Cyclometallation of Azine Phosphines of Type *Z,E*-$PPh_2CH_2C(Bu^t)=N-N=CHR$ (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*-$PPh_2CH_2C(Bu^t)=NNH_2$ **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*-$PPh_2CH_2C(Bu^t)=N-N=CHR$ [R = Ph **2a**, $C_6H_2(OMe)_3$-3,4,5 **2b**, $C_6H_4NO_2$-4 **2c**, C_6H_4I-2 **2d**, C_6H_4Br-2 **2e**, C_6H_4Cl-2 **2f** or $C_6H_2(OH\text{-}2)(OMe)_2$-4,6 **2g**]. The azines **2a**–**2f** reacted with $[PtMe_2(cod)]$ (cod = cycloocta-1,5-diene) at 20 °C to give dimethylplatinum(II) complexes $[PtMe_2\{PPh_2CH_2C(Bu^t)=N-N=CHR\}]$ **3a**–**3f** respectively, containing six-membered chelate rings. Treatment of **2g** with $[PtMe_2(cod)]$ effected O–H bond fission to give the *O*-cyclometallated methylplatinum(II) complex $[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH[C_6H_2O(OMe)_2\text{-}4,6]\}]$ **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 $[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4)\}]$ **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*-$[PtIMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4)\}]$ **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*-$[PtBrMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4)\}]$ **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 $[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_3Cl\text{-}6)\}]$ **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 $[PtMe_2(cod)]$ 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 $[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH(C_4H_3N)\}]$ **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 $[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH(C_4H_2X)\}]$ (X = S **10a** or O **10b**), which oxidatively added MeI to give the iododimethylplatinum(IV) complexes *mer,cis*-$[PtIMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH(C_4H_2X)\}]$ (X = S **11a** or O **11b**), respectively. Proton, ^{31}P-$\{^1H\}$ and some ^{13}C-$\{^1H\}$ NMR data have been obtained.

In a previous paper[1] we described the synthesis of a new phosphino hydrazone *Z*-$PPh_2CH_2C(Bu^t)=NNH_2$ **1** from the corresponding phosphino dimethylhydrazone *Z*-$PPh_2CH_2C(Bu^t)=NNMe_2$ 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 $PPh_2CH_2C(Bu^t)=N-N=CHR$[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 co-ordination (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.

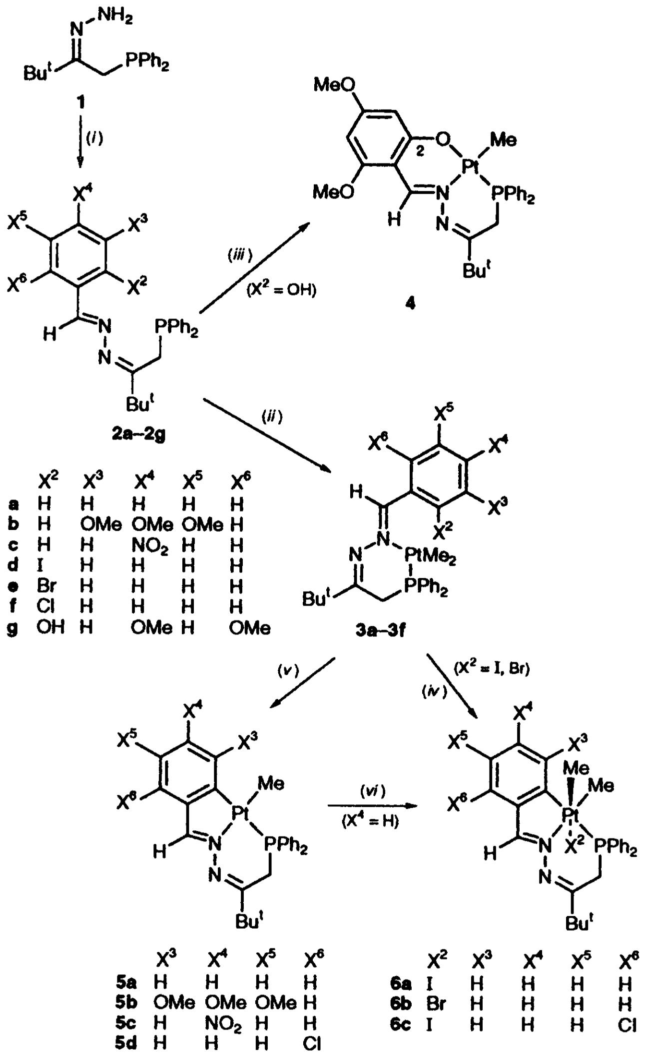
In 1965, Cope and Siekman[8] reported the first example of cyclometallation (or orthometallation) involving aryl C–H bond fission by platinum(II) with the complex $[\{PtCl(C_6H_4N=N\text{-}Ph)\}_2]$ derived from azobenzene. Since then many examples of cyclometallation have been reported involving aryl 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-$XC_6H_4CH=NCH_2CH_2NMe_2$ with $[\{PtMe_2(\mu\text{-}SMe_2)\}_2]$ to give $[Pt(X)Me_2(C_6H_4CH=NCH_2CH_2NMe_2)]$. The stereochemistry of this cyclometallated complex was 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(PC) and ^1J(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-$XC_6H_4CH{=}NR$ (R = Ph or CH_2Ph),[17,19,20] (2-XC_6H_4)-$CH{=}NCH_2$(2′-$X'C_6H_4$),[19] $C_6F_5CH{=}NCH_2CH_2NMe_2$[16,18] and $C_6F_5CH{=}NCH_2$(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-{^1H} 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-{^1H} NMR spectroscopy and by mass spectrometry.

