Reactions of an Azine Diphosphine with Platinum(II) and Palladium(II) and the Formation of a Novel Heterocyclic Diphosphine Ligand. Crystal Structure of $[PdI_2\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh\}]$†

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The azine diphosphine *Z,Z*-$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$ **I** was treated with $[PtMe_2(cod)]$ (cod = cycloocta-1,5-diene) to give the dimethylplatinum(II) complex $[PtMe_2\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ **1a** containing a nine-membered chelate ring with an *E,Z* configuration for the bidentate azine diphosphine ligand. This complex undergoes oxidative addition with MeI to give the *fac*-trimethylplatinum(IV) complex $[PtMe_3I\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ **2**. The corresponding platinum(II) complexes $[PtX_2\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ ($X = C{\equiv}CC_6H_4Me$-*p* **1b** or Cl **1c**) were also prepared. Treatment of *trans*-$[PtCl_2(NCR)_2]$ (R = Me or Ph) with **I** gave a hexanuclear species *trans*-$[\{PtCl_2[PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2]\}_6]$ **3a** in which the azine diphosphine is acting as a bridging group and is still symmetrical, *i.e.* the configuration is still *Z,Z*. The palladium analogue **3b** was made by treating $[PdCl_2(NCPh)_2]$ or $Na_2[PdCl_4]$ with **I** but might only be binuclear. This complex was unstable in hot chloroform and at 60 °C (30 min) was completely converted into the salt $[PdCl\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]Cl$ **4a** in which the azine diphosphine is tridentate with *E,Z* configuration and mutually *trans*-co-ordinated phosphorus donors and one of the azine nitrogens is co-ordinated. Treatment of $[PtCl_2(cod)]$ with **I** and addition of NH_4PF_6 gave the platinum salt $[PtCl\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]PF_6$ **4c**; $[PtI\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]I$ **4d** was also prepared. On prolonged (8 d) heating in chloroform solution the bridged complex **3b** was quantitatively converted into the novel and very stable heterocyclic complex $[PdCl_2\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh\}]$ **5a** with loss of a molecule of benzene. Treatment of **5a** with LiBr or NaI gave the corresponding dibromide **5b** or diiodide **5c** complexes. The crystal structure of **5c** has been determined. The corresponding platinum complexes $[PtX_2\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh\}]$ **5d**–**5f** (X = Cl, Br or I) were also prepared and treatment of the dichloro complex with MgMeI gave the dimethyl complex **5g**. Treatment of this dimethyl complex with an excess of MeI gave $[PtMe_3I\{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh\}]$ **6**. Proton, ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR and infrared data are given.

We have shown that the azine $MeC(Bu^t){=}N{-}N{=}C(Bu^t)Me$, readily made from *tert*-butyl methyl ketone (pinacolone) and hydrazine, can be dilithiated with $LiBu^n$ and the resultant dianion treated with PPh_2Cl to give the novel diphosphine *Z,Z*-$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$ **I**.[1] This diphosphine cannot chelate through both phosphorus atoms, because of the *Z,Z* configuration, but the energy barrier to rotation around C=N bonds in azines is low[2] and we showed that, when treated with derivatives of type $[M(CO)_4(nbd)]$ (nbd = norbornadiene; M = Cr, Mo or W), derivatives of the type $[M(CO)_4\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ are formed in which the corresponding *E,Z*-azine diphosphine is chelated to the metal in a nine-membered ring.[1] The structure of the tetracarbonylchromium(0) complex has been determined by X-ray crystallography and the nine-membered chelate ring confirmed.[3] These tetracarbonyl complexes, on heating, lose carbon monoxide to give *fac*-tricarbonyl derivatives in which the *E,Z*-diphosphine acts as a tridentate ligand, through two P and one N atom.[1] We now show that the *Z,Z*-diphosphine can act as a bridging ligand to Pt^{II} or Pd^{II} giving polynuclear complexes with very large chelate rings; or when converted into the *E,Z* isomer it can give nine-membered bidentate chelate rings, or act as a tridentate *P,P′,N* ligand in cationic species; and finally it can be converted into an unusual heterocyclic diphosphine ligand by intramolecular attack of an azine nitrogen on phosphorus with loss of a molecule of benzene. The crystal structure of one example of the latter novel type of heterocyclic diphosphine ring system has been determined.

Results and Discussion

We reasoned that, in order to get a stable nine-membered chelate ring at Pt with the *E,Z*-azine diphosphine, the other ligands on Pt should not be ionizable and have a preference to be mutually *cis*. We therefore treated $[PtMe_2(cod)]$[4] (cod = cycloocta-1,5-diene) with compound **I** at 20 °C in benzene solution and isolated the hoped for dimethyl complex **1a** in 70% yield. This complex, along with all the new complexes described in this paper, was fully characterized and the reactions of the azine diphosphine **I** are summarized in Scheme 1. Preparative details, elemental analyses, infrared and some carbon-13 NMR data are in the Experimental section; phosphorus-31 NMR data are in Table 1; proton NMR data (Table 2) were determined by recording both the ^1H and ^1H-$\{^{31}P\}$ spectra. In particular for complex **1a**, the values of $^1J(PtP)$, *viz.* 1980 and 1975 Hz, are typical for a tertiary phosphine *trans* to a methyl group[5,6] and

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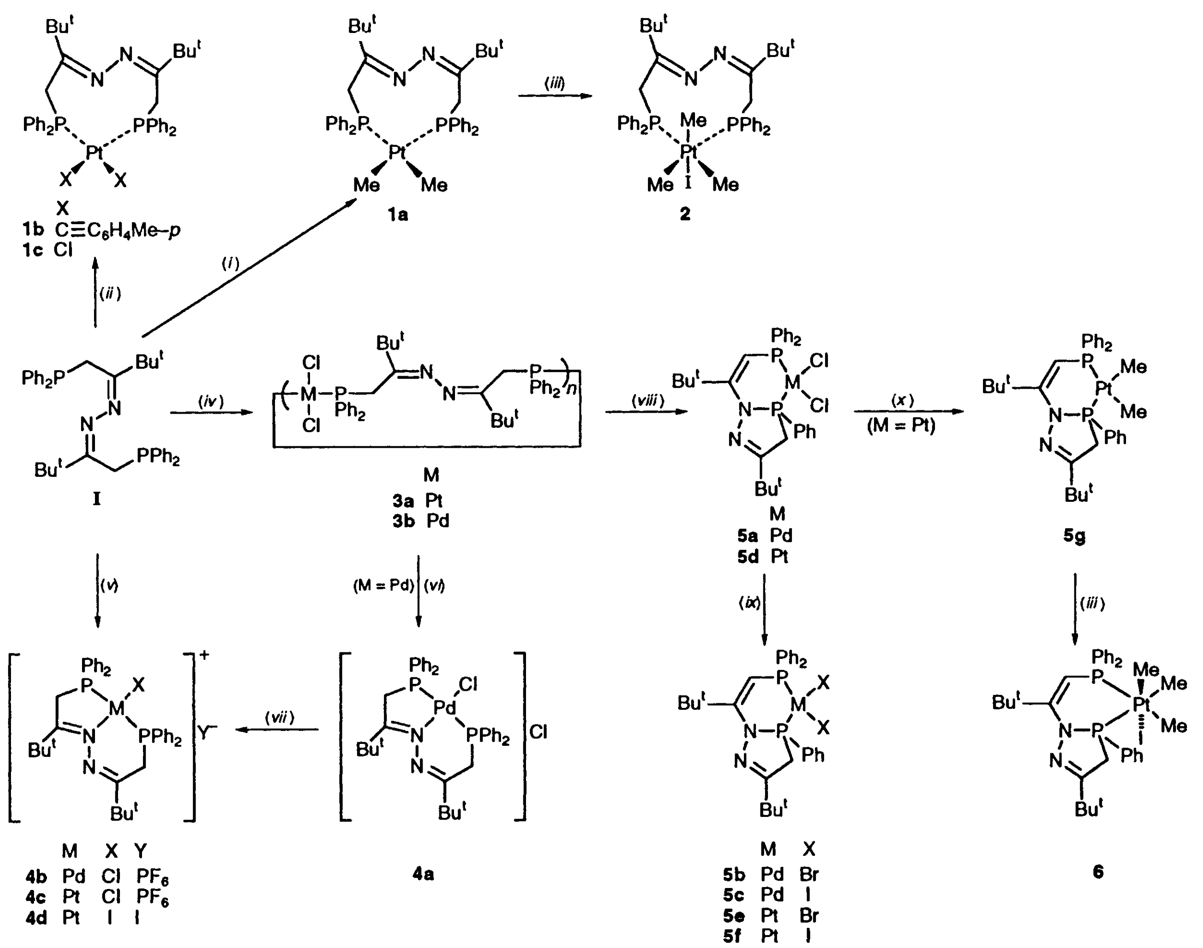
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 (*i*) $[PtMe_2(cod)]$; (*ii*) $[Pt(C{\equiv}CC_6H_4Me\text{-}p)_2(cod)]$ or $[PtCl_2(cod)]$–acetone; (*iii*) MeI; (*iv*) $[PtCl_2(NCMe)_2]$ or $[PdCl_2(NCPh)_2]$; (*v*) For **4c** $[PtCl_2(cod)]$–NH_4PF_6, for **4d** $[PtI_2(cod)]$; (*vi*) heat, $CHCl_3$, 30 min; (*vii*) for **4b** NH_4PF_6; (*viii*) heat, $CHCl_3$, 8 d; (*ix*) LiBr or NaI; (*x*) MgMeI

