

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 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 $[\text{PtMe}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{Cl}-6)\}]$ **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}P - $\{^1\text{H}\}$ and some ^{13}C - $\{^1\text{H}\}$ NMR data have been obtained.

In a previous paper¹ 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 $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CHR}$ ^{1–7} 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),³ or aryl fluoride coordination (RF→Ru)⁴ with ruthenium(II), and also to promote

cyclometallation with iridium(I)⁵ or tungsten(0).⁶ 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 Siekman⁸ 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.^{9–15} 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.*,^{16,17} 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-

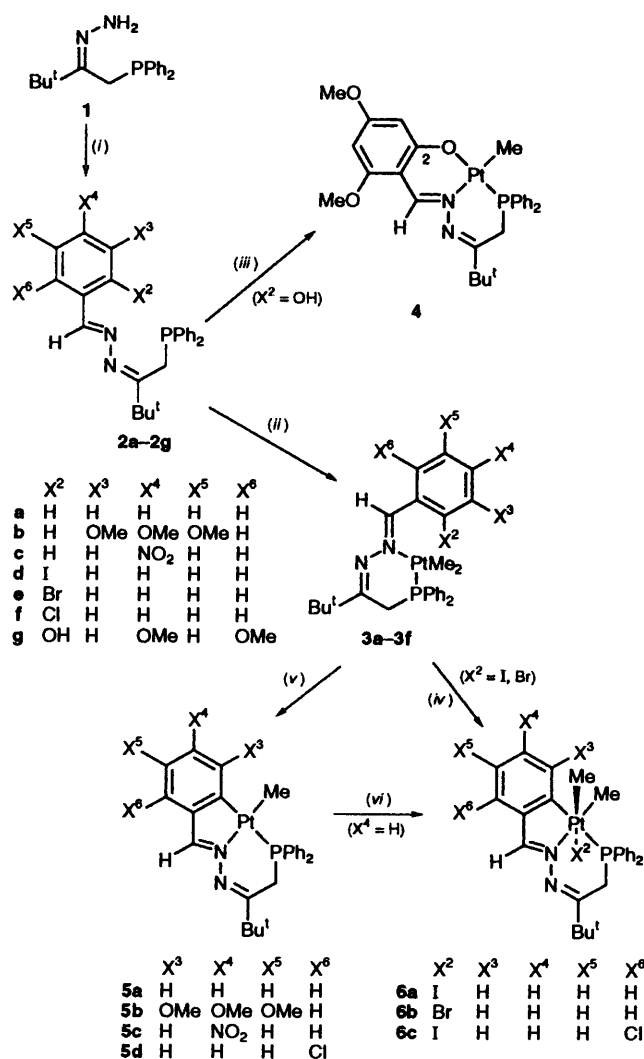
chemistry of this cyclometallated complex was⁴ not assigned from NMR data but molecular mechanics calculations suggested that the *mer,cis* complex was more stable than the *fac,cis* complex.¹⁷ We have been able to assign the geometries of all the complexes described herein from NMR data such as $J(\text{PC})$ and $^1J(\text{PtP})$ values. Other recent reports^{18–21} 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 CH_2Ph),^{17,19,20} (2- XC_6H_4)- $\text{CH}=\text{NCH}_2$ (2'- $\text{X}'\text{C}_6\text{H}_4$),¹⁹ $\text{C}_6\text{F}_5\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2$,^{16,18} and $\text{C}_6\text{F}_5\text{CH}=\text{NCH}_2$ (2- XC_6H_4),^{20,21} 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,^{22–26} 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}P - $\{^1\text{H}\}$ NMR spectroscopy, only.¹⁷ The iodo-mixed azine phosphine **2d** was prepared *in situ*⁶ 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}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 $[\text{PtMe}_2(\text{cod})]$ ²⁷ (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**,² derived from benzaldehyde. The NMR data for **3a** in C_6D_6 are as follows: δ_{p} 31.1 with platinum-195 satellites [$^1J(\text{PtP})$ 2126 Hz], typical of a phosphorus *trans* to a methyl group^{2,27–29}; 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 δ 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^{2,27} whilst a resonance absorbing at ≈ 1.5 with $^2J(\text{PtH}) \approx 90$ Hz, was assigned to the PtMe *trans* to nitrogen.^{2,17–19}

