

# Terdentate (P–N–O) Complexes formed from *Z,E*-PPh<sub>2</sub>CH<sub>2</sub>C-(Bu<sup>t</sup>)=N–N=CH(C<sub>6</sub>H<sub>4</sub>OH-2) or *Z,E*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH-[C<sub>6</sub>H<sub>2</sub>(OH-2)(OMe)<sub>2</sub>-4,6] and Nickel, Palladium, Platinum, Rhodium or Iridium

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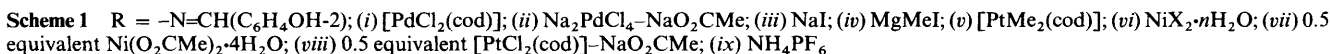
Condensation of *Z*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNH<sub>2</sub> with salicylaldehyde or 4,6-dimethoxysalicylaldehyde gave the azine phosphines *Z,E*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH(C<sub>6</sub>H<sub>4</sub>OH-2) **1a** or *Z,E*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH[C<sub>6</sub>H<sub>2</sub>(OH-2)(OMe)<sub>2</sub>-4,6] **1b**, respectively. Treatment of **1a** with [PdCl<sub>2</sub>(cod)] (cod = cycloocta-1,5-diene) gave the bidentate chelate complex [PdCl<sub>2</sub>{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH(C<sub>6</sub>H<sub>4</sub>OH-2)}] **3**. The phosphine **1a** reacts with Na<sub>2</sub>PdCl<sub>4</sub> in the presence of NaO<sub>2</sub>CMe to give the terdentate chelate complex [PdCl{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH(C<sub>6</sub>H<sub>4</sub>O)}] **4a**. Treatment of the latter with NaI or MgMeI gave the corresponding iodopalladium(II) complex **4b** or the methylpalladium(II) complex **4c**, respectively. The analogous methylplatinum(II) complex [PtMe{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH(C<sub>6</sub>H<sub>4</sub>O)}] **4d** was prepared by treating [PtMe<sub>2</sub>(cod)] with **1a**. Fluxional nickel(II) complexes of type [NiX{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH(C<sub>6</sub>H<sub>4</sub>O)}] (X = Cl **4e** or Br **4f**) were also prepared from NiX<sub>2</sub>·*n*H<sub>2</sub>O. When Ni(O<sub>2</sub>CMe)<sub>2</sub>·4H<sub>2</sub>O was treated with two mol equivalents of **1a** a paramagnetic octahedral nickel(II) complex [Ni{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH(C<sub>6</sub>H<sub>4</sub>O)}] **5** was formed. Treatment of [PtCl<sub>2</sub>(cod)] with two mol equivalents of **1a** in the presence of NaO<sub>2</sub>CMe gave a monocationic platinum(II) chloride salt, which with NH<sub>4</sub>PF<sub>6</sub> gave the PF<sub>6</sub> salt. Treatment of **1b** with [IrCl(CO)<sub>2</sub>(MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-*p*)] or 0.5 equivalents of [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>] in the presence of NEt<sub>3</sub> gave the square-planar complexes [M(CO){PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH[C<sub>6</sub>H<sub>2</sub>O(OMe)<sub>2</sub>-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){PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH[C<sub>6</sub>H<sub>2</sub>O(OMe)<sub>2</sub>-4,6]}] **8a–8d** respectively. In contrast, the reaction of the carbonylrhodium(I) complex **7b** with allyl chloride gave the  $\pi$ -allylrhodium(III) complex [RhCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>){PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH[C<sub>6</sub>H<sub>2</sub>O(OMe)<sub>2</sub>-4,6]}] **9**. Proton, <sup>31</sup>P-{<sup>1</sup>H} and some <sup>13</sup>C-{<sup>1</sup>H} NMR data have been attained.