Table 1 $^{31}P\text{-}\{^1H\}$ NMR data[a]

Compound	δ(P_A)	δ(P_B)	^2J(PP)	^1J(PtP_A)	^1J(PtP_B)
I	−14.4				
1a[b]	21.5	19.7	15	1980	1975
1b[b]	14.9	6.8	18	2487	2500
1c	17.1	−1.9	11	4132	4118
2[b]	11.0	−1.3	11	1351	1160
3a	10.4			2558	
3b	16.0				
4a	57.6	40.8	510		
4b[c]	54.4	41.7	505		
4c[d]	49.1	39.3	459	2803	2549
4d[e]	53.8	41.3	444	2725	2447
5a	77.4	2.8	15		
5b	74.6	0.9	13		
5c	69.2	−4.1	20		
5d	52.7	−17.7	31	3775	3207
5e	51.9	−17.9	28	3699	3159
5f	49.9	−20.2	24	3511	3030
5g[b]	71.8	−13.4	33	1923	1734
6[b]	41.6	−41.6	29	1165	1135

[a] Recorded at 36.2 MHz, chemical shifts (δ) in ppm relative to 85% H_3PO_4, solvent $CDCl_3$ unless otherwise stated, ^1J(PtP) in Hz. [b] In C_6D_6. [c] In CD_3COCD_3. [d] In CD_2Cl_2. [e] In MeCN–C_6D_6.

the value of ^2J(PP) (15 Hz) is typical for mutually *cis*-phosphine ligands.[5,6] This nine-membered ring complex was stable for several days in benzene solution at 20 °C and the ring survived oxidative addition of methyl iodide to the platinum so that the *fac*-trimethylplatinum(IV) complex **2** was isolated in 73% yield, and fully characterized. We also made the di-*p*-tolylacetylide complex **1b** by treating $[Pt(C{\equiv}CC_6H_4Me\text{-}p)_2(cod)]$[7] with **I** at 20 °C for 1 h in benzene solution. We subsequently found that we could make the dichloro complex $[PtCl_2\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ **1c**, containing a nine-membered chelate ring, and which was surprisingly stable, by treating $[PtCl_2(cod)]$[8,9] with the azine diphosphine **I** in refluxing acetone for 1.5 h; the isolated yield was 32%. A feature of the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1c** was the large values of ^1J(PtP), *viz.* 4132 and 4118 Hz, see Table 1, indicative of phosphorus *trans* to chlorine;[6] the value of ^2J(PP) of 11 Hz indicated mutually *cis* phosphines. When $[PtCl_2(cod)]$ was treated with **I** in dichloromethane a mixture was formed, but in acetone as reaction solvent some insoluble platinum complexes formed and were filtered off whilst the filtrate contained **1c** and what was probably the platinum analogue of the salt **4a** (see below). Complex **1c** was readily separated from this salt by recrystallization from CH_2Cl_2–MeOH, in which the salt was soluble.

As reported previously,[1] when we treated a Group VI metal carbonyl derivative $[M(CO)_4(nbd)]$ with the *Z*,*Z*-diphosphine **I**, chelates of the corresponding *E*,*Z*-diphosphine were formed but we thought it possible that attack by **I** on a more labile metal centre such as Pt^{II} or Pd^{II} could give complexes in which **I** was acting as a bridging ligand through two phosphorus atoms. We therefore treated *trans*-$[PtCl_2(NCMe)_2]$[10] with **I** in dichloromethane at 20 °C and obtained in high yield (90%) a yellow product of the hoped-for composition $[\{PtCl_2(diphosphine)\}_n]$ with a single phosphorus resonance and satellites, ^1J(PtP) = 2558 Hz, a value typical of two mutually *trans*-

