

## Cyclometallation of Azine Phosphines of Type *Z,E*- $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CHR}$ (R = an Aromatic or Heterocyclic Group) involving X–Y (X = C, N or O; Y = H, I or Br) Bond Fission by Platinum(II)

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The phosphino hydrazone *Z*- $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2$  **1** is shown to be a convenient 'reagent' for converting aryl or heterocyclic aldehydes into azines which can then be cycloplatinated readily with C–H, C–I, C–Br, N–H or O–H bond fission. Condensation of **1** with benzaldehyde derivatives (RCHO) gave mixed azines of type *Z,E*- $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CHR}$  [R = Ph **2a**,  $\text{C}_6\text{H}_2(\text{OMe})_{3-3,4,5}$  **2b**,  $\text{C}_6\text{H}_4\text{NO}_2$ -**4** **2c**,  $\text{C}_6\text{H}_4\text{I}$ -**2** **2d**,  $\text{C}_6\text{H}_4\text{Br}$ -**2** **2e**,  $\text{C}_6\text{H}_4\text{Cl}$ -**2** **2f** or  $\text{C}_6\text{H}_2(\text{OH}-2)(\text{OMe})_{2-4,6}$  **2g**]. The azines **2a–2f** reacted with  $[\text{PtMe}_2(\text{cod})]$  (cod = cycloocta-1,5-diene) at 20 °C to give dimethylplatinum(II) complexes  $[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CHR}\}]$  **3a–3f** respectively, containing six-membered chelate rings. Treatment of **2g** with  $[\text{PtMe}_2(\text{cod})]$  effected O–H bond fission to give the *O*-cyclometallated methylplatinum(II) complex  $[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_{2-4,6}]\}]$  **4**. When the dimethylplatinum(II) complex **3a** was heated in toluene at 100 °C, it underwent C–H bond fission with elimination of  $\text{CH}_4$  to give the cyclometallated methylplatinum(II) complex  $[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$  **5a**. Similarly, **3b** and **3c** were converted into the corresponding cyclometallated methylplatinum(II) complexes **5b** and **5c**, respectively. The square-planar dimethylplatinum(II) complex **3d** in benzene at 20 °C underwent oxidative addition of the C–I bond to give the cyclometallated iododimethylplatinum(IV) complex *mer,cis*- $[\text{PtI}(\text{Me})_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$  **6a**. When the bromo-mixed azine complex **3e** was heated in benzene at 75 °C for 16 h the cyclometallated bromodimethylplatinum(IV) complex *mer,cis*- $[\text{PtBr}(\text{Me})_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$  **6b** formed. In contrast the chloro-mixed azine complex **3f** underwent the C–H bond fission and not C–Cl bond fission to give the cyclometallated square-planar methylplatinum(II) complex  $[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{Cl}-6)\}]$  **5d**. The methylplatinum(II) complexes **5a** and **5d** oxidatively added MeI to give the *mer,cis*-iododimethylplatinum(IV) complexes **6a** and **6c**, respectively. Treatment of **1** with 2-carbaldehydes of pyrrole, thiophene or furan gave the corresponding phosphines **7a–7c**, which with  $[\text{PtMe}_2(\text{cod})]$  at 20 °C gave the dimethylplatinum(II) complexes **8a–8c**, respectively. When **8a**, derived from the pyrrole azine phosphine, was heated at 50 °C for 10 min, the *N*-cyclometallated methylplatinum(II) complex  $[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{N})\}]$  **9** and methane were formed *via* a N–H bond fission. When the dimethylplatinum(II) complexes **8b** or **8c**, derived from the thiophene or furan azine phosphines, were heated at 100 °C in toluene they underwent C–H bond fission to give the cyclometallated methylplatinum(II) complexes  $[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_4\text{H}_2\text{X})\}]$  (X = S **10a** or O **10b**), which oxidatively added MeI to give the iododimethylplatinum(IV) complexes *mer,cis*- $[\text{PtI}(\text{Me})_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_4\text{H}_2\text{X})\}]$  (X = S **11a** or O **11b**), respectively. Proton,  $^{31}\text{P}$ - $\{^1\text{H}\}$  and some  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR data have been obtained.

In a previous paper<sup>1</sup> we described the synthesis of a new phosphino hydrazone *Z*- $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2$  **1** from the corresponding phosphino dimethylhydrazone *Z*- $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNMe}_2$  by a hydrazine-exchange reaction. This very reactive functionalised phosphine **1** condenses readily and completely with a range of aldehydes (RCHO) (R = aryl or heterocycle) to give mixed-azine monophosphines of type  $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CHR}$ <sup>1–7</sup> having the *Z,E* configuration as shown in **2**, since the R group is much more sterically demanding than H. Under mild conditions, one would expect that azines of type **2** would chelate to a metal centre through phosphorus and N=CHR nitrogen to give six-membered chelate rings, and that this would force the sterically demanding R group against the metal and cause an atom or bond in the R group to interact with the metal. We have used this strategy to promote agostic interaction (C–H→Ru),<sup>3</sup> or aryl fluoride coordination (RF→Ru)<sup>4</sup> with ruthenium(II), and also to promote

cyclometallation with iridium(I)<sup>5</sup> or tungsten(0).<sup>6</sup> In this paper we describe how we have used this strategy to promote X–Y (X = C, N or O; Y = H, I or Br) bond fission by platinum(II) using azine phosphines derived from aryl aldehydes and heterocyclic aldehydes.

In 1965, Cope and Siekman<sup>8</sup> reported the first example of cyclometallation (or orthometallation) involving aryl C–H bond fission by platinum(II) with the complex  $[\{\text{PtCl}(\text{C}_6\text{H}_4\text{N}=\text{N}-\text{Ph})\}_2]$  derived from azobenzene. Since then many examples of cyclometallation have been reported involving aryl C–X (X = H, I, Br, Cl or F) bond fission using ligands containing nitrogen, phosphorus or sulfur donor atoms. The area has been well reviewed.<sup>9–15</sup> The first example of oxidative addition of an aryl C–X (X = Br or Cl) bond to platinum(II) was described recently by Anderson *et al.*,<sup>16,17</sup> who treated the imine ligand 2- $\text{XC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2$  with  $[\{\text{PtMe}_2(\mu\text{-SMe}_2)\}_2]$  to give  $[\text{Pt}(\text{X})\text{Me}_2(\text{C}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ . The stereo-

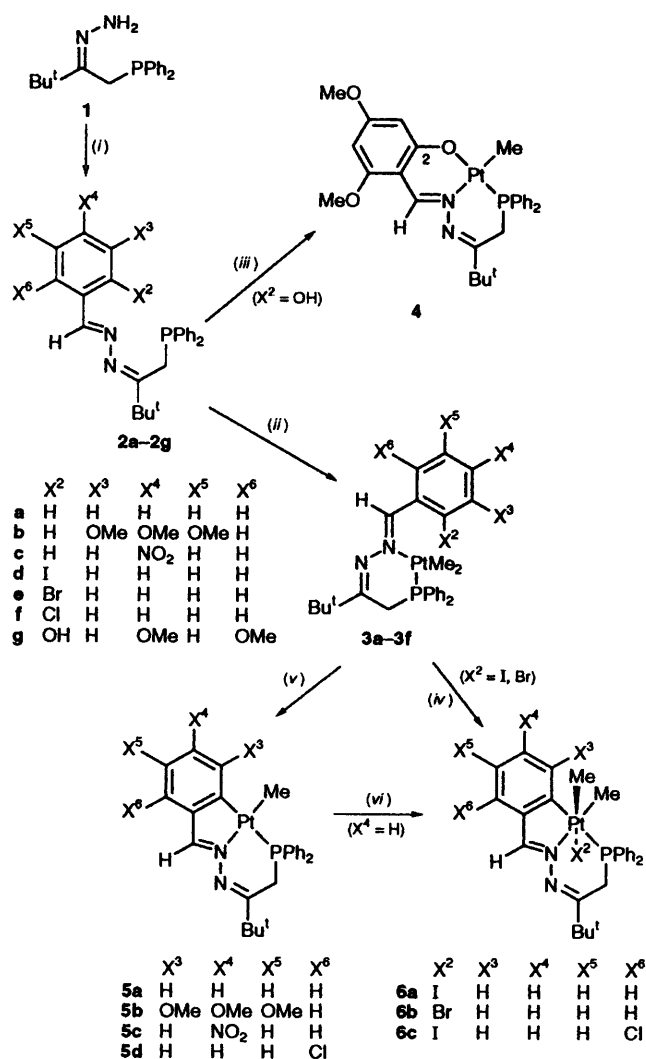
chemistry of this cyclometallated complex was<sup>4</sup> not assigned from NMR data but molecular mechanics calculations suggested that the *mer,cis* complex was more stable than the *fac,cis* complex.<sup>17</sup> We have been able to assign the geometries of all the complexes described herein from NMR data such as  $J(\text{PC})$  and  $^1J(\text{PtP})$  values. Other recent reports<sup>18–21</sup> on intramolecular aryl C–X (X = H, I, Br, Cl or F) bond activations by platinum(II) were with imine ligands such as 2- $\text{XC}_6\text{H}_4\text{CH}=\text{NR}$  (R = Ph or  $\text{CH}_2\text{Ph}$ ),<sup>17,19,20</sup> (2- $\text{XC}_6\text{H}_4$ )- $\text{CH}=\text{NCH}_2$  (2'- $\text{X}'\text{C}_6\text{H}_4$ ),<sup>19</sup>  $\text{C}_6\text{F}_5\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2$ ,<sup>16,18</sup> and  $\text{C}_6\text{F}_5\text{CH}=\text{NCH}_2$  (2- $\text{XC}_6\text{H}_4$ ),<sup>20,21</sup> etc.