In recent papers<sup>1,2</sup> we have described the syntheses of bidentate *P,N*-donor ligands such as the phosphino hydrazones *Z*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNMe<sub>2</sub> and *Z*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNH<sub>2</sub> and the corresponding mixed azine–phosphine from benzaldehyde, *viz.* *Z,E*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CHPh. We have described the co-ordination chemistry of these ligands with Group 6 metal carbonyls,<sup>1</sup> and also with palladium and platinum.<sup>2</sup> 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]<sup>3–5</sup> or (1*R*)-(–)-fenchone [(1*R*)-(–)-1,3,3-trimethylnorbornan-2-one].<sup>6</sup> In this paper we report the syntheses of the new azine phosphines *Z,E*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH(C<sub>6</sub>H<sub>4</sub>OH-2) **1a** and *Z,E*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CH[C<sub>6</sub>H<sub>2</sub>(OH-2)(OMe)<sub>2</sub>-4,6] **1b** and complexes formed from **1a** with Ni<sup>II</sup>, Pd<sup>II</sup> and Pt<sup>II</sup>, and from **1b** with Rh<sup>I</sup>, Rh<sup>III</sup>, Ir<sup>I</sup> and Ir<sup>III</sup>. 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.*<sup>7</sup> and Banbery *et al.*<sup>8</sup> have reported some imine–phosphine ligands derived from salicylaldehyde, *viz.* PPh<sub>2</sub>(CH<sub>2</sub>)<sub>*n*</sub>N=CH(C<sub>6</sub>H<sub>4</sub>OH-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*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNH<sub>2</sub>, 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 <sup>31</sup>P-{<sup>1</sup>H} NMR spectroscopy (Table 1), <sup>1</sup>H NMR spectroscopy (Table 2) and <sup>13</sup>C-{<sup>1</sup>H} NMR spectroscopy (Table 3). The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum of **1a** showed a singlet at  $\delta$  –14.1. In the <sup>1</sup>H NMR spectrum the O–H proton gave a singlet at  $\delta$  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 PPh<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>N=CH(C<sub>6</sub>H<sub>4</sub>OH-2).<sup>8</sup> The phosphine **1a** was converted into the corresponding sulfide **2** by treating it with monoclinic sulfur.

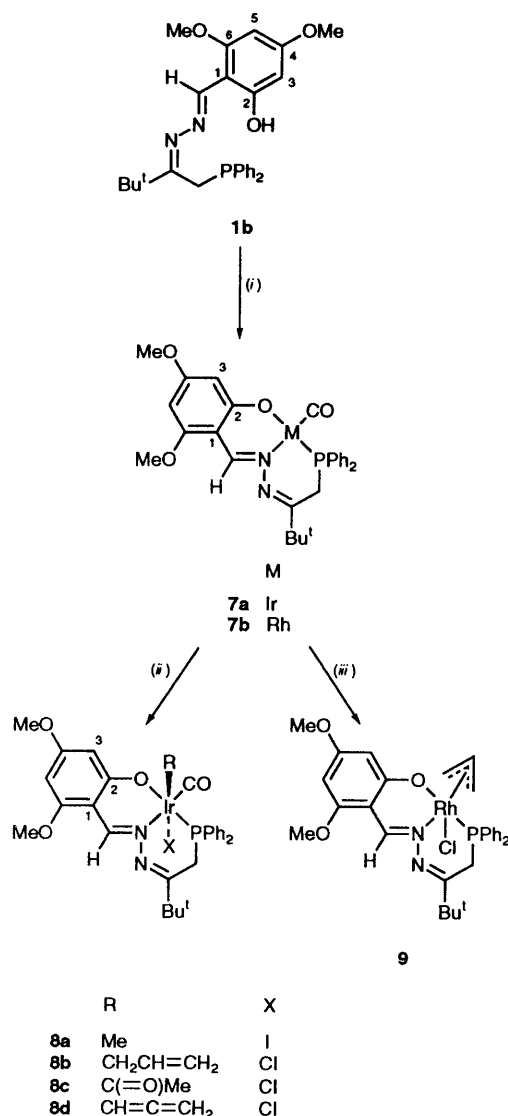
Treatment of [PdCl<sub>2</sub>(cod)] (cod = cycloocta-1,5-diene)<sup>9</sup> with **1a** gave a bright yellow solid, which was quite insoluble in most of the organic solvents and we were unable to record its NMR spectra. The IR spectrum of this complex shows two bands at 280 and 340 cm<sup>–1</sup> due to  $\nu$ (Pd–Cl), typical of a *cis*-PdCl<sub>2</sub> moiety.<sup>4,10,11</sup> The strong IR band at 3270 cm<sup>–1</sup>



