Deprotonation, Deuteriation and Substitution of the Backbone of Some Azine Diphosphine Complexes of Palladium and Platinum: Crystal Structures of [PtI(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] and [PtCl(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)][OC$_6$H$_2$(NO$_2$)$_3$-2,4,6]†

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Treatment of the azine diphosphine *Z,Z*-PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$ **I** with [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene) in CHCl$_3$ in the presence of NEt$_3$ gave the neutral deprotonated chloroplatinum(II) complex [PtCl(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)], containing an ene–hydrazone backbone. The corresponding bromo- and iodo-analogues were prepared from it by metathesis. The analogous chloropalladium(II) complex was prepared by treating **I** with [PdCl$_2$(NCPh)$_2$] in the presence of NEt$_3$. Treatment of it with LiBr or MgMeI gave the corresponding bromo- and methyl-palladium(II) complexes, respectively. Treatment of the neutral complexes [MCl(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] (M = Pt or Pd) with acids (HX) reprotonated the ene–hydrazone backbone to give the salts [MCl(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)]X **4** [X = picrate, formate or (1*S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-methanesulfonate, M = Pt or Pd]. Treatment of [PtCl(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] with 0.5 equivalent of NH$_2$NH$_2$·2HCl gave a mixture of the nine-membered ring complex [PtCl$_2$(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)] and its isomeric chloride salt [PtCl(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)]Cl. When [PtMe$_2$(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)], containing a nine-membered chelate ring, was heated to 75 °C in C$_6$H$_6$ the methylplatinum(II) complex, [PtMe(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)], containing the terdentate dehydroazine ligand, was formed by oxidative addition of NH followed by reductive elimination of CH$_4$. Treatment of the same PtMe$_2$ complex with 1 equivalent of picric acid gave the picrate salt [PtMe(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)][OC$_6$H$_2$(NO$_2$)$_3$], which with 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) gave [PtMe(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)], and with MeI followed by NH$_4$PF$_6$ gave *fac*-[PtMe$_3$(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)]PF$_6$ which with dbu gave *fac*-[PtMe$_3$(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)]. Treatment of [Pt(C≡CC$_6$H$_4$Me-*p*)$_2$(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)] with 1 equivalent of picric acid gave [Pt(C≡CC$_6$H$_4$Me-*p*)(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)][OC$_6$H$_2$(NO$_2$)$_3$] which with dbu gave [Pt(C≡C$_6$H$_4$Me-*p*)(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)]. Treatment of **I** with [Pt(nb)$_3$] (nb = norbornene) gave the bridged binuclear platinum(0) complex [Pt$_2$(nb)$_2$(μ-PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)$_2$], containing an 18-atom ring. Treatment of this with MeO$_2$CC≡C-CO$_2$Me displaced the norbornene to form the corresponding bis(dimethyl acetylenedicarboxylate) complex. When the former was heated to 75 °C in benzene [PtH(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] was formed. The bis(norbornene)platinum(0) complex also underwent oxidative addition with MeI to give [PtMe(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)]I, which with dbu gave [PtMe(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)]. Methods of forming the di- and tetra-deuteriated complexes containing the azine backbone, and also mono- and tri-deuteriated complexes containing the dehydroazine backbone are discussed (M = Pt or Pd). A novel method of functionalising (*e.g.* alkylation and halogenation) the ligand backbone by electrophilic attack on the enamine carbon in complexes of type **4** is described. The crystal structures of [PtI(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] and [PtCl(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)][OC$_6$H$_2$(NO$_2$)$_3$] were determined. Proton, ^{31}P and some ^{13}C NMR data are given.

We have shown that the azine diphosphine *Z,Z*-PPh$_2$CH$_2$-CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$ **I** does not chelate through phosphorus atoms owing to its *Z,Z* configuration.[1,2] However, rotation around C=N can occur quite readily and the azine diphosphine in the *E,Z* configuration can chelate to a metal giving a nine-membered ring (*e.g.* **1a**–**1c**)[2] or act as a terdentate ligand with P,P and N donor atoms.[1,2] We also showed that **I** could bridge two metal atoms to give binuclear species with an

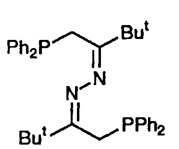
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

