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Synthesis and reactions of ene–hydrazone diphosphine iridium complexes and related species †

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Treatment of the azine diphosphine *Z*,*Z*-$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$ **I** with $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}4)]$ in benzene gave the ene–hydrazone diphosphine iridium(III) hydride $[IrH(Cl)(CO)\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh_2\}]$, **1**, which isomerised reversibly to the ionic square planar iridium(I) complex $[Ir(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]Cl$ **2a**, containing an azine diphosphine. Treatment of **1** with NEt_3 gave the neutral ene–hydrazone diphosphine iridium(I) complex $[Ir(CO)\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ **3** which is reactive and undergoes oxidative addition of H_2 to give the iridium(III) dihydride *mer*,*cis*-$[IrH_2(CO)\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ **4** and oxidative addition of MeI to give the methyliridium(III) complex $[IrMe(I)(CO)\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ **5**. It reacted rapidly with olefins or acetylenes (L), *i.e. N*-methylmaleimide, ethene or dimethyl acetylenedicarboxylate, to give the five-co-ordinate adducts $[Ir(CO)L\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh_2\}]$, **6a**, **6b** or **6c**, respectively, also with O_2 to give the η^2-dioxygen adduct $[Ir(CO)(\eta^2\text{-}O_2)\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ **7**. Treatment of **3** with 1 mol of picric acid protonated the ene–hydrazone diphosphine backbone to give the azine diphosphine iridium(I) salt $[Ir(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}][OC_6H_2(NO_2)_3]$ **2b**. The *N*-methylmaleimide adduct **6a** was similarly protonated to give the corresponding azine diphosphine iridium(I) salt $[Ir(CO)(\eta^2\text{-}COCH{=}CHCONMe)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}][OC_6H_2(NO_2)_3]$ **8**. Complex **1** was protonated by HCl to give the corresponding azine diphosphine iridium(III) salt $[IrH(Cl)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]Cl$ **9a**, which is converted into **3** when treated with NEt_3. The ^1H, ^{13}C and ^{31}P NMR and some IR data are given.

Azines, $R_2C{=}N{-}N{=}CR_2$, formed by condensing hydrazine with a ketone (or aldehyde) are often very stable entities and we have used azine backbones to generate new kinds of tertiary phosphine–metal chemistry very successfully. We have described, for example, the azine diphosphine $PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$, prepared by lithiation of *tert*-butyl methyl ketazine, followed by treatment with Ph_2PCl.[1] This diphosphine is in a *Z*,*Z* configuration and commonly bridges metals. Using it as a bridging ligand, we have made binuclear palladium(II) complexes with 18 atom rings or a polynuclear complex with platinum(II), probably hexanuclear, with a 54 atom ring.[2,3] However, it can form a nine-membered chelate ring with gold(I).[4] The energy barrier to rotation around a C=N bond is low and $PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$ frequently reacts in the *E*,*Z* configuration with metals. Again a nine-membered chelate ring can form, *e.g.* with Cr, Mo or W[1] or Pt.[2,3] More commonly, *E*,*Z*-$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$ acts as a terdentate *P*,*N*,*P* bonded ligand with five- and six-membered fused chelate rings as with Cr, Mo or W,[1] Pd^{II}, Pt^{II} or Pt^{IV} [2,3] or Ir^I.[5,6] We have also shown that in some metal complexes containing the terdentate *E*,*Z*-diphosphine ligand $PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$ reversible deprotonation of a CH_2 group adjacent to co-ordinated PPh_2 can occur giving a terdentate ene–hydrazone diphosphine ligand, $PPh_2CH{=}C(Bu^t){-}N{-}N{=}C(Bu^t)CH_2PPh_2$; this has been developed into a new method of generating co-ordinative unsaturation.[5,6]

In the present paper we describe a new, highly reactive neutral iridium(I) complex containing this ene–hydrazone ligand together with its reactions. For the convenience of the reader the various reactions are shown in Schemes 1–3 and the characterising NMR data for the various complexes are given in Tables 1–3.

† Dedicated to Professor Warren Roper on the occasion of his 60th birthday.