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}P - $\{^1\text{H}\}$ NMR spectrum of **4** showed a singlet at δ 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.^{28,29} In the proton NMR spectrum of **4** the methylene protons were chemically equivalent and absorbed at δ 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 δ 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 δ_{p} 28.2 and $^1J(\text{PtP})$ 2226 Hz (the progress of the reaction was monitored by ^{31}P - $\{^1\text{H}\}$ NMR spectroscopy). The proton NMR spectrum showed a doublet with platinum-195 satellites at δ 1.69 [$^3J(\text{PH})$ 7.0 and $^2J(\text{PtH})$ 87.0 Hz] for the PtMe protons whereas the CH_2 protons absorbed at δ 2.88 with $^2J(\text{PH})$ 11.6 and $^3J(\text{PtH})$ 20.2 Hz. In the ^{13}C - $\{^1\text{H}\}$ NMR spectrum a doublet was observed at δ 171.5 with a large $^2J(\text{PC})$ value of 127.9 Hz for the quaternary carbon C², confirming that C² 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*- $[\text{PtPh}_2(\text{PEt}_3)_2]$,²³ *trans*- $[\text{PtPh}_2(\text{PEt}_3)_2]$,²³ $[\text{W}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$ ⁶ and $[\text{Ir}(\text{H})\text{Cl}(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$.^{5,30} 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 H⁶ 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^a [$^2J(\text{HH})$, $^cJ(\text{PH})$, $^dJ(\text{PtH})$, $^eJ(\text{PH})$, $^fJ(\text{PtH})$ and $^gJ(\text{PH})$]

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

^a Recorded at 100 MHz, chemical shifts are in ppm relative to SiMe_4 , J values are in Hz, solvent C_6D_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 PPh_2 group. $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra are recorded in C_6D_6 at 36.2 MHz, chemical shifts are in ppm relative to 85% H_3PO_4 , $^1J(\text{PtP})$ in Hz. ^b δ 3.73 (6 H, s, 2 \times OMe) and 3.87 (3 H, s, OMe). ^c δ 8.03 (2 H, d, $^3J(\text{HH})$ 8.6, H^3 and H^5). ^d In thf . ^e δ 3.79 (6 H, s, 2 \times OMe), 5.90 [1 H, d, $^4J(\text{HH})$ 2.2, H^3 or H^5] and 6.02 [1 H, d, $^4J(\text{HH})$ 2.2, H^3 or H^5]. ^f δ 3.49 (6 H, s, 2 \times OMe) and 3.78 (3 H, s, OMe). ^g δ 7.50 [2 H, d, $^3J(\text{HH})$ 8.6, H^2 and H^6] and 8.32 [2 H, d, $^3J(\text{HH})$ 8.6, H^3 and H^5]. ^h δ 3.20 (3 H, s, OMe), 3.31 (3 H, s, OMe), 5.81 [1 H, d, $^4J(\text{HH})$ 2.3, H^3 or H^5] and 6.53 [1 H, d, $^4J(\text{HH})$ 2.3, H^3 or H^5]. ⁱ δ 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, H^6]. ^j δ 6.09 (1 H, m, pyrrole-H), 6.41 (1 H, m, pyrrole-H) and 6.50 (1 H, m, pyrrole-H). ^k δ 6.69 (1 H, m, thiophene-H) and 7.13 (1 H, m, thiophene-H). ^l δ 6.40 (1 H, m, furan-H) and 6.50 (1 H, m, furan-H). ^m δ 6.69 [1 H, dd, $J(\text{HH})$ 2.7, 5.9, pyrrole-H] and 7.13 (2 H, m, pyrrole-H). ⁿ δ 6.45 [1 H, dd, $J(\text{HH})$ 3.8, 5.0, thiophene-H]. ^o δ 5.86 (1 H, m, furan-H). ^p δ 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 H^3 proton gave a doublet of doublets resonance with platinum-195 satellites at δ 9.17 [$^4J(\text{HH})$ 2.2, $^4J(\text{PH})$ 6.4 and $^3J(\text{PtH})$ 55.9 Hz].