18-atom ring (Pd) or what appeared to be a hexanuclear complex with a 54-atom ring (Pt).[2] When these complexes were heated for prolonged periods in chloroform a remarkable transformation occurred, in which the heterocyclic disphosphine complexes **2a** and **2b** were formed essentially quantitatively, with loss of a molecule of benzene.[2] We reason that the methylene protons in the azine backbone of the terdentate complexes of type $[\overline{MX(PPh_2CH_2CBu^t{=}N{-}N{=}CBu^tCH_2P}Ph_2)]^+$ (M = Pd or Pt; X = halide or an organic group) should be activated *i.e.* deprotonation should occur. We have found this to be the case and have developed a lot of novel chemistry from such systems which are now described.

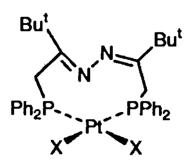
Results and Discussion

Treatment of the azine diphosphine **I** with $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) in hot chloroform, followed by an excess of triethylamine and further heating, gave the neutral deprotonated chloroplatinum(II) complex **3a** in 68% yield. Deprotonation has converted the azine backbone into a novel terdentate ligand containing an enamine (or ene–hydrazone) grouping. The $^{31}P-\{^1H\}$ NMR data (Table 1) show $^2J(PP)$ = 435 Hz, indicative of mutually *trans* co-ordinating phosphorus atoms.[2,3] In the ^1H NMR spectrum (Table 2) the CH= proton appeared as a triplet at δ 4.59 with satellites due to coupling to platinum-195, $^3J(PtH)$ = 29.3 and with $^2J(PH) = {^4J(PH)}$ = 4.5 Hz. The carbon-13 NMR spectrum (Experimental section) shows a doublet at δ 20.4 with $^1J(PC)$ = 25.0 Hz for the CH_2 carbon, typical of a methylene carbon in a six-membered ring;[2,4–6] the CH= carbon gives a doublet at δ 78.1 with $^1J(PC)$ = 64.4 Hz. The corresponding bromo- (**3b**) and iodo- (**3c**) analogues were prepared from the chloro-complex **3a** by metathesis. The crystal structure of the iodo-complex **3c** was determined (Fig. 1) and is described below. Treatment of $[PdCl_2(NCPh)_2]$ with **I** followed by triethylamine gave the corresponding chloropalladium(II) complex **3d**, containing the ene–hydrazone backbone, in excellent yield (78%); the characterising data for this purple complex are in the Experimental section and in Tables 1 and 2. It was converted into the corresponding dark purple bromopalladium(II) complex **3e** by treatment with LiBr in acetone.

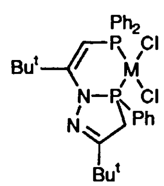
Treatment of the neutral complexes **3** with acids reprotonated the ene–hydrazone backbone to reform the azine moiety. Thus, the chloroplatinum(II) complex **3a** with 1 equivalent of picric acid $[HOC_6H_2(NO_2)_3$-2,4,6] gave the picrate salt **4a** in 96% yield. The structure of this complex was determined by X-ray diffraction analysis (see below) and is shown in Fig. 2. The proton and phosphorus-31 NMR data for this complex and the others of type **4** are in agreement with those for the published terdentate azine diphosphine complexes of platinum(II) and palladium(II).[2] The analogous picrate salt of palladium, **4b**, was similarly prepared in 86% yield and characterised. The formate salts **4c** and **4d** were prepared *in situ* by adding a slight excess of formic acid to CD_2Cl_2 solutions of **3a** or **3d** respectively. The salt **4e** was prepared and isolated in 91% yield by adding (1*S*)-



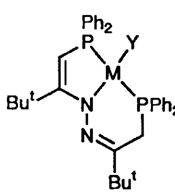
I



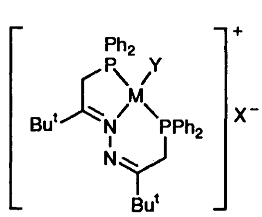
	X
1a	Me
1b	C≡CC$_6$H$_4$Me-*p*
1c	Cl



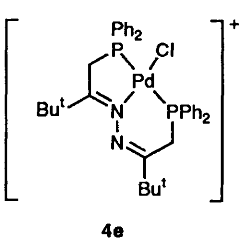
	M
2a	Pt
2b	Pd



	M	Y
3a	Pt	Cl
3b	Pt	Br
3c	Pt	I
3d	Pd	Cl
3e	Pd	Br
3g	Pd	Me



	M	Y	X
4a	Pt	Cl	OC$_6$H$_2$(NO$_2$)$_3$
4b	Pd	Cl	OC$_6$H$_2$(NO$_2$)$_3$
4c	Pt	Cl	O$_2$CH
4d	Pd	Cl	O$_2$CH