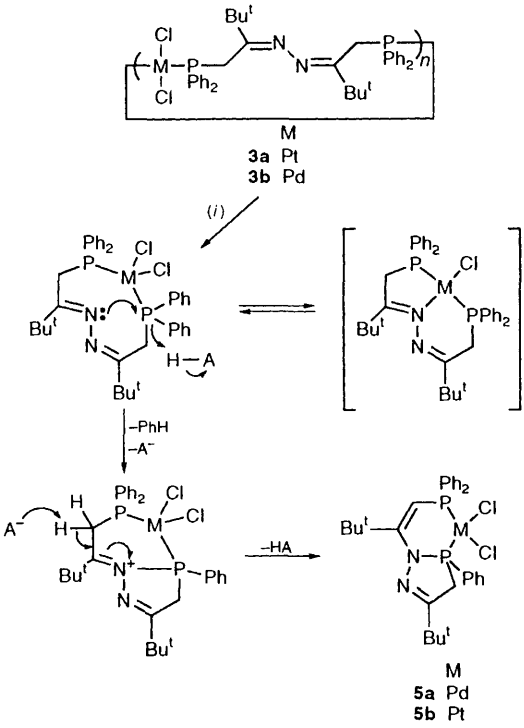
Table 2 Proton NMR data^a

Compound	δ(Bu^t)	δ(CH_2)/δ(CH=)	Others
I	0.90 (18 H, s)	3.26 (4 H, d, 3.9,^{b} CH_2)	
1a^{c,d}	0.77 (9 H, s)	3.02 (2 H, d, 11.6,^{b} 18.5,^{e} CH_2)	0.99 (3 H, dd, 7.3,^{f} 9.0,^{f} 69.1,^{g} PtMe)
	1.45 (9 H, s)	3.48 (2 H, d, 8.2,^{b} 17.7,^{e} CH_2)	1.16 (3 H, dd, 7.3,^{f} 9.2,^{f} 69.5,^{g} PtMe)
1b^d	0.79 (9 H, s)	3.07 (2 H, d, 12.7,^{b} 26.5,^{e} CH_2)	1.97 (6 H, s, 2 × C_6H_4*Me*)
	1.28 (9 H, s)	3.41 (2 H, d, 10.2,^{b} 18.8,^{e} CH_2)	
1c	1.13 (9 H, s)	2.68 (2 H, d, 12.9,^{b} 30.0,^{e} CH_2)	
	1.17 (9 H, s)	3.35 (2 H, d, 12.2,^{b} 36.9,^{e} CH_2)	
2^{c,d}	1.11 (9 H, s)	3.06 (1 H, dd, 13.7,^{h} 12.6,^{b} CH_2)	0.76 (3 H, dd, 6.6,^{f} 8.9,^{f} 54.0,^{g} PtMe)
	1.56 (9 H, s)	3.86 (1 H, dd, 18.5,^{h} 5.5,^{b} CH_2)	0.92 (3 H, t, 7.0,^{f} 56.1,^{g} PtMe)
		4.22 (2 H, m, 13.4,^{h} 18.5,^{h} CH_2)	1.64 (3 H, t, 6.7,^{f} 70.4,^{g} PtMe)
3a	0.76 (18 H, s)	4.02 (4 H, s, br, CH_2)	
3b	0.79 (18 H, s)	3.96 (4 H, s, br, CH_2)	
4a	0.75 (9 H, s)	3.97 (2 H, d, br, 12.0,^{b} CH_2)	
	1.32 (9 H, s)	4.79 (2 H, d, br, 7.6,^{b} CH_2)	
4b^i	0.79 (9 H, s)	3.24 (2 H, dd, 10.8,^{b} 2.5,^{j} CH_2)	
	1.23 (9 H, s)	4.16 (2 H, dd, 9.3,^{b} 3.9,^{j} CH_2)	
4c^i	0.80 (9 H, s)	3.40 (2 H, dd, 10.2,^{b} 0.8,^{j}, 31.0,^{g} CH_2)	
	1.26 (9 H, s)	4.05 (2 H, dd, 8.3,^{b} 2.7,^{j} CH_2)	
4d^k	0.76 (9 H, s)	3.66 (2 H, dd, 11.5,^{b} 1.7,^{j} 28.1,^{g} CH_2)	
	1.24 (9 H, s)	4.47 (2 H, dd, 9.2,^{b} 3.4,^{j} CH_2)	
5a^c	1.26 (9 H, s)	3.51 (1 H, dd, 20.3,^{h} 9.7,^{b} CH_2)	
	1.47 (9 H, s)	4.55 (1 H, ddd, 20.2,^{h} 8.2,^{b} 0.8,^{d} CH_2)^l	
		4.99 (1 H, d, 8.8,^{j} CH=)^l	
5b	1.27 (9 H, s)	3.57 (1 H, dd, 20.3,^{h} 9.5,^{b} CH_2)	
	1.47 (9 H, s)	4.69 (1 H, dd, 20.3,^{h} 7.6,^{b} CH_2)	
		5.05 (1 H, d, 9.0,^{j} CH=)	
5c	1.27 (9 H, s)	3.62 (1 H, dd, 20.0,^{h} 10.0,^{b} CH_2)	
	1.46 (9 H, s)	4.82 (1 H, dd, 20.0,^{h} 6.1,^{b} CH_2)	
		5.15 (1 H, d, 8.5,^{j} CH=)	
5d^c	1.27 (9 H, s)	3.54 (1 H, dd, 20.1,^{h} 8.6,^{b} 22.2,^{e} CH_2)	
	1.39 (9 H, s)	4.52 (1 H, dd, 20.1,^{h} 8.3,^{b} 40.7,^{e} CH_2)	
		5.12 (1 H, dd, 3.0,^{b} 3.7,^{j} 105.5,^{e}, CH=)^l	
5e	1.20 (9 H, s)	3.54 (1 H, dd, 20.0,^{h} 8.6,^{b} 22.4,^{e} CH_2)	
	1.32 (9 H, s)	4.54 (1 H, dd, 20.0,^{h} 8.0,^{b} 41.4,^{e} CH_2)	
		5.08 (1 H, t, 3.7,^{b,j} 102.6,^{e} CH=)	
5f	1.27 (9 H, s)	3.71 (1 H, dd, 19.8,^{h} 9.2,^{b} 19.8,^{e} CH_2)	
	1.35 (9 H, s)	4.68 (1 H, dd, 19.8,^{h} 7.3,^{b} 42.0,^{e} CH_2)	
		5.27 (1 H, t, 3.5,^{b,j} 93.4,^{e} CH=)	
5g^d	0.88 (9 H, s)	2.90 (1 H, dd, 19.1,^{h} 6.6,^{b} 8.8,^{e} CH_2)	1.41 (3 H, dd, 4.6,^{f} 6.8,^{f} 69.6,^{g} PtMe)
	1.31 (9 H, s)	3.39 (1 H, dd, 19.1,^{h} 2.2,^{b} 21.2,^{e} CH_2)	1.46 (3 H, dd, 4.4,^{f} 8.0,^{f} 70.0,^{g} PtMe)
		5.61 (1 H, t, 1.2,^{b,j} 35.1,^{e} CH=)	
6^d	0.84 (9 H, s)	2.70 (2 H, s, 5.2,^{e} CH_2)	0.98 (3 H, dd, 6.7,^{f} 8.0,^{f}, 67.4,^{g} PtMe)
	1.34 (9 H, s)	5.82 (1 H, dd, 1.0,^{b} 3.2,^{j} 9.7,^{e} CH=)	1.64 (3 H, dd, 7.1,^{f} 9.3,^{f} 57.6,^{g} PtMe)
			2.01 (3 H, t, 7.9,^{f} 60.0,^{g} PtMe)

^{a} Recorded at 100 MHz, chemical shifts (δ) are in ppm relative to $SiMe_4$, *J* in Hz, solvent $CDCl_3$ unless otherwise stated. ^{b} ^2J(PH). ^{c} Recorded at 400 MHz. ^{d} In C_6D_6. ^{e} ^3J(PtH). ^{f} ^3J(PH), ^{g} ^2J(PtH). ^{h} ^2J(HH) ^{i} In CD_2Cl_2. ^{j} ^4J(PH). ^{k} In CD_3CN. ^{l} Coupling to phosphorus was resolved by selective-decoupling experiments at 400 Mz.

