.4 Hz for the quaternary olefinic carbon Ir*C*Ph, confirming that it was *trans* to the phosphorus atom; *i.e.* as expected the cyclometallated azine ligand is in the *mer* arrangement. Similarly, the azine phosphine **Vb**, derived from 3-methylpent-3-en-2-one, gave the corresponding iridium(III) hydride **8b** as a yellow solid in 72% yield.

When we attempted to activate a C–H bond in the *tert*-butyl $[MeC(Bu^t)=]$ group of the azine phosphine **VI**,[3] by treating it with $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ in benzene at 75 °C, it yielded the iridium(III) hydride **9** as a white crystalline solid in 62% yield; *i.e.* metallation had occurred on the single methyl group *Me*C(Bu^t)= due to isomerisation around the C=N bond of the $PPh_2CH_2C(Bu^t)=N$ moiety. The $^1H\text{-}\{^{31}P\}$ NMR spectrum showed (*i*) a singlet at δ −17.77 for the hydride ligand, (*ii*) two singlets at δ 1.29 and 1.44 for the two *tert*-butyl groups, and (*iii*) two AB patterns for the CH_2P and CH_2Ir groups with $^2J(HH)$ values 18.3 and 17.6 Hz, respectively. The $^{13}C\text{-}\{^1H\}$ NMR spectrum showed a doublet at δ 22.4 with a large $^2J(PC)$ value of 71.6 Hz for the $IrCH_2$ carbon *trans* to the phosphorus atom, and a doublet at δ 46.8 for the CH_2P carbon as expected for a methylene carbon in a five-membered chelate ring.[2,29,39]

Crystal Structure of $[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t)=N\text{-}N=CH[C_6H(OMe)_3\text{-}3,4,5]\}]$ **1a**.—The hydridoiridium(III) complex **1a** crystallised from benzene–ethanol as triclinic crystals in the space group *P*$\bar{1}$. The molecular structure is shown in Fig. 2 with atom coordinates in Table 2 and selected bond lengths and angles in Table 3. The iridium atom has a distorted octahedral coordination sphere. The metallated ligand is in the *mer* arrangement and the hydride ligand is *trans* to the chloride. The cyclometallated aryl ring and the adjacent five-membered chelate ring are essentially in the same plane. The structure showed that the distances and angles are quite normal as found in similar azines, or hydrazones[1,2,29,39–41] and iridium complexes.[42–53] The Ir–$C_6H(OMe)_3$ bond distance of 2.077(3) Å is close to those observed previously [2.03(1)–2.081(17) Å].[42,44,45] The Ir–P distance of 2.328(1) Å falls within the range of 2.22–2.37 Å normally observed for other iridium complexes.[42–52] The Ir–H distance of 1.664 Å is within the values (1.47–1.71 Å) reported for other iridium hydrides.[24,45,47–53] The Ir–Cl bond length of 2.490(1) Å is at the high end of the range normally found (2.361–2.492 Å),[43,47,49,52] presumably as a result of the strong *trans* influence of the hydride ligand.

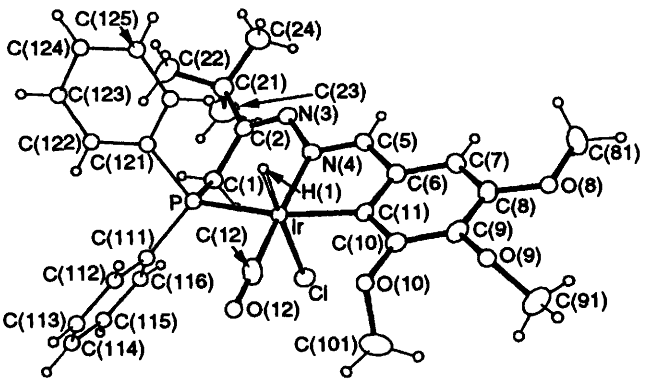


Fig. 2 Molecular structure of $[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t)=N\text{-}N=CH[C_6H(OMe)_3\text{-}3,4,5]\}]$ **1a**. Ellipses are shown at the 50% probability level. In the interest of clarity both phenyl carbon atoms and hydrogen atoms are drawn as circles each with an arbitrarily small radius

Experimental

All the reactions were carried out in an inert atmosphere of dry nitrogen or dry argon. Benzene was distilled from sodium under nitrogen immediately before use. Infrared spectra were recorded using a Perkin-Elmer model 457 grating spectrometer, NMR spectra using a JEOL FX-90Q (operating frequencies for ^1H and ^{31}P of 89.5 and 36.2 MHz respectively), a JEOL FX-100 (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively). The ^1H and ^{13}C chemical shifts are relative to tetramethylsilane and the ^{31}P shifts to 85% phosphoric acids. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec spectrometer with 8 kV acceleration, and for metal complexes *m*/*z* values are quoted for ^{193}Ir.

Preparation of Phosphines.—The compound *Z*-$PPh_2CH_2C(Bu^t)=NNH_2$ **I**[1] and the azine phosphines **IIa**–**IIi**,[6,7,9] **IIIa**[6] and **IIIc**[6] were prepared according to our published procedures.