## Results and Discussion

For the convenience of the reader the mixed azines and the complexes prepared from them are shown in Schemes 1 and 2. Elemental analytical, mass spectral and some carbon-13 NMR data are given in the Experimental section and proton and phosphorus-31 NMR data are given in Table 1. Carbon-13 NMR spectra were assigned using attached proton tests and by comparison with published data,<sup>22–26</sup> some satellites due to platinum-195 coupling were not identified due to their low intensities or broadness. Some cyclometallated complexes were very soluble and were not isolated in the pure state; these were characterised by proton and  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopy, only.<sup>17</sup> The iodo-mixed azine phosphine **2d** was prepared *in situ*<sup>6</sup> and characterised by phosphorus-31 NMR spectroscopy whereas the other mixed azine phosphines of types **2** and **7** were isolated in 70–85% yield as pale yellow crystalline solids and characterised by C, H, N analyses, proton and  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopy and by mass spectrometry.

The phosphino hydrazone  $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{NNH}_2$  **1** readily condensed with a range of benzaldehyde derivatives (RCHO) to give mixed azine phosphines of type  $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CHR}$  [R = Ph **2a**,  $\text{C}_6\text{H}_2(\text{OMe})_3$ -**3,4,5** **2b**,  $\text{C}_6\text{H}_4\text{NO}_2$ -**4** **2c**,  $\text{C}_6\text{H}_4\text{I}$ -**2** **2d**,  $\text{C}_6\text{H}_4\text{Br}$ -**2** **2e**,  $\text{C}_6\text{H}_4\text{Cl}$ -**2** **2f** or  $\text{C}_6\text{H}_2(\text{OH}-2)(\text{OMe})_2$ -**4,6** **2g**] (Scheme 1). The phosphorus-31 resonances for the azine phosphines **2a–2f** were singlets at  $\delta \approx -10$  whereas the resonance for **2g** was at  $\delta -14.2$ . The azine phosphines **2a–2f** displaced cod from the labile  $[\text{PtMe}_2(\text{cod})]$ <sup>27</sup> (cod = cycloocta-1,5-diene) at 20 °C to give yellow dimethylplatinum(II) complexes of type  $[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CHR}\}]$  **3a–3f**, containing six-membered chelate rings. We have previously described the dimethylplatinum(II) complex  $[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CHPh}\}]$  **3a**,<sup>2</sup> derived from benzaldehyde. The NMR data for **3a** in  $\text{C}_6\text{D}_6$  are as follows:  $\delta_{\text{p}}$  31.1 with platinum-195 satellites [ $^1J(\text{PtP})$  2126 Hz], typical of a phosphorus *trans* to a methyl group<sup>2,27–29</sup>; and in the proton NMR spectrum, the methylene protons are non-equivalent with  $^2J(\text{HH})$  12.6 and  $^2J(\text{PH})$  10.7 Hz, for each proton; the imine proton  $\text{CH}=\text{N}$  is at  $\delta$  8.40 with platinum-195 satellites [ $^3J(\text{PtH})$  37.0 Hz]. As expected, the related dimethylplatinum(II) complexes **3b–3f** showed similar NMR properties to **3a**, derived from benzaldehyde. In particular, in the proton NMR spectra of complexes of type **3**, a platinum methyl absorbing at  $\delta \approx 1.1$  with satellites due to coupling to platinum-195 [ $^2J(\text{PtH}) \approx 70$  Hz] was assigned to the PtMe *trans* to phosphorus<sup>2,27</sup> whilst a resonance absorbing at  $\approx 1.5$  with  $^2J(\text{PtH}) \approx 90$  Hz, was assigned to the PtMe *trans* to nitrogen.<sup>2,17–19</sup>

Treatment of  $[\text{PtMe}_2(\text{cod})]$  in benzene with the azine **2g**, derived from 4,6-dimethoxybenzaldehyde, at 50 °C for 10 min effected fission of the O–H bond to give the *O*-cyclometallated methylplatinum(II) complex **4** and methane. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of **4** showed a singlet at  $\delta$  22.9 with platinum-195 satellites [ $^1J(\text{PtP})$  4599 Hz]; the large value of  $^1J(\text{PtP})$  is typical for a tertiary phosphine ligand *trans* to an oxygen donor ligand.<sup>28,29</sup> In the proton NMR spectrum of **4** the methylene protons were chemically equivalent and absorbed at  $\delta$  2.84 ppm with  $^2J(\text{PH})$  13.7 and  $^3J(\text{PtH})$  48.4 Hz whilst



Scheme 1 (i) RCHO; (ii)  $[\text{PtMe}_2(\text{cod})]$ , 20 °C; (iii)  $[\text{PtMe}_2(\text{cod})]$ , 50 °C, 10 min,  $-\text{CH}_4$ ; (iv) for **6a**, 20 °C, 4 h; for **6b**, heat, 75 °C, 16 h; (v) heat, 100 °C,  $-\text{CH}_4$ ; (vi) MeI

the PtMe protons were at  $\delta$  1.20 with  $^3J(\text{PH})$  2.7 and  $^2J(\text{PtH})$  69.0 Hz.

When the dimethylplatinum(II) complex **3a** was heated in toluene at 100 °C for 40 h, it was completely converted into the methylplatinum(II) complex **5a** with  $\delta_{\text{p}}$  28.2 and  $^1J(\text{PtP})$  2226 Hz (the progress of the reaction was monitored by  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopy). The proton NMR spectrum showed a doublet with platinum-195 satellites at  $\delta$  1.69 [ $^3J(\text{PH})$  7.0 and  $^2J(\text{PtH})$  87.0 Hz] for the PtMe protons whereas the  $\text{CH}_2$  protons absorbed at  $\delta$  2.88 with  $^2J(\text{PH})$  11.6 and  $^3J(\text{PtH})$  20.2 Hz. In the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum a doublet was observed at  $\delta$  171.5 with a large  $^2J(\text{PC})$  value of 127.9 Hz for the quaternary carbon C<sup>2</sup>, confirming that C<sup>2</sup> is directly bonded to platinum and also that it is *trans* to the phosphorus atom. Similar carbon-13 chemical shifts have been reported for aryl carbons bound to metals in other complexes such as *cis*- $[\text{PtPh}_2(\text{PEt}_3)_2]$ ,<sup>23</sup> *trans*- $[\text{PtPh}_2(\text{PEt}_3)_2]$ ,<sup>23</sup>  $[\text{W}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$ <sup>6</sup> and  $[\text{Ir}(\text{H})\text{Cl}(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$ .<sup>5,30</sup> Similarly, the dimethylplatinum(II) complex **3b**, derived from the 3,4,5-trimethoxybenzaldehyde azine, was converted into the cyclometallated methylplatinum(II) complex **5b**, in which the H<sup>6</sup> proton showed coupling to phosphorus [ $^5J(\text{PH})$  1.6 Hz] and to platinum-195 [ $^4J(\text{PtH})$  6.7 Hz], confirming that bond formation between the aryl group and platinum had occurred. The dimethylplatinum(II) complex **3c**, derived from the 4-