4e

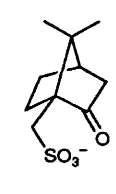


Table 1 $^{31}P-\{^1H\}$ NMR data [a]

Compd.	δ(P_A)	δ(P_B)	^2J(PP)/ Hz	$^1J(PtP_A)$/ Hz	$^1J(PtP_B)$/ Hz
I	−14.4				
1a [b,c]	21.5	19.7	15	1980	1975
1b [b,c]	14.9	6.8	18	2487	2500
1c [b]	17.1	−1.9	11	4132	4118
3a	58.8	21.6	435	3024	2755
3b	61.0	22.8	433	3004	2733
3c [d]	64,8	24.9	427	2960	2639
3d	64.5	29.6	457		
3e	67.7	31.6	459		
3f [c]	54.6	26.4	424	3080	2940
3g [c]	47.2	25.2	409		
3h	53.0	21.7	409	2821	2663
3i [c]	56.5	32.7	386	3029	2850
4a [d]	48.2	40.1	455	2795	2571
4b	54.4	43.4	508		
4c [d]	47.2	39.4	455	2777	2558
4d [d]	53.4	41.9	508		
4e	57.6	41.6	508		
4f [c]	56.4	44.3	439	3116	2900
4g	49.2	37.9	426	2764	2566
4h [d]	54.7	41.1	441	3127	2938
5 [d]	6.8	−2.6	11	1335	1131
6	−2.7	−14.9	13	1419	1200
7a [c]	39.4			3663	
7b [c]	30.9			3903	
8 [c]	23.9	15.1	6.5	3821	3802
9a [d]	47.8	39.9	454	2793	2564
9b [d]	47.3	39.7	455	2786	2560
9c	53.3	41.9	508		
10a [d]	47.4	39.0	455	2793	2562
10b [d]	53.2	41.7	509		
11a	58.9	21.4	434	3021	2753
11b	64.7	29.4	456		
12a	58.6	21.6	433	3019	2760
12b	64.4	29.4	456		
13a [d]	53.9	46.7	443	2729	2531
13b	52.6	47.3	444	2690	2562
13c [d]	50.6	45.8	449	2784	2668
13d [d]	49.3	44.5	448	2789	2668
14	79.1	50.7	429	3186	2782

[a] Recorded at 36.2 MHz, chemical shifts (δ) are in ppm relative to 85% H_3PO_4, solvent $CDCl_3$ unless otherwise stated. [b] From ref. 2. [c] In C_6D_6. [d] In CD_2Cl_2.

Table 2 Proton NMR data[a]