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

[PdIme<sub>2</sub>{PPh<sub>2</sub>CH<sub>2</sub>C(Bu)<sup>t</sup>=N=N=CH(C<sub>6</sub>H<sub>4</sub>O)}]. The analogous methylplatinum(II) complex **4d** was prepared by the reaction of [PtMe<sub>2</sub>(cod)]<sup>12</sup> with the phosphine **1a** in benzene. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum of **4d** showed a singlet at δ 20.6 with <sup>1</sup>J(PtP) 4542 Hz; the large value of <sup>1</sup>J(PtP) is typical for a tertiary phosphine *trans* to an oxygen ligand.<sup>4,15,16</sup> In the <sup>1</sup>H NMR spectrum, the methylene protons appeared as a doublet at δ 3.34 with <sup>2</sup>J(PH) 13.9 and <sup>3</sup>J(PtH) 48.8 Hz, and the imine CHPh proton appeared as a singlet at δ 8.67 with <sup>3</sup>J(PtH) 16.8 Hz. The resonance of the PtMe protons at δ 0.50 was split into a doublet with <sup>3</sup>J(PH) 2.9 Hz together with platinum-195 satellites, <sup>2</sup>J(PtH) 70.3 Hz.

The phosphine **1a** complexes react readily with  $\text{NiX}_2 \cdot n\text{H}_2\text{O}$  to give deep red complexes of type  $[\text{NiX}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu})=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}]$  ( $\text{X} = \text{Cl}$  **4e** or  $\text{Br}$  **4f**). These complexes gave broad  $^1\text{H}$  NMR spectra at  $20^\circ\text{C}$ , but at  $-60^\circ\text{C}$  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  $340\text{ cm}^{-1}$  for  $\nu(\text{Ni}-\text{Cl})$ , and in the  $^1\text{H}$  NMR spectrum at  $-60^\circ\text{C}$  the methylene protons gave a doublet at  $\delta$  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  $\delta$  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 ( $\Lambda_m = 4.25 \times 10^{-2} \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ ).<sup>17</sup> 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.  $\text{NiO}_2\text{N}_2\text{X}_2$  ( $\text{X} = \text{S}$  or  $\text{O}$ )] have been characterised by X-ray crystallography.<sup>18</sup>

Treatment of  $[\text{PtCl}_2(\text{cod})]$ <sup>12</sup> in  $\text{CH}_2\text{Cl}_2$  with 2 mol equivalents of **1a** in the presence of  $\text{NaO}_2\text{CMe}$  gave the monocationic salt **6a** in 50% yield. The corresponding  $\text{PF}_6$  salt **6b** was prepared by the addition of  $\text{NH}_4\text{PF}_6$  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 ( $\text{cm}^{-1}$ ) and  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR <sup>a</sup> data