**Table 1** Proton and  $^{31}\text{P}\{-^1\text{H}\}$  NMR data<sup>a</sup> [ $^b J(\text{HH})$ ,  $^c J(\text{PH})$ ,  $^d J(\text{PtH})$ ,  $^e J(\text{PH})$ ,  $^f J(\text{PtH})$  and  $^g J(\text{PH})$ ]

Complex	$\delta(\text{Bu}^t)$	$\delta(\text{CH}_2)$	$\delta(\text{CH}=\text{N})$	$\delta(\text{PtMe})$	$\delta_{\text{P}}$	$^1J(\text{PtP})$
<b>1</b>	0.98	3.10 (2 H, d, 2.2 <sup>c</sup> )	—	—	-22.6	—
<b>2a</b>	1.22	3.52 (2 H, d, 3.2 <sup>c</sup> )	8.04 (s)	—	-10.0	—
<b>2b<sup>h</sup></b>	1.50	3.48 (2 H, d, 3.4 <sup>c</sup> )	8.02 [1 H, d, $^6J(\text{PH})$ 1.0]	—	-9.2	—
<b>2c<sup>i</sup></b>	1.25	3.50 (2 H, d, 2.9 <sup>c</sup> )	8.14 (s)	—	-10.4	—
<b>2d</b>	—	—	—	—	-10.1 <sup>j</sup>	—
<b>2e</b>	1.24	3.49 (2 H, d, 2.5 <sup>c</sup> )	8.33 (s)	—	-10.8	—
<b>2f</b>	1.24	3.50 (2 H, d, 2.7 <sup>c</sup> )	8.39 (s)	—	-10.7	—
<b>2g<sup>k</sup></b>	1.21	3.41 (2 H, d, 1.2 <sup>c</sup> )	8.38 (s)	—	-14.2	—
<b>3a</b>	0.79	2.28 (1 H, dd, 12.6, <sup>b</sup> 10.7, <sup>c</sup> 10.3 <sup>f</sup> ) 3.11 (1 H, dd, 12.6, <sup>b</sup> 10.7, <sup>c</sup> 18.8 <sup>f</sup> )	8.40 (d, 1.9, <sup>g</sup> 37.0 <sup>f</sup> )	1.23 (3 H, d, 7.8, <sup>e</sup> 70.4 <sup>d</sup> ) 1.53 (3 H, d, 7.8, <sup>e</sup> 89.4 <sup>d</sup> )	31.1	2126
<b>3b<sup>l</sup></b>	0.83	2.33 (1 H, dd, 12.6, <sup>b</sup> 10.8, <sup>c</sup> 9.9 <sup>f</sup> ) 3.12 (1 H, dd, 12.6, <sup>b</sup> 10.8, <sup>c</sup> 18.9 <sup>f</sup> )	8.30 (d, 2.2, <sup>g</sup> 35.9 <sup>f</sup> )	1.26 (3 H, d, 7.8, <sup>e</sup> 69.8 <sup>d</sup> ) 1.45 (3 H, d, 7.8, <sup>e</sup> 89.7 <sup>d</sup> )	31.4	2110
<b>3c<sup>m</sup></b>	0.79	2.22 (1 H, dd, 12.6, <sup>b</sup> 10.7, <sup>c</sup> 9.9 <sup>f</sup> ) 3.14 (1 H, dd, 12.6, <sup>b</sup> 10.4, <sup>c</sup> 18.9 <sup>f</sup> )	8.20 (d, 2.1, <sup>g</sup> 35.9 <sup>f</sup> )	1.10 (3 H, d, 7.8, <sup>e</sup> 70.1 <sup>d</sup> ) 1.54 (3 H, d, 8.1, <sup>e</sup> 89.7 <sup>d</sup> )	29.6	2109
<b>3d</b>	0.76	2.22 (1 H, dd, 12.8, <sup>b</sup> 10.5, <sup>c</sup> 10.2 <sup>f</sup> ) 3.14 (1 H, dd, 12.8, <sup>b</sup> 10.6, <sup>c</sup> 18.6 <sup>f</sup> )	8.91 (d, 2.1, <sup>g</sup> 33.8 <sup>f</sup> )	1.08 (3 H, d, 7.9, <sup>e</sup> 70.4 <sup>d</sup> ) 1.44 (3 H, d, 8.1, <sup>e</sup> 89.7 <sup>d</sup> )	32.4	2125
<b>3e</b>	0.76	2.21 (1 H, dd, 12.9, <sup>b</sup> 10.6, <sup>c</sup> 10.5 <sup>f</sup> ) 3.11 (1 H, dd, 12.9, <sup>b</sup> 10.6, <sup>c</sup> 18.2 <sup>f</sup> )	9.07 (d, 2.4, <sup>g</sup> 34.6 <sup>f</sup> )	1.13 (3 H, d, 7.9, <sup>e</sup> 69.7 <sup>d</sup> ) 1.47 (3 H, d, 7.9, <sup>e</sup> 89.7 <sup>d</sup> )	30.5	2109
<b>3f</b>	0.75	2.22 (1 H, dd, 12.9, <sup>b</sup> 10.6, <sup>c</sup> 10.2 <sup>f</sup> ) 3.13 (1 H, dd, 12.9, <sup>b</sup> 10.7, <sup>c</sup> 18.5 <sup>f</sup> )	9.11 (d, 2.2, <sup>g</sup> 34.9 <sup>f</sup> )	1.13 (3 H, d, 8.1, <sup>e</sup> 70.4 <sup>d</sup> ) 1.46 (3 H, d, 7.8, <sup>e</sup> 89.7 <sup>d</sup> )	30.4	2109
<b>4<sup>n</sup></b>	0.69	2.84 (2 H, d, 13.7, <sup>c</sup> 48.4 <sup>f</sup> )	9.62 (s, 17.4 <sup>f</sup> )	1.20 (3 H, d, 2.7, <sup>e</sup> 69.0 <sup>d</sup> )	22.9	4599
<b>5a</b>	0.75	2.88 (2 H, d, 11.6, <sup>c</sup> 20.2 <sup>f</sup> )	9.02 (s, 35.5 <sup>f</sup> )	1.69 (3 H, d, 7.0, <sup>e</sup> 87.0 <sup>d</sup> )	28.2	2226
<b>5b<sup>o</sup></b>	0.78	2.92 (2 H, d, 11.8, <sup>c</sup> 23.9 <sup>f</sup> )	9.08 (s, 32.8 <sup>f</sup> )	1.98 (3 H, d, 8.8, <sup>e</sup> 88.4 <sup>d</sup> )	25.5	2441
<b>5c<sup>p</sup></b>	0.74	2.87 (2 H, d, 11.6, <sup>c</sup> 21.2 <sup>f</sup> )	8.85 (s, 35.5 <sup>f</sup> )	1.62 (3 H, d, 6.7, <sup>e</sup> 85.9 <sup>d</sup> )	28.6	2347
<b>5d<sup>q</sup></b>	0.69	2.85 (2 H, d, 11.7, <sup>c</sup> 22.3 <sup>f</sup> )	9.91 (s, 37.8 <sup>f</sup> )	1.60 (3 H, d, 7.0, <sup>e</sup> 85.8 <sup>d</sup> )	29.5	2281
<b>6a</b>	0.87	3.59 (1 H, t, 13.7, <sup>b</sup> 13.9, <sup>c</sup> 10.3 <sup>f</sup> ) 4.70 (1 H, dd, 13.7, <sup>b</sup> 12.3, <sup>c</sup> 6.2 <sup>f</sup> )	8.63 (s, 29.8 <sup>f</sup> )	0.99 (3 H, d, 6.7, <sup>e</sup> 69.8 <sup>d</sup> ) 1.92 (3 H, d, 6.5, <sup>e</sup> 70.9 <sup>d</sup> )	-11.4	1466
<b>6b</b>	0.79	3.36 (1 H, t, 13.5, <sup>b</sup> 13.9, <sup>c</sup> 10.3 <sup>f</sup> ) 4.61 (1 H, t, 13.5, <sup>b</sup> 13.2, <sup>c</sup> 6.2 <sup>f</sup> )	8.59 (s, 29.0 <sup>f</sup> )	0.86 (3 H, d, 6.7, <sup>e</sup> 72.1 <sup>d</sup> ) 1.77 (3 H, d, 6.4, <sup>e</sup> 70.3 <sup>d</sup> )	-5.4	1441
<b>6c</b>	0.80	3.61 (1 H, t, 13.9, <sup>b</sup> 14.1, <sup>c</sup> 11.2 <sup>f</sup> ) 4.66 (1 H, t, 13.9, <sup>b</sup> 13.9, <sup>c</sup> 6.8 <sup>f</sup> )	9.63 (s, 31.5 <sup>f</sup> )	0.93 (3 H, d, 6.6, <sup>e</sup> 69.3 <sup>d</sup> ) 1.85 (3 H, d, 6.2, <sup>e</sup> 70.3 <sup>d</sup> )	-10.9	1507
<b>7a<sup>r</sup></b>	1.23	3.50 (2 H, d, 2.9 <sup>c</sup> )	8.10 (s)	—	-9.0	—
<b>7b<sup>s</sup></b>	1.20	3.54 (2 H, d, 2.7 <sup>c</sup> )	8.15 (s)	—	-9.5	—
<b>7c<sup>t</sup></b>	1.21	3.53 (2 H, d, 2.9 <sup>c</sup> )	7.82 (s)	—	-9.0	—
<b>8a<sup>u</sup></b>	1.43	3.02 (1 H, dd, 12.8, <sup>b</sup> 11.1, <sup>c</sup> 10.1 <sup>f</sup> ) 3.82 (1 H, dd, 12.8, <sup>b</sup> 11.0, <sup>c</sup> 20.4 <sup>f</sup> )	8.72 (d, 1.6, <sup>g</sup> 41.7 <sup>f</sup> )	1.56 (3 H, d, 7.8, <sup>e</sup> 69.0 <sup>d</sup> ) 1.78 (3 H, d, 7.5, <sup>e</sup> 87.3 <sup>d</sup> )	34.9	2045
<b>8b<sup>v</sup></b>	0.79	2.13 (1 H, dd, 12.8, <sup>b</sup> 11.0, <sup>c</sup> 10.2 <sup>f</sup> ) 3.06 (1 H, dd, 12.8, <sup>b</sup> 10.7, <sup>c</sup> 20.1 <sup>f</sup> )	8.35 (d, 2.1, <sup>g</sup> 38.9 <sup>f</sup> )	1.43 (3 H, d, 7.8, <sup>e</sup> 71.2 <sup>d</sup> ) 1.59 (3 H, d, 8.1, <sup>e</sup> 88.3 <sup>d</sup> )	30.1	2116
<b>8c<sup>w</sup></b>	0.74	2.12 (1 H, dd, 12.9, <sup>b</sup> 11.4, <sup>c</sup> 10.2 <sup>f</sup> ) 3.04 (1 H, dd, 12.9, <sup>b</sup> 10.6, <sup>c</sup> 20.0 <sup>f</sup> )	8.31 (d, 2.4, <sup>g</sup> 39.7 <sup>f</sup> )	1.37 (3 H, d, 8.1, <sup>e</sup> 70.6 <sup>d</sup> ) 1.52 (3 H, d, 7.8, <sup>e</sup> 88.6 <sup>d</sup> )	30.8	2096
<b>9<sup>x</sup></b>	0.76	2.83 (2 H, d, 13.4, <sup>c</sup> 38.9 <sup>f</sup> )	8.49 (s, 20.7 <sup>f</sup> )	1.19 (3 H, d, 3.8, <sup>e</sup> 78.4 <sup>d</sup> )	16.3	3987
<b>10a</b>	0.75	2.84 (2 H, d, 11.6, <sup>c</sup> 21.2 <sup>f</sup> )	9.08 (s, 33.8 <sup>f</sup> )	1.82 (3 H, d, 7.0, <sup>e</sup> 87.8 <sup>d</sup> )	23.5	2470
<b>10b</b>	0.71	2.83 (2 H, d, 11.8, <sup>c</sup> 21.0 <sup>f</sup> )	9.02 (s, 34.9 <sup>f</sup> )	1.79 (3 H, d, 7.0, <sup>e</sup> 88.6 <sup>d</sup> )	23.2	2588
<b>11a</b>	0.87	3.56 (1 H, t, 13.9, <sup>b</sup> 13.9, <sup>c</sup> 12.2 <sup>f</sup> ) 4.61 (1 H, t, 13.9, <sup>b</sup> 13.7, <sup>c</sup> 6.8 <sup>f</sup> )	8.32 (s, 28.8 <sup>f</sup> )	0.90 (3 H, d, 6.6, <sup>e</sup> 69.1 <sup>d</sup> ) 2.04 (3 H, d, 6.6, <sup>e</sup> 71.3 <sup>d</sup> )	-14.6	1639
<b>11b</b>	0.83	3.57 (1 H, t, 13.7, <sup>b</sup> 13.9, <sup>c</sup> 12.5 <sup>f</sup> ) 4.61 (1 H, t, 13.7, <sup>b</sup> 13.7, <sup>c</sup> 7.1 <sup>f</sup> )	8.47 (s, 29.8 <sup>f</sup> )	0.98 (3 H, d, 6.6, <sup>e</sup> 68.6 <sup>d</sup> ) 2.03 (3 H, d, 6.3, <sup>e</sup> 72.3 <sup>d</sup> )	-14.7	1727