bonded phosphine ligands in a complex of type *trans*-$[PtCl_2(phosphine)_2]$,[6,11] *i.e.* there were no unco-ordinated phosphorus atoms. In the proton spectrum there was only one type of Bu^t group and only one kind of CH_2 group, and in the infrared spectrum there was a very strong band at 340 cm^{-1} due to ν(Pt–Cl), typical of a mutually *trans* Cl–Pt–Cl moiety.[11–13] The product was sufficiently soluble in chloroform to measure its molecular weight at 4870, *i.e.* we suggest that the compound **3a** is a hexamer with a 54-atom ring but have been unable to grow crystals suitable for a crystal structure determination. We have previously described some binuclear complexes with bridging diphosphines including the crystal structures of 26- and 20-atom rings,[14,15] and also described the synthesis of a complex of type *trans*-$[\{PtCl_2[Bu^t_2PC{\equiv}C(CH_2)_5C{\equiv}CPBu^t_2]\}_n]$ in which '*n*' appears to be 6, *i.e.* with a 72-atom ring.[16] Treatment of *trans*-$[PtCl_2(NCPh)_2]$ with **I** gave the product **3a**, in 89% yield. Similarly, treatment of either *trans*-$[PdCl_2(NCPh)_2]$[17] or $Na_2[PdCl_4]$ with **I** gave a complex $[\{PdCl_2(diphosphine)\}_n]$, which gave a singlet phosphorus resonance in the NMR spectrum and a very strong band at 345 cm^{-1} in the infrared spectrum, typical of a mutually *trans* Cl–Pd–Cl moiety;[13] this palladium complex was slow to dissolve completely in chloroform and was probably at least partially converted into the salt **4a**, hence an attempt to measure its molecular weight was not successful. However, since the NMR data showed the azine diphosphine ligand to be symmetrical (Tables 1 and 2) it must therefore have at least an 18-atom ring. This complex **3b** was unstable in hot chloroform and on heating the solution to 60 °C for 30 min it was completely transformed into a yellow complex, characterized by an AB pattern in its $^{31}P-\{^1H\}$ spectrum; δ(P_A) 57.6 and δ(P_B) 40.8, ^2J(PP) = 510 Hz, the large value of the coupling constant indicating mutually *trans* phosphines.[6] This complex is formulated as the chloride salt **4a** and was readily converted into the corresponding hexafluorophosphate **4b** by treating it in methanol with ammonium hexafluorophosphate. The $^{13}C-\{^1H\}$ NMR spectrum of **4b** showed a doublet of doublets at δ 23.5, which we assign to the carbon of the CH_2 group in the six-membered ring, and a doublet of doublets at δ 41.0 which we assign to the CH_2 in the five-membered ring. A $^1H-^{13}C$ correlation spectroscopy (COSY) experiment established that the resonance at δ 41.0 is associated with the two hydrogens absorbing at δ 4.16 and the resonance at δ 23.5 is associated with the two hydrogens absorbing at δ 3.24. On shaking a deuteriodichloromethane solution of **4b** with D_2O in the presence of acid (HCO_2H) the hydrogens absorbing at δ 4.16 exchange immediately with deuterium whereas the other two (at δ 3.24) take several hours to exchange completely. Clearly, the CH_2 hydrogens in the five-membered ring will be much more activated to exchange than the ones in the six-membered ring. In extensive studies of azine diphosphines acting as tridentates with metals such as Cr, Mo, W, Ir and Pt we have found that protons in the CH_2 groups of the six-membered chelate rings give resonances at lower δ values than the ones in five-membered chelate rings, as do the carbon-13 resonances. Interestingly, in extensive work by Lindner *et al.*[18] with diphosphinemetal chelates, phosphorus-31 chemical shifts and ^1J(PtP) values are invariably higher for five than for six-membered chelate rings. When the corresponding platinum complex **3a** was heated in chloroform it gave a mixture of **1c** and the corresponding platinum salt analogous to **4a**, but on prolonged heating another product was formed; see below. However, a hexafluorophosphate salt **4c**, analogous to **4b**, was readily prepared by treating [$PtCl_2$(cod)] with **I** in hot chloroform and then extracting the product into methanol and adding ammonium hexafluorophosphate; this salt was fully characterized. An iodide salt **4d** was prepared by treating [PtI_2(cod)] with **I** and showed a large value of ^2J(PP) of 444 Hz, indicative of mutually *trans* phosphorus atoms.[6]

When complex **3b** in chloroform solution was heated for 8 d it was quantitatively converted into a single product **5a** characterized by an AX phosphorus NMR pattern, δ(P_A) 77.4 and δ(P_X) 2.8, ^2J(PP) = 15 Hz; this product was isolated in 82% yield as an extremely stable white solid with ν(Pd–Cl) 315 and 290 cm^{-1}, indicative of mutually *cis*-chloride ligands.[12] Treatment of this dichloride with lithium bromide or sodium iodide gave the corresponding dibromo-or diiodo-complexes, **5b** and **5c**, respectively. The crystal structure of the diiodide was determined and is shown in Fig. 1. It contains an unusual heterocyclic chelating diphosphine ligand formed by attack of an azine nitrogen on one of the phosphorus atoms, with loss of a molecule of benzene; the corresponding dichloro- and dibromo-complexes, from the elemental and spectroscopic data, clearly have corresponding structures **5a** and **5b**. When **3b** in deuteriochloroform was heated for several days, 1 mol of benzene gradually formed as the conversion into **5a** took place (proton NMR evidence). When a chloroform solution of the platinum hexamer **3a** was heated for 8 d at 60 °C it formed the very stable platinum complex **5d**, quantitatively (phosphorus-31 NMR evidence); this complex was isolated in 94% yield and fully characterized. It was converted into the corresponding dibromide **5e** or diiodide **5f** by treatment with lithium bromide or sodium iodide, respectively. It is possible that these very unusual and very stable complexes of type **5** are formed by attack by nitrogen on phosphorus, as depicted in Scheme 2, followed by take up of a proton, present in the chloroform solvent as *e.g.* ethanol (HA in Scheme 2). We also



Scheme 2 A possible mechanism for the conversion of complex **3** to **5**. (*i*) Heat, C=N bond isomerization

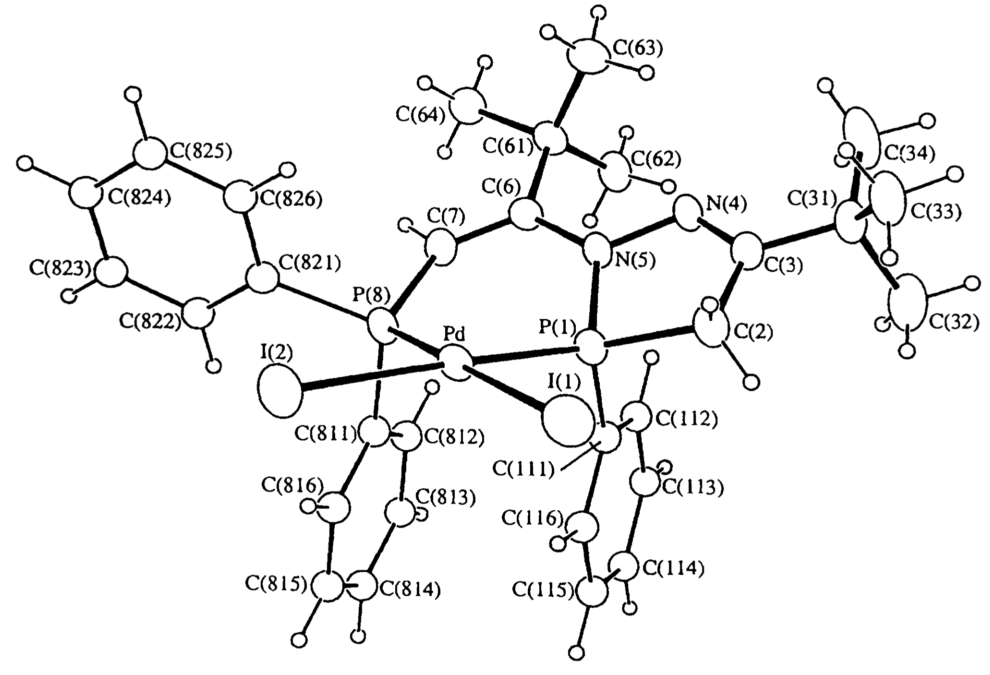


Fig. 1 An ORTEP[19] representation of the crystal and molecular structure of [PdI_2{$PPh_2CH=C(Bu^t)N–N=C(Bu^t)CH_2PPh$}] **5c**. For clarity phenyl carbon and all H atoms are shown as small circles of arbitrary radius; ellipses for all other atoms are at the 30% probability level

Table 3 Bond lengths (pm) and angles (°) for compound **5c** with estimated standard deviations (e.s.d.s) in parentheses