Compound	δ(Bu^t)	δ(CH_2), δ(CH=), δ(C*H*Me), δ(C*H*Br)	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[c,d]	0.79 (9 H, s)	3.07 (2 H, d, 12.7,[b] 26.5,[e] CH_2)	1.97 (6 H, s, C_6H_4*Me*)
	1.28 (9 H, s)	3.41 (2 H, d, 10.2,[b] 18.8,[e] CH_2)	
1c[c]	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)	
3a	0.76 (9 H, s)	3.04 (2 H, dd, 12.2,[b] 2.9,[h] 35.7,[e] CH_2)	
	1.35 (9 H, s)	4.59 (1 H, t, 4.5,[b,h] 29.3,[e] CH=)	
3b	0.76 (9 H, s)	3.04 (2 H, dd, 12.1[b], 3.0,[h] 35.2,[e] CH_2)	
	1.36 (9 H, s)	4.57 (1 H, t, 4.5,[b,h] 26.6,[e] CH=)	
3c[i]	0.75 (9 H, s)	3.09 (2 H, dd, 12.1,[b] 3.1,[h] 34.2,[e] CH_2)	
	1.37 (9 H, s)	4.59 (1 H, dd, 3.9,[j] 5.1,[j] 22.5,[e] CH=)	
3d	0.75 (9 H, s)	2.89 (2 H, dd, 11.0,[b] 3.2,[h] CH_2)	
	1.32 (9 H, s)	4.45 (1 H, dd, 2.7,[j] 4.6,[j] CH=)	
3e	0.75 (9 H, s)	2.90 (2 H, dd, 10.8,[b] 3.2,[h] CH_2)	
	1.34 (9 H, s)	4.42 (1 H, dd, 2.9,[j] 4.6,[j] CH=)	
3f[d]	0.90 (9 H, s)	3.06 (2 H, dd, 12.2,[b] 2.7,[h] 30.0,[e] CH_2)	1.06 (3 H, t, 6.2,[f] 73.8,[g] PtMe)
	1.75 (9 H, s)	4.73 (1 H, t, 4.2,[b,h] 28.5,[e] CH=)	
3g[d]	0.90 (9 H, s)	2.91 (2 H, dd, 10.7,[b] 2.2,[h] CH_2)	0.74 (3 H, dd, 6.9,[f] 5.1,[f] PdMe)
	1.75 (9 H, s)	4.56 (1 H, d, 4.9,[j] CH=)	
3h	0.78 (9 H, s)	3.11 (2 H, dd, 12.2,[b] 3.0,[h] 28.1,[e] CH_2)	2.24 (3 H, s, C_6H_4*Me*)
	1.42 (9 H, s)	4.63 (1 H, t, 4.6,[b,h] 26.1,[e] CH=)	
3i[d]	0.64 (9 H, s)	2.68 (2 H, dd, 12.2,[b] 2.2,[h] 27.8,[e] CH_2)	−12.80 (1 H, dd, 17.6,[b] 12.2,[b] 1047,[l] PtH)
	1.50 (9 H, s)	4.59 (1 H, t, 3.9,[b,h] 22.9,[e] CH=)	
4a[i]	0.83 (9 H, s)	3.59 (2 H, d, 9.5,[b] 31.0,[e] CH_2)	8.67 [2 H, s, $OC_6H_2(NO_2)_3$-2,4,6]
	1.21 (9 H, s)	4.24 (2 H, dd, 7.3,[b] 2.0,[h] CH_2)	
4b[i]	0.82 (9 H, s)	3.44 (2 H, dd, 10.0,[b] 1.7,[h] CH_2)	8.64 [2 H, s, $OC_6H_2(NO_2)_3$-2,4,6]
	1.18 (9 H, s)	4.39 (2 H, dd, 8.3,[b] 3.2,[h] CH_2)	
4c[i]	0.80 (9 H, s)	3.45 (2 H, d, 9.5,[b] 31.0,[e] CH_2)	8.23 (1 H, s, HCO_2)
	1.22 (9 H, s)	4.08 (2 H, s, br, CH_2)	
4d[i]	0.80 (9 H, s)	3.27 (2 H, dd, 10.5,[b] 1.8,[h] CH_2)	8.19 (1 H, s, HCO_2)
	1.19 (9 H, s)	4.18 (2 H, d, br, 6.1,[b] CH_2)	
4e	0.75 (9 H, s)	3.73 (2 H, m, 12.4,[m] 12.4,[b] CH_2)	0.78 (3 H, s, Me), 1.08 (3 H, s, Me)
	1.32 (9 H, s)	4.72 (2 H, m, br, CH_2)	2.65 (1 H, d, 14.9,[m] CH_2S)
			3.28 (1 H, d, 14.9,[m] CH_2S)