<sup>a</sup> Recorded at 100 MHz, chemical shifts are in ppm relative to  $\text{SiMe}_4$ ,  $J$  values are in Hz, solvent  $\text{C}_6\text{D}_6$  unless otherwise stated; some of the heterocyclic ring protons of compounds **7b**, **7c**, **8b**, **8c**, **9**, **10a**, **10b**, **11a** and **11b** were obscured by phenyl protons of the  $\text{PPh}_2$  group.  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra are recorded in  $\text{C}_6\text{D}_6$  at 36.2 MHz, chemical shifts are in ppm relative to 85%  $\text{H}_3\text{PO}_4$ ,  $^1J(\text{PtP})$  in Hz. <sup>b</sup>  $\delta$  3.73 (6 H, s, 2  $\times$  OMe) and 3.87 (3 H, s, OMe). <sup>c</sup>  $\delta$  8.03 (2 H, d,  $^3J(\text{HH})$  8.6,  $\text{H}^3$  and  $\text{H}^5$ ). <sup>d</sup> In  $\text{thf}$ . <sup>e</sup>  $\delta$  3.79 (6 H, s, 2  $\times$  OMe), 5.90 [1 H, d,  $^4J(\text{HH})$  2.2,  $\text{H}^3$  or  $\text{H}^5$ ] and 6.02 [1 H, d,  $^4J(\text{HH})$  2.2,  $\text{H}^3$  or  $\text{H}^5$ ]. <sup>f</sup>  $\delta$  3.49 (6 H, s, 2  $\times$  OMe) and 3.78 (3 H, s, OMe). <sup>g</sup>  $\delta$  7.50 [2 H, d,  $^3J(\text{HH})$  8.6,  $\text{H}^2$  and  $\text{H}^6$ ] and 8.32 [2 H, d,  $^3J(\text{HH})$  8.6,  $\text{H}^3$  and  $\text{H}^5$ ]. <sup>h</sup>  $\delta$  3.20 (3 H, s, OMe), 3.31 (3 H, s, OMe), 5.81 [1 H, d,  $^4J(\text{HH})$  2.3,  $\text{H}^3$  or  $\text{H}^5$ ] and 6.53 [1 H, d,  $^4J(\text{HH})$  2.3,  $\text{H}^3$  or  $\text{H}^5$ ]. <sup>i</sup>  $\delta$  3.46 (3 H, s, OMe), 3.93 (3 H, s, OMe), 3.97 (3 H, s, OMe) and 6.85 [1 H, d,  $^5J(\text{PH})$  1.6,  $^4J(\text{PtH})$  6.7,  $\text{H}^6$ ]. <sup>j</sup>  $\delta$  6.09 (1 H, m, pyrrole-H), 6.41 (1 H, m, pyrrole-H) and 6.50 (1 H, m, pyrrole-H). <sup>k</sup>  $\delta$  6.69 (1 H, m, thiophene-H) and 7.13 (1 H, m, thiophene-H). <sup>l</sup>  $\delta$  6.40 (1 H, m, furan-H) and 6.50 (1 H, m, furan-H). <sup>m</sup>  $\delta$  6.69 [1 H, dd,  $J(\text{HH})$  2.7, 5.9, pyrrole-H] and 7.13 (2 H, m, pyrrole-H). <sup>n</sup>  $\delta$  6.45 [1 H, dd,  $J(\text{HH})$  3.8, 5.0, thiophene-H]. <sup>o</sup>  $\delta$  5.86 (1 H, m, furan-H). <sup>p</sup>  $\delta$  6.63 [1 H, m,  $J(\text{HH})$  1.6, 3.8,  $J(\text{PtH})$  15.0, pyrrole-H].

nitrobenzaldehyde azine **2c**, also underwent C–H bond fission to give the cyclometallated methylplatinum(II) complex **5c**, in which the  $\text{H}^3$  proton gave a doublet of doublets resonance with platinum-195 satellites at  $\delta$  9.17 [ $^4J(\text{HH})$  2.2,  $^4J(\text{PH})$  6.4 and  $^3J(\text{PtH})$  55.9 Hz].