Results and Discussion

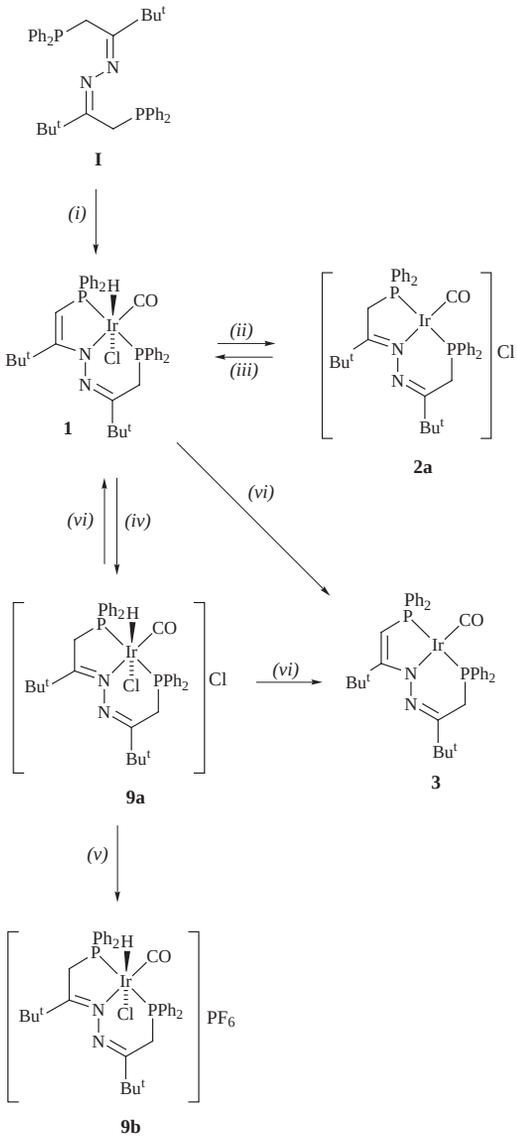
Previously[6] we have reported that treatment of $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}4)]$[7] with *Z*,*Z*-$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$ **I**, in benzene, gives the octahedral iridium(III) hydride **1** containing the ene–hydrazone diphosphine ligand. However, when **1** is dissolved in a polar solvent such as ethanol or methanol it very rapidly isomerises to the square planar iridium(I) salt **2a** containing the terdentate diphosphine ligand *E*,*Z*-$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$. Hydrogen migration from the azine backbone is rapid and, on dissolution of **2a** in benzene or dichloromethane, isomerisation back to **1** occurs rapidly and essentially completely. We now find that when the neutral octahedral iridium(III) hydride **1** is treated with triethylamine, 1 molecule of HCl is removed and the orange square planar neutral iridium(I) complex **3** is formed in good (>70%) yield. Complex **3** contains a terdentate ene–hydrazone diphosphine ligand. This iridium(I) carbonyl complex shows ν(C≡O) at 1945 cm^{-1} in dichloromethane solution (see Experimental section for IR and elemental analytical data). The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows an AX pattern with strongly coupled *trans*-phosphorus atoms [$^2J(PP) = 299$ Hz]. The ^1H and $^1H\text{-}\{^{31}P\}$ NMR data are in complete accord with the assigned structure, in particular, the olefinic proton of the ene–hydrazone system gave a doublet of doublets at δ 5.04 [$J(PH) = 3.9$, 3.2 Hz]. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the resonances of all four carbons of the ene–hydrazone backbone and of the C≡O carbon and also of the two *tert*-butyl groups are assigned (see Table 3). The methylene carbon gave a doublet at δ 20.0 [$^1J(PC) = 23.4$ Hz]; this chemical shift is typical of methylene carbon in a six-membered chelate ring.[2,3,8,9]

On maintaining a C_6D_6 solution of the iridium(I) complex **3** under 1 atm (101 325 Pa) of dihydrogen the orange solution gradually became paler and a new species was formed over 20 h, as shown by $^{31}P\text{-}\{^1H\}$, ^1H and $^1H\text{-}\{^{31}P\}$ NMR studies. We formulate this new species as the iridium(III) dihydride **4** (Scheme 2). This dihydride was labile and we were unable to isolate it; the

assigned structure **4** is based on the NMR evidence. The ^{31}P-$\{^1H\}$ NMR spectrum showed that the two phosphorus were mutually *trans* with $^2J(PP) = 301$ Hz (Table 1). The ^1H and ^1H-$\{^{31}P\}$ NMR spectra (data in Table 2) show two hydrides mutually *cis*, $^2J(HH) = 4.2$ Hz. The hydride resonating at δ −15.78 is probably *trans* to nitrogen and other iridium hydrides with hydride *trans* to a nitrogen donor ligand typically resonate at *ca.* δ −16.[6] The other hydride resonance at δ −8.62 is assigned to the hydride *trans* to C≡O; other iridium hydrides with H *trans* to C≡O resonate at δ *ca.* −8.[10–13] The small coupling constants to phosphorus of 10.0 and 14.3 (δ −15.78) and 9.4 Hz (δ −8.62) show that both hydrides are *cis* to both phosphorus atoms.

The iridium(I) complex **3** reacts with methyl iodide over 3 h to give a methyliridium(III) complex formulated as **5**. The elemental analysis (Experimental section) and value of ν(C≡O) 2015 cm^{-1} are in agreement with the assigned structure. The ^{31}P-$\{^1H\}$ NMR spectrum showed that the *mer* geometry of the terdentate phosphine was retained with $^2J(PP) = 353$ Hz. In the ^1H NMR spectrum the $IrCH_3$ gave a triplet at δ 0.14 with $^3J(PH) = 5.3$ Hz and in the ^{13}C-$\{^1H\}$ NMR spectrum the CH_3 carbon gave a triplet at δ −8.6, $^2J(PC) = 3.5$ Hz. These triplets might be deceptively simple and arise because of a second order phenomenon, since the phosphorus atoms are very strongly coupled, although non-equivalent. The other proton and carbon-13 data are consistent with the assigned structure **5**.

