

Terdentate (P–N–O) Complexes formed from *Z,E*-PPh₂CH₂C(Bu^t)=N–N=CH(C₆H₄OH-2) or *Z,E*-PPh₂CH₂C(Bu^t)=N–N=CH[C₆H₂(OH-2)(OMe)₂-4,6] and Nickel, Palladium, Platinum, Rhodium or Iridium

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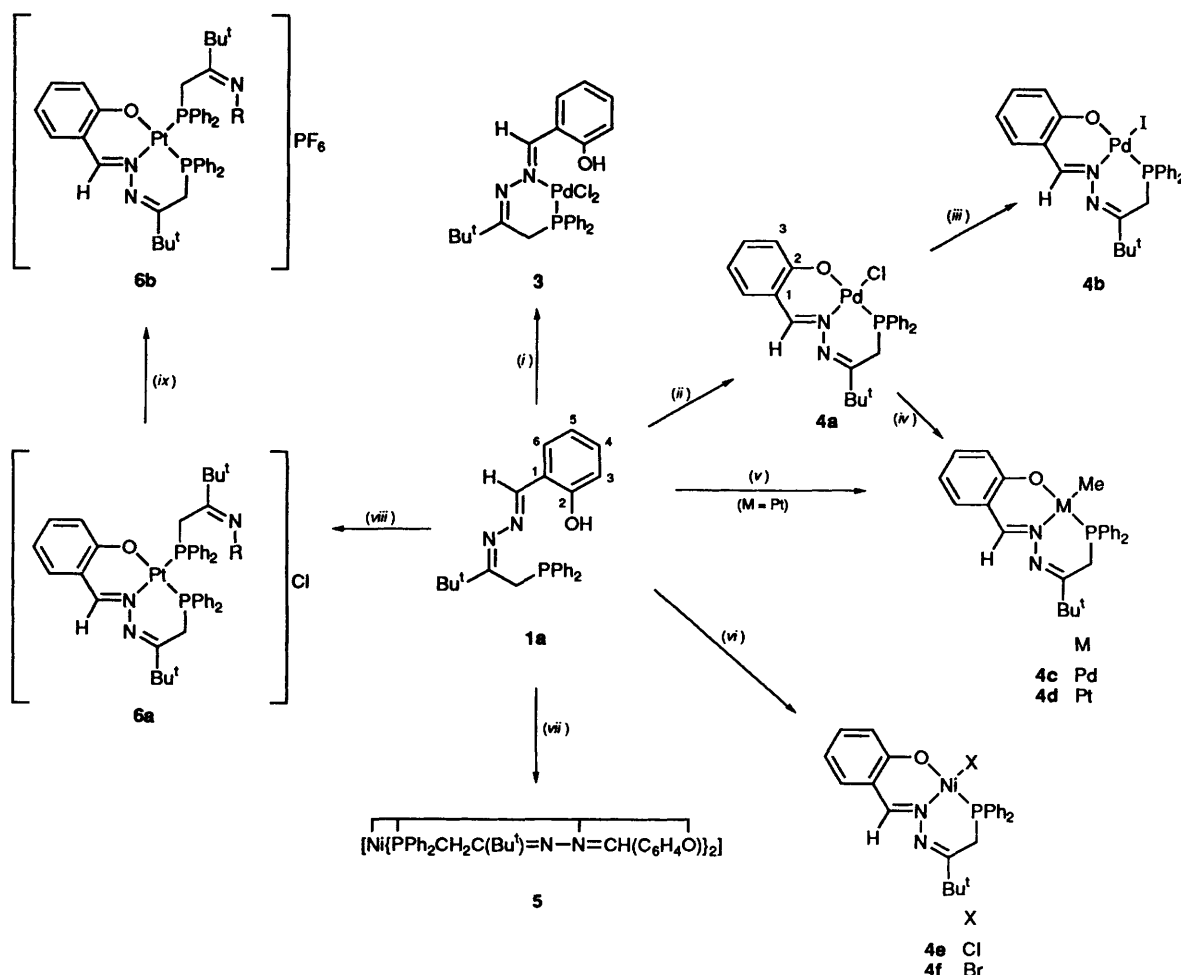
Condensation of *Z*-PPh₂CH₂C(Bu^t)=NNH₂ with salicylaldehyde or 4,6-dimethoxysalicylaldehyde gave the azine phosphines *Z,E*-PPh₂CH₂C(Bu^t)=N–N=CH(C₆H₄OH-2) **1a** or *Z,E*-PPh₂CH₂C(Bu^t)=N–N=CH[C₆H₂(OH-2)(OMe)₂-4,6] **1b**, respectively. Treatment of **1a** with [PdCl₂(cod)] (cod = cycloocta-1,5-diene) gave the bidentate chelate complex [PdCl₂{PPh₂CH₂C(Bu^t)=N–N=CH(C₆H₄OH-2)}] **3**. The phosphine **1a** reacts with Na₂PdCl₄ in the presence of NaO₂CMe to give the terdentate chelate complex [PdCl{PPh₂CH₂C(Bu^t)=N–N=CH(C₆H₄O)}] **4a**. Treatment of the latter with NaI or MgMel gave the corresponding iodopalladium(II) complex **4b** or the methylpalladium(II) complex **4c**, respectively. The analogous methylplatinum(II) complex [PtMe{PPh₂CH₂C(Bu^t)=N–N=CH(C₆H₄O)}] **4d** was prepared by treating [PtMe₂(cod)] with **1a**. Fluxional nickel(II) complexes of type [NiX{PPh₂CH₂C(Bu^t)=N–N=CH(C₆H₄O)}] (X = Cl **4e** or Br **4f**) were also prepared from NiX₂·*n*H₂O. When Ni(O₂CMe)₂·4H₂O was treated with two mol equivalents of **1a** a paramagnetic octahedral nickel(II) complex [Ni{PPh₂CH₂C(Bu^t)=N–N=CH(C₆H₄O)}] **5** was formed. Treatment of [PtCl₂(cod)] with two mol equivalents of **1a** in the presence of NaO₂CMe gave a monocationic platinum(II) chloride salt, which with NH₄PF₆ gave the PF₆ salt. Treatment of **1b** with [IrCl(CO)₂(MeC₆H₄NH₂-*p*)] or 0.5 equivalents of [Rh₂Cl₂(CO)₄] in the presence of NEt₃ gave the square-planar complexes [M(CO){PPh₂CH₂C(Bu^t)=N–N=CH[C₆H₂O(OMe)₂-4,6]}] (M = Ir **7a** or Rh **7b**). The carbonyliridium(I) complex **7a** underwent oxidative-addition reactions with MeI, allyl chloride, acetyl chloride or propargyl chloride to give the halogenocarbonyliridium(III) complexes [IrX(R)(CO){PPh₂CH₂C(Bu^t)=N–N=CH[C₆H₂O(OMe)₂-4,6]}] **8a–8d** respectively. In contrast, the reaction of the carbonylrhodium(I) complex **7b** with allyl chloride gave the π-allylrhodium(III) complex [RhCl(η³-C₃H₅{PPh₂CH₂C(Bu^t)=N–N=CH[C₆H₂O(OMe)₂-4,6]}] **9**. Proton, ³¹P-{¹H} and some ¹³C-{¹H} NMR data have been attained.