The phosphino hydrazone *Z*-$PPh_2CH_2C(Bu^t){=}NNH_2$ **1** readily condensed with a range of benzaldehyde derivatives (RCHO) to give mixed azine phosphines of type *Z,E*-$PPh_2CH_2C(Bu^t){=}N{-}N{=}CHR$ [R = Ph **2a**, $C_6H_2(OMe)_3$-3,4,5 **2b**, $C_6H_4NO_2$-4 **2c**, C_6H_4I-2 **2d**, C_6H_4Br-2 **2e**, C_6H_4Cl-2 **2f** or C_6H_2(OH-2)$(OMe)_2$-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 δ −14.2. The azine phosphines **2a**–**2f** displaced cod from the labile $[PtMe_2(cod)]$[27] (cod = cycloocta-1,5-diene) at 20 °C to give yellow dimethylplatinum(II) complexes of type $[PtMe_2\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CHR\}]$ **3a**–**3f**, containing six-membered chelate rings. We have previously described the dimethylplatinum(II) complex $[PtMe_2\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CHPh\}]$ **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(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(HH) 12.6 and ^2J(PH) 10.7 Hz, for each proton; the imine proton C*H*=N is at δ 8.40 with platinum-195 satellites [^3J(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 [$^2J(PtH) \approx 70$ Hz] was assigned to the PtMe *trans* to phosphorus[2,27] whilst a resonance absorbing at ≈ 1.5 with $^2J(PtH) \approx 90$ Hz, was assigned to the PtMe *trans* to nitrogen.[2,17–19]

Treatment of $[PtMe_2(cod)]$ in benzene with the azine **2g**, derived from 4,6-dimethoxysalicylaldehyde, 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-{^1H} NMR spectrum of **4** showed a singlet at δ 22.9 with platinum-195 satellites [^1J(PtP) 4599 Hz]; the large value of ^1J(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(PH) 13.7 and ^3J(PtH) 48.4 Hz whilst the PtMe protons were at δ 1.20 with ^3J(PH) 2.7 and ^2J(PtH) 69.0 Hz.



	X^2	X^3	X^4	X^5	X^6
a	H	H	H	H	H
b	H	OMe	OMe	OMe	H
c	H	H	NO_2	H	H
d	I	H	H	H	H
e	Br	H	H	H	H
f	Cl	H	H	H	H
g	OH	H	OMe	H	OMe