The iridium(I) complex **3** reacted rapidly with olefins (*N*-methylmaleimide or ethene), or with the acetylene $MeO_2CC{\equiv}CCO_2Me$, to give adducts (Scheme 2). We formulate these as **6a**, **6b**, and **6c**, respectively. *N*-Methylmaleimide when added to an orange solution of **3** in dichloromethane reacted over 15 min (^{31}P-$\{^1H\}$ NMR evidence) and the yellow *N*-methylmaleimide adduct **6a** was isolated in 86% yield. It was characterised by elemental analysis and the IR spectrum. The ^{31}P-

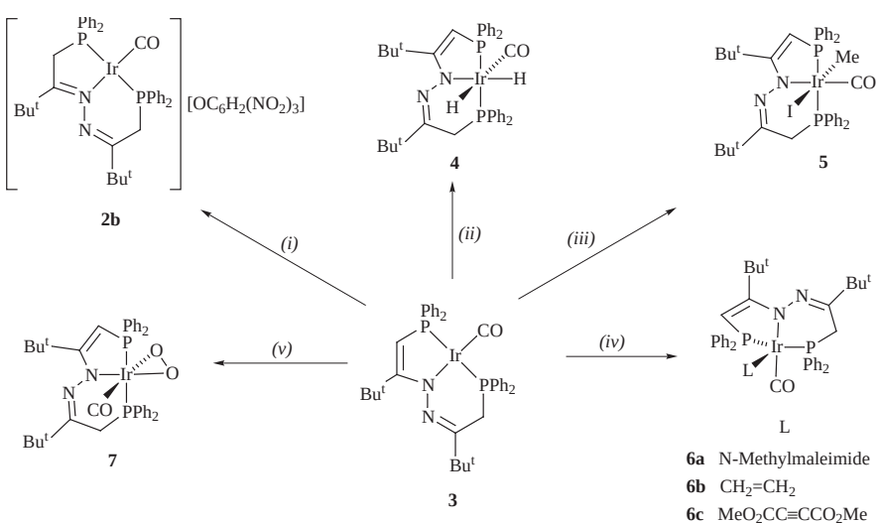


Scheme 1 (*i*) $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}4)]$; (*ii*) EtOH or MeOH; (*iii*) CH_2Cl_2 or C_6H_6; (*iv*) HCl; (*v*) NH_4PF_6; (*iv*) NEt_3

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

Compound	$\delta(P_A)$	$\delta(P_B)$	$^2J(PP)$/Hz
I[b]	−14.4		
1[b]	44.3	20.3	312
2a[b]	60.6	56.0	303
2b[c,d]	60.8	55.5	306
3[e]	60.3	34.1	299
4[e]	46.6	13.8	301
5[d]	37.3	17.0	353
6a[c,d]	12.0	9.3	22
6b[d,f]	43.4	15.8	49
6c[d]	8.5	3.3	25
7[e]	14.6	1.1	396
8[d]	35.8	9.3	32
9a[c]	40.7	25.4	318
9b[c]	41.9	25.6	317

[a] Recorded at 36.2 MHz, chemical shifts (δ) in ppm relative to 85% H_3PO_4, solvent CD_2Cl_2 unless otherwise stated. [b] From ref. 6. [c] In $CDCl_3$. [d] At 101.2 MHz. [e] In C_6D_6. [f] Recorded at −80 °C, but at 20 °C, $\delta(P_A)$ 55.1, $\delta(P_B)$ 26.3 and $^2J(PP) = 210$ Hz.



Scheme 2 (*i*) $HOC_6H_2(NO_2)_3$-2,4,6; (*ii*) H_2; (*iii*) MeI; (*iv*) for complex **6a**, *N*-methylmaleimide; for **6b**, ethene; for **6c**, $MeO_2CC{\equiv}CCO_2Me$; (*v*) O_2

Table 2 Proton NMR data[a]