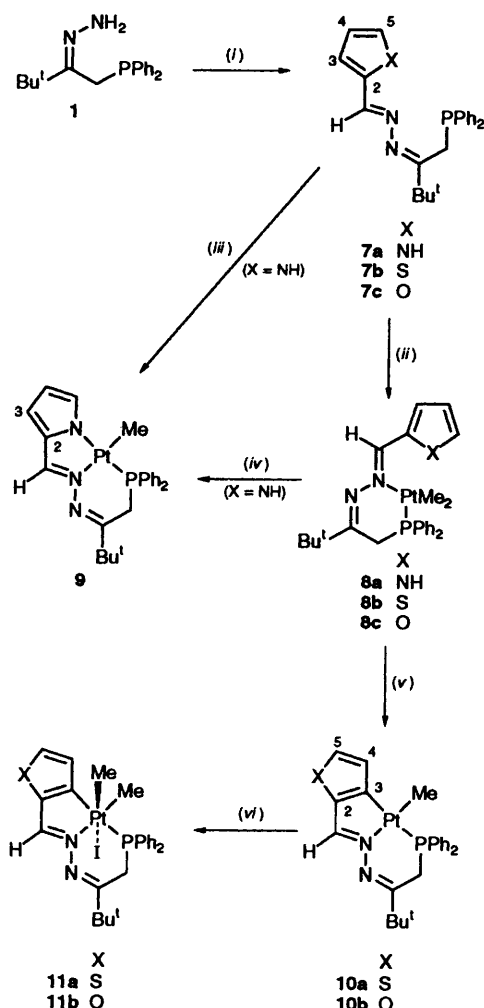
We have also investigated the tendency of C-X bonds ($X = \text{I}$, Br or Cl) to undergo oxidative addition to a platinum(II) centre using azine phosphines derived from 2-halogenobenzaldehydes. The factors which influence the oxidative addition of a C-X ($X = \text{I}$, Br, Cl, F or H) bond to a metal centre are complex and several mechanisms have been proposed.^{13-21,31,32} 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^{6,14-17} 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).^{5,14,19-21,32}