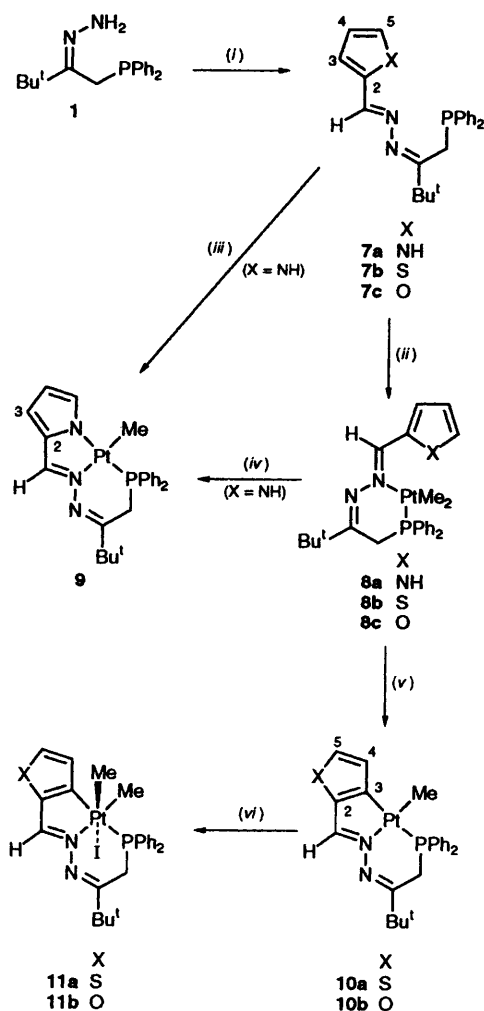
We have also investigated the tendency of C–X bonds ( $X = \text{I}$ , Br or Cl) to undergo oxidative addition to a platinum(II) centre using azine phosphines derived from 2-halogenobenzaldehydes. The factors which influence the oxidative addition of a C–X ( $X = \text{I}$ , Br, Cl, F or H) bond to a metal centre are complex and several mechanisms have been proposed.<sup>13–21,31,32</sup> For many systems, the reactivity ( $\text{C–I} > \text{C–Br} > \text{C–Cl} > \text{C–H} > \text{C–F}$ )

of the aryl C–X bond follows the inverse order of C–X bond energies<sup>6,14–17</sup> but there are also reports on the activation of strong bonds (e.g. C–F or C–H) in the presence of much weaker C–X bonds ( $X = \text{Br}$ , Cl or H).<sup>5,14,19–21,32</sup>

In benzene solution at room temperature (20 °C) the dimethylplatinum(II) complex **3d**, derived from the 2-iodobenzaldehyde azine **2d**, underwent an intramolecular oxidative addition of the C–I bond to form the iododimethylplatinum(IV) complex **6a** as the only product, after a reaction time of 4 h. Complex **6a** was also prepared by the oxidative addition of MeI to the cyclometallated methylplatinum(II) complex **5a**, derived from the benzaldehyde azine phosphine **2a**. The small  $^1J(\text{PtP})$

value of 1466 Hz is typical for platinum(IV) complexes.<sup>2,28,29,33</sup> In the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum, the resonances for the platinum methyl carbons appeared as a doublet with platinum-195 satellites at  $\delta -6.0$  [ $^2J(\text{PC})$  3.3 and  $^1J(\text{PtC})$  616 Hz] and a singlet at  $\delta 8.1$  with  $^1J(\text{PtC})$  590 Hz, indicating that both carbons are *cis* to phosphorus. The resonance at  $\delta 162.4$  with a large  $^2J(\text{PC})$  value of 145.4 Hz is assigned to the quaternary carbon directly bonded to platinum, *i.e.* C<sup>2</sup>, thus the ligand has retained the *mer* arrangement. The observed low  $\delta_{\text{C}}$  value of  $\delta 26.6$  for the methylene carbon is consistent with other values obtained for methylene carbons in six-membered rings.<sup>2,6,27</sup> In the proton NMR spectrum, the occurrence of two chemically inequivalent platinum methyl resonances with  $^2J(\text{PtH})$  values of  $\approx 70$  Hz suggests that one of the PtMe groups is *trans* to nitrogen<sup>2,18,19</sup> and the other *trans* to iodine.<sup>2,34</sup> Therefore, this iododimethylplatinum(IV) complex has the *mer,cis* geometry **6a**, confirming that the intramolecular oxidative addition of the C–I bond is *cis*<sup>16–21</sup> whereas the intermolecular oxidative addition of MeI is *trans*.<sup>2,16,17</sup> The dimethylplatinum(II) complex **3e**, derived from the bromo azine **2e**, when heated in benzene at 75 °C underwent oxidative addition of the C–Br bond to give the *mer,cis*-bromodimethylplatinum(IV) complex **6b**, which showed similar NMR properties to the analogous iododimethylplatinum(IV) complex **6a**. Somewhat surprisingly, when the dimethylplatinum(II) complex **3f**, derived from the chloro azine **2f**, was heated in toluene at 100 °C C–H bond fission took place instead of the oxidative addition of the C–Cl bond, to give the cyclometallated methylplatinum(II) complex **5d**; this was shown by the NMR data and subsequent chemistry. The  $^1J(\text{PtP})$  value of 2281 Hz is similar to other values observed for the methylplatinum(II) complexes of type **5** with phosphorus *trans* to aryl groups. If the C–Cl bond fission took place with a loss of MeCl it would give the methylplatinum(II) complex **5a**. Treatment of the chloro azine **2f** with  $[\text{IrCl}(\text{CO})_2(\text{NH}_2\text{C}_6\text{H}_4\text{Me}-p)]$  underwent C–H bond fission to give the iridium(III) hydride  $[\text{Ir}(\text{H})\text{Cl}(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{Cl}-6)\}]$ <sup>5</sup> whereas **2f** with  $[\text{W}(\text{CO})_3(\text{NCEt}_3)_3]$  gave  $[\text{WCl}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$ <sup>6</sup> via a C–Cl bond fission. In the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum of **5d**, the carbon-13 resonance at  $\delta 173.8$  [ $^2J(\text{PC})$  128.1 and  $^1J(\text{PtC})$  961 Hz] was assigned to the quaternary aryl carbon directly bonded to platinum, *i.e.* C<sup>2</sup>, whilst the resonances for the quaternary carbons C<sup>1</sup> and C<sup>6</sup> were at  $\delta 135.9$  or 142.2. The methylplatinum(II) complex **5d** reacted with MeI to give the *mer,cis*-iododimethylplatinum(IV) complex **6c**, which was characterised in a similar fashion to the analogous bromodimethylplatinum(IV) complex **6b**.