4f[d]	0.58 (9 H, s)	3.69 (2 H, d, 11.5,[b] 28.9,[e] CH_2)	0.71 (3 H, t, 6.5,[f] 80.1,[g] PtMe)
	1.02 (9 H, s)	4.19 (2 H, dd, 8.3,[b] 2.2,[h] 17.1,[e] CH_2)	8.70 [2 H, s, $OC_6H_2(NO_2)_3$-2,4,6]
4g	0.87 (9 H, s)	3.68 (2 H, d, 11.5,[b] 1.1,[h] 25.9,[e] CH_2)	2.23 (3 H, s, C_6H_4*Me*)
	1.28 (9 H, s)	4.34 (2 H, dd, 8.6,[b] 3.1,[h] 10.7,[e] CH_2)	6.87 (2 H, d, 8.2,[n] C_6*H_4*Me)
			8.73 [2 H, s, $OC_6H_2(NO_2)_3$-2,4,6]
4h[i]	0.76 (9 H, s)	3.69 (2 H, dd, 11.6,[b] 1.9,[h] 29.3,[e] CH_2)	0.56 (3 H, t, 6.6,[f] 80.6,[g] PtMe)
	1.29 (9 H, s)	4.40 (2 H, dd, 8.9,[b] 3.2,[h] 17.5,[e] CH_2)	
5[i]	1.04 (9 H, s)	2.45 (1 H, dd, 13.4,[m] 11.6,[b] 3.6,[e] CH_2)	0.79 (3 H, dd, 8.9,[f] 6.4,[f] 54.7,[g] PtMe)
	1.51 (9 H, s)	3.86 (1 H, m, 13.4,[m] CH_2)[o]	0.92 (3 H, t, 7.1,[f] 56.6,[g] PtMe)
		3.87 (1 H, m, 18.2,[m] CH_2)[o]	1.67 (3 H, t, 6.9,[f] 70.3,[g] PtMe)
		4.24 (1 H, dd, 18.2,[m], 11.3,[b], 8.0,[e] CH_2)	
6	1.24 (9 H, s)	1.92 (1 H, dd, 17.3,[m] 13.9,[b] 8.0,[e] CH_2)	0.32 (3 H, t, 7.6,[f] 53.2,[g] PtMe)
	1.53 (9 H, s)	3.06 (1 H, dd, 17.3,[m] 9.4,[b] 2.7,[e] CH_2)	0.39 (3 H, t, 8.1,[f] 58.6,[g] PtMe)
		4.08 (1 H, s, 10.2,[e] CH=)	0.86 (3 H, t, 5.8,[f] 66.7,[g] PtMe)
7a[d,p]	0.93 (9 H, s)	3.41 (1 H, m, 12.9,[m] 26.8,[e] CH_2)	2.12 (1 H, m, 5.8,[n] 65.8,[g] =CH)
	0.94 (9 H, s)	3.44 (1 H, m, 12.9,[m] 33.2,[e] CH_2)	2.56 (1 H, m, 5.7,[n] 65.7,[g] =CH)
		4.32 (1 H, m, 12.9,[m] 9.3,[e] CH_2)	
		4.34 (1 H, m, 12.9,[m] CH_2)	
7b[p]	0.60 (18 H, s)	3.04 (2 H, m, 12.7,[m] 12.6,[b] 25.7,[e] CH_2)[o]	3.07 (6 H, s, OMe)
		4.26 (2 H, m, 12.7,[m] 13.1,[b] 10.8,[e] CH_2)	
8	0.68 (9 H, s)	*q*	3.26 (3 H, s, OMe)
	1.26 (9 H, s)		3.49 (3 H, s, OMe)
9a[i]	0.82 (9 H, s)	3.56 (2 H, d, 9.6,[b] 31.0,[e] CH_2)	8.75 [2 H, s, $OC_6H_2(NO_2)_3$-2,4,6]
	1.21 (9 H, s)		
9b[i]	0.81 (9 H, s)	3.47 (2 H, d, 9.5,[b] 31.5,[e] CH_2)	8.27 (1 H, s, HCO_2)
	1.22 (9 H, s)		
9c[i]	0.80 (9 H, s)	3.31 (2 H, d, 10.2,[b] 2.2,[h] CH_2)	8.24 (1 H, s, HCO_2)
	1.19 (9 H, s)		
10a[i]	0.81 (9 H, s)		8.27 (1 H, s, HCO_2)
	1.22 (9 H, s)		
10b[i]	0.80 (9 H, s)		8.24 (1 H, s, HCO_2)
	1.19 (9 H, s)		
11a	0.76 (9 H, s)	3.05 (2 H, d, 11.9,[b] 2.9,[h] 35.7,[e] CH_2)	
	1.35 (9 H, s)		
11b	0.75 (9 H, s)	2.89 (2 H, dd, 11.0,[b] 3.2,[h] CH_2)	
	1.32 (9 H, s)		