The following azine phosphines were prepared in a similar manner and on a similar scale:[7] *Z*,*E*-$PPh_2CH_2C(Bu^t)=N\text{-}N=CH(C_5H_4)Fe(C_5H_5)$ **3**, yield 86% (Found: C, 70.15; H, 6.25; N, 5.8. $C_{29}H_{31}FeN_2P$ requires C, 70.45; H, 6.3; N, 5.65%), *m*/*z* (EI) 494 (*M* − 1) and 437 (*M* − Bu^t); *Z*,*E*-$PPh_2CH_2C(Bu^t)=N\text{-}N=CH(C_4H_3NMe)$ **IIIb**, yield 77% (Found: C, 74.0; H, 7.4; N, 10.9. $C_{24}H_{28}N_3P$ requires C, 74.0; H, 7.25; N, 10.8%), *m*/*z* (EI) 388 (*M* − 1) 374 (*M* − Me) and 332 (*M* − Bu^t); *Z*,*E*-$PPh_2CH_2C(Bu^t)=N\text{-}N=CH(C_8H_5NH)$ **IV**, yield 79% (Found: C, 75.9; H, 6.6; N, 9.7. $C_{27}H_{28}N_3P$ requires C, 76.2; H, 6.65; N,

Table 2 Fractional non-hydrogen atomic coordinates ($\times 10^4$) for compound **1a** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ir	721.12(10)	3085.94(9)	2413.54(6)
Cl	2618.8(7)	5224.7(6)	2539.1(4)
P	2280.8(7)	2135.8(6)	2710.0(4)
C(111)	3479(3)	2746(2)	3711(2)
C(112)	2967(3)	2439(3)	4429(2)
C(113)	3838(3)	2855(3)	5211(2)
C(114)	5208(3)	3563(3)	5279(2)
C(115)	5713(3)	3872(3)	4573(2)
C(116)	4847(3)	3470(3)	3783(2)
C(121)	1651(2)	350(2)	2545(2)
C(122)	2442(3)	−273(3)	2885(2)
C(123)	2000(3)	−1631(3)	2668(2)
C(124)	786(3)	−2376(3)	2110(2)
C(125)	−6(3)	−1766(3)	1782(2)
C(126)	418(3)	−409(2)	2002(2)
C(1)	3328(3)	2471(3)	1912(2)
C(2)	2531(3)	1824(2)	1016(2)
C(21)	3092(3)	988(3)	454(2)
C(22)	3131(3)	−170(3)	837(2)
C(23)	4516(3)	1848(3)	383(2)
C(24)	2197(3)	428(3)	−430(2)
N(3)	1465(2)	1948(2)	663.2(13)
N(4)	842(2)	2677(2)	1127.3(13)
C(5)	88(3)	3050(2)	634(2)
C(6)	−731(3)	3686(2)	1007(2)
C(7)	−1588(3)	4094(2)	504(2)
C(8)	−2451(3)	4577(2)	875(2)
O(81)	−3370(2)	4962(2)	451.4(12)
C(82)	−3520(3)	4741(3)	−446(2)
C(9)	−2442(3)	4649(2)	1744(2)
O(91)	−3415(2)	4947(2)	2109.2(12)
C(92)	−3392(3)	6248(3)	2180(2)
C(10)	−1540(3)	4289(2)	2232(2)
O(101)	−1567(2)	4357(2)	3081.8(11)
C(102)	−933(5)	5638(3)	3609(2)
C(11)	−657(3)	3788(2)	1879(2)
C(12)	486(3)	3425(3)	3514(2)
O(12)	366(3)	3629(3)	4204.0(13)

Table 3 Selected bond lengths (Å) and angles (°) for compound **1a** with e.s.d.s in parentheses