Compound	δ(Bu^t)	δ(CH_2P)	Others
I[b]	0.90 (18 H, s)	3.26 [4 H, d, ^2J(PH) 3.9]	
1[b]	0.77 (9 H, s)	3.03 [1 H, m, ^2J(HH) 11.7]	−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, PCH=]
2b[c,d]	0.83 (9 H, s)	3.63 [2 H, dd, ^2J(PH) 11.8, ^4J(PH) 2.0]	8.73 [2 H, s, $OC_6H_2(NO_2)_3$]
	1.20 (9 H, s)	4.35 [2 H, dd, ^2J(PH) 8.9, ^4J(PH) 4.2]	
3[e]	0.85 (9 H, s)	3.13 [2 H, dd, ^2J(PH) 12.0, ^4J(PH) 2.7]	5.04 [1 H, dd, J(PH) 3.9, 3.2, PCH=]
	1.66 (9 H, s)		
4[e]	0.96 (9 H, s)	2.82 [1 H, dd, ^2J(HH) 11.7, ^2J(PH) 12.8]	−15.78 [1H, ddd, ^2J(HH) 4.2, ^2J(PH) 10.0, 14.3, IrH]
	1.68 (9 H, s)	3.44 [1 H, m, ^2J(HH) 11.7, ^2J(PH) 12.5, ^4J(PH) 2.9]	−8.62 [1 H, dt, ^2J(HH) 4.2, ^2J(PH) 9.4, IrH]
			4.81 [1 H, dd, J(PH) 5.1, 3.0, PCH=]
5[d]	1.02 (9 H, s)	3.24 [1 H, dt, ^2J(HH) = ^2J(PH) 12.3, ^4J(PH) 3.5]	0.14 [3 H, t, ^3J(PH) 5.3, IrMe]
	1.42 (9 H, s)	3.53 [1 H, dt, ^2J(HH) = ^2J(PH) 12.3, ^4J(PH) 2.1]	4.87 [1 H, dd, J(PH) 5.1, 3.9, PCH=]
6a[c,d]	0.97 (9 H, s)	2.59 [1 H, dt, ^2J(HH) = ^2J(PH) 14.2, ^4J(PH) 1.5]	2.85 (3 H, s, NMe)
	1.30 (9 H, s)	3.26 [1 H, dd, ^2J(HH) 14.2, ^2J(PH) 11.7]	3.17 [1 H, m, ^3J(HH) 4.8, ^3J(PH) 8.7, 4.1, =CH]
			3.52 [1 H, m, ^3J(HH) 4.8, ^3J(PH) 10.4, 2.7, =CH]
			4.26 [1 H, d, J(PH) 4.4, PCH=]
6b[d,f]	0.64 (9 H, s)	2.34 [1H, t, ^2J(HH) = ^2J(PH) 12]	1.15 (1 H, m, CH_2=CH_2)
	1.13 (9 H, s)	3.29 [1H, t, ^2J(HH) = ^2J(PH) 12]	1.83 (1 H, m, CH_2=CH_2)
			2.06 (1 H, m, CH_2=CH_2)
			2.41 (1 H, m, CH_2=CH_2)
			3.98 [1 H, d, J(PH) 2.3, PCH=]
6c[d]	1.01 (9 H, s)	2.59 [1 H, ddd, ^2J(HH) 15.6, ^2J(PH) 13.8, ^4J(PH) 2.0]	3.41 (3 H, s, OMe)
	1.33 (9 H, s)	3.43 [1 H, dd, ^2J(HH) 15.6, ^2J(PH) 11.7]	3.69 (3 H, s, OMe)
			4.15 [1 H, d, J(PH) 3.9, PCH=]
7[e]	0.81 (9 H, s)	2.91 [1 H, m, ^2J(HH) 12.8, ^2J(PH) 13.0, ^4J(PH) 2.5]	4.90 [1 H, dd, J(PH) 5.1, 4.2, PCH=]
	1.73 (9 H, s)	3.33 [1 H, t, ^2J(HH) = ^2J(PH) 12.8]	
8[d]	0.89 (9 H, s)	2.52 [1 H, t, ^2J(HH) = ^2J(PH) 12.8]	3.06 (3 H, s, NMe)
	1.47 (9 H, s)	3.89 [1 H, t, ^2J(HH) 12.8, ^2J(PH) 13.0]	3.19 [1 H, dt, ^3J(HH) 5.2, ^3J(PH) 6.2, 5.1, =CH]
		4.03 [1 H, m, ^2J(HH) 19.2][g]	4.02 [1 H, m, ^3J(HH) 5.2, PCH=][g]
		4.73 [1 H, dd, ^2J(HH) 19.2, ^2J(PH) 12.0]	8.75 [2 H, s, $OC_6H_2(NO_2)_3$]
9a[d]	0.79 (9 H, s)	3.33 [1 H, dt, ^2J(HH) = ^2J(PH) 12.0, ^4J(PH) 1.8]	−15.35 [1 H, dd, ^2J(PH) 10.0, 7.7, IrH]
	1.21 (9 H, s)	3.70 [1 H, m, ^2J(HH) 12.0, ^2J(PH) 14.5, ^4J(PH) 5.5]	
		4.45 [1 H, ddd, ^2J(HH) 17.8, ^2J(PH) 12.8, ^4J(PH) 8.0]	
		4.70 [1 H, ddd, ^2J(HH) 17.8, ^2J(PH) 10.0, ^4J(PH) 2.6]	
9b[d]	0.74 (9 H, s)	3.46 [1 H, dt, ^2J(HH) = ^2J(PH) 12.1, ^4J(PH) 1.3]	−15.11 [1H, dd, ^2J(PH) 9.5, 7.5, IrH]
	1.29 (9 H, s)	3.71 [1 H, m, ^2J(HH) 12.1, ^2J(PH) 15.1, ^4J(PH) 6.3]	
		4.34 [1 H, ddd, ^2J(HH) 17.6, ^2J(PH) 12.8, ^4J(PH) 8.0]	
		4.79 [1 H, ddd, ^2J(HH) 17.6, ^2J(PH) 10.3, ^4J(PH) 2.4]	

[a] Recorded at 100 MHz, chemical shifts 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, ddd = double doublet of doublets, m = multiplet. [b] From ref. 6. [c] In $CDCl_3$. [d] At 250 Mz. [e] In C_6D_6. [f] At −80 °C. At 20 °C the free ethene and complexed ethene gave a broad peak at δ 5.12, $w_{\frac{1}{2}}$ *ca.* 7.7 Hz, whilst on the NMR timescale the CH_2 protons gave a doublet at δ 3.09, ^2J(PH) = 10.8 Hz and the PCH= proton a broad peak at δ 4.56 with unresolved coupling to P, the two Bu^t groups absorbed as singlets at δ 0.80 and 1.34. [g] Coupling to phosphorus nuclei not resolved.