We also studied the C–H/N–H bond fission processes of azine phosphines of type *Z,E*-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N–N=CHR where R is a 2-substituted pyrrole, thiophene or furan moiety. Treatment of the phosphino hydrazone **1** with 2-carbaldehydes of pyrrole, thiophene or furan gave the heterocyclic azines **7a**, **7b** or **7c**, respectively (Scheme 2). The phosphorus-31 resonances for these phosphines **7a–7c** were observed as singlets at  $\delta \approx -9$  and the proton resonances for the CH<sub>2</sub> groups as doublets at  $\delta \approx 3.5$  with  $^2J(\text{PH}) \approx 2.8$  Hz. Treatment of **7a–7c** with  $[\text{PtMe}_2(\text{cod})]$  gave the expected dimethylplatinum(II) complexes **8a–8c**, respectively. Their NMR data are similar to those of **3**, derived from benzaldehyde derivatives. When the dimethylplatinum(II) complex **8a**, derived from the pyrrole azine, was heated in C<sub>6</sub>D<sub>6</sub> at 50 °C for 10 min, it gave the *N*-cyclometallated methylplatinum(II) complex **9**; this was also formed by treatment of the pyrrole azine **7a** with  $[\text{PtMe}_2(\text{cod})]$  in benzene at 50 °C for 10 min. Probably, the *N*-cyclometallated methylplatinum(II) complex **9** was formed from **8a** by oxidative addition of the N–H bond followed by reductive elimination of CH<sub>4</sub>. We have shown that a pyrrole N–H bond could undergo oxidative addition to a d<sup>8</sup> iridium(III) centre to give the d<sup>6</sup> iridium(III) hydride  $[\text{Ir}(\text{H})\text{Cl}(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{N})\}]$ .<sup>5</sup> The



Scheme 2 (i) RCHO; (ii)  $[\text{PtMe}_2(\text{cod})]$ , 20 °C; (iii)  $[\text{PtMe}_2(\text{cod})]$ , 50 °C, 10 min,  $-\text{CH}_4$ ; (iv) heat, 50 °C, 10 min,  $-\text{CH}_4$ ; (v) heat, 100 °C,  $-\text{CH}_4$ ; (vi) MeI

large  $^1J(\text{PtP})$  value of 3987 Hz observed for the *N*-cyclometallated methylplatinum(II) complex **9** is typical of phosphorus *trans* to nitrogen donor atom.<sup>2,35–39</sup> When a solution of the dimethylplatinum(II) complex **8b**, derived from the thiophene azine, was heated in toluene at 100 °C for 24 h, it gave a single product [ $\delta_{\text{P}}$  23.5 with platinum-195 satellites  $^1J(\text{PtP})$  2470 Hz] which we formulate as the cyclometallated methylplatinum(II) complex **10a**. In the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum of **10a**, one of the thienyl carbons ( $\delta_{\text{C}}$  135.9 for C<sup>4</sup> or C<sup>5</sup>) is coupled to both phosphorus [ $J(\text{PC})$  10.6 Hz] and platinum-195 [ $J(\text{PtC})$  74.2 Hz] indicating that the thienyl moiety is directly bonded to platinum. Moreover, the large  $^2J(\text{PC})$  value of 128.7 Hz suggests that the C<sup>3</sup> is *trans* to phosphorus, in agreement with other  $^2J(\text{P–Pt–C})$  values reported for similar metal complexes.<sup>25,26</sup> The analogous furan complex **10b** was similarly prepared and characterised. These cyclometallated methylplatinum(II) complexes **10a** and **10b** reacted with MeI to give the *mer,cis*-iododimethylplatinum(IV) complexes **11a** and **11b**, which showed similar proton and phosphorus-31 NMR properties to the *mer,cis*-iododimethylplatinum(IV) complexes of type **6**, derived from benzaldehyde derivatives.

## Experimental

All the reactions were carried out in an inert atmosphere of dry nitrogen or dry argon. Infrared spectra were recorded using a Perkin-Elmer model 457 grating spectrometer. The NMR

spectra were recorded using a JEOL FX-90Q spectrometer (operating frequencies for  $^1\text{H}$  and  $^{31}\text{P}$  of 89.5 and 36.2 MHz respectively), a JEOL FX-100 spectrometer (operating frequencies for  $^1\text{H}$  and  $^{31}\text{P}$  of 99.5 and 40.25 MHz respectively) or a Bruker AM-400 spectrometer (operating frequencies for  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  of 400.13, 161.9 and 100.6 MHz respectively). Proton and  $^{13}\text{C}$  chemical shifts are relative to  $\text{SiMe}_4$  and  $^{31}\text{P}$  shifts to 85% phosphoric acids; all coupling constants are in Hz. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec spectrometer with 8 kV acceleration. For metal complexes  $m/z$  values are quoted for  $^{195}\text{Pt}$ .

**Preparation of Phosphine Ligands.**—The hydrazone  $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2$  **1** was prepared according to our published procedure.<sup>1</sup> The azine  $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{I-2})$  **2d** was prepared *in situ* by treating 2-iodobenzaldehyde with  $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2$  **1** in dry tetrahydrofuran (thf).<sup>6</sup>  $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{Ph})$  **2a** was prepared in a similar manner to our published procedure<sup>1</sup> using ethanol instead of benzene as the solvent [yield 77%;  $m/z$  (EI): 409 ( $M - \text{Bu}^t$ )].

Similarly, the following eight mixed azine phosphines were prepared and isolated as crystalline solids.

$Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2(\text{OMe})_3\text{-3,4,5}]$  **2b**. Yield 86% (Found: C, 70.3; H, 7.1; N, 5.95.  $\text{C}_{28}\text{H}_{33}\text{N}_2\text{O}_3\text{P}$  requires C, 70.55; H, 7.0; N, 5.85%).  $m/z$  (EI): 419 ( $M - \text{Bu}^t$ ).

$Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{NO}_2\text{-4})$  **2c**. Yield 79% (Found: C, 70.0; H, 5.9; N, 10.0.  $\text{C}_{25}\text{H}_{26}\text{N}_3\text{O}_2\text{P}$  requires C, 69.6; H, 6.05; N, 9.75%).  $m/z$  (EI): 374 ( $M - \text{Bu}^t$ ).

$Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{Br-2})$  **2e**. Yield 68% (Found: C, 64.35; H, 5.7; N, 6.05.  $\text{C}_{25}\text{H}_{26}\text{BrN}_2\text{P}$  requires C, 64.5; H, 5.6; N, 6.0%).  $m/z$  (EI): 409 and 407 ( $M - \text{Bu}^t$ ).

$Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{Cl-2})$  **2f**. Yield 69% (Found: C, 70.9; H, 6.2; Cl, 8.5; N, 6.5.  $\text{C}_{25}\text{H}_{26}\text{ClN}_2\text{P}$  requires C, 71.3; H, 6.2; Cl, 8.4; N, 6.65%).  $m/z$  (EI): 420 ( $M^+$ ) and 363 ( $M - \text{Bu}^t$ ).

$Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_4(\text{OH-2})(\text{OMe})_2\text{-4,6}]$  **2g**. Yield 82% (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, 70.1; H, 6.75; N, 6.05%).  $m/z$  (EI): 405 ( $M - \text{Bu}^t$ ).

$Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{NH})$  **7a**. Yield 81% (Found: C, 73.7; H, 7.1; N, 11.2.  $\text{C}_{23}\text{H}_{26}\text{N}_3\text{P}$  requires C, 73.55; H, 7.0; N, 11.2%). IR (KBr disc)  $\nu(\text{N-H})$  3405  $\text{cm}^{-1}$ .  $m/z$  (EI): 318 ( $M - \text{Bu}^t$ ).

$Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{S})$  **7b**. Yield 77% (Found: C, 70.15; H, 6.35; N, 6.95.  $\text{C}_{23}\text{H}_{25}\text{N}_2\text{PS}$  requires C, 70.4; H, 6.4; N, 7.15%).  $m/z$  (EI): 391 ( $M - 1$ ) and 335 ( $M - \text{Bu}^t$ ).

$Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{O})$  **7c**. Yield 77% (Found: C, 73.4; H, 6.8; N, 7.4.  $\text{C}_{23}\text{H}_{25}\text{N}_2\text{PO}$  requires C, 73.4; H, 6.7; N, 7.45%).  $m/z$  (EI): 319 ( $M - \text{Bu}^t$ ).

**Preparation of Platinum Complexes.**—Complex  $[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{Ph})\}]$  **3a** was prepared according to our published procedure.<sup>2</sup> The following dimethylplatinum(II) complexes **3b**, **3c**, **3e** and **3f** were prepared as yellow crystalline solids in a similar manner to that described for **3a**.