In recent papers^{1,2} we have described the syntheses of bidentate *P,N*-donor ligands such as the phosphino hydrazones *Z*-PPh₂CH₂C(Bu^t)=NNMe₂ and *Z*-PPh₂CH₂C(Bu^t)=NNH₂ and the corresponding mixed azine–phosphine from benzaldehyde, *viz.* *Z,E*-PPh₂CH₂C(Bu^t)=N–N=CHPh. We have described the co-ordination chemistry of these ligands with Group 6 metal carbonyls,¹ and also with palladium and platinum.² We have also described some co-ordination chemistry of novel, chiral hydrazone, imine or azine *P,N*-donor ligands derived from (1*R*)-(+)-camphor [(1*R*-(+)-1,7,7-trimethylnorbornan-2-one)]^{3–5} or (1*R*)-(–)-fenchone [(1*R*-(–)-1,3,3-trimethylnorbornan-2-one)].⁶ In this paper we report the syntheses of the new azine phosphines *Z,E*-PPh₂CH₂C(Bu^t)=N–N=CH(C₆H₄OH-2) **1a** and *Z,E*-PPh₂CH₂C(Bu^t)=N–N=CH[C₆H₂(OH-2)(OMe)₂-4,6] **1b** and complexes formed from **1a** with Ni^{II}, Pd^{II} and Pt^{II}, and from **1b** with Rh^I, Rh^{III}, Ir^I and Ir^{III}. The azine phosphines **1a** and **1b** were prepared with the object of incorporating a third donor atom (oxygen), in the form of a phenolate group, into the azine backbone. We expected that the azines **1a** and **1b** would be terdentate, *i.e.* P–N–O ligands, and would co-ordinate to metal centres using both soft- and hard-donor atoms. Gray *et al.*⁷ and Banbery *et al.*⁸ have reported some imine–phosphine ligands derived from salicylaldehyde, *viz.* PPh₂(CH₂)_{*n*}N=CH(C₆H₄OH-2) (*n* = 3 or 4). They described some complexes of these ligands with Cr, W, Re, Ni, Zn and Cu, but their complexes with Pd, Pt, Rh or Ir are not known.

Results and Discussion

Reactions of 1a with the Nickel Triad.—Condensation of *tert*-butyldiphenylphosphinomethyl ketone hydrazone, *Z*-PPh₂CH₂C(Bu^t)=NNH₂, with salicylaldehyde gave the salicylaldehyde azine phosphine (P–N–OH) **1a** as pale yellow needles in excellent yield (90%). The various reactions of **1a** are summarised in Scheme 1 and those of **1b** in Scheme 2. The compounds described in this paper have been characterised by elemental analysis and mass spectrometry (data in the Experimental section), IR and ³¹P-{¹H} NMR spectroscopy (Table 1), ¹H NMR spectroscopy (Table 2) and ¹³C-{¹H} NMR spectroscopy (Table 3). The ³¹P-{¹H} NMR spectrum of **1a** showed a singlet at δ –14.1. In the ¹H NMR spectrum the O–H proton gave a singlet at δ 11.2. No IR band for an O–H stretch was observed, probably due to intramolecular hydrogen bonding between the hydroxy hydrogen and the azine nitrogen N=CH. Such an intramolecular hydrogen bond was found in the solid state of the imine ligand PPh₂(CH₂)₃N=CH(C₆H₄OH-2).⁸ The phosphine **1a** was converted into the corresponding sulfide **2** by treating it with monoclinic sulfur.

Treatment of [PdCl₂(cod)] (cod = cycloocta-1,5-diene)⁹ with **1a** gave a bright yellow solid, which was quite insoluble in most of the organic solvents and we were unable to record its NMR spectra. The IR spectrum of this complex shows two bands at 280 and 340 cm^{–1} due to ν(Pd–Cl), typical of a *cis*-PdCl₂ moiety.^{4,10,11} The strong IR band at 3270 cm^{–1}



Scheme 1 R = -N=CH(C₆H₄OH-2); (i) [PdCl₂(cod)]; (ii) Na₂PdCl₄-NaO₂CMe; (iii) NaI; (iv) MgMeI; (v) [PtMe₂(cod)]; (vi) NiX₂·nH₂O; (vii) 0.5 equivalent Ni(O₂CMe)₂·4H₂O; (viii) 0.5 equivalent [PtCl₂(cod)]-NaO₂CMe; (ix) NH₄PF₆

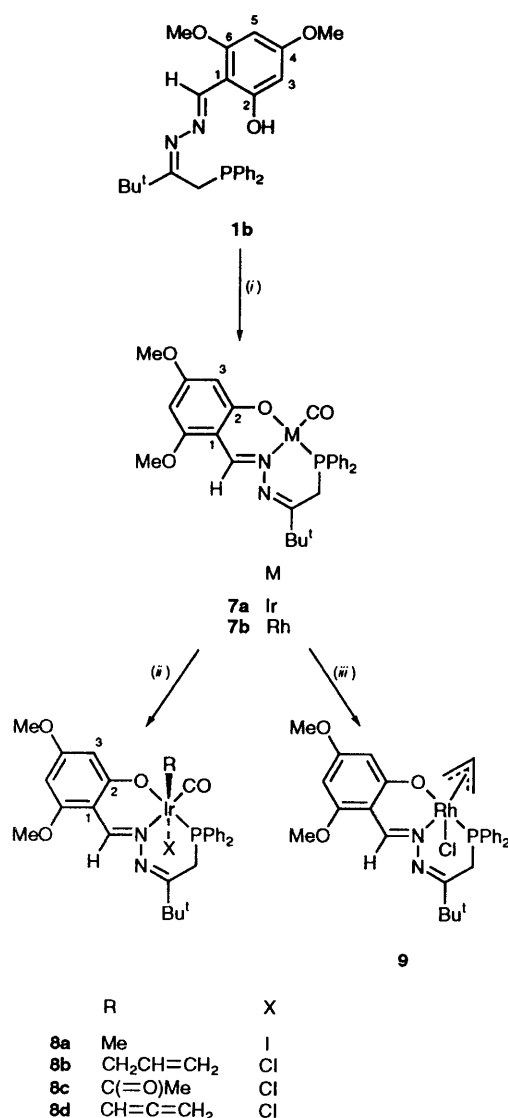
is assigned to the O-H stretching vibration of an uncoordinated hydroxy group. Elemental analyses are in agreement with the composition C₂₅H₂₇Cl₂N₂OPPd·CH₂Cl₂. We therefore tentatively suggest that it has the structure **3** containing a six-membered chelate ring. Treatment of the phosphine **1a** with sodium tetrachloropalladate(II) in the presence of sodium acetate gave the expected neutral chloropalladium(II) complex **4a** as a bright orange solid in over 90% yield. Complex **4a** is slightly soluble in dichloromethane and in the ¹H NMR spectrum the methylene protons gave a doublet at δ 2.99 with ²J(PH) 14.4 Hz. Consistent with the proposed structure for **4a**, only one IR band for ν(Pd-Cl) was observed at 330 cm⁻¹. The corresponding iodopalladium(II) complex **4b** was prepared as bright red needles by treatment of **4a** with NaI in acetone. This iodo complex is much more soluble in CDCl₃, and the ¹H NMR spectrum is very similar to that of **4a**, but a four-bond coupling of 1.5 Hz between the imine proton N=CH and phosphorus is also observed (Table 2). The ¹³C-{¹H} NMR spectrum showed that four of the aryl carbons of the salicylaldehyde moiety were each attached to a single hydrogen (attached proton test experiment). This confirmed that the O-H bond had been split and not the C-H bond in the 6 position. The carbon resonance for the CH₂ carbon gave a doublet at δ 21.5, consistent with the δ_C values observed for methylene carbons in six-membered chelate rings.^{2,12,13} Interestingly, a significantly large four-bond coupling of 7.5 Hz was observed between C³ and phosphorus.