Ir–C(12)	1.842(3)	Ir–C(11)	2.077(3)
Ir–N(4)	2.105(2)	Ir–P	2.328(1)
Ir–Cl	2.490(1)	Ir–H(1)	1.664
C(1)–C(2)	1.517(3)	C(2)–N(3)	1.282(3)
C(2)–C(21)	1.528(4)	C(21)–C(23)	1.522(4)
C(21)–C(24)	1.528(4)	C(21)–C(22)	1.540(4)
N(3)–N(4)	1.413(3)	N(4)–C(5)	1.294(3)
C(5)–C(6)	1.444(4)	C(6)–C(11)	1.399(4)
C(6)–C(7)	1.405(4)	C(7)–C(8)	1.381(4)
C(8)–O(81)	1.370(3)	C(8)–C(9)	1.407(4)
O(81)–C(82)	1.425(3)	C(9)–O(91)	1.378(3)
C(9)–C(10)	1.391(4)	O(91)–C(92)	1.432(3)
C(10)–O(101)	1.381(3)	C(10)–C(11)	1.398(4)
O(101)–C(102)	1.419(4)	C(12)–O(12)	1.145(3)
C(12)–Ir–C(11)	97.60(11)	C(12)–Ir–N(4)	175.86(11)
C(11)–Ir–N(4)	78.86(9)	C(12)–Ir–P	94.65(9)
C(11)–Ir–P	167.61(7)	N(4)–Ir–P	88.83(6)
C(12)–Ir–Cl	95.84(10)	C(11)–Ir–Cl	90.68(7)
N(4)–Ir–Cl	86.39(6)	P–Ir–Cl	89.94(3)
C(12)–Ir–H(1)	85.24	C(11)–Ir–H(1)	87.13
N(4)–Ir–H(1)	92.40	P–Ir–H(1)	92.03
Cl–Ir–H(1)	177.67(2)	C(1)–P–Ir	103.65(9)
C(2)–C(1)–P	112.8(2)	N(3)–C(2)–C(1)	127.1(2)
N(3)–C(2)–C(21)	116.0(2)	C(1)–C(2)–C(21)	116.9(2)
C(2)–N(3)–N(4)	120.9(2)	C(5)–N(4)–N(3)	111.6(2)
C(5)–N(4)–Ir	114.6(2)	N(3)–N(4)–Ir	133.4(2)
N(4)–C(5)–C(6)	118.2(2)	C(11)–C(6)–C(7)	123.7(2)
C(11)–C(6)–C(5)	115.3(2)	C(7)–C(6)–C(5)	120.9(2)
C(8)–C(7)–C(6)	118.8(2)	O(81)–C(8)–C(7)	124.8(2)
O(81)–C(8)–C(9)	116.2(2)	C(7)–C(8)–C(9)	119.1(2)
C(8)–O(81)–C(82)	117.1(2)	O(91)–C(9)–C(10)	118.4(2)
O(91)–C(9)–C(8)	120.6(2)	C(10)–C(9)–C(8)	120.7(2)
C(9)–O(91)–C(92)	118.1(2)	O(101)–C(10)–C(9)	119.2(2)
O(101)–C(10)–C(11)	118.8(2)	C(9)–C(10)–C(11)	121.9(2)
C(10)–O(101)–C(102)	115.0(2)	C(10)–C(11)–C(6)	115.8(2)
C(10)–C(11)–Ir	131.2(2)	C(6)–C(11)–Ir	113.0(2)
O(12)–C(12)–Ir	178.4(3)		

9.9%), IR (KBr disc) ν(N–H) 3400 cm^{-1}, *m*/*z* (EI) 424 (*M* − 1) and 368 (*M* − Bu^t); *Z*,*E*-PPh$_2$CH$_2$C(Bu^t)=N–N=CHCH=CHPh **Va**, yield 62% (Found: C, 78.35; H, 7.0; N, 6.95. $C_{27}H_{29}N_2P$ requires C, 78.6; H, 7.1; N, 6.8%), *m*/*z* (EI) 412 (M^+) and 355 (*M* − Bu^t); *Z*,*E*-PPh$_2$CH$_2$C(Bu^t)=N–N=C(Me)C(Me)=CHMe **VIb**, yield 34% (Found: C, 76.25; H, 8.3; N, 7.4. $C_{24}H_{31}N_2P$ requires C, 76.15; H, 8.25; N, 7.4%), *m*/*z* (EI) 321 (*M* − Bu^t); *Z*,*E*-PPh$_2$CH$_2$C(Bu^t)=N–N=C(Me)Bu^t **VI**, yield 61% (Found: C, 75.15; H, 8.85; N, 7.15. $C_{24}H_{33}N_2P \cdot 0.25EtOH$ requires C, 75.05; H, 8.85; N, 7.15%), *m*/*z* (EI) 323 (*M* − Bu^t).

Preparation of Hydridoiridium(III) *Complexes*.—[IrH(Cl)(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=CH[C$_6$H(OMe)$_3$-3,4,5]}] **1a**. A mixture of [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)] (50 mg, 0.13 mmol) and the azine phosphine **IIa** (62 mg, 0.13 mmol) in benzene (*ca.* 2 cm^3) was warmed to *ca.* 75 °C for 5 min. The resultant yellow solution was concentrated to low volume (*ca.* 0.5 cm^3) under reduced pressure. Addition of hexane to the residue gave the hydridoiridium(III) complex **1a** as pale yellow microcrystals (90 mg, 96%) (Found: C, 48.9; H, 4.7; Cl, 4.65; N, 4.05. $C_{29}H_{33}ClIrN_2O_4P \cdot 0.25C_6H_6$ requires C, 48.75; H, 4.65; Cl, 4.7; N, 3.75%). IR (KBr disc): ν(Ir–H) 2195 and ν(C≡O) 2040 cm^{-1}. *m*/*z* (FAB): 731 (*M* − H) and 697 (*M* − Cl). ^{13}C-{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$): δ 21.6 [1 C, d, ^1J(PC) 26.8, CH$_2$], 27.2 (3 C, s, C*Me*$_3$), 41.2 [1 C, d, ^3J(PC) 3.0, *C*Me$_3$], 56.7 (1 C, s, OMe), 60.9 (1 C, s, OMe), 61.1 (1 C, s, OMe), 111.2 [1 C, d, ^4J(PC) 5.5, C^2], 128.8 [2 C, d, ^3J(PC) 10.3, C$_m$], 129.1 [2 C, d, ^3J(PC) 10.7, C$_m$], 130.0 [1 C, d, ^1J(PC) 48.9, C$_i$], 131.0 [1 C, d, ^1J(PC) 51.3, C$_i$], 131.2 [1 C, d, ^4J(PC) 1.8, C$_p$], 132.2 [2 C, d, ^2J(PC) 9.8, C$_o$], 132.3 [1 C, d, ^4J(PC) 2.3, C$_p$], 135.0 [2 C, d, ^2J(PC) 12.3, C$_o$], 135.6 (1 C, s, aryl), 147.3 [1 C, d, *J*(PC) 5.3, aryl], 151.7 (1 C, s, aryl), 151.9 [1 C, d, ^2J(PC) 92.6, C^6], 156.4 (1 C, s, aryl), 167.6 [1 C, d, ^2J(PC) 5.2, C≡O], 171.1 (1 C, s, Bu^t*C*=N) and 180.3 [1 C, d, ^3J(PC) 5.3 Hz, HC=N].