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

<sup>a</sup> Recorded at 36.2 MHz, chemical shifts ( $\pm 0.1$  ppm) relative to 85%  $\text{H}_3\text{PO}_4$ , solvent  $\text{CDCl}_3$  unless otherwise indicated. <sup>b</sup>  $^1J(\text{MP})$  values (Hz) in parentheses. <sup>c</sup> As compressed KBr disc. <sup>d</sup> As Nujol mull between polythene plates. <sup>e</sup>  $\nu(\text{O}-\text{H})$  3270  $\text{cm}^{-1}$ . <sup>f</sup> Reaction mixture in  $\text{CH}_2\text{Cl}_2$  with  $\text{C}_6\text{D}_6$  as external lock. <sup>g</sup> In  $\text{C}_6\text{D}_6$ . <sup>h</sup> Recorded at  $-60^\circ\text{C}$ . <sup>i</sup> NMR not observed. <sup>j</sup>  $\nu(\text{C}=\text{O})$  1650  $\text{cm}^{-1}$ . <sup>k</sup>  $\nu(\text{C}=\text{C})$  1930  $\text{cm}^{-1}$ .

suggesting that the two phosphorus atoms are *cis* to each other. In the  $^1\text{H}$  NMR spectra, two sets of *tert*-butyl,  $\text{CH}_2$  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.<sup>19</sup> 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  $\text{CH}_2\text{Cl}_2$  with  $[\text{IrCl}(\text{CO})_2(\text{MeC}_6\text{H}_4\text{NH}_2\text{-}p)]$ <sup>20</sup> in the presence of  $\text{NEt}_3$  gave the square-planar carbonyliridium(I) complex **7a**, which has a  $\delta_p$  value of 24.0. The IR spectrum showed a band at 1965  $\text{cm}^{-1}$  for  $\nu(\text{C}=\text{O})$ , in agreement with literature values reported for carbonyliridium(I) complexes.<sup>21,22</sup> In the  $^{13}\text{C}\text{-}\{^1\text{H}\}$  NMR spectrum, the doublets at  $\delta$  22.0, 95.8 and 175.1 are assigned to the  $\text{CH}_2$ ,  $\text{C}^3$  and  $\text{C}=\text{O}$  carbons, respectively. The  $^1\text{H}$  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  $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ .<sup>23</sup> The  $\nu(\text{C}=\text{O})$  value of 1985  $\text{cm}^{-1}$  is similar to values reported for carbonylrhodium(I) complexes.<sup>24</sup> The  $^{13}\text{C}\text{-}\{^1\text{H}\}$  NMR spectrum showed a doublet of doublets at  $\delta$  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<sup>a</sup>

Compd.	$\delta(\text{Bu}^t)$	$\delta(\text{CH}_2)$	$\delta(=\text{CH})$	Others
<b>1a</b>	1.26 (s)	3.45 [2 H, d, $^2J(\text{PH})$ 1.2]	7.95 (s)	11.2 (1 H, s, br, OH)
<b>1b</b>	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)
<b>2</b>	1.23 (s)	4.04 [2 H, d, $^2J(\text{PH})$ 14.9]	8.11 (s)	—
<b>4a<sup>b</sup></b>	0.80 (s)	2.99 [2 H, d, $^2J(\text{PH})$ 14.4]	8.30 (s)	—
<b>4b</b>	0.79 (s)	2.91 [2 H, d, $^2J(\text{PH})$ 13.9]	8.27 [1 H, d, $^4J(\text{PH})$ 1.5]	—
<b>4c<sup>c</sup></b>	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]
<b>4d</b>	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]
<b>4e<sup>b,d</sup></b>	0.61 (s)	2.59 [2 H, d, $^2J(\text{PH})$ 13.9]	8.77 (s, br)	—
<b>4f<sup>b,d</sup></b>	0.59 (s)	2.58 [2 H, br d, $^2J(\text{PH}) \approx 7$ ]	8.76 (s)	—
<b>6a</b>	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]	—
<b>6b</b>	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]	—
<b>7a<sup>e</sup></b>	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)
<b>7b<sup>e</sup></b>	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)
<b>8a<sup>e</sup></b>	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)
<b>8b<sup>e</sup></b>	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 <sub>2</sub> ) 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 <sub>2</sub> ] 4.47 [1 H, m, $^2J(\text{HH})$ 2.3, $^3J(\text{HH})$ 9.9, =CH <sub>2</sub> ] 5.73 [1 H, m, $^3J(\text{HH})$ 16.7, $^3J(\text{HH})$ 9.9, CH=]
<b>8c<sup>e</sup></b>	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)
<b>8d<sup>e</sup></b>	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 <sub>2</sub> ] 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 <sub>2</sub> ] 5.49 [1 H, t, $^4J(\text{HH})$ 6.2, IrCH]
<b>9<sup>e</sup></b>	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 <sub>anti</sub> ] 3.14 [1 H, d, $^3J(\text{HH})$ 12.5, H <sub>anti</sub> ] 3.68 [1 H, d, $^3J(\text{HH})$ 7.1, H <sub>syn</sub> ] 3.73 (3 H, s, OMe) 3.82 (3 H, s, OMe) 3.82 <sup>f</sup> 4.65 (1 H, m, CH <sub>2</sub> CHCH <sub>2</sub> )