I(1)–Pd(9)	264.2(1)	I(2)–Pd(9)	264.6(1)
P(1)–Pd(9)	222.9(3)	P(8)–Pd(9)	226.9(3)
N(5)–P(1)	171.6(4)	C(2)–P(1)	182.0(5)
C(111)–P(1)	180.4(3)	C(7)–P(8)	178.0(5)
C(811)–P(8)	181.8(3)	C(821)–P(8)	182.0(3)
N(5)–N(4)	141.7(4)	C(3)–N(4)	127.8(4)
C(6)–N(5)	140.4(4)	C(3)–C(2)	150.5(6)
C(31)–C(3)	151.6(5)	C(32)–C(31)	154.2(6)
C(33)–C(31)	152.6(6)	C(34)–C(31)	152.3(6)
C(61)–C(6)	154.1(5)	C(7)–C(6)	135.0(4)
C(62)–C(61)	154.0(6)	C(63)–C(61)	154.6(6)
C(64)–C(61)	154.2(5)		
I(2)–Pd(9)–I(1)	91.5(1)	P(1)–Pd(9)–I(1)	89.9(1)
P(1)–Pd(9)–I(2)	176.7(1)	P(8)–Pd(9)–I(1)	173.6(1)
P(8)–Pd(9)–I(2)	93.6(1)	P(8)–Pd(9)–P(1)	84.8(1)
N(5)–P(1)–Pd(9)	116.4(2)	C(2)–P(1)–Pd(9)	122.3(2)
C(2)–P(1)–N(5)	90.8(2)	C(111)–P(1)–Pd(9)	113.8(2)
C(111)–P(1)–N(5)	104.1(2)	C(111)–P(1)–C(2)	106.1(2)
C(7)–P(8)–Pd(9)	114.7(2)	C(811)–P(8)–Pd(9)	106.6(2)
C(811)–P(8)–C(7)	109.9(2)	C(821)–P(8)–Pd(9)	120.4(2)
C(821)–P(8)–C(7)	99.9(2)	C(821)–P(8)–C(811)	104.8(2)
C(3)–N(4)–N(5)	112.1(3)	N(4)–N(5)–P(1)	113.6(2)
C(6)–N(5)–P(1)	126.1(3)	C(6)–N(5)–N(4)	120.2(3)
H(21)–C(2)–P(1)	110.9(2)	H(22)–C(2)–P(1)	111.0(2)
C(3)–C(2)–P(1)	103.6(3)	C(3)–C(2)–H(21)	111.0(3)
C(3)–C(2)–H(22)	110.9(3)	C(2)–C(3)–N(4)	118.0(3)
C(31)–C(3)–N(4)	120.7(3)	C(31)–C(3)–C(2)	121.3(3)
C(32)–C(31)–C(3)	107.9(3)	C(33)–C(31)–C(3)	109.0(3)
C(33)–C(31)–C(32)	109.3(3)	C(34)–C(31)–C(3)	111.1(3)
C(34)–C(31)–C(32)	110.5(4)	C(34)–C(31)–C(33)	109.0(4)
C(61)–C(6)–N(5)	117.5(3)	C(7)–C(6)–N(5)	121.0(3)
C(7)–C(6)–C(61)	121.6(3)	C(62)–C(61)–C(6)	109.3(3)
C(63)–C(61)–C(6)	111.5(3)	C(63)–C(61)–C(62)	112.0(3)
C(64)–C(61)–C(6)	110.5(3)	C(64)–C(61)–C(62)	107.5(3)
C(64)–C(61)–C(63)	106.0(3)	H(622)–C(62)–C(61)	114.4(2)
C(6)–C(7)–P(8)	132.6(2)	H(71)–C(7)–P(8)	113.7(2)
H(71)–C(7)–C(6)	113.6(2)		

Table 4 Atom coordinates (× 10^4) for compound **5c** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pd(9)	1742.1(2)	1506.2(1)	1843.9(1)
I(1)	−251.4(2)	2623.7(1)	1928.7(1)
I(2)	2220.3(2)	2001.3(1)	692.2(1)
P(1)	1295.9(7)	1021.9(4)	2790.2(3)
P(8)	3300.6(7)	452.6(4)	1830.8(3)
N(4)	2536(2)	1075(1)	3941(1)
N(5)	2742(2)	841(1)	3312(1)
C(2)	485(3)	1644(2)	3375(1)
C(3)	1375(3)	1465(2)	3979(1)
C(31)	934(3)	1757(2)	4613(1)
C(32)	−403(4)	1277(2)	4761(2)
C(33)	581(4)	2666(2)	4568(2)
C(34)	2121(4)	1628(3)	5132(2)
C(6)	4003(2)	451(2)	3173(1)
C(61)	5110(3)	273(2)	3729(1)
C(62)	4496(3)	−352(2)	4177(1)
C(63)	5596(3)	1066(2)	4078(2)
C(64)	6458(3)	−106(2)	3486(1)
C(7)	4219(3)	226(2)	2576(1)
C(111)	347(2)	64(1)	2757(1)
C(112)	656(2)	−543(1)	3209(1)
C(113)	−89(2)	−1280(1)	3172(1)
C(114)	−1142(2)	−1409(1)	2684(1)
C(115)	−1451(2)	−801(1)	2233(1)
C(116)	−707(2)	−65(1)	2269(1)
C(811)	2287(2)	−434(1)	1542(1)
C(812)	2331(2)	−1172(1)	1872(1)
C(813)	1519(2)	−1833(1)	1639(1)
C(814)	662(2)	−1757(1)	1076(1)
C(815)	618(2)	−1019(1)	746(1)
C(816)	1430(2)	−357(1)	979(1)
C(821)	4794(2)	503(1)	1340(1)
C(822)	5106(2)	−151(1)	953(1)
C(823)	6328(2)	−134(1)	625(1)
C(824)	7238(2)	537(1)	684(1)
C(825)	6926(2)	1192(1)	1071(1)
C(826)	5704(2)	1175(1)	1399(1)

converted the heterocyclic chelating diphosphine–platinum dichloride complex **5d** into the corresponding dimethyl complex **5g** by treating it with an excess of methylmagnesium iodide; **5g** was isolated in 68% yield and when treated with an excess of methyl iodide underwent oxidative addition to the trimethylplatinum(IV) complex **6** in 70% yield. The complexes **5a** and **5d** were also characterized by carbon-13 NMR spectroscopy.

Crystal Structure of the Heterocyclic Diphosphine Diiodide **5c**.—The crystal structure of this diiodide containing the novel type of diphosphine is shown in Fig. 1 with selected bond lengths and angles in Table 3 and atom coordinates, excluding hydrogen, in Table 4. The most important features are (*i*) one of the phenyls on phosphorus has been lost and (*ii*) a nitrogen–phosphorus bond has formed by attack of an azine-type nitrogen on phosphorus. The four atoms co-ordinated to palladium are essentially planar. The two palladium–iodide distances 264.2(1) and 264.6(1) pm are very similar to those found for other diphosphinepalladium diiodides.[20–22] The two palladium–phosphorus distances are significantly different, *viz.* 222.9(3) (P bonded to nitrogen and two carbons) and 226.9(3) pm (P bonded to three carbons). In the crystal structure of the hydrazone–diphosphine tungsten complex $[(OC)_4W\{PPh_2NHN{=}C(Ph)CH_2PPh_2\}]$[23] the P–W bond for the phosphorus bonded to three carbons is longer [251.3(2) pm] than that for the phosphorus bonded to two carbons and one nitrogen [249.7(1) pm], as found for **5c**.