The following six hydridoiridium(III) complexes were prepared in a similar manner and on a similar scale to those of **1a**.

[IrH(Cl)(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_6$H$_4$)}] **1b**. Yield 94% (Found: C, 53.0; H, 4.5; Cl, 5.15; N, 3.9. $C_{26}H_{27}ClIrN_2OP \cdot C_6H_6$ requires C, 53.35; H, 4.6; Cl, 4.9; N, 3.9%). IR (KBr disc) ν(Ir–H) 2190 and ν(C≡O) 2040 cm^{-1} *m*/*z* (FAB): 642 (M^+) and 614 (*M* − CO). ^{13}C-{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$): δ 21.9 [1 C, d, ^1J(PC) 25.6, CH$_2$], 27.2 (3 C, s, C*Me*$_3$), 41.3 [1 C, d, ^3J(PC) 3.0, *C*Me$_3$], 124.3 (1 C, s, C^3), 128.9 [2 C, d, ^3J(PC) 10.3, C$_m$], 129.1 [2 C, d, ^3J(PC) 10.6, C$_m$], 130.2 [1 C, d, ^1J(PC) 47.2, C$_i$], 131.0 [1 C, d, *J*(PC) 4.8, aryl], 131.2 [1 C, d, ^1J(PC) 51.2, C$_i$], 130.3 [1 C, d, ^4J(PC) 2.4, C$_p$], 132.1 [2 C, d, ^2J(PC) 10.4, C$_o$], 132.3 [1 C, d, ^4J(PC) 2.4, C$_p$], 133.5 [1 C, d, *J*(PC) 6.1, aryl], 134.8 [2 C, d, ^2J(PC) 12.5, C$_o$], 137.6 [1 C, d, *J*(PC) 1.4, aryl], 141.2 [1 C, d, ^3J(PC) 2.5, C^1], 163.4 [1 C, d, ^2J(PC) 91.5, C^6], 168.7 [1 C, d, ^2J(PC) 5.2, C≡O], 172.3 (1 C, s, Bu^t*C*=N) and 180.6 [1 C, d, ^3J(PC) 5.2 Hz, HC=N].

[IrH(Cl)(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_6$H$_3$OMe-4)}] **1c**. Yield 84% (Found: C, 49.35; H, 4.2; N, 4.1. $C_{27}H_{29}ClIrN_2O_2P \cdot 0.2C_6H_6$ requires C, 49.25; H, 4.4; N, 4.05%). IR (KBr disc): ν(Ir–H) 2190 and ν(C≡O) 2035 cm^{-1}. *m*/*z* (FAB): 671 (*M* − H), 644 (*M* − CO) and 637 (*M* − Cl).

[IrH(Cl)(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_6$H$_3$NO$_2$-4)}]

1d. Yield 77% (Found: C, 50.9; H, 4.20; Cl, 4.6; N, 5.65. $C_{26}H_{26}ClIrN_3O_3P{\cdot}1.1C_6H_6$ requires C, 50.65; H, 4.25; Cl, 4.6; N, 5.45%). IR (KBr disc): ν(Ir–H) 2170, ν(C≡O) 2030 and ν(NO_2) 1510 and 1340 cm^{-1}. *m/z* (FAB): 687 (M^+) and 651 (*M* – HCl).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_3Br\text{-}2)\}]$ **1e**. Yield 97% (Found: C, 45.5; H, 3.85; N, 3.85. $C_{26}H_{26}BrClIrN_2OP{\cdot}0.5C_6H_6$ requires C, 45.8; H, 3.85; N, 3.7%). IR (KBr disc): ν(Ir–H) 2195 and ν(C≡O) 2045 cm^{-1}. *m/z* (FAB): 721 (*M* – H) and 687 (*M* – Cl).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_3Cl\text{-}2)\}]$ **1f**. Yield 86% (Found: C, 46.7; H, 3.9; Cl, 10.55; N, 4.0. $C_{26}H_{26}Cl_2IrN_2OP{\cdot}0.1C_6H_6$ requires C, 46.65; H, 3.9; Cl, 10.35; N, 4.1%). IR (KBr disc): ν(Ir–H) 2170 and ν(C≡O) 2040 cm^{-1}. *m/z* (FAB): 675 (*M* – H) and 641 (*M* – Cl).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_3F\text{-}2)\}]$ **1g**. Yield 75% (Found: C, 47.9; H, 4.0; Cl, 5.15; N, 4.05. $C_{26}H_{26}ClFIrN_2OP{\cdot}0.1C_6H_6$ requires C, 47.8; H, 4.0; Cl, 5.3; N, 4.2%). ν(Ir–H) 2190 and ν(C≡O) 2040 cm^{-1}. *m/z* (FAB): 660 (M^+) and 625 (*M* – Cl). $^{13}C\text{-}\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 21.9 [1 C, d, ^1J(PC) 26.0, CH_2], 27.2 (3 C, s, C*Me*$_3$), 41.4 [1 C, d, ^3J(PC) 2.9, *C*Me$_3$], 110.2 [1 C, d, ^2J(FC) 19.1, C^3], 128.9 [2 C, d, ^3J(PC) 10.5, C_m], 129.2 [2 C, d, ^3J(PC) 10.7, C_m], 129.2 [1 C, C^1(obscured)], 129.8 [1 C, d, ^1J(PC) 48.0, C_i], 130.9 [1 C, d, ^1J(PC) 53.0, C_i), 131.4 [1 C, d, ^4J(PC) 2.4, C_p], 132.1 [2 C, d, ^2J(PC) 10.3, C_o], 132.4 [1 C, d, ^4J(PC) 2.5, C_p], 133.3 [1 C, dd, ^3J(PC) 3.0, ^4J(FC) 1.2, C^5], 134.8 [2 C, d, ^2J(PC) 12.4, C_o], 136.2 [1 C, t, ^4J(PC) = ^3J(FC) 7.6, C^4], 163.4 [1 C, dd, ^1J(FC) 262.6, ^4J(PC) 7.2, C^2], 165.9 [1 C, dd, ^2J(PC) 92.4, ^3J(FC) 3.3, C^6], 168.2 [1 C, d, ^2J(PC) 5.6, C≡O], 173.0 (1 C, s, Bu^t*C*=N) and 175.3 [1 C, d, ^3J(PC) 5.5 Hz, HC=N].