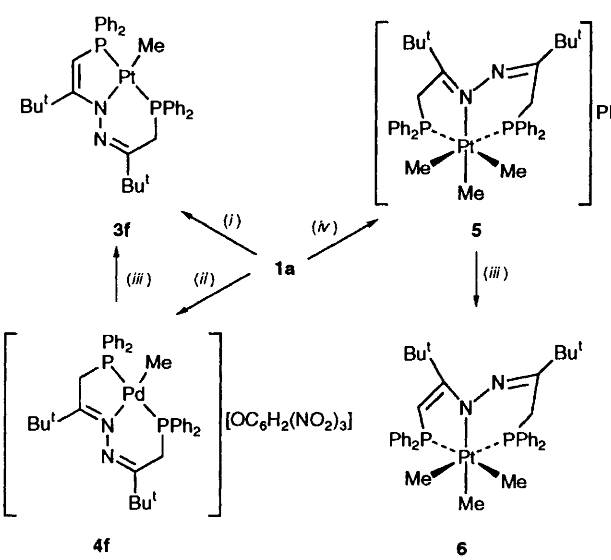
Table 2 (*continued*)

Compound	δ(Bu^t)	δ(CH_2), δ(CH=), δ(C*H*Me), δ(C*H*Br)	Others
12a	0.76 (9 H, s) 1.135 (9 H, s)	—	
12b	0.75 (9 H, s) 1.32 (9 H, s)	—	
13a	0.77 (9 H, s) 1.42 (9 H, s)	3.64 (1 H, m, 13.2,^{m} 9.2,^{b} 2.5,^{h} 25.4,^{e} CH_2) 3.91 (1 H, m, 13.2,^{m} 31.2,^{e} CH_2) 4.42 (1 H, m, 7.0,^{n} C*H*Me)	1.89 (3 H, m, 7.1,^{n} CH*Me*)
13b^i	0.76 (9 H, s) 1.31 (9 H, s)	3.05 (1 H, m, 13.0,^{m} 29.8,^{e} CH_2) 3.66 (1 H, dd, 13.0,^{m} 6.6,^{b} 22.9,^{e} CH_2) 4.44 (1 H, m, 6.8,^{n} C*H*Me)	1.72 (3 H, ddd, 7.1,^{n} 11.7,^{b} 4.4,^{r} CH*Me*)
13c^i	0.82 (9 H, s) 1.29 (9 H, s)	2.94 (1 H, ddd, 13.2,^{m} 8.5,^{b} 3.3,^{h} 54.0,^{e} CH_2) 3.91 (1 H, dd, 13.2,^{m} 6.6,^{b} 28.4,^{e} CH_2) 6.15 (1 H, dd, 2.9,^{b} 2.2,^{h} 21.5,^{e} CHBr)	
13d^i	0.82 (9 H, s) 1.28 (9 H, s)	2.87 (1 H, ddd, 13.2,^{m} 8.3,^{b} 3.4,^{h} 54.0,^{e} CH_2) 3.77 (1 H, ddd, 13.2,^{m} 7.3,^{b} 1.0,^{h} 31.8,^{e} CH_2) 5.77 (1 H, dd, 3.2,^{b} 2.2,^{h} 21.5,^{e} CHBr)	
14^i	0.73 (9 H, s) 1.29 (9 H, s)	3.08 (2 H, dd, 11.7,^{b} 2.2,^{h} 35.5,^{e} CH_2)	1.91 (3 H, dd, 10.7,^{f} 2.2,^{r} =C*Me*)

^{a} Recorded at 100 MHz, chemical shifts (δ) in ppm relative to $SiMe_4$, *J* values in Hz, solvent $CDCl_3$ unless otherwise stated. ^{b} ^2J(PH). ^{c} From ref. 2. ^{d} In C_6D_6. ^{e} ^3J(PtH). ^{f} ^3J(PH). ^{g} ^2J(PtH). ^{h} ^4J(PH). ^{i} In CD_2Cl_2. ^{j} ^2J(PH) or ^4J(PH). ^{l} ^1J(PtH). ^{m} ^2J(HH). ^{n} ^3J(HH). ^{o} Signal obscured. ^{p} Recorded at 400 MHz. ^{q} Not resolved. ^{r} ^5J(PH).