Experimental

All the reactions were carried out in an atmosphere of dry nitrogen or dry argon. Tetrahydrofuran and benzene were distilled from sodium under argon immediately before use. Infrared spectra were recorded using a Perkin Elmer 257 grating spectrometer, NMR spectra using a JEOL FX-90Q (operating frequencies of ^1H and ^{31}P of 89.5 and 36.2 MHz respectively), a JEOL FX-100 (operating frequencies of ^1H and ^{31}P of 99.5 and 40.25 MHz respectively) or a Bruker AM400 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively). The ^1H and ^{13}C shifts are in ppm relative to tetramethylsilane, ^{31}P shifts are in ppm relative to 85% phosphoric acid and all coupling constants are in Hz. Mass spectra were recorded using a VG Autospec spectrometer with 8 kV acceleration. Molecular weights were determined on a Hitachi–Perkin Elmer model 115 apparatus in chloroform solution at 30 °C.

Preparations.—*cis*-$[PtMe_2\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}]$ **1a**. A solution containing $[PtMe_2(cod)]$ (0.24 g, 0.72 mmol) and the azine diphosphine **I** (0.41 g, 0.73 mmol) in benzene (8 cm^3) was put aside for 4.5 h. The solution was filtered and the filtrate concentrated to a low volume (*ca.* 0.5 cm^3) under reduced pressure, then triturated with methanol to give the required dimethyl complex **1a** as a pale yellow solid (0.40 g, 70%) (Found: C, 57.9; H, 6.3; N, 3.5. $C_{38}H_{48}N_2P_2Pt$ requires C, 57.8; H, 6.1; N, 3.55%). IR (KBr): ν(C=N) 1620m cm^{-1}. Mass spectrum (electron impact, EI): *m*/*z* 773 ($M - CH_4$); molecular weight 749 (calc. 790). ^{13}C-{^1H} NMR (100.6 MHz, C_6D_6): δ_C 7.2 [1C, dd, $^2J(PC)$ 107.8, 6.9, $^1J(PtC)$ 617, PtMe], 7.6 [1C, dd, $^2J(PC)$ 107.6, 6.5, $^1J(PtC)$ 626, PtMe], 26.9 [1C, dd, $^1J(PC)$ 16.8, $^3J(PC)$ 3.3, $^2J(PtC)$ 8.1, CH_2], 28.3 (3C, s, C*Me*$_3$), 28.8 (3C s, C*Me*$_3$), 31.4 [1C, d, $^1J(PC)$ 33.9, $^2J(PtC)$ 13.7, CH_2], 38.9 [1C, d, $^3J(PC)$ 2.0, *C*Me$_3$], 39.4 [1C, d, $^3J(PC)$ 2.9, *C*Me$_3$], 172.2 [1C, d, ^2J(PC) 2.1, C=N] and 175.2 [1C, d, ^2J(PC) 6.9 Hz, C=N].

cis-$[\mathrm{Pt(C{\equiv}CC_6H_4Me}\text{-}p)_2\{\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2}\}]$ **1b**. A solution containing $[\mathrm{Pt(C{\equiv}CC_6H_4Me}\text{-}p)_2\mathrm{(cod)}]$ (80 mg, 0.15 mmol) and the azine diphosphine **I** (85 mg, 0.15 mmol) in benzene (3 $\mathrm{cm^3}$) was put aside for 1 h. The solvent was then removed under pressure and the residue dissolved in methanol (*ca.* 0.5 $\mathrm{cm^3}$). The slow addition of water then precipitated the diacetylide complex **1b** as a white solid (88 mg, 59%) (Found: C, 64.75; H, 5.65; N, 2.65. $\mathrm{C_{54}H_{56}N_2P_2Pt{\cdot}MeOH}$ requires C, 64.65; H, 5.9; N, 2.75%). IR (KBr disc): ν(C=N) 1615 and ν(C≡C) 2120 $\mathrm{cm^{-1}}$.

cis-$[\mathrm{PtCl_2}\{\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2}\}]$ **1c**. A mixture of $[\mathrm{PtCl_2(cod)}]$ (40 mg, 0.11 mmol) and the azine diphosphine **I** (60 mg, 0.11 mmol) was heated under reflux in acetone (2 $\mathrm{cm^3}$) for 1.5 h. The resultant white precipitate was filtered off and the filtrate evaporated to dryness. The residue was crystallized from dichloromethane–methanol to give the dichloride **1c** as a white crystalline solid (29 mg, 32%) (Found: C, 51.75; H, 4.95; Cl, 8.7; N, 3.3. $\mathrm{C_{36}H_{42}Cl_2N_2P_2Pt}$ requires C, 52.05; H, 5.1; Cl, 8.55; N, 3.35%). IR (KBr disk): ν(C=N) 1620 and ν(Pt–Cl) 310 and 285 $\mathrm{cm^{-1}}$.

$[\mathrm{PtIMe_3}\{\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2}\}]$ **2**. An excess of methyl iodide (0.1 $\mathrm{cm^3}$) was added to a solution of **1a** (51 mg, 0.06 mmol) in benzene (0.5 $\mathrm{cm^3}$); the required product **2** crystallized as white prisms (44 mg, 73%) (Found: C, 50.05; H, 5.5; N, 2.85. $\mathrm{C_{39}H_{51}IN_2P_2Pt}$ requires C, 50.25; H, 5.5; N, 3.0%). IR(KBr disc): ν(C=N) 1605 $\mathrm{cm^{-1}}$. Mass spectrum (FAB): *m/z* 804 (*M* − I).

trans-$[\{\mathrm{PtCl_2[PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2]}\}_6]$ **3a**. The complex $[\mathrm{PtCl_2(NCMe)_2}]$ (0.84 g, 2.3 mmol) was added to a solution of azine diphosphine **I** (1.34 g, 2.35 mmol) in dichloromethane (50 $\mathrm{cm^3}$). After 30 min the resulting pale yellow solution was concentrated to a low volume (*ca.* 5 $\mathrm{cm^3}$) and the complex **3a** was precipitated by the addition of methanol (1.7 g, 89%) (Found: C, 52.3; H, 5.15; Cl, 8.4; N, 3.35. $\mathrm{C_{36}H_{42}Cl_2N_2P_2Pt}$ requires C, 52.05; H, 5.1; Cl, 8.55; N, 3.35%). IR (KBr disc): ν(C=N) 1605 and ν(Pt–Cl) 340 $\mathrm{cm^{-1}}$. Molecular weight 4870 (calculated for a hexamer 4985).

trans-$[\{\mathrm{PdCl_2[PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2]}\}_2]$ **3b**. A solution of the azine diphosphine **I** (1.0 g, 1.77 mmol) in dichloromethane (15 $\mathrm{cm^{-3}}$) was added to a solution of $[\mathrm{PdCl_2(NCPh)_2}]$ (0.67 g, 1.75 mmol) in dichloromethane (15 $\mathrm{cm^3}$) at *ca.* 20 °C. After 30 min the solution was concentrated to a low volume (*ca.* 8 $\mathrm{cm^3}$). The complex **3b** was precipitated by the addition of methanol as a yellow solid (1.1 g, 84%) (Found: C, 58.4; H, 5.65; Cl, 9.7; N, 3.6. $\mathrm{C_{36}H_{42}Cl_2N_2P_2Pd}$ requires C, 58.25; H, 5.7; Cl, 9.55; N, 3.75%). IR (KBr disc): ν(C=N) 1605 and ν(Pd–Cl) 345 $\mathrm{cm^{-1}}$. The complex was slow to dissolve in chloroform and on dissolution underwent partial transformation to **4a**; hence the molecular weight measurement was unreliable (see Discussion).