$[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2(\text{OMe})_3\text{-3,4,5}]\}]$  **3b**. Yield 78% (Found: C, 51.55; H, 5.7; N, 4.15.  $\text{C}_{30}\text{H}_{39}\text{N}_2\text{O}_3\text{Pt}$  requires C, 51.35; H, 5.6; N, 4.0%).  $m/z$  (FAB): 670 ( $M - \text{Bu}^t$ ).

$[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{NO}_2\text{-2})\}]$  **3c**. Yield 69% (Found: C, 49.35; H, 5.05; N, 6.35.  $\text{C}_{27}\text{H}_{32}\text{N}_3\text{PO}_2\text{Pt}$  requires C, 49.4; H, 4.9; N, 6.3%).  $m/z$  (FAB): 631 ( $M - \text{Me}$ ) and 615 ( $M - \text{Me} - \text{Bu}^t$ ). IR (KBr disc):  $\nu(\text{NO}_2)$  1345 and 1520  $\text{cm}^{-1}$ .

$[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{I-2})\}]$  **3d**. A solution containing  $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2$  (45 mg, 0.15 mmol)

and 2-iodobenzaldehyde (35 mg, 0.15 mmol) in dry thf (*ca.* 2  $\text{cm}^3$ ) was put aside for 20 min at *ca.* 20 °C. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the resulting pale yellow solution showed a singlet at  $\delta - 10.1$  which we assigned to the azine phosphine **2d**.<sup>6</sup> To this solution  $[\text{PtMe}_2(\text{cod})]$  (50 mg, 0.15 mmol) was then added. After 15 min, the resultant solution was concentrated to a low volume (*ca.* 0.2  $\text{cm}^3$ ) under reduced pressure. Addition of MeOH to the residue gave the dimethylplatinum(II) complex **3d** as yellow microcrystals (55 mg, 50%) (Found: C, 43.7; H, 4.25; N, 3.8.  $\text{C}_{27}\text{H}_{32}\text{IN}_2\text{PPT}$  requires C, 43.95; H, 4.35; N, 3.8%).  $m/z$  (FAB): 721 ( $M - \text{CH}_4$ ) and 595 ( $M - \text{MeI}$ ).

$[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{Br-2})\}]$  **3e**. Yield 60 mg, 72% (Found: C, 46.65; H, 4.6; N, 3.85.  $\text{C}_{27}\text{H}_{32}\text{BrN}_2\text{PPT}$  requires C, 46.95; H, 4.65; N, 4.05%).  $m/z$  (FAB): 674 ( $M - \text{CH}_4$ ).

$[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{Cl-2})\}]$  **3f**. Yield 65% (Found: C, 49.85; H, 4.75; Cl, 5.55; N, 4.3.  $\text{C}_{27}\text{H}_{32}\text{ClN}_2\text{PPT}$  requires C, 50.2; H, 5.0; Cl, 5.5; N, 4.35%).  $m/z$  (FAB): 631 ( $M - \text{Me}$ ) and 615 ( $M - \text{Me} - \text{Bu}^t$ ).

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}_2\text{O}(\text{OMe})_2\text{-4,6}]\}]$

**4**. A solution containing the phosphine **2g** (56 mg, 0.12 mmol) and  $[\text{PtMe}_2(\text{cod})]$  (40 mg, 0.12 mmol) in benzene (*ca.* 2  $\text{cm}^3$ ) was heated at 50 °C for 10 min. The solution was then concentrated to a low volume (*ca.* 0.2  $\text{cm}^3$ ) under reduced pressure. Addition of EtOH to the residue gave the *O*-methylplatinum(II) complex **4** as yellow microcrystals (53 mg, 66%) (Found: C, 50.6; H, 5.05; N, 4.2.  $\text{C}_{28}\text{H}_{33}\text{N}_2\text{O}_3\text{PPT}$  requires C, 50.55; H, 5.0; N, 4.1%).  $m/z$  (FAB): 671 ( $M^+$ ) and 656 ( $M - \text{Me}$ ).

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$  **5a**. A solution containing the dimethylplatinum(II) complex **3a** (35 mg, 0.055 mmol) in toluene (0.5  $\text{cm}^3$ ) was heated at 100 °C for 40 h. The solvent was then removed and the residue triturated with methanol to give the cyclometallated methylplatinum(II) complex **5a** as pale yellow microcrystals (15 mg, 45%).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{C}} - 15.6$  [1 C, d,  $^2J(\text{PC})$  4.7,  $^1J(\text{PtC})$  752, PtMe], 22.8 [1 C, d,  $^1J(\text{PC})$  23.2  $\text{CH}_2$ ], 27.8 (3 C, s,  $\text{CMe}_3$ ), 40.6 [1 C, d,  $^3J(\text{PC})$  3.0,  $\text{CMe}_3$ ], 124.7 (1 C, s, Pt-aryl), 129.0 [1 C, d,  $J(\text{PC})$  5.3,  $J(\text{PtC})$  34.2, Pt-aryl], 132.3 [1 C, d,  $J(\text{PC})$  7.0, Pt-aryl], 132.6 (1 C, s, Pt-aryl), 145.3 (1 C, s,  $\text{C}^1$ ), 171.4 (1 C, s,  $\text{Bu}^t\text{C}=\text{N}$ ), 171.5 [1 C, d,  $^2J(\text{PC})$  127.9,  $\text{C}^2$ ] and 177.4 [1 C, d,  $^3J(\text{PC})$  5.5,  $^2J(\text{PtC})$  76.2,  $\text{HC}=\text{N}$ ].

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}[\text{C}_6\text{H}(\text{OMe})_3\text{-3,4,5}]\}]$  **5b**. The cyclometallated methylplatinum(II) complex **5b** was prepared in a similar manner to the analogous methylplatinum(II) complex **5a**, after a reaction time of 55 h.

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{NO}_2\text{-4})\}]$  **5c**. The cyclometallated methylplatinum(II) complex **5c** was prepared in a similar manner to the analogous methylplatinum(II) complex **5a**, after a reaction time of 16 h.

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{Cl-2})\}]$  **5d**. The cyclometallated methylplatinum(II) complex **5d** was prepared in 62% yield in a similar manner to the analogous methylplatinum(II) complex **5a**, after a reaction time of 16 h.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{C}} - 14.8$  [1 C, d,  $^2J(\text{PC})$  4.7,  $^1J(\text{PtC})$  741, PtMe], 22.6 [1 C, d,  $^1J(\text{PC})$  23.7,  $\text{CH}_2$ ], 27.6 (3 C, s,  $\text{CMe}_3$ ), 40.7 [1 C, d,  $^3J(\text{PC})$  2.7,  $\text{CMe}_3$ ], 125.2 (1 C, s, Pt-aryl), 130.0 (1 C, s, Pt-aryl), 134.0 [1 C, d,  $J(\text{PC})$  8.5, Pt-aryl], 135.9 (1 C, s,  $\text{C}^1$  or  $\text{C}^6$ ), 142.2 (1 C, s,  $\text{C}^1$  or  $\text{C}^6$ ), 172.6 (1 C, s,  $\text{Bu}^t\text{C}=\text{N}$ ), 173.8 [1 C, d,  $^2J(\text{PC})$  128.1,  $^1J(\text{PtC})$  961,  $\text{C}^2$ ] and 174.3 [1 C, d,  $^3J(\text{PC})$  4.9,  $^2J(\text{PtC})$  73.0,  $\text{HC}=\text{N}$ ].

*mer,cis*- $[\text{PtIME}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$  **6a**. A solution containing the dimethylplatinum(II) complex **3d** (24 mg, 0.032 mmol) in  $\text{C}_6\text{H}_6$  (0.5  $\text{cm}^3$ ) was put aside for 4 h. The solution was concentrated to a low volume and methanol (*ca.* 1  $\text{cm}^3$ ) added to give the dimethylplatinum(IV) complex **6a** as pale yellow microcrystals (17 mg, 71%) (Found: C, 45.95; H, 4.5; N, 3.65.  $\text{C}_{27}\text{H}_{32}\text{IN}_2\text{PPT}\cdot 0.6\text{C}_6\text{H}_6$  requires C, 45.9; H, 4.45; N,

3.65%).  $m/z$  (FAB): 721 ( $M - \text{CH}_4$ ) and 595 ( $M - \text{MeI}$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{C}} - 6.0$  [1 C, d,  $^2J(\text{PC})$  3.3,  $^1J(\text{PtC})$  616, PtMe], 8.1 [1 C, s,  $^1J(\text{PtC})$  590, PtMe], 26.6 [1 C, d,  $^1J(\text{PC})$  27.5,  $\text{CH}_2$ ], 27.7 (3 C, s,  $\text{CMe}_3$ ), 41.7 [1 C, d,  $^3J(\text{PC})$  3.5,  $\text{CMe}_3$ ], 124.5 [1 C, s, Pt-aryl], 130.2 [1 C, s,  $J(\text{PtC})$  41.6, Pt-aryl], 131.5 [1 C, d,  $J(\text{PC})$  6.7, Pt-aryl], 133.3 [1 C, d,  $J(\text{PC})$  8.5, Pt-aryl], 139.7 (1 C, s,  $\text{C}^1$ ), 162.4 [1 C, d,  $^2J(\text{PC})$  145.4,  $\text{C}^2$ ], 171.6 (1 C, s,  $\text{Bu}^1\text{C}=\text{N}$ ) and 177.4 [1 C, d,  $^3J(\text{PC})$  5.8,  $^2J(\text{PtC})$  47.5,  $\text{HC}=\text{N}$ ].