The methylpalladium(II) complex **4c** was prepared by treating **4a** with MgMeI. In the ¹H NMR spectrum of **4c** the reson-

ance of the PdMe group was a doublet at δ 1.05 with ³J(PH) 2.9 Hz. Complex **4c** is stable in benzene for 24 h at room temperature (ca. 20 °C) or for 3 h at 60 °C. It did not react with MeI at room temperature, but when the reaction mixture was heated to 60 °C for 30 min the iodopalladium(II) complex **4b** was formed. The iodopalladium(II) complex **4b** was probably formed via a palladium(IV) intermediate¹⁴

[PdIme₂{PPh₂CH₂C(Bu')=N-N=CH(C₆H₄O)}]. The analogous methylplatinum(II) complex **4d** was prepared by the reaction of [PtMe₂(cod)]¹² with the phosphine **1a** in benzene. The ³¹P-{¹H} NMR spectrum of **4d** showed a singlet at δ 20.6 with ¹J(PtP) 4542 Hz; the large value of ¹J(PtP) is typical for a tertiary phosphine *trans* to an oxygen ligand.^{4,15,16} In the ¹H NMR spectrum, the methylene protons appeared as a doublet at δ 3.34 with ²J(PH) 13.9 and ³J(PtH) 48.8 Hz, and the imine CHPh proton appeared as a singlet at δ 8.67 with ³J(PtH) 16.8 Hz. The resonance of the PtMe protons at δ 0.50 was split into a doublet with ³J(PH) 2.9 Hz together with platinum-195 satellites, ²J(PtH) 70.3 Hz.

The phosphine **1a** complexes react readily with NiX₂·nH₂O to give deep red complexes of type [NiX{PPh₂CH₂C(Bu')=N-N=CH(C₆H₄O)}] (X = Cl **4e** or Br **4f**). These complexes gave broad ¹H NMR spectra at 20 °C, but at -60 °C the spectra were similar to that of **4a**. The elemental analyses agreed well with the proposed structures for **4e** and **4f**. The chloronickel(II) complex **4e** showed one IR band at 340 cm⁻¹ for ν(Ni-Cl), and in the ¹H NMR spectrum at -60 °C the methylene protons gave a doublet at δ 2.59 with



Scheme 2 (i) $[\text{IrCl}(\text{CO})_2(\text{MeC}_6\text{H}_4\text{NH}_2\text{-}p)]\text{-NEt}_3$ or 0.5 equivalent $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]\text{-NEt}_3$; (ii) MeI, allyl chloride, acetyl chloride or propargyl chloride; (iii) allyl chloride

$^2J(\text{PH})$ 13.9 Hz; for the bromonickel(II) complex **4f** a broad doublet was observed at δ 2.58 with $^2J(\text{PH}) \approx 7$ Hz. When two equivalents of the azine phosphine **1a** were treated with nickel(II) acetate tetrahydrate in acetone, a green paramagnetic complex was isolated in 83% yield. The conductimetric measurement showed it to be a non-electrolyte in acetone ($\Lambda_m = 4.25 \times 10^{-2} \Omega^{-1} \text{mol}^{-1} \text{cm}^2$).¹⁷ Elemental analyses agreed with the composition $\text{C}_{50}\text{H}_{52}\text{N}_4\text{NiO}_2\text{P}_2$, and we tentatively suggest that this complex has an octahedral structure of type $[\text{Ni}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}_2]$ **5** containing two terdentate (P-N-O) fragments. No NMR data could be obtained due to its paramagnetism, and attempts to obtain suitable crystals for X-ray studies were unsuccessful. Some ter- and hexa-dentate paramagnetic octahedral nickel(II) azo-phenolate complexes [e.g. $\text{NiO}_2\text{N}_2\text{X}_2$ (X = S or O)] have been characterised by X-ray crystallography.¹⁸

Treatment of $[\text{PtCl}_2(\text{cod})]$ ¹² in CH_2Cl_2 with 2 mol equivalents of **1a** in the presence of NaO_2CMe gave the monocationic salt **6a** in 50% yield. The corresponding PF_6 salt **6b** was prepared by the addition of NH_4PF_6 to a solution of **6a** in methanol. The $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR spectra of the platinum(II) complexes **6** showed an AB pattern with $^2J(\text{PP})$ 22 Hz,

Table 1 IR (cm^{-1}) and $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR^a data

Compound	$\nu(\text{C}=\text{N})^b$	$\nu(\text{Pd}-\text{Cl})^c$	$\nu(\text{C}=\text{O})^b$	δ_p
1a	1610s	—	—	-14.1
1b	1645s	—	—	-14.2
2	1630s	—	—	37.2
3^d	1610s	280m, 340m	—	26.8 ^e
4a	1610m	330m	—	46.7 ^f
4b	1625s	—	—	47.0
4c	1620s	—	—	47.1 ^g
4d	1620s	—	—	20.6 (4542)
4e	1630s	—	—	26.8 ^{f,h}
4f	1625s	—	—	29.3 ^{f,h}
5	1605s	—	—	— ⁱ
6a	1630m	—	—	19.7 (3744), 1.5 (3573), $^2J(\text{PP})$ 22.0
6b	1625m	—	—	20.2 (3739), 2.1 (3568), $^2J(\text{PP})$ 22.0
7a	1620s	—	1965s	24.0
7b	1620s	—	1985s	60.6 (165)
8a	1620s	—	2060s	-4.7
8b	1620s	—	2060s	-4.9
8c^j	1620s	—	2060s	-6.3
8d^k	1625s	—	2070s	-10.3
9	1620s	—	—	42.0 (107)

^a Recorded at 36.2 MHz, chemical shifts (± 0.1 ppm) relative to 85% H_3PO_4 , solvent CDCl_3 unless otherwise indicated. ¹ $J(\text{MP})$ values (Hz) in parentheses. ^b As compressed KBr disc. ^c As Nujol mull between polythene plates. ^d $\nu(\text{O}-\text{H})$ 3270 cm^{-1} . ^e Reaction mixture in CH_2Cl_2 with C_6D_6 as external lock. ^f In CD_2Cl_2 . ^g In C_6D_6 . ^h Recorded at -60°C . ⁱ NMR not observed. ^j $\nu(\text{C}=\text{O})$ 1650 cm^{-1} . ^k $\nu(\text{C}=\text{C})$ 1930 cm^{-1} .

suggesting that the two phosphorus atoms are *cis* to each other. In the ^1H NMR spectra, two sets of *tert*-butyl, CH_2 and $\text{CH}=\text{N}$ protons were observed; in particular, one $\text{CH}=\text{N}$ proton is not coupled to platinum-195 (*i.e.* the $\text{CH}=\text{N}$ proton of the non-chelating ligand) and the other $\text{CH}=\text{N}$ proton of the chelating ligand is coupled to platinum-195 [$^3J(\text{PtH}) \approx 38$ Hz], in agreement with the proposed structures.