<sup>a</sup> Recorded at 100 MHz, chemical shifts ( $\pm 0.01$  ppm) relative to SiMe<sub>4</sub>, solvent CDCl<sub>3</sub> unless otherwise stated. <sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>d</sup> Recorded at  $-60^\circ\text{C}$ . <sup>e</sup> Recorded at 400 MHz. <sup>f</sup> H<sub>syn</sub> 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 [IrX(R)(CO){PPh<sub>2</sub>CH<sub>2</sub>C(Bu)<sup>t</sup>=N-N=CH[C<sub>6</sub>H<sub>4</sub>O(OMe)<sub>2</sub>-4,6]}] **8** (X = I or Cl, R = an organic group). The observed shifts of  $\delta_p$  to high field and the high frequency values of  $\nu(\text{C}\equiv\text{O})$  (up to ca. 2060 cm<sup>-1</sup>) 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 <sup>31</sup>P-<sup>1</sup>H NMR spectrum showed a singlet at  $\delta -4.7$ , and in the <sup>1</sup>H NMR spectrum, the doublet at

$\delta 0.98$  with  $^3J(\text{PH})$  1.9 Hz was assigned to the IrMe protons. The <sup>13</sup>C-<sup>1</sup>H 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 C<sup>3</sup> 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<sup>21,25,26</sup> and acyl chlorides<sup>22,25</sup> 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 ( $\delta$ )<sup>a</sup>

Compd.	$\text{CMe}_3$	$\text{CH}_2\text{P}$	$\text{CMe}_3$	OMe	$\text{C}^1$	$\text{C}^2$	$\text{C}^3$	$\text{C}^4$ and $\text{C}^6$	$\text{C}^5$	$\text{C}_{\text{ipso}}$	$\text{C}_{\text{ortho}}$	$\text{C}_{\text{meta}}$	$\text{C}_{\text{para}}$	$\text{HC}\equiv\text{N}$	$\text{Bu}^t\text{C}\equiv\text{N}$	Others
<b>1a</b>	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) (16.5)	128.2 (d) (6.9)	128.9 (s)	160.5 (s)	174.9 (d) (2.6)	—
<b>1b</b>	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)	173.1 (d) (1.4)	—
<b>4b</b>	27.3 (s)	21.5 (d) (22.9)	39.8 (d) (2.2)	—	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)	—
<b>4d</b>	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)
<b>7a</b>	27.3 (s)	22.0 (d) (32.0)	39.8 (d) (3.2)	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 $\equiv$ O)
<b>7b</b>	27.5 (s)	23.2 (d) (24.9)	39.9 (d) (2.3)	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, <sup>b</sup> C $\equiv$ O)
<b>8a</b>	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 $\equiv$ O)
<b>8b</b>	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 <sub>2</sub> ) 110.0 (s) (CH=CH <sub>2</sub> ) 144.1 (s) (CH=CH <sub>2</sub> )
<b>8c</b>	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)	164.0 (d) (11.0, C $\equiv$ O) 42.9 (s) (MeC=O) 163.2 (9.7, C $\equiv$ O) 203.2 (d) (4.8, MeC=O)
<b>8d</b>	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 <sub>2</sub> ) 164.0 (d) (11.0, C $\equiv$ O) 208.6 (s) (=C=CH <sub>2</sub> )