$[\mathrm{PdCl}\{\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2}\}]\mathrm{Cl}$ **4a**. A suspension of complex **3b** (0.53 g, 0.71 mmol) in $\mathrm{CHCl_3}$ (25 $\mathrm{cm^3}$) was heated under reflux for 30 min. It was then concentrated to a low volume (1 $\mathrm{cm^3}$). The slow addition of diethyl ether gave complex **4a** as a yellow solid (0.42 g, 79%) (Found: C, 54.85; H, 5.5; N, 3.55. $\mathrm{C_{36}H_{42}Cl_2N_2P_2Pd{\cdot}0.75CH_2Cl_2}$ requires C, 54.9; H, 5.45; N, 3.45%). IR (KBr disc): ν(C=N) 1600 and ν(Pd–Cl) 340 $\mathrm{cm^{-1}}$. Mass spectrum (EI): *m/z* 704 (*M* − HCl).

$[\mathrm{PdCl}\{\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2}\}]\mathrm{PF_6}$ **4b**. An excess of ammonium hexafluorophosphate (0.12 g, 0.73 mmol) in ethanol (1 $\mathrm{cm^3}$) was added to a solution of complex **4a** (0.12 g, 0.16 mmol) in ethanol (2 $\mathrm{cm^3}$). Complex **4b** deposited as yellow microcrystals (95 mg, 69%) (Found: C, 50.6; H, 5.05; Cl, 4.2; N, 3.5. $\mathrm{C_{36}H_{42}ClF_6N_2P_3Pd}$ requires C, 50.75; H, 4.95; Cl, 4.15; N, 3.3%). IR (KBr disc): ν(C=N) 1600 and ν(Pd–Cl) 340 $\mathrm{cm^{-1}}$. ^{13}C-{^{1}H} NMR (100.6 MHz, $\mathrm{CD_2Cl_2}$): δ_C 23.5 [1C, dd, ^1J(PC) 15.7, ^3J(PC) 2.6, $\mathrm{CH_2}$ of six-membered ring], 26.9 (3C, s, C*Me*$_3$), 27.9 (3C, s, C*Me*$_3$), 40.90 [1C, d, ^3J(PC) 1.5, *C*Me$_3$], 40.97 [1C, dd, ^1J(PC) 25.9, ^3J(PC) 2.3, $\mathrm{CH_2}$ of five-membered ring], 41.9 [1C, d, ^3J(PC) 5.5, *C*Me$_3$], 174.9 (1C, s, C=N of six-membered ring) and 190.4 [1C, dd, ^2J(PC) 5.9, ^3J(PC) 1.5 Hz, *c*=N of five-membered ring].

$[\mathrm{PtCl}\{\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2}\}]\mathrm{PF_6}$ **4c**. A mixture of $[\mathrm{PtCl_2(cod)}]$ (0.20 g, 0.53 mmol) and the azine diphosphine **I** (0.30 g, 0.53 mmol) in $\mathrm{CHCl_3}$ (8 $\mathrm{cm^3}$) was heated under reflux for 3 h. The solvent was then removed, the residue extracted into hot methanol (5 $\mathrm{cm^3}$) and an excess of $\mathrm{NH_4PF_6}$ (0.25 g) in methanol (1.5 $\mathrm{cm^3}$) added. The required salt **4c** deposited as a white solid (0.20 g, 40%) (Found: C, 45.95; H, 4.5; Cl, 4.0; N, 3.0. $\mathrm{C_{36}H_{42}ClF_6N_2P_3Pt}$ requires C, 46.0; H, 4.5; Cl, 3.75; N, 3.0%). IR (KBr): ν(C=N) 1605 and ν(Pt–Cl) 345 $\mathrm{cm^{-1}}$.

$[\mathrm{PtI}\{\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2}\}]\mathrm{I}$ **4d**. A solution containing $[\mathrm{PtI_2(cod)}]$ (0.22 g, 0.40 mmol) and the azine diphosphine **I** (0.23 g, 0.40 mmol) in dichloromethane (5 $\mathrm{cm^3}$) was put aside for 30 min. The solution was concentrated to a low volume (*ca.* 1 $\mathrm{cm^3}$); addition of ether then gave complex **4d** as a pale yellow solid (0.33 g, 80%) (Found: C, 39.4; H, 3.85; I, 23.0; N, 2.55. $\mathrm{C_{36}H_{42}I_2N_2P_2Pt{\cdot}1.5\ CH_2Cl_2}$ requires C, 39.45; H, 3.95; I, 22.2; N, 2.45%). IR (KBr disc): ν(C=N) 1600 $\mathrm{cm^{-1}}$.

$[\{\mathrm{PdCl_2}\{\mathrm{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh}\}]$ **5a**. A suspension of complex **3b** (1.65 g, 2.22 mmol) in $\mathrm{CHCl_3}$ (60 $\mathrm{cm^3}$) was heated under reflux for 8 d. The resultant yellow solution was concentrated to a low volume (*ca.* 3 $\mathrm{cm^3}$) and addition of hexane (*ca.* 3 $\mathrm{cm^3}$) gave complex **5a** as an off-white solid (1.21 g, 82%). An analytical sample was obtained by crystallization from $\mathrm{CH_2Cl_2}$–MeOH (Found: C, 49.95; H, 5.2; Cl, 18.6; N, 3.85. $\mathrm{C_{30}H_{36}Cl_2N_2P_2Pd{\cdot}CH_2Cl_2}$ requires C, 49.7; H, 5.1; Cl, 18.95; N, 3.95%). IR (KBr disc): ν(Pd–Cl) 315 and 290 $\mathrm{cm^{-1}}$. Mass spectrum (EI): *m/z* 626 (*M* − HCl). ^{13}C-{^{1}H} NMR ($\mathrm{CDCl_3}$, 100.6 MHz): δ_C 28.3 (3C, s, C*Me*$_3$), 29.7 (3C, s, C*Me*$_3$), 36.0 [1C, d, ^3J(PC) 3.2, *C*Me$_3$], 38.2 [1C, d, ^1J(PC) 48.6, $\mathrm{CH_2}$], 87.3 [1C, dd, ^1J(PC) 64.0, ^3J(PC) 13.7, PCH=], 163.3 [1C, d, ^2J(PC) 1.7, NC=] and 166.8 [1C, d, ^2J(PC) 6.7 Hz, C=N].

$[\mathrm{PdBr_2}\{\mathrm{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh}\}]$ **5b**. A mixture of complex **5a** (0.15 g, 0.226 mmol) and LiBr (0.2 g, 2.3 mmol) was stirred in acetone (10 $\mathrm{cm^3}$) for 16 h. The solvent was then removed, the residue was extracted into $\mathrm{CH_2Cl_2}$ (3 × 2 $\mathrm{cm^3}$), and the product crystallized from $\mathrm{CH_2Cl_2}$–MeOH as pale yellow microcrystals (95 mg, 56%) (Found: C, 47.7; H, 4.8; N, 3.75. $\mathrm{C_{30}H_{36}Br_2N_2P_2Pd}$ requires C, 47.85; H, 4.8; N, 3.70%).

$[\mathrm{PdI_2}\{\mathrm{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh}\}]$ **5c**. Complex **5c** was prepared from **5a** using NaI, in an analogous manner to **5b**, as orange crystals. Yield 76% (Found: C, 42.45; H, 4.2; N, 3.25. $\mathrm{C_{30}H_{36}I_2N_2P_2Pd}$ requires C, 42.55; H, 4.25; N, 3.3%).