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_3OH{-}2)\}]$ **1h**. This complex was prepared in a similar manner to that of **1a** except with a reaction time of 3 h. Yield 68% (Found: C, 47.8; H, 4.15; Cl, 5.8; N, 4.2. $C_{26}H_{27}ClIrN_2O_2P$ requires C, 47.45; H, 4.15; Cl, 5.4; N, 4.25%). IR (KBr disc): ν(O–H) 3225, ν(Ir–H) 2215 and ν(C≡O) 2040 cm^{-1}. *m/z* (FAB): 657 (*M* – H) and 623 (*M* – Cl).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4O)\}]$ **2a**. A mixture of $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ (50 mg, 0.13 mmol) and the azine phosphine **IIh** (48 mg, 0.12 mmol) in CH_2Cl_2 (*ca.* 2 cm^3) was put aside at 20 °C for 20 min. The resultant yellow solution was concentrated to low volume (*ca.* 0.3 cm^3) under reduced pressure. Addition of cyclohexane to the residue gave the hydridoiridium(III) complex **2a** as yellow microcrystals (66 mg, 78%) (Found: C, 50.25; H, 4.7; Cl, 5.3; N, 4.35. $C_{26}H_{27}ClIrN_2O_2P{\cdot}0.6C_6H_{12}$ requires C, 50.15; H, 4.85; Cl, 5.0; N, 3.95%). IR (KBr disc): ν(Ir–H) 2185 and ν(C≡O) 2050 cm^{-1}. *m/z* (FAB): 657 (*M* – H) and 623 (M – Cl).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH[C_6H_2O(OMe)_2\text{-}4.6]\}]$ **2b**. Yield 78% (Found: C, 50.8; H, 4.95; Cl, 4.8; N, 3.55. $C_{28}H_{31}ClIrN_2O_4P{\cdot}0.9C_6H_6$ requires C, 50.85; H, 4.65; Cl, 4.5; N, 3.55%). IR (KBr disc): ν(Ir–H) 2200 and ν(C≡O) 2055 cm^{-1}. *m/z* (FAB): 717 (*M* – H) and 683 (*M* – Cl).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_5H_3)Fe(C_5H_5)\}]$ **4**. Yield 68% (Found: C, 48.0; H, 4.0; Cl, 4.85; N, 3.6. $C_{30}H_{31}ClFeIrN_2OP$ requires C, 48.05; H, 4.15; Cl, 4.75; N, 3.75%). IR (KBr disc): ν(Ir–H) 2200 and ν(C≡O) 2030 cm^{-1}.

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_4H_3N)\}]$ **5**. Yield 85% (Found: C, 49.15; H, 4.65; Cl, 4.9; N, 6.65. $C_{24}H_{26}ClIrN_3OP{\cdot}0.6C_6H_6$ requires C, 48.9; H, 4.4; Cl, 5.2; N, 6.2%). IR (KBr disc): ν(Ir–H) 2190 and ν(C≡O) 2050 cm^{-1}. *m/z* (FAB): 631 (M^+) and 596 (*M* – Cl). $^{13}C\text{-}\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 21.6 [1 C, d, ^1J(PC) 34.7, CH_2], 27.3 (3C, s, C*Me*$_3$), 40.8 [1 C, d, ^3J(PC) 3.4, *C*Me$_3$], 116.0 [1 C, d, ^4J(PC) 4.7, C^4], 121.0 [1 C, d, ^4J(PC) 2.4, C^3], 128.3 [1 C, d, ^1J(PC) 61.6, C_i], 129.0 [2 C, d, ^3J(PC) 13.1, C_m], 129.2 [2 C, d, ^3J(PC) 11.9, C_m], 129.7 [1 C, d, ^1J(PC) 64.6, C_i], 132.1 (1 C, s, C_p), 132.2 [2 C, d, ^2J(PC) 9.5, C_o], 132.9 (1 C, s, C_p), 134.7 [2 C, d, ^2J(PC) 11.5, C_o], 135.9 (1 C, s, C^2), 139.9 (1 C, s, C^5), 161.7 (1 C, s, HC=N), 164.5 [1 C, d, ^3J(PC) 2.2, Bu^t*C*=N] and 165.4 [1 C, d, ^2J(PC) 8.3 Hz, C≡O].