(+)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-methanesulfonic acid to a solution of **3d** in chloroform. Treatment of the neutral chloroplatinum(II) complex **3a** with 0.5 equivalent of $NH_2NH_2{\cdot}2HCl$ in tetrahydrofuran for 5 h gave a mixture of the nine-membered chelate ring complex **1c** and its isomeric chloride salt [PtCl($PPh_2CH_2CBu^t$=N–N=$CBu^tCH_2PPh_2$)]Cl in the ratio *ca.* 4:1, and prolonged heating (60 °C, 8 d) of this mixture gave the heterocyclic complex **2a** essentially quantitatively (^{31}P-{^{1}H} NMR evidence).

We have previously described the dimethylplatinum(II) complex **1a**,[2] containing the *E,Z*-azine backbone in a nine-membered chelate ring, and some new reactions of this complex are summarised in Scheme 1. When heated to 75 °C in benzene for 5 h the monomethylplatinum(II) complex **3f** containing a dehydroazine backbone was formed, possibly by the oxidative addition of NH (formed by azine ⟷ ene–hydrazone tautomerism, *i.e.* a 1,3-proton shift) followed by reductive elimination of methane; a four-centre mechanism involving NH and PtMe is also possible. In the proton NMR spectrum the CH= proton appeared as a triplet at δ 4.73 with ^2J(PH) = ^4J(PH) = 4.2 and ^3J(PtH) = 28.5 Hz, whilst the PtMe protons showed a triplet at δ 1.06 with ^3J(PH) = 6.2 and ^2J(PtH) = 73.8 Hz. The analogous methylpalladium(II) complex **3g** was prepared from the chloropalladium(II) complex **3d** by treating it with MgMeI. It was not isolated in the pure state and was characterised by proton and phosphorus-31 NMR spectroscopy. Addition of 1 equivalent of picric acid to a solution of complex **1a** gave methane and the monomethylplatinum(II) picrate salt **4f** in 82% yield, which with dbu (1,8-diazabicyclo[5.4.0]undec-7-ene) gave the neutral methylplatinum(II) complex **3f**. Treatment of complex **1a** with MeI, followed by the addition of NH_4PF_6, gave the *fac*-trimethylplatinum(IV) salt **5** containing an *E,Z*-azine backbone. In the carbon-13 NMR spectrum the two methyl carbons *trans* to phosphorus appeared as doublet of doublets with a large $^2J(PC_{trans})$ value of *ca.* 110 Hz and a small $^2J(PC_{cis})$ value of *ca.* 5 Hz, whilst the methyl carbon *trans* to nitrogen showed small coupling (*ca.* 3.0 Hz) to both the phosphorus nuclei in *cis* positions. The phosphorus-31 NMR showed a AB pattern with ^2J(PP) = 11 Hz, consistent with the *fac* geometry. As in our previous work[2,4–6] the methylene carbon in the six-membered chelate ring was presumably the one which absorbed at a lower δ_C value (24.5) than the methylene carbon in the five-membered ring (41.9); similarly we assign the methylene hydrogens in the six-membered chelate ring to the resonances at δ 2.45 and 3.86, whilst those in the five-