Reactions of 1b with Iridium and Rhodium.—We have extended the co-ordination chemistry of this type of terdentate (P-N-O) ligand to Group 9 metal centres such as iridium and rhodium. The 6-unsubstituted salicyl moiety in the phosphine **1a** showed the tendency to undergo both aryl C-H and O-H bond activations to give a mixture of *C*-cyclometalated and *O*-cyclometalated iridium(III) complexes.¹⁹ We therefore studied reactions (Scheme 2) of the azine phosphine **1b** derived from 4,6-dimethoxysalicylaldehyde, in which the methoxy group at the 6 position would block aryl C-H bond activation. Treatment of the phosphine **1b** in CH_2Cl_2 with $[\text{IrCl}(\text{CO})_2(\text{MeC}_6\text{H}_4\text{NH}_2\text{-}p)]$ ²⁰ in the presence of NEt_3 gave the square-planar carbonyliridium(I) complex **7a**, which has a δ_p value of 24.0. The IR spectrum showed a band at 1965 cm^{-1} for $\nu(\text{C}=\text{O})$, in agreement with literature values reported for carbonyliridium(I) complexes.^{21,22} In the $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum, the doublets at δ 22.0, 95.8 and 175.1 are assigned to the CH_2 , C^3 and $\text{C}=\text{O}$ carbons, respectively. The ^1H NMR spectrum is very similar to those of square-planar palladium(II) complexes of type **4**. The analogous carbonylrhodium(I) complex **7b** was similarly prepared in 87% yield by treating **1b** with 0.5 equivalents of $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$.²³ The $\nu(\text{C}=\text{O})$ value of 1985 cm^{-1} is similar to values reported for carbonylrhodium(I) complexes.²⁴ The $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum showed a doublet of doublets at δ 189.8 with $^1J(\text{RhC})$ 73.6 and $^2J(\text{PC})$ 22.9 Hz for the carbon of the carbonyl ligand.

The co-ordinatively unsaturated iridium(I) complex

Table 2 Proton NMR data^a

Compd.	$\delta(\text{Bu}^t)$	$\delta(\text{CH}_2)$	$\delta(=\text{CH})$	Others
1a	1.26 (s)	3.45 [2 H, d, $^2J(\text{PH})$ 1.2]	7.95 (s)	11.2 (1 H, s, br, OH)
1b	1.21 (s)	3.42 [2 H, d, $^2J(\text{PH})$ 1.2]	8.38 (s)	3.78 (6 H, s, OMe) 11.4 (1 H, s, br, OH)
2	1.23 (s)	4.04 [2 H, d, $^2J(\text{PH})$ 14.9]	8.11 (s)	—
4a^b	0.80 (s)	2.99 [2 H, d, $^2J(\text{PH})$ 14.4]	8.30 (s)	—
4b	0.79 (s)	2.91 [2 H, d, $^2J(\text{PH})$ 13.9]	8.27 [1 H, d, $^4J(\text{PH})$ 1.5]	—
4c^c	0.69 (s)	2.64 [2 H, d, $^2J(\text{PH})$ 13.2]	8.67 [1 H, d, $^4J(\text{PH})$ 2.9]	1.05 [2 H, d, $^3J(\text{PH})$ 2.9, PdMe]
4d	0.82 (s)	3.34 [2 H, d, $^2J(\text{PH})$ 13.9, $^3J(\text{PtH})$ 48.8]	8.67 [1 H, s, $^3J(\text{PtH})$ 16.8]	0.50 [3 H, d, $^3J(\text{PH})$ 2.9, $^2J(\text{PtH})$ 70.3, PtMe]
4e^{b,d}	0.61 (s)	2.59 [2 H, d, $^2J(\text{PH})$ 13.9]	8.77 (s, br)	—
4f^{b,d}	0.59 (s)	2.58 [2 H, br d, $^2J(\text{PH}) \approx 7$]	8.76 (s)	—
6a	0.63 (s)	3.53 [2 H, d, $^2J(\text{PH})$ 13.9, $^3J(\text{PtH})$ 44.7]	7.91 (s)	—
	1.17 (s)	4.24 [2 H, d, $^2J(\text{PH})$ 16.1, $^3J(\text{PtH})$ 31.5]	8.59 [1 H, d, $^4J(\text{PH})$ 10.7, $^3J(\text{PtH})$ 37.8]	—
6b	0.63 (s)	3.33 [2 H, d, $^2J(\text{PH})$ 13.4, $^3J(\text{PtH})$ 45.9]	7.80 (s)	—
	1.21 (s)	4.26 [2 H, d, $^2J(\text{PH})$ 16.1, $^3J(\text{PtH})$ 32.5]	8.55 [1 H, d, $^4J(\text{PH})$ 11.0, $^3J(\text{PtH})$ 38.5]	—
7a^e	0.79 (s)	3.43 [2 H, d, $^2J(\text{PH})$ 13.2]	8.91 [1 H, d, $^4J(\text{PH})$ 0.5]	3.80 (3 H, s, OMe) 3.82 (3 H, s, OMe)
7b^e	0.78 (s)	3.18 [2 H, dd, $^2J(\text{PH})$ 12.9, $^3J(\text{RhH})$ 1.2]	8.85 (s)	3.79 (3 H, s, OMe) 3.80 (3 H, s, OMe)
8a^e	0.93 (s)	3.40 [1 H, dd, $^2J(\text{PH})$ 14.3, $^2J(\text{HH})$ 14.2] 4.06 [1 H, dd, $^2J(\text{PH})$ 14.3, $^2J(\text{HH})$ 14.2]	8.60 (s)	0.98 [3 H, d, $^3J(\text{PH})$ 1.9, IrMe] 3.69 (3 H, s, OMe) 3.70 (3 H, s, OMe)
8b^e	0.97 (s)	3.17 [1 H, t, $^2J(\text{PH})$ 13.9, $^2J(\text{HH})$ 13.9] 3.97 [1 H, dd, $^2J(\text{PH})$ 14.2, $^2J(\text{HH})$ 13.9]	8.81 (s)	2.37 (2 H, m, IrCH ₂) 3.79 (3 H, s, OMe) 3.80 (3 H, s, OMe) 4.37 [1 H, m, $^2J(\text{HH})$ 2.3, $^3J(\text{HH})$ 16.7, =CH ₂) 4.47 [1 H, m, $^2J(\text{HH})$ 2.3, $^3J(\text{HH})$ 9.9, =CH ₂] 5.73 [1 H, m, $^3J(\text{HH})$ 16.7, $^3J(\text{HH})$ 9.9, CH=]
8c^e	0.84 (s)	3.75 [2 H, d, $^2J(\text{PH})$ 14.0]	8.64 (s)	2.09 (3 H, s, MeC=O) 3.77 (3 H, s, OMe) 3.78 (3 H, s, OMe)
8d^e	0.84 (s)	3.23 [1 H, dd, $^2J(\text{PH})$ 12.9, $^2J(\text{HH})$ 13.6] 4.19 [1 H, dd, $^2J(\text{PH})$ 13.7, $^2J(\text{HH})$ 13.6]	8.84 (s)	3.43 [1 H, dd, $^2J(\text{HH})$ 8.8, $^4J(\text{HH})$ 6.2, C=CH ₂] 3.77 (3 H, s, OMe) 3.80 (3 H, s, OMe) 3.92 [1 H, dd, $^2J(\text{HH})$ 8.8, $^4J(\text{HH})$ 6.2, C=CH ₂] 5.49 [1 H, t, $^4J(\text{HH})$ 6.2, IrCH]
9^e	0.74 (s)	2.88 [1 H, dd, $^2J(\text{PH})$ 16.0, $^2J(\text{HH})$ 13.1] 4.14 [1 H, dd, $^2J(\text{PH})$ 13.1, $^2J(\text{HH})$ 13.1]	9.07 (s)	2.53 [1 H, d, $^3J(\text{HH})$ 11.8, H _{anti}] 3.14 [1 H, d, $^3J(\text{HH})$ 12.5, H _{anti}] 3.68 [1 H, d, $^3J(\text{HH})$ 7.1, H _{syn}] 3.73 (3 H, s, OMe) 3.82 (3 H, s, OMe) 3.82 ^f 4.65 (1 H, m, CH ₂ CHCH ₂)