<sup>a</sup> Recorded at 100.6 MHz, chemical shifts ( $\pm 0.1$  ppm) relative to SiMe<sub>4</sub>, solvent CDCl<sub>3</sub>,  $J(\text{PC})$  values (Hz) in parentheses. <sup>b</sup>  $^1J(\text{RhC})$ .



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  $\sigma$ -allyliridium(iii) complex **8b**. In the  $^1\text{H}$  NMR spectrum, the olefinic protons of the  $\sigma$ -allyl group appeared as multiplets at  $\delta$  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.<sup>27</sup> In the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum, the resonances at  $\delta$  12.6 [d,  $^2J(\text{PC})$  2.9 Hz], 110.0 (s) and 144.1 (s) are assigned to the  $\text{IrCH}_2$ ,  $=\text{CH}_2$  and  $\text{CH=}$  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  $1650\text{ cm}^{-1}$  for  $\nu(\text{C=O})$  of the acetyl group.<sup>22</sup> The  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum showed a doublet at  $\delta$  203.2 with  $^2J(\text{PC})$  4.8 Hz for the carbonyl carbon of the acetyl group.

The  $\sigma$ -allenyliridium(iii) complex **8d**, prepared from **7a** and propargyl chloride, showed three inequivalent proton resonances at  $\delta$  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  $\text{IrCH}$  proton, respectively. In the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum, the resonances at  $\delta$  62.8 [d,  $^2J(\text{PC})$  5.8 Hz], 69.0 (s) and 208.6 (s) are assigned to the  $\text{IrCH}$ ,  $=\text{CH}_2$  and  $\text{C=}$  carbons, respectively. These  $\delta_{\text{C}}$  values are in agreement with literature values for allenes<sup>28</sup> and other allenylmetal compounds.<sup>29</sup> The formation of the  $\sigma$ -allenyliridium(iii) complex **8d** suggests that the addition of propargyl chloride proceeds *via* a  $\text{S}_{\text{N}}2'$  type mechanism.<sup>30,31</sup>

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  $60^\circ\text{C}$  for 1 h. However, the reaction of allyl chloride with **7b** very rapidly gave the  $\pi$ -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  $\delta$  42.0 with a much smaller coupling constant,  $^1J(\text{RhP})$ , of 107 Hz as expected for rhodium(iii) complexes.<sup>16</sup> In the  $^1\text{H}$  NMR spectrum, the *anti* protons appeared as doublets at  $\delta$  2.53 and 3.14 with  $^3J(\text{HH})$  vicinal couplings of about 12 Hz, and the *syn* protons appeared at  $\delta$  3.68 and 3.82 with  $^3J(\text{HH})$  coupling of about 7 Hz, which are in good agreement with the literature values for  $\pi$ -allylrhodium complexes.<sup>32,33</sup>