$[\mathrm{PtCl_2}\{\mathrm{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh}\}]$ **5d**. Complex **5d** was prepared from **3a** and isolated in an analogous manner to **5a** as an off-white solid. Yield 94%. An analytical sample was obtained by crystallization from benzene–ethanol (Found: C, 49.1; H, 5.1; Cl, 9.5; N, 3.6. $\mathrm{C_{30}H_{36}Cl_2N_2P_2Pt{\cdot}0.25\ C_6H_6}$ requires C, 49.0; H, 4.9; Cl, 9.2; N, 3.65%). IR (KBr disc): ν(Pt–Cl) 320 and 295 $\mathrm{cm^{-1}}$. Mass spectrum (EI): *m/z* 716 (*M* − Cl). Molecular weight 821 (calculated 753). ^{13}C-{^{1}H} NMR (100.6 MHz, $\mathrm{CDCl_3}$): δ_C 28.3 (3C, s, C*Me*), 29.4 (3C, s, C*Me*$_3$), 35.7 [1C, d, ^1J(PC) 56.0, ^2J(PtC) 32, $\mathrm{CH_2}$], 35.8 [1C, d, ^3J(PC) 3.2, *C*Me$_3$], 40.7 [1C, dd, ^3J(PC) 8.3, 2.1, *C*Me$_3$], 86.6 [1C, dd, ^1J(PC) 72.4, ^3J(PC) 9.8, ^2J(PtC) 50, PCH=], 162.5 [1C, s, ^3J(PtC) 28, NC=] and 165.8 [1C, d, ^2J(PC) 5.1 Hz, C=N].

$[\mathrm{PtBr_2}\{\mathrm{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh}\}]$ **5e**. Complex **5e** was prepared from **5d** and isolated in an analogous manner to **5b**; yield 72% (Found: C, 43.1; H, 4.25; Br, 19.2; N, 3.2. $\mathrm{C_{30}H_{36}Br_2N_2P_2Pt}$ requires C, 42.8; H, 4.3; Br, 19.0; N, 3.35%).

$[\mathrm{PtI_2}\{\mathrm{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh}\}]$ **5f**. Complex **5f** was prepared from **5d** and isolated in an analogous manner to **5c**: yield 51% (Found: C, 38.7; H, 3.8; I, 27.3; N, 2.9. $\mathrm{C_{30}H_{36}I_2N_2P_2Pt}$ requires C, 38.5; H, 3.9; I, 27.15; N, 3.0%).

$[\mathrm{PtMe_2}\{\mathrm{PPh_2CH{=}C(Bu^t)N{-}N{=}C(Bu^t)CH_2PPh}\}]$ **5g**. An excess of methylmagnesium iodide (0.5 mol $\mathrm{dm^{-3}}$) in ether (0.5

cm^3) was added to a solution of complex **5d** (100 mg, 0.13 mmol) in dry tetrahydrofuran (2 cm^3). After 30 min the solution was cooled to −78 °C and an excess of MgMeI was hydrolysed with water. The solvent was then removed under reduced pressure and the product was extracted into CH_2Cl_2 (2 × 2 cm^3). The required product was crystallized from CH_2Cl_2–MeOH as a white solid (64 mg, 68%) (Found: C, 53.15; H, 5.9; N, 3.7. $C_{32}H_{42}N_2P_2Pt{\cdot}0.2CH_2Cl_2$ requires C, 53.05; H, 5.85; N, 3.85%).

$[PtMe_3I\{PPh_2CH{=}C(Bu^t)\overline{N{-}N{=}C(Bu^t)CH_2P}Ph\}]$ **6**. An excess of MeI (0.1 cm^3) was added to a solution of **5g** (25 mg, 0.035 mmol) in benzene (0.5 cm^3). After 16 h the solvent was removed and the residue triturated with ethanol to give complex **6** as white microcrystals (22 mg, 70%) (Found: C, 48.45; H, 5.15; N, 3.1. $C_{33}H_{45}IN_2P_2Pt{\cdot}0.5\ C_6H_6$ requires C, 48.45; H, 5.4; N, 3.15%).

Single-crystal X-Ray Diffraction Analysis of Complex **5c**.—All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using an on-line profile-fitting method[24] and graphite-monochromated Mo-Kα X-radiation (λ = 71.069 pm). The data set was corrected for absorption semiempirically using azimuthal ψ scans (maximum and minimum transmission factors = 0.3972 and 0.4557 respectively).

The structure was determined *via* standard heavy-atom (for the two iodine atoms) and Fourier difference techniques and was refined by full-matrix least squares using the SHELX program system.[25] All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl groups were treated as rigid bodies with idealized hexagonal symmetry (C–C 139.5 pm). All hydrogen atoms were included in calculated positions (C–H 96 pm) and were refined with an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o) + 0.0008(F_o)^2]^{-1}$ was used. The final difference synthesis contained no features of chemical significance (maximum and minimum residual electron density = 0.75 and −0.77 e Å^{-3} respectively). Final non-hydrogen atomic coordinates are given in Table 4.

Crystal data. $C_{30}H_{36}I_2N_2P_2Pd$, size = 0.3 × 0.2 × 0.21 mm, M = 846.81, monoclinic, space group $P2_1/n$, a = 945.23(7), b = 1636.6(2), c = 2121.3(2) pm, β = 94.513(8)°, U = 3.2714(6) nm^3, Z = 4, D_c = 1.72 Mg m^{-3}, μ = 25.45 cm^{-1}, $F(000)$ = 1648.

Data collection. $4.0 < 2\theta < 55.0°$, 7804 data collected, 6363 with $I > 2.0\sigma(I)$ considered observed, T = 200 K.

Structure refinement. Number of parameters = 317, R = 0.0239, R' = 0.0304, maximum Δ/σ = 0.001 [in U_{12} of C(34)], mean Δ/σ = 0.000.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1992, 1469.

2 C. G. MaCarty, in *The Chemistry of the Carbon–Nitrogen Double Bond*, ed. S. Patai, Interscience, London, New York, Sydney and Toronto, 1970, p. 363.

3 S. D. Perera, B. L. Shaw and M. Thornton-Pett, unpublished work.

4 H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, 1973, **59**, 411.

5 K. D. Tau, R. Uriarte, T. J. Mazanec and D. W. Meek, *J. Am. Chem. Soc.*, 1979, **101**, 6614.

6 P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer, Berlin, Heidelberg, New York, 1979.

7 R. J. Cross and M. F. Davidson, *J. Chem. Soc., Dalton Trans.*, 1986, 1987.

8 J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2496.

9 J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.

10 F. R. Hartley, S. G. Murray and C. A. McAuliffe, *Inorg. Chem.*, 1979, **18**, 1394.

11 A. Pryde, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 1976, 322.

12 D. M. Adams, J. Chatt, J. Gerratt and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

13 D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton and J. G. Smith, *J. Chem. Soc. A*, 1970, 545.

14 N. A. Al-Salem, H. D. Empsall, R. Markham, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 1979, 1972.

15 W. S. McDonald and M. C. Norton, *Acta Crystallogr., Sect. A*, 1978, **34**, S99.

16 H. D. Empsall, E. Mentzer, D. Pawson, B. L. Shaw, R. Mason and G. A. Williams, *J. Chem. Soc., Chem. Commun.*, 1977, 311.

17 M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Am. Chem. Soc.*, 1938, **60**, 882.

18 E. Lindner, R. Fawzi, H. A. Mayer, K. Eichele and W. Hiller, *Organometallics*, 1992, **11**, 1033.

19 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

20 L. R. Gray, D. J. Gulliver, W. Levason and M. Webster, *Inorg. Chem.*, 1983, **22**, 2362.

21 J. A. Davies, A. A. Pinkerton, R. Syed and M. Vilmer, *J. Chem. Soc., Chem. Commun.*, 1988, 47.

22 M. A. Bennett and P. N. Kapoor, *J. Organometallic Chem.*, 1987, **336**, 257.

23 S. Al-Jibori, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 287.

24 W. Clegg, *Acta Crystallogr., Sect. A*, 1987, **37**, 22.

25 G. M. Sheldrick, SHELX 76, program system for X-ray structure determinations, University of Cambridge, 1976.

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