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_4H_2NMe)\}]$ **6a**. Yield 84% (Found: C, 49.8; H, 4.6; Cl, 5.05; N, 6.15. $C_{25}H_{28}ClIrN_3OP{\cdot}0.6C_6H_6$ requires C, 49.65; H, 4.6; Cl, 5.1; N, 6.05%). IR (KBr disc): ν(Ir–H) 2195 and ν(C≡O) 2040 cm^{-1}. *m/z* (FAB): 645 (M^+), 617 (*M* – CO) and 609 (*M* – HCl).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_4H_2S)\}]$ **6b**. This complex was prepared in a similar manner to that of **1a** except with a reaction time of 1 h. Yield 87% (Found: C, 46.6; H, 4.4; Cl, 5.3; N, 4.45. $C_{24}H_{25}ClIrN_2OPS{\cdot}0.4C_6H_6$ requires C, 46.65; H, 4.05; Cl, 5.2; N, 4.15%). IR (KBr disc): ν(Ir–H) 2180 and ν(C≡O) 2030 cm^{-1}. *m/z* (FAB): 648 (M^+), 620 (*M* – CO) and 613 (*M* – Cl).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_8H_4NH)\}]$ **7**. Yield 83% (Found: C, 50.85; H, 4.15; Cl, 5.3; N, 5.85. $C_{28}H_{28}ClIrN_3OP{\cdot}0.25C_6H_6$ requires C, 50.55; H, 4.25; Cl, 5.05; N, 6.0%). IR (KBr disc): ν(N–H) 3290, ν(Ir–H) 2195 and ν(C≡O) 2050 cm^{-1}. *m/z* (FAB): 681 (M^+).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CHCH{=}CPh\}]$ **8a**. Yield 92% (Found: C, 47.65; H, 4.95; Cl, 5.4; N, 4.55. $C_{28}H_{29}ClIrN_2OP$ requires C, 47.35; H, 4.95; Cl, 5.6; N, 4.4%). IR (KBr disc): ν(Ir–H) 2180 and ν(C≡O) 2030 cm^{-1}. *m/z* (FAB): 668 (M^+), 640 (*M* – CO) and 632 (*M* – HCl). $^{13}C\text{-}\{^1H\}$ NMR (62.9 MHz, CD_2Cl_2): δ 21.0 [1 C, d, ^1J(PC) 26.6, CH_2], 26.9 (3 C, s, C*Me*$_3$), 40.7 [1 C, d, ^3J(PC) 3.1, *C*Me$_3$], 126.1 [1 C, d, ^3J(PC) 2.1, *C*H=CPh], 126.4 [2 C, d, ^4J(PC) 2.8, =C*Ph*], 128.2 (2 C, s, =C*Ph*), 128.3 (1 C, s, =C*Ph*), 128.8 [2 C, d, ^3J(PC) 10.3, C_m], 128.8 [2 C, d, ^3J(PC) 10.8, C_m], 129.2 [1 C, d, ^1J(PC) 54.6, C_i], 129.9 [1 C, d, ^1J(PC) 51.6, C_i], 131.0 [1 C, d, ^4J(PC) 2.4, C_p], 131.8 [2 C, d, ^2J(PC) 10.8, C_o], 132.0 [1 C, d, ^4J(PC) 2.5, C_p], 134.6 [2 C, d, ^2J(PC) 12.1, C_o], 149.7 [1 C, d, ^3J(PC) 2.3, =C*Ph*], 167.7 [1 C, d, ^2J(PC) 3.8, C=O], 167.8 (1 C, s, C=N), 179.2 [1 C, d, ^3J(PC) 6.7, HC=N] and 205.6 [1 C, d, ^3J(PC) 89.4 Hz, Ir*C*Ph].

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)C(Me){=}CMe\}]$ **8b**. Yield 72% (Found: C, 47.65; H, 4.95; Cl, 5.4; N, 4.55. $C_{25}H_{31}ClIrN_2OP$ requires C, 47.35; H, 4.95; Cl, 5.6; N, 4.4%). IR (KBr disc): ν(Ir–H) 2195 and ν(C≡O) 2025 cm^{-1}. *m/z* (FAB): 634 (M^+), 606 (*M* – CO) and 598 (*M* – HCl).