$\text{mer,cis-}[\text{PtBrMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$  **6b**. A solution containing the dimethylplatinum(II) complex **3e** (28 mg, 0.032 mmol) in  $\text{C}_6\text{D}_6$  (0.5  $\text{cm}^3$ ) was heated at 75 °C for 16 h. The solution was concentrated to a low volume and ethanol (1  $\text{cm}^3$ ) added to give the dimethylplatinum(IV) complex **6b** as pale yellow microcrystals (14 mg, 50%) (Found: C, 47.15; H, 4.5; N, 4.0.  $\text{C}_{27}\text{H}_{32}\text{BrN}_2\text{PPT}$  requires C, 46.95; H, 4.65; N, 4.05%).  $m/z$  (FAB): 675 ( $M - \text{Me}$ ) and 595 ( $M - \text{MeBr}$ ).

$\text{mer,cis-}[\text{PtIme}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{Cl-6})\}]$  **6c**. A solution containing the methylplatinum(II) complex **5d** (20 mg, 0.031 mmol) and MeI (0.1  $\text{cm}^3$ ) in  $\text{C}_6\text{H}_6$  (1  $\text{cm}^3$ ) was put aside for 2 h. The solution was concentrated to a low volume and methanol (*ca.* 1  $\text{cm}^3$ ) added to give the dimethylplatinum(IV) complex **6c** as pale yellow microcrystals (12 mg, 52%).  $m/z$  (FAB): 644 ( $M - \text{I}$ ) and 629 ( $M - \text{MeI}$ ).

$[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{NH})\}]$  **8a**. The dimethylplatinum(II) complex **8a** was prepared in a similar manner to the analogous dimethylplatinum(II) complex **3a** in 80% yield, after a reaction time of 10 min (Found: C, 49.7; H, 5.35; N, 6.9.  $\text{C}_{25}\text{H}_{32}\text{N}_3\text{PPT}$  requires C, 50.0; H, 5.35; N, 7.0%). IR (KBr disc):  $\nu(\text{N}-\text{H})$  3160  $\text{cm}^{-1}$ .

$[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{S})\}]$  **8b**. The dimethylplatinum(II) complex **8b** was prepared in a similar manner to the analogous dimethylplatinum(II) complex **8a** in 77% yield (Found: C, 48.55; H, 5.0; N, 4.35.  $\text{C}_{25}\text{H}_{31}\text{N}_2\text{PPTS}$  requires C, 48.6; H, 5.05; N, 4.55%).  $m/z$  (FAB): 602 ( $M - \text{Me}$ ) and 586 ( $M - \text{Me} - \text{CH}_4$ ).

$[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{O})\}]$  **8c**. The dimethylplatinum(II) complex **8c** was prepared in a similar manner to the analogous dimethylplatinum(II) complex **8a** in 70% yield (Found: C, 49.85; H, 5.15; N, 4.55.  $\text{C}_{25}\text{H}_{31}\text{N}_2\text{OPPT}$  requires C, 49.9; H, 5.2; N, 4.65%).  $m/z$  (FAB): 586 ( $M - \text{Me}$ ) and 570 ( $M - \text{Me} - \text{CH}_4$ ).

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{N})\}]$  **9**. A solution containing the azine phosphine **7a** (45 mg, 0.12 mmol) and  $[\text{PtMe}_2(\text{cod})]$  (40 mg, 0.12 mmol) in benzene (1.5  $\text{cm}^3$ ) was heated at 50 °C for 10 min. The solvent was then removed and the residue triturated with ethanol to give the *N*-cyclo-metallated methylplatinum(II) complex **9** as orange microcrystals (57 mg, 81%) (Found: C, 49.85; H, 4.75; N, 6.9.  $\text{C}_{24}\text{H}_{28}\text{N}_3\text{PPT}$  requires C, 49.3; H, 4.85; N, 7.2%).  $m/z$  (EI): 584 ( $M^+$ ), 569 ( $M - \text{Me}$ ) and 527 ( $M - \text{Bu}^1$ ).

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_2\text{S})\}]$  **10a**. The cyclometallated methylplatinum(II) complex **10a** was prepared in a similar manner to the analogous methylplatinum(II) complex **5a**, after a reaction time of 24 h.  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{C}} - 20.1$  [1 C, d,  $^2J(\text{PC})$  5.0,  $^1J(\text{PtC})$  719, PtMe], 22.5 [1 C, d,  $^1J(\text{PC})$  24.0,  $\text{CH}_2$ ], 27.8 (3 C, s,  $\text{CMe}_3$ ), 40.5 [1 C, d,  $^3J(\text{PC})$  3.2,  $\text{CMe}_3$ ], 133.3 [1 C, d,  $J(\text{PC})$  6.8,  $\text{C}^4$  or  $\text{C}^5$ ], 135.9 [1 C, d,  $J(\text{PC})$  10.6,  $J(\text{PtC})$  74.2,  $\text{C}^4$  or  $\text{C}^5$ ], 140.8 [1 C, d,  $^3J(\text{PC})$  6.1,  $\text{C}^2$ ], 167.4 [1 C, d,  $^3J(\text{PC})$  4.3,  $^2J(\text{PtC})$  54.0,  $\text{HC}=\text{N}$ ], 168.1 (1 C, s,  $\text{Bu}^1\text{C}=\text{N}$ ) and 184.4 [1 C, d,  $^2J(\text{PC})$  128.7,  $\text{C}^3$ ].

$[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_2\text{O})\}]$  **10b**. The cyclometallated methylplatinum(II) complex **10b** was prepared in a similar manner to the analogous methylplatinum(II) complex **5a**, after a reaction time of 36 h.  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{C}} - 22.6$  [1 C, d,  $^2J(\text{PC})$  4.7,  $^1J(\text{PtC})$  706, PtMe], 22.2 [1 C, d,  $^1J(\text{PC})$  24.2,  $\text{CH}_2$ ], 27.8 (3 C, s,  $\text{CMe}_3$ ), 40.5 [1 C, d,  $^3J(\text{PC})$  3.1,  $\text{CMe}_3$ ], 117.5 [1 C, d,  $^3J(\text{PC})$  6.4,  $^2J(\text{PtC})$  118.2,  $\text{C}^4$ ],

145.3 (1 C, s,  $\text{C}^2$ ), 149.5 [1 C, d,  $^4J(\text{PC})$  7.2,  $^3J(\text{PtC})$  43.8,  $\text{C}^5$ ], 159.0 [1 C, d,  $^3J(\text{PC})$  2.4,  $^2J(\text{PtC})$  36.8,  $\text{HC}=\text{N}$ ], 164.3 [1 C, d,  $^2J(\text{PC})$  135.6,  $\text{C}^3$ ] and 167.3 [1 C, d,  $^2J(\text{PC})$  2.6,  $\text{Bu}^1\text{C}=\text{N}$ ].

$\text{mer,cis-}[\text{PtIme}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_2\text{S})\}]$  **11a**. The dimethylplatinum(IV) complex **10a** was prepared in a similar manner to the analogous dimethylplatinum(IV) complex **6c**.

$\text{mer,cis-}[\text{PtIme}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_2\text{O})\}]$  **11b**. The dimethylplatinum(IV) complex **11b** was prepared in a similar manner to the analogous dimethylplatinum(IV) complex **6c**.

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