$\{^1H\}$ NMR spectrum showed that the phosphorus atoms were no longer *trans* with ^2J(PP) = 22 Hz. The proton NMR data showed that the co-ordinated *N*-methylmaleimide moiety was bonded to iridium in a static fashion on the NMR timescale and that the CO–CH=CH–CO hydrogens were non-equivalent, δ 3.17 and 3.52 and mutually coupled, with ^3J(HH) = 4.8 Hz, and each coupled to phosphorus. The CH proton of the ene–hydrazone backbone absorbed at δ 4.26 [J(PH) = 4.4 Hz]. We formulate the complex as having the *N*-methylmaleimide in approximately the same plane as the P–Ir–P moiety, as found for many other trigonal bipyramidal five-co-ordinate olefinic phosphine complexes.[14] In the ^{13}C-$\{^1H\}$ NMR spectrum both CH=CH carbons gave a doublet of doublets, *i.e.* they are coupled to both phosphorus atoms. One coupling (presumably due to the *trans* phosphorus) was much larger than the other coupling, *viz*. for δ_C 36.9, ^2J(PC) = 27.5 and 5.5 Hz and for δ_C 39.1, ^2J(PC) = 33.5 and 4.6 Hz. The other proton (Table 2) and carbon-13 (Table 3) data are consistent with the assigned structure **6a**.

A CD_2Cl_2 solution of complex **3** reacted rapidly with ethene to give essentially a single product (adduct) which we formulate as **6b** and which was characterised only in solution. At −80 °C, the ^{31}P-$\{^1H\}$ NMR spectrum showed ^2J(PP) = 49 Hz, *i.e.* the phosphorus atoms are no longer mutually *trans*. The proton NMR data show that at −80 °C all four ethene hydrogens are non-equivalent [δ 1.15 (m), 1.83 (m), 2.06 (m) and 2.41 (m)], *i.e.* it is not rotating fast on the NMR timescale. All four hydrogens were also coupled to phosphorus. The other data, *e.g.* for PC*H*= and PCH_2, are consistent with the structure **6b**. At 20 °C (see Table 2) the free ethene and complexed ethene were exchanging rapidly, giving a single broadened peak and this caused equivalence of the two CH_2P protons of the ene–hydrazone backbone.

Dimethyl acetylenedicarboxylate reacted over a period of a few minutes at *ca.* 20 °C with complex **3** to give an adduct **6c**. This was characterised by elemental analytical and IR data, *e.g.* ν(C≡O) 1990 and ν(C=O) 1700 and 1680 cm^{-1}. As with the *N*-methylmaleimide adduct the ^2J(PP) for **6c** was small (25 Hz). The proton NMR data for **6c** show non-equivalent OCH_3 groups, a PCH= proton and two non-equivalent PCH_2 protons, as for **6a**. This complex was very labile in CD_2Cl_2 solution and had decomposed extensively within 2 h at 20 °C.

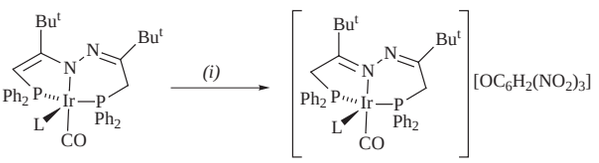
An orange solution of complex **3** in C_6D_6 reacted slowly over a period of 7 h at *ca.* 20 °C with dioxygen to give a single product, as evidenced by the ^{31}P-$\{^1H\}$, ^1H, ^1H-$\{^{31}P\}$ and ^{13}C-$\{^1H\}$ NMR data. We tentatively formulate this as the η^2-O_2 complex **7**. This showed a large value for ^2J(PP) of 396 Hz indicating that the ene–hydrazone diphosphine was still co-ordinated with the two phosphorus atoms mutually *trans*. The proton NMR data showed two *tert*-butyls, a CH_2 group with non-equivalent hydrogens and a single CH= hydrogen. This dioxygen adduct was labile and decomposed on attempted isolation.