$[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2\}]$ **9**. This complex was prepared in a similar manner that to of **1a** except with a reaction time of 1.5 h. Yield 62%. An analytical sample was crystallised from CH_2Cl_2–EtOH (Found: C, 46.3; H, 5.45; Cl, 7.2; N, 4.3. $C_{25}H_{33}ClIrN_2OP{\cdot}0.2CH_2Cl_2$ requires C, 46.35; H, 5.15; Cl, 7.6; N, 4.3%). IR (KBr disc): ν(Ir=H) 2085 and ν(C≡O) 2010 cm^{-1}. *m/z* (FAB): 636 (M^+), 608 (*M* – CO) and 601 (*M* – Cl). $^{13}C\text{-}\{^1H\}$ NMR (62.9 MHz, CD_2Cl_2): δ 22.4 [1 C, d, ^2J(PC) 71.6, CH_2Ir], 29.1 (3 C, s, C*Me*$_3$), 29.4 (3 C, s, C*Me*$_3$), 37.4 [1 C, d, ^4J(PC) 3.1, *C*Me$_3$], 39.7 [1 C, d, ^3J(PC) 7.0, *C*Me$_3$], 46.8 [1 C, d, ^1J(PC) 30.3, CH_2P], 128.9 [2 C, d, ^3J(PC) 10.7, C_m], 129.0 [2 C, d, ^3J(PC) 10.3, C_m], 130.1 [1 C, d, ^1J(PC) 45.9, C_i], 130.8 [1 C, d, ^4J(PC) 2.4, C_p], 131.4 [2 C, d, ^2J(PC) 11.8, C_o], 131.5 (1 C, s, C_p), 133.8 [2 C, d, ^2J(PC) 12.1, C_o], 136.1 [1 C, d, ^1J(PC) 48.8, C_i], 173.6 [1 C, d, ^2J(PC) 4.8, C≡O], 185.7 [1 C, d, *J*(PC) 3.5, C=N] and 198.4 [1 C, d, *J*(PC) 3.3 Hz, C=N].

Single-crystal X-Ray Diffraction Analysis of Compound **1a**.—All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated Mo-Kα radiation (λ = 71.069 pm) and an on-line profile-fitting method.[54] The data set was corrected for absorption using azimuthal Ψ scans (maximum and minimum transmission factors 0.1894 and 0.3458 respectively).

The structure was determined by heavy-atom methods using SHELXS 86[55] and refined by full-matrix least squares (based on F^2) using SHELXL 93.[56] All data were used in the refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters including those of two independent benzene solvate molecules (one positioned across a centre of symmetry). Restraints were applied to the phosphine phenyl groups and benzene solvate molecules so each remained flat with overall C_{2v} symmetry. All hydrogen atoms, with the exception of the metal hydride H(1), were constrained to calculated positions (C–H 0.93, 0.96, 0.97 and 0.99 Å for phenyl, methyl, methylene and methine hydrogen atoms respectively) with fixed isotropic thermal parameters of $n(U_{eq})$ of the parent carbon atom where n was 1.5 for methyl hydrogens and 1.2 for all others. The highest peak in the Fourier-difference synthesis gave an acceptable hydride position but the atomic coordinates had to be constrained as the atom moved to an unrealistic position during refinement. The weighting scheme $w = [\sigma^2(F_o^2) + (0.0216P)^2 + 1.0201P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3]$, was used. The final Fourier-difference synthesis was flat and showed no features of chemical significance (maximum and minimum residual densities 0.592 and -0.515 e Å^{-3}). Final non-hydrogen atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3. An ORTEP[57] diagram is given in Fig. 2.

Crystal data. $C_{29}H_{33}ClIrN_2O_4P\cdot1.5C_6H_6$, 0.54 × 0.38 × 0.31 mm, $M = 849.36$ (includes solvate molecules), triclinic, space group $P\bar{1}$, $a = 10.758(2)$, $b = 11.190(2)$, $c = 16.335(3)$ Å, $\alpha = 99.534(9)$, $\beta = 97.023(9)$, $\gamma = 110.801(10)°$, $U = 1777.6(6)$ Å^3.

Data collection. $4.0 < 2\theta < 50.0°$; each scan divided into 30 steps, scan widths and step sizes calculated from a learnt profile; scan speeds 1.0–8.0° min^{-1} (subject to a fast pre-scan). Number of data collected = 6436; number of unique data, $n = 6261$; number with $F_o > 4.0\ \sigma(F_o) = 5706$; $R_{sig} = \Sigma(\sigma F_o^2)/\Sigma(F_o^2) = 0.0217$; $T = 173$ K.

Structure refinement. Number of parameters, $p = 431$; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0174$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.0423$; goodness of fit $s = \Sigma[w(F_o^2 - F_c^2)^2]/(n - p)^{\frac{1}{2}} = 1.022$; maximum $\Delta/\sigma = 0.001$ (in Y/b of Ir), mean $\Delta/\sigma = 0.000$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the SERC for a fellowship (to S. D. P.) and for other support, and Johnson Matthey for the generous loan of iridium salts.