^a Recorded at 100 MHz, chemical shifts (± 0.01 ppm) relative to SiMe₄, solvent CDCl₃ unless otherwise stated. ^b In CD₂Cl₂. ^c In C₆D₆. ^d Recorded at -60 °C. ^e Recorded at 400 MHz. ^f H_{syn} is obscured by an OMe signal.

7a underwent oxidative-addition reactions with a range of organic halides such as iodomethane, allyl chloride, acetyl chloride or propargyl chloride to give saturated halogenocarbonyliridium(III) complexes of type $[\text{IrX}(\text{R})(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6\}]]$ **8** (X = I or Cl, R = an organic group). The observed shifts of δ_p to high field and the high frequency values of $\nu(\text{C}=\text{O})$ (up to ca. 2060 cm⁻¹) clearly indicate the oxidation of iridium(I) to iridium(III). The carbonyliridium(I) complex **7a** reacted rapidly with MeI to give the iridium(III) complex **8a** in 87% yield as a yellow solid. The ³¹P-¹H NMR spectrum showed a singlet at $\delta -4.7$, and in the ¹H NMR spectrum, the doublet at

$\delta 0.98$ with $^3J(\text{PH})$ 1.9 Hz was assigned to the IrMe protons. The ¹³C-¹H NMR spectrum showed two sets of doublets at $\delta -2.10$ with $^2J(\text{PC})$ 3.5 Hz and $\delta 166.0$ with $^2J(\text{PC})$ 10.3 Hz for the IrMe and IrC=O carbons respectively; such small $^2J(\text{PC})$ values suggest that both carbons are *cis* to phosphorus. Like other square-planar complexes, the C³ carbon was observed as a doublet at $\delta 96.1$ with $^4J(\text{PC})$ 6.1 Hz indicating that the ligand remains in a planar *mer* arrangement. Since the alkyl halides^{21,25,26} and acyl chlorides^{22,25} are known to undergo *trans* additions to iridium(I) centres, we tentatively suggest that the stereochemistry around iridium(III) centre is as shown in **8a**. We propose the same stereochemistry for the other iridium(III)

Table 3 $^{13}\text{C}\{-^1\text{H}\}$ NMR data (δ)^a

Compd.	CMe_3	CH_2P	CMe_3	OMe	C^1	C^2	C^3	C^4 and C^6	C^5	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	$\text{HC}\equiv\text{N}$	$\text{Bu}^1\text{C}\equiv\text{N}$	Others
1a	29.1 (d) (3.2)	29.3 (d) (29.3)	39.0 (s)	—	118.9 (s)	159.0 (s)	118.2 (s)	131.8 (s), 131.9 (s)	116.6 (s)	137.2 (d) (16.5)	132.9 (d) (6.9)	128.2 (d)	128.9 (s)	160.5 (s) (2.6)	174.9 (d) (2.6)	—
1b	29.1 (d) (2.7)	29.0 (d) (22.2)	38.8 (s)	55.4 (s), 55.5 (s)	102.0 (s)	160.3 (s)	93.1 (s)	164.0 (s), 162.5 (s)	90.1 (s)	137.5 (d) (16.6)	132.9 (d) (20.2)	128.2 (d) (6.8)	128.7 (s)	156.6 (s) (1.4)	173.1 (d) (1.4)	—
4b	27.3 (s)	21.5 (d) (22.9)	39.8 (d)	—	116.6 (s)	167.4 (s)	122.3 (d) (7.5)	134.7 (s), 136.3 (s)	115.1 (s)	129.0 (d) (59.9)	134.2 (d) (10.7)	128.6 (d) (11.6)	132.2 (d) (2.7)	161.6 (s)	167.0 (s)	—
4d	27.7 (s)	21.6 (d) (34.1)	40.1 (d) (2.7)	—	115.4 (s)	167.2 (d) (3.3)	122.7 (d) (5.7)	134.4 (s), 134.6 (s)	115.3 (s)	128.3 (d) (62.6)	133.7 (d) (10.9)	128.6 (d) (11.1)	131.3 (s)	160.8 (s)	165.6 (s)	-11.7 (d) (7.6, PtMe)
7a	27.3 (s)	22.0 (d) (32.0)	39.8 (d)	55.4 (s), 55.6 (s)	103.8 (s)	161.0 (s)	95.8 (d) (4.3)	165.5 (s), 165.9 (s)	89.0 (s)	131.8 (d) (60.6)	133.3 (d) (11.0)	128.5 (d) (10.9)	130.9 (d) (2.3)	156.1 (s)	167.6 (s)	175.1 (d) (6.4, C=O)
7b	27.5 (s)	23.2 (d) (24.9)	39.9 (d)	56.0 (s), 55.7 (s)	103.4 (s)	158.0 (s)	96.0 (d) (4.3)	166.4 (s), 162.0 (s)	88.2 (s)	133.0 (d) (51.1)	133.6 (d) (11.9)	129.0 (d) (10.6)	131.4 (d) (2.3)	165.0 (s)	170.0 (s)	189.8 (dd) (22.9, 73.6, ^b C=O)
8a	27.8 (s)	23.9 (d) (38.1)	41.1 (d) (3.6)	55.3 (s), 55.6 (s)	104.7 (s)	161.7 (s)	96.1 (d) (6.1)	167.1 (s), 167.7 (s)	88.9 (s)	127.7 (d) (59.9)	132.6 (d) (9.2)	128.4 (d) (11.3)	131.5 (d) (2.6)	157.2 (s)	164.0 (d) (2.6)	-2.10 (d) (3.5, IrMe) 166.0 (d) (10.3, C=O)
8b	27.7 (s)	20.9 (d) (36.7)	40.9 (d) (3.2)	55.4 (s), 55.7 (s)	103.5 (s)	161.7 (s)	96.6 (d) (6.2)	167.0 (s), 167.1 (s)	—	129.1 (d) (68.8)	133.7 (d) (9.4)	128.5 (d) (10.8)	131.9 (d) (2.6)	156.7 (s)	163.7 (d) (2.8)	12.6 (d) (2.9, IrCH ₂) 110.0 (s) (CH=CH ₂) 144.1 (s) (CH=CH ₂) 164.0 (d) (11.0, C=O)
8c	27.3 (s)	20.8 (d) (34.3)	40.2 (d) (2.7)	55.3 (s), 55.6 (s)	104.3 (s)	161.7 (s)	95.9 (d) (5.6)	166.9 (s), 166.9 (s)	89.1 (s)	127.8 (d) (61.5)	132.1 (d) (9.4)	128.8 (d) (11.1)	131.7 (d) (2.6)	155.3 (s)	166.4 (s)	42.9 (s) (MeC=O) 163.2 (9.7, C=O) 203.2 (d) (4.8, MeC=O)
8d	27.2 (s)	21.5 (d) (38.2)	40.8 (d) (3.5)	55.3 (s), 55.7 (s)	103.6 (s)	161.8 (s)	96.4 (d) (6.3)	167.2 (s), 167.4 (s)	89.1 (s)	126.5 (d) (63.1)	133.1 (d) (9.5)	128.3 (d) (11.1)	131.5 (d) (2.7)	156.6 (s)	163.7 (d) (2.4)	62.8 (d) (5.8, IrCH) 69.0 (s) (C=CH ₂) 164.0 (d) (11.0, C=O) 208.6 (s) (=C=CH ₂)