We have shown previously[3] that ene–hydrazone diphosphine

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

Compound	δ(C*Me*$_3$)	δ(*C*Me$_3$)	δ(CH$_2$)	δ(C=N)	δ(C≡O)	Others
1[b]	28.8 (s) 31.7 (s)	39.4 (d, 15.2) 39.5 (d, 3.6)	20.5 (d, 26.2)	190.6 (dd, 17.2, 1.8)	169.9 (t, 7.9)	74.4 (d, 66.5, PCH=) 149.6 (d, 3.7, =CN)
3[c]	28.6 (d, 1.4) 31.2 (s)	38.9 (d, 13.9) 39.0 (d, 2.2)	20.0 (d, 23.4)	191.7 (dd, 21.0, 2.0)	184.0 (t, 9.7)	77.6 (d, 60.5, PCH=) 150.6 (d, 3.5, =CN)
5[d]	29.2 (s) 30.8 (s)	39.0 (d, 13.9) 39.2 (d, 3.2)	19.2 (d, 24.8)	190.5 (dd, 15.5, 2.2)	171.7 (t, 8.0)	−8.6 (t, 3.5, IrMe) 73.5 (d, 68.1, PCH=) 151.3 (d, 4.1, =CN)
6a[c,d]	28.4 (s) 30.2 (s)	37.1 (d, 14.2) 39.4 (d, 4.3)	26.8 (dd, 24.8)[e]	184.7 (d, 15.7)	158.4 (t, 4.1)	22.5 (s, NMe) 36.9 (dd, 27.5, 5.5, CH=) 39.1 (dd, 33.5, 4.6, CH=) 72.6 (d, 65.5, PCH=) 137.9 (dd, 46.7, 1.9, =CN) 178.6 (d, 3.7, C=O) 179.8 (dd, 3.7, 1.6, C=O)
7[f]	28.8 (s) 31.7 (s)	39.7 (d, 12.4) 40.0 (d, 2.8)	19.8 (d, 27.6)	192.9 (d, 13.3)	168.9 (t, 8.5)	76.0 (d, 66.8, PCH=) 147.4 (d, 3.0, =CN)
9a[c]	27.0 (s) 28.4 (s)	40.7 (d, 1.9) 41.3 (d, 5.4)	23.8 (d, 24.6) 42.1 (d, 35.7)	173.5 (d, 2.3) 191.7 (t, 2.8)	162.2 (t, 7.3)	
9b	26.9 (s) 28.3 (s)	41.2 (d, 1.9) 41.7 (d, 5.5)	23.3 (d, 25.4) 41.5 (d, 35.7)	174.5 (s) 192.8 (t, 2.7)	162.0 (t, 7.7)	

[a] Recorded at 100.6 MHz, chemical shifts are in ppm relative to SiMe$_4$, solvent CD_2Cl_2 unless otherwise stated and *J*(PC)/Hz values are given in parentheses. [b] From ref. 6. [c] In $CDCl_3$. [d] At 62.9 MHz. [e] $^4J(PC) = 2.3$ Hz. [f] In C_6D_6.



6a **8**

Scheme 3 L = *N*-Methylmaleimide. (*i*) $HOC_6H_2(NO_2)_3$-2,4,6

ligands on platinum or palladium are reversibly protonated at the ene–hydrazone carbon, *viz*. PCH= to give PCH_2 thereby generating the corresponding azine diphosphine complex. However, square planar iridium(I) phosphine complexes, *e.g.* of type *trans*-[IrX(CO)(PR_3)$_2$] (X = Cl, Br or I; R = alkyl or aryl), are well known to protonate on iridium giving an iridium hydride. We find that the ene–hydrazone diphosphine iridium(I) complex **3** reacts rapidly and exclusively with 1 mol of picric acid to give the square planar azine diphosphine iridium(I) cation, isolated as the picrate salt **2b**. This was fully characterised by elemental analysis, its IR spectrum, and by ^{31}P-{^1H}, ^1H and ^1H-{^{31}P} NMR spectroscopy, see Experimental section and Tables 1 and 2.

We now show that the five-co-ordinate *N*-methylmaleimide adduct **6a** is protonated by picric acid, exclusively on the ene–hydrazone diphosphine backbone to give an azine diphosphine backbone, *i.e.* conversion into an *N*-methylmaleimide–iridium(I) cationic complex containing an azine moiety occurred and this was isolated as the picrate salt **8** (Scheme 3). We have previously prepared the cation [Ir(CO)-(η^2-COCH=CHCONMe){$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2$-PPh_2}]$^+$ directly by treating **2a** with *N*-methylmaleimide[6] and determined the crystal structure of its PF_6 salt [Ir(CO)-(η^2-COCH=CHCONMe){$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2$-PPh_2}]PF_6.[6]

We have now converted the ene–hydrazone backbone of the neutral iridium(III) hydride complex **1** into the corresponding cationic azine diphosphine complex hydride **9a** by bubbling hydrogen chloride into a benzene solution of **1** (Scheme 1). The salt **9a** separated as a white solid. This was somewhat labile but was readily converted into the corresponding PF_6 salt **9b** by treating a solution of **9a** in methanol with NH_4PF_6. This azine diphosphine iridium(III) hydride **9b** was characterized by elemental analysis and infrared spectroscopy, ν(Ir−H) 2205, ν(C≡O) 2075 cm^{-1}. The ^{31}P-{^1H} NMR spectrum established that the azine diphosphine was *mer* with $^2J(PP) = 317$ Hz; and in the ^1H and ^1H-{^{31}P} NMR spectra the hydride resonance occurred at δ −15.11 with $^2J(PH) = 9.5$ and 7.5 Hz. Both *tert*-butyl resonances and the resonances of all four hydrogens of the two CH_2 groups were identified. The ^{13}C-{^1H} NMR data for **9b** are in Table 3. Although the corresponding chloride salt **9a** was not sufficiently pure for elemental analysis it was characterised by infrared spectroscopy and by ^{31}P-{^1H}, ^1H, ^1H-{^{31}P} and ^{13}C-{^1H} NMR spectroscopy (Tables 1–3). Complex **9a**, when treated with an excess of triethylamine, gave the iridium(I) complex **3** in 72% isolated yield.