	X^3	X^4	X^5	X^6
5a	H	H	H	H
5b	OMe	OMe	OMe	H
5c	H	NO_2	H	H
5d	H	H	H	Cl

	X^2	X^3	X^4	X^5	X^6
6a	I	H	H	H	H
6b	Br	H	H	H	H
6c	I	H	H	H	Cl

Scheme 1 (*i*) RCHO; (*ii*) $[PtMe_2(cod)]$, 20 °C; (*iii*) $[PtMe_2(cod)]$, 50 °C, 10 min, $-CH_4$; (*iv*) for **6a**, 20 °C, 4 h; for **6b**, heat, 75 °C, 16 h; (*v*) heat, 100 °C, $-CH_4$; (*vi*) MeI

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(PtP) 2226 Hz (the progress of the reaction was monitored by ^{31}P-{^1H} NMR spectroscopy). The proton NMR spectrum showed a doublet with platinum-195 satellites at δ 1.69 [^3J(PH) 7.0 and ^2J(PtH) 87.0 Hz] for the PtMe protons whereas the CH_2 protons absorbed at δ 2.88 with ^2J(PH) 11.6 and ^3J(PtH) 20.2 Hz. In the ^{13}C-{^1H} NMR spectrum a doublet was observed at δ 171.5 with a large ^2J(PC) value of 127.9 Hz for the quaternary carbon C^2, confirming that C^2 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*-$[PtPh_2(PEt_3)_2]$,[23] *trans*-$[PtPh_2(PEt_3)_2]$,[23] $[WI(CO)_3\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4)\}]$[6] and $[Ir(H)Cl(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4)\}]$.[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 H^6 proton showed coupling to phosphorus [^5J(PH) 1.6 Hz] and to platinum-195 [^4J(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 $^{31}P-\{^1H\}$ NMR data[a] [[b] ^2J(HH), [c] ^2J(PH), [d] ^2J(PtH), [e] ^3J(PH), [f] ^3J(PtH) and [g] ^4J(PH)]

Complex	δ(Bu^t)	δ(CH_2)	δ(CH=N)	δ(PtMe)	δ_P	^1J(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(PH) 1.0]		−9.2	
2c[i]	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
4[n]	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

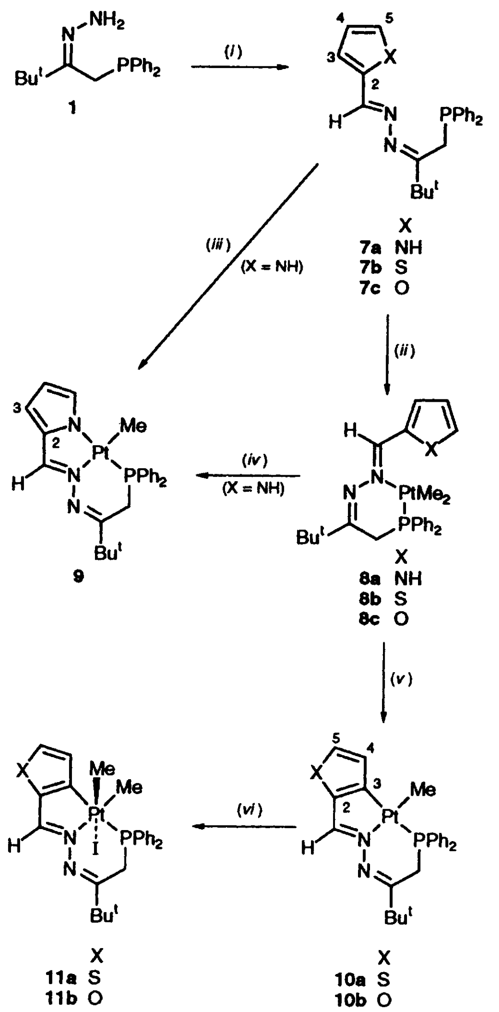
[a] Recorded at 100 MHz, chemical shifts are in ppm relative to $SiMe_4$, J values are in Hz, solvent C_6D_6 unless otherwise stated; some of the heterocyclic ring protons of compounds **7b**, **7c**, **8b**, **8c**, **9**, **10a**, **10b**, **11a** and **11b** were obscured by phenyl protons of the PPh_2 group. $^{31}P-\{^1H\}$ NMR spectra are recorded in C_6D_6 at 36.2 MHz, chemical shifts are in ppm relative to 85% H_3PO_4, ^1J(PtP) in Hz. [h] δ 3.73 (6 H, s, 2 × OMe) and 3.87 (3 H, s, OMe). [i] δ 8.03 (2 H, d, ^3J(HH) 8.6, H^3 and H^5). [j] In thf. [k] δ 3.79 (6 H, s, 2 × OMe), 5.90 [1 H, d, ^4J(HH) 2.2, H^3 or H^5] and 6.02 [1 H, d, ^4J(HH) 2.2, H^3 or H^5]. [l] δ 3.49 (6 H, s, 2 × OMe) and 3.78 (3 H, s, OMe). [m] δ 7.50 [2 H, d, ^3J(HH) 8.6, H^2 and H^6] and 8.32 [2 H, d, ^3J(HH) 8.6, H^3 and H^5]. [n] δ 3.20 (3 H, s, OMe), 3.31 (3 H, s, OMe), 5.81 [1 H, d, ^4J(HH) 2.3, H^3 or H^5] and 6.53 [1 H, d, ^4J(HH) 2.3, H^3 or H^5]. [o] 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(PH) 1.6, ^4J(PtH) 6.7, H^6]. [p] δ 9.17 [1 H, dd, ^4J(HH) 2.2, ^4J(PH) 6.4, ^3J(PtH) 55.9, H^3]. [q] δ 8.21 [1 H, m, ^3J(HH) 7.0, ^4J(HH) 1.1, ^4J(PH) 6.4, ^3J(PtH) 49.4, H^3] at 400 MHz. [r] δ 6.09 (1 H, m, pyrrole-H), 6.41 (1 H, m, pyrrole-H) and 6.50 (1 H, m, pyrrole-H). [s] δ 6.69 (1 H, m, thiophene-H) and 7.13 (1 H, m, thiophene-H). [t] δ 6.40 (1 H, m, furan-H) and 6.50 (1 H, m, furan-H). [u] δ 6.69 [1 H, dd, J(HH) 2.7, 5.9, pyrrole-H] and 7.13 (2 H, m, pyrrole-H). [v] δ 6.45 [1 H, dd, J(HH) 3.8, 5.0, thiophene-H). [w] δ 5.86 (1 H, m, furan-H). [x] δ 6.63 [1 H, m, J(HH) 1.6, 3.8, J(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(HH) 2.2, ^4J(PH) 6.4 and ^3J(PtH) 55.9 Hz].