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.^{2,28,29,33} 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.* C², thus the ligand has retained the *mer* arrangement. The observed low δ_{C} value of $\delta 26.6$ for the methylene carbon is consistent with other values obtained for methylene carbons in six-membered rings.^{2,6,27} In the proton NMR spectrum, the occurrence of two chemically inequivalent platinum methyl resonances with $^2J(\text{PtH})$ values of ≈ 70 Hz suggests that one of the PtMe groups is *trans* to nitrogen^{2,18,19} and the other *trans* to iodine.^{2,34} Therefore, this iododimethylplatinum(IV) complex has the *mer,cis* geometry **6a**, confirming that the intramolecular oxidative addition of the C–I bond is *cis*^{16–21} whereas the intermolecular oxidative addition of MeI is *trans*.^{2,16,17} 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 $[\text{Ir}(\text{H})\text{Cl}(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{Cl}-6)\}]$ ⁵ whereas **2f** with $[\text{W}(\text{CO})_3(\text{NCEt}_3)_3]$ gave $[\text{WCl}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_4)\}]$ ⁶ 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.* C², whilst the resonances for the quaternary carbons C¹ and C⁶ 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*-PPh₂CH₂C(Bu^t)=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 CH₂ 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 C₆D₆ 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 CH₄. We have shown that a pyrrole N–H bond could undergo oxidative addition to a d⁸ iridium(III) centre to give the d⁶ iridium(III) hydride $[\text{Ir}(\text{H})\text{Cl}(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CH}(\text{C}_4\text{H}_3\text{N})\}]$.⁵ 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.^{2,35–39} 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 [δ_{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 (δ_{C} 135.9 for C⁴ or C⁵) 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 C³ is *trans* to phosphorus, in agreement with other $^2J(\text{P–Pt–C})$ values reported for similar metal complexes.^{25,26} 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 ^1H and ^{31}P of 89.5 and 36.2 MHz respectively), a JEOL FX-100 spectrometer (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^1H , ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively). Proton and ^{13}C chemical shifts are relative to SiMe_4 and ^{31}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}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.¹ 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).⁶ $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CH}(\text{Ph})$ **2a** was prepared in a similar manner to our published procedure¹ 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 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 ($M - \text{I}$) 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.² 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 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 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**.⁶ 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 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 cm^3) was heated at 50 °C for 10 min. The solution was then concentrated to a low volume (*ca.* 0.2 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 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, C_6D_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 CH_2], 27.8 (3 C, s, CMe_3), 40.6 [1 C, d, $^3J(\text{PC})$ 3.0, 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, C^1), 171.4 (1 C, s, $\text{Bu}^t\text{C}=\text{N}$), 171.5 [1 C, d, $^2J(\text{PC})$ 127.9, 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, C_6D_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, CH_2], 27.6 (3 C, s, CMe_3), 40.7 [1 C, d, $^3J(\text{PC})$ 2.7, 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, C^1 or C^6), 142.2 (1 C, s, C^1 or 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, 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 C_6H_6 (0.5 cm^3) was put aside for 4 h. The solution was concentrated to a low volume and methanol (*ca.* 1 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 ($M - CH_4$) and 595 ($M - MeI$). ^{13}C - $\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta_C -6.0$ [1 C, d, $^2J(PC)$ 3.3, $^1J(PtC)$ 616, PtMe], 8.1 [1 C, s, $^1J(PtC)$ 590, PtMe], 26.6 [1 C, d, $^1J(PC)$ 27.5, CH_2], 27.7 (3 C, s, CMe_3), 41.7 [1 C, d, $^3J(PC)$ 3.5, CMe_3], 124.5 [1 C, s, Pt-aryl], 130.2 [1 C, s, $J(PtC)$ 41.6, Pt-aryl], 131.5 [1 C, d, $J(PC)$ 6.7, Pt-aryl], 133.3 [1 C, d, $J(PC)$ 8.5, Pt-aryl], 139.7 (1 C, s, C^1), 162.4 [1 C, d, $^2J(PC)$ 145.4, C^2], 171.6 (1 C, s, $Bu^1C=N$) and 177.4 [1 C, d, $^3J(PC)$ 5.8, $^2J(PtC)$ 47.5, $HC=N$].

mer,cis - $[PtBrMe_2\{PPh_2CH_2C(Bu^1)=N-N=CH(C_6H_4)\}]$ **6b**. A solution containing the dimethylplatinum(II) complex **3e** (28 mg, 0.032 mmol) in C_6D_6 (0.5 cm^3) was heated at 75 °C for 16 h. The solution was concentrated to a low volume and ethanol (1 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. $C_{27}H_{32}BrN_2Ppt$ requires C, 46.95; H, 4.65; N, 4.05%). m/z (FAB): 675 ($M - Me$) and 595 ($M - MeBr$).

mer,cis - $[PtIme_2\{PPh_2CH_2C(Bu^1)=N-N=CH(C_6H_4Cl-6)\}]$ **6c**. A solution containing the methylplatinum(II) complex **5d** (20 mg, 0.031 mmol) and MeI (0.1 cm^3) in C_6H_6 (1 cm^3) was put aside for 2 h. The solution was concentrated to a low volume and methanol (*ca.* 1 cm^3) added to give the dimethylplatinum(IV) complex **6c** as pale yellow microcrystals (12 mg, 52%). m/z (FAB): 644 ($M - I$) and 629 ($M - MeI$).