Enamines react with electrophiles in what is a very useful and selective synthetic method in organic chemistry. We have shown in our previous work[3] that neutral square planar complexes of Pt^{II} containing the terdentate ene–hydrazone diphosphine PPh_2CH=$C(Bu^t)$N−N=$C(Bu^t)CH_2PPh_2$ undergo electrophilic attack by MeI exclusively on the backbone to give corresponding methyl-substituted azine diphosphine–platinum complexes. However, in the present paper we have shown that, in contrast with the behaviour of the platinum(II) complex, the ene–hydrazone diphosphine iridium(I) complex **3** undergoes electrophilic attack by MeI at iridium (*i.e.* oxidative addition). This reflects the greater tendency of iridium(I) to undergo oxidative addition than platinum(II).

It is possible that treatment of the various adducts **4**, **5**, **6a**–**6c** and even **8** with electrophiles for longer periods or with more vigorous conditions than described here might cause electrophilic attack on the backbone at the PCH= carbon. We have not studied this apart from protonation.

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 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 FX-100 (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz, respectively), a Bruker ARX-250 (operating frequencies for ^1H, ^{31}P and ^{13}C of 250.1, 101.3 and 62.9 MHz respectively), or a 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, the ^{31}P shifts to 85% phosphoric acid.

The azine diphosphine *Z*,*Z*-$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)$-CH_2PPh_2 **I** and the iridium(III) complex **1** were prepared according to our published procedure.[1,6]

Preparations

[Ir(CO){$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$}][$OC_6H_2(NO_2)_3$] 2b. Picric acid (12 mg, 0.052 mmol) was added to a solution of complex **3** (40 mg, 0.051 mmol) in dichloromethane (*ca.* 1.5 cm^3). After 10 min the solvent was removed under reduced pressure and the residue triturated with methanol to give the required product **2b** as yellow microcrystals (36 mg, 69%) (Found: C, 48.6; H, 4.55; N, 6.8. $C_{43}H_{44}IrN_5O_8P_2 \cdot 0.75CH_2Cl_2$ requires C, 48.8; H, 4.25; N, 6.5%). IR (KBr): ν(C≡O) 1980 cm^{-1}.

[Ir(CO){PPh_2CH=$C(Bu^t)$N−N=$C(Bu^t)CH_2PPh_2$}] 3. An excess of NEt_3 (2.5 cm^3) was added to a solution of complex **1** (0.57 g, 0.69 mmol) in benzene (10 cm^3). After 3 h the resultant orange solution was concentrated to low volume (*ca.* 1 cm^3) under reduced pressure. Addition of ethanol to the residue gave the iridium(I) complex **3** as orange microcrystals (0.39 g, 72%) (Found: C, 59.3; H, 5.65; N, 3.35. $C_{37}H_{41}IrN_2OP_2 \cdot 0.75C_6H_6$ requires C, 59.15; H, 5.45; N, 3.35%). IR (CH_2Cl_2): ν(C≡O) 1945 cm^{-1}.

From complex **9a**. An excess of NEt_3 (0.5 cm^3) was added to a suspension of complex **9a** (53 mg, 0.059 mmol) in benzene (2 cm^3). After 3 h the solvent was removed under reduced pressure and the residue triturated with ethanol to give the required product **3** as orange microcrystals (33 mg, 72%)

***mer*,*cis*-[IrH_2(CO){PPh_2CH=$C(Bu^t)$N−N=$C(Bu^t)CH_2PPh_2$}] 4.** A solution of complex **3** (50 mg, 0.064 mmol) in C_6D_6 (*ca.* 1 cm^3) was kept in an atmosphere of dihydrogen for 20 h. The ^{31}P-{^1H}, ^1H and ^1H-{^{31}P} NMR spectra were recorded, see Discussion and Tables.

[IrMe(I)(CO){PPh_2CH=$C(Bu^t)$N−N=$C(Bu^t)CH_2PPh_2$}] 5. An excess of MeI (0.25 cm^3) was added to a solution of complex **3** (40 mg, 0.098 mmol) in CH_2Cl_2 (1 cm^3). After 3 h the resultant yellow solution was concentrated to low volume (*ca.* 0.1 cm^3) under reduced pressure. Addition of methanol to the residue gave the methyliridium(III) complex **5** as yellow microcrystals (37 mg, 78%) (Found: C, 49.05; H, 4.8; N, 2.95. $C_{38}H_{44}IIrN_2OP_2$ requires C, 49.3; H, 4.8; N, 3.0%). IR (CH_2Cl_2): ν(C≡O) 2015 cm^{-1}.