We have also investigted the tendency of C–X bonds (X = 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 = 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 (C–I > C–Br > C–Cl > C–H > 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 = 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(PtP) value of 1466 Hz is typical for platinum(IV) complexes.[2,28,29,33] In the ^{13}C-{^{1}H} NMR spectrum, the resonances for the platinum methyl carbons appeared as a doublet with platinum-195 satellites at δ −6.0 [^{2}J(PC) 3.3 and ^{1}J(PtC) 616 Hz] and a singlet at δ 8.1 with ^{1}J(PtC) 590 Hz, indicating that both carbons are *cis* to phosphorus. The resonance at δ 162.4 with a large ^{2}J(PC) value of 145.4 Hz is assigned to the quaternary carbon directly bonded to platinum, *i.e.* C^{2}, thus the ligand has retained the *mer* arrangement. The observed low δ_C value of δ 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 ^{2}J(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 ^{1}J(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 [IrCl(CO)$_2$(NH$_2$C$_6$H$_4$Me-*p*)] underwent C–H bond fission to give the iridium(III) hydride [Ir(H)Cl(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_6$H$_3$Cl-6)}][5] whereas **2f** with [W(CO)$_3$(NCEt)$_3$] gave [WCl(CO)$_3${PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_6$H$_4$)}][6] *via* a C–Cl bond fission. In the ^{13}C-{^{1}H} NMR spectrum of **5d**, the carbon-13 resonance at δ 173.8 [^{2}J(PC) 128.1 and ^{1}J(PtC) 961 Hz] was assigned to the quaternary aryl carbon directly bonded to platinum, *i.e.* C^{2}, whilst the resonances for the quaternary carbons C^{1} and C^{6} were at δ 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$_2$CH$_2$C(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 δ ≈ −9 and the proton resonances for the CH$_2$ groups as doublets at δ ≈ 3.5 with ^{2}J(PH) ≈ 2.8 Hz. Treatment of **7a**–**7c** with [PtMe$_2$(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$_6$D$_6$ 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 [PtMe$_2$(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$_4$. We have shown that a pyrrole N–H bond could undergo oxidative addition to a d^{8} iridium(I) centre to give the d^{6} iridium(III) hydride [Ir(H)Cl(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_4$H$_3$N)}].[5] The large ^{1}J(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 ^{1}J(PtP) 2470 Hz] which we formulate as the cyclometallated methylplatinum(II) complex **10a**. In the ^{13}C-{^{1}H} NMR spectrum of **10a**, one of the thienyl carbons (δ_C 135.9 for C^{4} or C^{5}) is coupled to both phosphorus [*J*(PC) 10.6 Hz] and platinum-195 [*J*(PtC) 74.2 Hz] indicating that the thienyl moiety is directly bonded to platinum. Moreover, the large ^{2}J(PC) value of 128.7 Hz suggests that the C^{3} is *trans* to phosphorus, in agreement with other ^{2}J(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.