^a Recorded at 100.6 MHz, chemical shifts (± 0.1 ppm) relative to SiMe_4 , solvent CDCl_3 , $J(\text{PC})$ values (Hz) in parentheses. ^b $^1J(\text{RhC})$.

complexes **8b**, **8c** and **8d** because they exhibit similar spectroscopic properties to **8a**. The oxidative addition of allyl chloride to the carbonyliridium(i) complex **7a** gave the σ -allyliridium(iii) complex **8b**. In the ^1H NMR spectrum, the olefinic protons of the σ -allyl group appeared as multiplets at δ 4.37, 4.47 and 5.73 with $^2J(\text{HH})$ 2.3, $^3J(\text{HH}_{\text{trans}})$ 16.7 and $^3J(\text{HH}_{\text{cis}})$ 9.9 Hz, in agreement with the literature values for similar complexes.²⁷ In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum, the resonances at δ 12.6 [d, $^2J(\text{PC})$ 2.9 Hz], 110.0 (s) and 144.1 (s) are assigned to the IrCH_2 , $=\text{CH}_2$ and $\text{CH}=\text{C}$ carbons, respectively. The oxidative addition of acetyl chloride to the carbonyliridium(i) complex **7a** gave the acetyliridium(iii) complex **8c** in 73% yield. The IR spectrum showed a strong band at 1650 cm^{-1} for $\nu(\text{C}=\text{O})$ of the acetyl group.²² The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum showed a doublet at δ 203.2 with $^2J(\text{PC})$ 4.8 Hz for the carbonyl carbon of the acetyl group.

The σ -allenyliridium(iii) complex **8d**, prepared from **7a** and propargyl chloride, showed three inequivalent proton resonances at δ 3.43 (dd), 3.92 (dd) and 5.49 (t) with $^2J(\text{HH})$ 8.8 and $^4J(\text{HH})$ 6.2 Hz for the two $=\text{CH}_2$ protons and IrCH proton, respectively. In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum, the resonances at δ 62.8 [d, $^2J(\text{PC})$ 5.8 Hz], 69.0 (s) and 208.6 (s) are assigned to the IrCH , $=\text{CH}_2$ and $=\text{C}=\text{C}$ carbons, respectively. These δ_{C} values are in agreement with literature values for allenes²⁸ and other allenylmetal compounds.²⁹ The formation of the σ -allenyliridium(iii) complex **8d** suggests that the addition of propargyl chloride proceeds *via* a $\text{S}_{\text{N}}2'$ type mechanism.^{30,31}

Unlike the analogous iridium(i) complex **7a**, the carbonylrhodium(i) complex **7b** was reluctant to undergo oxidative-addition reactions with organic halides such as iodomethane or propargyl chloride. The rhodium(i) complex **7b** showed no reaction with iodomethane even at 60°C for 1 h. However, the reaction of allyl chloride with **7b** very rapidly gave the π -allylrhodium(iii) complex **9**. The carbonyl ligand has been displaced as shown by the absence of any IR bands in the carbonyl region in the IR spectrum. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum showed a doublet at δ 42.0 with a much smaller coupling constant, $^1J(\text{RhP})$, of 107 Hz as expected for rhodium(iii) complexes.¹⁶ In the ^1H NMR spectrum, the *anti* protons appeared as doublets at δ 2.53 and 3.14 with $^3J(\text{HH})$ vicinal couplings of about 12 Hz, and the *syn* protons appeared at δ 3.68 and 3.82 with $^3J(\text{HH})$ coupling of about 7 Hz, which are in good agreement with the literature values for π -allylrhodium complexes.^{32,33}

Experimental

The apparatus used and general techniques were the same as in other recent papers from this laboratory.⁶ The IR spectra were recorded using a Perkin-Elmer model 257 grating spectrometer and NMR spectra using a JEOL FX-90Q (operating frequencies for ^1H and ^{31}P of 89.5 and 36.2 MHz respectively), JEOL FX-100 (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz respectively) or Bruker AM400 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 shifts are relative to SiMe_4 and ^{31}P shifts are relative to 85% phosphoric acid. The ^{13}C resonances were assigned with the aid of attached proton test experiments. The ^{13}C chemical shifts are comparable to the literature values.^{2,7,12,13,34,35} Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec with 8 kV acceleration, and for metal complexes m/z values are quoted for ^{58}Ni , ^{106}Pd , ^{195}Pt , ^{103}Rh and ^{193}Ir .

The compound $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}$ was prepared as reported in a previous paper.¹

Preparations.— $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{OH}-2)$ **1a**. Salicylaldehyde (0.6 g, 5.0 mmol) was added to a solution of $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}$ (1.5 g, 5.0 mmol) in ethanol (5 cm^3). On standing, the required azine phosphine crystallised as

pale yellow needles (1.77 g, 90%) (Found: C, 74.5; H, 6.65; N, 6.85. $\text{C}_{25}\text{H}_{27}\text{N}_2\text{OP}$ requires C, 74.6; H, 6.75; N, 6.95%); m/z (EI) 403 ($M + 1$) and 345 ($M - \text{Bu}^t$).

$Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_4(\text{OH}-2)(\text{OMe})_2-4,6]$ **1b**. A mixture of $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}$ (1.5 g, 5.03 mmol) and 4,6-dimethoxysalicylaldehyde (0.92 g, 5.05 mmol) in ethanol (5 cm^3) was left at room temperature for 2.5 h and then cooled to -30°C . The required azine phosphine **1b** was separated as a yellow solid (1.99 g, 86%) (Found: C, 69.95; H, 6.8; N, 6.1. $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}_3\text{P}$ requires C, 70.10; H, 6.8; N, 6.1%); m/z (EI) 405 ($M - \text{Bu}^t$).

$Z,E\text{-P}(\text{S})\text{Ph}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{OH}-2)$ **2**. A mixture of the azine phosphine **1a** (100 mg, 0.25 mmol) and monoclinic sulfur (8 mg, 0.25 mmol) was refluxed in benzene (2 cm^3) for 1 h. The reaction mixture was filtered and the solvent removed under reduced pressure. The residue was triturated with methanol to give the phosphine sulfide **2** as a white solid (80 mg, 75%) (Found: C, 69.35; H, 6.55; N, 6.4. $\text{C}_{25}\text{H}_{27}\text{N}_2\text{OPS}$ requires C, 69.1; H, 6.25; N, 6.45%).

$[\text{PdCl}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{OH}-2)\}]$ **3**. A solution of the azine phosphine **1a** (85 mg, 0.21 mmol) in dichloromethane (1.5 cm^3) was added to a solution of $[\text{PdCl}_2(\text{cod})]$ (60 mg, 0.21 mmol) in dichloromethane (1.5 cm^3). The dichloropalladium(ii) complex **3** deposited as a bright yellow solid (95 mg, 78%) (Found: C, 50.3; H, 4.5; N, 4.8. $\text{C}_{25}\text{H}_{27}\text{Cl}_2\text{N}_2\text{OPPd}\cdot\text{CH}_2\text{Cl}_2$ requires C, 50.3; H, 4.6; N, 4.65%).

$[\text{PdCl}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}]$ **4a**. A solution containing the azine phosphine **1a** (100 mg, 0.25 mmol) and sodium acetate (20 mg) in hot methanol (1.5 cm^3) was added to a solution of sodium tetrachloropalladate(ii) (70 mg, 0.24 mmol) in methanol (2.0 cm^3). The reaction mixture was stirred at 20°C for 4 h to give the required monochloropalladium(ii) complex **4a** as a bright orange solid (99 mg, 94%) (Found: C, 54.95; H, 4.9; N, 5.1. $\text{C}_{25}\text{H}_{26}\text{ClN}_2\text{OPPd}\cdot 0.3\text{CH}_3\text{OH}$ requires C, 54.95; H, 4.85; N, 5.1%); m/z (EI) 543 ($M + 1$) and 509 ($M - \text{Cl}$).

$[\text{PdI}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}]$ **4b**. A solution of sodium iodide (30 mg, 0.2 mmol) in methanol (2 cm^3) was added to a stirred suspension of the chloropalladium(ii) complex **4a** (60 mg, 0.11 mmol) in acetone (1.5 cm^3). The resultant clear red solution was put aside at *ca.* 20°C for 12 h. The iodopalladium(ii) complex **4b** crystallized as bright red needles which were filtered off and dried. Yield 54 mg, 77%. A second crop of **4b** was recovered by evaporating the mother-liquor to dryness and recrystallizing the residue from acetone-methanol. Yield 10 mg, 14% (Found: C, 46.75; H, 4.0; N, 4.3. $\text{C}_{25}\text{H}_{26}\text{IN}_2\text{OPPd}\cdot 0.3\text{CH}_3\text{OH}$ requires C, 46.95; H, 4.2; N, 4.3%); m/z (EI) 634 (M^+) and 507 ($M - \text{I}$).

$[\text{PdMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}]$ **4c**. The chloropalladium(ii) complex **4a** (150 mg, 0.28 mmol) was treated with an excess of MgMeI (3.5 mmol) in diethyl ether (5 cm^3). The reaction mixture was cooled to 0°C and excess MgMeI was destroyed by careful addition of saturated aqueous ammonium chloride solution until effervescence ceased. The solution was then extracted with benzene (2 \times 5 cm^3). The combined benzene extracts were dried with MgSO_4 and evaporated to dryness. The methylpalladium(ii) complex **4c** was obtained as a bright yellow solid (83 mg, 58%) (Found: C, 62.0; H, 5.8; N, 4.9. $\text{C}_{26}\text{H}_{29}\text{N}_2\text{OPPd}\cdot 0.5\text{C}_6\text{H}_6$ requires C, 62.0; H, 5.8; N, 5.0%); m/z (FAB) 522 (M^+) and 507 ($M - \text{Me}$).

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}]$ **4d**. A mixture of the azine phosphine **1a** (75 mg, 0.19 mmol) and $[\text{PtMe}_2(\text{cod})]$ (60 mg, 0.18 mmol) in benzene (3 cm^3) was put aside for 40 min at 20°C . The reaction mixture was then filtered and the solvent removed under reduced pressure. Addition of methanol to the residue gave the required methylplatinum(ii) complex **4d** as yellow prisms (76.5 mg, 70%) (Found: C, 50.8; H, 4.85; N, 4.55. $\text{C}_{26}\text{H}_{29}\text{N}_2\text{OPPt}$ requires C, 51.0; H, 4.8; N, 4.6%); m/z (FAB) 611 (M^+) and 596 ($M - \text{Me}$).

$[\text{NiCl}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}]$ **4e**. A mixture of the azine phosphine **1a** (60 mg, 0.15 mmol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (35 mg, 0.15 mmol) in ethanol (2 cm³) was stirred at 20 °C for 20 min. The required chloronickel(II) complex **4e** precipitated as a dark red solid (40 mg, 55%) (Found: C, 60.6; H, 5.25; N, 5.8. $\text{C}_{25}\text{H}_{26}\text{ClN}_2\text{NiOP}$ requires C, 60.6; H, 5.3; N, 5.7%); m/z (EI) 494 (M^+) and 458 ($M - \text{Cl}$).

$[\text{NiBr}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}]$ **4f**. A mixture of the azine phosphine **1a** (60 mg, 0.15 mmol) and $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ (40 mg, 0.15 mmol) was stirred in ethanol (3 cm³) at room temperature for 15 min. The required bromonickel(II) complex **4f** was isolated as a brownish red solid (40 mg, 50%) (Found: C, 55.45; H, 4.7; N, 5.25. $\text{C}_{25}\text{H}_{26}\text{BrN}_2\text{NiOP}$ requires C, 55.6; H, 4.8; N, 5.2%); m/z (EI) 540 (M^+).