[Ir(CO)(η²-COCH=CHCONMe){PPh_2CH=$C(Bu^t)$N−N=$C(Bu^t)CH_2PPh_2$}] 6a. *N*-Methylmaleimide (15 mg, 0.135 mmol) was added to a solution of complex **3** (60 mg, 0.077 mmol) in CH_2Cl_2 (1.5 cm^3). After 15 min the resultant yellow solution was concentrated to low volume (*ca.* 0.1 cm^3) under reduced pressure. Addition of methanol to the residue gave the required complex **6a** as yellow microcrystals (59 mg, 86%) (Found: C, 55.25; H, 5.25; N, 4.55. $C_{42}H_{46}IrN_3O_3P_2 \cdot 0.75CH_2Cl_2$ requires C, 55.35; H, 5.1; N, 4.6%). IR (KBr): ν(C≡O) 1995 and ν(C=O) 1740 and 1680 cm^{-1}.

[Ir(CO)(η²-CH_2=CH_2){PPh_2CH=$C(Bu^t)$N−N=$C(Bu^t)CH_2PPh_2$}] 6b. Ethene was bubbled through a solution of complex **3** (20 mg, 0.025 mmol) in CD_2Cl_2 (*ca.* 0.5 cm^3) for 3 min. The ^{31}P-{^1H}, ^1H and ^1H-{^{31}P} NMR spectra were recorded at both 20 and −80 °C (see Tables and Discussion).

[Ir(CO)(η²-MeO_2CC≡CCO_2Me){PPh_2CH=$C(Bu^t)$N−N=$C(Bu^t)CH_2PPh_2$}] 6c. Dimethyl acetylenedicarboxylate (20 mg, 0.14 mmol) was added to a solution of complex **3** (40 mg, 0.051 mmol) in CH_2Cl_2 (1.5 cm^3). After 10 min the resultant yellow solution was concentrated to low volume (*ca*. 0.1 cm^3) under reduced pressure. Addition of ethanol to the residue gave the required complex **6c** as yellow microcrystals (35 mg, 74%) (Found: C, 55.65; H, 5.15; N, 2.95. $C_{43}H_{47}IrN_2O_5P_2$ requires C, 55.75; H, 5.1; N, 3.05%). IR (KBr): ν(C≡O) 1990, ν(C≡C) 1800, and ν(C=O) 1700 and 1680 cm^{-1}.

[Ir(CO)(η²-O_2){PPh_2CH=$C(Bu^t)$N−N=$C(Bu^t)CH_2PPh_2$}] 7. A solution of complex **3** (59 mg, 0.075 mmol) in C_6D_6 (*ca.* 1 cm^3) was kept in an atmosphere of dioxygen for 7 h. The ^{31}P-{^1H}, ^{13}C-{^1H}, ^1H and ^1H-{^{31}P} NMR spectra were recorded, see Tables and Discussion.

[Ir(CO)(η²-COCH=CHCONMe){$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$}][$OC_6H_2(NO_2)_3$] 8. Picric acid (11 mg, 0.048 mmol) was added to a solution of complex **6a** (35 mg, 0.039 mmol) in chloroform (*ca.* 1.5 cm^3). After 30 min the solvent was removed under reduced pressure and the residue triturated with methanol to give the required product **8** as yellow microcrystals (35 mg, 79%) (Found: C, 48.1; H, 4.2; N, 6.6. $C_{48}H_{49}IrN_6O_{10}P_2 \cdot 0.75CHCl_3$ requires C, 48.2; H, 4.1; N, 6.9%). IR (KBr): ν(C≡O) 2035 and ν(C=O) 1745 and 1680 cm^{-1}.

[IrH(Cl)(CO){$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$}]Cl 9a. Hydrogen chloride was bubbled through a solution of complex **1** (82 mg, 0.10 mmol) in benzene (*ca.* 1.5 cm^3) for 1 min. The resulting white precipitate **9a** was filtered off and washed with benzene. Yield 83 mg, 93%. IR (CH_2Cl_2): ν(Ir−H) 2200 and ν(C≡O) 2070 cm^{-1}.

[IrH(Cl)(CO){$PPh_2CH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$}]PF_6 9b. A solution of NH_4PF_6 (65 mg, 0.40 mmol) in methanol (1 cm^3) was added to a solution of complex **9a** (60 mg, 0.067 mmol) in methanol (1 cm^3). The required iridium(III) complex **9b** deposited as white microcrystals. Yield 52 mg, 80% (Found: C, 45.7; H, 4.4; Cl, 3.75; N, 2.9. $C_{37}H_{43}ClF_6IrN_2OP_3$ requires C, 46.0; H, 4.5; Cl, 3.65; N, 2.9%). IR (CH_2Cl_2): ν(Ir−H) 2205 and ν(C≡O) 2075 cm^{-1}.

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