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

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}H and ^{31}P of 89.5 and 36.2 MHz respectively), a JEOL FX-100 spectrometer (operating frequencies for ^{1}H and ^{31}P of 99.5 and 40.25 MHz respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^{1}H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively). Proton and ^{13}C chemical shifts are relative to $\mathrm{SiMe_4}$ 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*-$\mathrm{PPh_2CH_2C(Bu^t)=NNH_2}$ **1** was prepared according to our published procedure.[1] The azine *Z*,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4I\text{-}2)}$ **2d** was prepared *in situ* by treating 2-iodobenzaldehyde with *Z*-$\mathrm{PPh_2CH_2C(Bu^t)=NNH_2}$ **1** in dry tetrahydrofuran (thf)[6] *Z*,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH(Ph)}$ **2a** was prepared in a similar manner to our published procedure[1] using ethanol instead of benzene as the solvent [yield 77%; *m*/*z* (EI): 409 (*M* − Bu^t)].

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

Z,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH[C_6H_2(OMe)_3\text{-}3,4,5]}$ **2b**. Yield 86% (Found: C, 70.3; H, 7.1; N, 5.95. $\mathrm{C_{28}H_{33}N_2O_3P}$ requires C, 70.55; H, 7.0; N, 5.85%). *m*/*z* (EI): 419 (*M* − Bu^t).

Z,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4NO_2\text{-}4)}$ **2c**. Yield 79% (Found: C, 70.0; H, 5.9; N, 10.0. $\mathrm{C_{25}H_{26}N_3O_2P}$ requires C, 69.6; H, 6.05; N, 9.75%). *m*/*z* (EI): 374 (*M* − Bu^t).

Z,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4Br\text{-}2)}$ **2e**. Yield 68% (Found: C, 64.35; H, 5.7; N, 6.05. $\mathrm{C_{25}H_{26}BrN_2P}$ requires C, 64.5; H, 5.6; N, 6.0%). *m*/*z* (EI): 409 and 407 (*M* − Bu^t).

Z,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4Cl\text{-}2)}$ **2f**. Yield 69% (Found: C, 70.9; H, 6.2; Cl, 8.5; N, 6.5. $\mathrm{C_{25}H_{26}ClN_2P}$ requires C, 71.3; H, 6.2; Cl, 8.4; N, 6.65%). *m*/*z* (EI): 420 (M^+) and 363 (*M* − Bu^t).

Z,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH[C_6H_4(OH\text{-}2)(OMe)_2\text{-}4,6]}$ **2g**. Yield 82% (Found: C, 69.95; H, 6.8; N, 6.1. $\mathrm{C_{27}H_{31}N_2O_3P}$ requires C, 70.1; H, 6.75; N, 6.05%). *m*/*z* (EI): 405 (*M* − Bu^t).

Z,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH(C_4H_3NH)}$ **7a**. Yield 81% (Found: C, 73.7; H, 7.1; N, 11.2. $\mathrm{C_{23}H_{26}N_3P}$ requires C, 73.55; H, 7.0; N, 11.2%). IR (KBr disc) ν(N–H) 3405 cm^{-1}. *m*/*z* (EI): 318 (*M* − Bu^t).