## Experimental

The apparatus used and general techniques were the same as in other recent papers from this laboratory.<sup>6</sup> The IR spectra were recorded using a Perkin-Elmer model 257 grating spectrometer and NMR spectra using a JEOL FX-90Q (operating frequencies for  $^1\text{H}$  and  $^{31}\text{P}$  of 89.5 and 36.2 MHz respectively), JEOL FX-100 (operating frequencies for  $^1\text{H}$  and  $^{31}\text{P}$  of 99.5 and 40.25 MHz respectively) or Bruker AM400 spectrometer (operating frequencies for  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  of 400.13, 161.9 and 100.6 MHz respectively). The  $^1\text{H}$  and  $^{13}\text{C}$  shifts are relative to  $\text{SiMe}_4$  and  $^{31}\text{P}$  shifts are relative to 85% phosphoric acid. The  $^{13}\text{C}$  resonances were assigned with the aid of attached proton test experiments. The  $^{13}\text{C}$  chemical shifts are comparable to the literature values.<sup>2,7,12,13,34,35</sup> 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  $^{58}\text{Ni}$ ,  $^{106}\text{Pd}$ ,  $^{195}\text{Pt}$ ,  $^{103}\text{Rh}$  and  $^{193}\text{Ir}$ .

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

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

$\text{Z,E-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N-N}=\text{CH}[\text{C}_6\text{H}_2(\text{OH-2})(\text{OMe})_2-4,6]$  **1b**. A mixture of  $\text{Z-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N-NH}_2$  (1.5 g, 5.03 mmol) and 4,6-dimethoxysalicylaldehyde (0.92 g, 5.05 mmol) in ethanol (5  $\text{cm}^3$ ) was left at room temperature for 2.5 h and then cooled to  $-30^\circ\text{C}$ . 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 ( $M-\text{Bu}^t$ )).

$\text{Z,E-P}(\text{S})\text{Ph}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N-N}=\text{CH}(\text{C}_6\text{H}_4\text{OH-2})$  **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  $\text{cm}^3$ ) 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%).

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

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

$[\text{PdI}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N-N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}]$  **4b**. A solution of sodium iodide (30 mg, 0.2 mmol) in methanol (2  $\text{cm}^3$ ) was added to a stirred suspension of the chloropalladium(ii) complex **4a** (60 mg, 0.11 mmol) in acetone (1.5  $\text{cm}^3$ ). The resultant clear red solution was put aside at *ca.*  $20^\circ\text{C}$  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.  $\text{C}_{25}\text{H}_{26}\text{IN}_2\text{OPPd-0.3CH}_3\text{OH}$  requires C, 46.95; H, 4.2; N, 4.3%;  $m/z$  (EI) 634 ( $M^+$ ) and 507 ( $M-\text{I}$ )).

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

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N-N}=\text{CH}(\text{C}_6\text{H}_4\text{O})\}]$  **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  $\text{cm}^3$ ) was put aside for 40 min at  $20^\circ\text{C}$ . 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 cm<sup>3</sup>) 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 cm<sup>3</sup>) 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 cm<sup>3</sup>) was added to a solution of the azine phosphine **1a** (195 mg, 48 mmol) in acetone (2 cm<sup>3</sup>). 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 cm<sup>3</sup>). 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.  $\text{C}_{50}\text{H}_{53}\text{ClN}_4\text{O}_2\text{Pt} \cdot 0.85\text{CH}_2\text{Cl}_2$  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  $\text{NH}_4\text{PF}_6$  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 cm<sup>3</sup>). After 15 min triethylamine (0.2 cm<sup>3</sup>, 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 cm<sup>3</sup>). After 10 min triethylamine (0.25 cm<sup>3</sup>, 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 cm<sup>3</sup>) was added to the iridium(I) complex **7a** (40 mg, 0.06 mmol) in benzene (1 cm<sup>3</sup>). 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**.

$[\text{IrCl}(\text{CO})(\sigma\text{-CH}_2\text{CH}=\text{CH}_2)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6]\}]$  **8b**. The  $\sigma$ -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 ( $M - \text{Cl} - \text{MeCO}$ )).

$[\text{IrCl}(\sigma\text{-CH}=\text{C}=\text{CH}_2)(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2-4,6]\}]$  **8d**. The  $\sigma$ -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 cm<sup>3</sup>) was added to a solution of the carbonylrhodium(I) complex **7b** (50 mg, 0.08 mmol) in dichloromethane (2 cm<sup>3</sup>). 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  $\pi$ -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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