$[\text{Ni}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}_2]$ **5**. A solution of nickel(II) acetate tetrahydrate (60 mg, 0.24 mmol) in water (1 cm³) was added to a solution of the azine phosphine **1a** (195 mg, 48 mmol) in acetone (2 cm³). Complex **5** was obtained as a green solid (173 mg, 83%) (Found: C, 69.7; H, 6.15; N, 6.45. $\text{C}_{50}\text{H}_{52}\text{N}_4\text{NiO}_2\text{P}_2$ requires C, 69.7; H, 6.1; N, 6.5%); m/z (FAB) 861 ($M + 1$), 459 ($M - 1a$) and 403 ($M - 1a - \text{Bu}'$).

$[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{OH}-2)\}]\text{Cl}$ **6a**. The compound $[\text{PtCl}_2(\text{cod})]$ (60 mg, 0.16 mmol) was added to the azine phosphine **1a** (0.13 g, 0.33 mmol) and sodium acetate (30 mg, 0.36 mmol) in dichloromethane (3 cm³). The reaction mixture was left at 20 °C for 3 d, whereupon **6a** deposited as yellow microcrystals which were filtered off and washed with cold methanol (81 mg, 50%) (Found: C, 55.2; H, 4.9; Cl, 8.05; N, 4.85. $\text{C}_{50}\text{H}_{53}\text{ClN}_4\text{O}_2\text{P}_2\text{Pt} \cdot 0.85\text{CH}_2\text{Cl}_2$ requires C, 55.2; H, 5.05; Cl, 8.65; N, 5.05%); m/z (FAB) 998 ($M - \text{Cl}$).

$[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{OH}-2)\}]\text{PF}_6$ **6b**. This compound was prepared by the dropwise addition of a saturated solution of NH_4PF_6 in methanol to a methanolic solution of **6a** (60 mg, 0.058 mmol). Complex **6b** deposited as a bright yellow solid (40 mg, 60%) (Found: C, 52.0; H, 4.65; N, 4.8. $\text{C}_{50}\text{H}_{53}\text{F}_6\text{N}_4\text{O}_2\text{P}_3\text{Pt} \cdot 0.8\text{CH}_3\text{OH}$ requires C, 52.2; H, 4.85; N, 4.80%).

$[\text{Ir}(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6]\}]$ **7a**. The compound $[\text{IrCl}(\text{CO})_2(\text{MeC}_6\text{H}_4\text{NH}_2-p)]$ (0.4 g, 1.02 mmol) was added to a solution of the azine phosphine **1b** (0.48 g, 1.04 mmol) in dichloromethane (5 cm³). After 15 min triethylamine (0.2 cm³, 1.43 mmol) was added. The solvent was then removed under reduced pressure and the residue triturated with methanol to give the carbonyliridium(I) complex **7a** as a yellow solid (0.53 g, 77%) (Found: C, 46.5; H, 4.3; N, 4.05. $\text{C}_{28}\text{H}_{30}\text{IrN}_2\text{O}_4\text{P} \cdot 0.7\text{CH}_2\text{Cl}_2$ requires C, 46.5; H, 4.3; N, 3.8%); m/z (FAB) 683 ($M + 1$).

$[\text{Rh}(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6]\}]$ **7b**. The compound $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ (0.30 g, 0.77 mol) was added to a solution of the azine phosphine **1b** (0.72 g, 1.6 mmol) in dichloromethane (5 cm³). After 10 min triethylamine (0.25 cm³, 1.8 mmol) was added. The solvent was then removed under reduced pressure and the residue triturated with methanol to give **7b** as a yellow solid (0.70 g, 87%) (Found: C, 55.7; H, 5.0; N, 4.65. $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4\text{PRh} \cdot \text{CH}_3\text{OH}$ requires C, 55.8; H, 5.5; N, 4.5%); m/z (FAB) 593 ($M + 1$).

$[\text{Ir}(\text{Me})(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6]\}]$ **8a**. An excess of iodomethane (0.4 cm³) was added to the iridium(I) complex **7a** (40 mg, 0.06 mmol) in benzene (1 cm³). After 15 min the solution was filtered and the solvent removed under reduced pressure. Addition of methanol to the residue gave the iridium(III) complex **8a** as a yellow microcrystalline solid (42 mg, 87%) (Found: C, 42.3; H, 4.05; N, 3.35. $\text{C}_{29}\text{H}_{33}\text{IrN}_2\text{O}_4\text{P}$ requires C, 42.3; H, 4.05; N, 3.40%); m/z (FAB) 825 ($M + 1$), 697 ($M - \text{I}$), 681 ($M - \text{I} - \text{Me}$) and 653 ($M - \text{I} - \text{Me} - \text{CO}$).

The following three compounds were prepared in a similar manner and on a similar scale to **8a**.

$[\text{IrCl}(\text{CO})(\sigma\text{-CH}_2\text{CH}=\text{CH}_2)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6]\}]$ **8b**. The σ -allyliridium(III) complex **8b** was prepared from **7a** using allyl chloride. Yield 72% (Found: C, 47.2; H, 4.1; N, 3.75. $\text{C}_{30}\text{H}_{33}\text{ClIrN}_2\text{O}_5\text{P}$ requires C, 47.4; H, 4.35; N, 3.70%).

$[\text{IrCl}(\text{CO})(\text{COMe})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6]\}]$ **8c**. The acetyliridium(III) complex **8c** was prepared and isolated in 73% yield by the addition of acetyl chloride to **7a** (Found: C, 47.15; H, 4.1; N, 3.75. $\text{C}_{30}\text{H}_{33}\text{ClIrN}_2\text{O}_5\text{P}$ requires C, 47.40; H, 4.4; N, 3.70%); m/z (FAB) 760 (M^+), 725 ($M - \text{Cl}$), 697 ($M - \text{Cl} - \text{CO}$) and 681 ($M - \text{Cl} - \text{MeCO}$).

$[\text{IrCl}(\sigma\text{-CH}=\text{C}=\text{CH}_2)(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6]\}]$ **8d**. The σ -allenyliridium(III) complex **8d** was prepared and isolated in 46% yield by the addition of propargyl chloride to **7a** (Found: C, 48.95; H, 4.25; N, 3.60. $\text{C}_{31}\text{H}_{33}\text{ClIrO}_4\text{N}_2\text{P}$ requires C, 49.15; H, 4.5; N, 3.7%); m/z (FAB) 757 ($M + 1$), 721 ($M - \text{Cl}$), 693 ($M - \text{Cl} - \text{CO}$) and 653 ($M - \text{Cl} - \text{CO} - \text{C}_3\text{H}_3$).

$[\text{RhCl}(\eta^3\text{-C}_3\text{H}_5)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6]\}]$ **9**. An excess of allyl chloride (0.1 cm³) was added to a solution of the carbonylrhodium(I) complex **7b** (50 mg, 0.08 mmol) in dichloromethane (2 cm³). The reaction mixture was left at room temperature for 2 min, and solvent was then removed under reduced pressure. Addition of methanol to the residue gave the π -allylrhodium(III) complex **9** as a bright yellow solid (28 mg, 52%) (Found: C, 55.20; H, 5.15; N, 4.45. $\text{C}_{30}\text{H}_{35}\text{ClN}_2\text{O}_3\text{PRh} \cdot 0.25\text{CH}_2\text{Cl}_2$ requires C, 54.9; H, 5.4; N, 4.25%).

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