Z,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH(C_4H_3S)}$ **7b**. Yield 77% (Found: C, 70.15; H, 6.35; N, 6.95. $\mathrm{C_{23}H_{25}N_2PS}$ requires C, 70.4; H, 6.4; N, 7.15%). *m*/*z* (EI): 391 (*M* − 1) and 335 (*M* − Bu^t).

Z,*E*-$\mathrm{PPh_2CH_2C(Bu^t)=N-N=CH(C_4H_3O)}$ **7c**. Yield 77% (Found: C, 73.4; H, 6.8; N, 7.4. $\mathrm{C_{23}H_{25}N_2PO}$ requires C, 73.4; H, 6.7; N, 7.45%). *m*/*z* (EI): 319 (*M* − Bu^t).

Preparation of Platinum Complexes.—Complex $\mathrm{[PtMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH(Ph)\}]}$ **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**.

$\mathrm{[PtMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH[C_6H_2(OMe)_3\text{-}3,4,5]\}]}$ **3b**. Yield 78% (Found: C, 51.55; H, 5.7; N, 4.15. $\mathrm{C_{30}H_{39}N_2O_3PPt}$ requires C, 51.35; H, 5.6; N, 4.0%). *m*/*z* (FAB): 670 (*M* − Bu^t).

$\mathrm{[PtMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4NO_2\text{-}2)\}]}$ **3c**. Yield 69% (Found: C, 49.35; H, 5.05; N, 6.35. $\mathrm{C_{27}H_{32}N_3PO_2Pt}$ requires C, 49.4; H, 4.9; N, 6.3%). *m*/*z* (FAB): 631 (*M* − Me) and 615 (*M* − Me − Bu^t). IR (KBr disc): ν(NO$_2$) 1345 and 1520 cm^{-1}.

$\mathrm{[PtMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4I\text{-}2)\}]}$ **3d**. A solution containing *Z*-$\mathrm{PPh_2CH_2C(Bu^t)=NNH_2}$ (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}P-{^{1}H} NMR spectrum of the resulting pale yellow solution showed a singlet at δ −10.1 which we assigned to the azine phosphine **2d**.[6] To this solution $\mathrm{[PtMe_2(cod)]}$ (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. $\mathrm{C_{27}H_{32}IN_2PPt}$ requires C, 43.95; H, 4.35; N, 3.8%). *m*/*z* (FAB): 721 (*M* − CH$_4$) and 595 (*M* − MeI).

$\mathrm{[PtMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4Br\text{-}2)\}]}$ **3e**. Yield 60 mg, 72% (Found: C, 46.65; H, 4.6; N, 3.85. $\mathrm{C_{27}H_{32}BrN_2PPt}$ requires C, 46.95; H, 4.65; N, 4.05%). *m*/*z* (FAB): 674 (*M* − CH$_4$).

$\mathrm{[PtMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4Cl\text{-}2)\}]}$ **3f**. Yield 65% (Found: C, 49.85; H, 4.75; Cl, 5.55; N, 4.3. $\mathrm{C_{27}H_{32}ClN_2PPt}$ requires C, 50.2; H, 5.0; Cl, 5.5; N, 4.35%). *m*/*z* (FAB): 631 (*M* − Me) and 615 (*M* − Me − Bu^t).

$\mathrm{[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH[C_6H_2O(OMe)_2\text{-}4,6]\}]}$ **4**. A solution containing the phosphine **2g** (56 mg, 0.12 mmol) and $\mathrm{[PtMe_2(cod)]}$ (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. $\mathrm{C_{28}H_{33}N_2O_3PPt}$ requires C, 50.55; H, 5.0; N, 4.1%). *m*/*z* (FAB): 671 (M^+) and 656 (*M* − Me).