References

1 K. K. Hii, S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1992, 2361.
2 K. K. Hii, S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1994, 103 and refs. therein.
3 S. D. Perera and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1994, 1201.
4 S. D. Perera and B. L. Shaw, *Inorg. Chim. Acta.*, 1995, **228**, 127.
5 S. D. Perera and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1994, 1203.
6 S. D. Perera and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1995, 641.
7 S. D. Perera and B. L. Shaw, *J. Organomet. Chem.*, 1994, **479**, 117.
8 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *Inorg. Chim. Acta*, 1995, **233**, 103.
9 K. K. Hii, S. D. Perera and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1994, 3589.
10 K. K. Hii, S. D. Perera and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1995, 625.
11 S. D. Perera, M. Shamsuddin and B. L. Shaw, *Can. J. Chem.*, in the press.
12 M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 73.
13 E. C. Constable, *Polyhedron*, 1984, **3**, 1037.
14 G. R. Newkome, W. E. Puckett, V. K. Gupta and G. E. Kieper, *Chem. Rev.*, 1986, **86**, 451.
15 V. V. Dunina, O. A. Zalevskaya and V. M. Potapov, *Russ. Chem. Rev.*, 1988, **57**, 250.
16 A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.
17 M. A. Bennett and D. L. Milner, *J. Am. Chem. Soc.*, 1969, **91**, 6983.
18 S. Hietkamp, D. J. Stufkens and K. Vrieze, *J. Organomet. Chem.*, 1976, **122**, 419.
19 S. Hietkamp, D. J. Stufkens and K. Vrieze, *J. Organomet. Chem.*, 1977, **139**, 189.
20 S. Hietkamp, D. J. Stufkens and K. Vrieze, *J. Organomet. Chem.*, 1978, **152**, 347.
21 H. D. Empsall, E. M. Hyde, R. Markham, W. S. McDonald, M. C. Norton, B. L. Shaw and B. Weeks, *J. Chem. Soc., Chem. Commun.*, 1977, 589.
22 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020.
23 E. F. Landvatter and T. B. Rauchfuss, *Organometallics*, 1982, **1**, 506.
24 S. Park, M. P. Johnson and D. M. Roundhill, *Organometallics*, 1989, **8**, 1700.
25 E. Farnetti, G. Nardin and M. Graziani, *J. Organomet. Chem.*, 1991, **417**, 163.
26 D. W. Stephan, *Inorg. Chem.*, 1984, **23**, 2207.
27 M. J. Auburn, R. D. Holmes-Smith and S. R. Stobart, *J. Am. Chem. Soc.*, 1984, **106**, 1314.
28 G. C. Levy, R. L. Lichter and G. L. Nelson, *Carbon-13 NMR Spectroscopy*, 2nd edn., Wiley, New York, Chichester, Brisbane, Toronto, 1980.
29 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1993, 3653 and refs. therein.
30 F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, 1969, **91**, 4940.
31 W. Kemp, *NMR in Chemistry—A Multinuclear Introduction*, MacMillan, Basingstoke and London, 1986.
32 U. Klabunde, *Inorg. Synth.*, 1974, **15**, 82.
33 C. E. Johnson, B. J. Fisher and R. Eisenberg, *J. Am. Chem. Soc.*, 1983, **105**, 7772.
34 J. R. Knorr and J. S. Merola, *Organometallics*, 1990, **9**, 3008.
35 C. V. Senoff, *Can. J. Chem.*, 1970, **48**, 2444.
36 J. R. Gaylor and C. V. Senoff, *Can. J. Chem.*, 1972, **50**, 1868.
37 B. L. Shaw and E. Singleton, *J. Chem. Soc. A*, 1967, 1683.
38 R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245.
39 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1992, 1469.
40 S. D. Perera, B. L. Shaw, M. Thornton-Pett and J. D. Vessey, *J. Organomet. Chem.*, 1993, **462**, 221.
41 S. D. Perera, B. L. Shaw, M. Thornton-Pett and J. D. Vessey, *Inorg. Chim. Acta.*, 1993, **207**, 175.
42 O. Blum, F. Frolow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1991, 258.
43 M. P. Anderson, A. L. Casalnuova, B. J. Johnson, B. M. Mattson, A. M. Mueting and L. H. Pignolet, *Inorg. Chem.*, 1988, **27**, 1649.
44 T. Yoshida, K. Tani, T. Yamagata, Y. Tatsuno and T. Saito, *J. Chem. Soc., Chem. Commun.*, 1990, 292.
45 F. Neve, M. Ghedini, A. Tiripicchio and F. Ugozzoli, *Inorg. Chem.*, 1989, **28**, 3084.
46 F. Neve, M. Ghedini, G. De Munno and A. Crispini, *Inorg. Chem.*, 1991, **10**, 1143.
47 A. M. Mueting, P. Boyle and L. H. Pignolet, *Inorg. Chem.*, 1984, **23**, 44.
48 G. R. Clark, B. W. Skelton and T. N. Waters, *Inorg. Chim. Acta*, 1975, **12**, 235.
49 M. Schulz and H. Werner, *Organometallics*, 1992, **11**, 2790.
50 P. O. Stoutland and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 5732.
51 L. Garlaschelli, S. I. Khan, R. Bau, G. Longoni and T. F. Koetzle, *J. Am. Chem. Soc.*, 1985, **107**, 7212.
52 T. H. Tulip and J. A. Ibers, *J. Am. Chem. Soc.*, 1979, **101**, 4201.
53 J. S. Ricci, jun., T. F. Koetzle, M. Fernandez and P. M. Maitlis, *Acta Crystallogr., Sect. A*, 1984, **40**, C301.
54 W. Clegg, *Acta Crystallogr., Sect. A*, 1987, **37**, 22.
55 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467.
56 G. M. Sheldrick, University of Göttingen, 1993.
57 C. K. Johnson, ORTEP II Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Received 16th *November* 1994; *Paper* 4/06993E