$[PtMe_2\{PPh_2CH_2C(Bu^1)=N-N=CH(C_4H_3NH)\}]$ **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. $C_{25}H_{32}N_3Ppt$ requires C, 50.0; H, 5.35; N, 7.0%). IR (KBr disc): $\nu(N-H)$ 3160 cm^{-1} .

$[PtMe_2\{PPh_2CH_2C(Bu^1)=N-N=CH(C_4H_3S)\}]$ **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. $C_{25}H_{31}N_2PptS$ requires C, 48.6; H, 5.05; N, 4.55%). m/z (FAB): 602 ($M - Me$) and 586 ($M - Me - CH_4$).

$[PtMe_2\{PPh_2CH_2C(Bu^1)=N-N=CH(C_4H_3O)\}]$ **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. $C_{25}H_{31}N_2OPpt$ requires C, 49.9; H, 5.2; N, 4.65%). m/z (FAB): 586 ($M - Me$) and 570 ($M - Me - CH_4$).

$[PtMe\{PPh_2CH_2C(Bu^1)=N-N=CH(C_4H_3N)\}]$ **9**. A solution containing the azine phosphine **7a** (45 mg, 0.12 mmol) and $[PtMe_2(cod)]$ (40 mg, 0.12 mmol) in benzene (1.5 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. $C_{24}H_{28}N_3Ppt$ requires C, 49.3; H, 4.85; N, 7.2%). m/z (EI): 584 (M^+), 569 ($M - Me$) and 527 ($M - Bu^1$).

$[PtMe\{PPh_2CH_2C(Bu^1)=N-N=CH(C_4H_2S)\}]$ **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}C - $\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta_C -20.1$ [1 C, d, $^2J(PC)$ 5.0, $^1J(PtC)$ 719, PtMe], 22.5 [1 C, d, $^1J(PC)$ 24.0, CH_2], 27.8 (3 C, s, CMe_3), 40.5 [1 C, d, $^3J(PC)$ 3.2, CMe_3], 133.3 [1 C, d, $J(PC)$ 6.8, C^4 or C^5], 135.9 [1 C, d, $J(PC)$ 10.6, $J(PtC)$ 74.2, C^4 or C^5], 140.8 [1 C, d, $^3J(PC)$ 6.1, C^2], 167.4 [1 C, d, $^3J(PC)$ 4.3, $^2J(PtC)$ 54.0, $HC=N$], 168.1 (1 C, s, $Bu^1C=N$) and 184.4 [1 C, d, $^2J(PC)$ 128.7, C^3].

$[PtMe\{PPh_2CH_2C(Bu^1)=N-N=CH(C_4H_2O)\}]$ **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}C - $\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta_C -22.6$ [1 C, d, $^2J(PC)$ 4.7, $^1J(PtC)$ 706, PtMe], 22.2 [1 C, d, $^1J(PC)$ 24.2, CH_2], 27.8 (3 C, s, CMe_3), 40.5 [1 C, d, $^3J(PC)$ 3.1, CMe_3], 117.5 [1 C, d, $^3J(PC)$ 6.4, $^2J(PtC)$ 118.2, C^4],

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

mer,cis - $[PtIme_2\{PPh_2CH_2C(Bu^1)=N-N=CH(C_4H_2S)\}]$ **11a**. The dimethylplatinum(IV) complex **10a** was prepared in a similar manner to the analogous dimethylplatinum(IV) complex **6c**.

mer,cis - $[PtIme_2\{PPh_2CH_2C(Bu^1)=N-N=CH(C_4H_2O)\}]$ **11b**. The dimethylplatinum(IV) complex **11b** was prepared in a similar manner to the analogous dimethylplatinum(IV) complex **6c**.

Acknowledgements

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

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Received 2nd September 1994; Paper 4/05358C