$\mathrm{[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4)\}]}$ **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}C-{^{1}H}NMR (100.6 MHz, $\mathrm{C_6D_6}$): δ_C −15.6 [1 C, d, ^2J(PC) 4.7, ^1J(PtC) 752, PtMe], 22.8 [1 C, d, ^1J(PC) 23.2 CH$_2$], 27.8 (3 C, s, CMe$_3$), 40.6 [1 C, d, ^3J(PC) 3.0, *C*Me$_3$], 124.7 (1 C, s, Pt-aryl), 129.0 [1 C, d, *J*(PC) 5.3, *J*(PtC) 34.2, Pt-aryl], 132.3 [1 C, d, *J*(PC) 7.0, Pt-aryl], 132.6 (1 C, s, Pt-aryl), 145.3 (1 C, s, C^1), 171.4 (1 C, s, Bu^t*C*=N), 171.5 [1 C, d, ^2J(PC) 127.9, C^2] and 177.4 [1 C, d, ^3J(PC) 5.5, ^2J(PtC) 76.2, HC=N].

$\mathrm{[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH[C_6H(OMe)_3\text{-}3,4,5]\}]}$ **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.

$\mathrm{[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_3NO_2\text{-}4)\}]}$ **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.

$\mathrm{[PtMe\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_3Cl\text{-}2)\}]}$ **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}C-{^{1}H} NMR (100.6 MHz, $\mathrm{C_6D_6}$): δ_C −14.8 [1 C, d, ^2J(PC) 4.7, ^1J(PtC) 741, PtMe], 22.6 [1 C, d, ^1J(PC) 23.7, CH$_2$], 27.6 (3 C, s, C*Me*$_3$), 40.7 [1 C, d, ^3J(PC) 2.7, *C*Me$_3$], 125.2 (1 C, s, Pt-aryl), 130.0 (1 C, s, Pt-aryl), 134.0 [1 C, d, *J*(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, Bu^t*C*=N), 173.8 [1 C, d, ^2J(PC) 128.1, ^1J(PtC) 961, C^2] and 174.3 [1 C, d, ^3J(PC) 4.9, ^2J(PtC) 73.0, HC=N].

mer,*cis*-$\mathrm{[PtIMe_2\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6H_4)\}]}$ **6a**. A solution containing the dimethylplatinum(II) complex **3d** (24 mg, 0.032 mmol) in $\mathrm{C_6H_6}$ (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. $\mathrm{C_{27}H_{32}IN_2PPt\cdot 0.6C_6H_6}$ requires C, 45.9; H, 4.45; N, 3.65%). *m/z* (FAB): 721 (*M* − CH_4) and 595 (*M* − MeI). ^{13}C-{^{1}H} NMR (100.6 MHz, C_6D_6): δ_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, C*Me*$_3$), 41.7 [1 C, d, ^3J(PC) 3.5, *C*Me$_3$], 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^t*C*=N) and 177.4 [1 C, d, ^3J(PC) 5.8, ^2J(PtC) 47.5, HC=N].

mer,cis-[PtBrMe$_2${PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_6$H$_4$)}] **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$_2$CH$_2$C(Bu^t)=N–N=CH(C$_6$H$_4$Cl-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$_2$CH$_2$C(Bu^t)=N–N=CH(C$_4$H$_3$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. $C_{25}H_{32}N_3PPt$ requires C, 50.0; H, 5.35; N, 7.0%). IR (KBr disc): ν(N–H) 3160 cm^{-1}.

[PtMe$_2${PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_4$H$_3$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. $C_{25}H_{31}N_2PPtS$ 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$_2$CH$_2$C(Bu^t)=N–N=CH(C$_4$H$_3$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. $C_{25}H_{31}N_2OPPt$ requires C, 49.9; H, 5.2; N, 4.65%). *m/z* (FAB): 586 (*M* − Me) and 570 (*M* − Me − CH_4).

[PtMe{PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_4$H$_3$N)}] **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*-cyclometallated 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^t).

[PtMe{PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_4$H$_2$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}C-{^{1}H} NMR (100.6 MHz, C_6D_6): δ_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, C*Me*$_3$), 40.5 [1 C, d, ^3J(PC) 3.2, *C*Me$_3$], 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^t*C*=N) and 184.4 [1 C, d, ^2J(PC) 128.7, C^3].

[PtMe{PPh$_2$CH$_2$C(Bu^t)=N–N=CH(C$_4$H$_2$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}C-{^{1}H} NMR (100.6 MHz, C_6D_6): δ_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, C*Me*$_3$), 40.5 [1 C, d, ^3J(PC) 3.1, *C*Me$_3$], 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^t*C*=N].

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

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

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