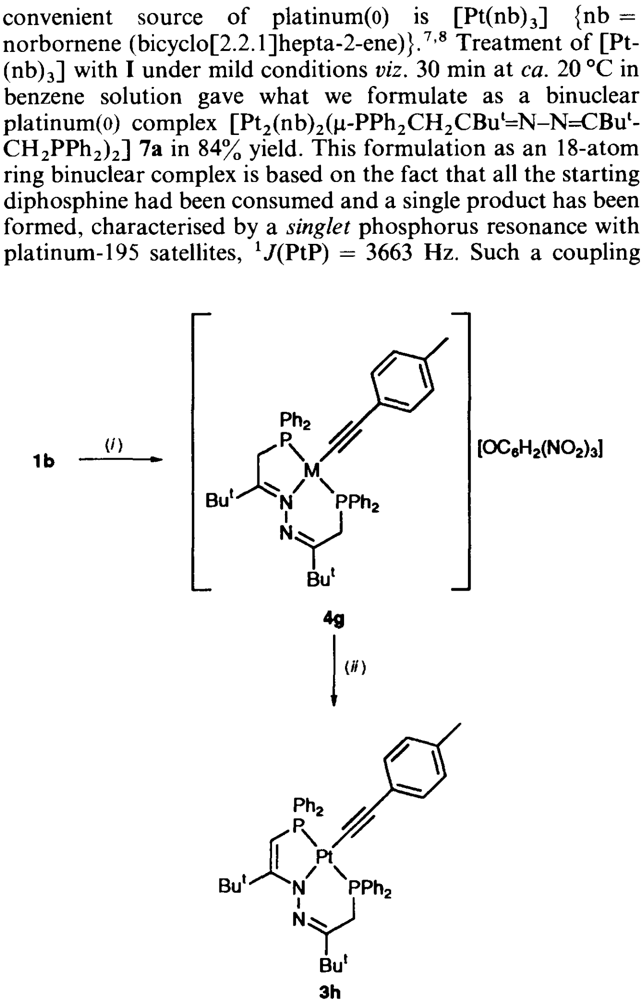


Scheme 1 (*i*) heat, $-CH_4$; (*ii*) picric acid, $-CH_4$; (*iii*) base; (*iv*) MeI–NH_4PF_6

membered ring absorbed at δ 3.87 and 4.24. The methylene proton in the five-membered ring of **5** was easily removed by dbu to give the neutral *fac*-trimethylplatinum(IV) complex **6**, which showed the CH= hydrogen resonance at δ 4.08 and two CH_2 hydrogen resonances at δ 1.92 and 3.06.

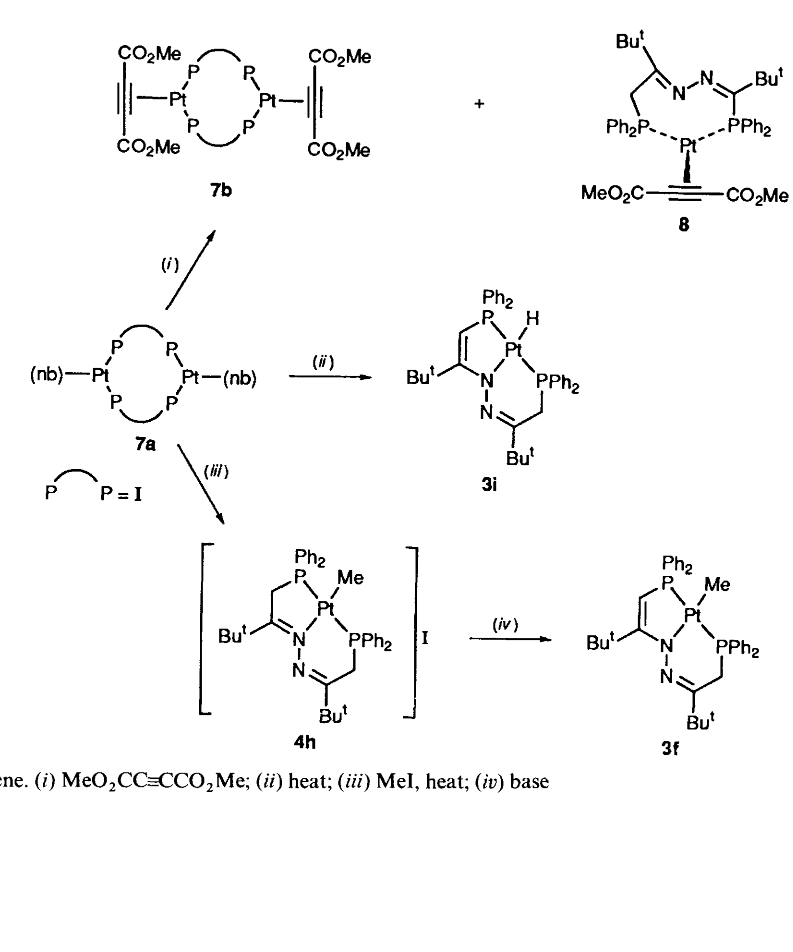
We have previously prepared and characterised the platinum(II) di-*p*-tolylacetylide complex **1b** containing a nine-membered chelate ring, by treating [Pt(C≡CC_6H_4Me-*p*)$_2$(cod)] with the azine diphosphine **I**.[2] This complex shows somewhat analogous chemistry (Scheme 2) to the dimethylplatinum(II) complex **1a** as shown in Scheme 1. Thus, treatment of a benzene solution of **1b**, prepared *in situ*, with 1 equivalent of picric acid gave the terdentate picrate salt **4g** containing an *E,Z*-azine backbone; characterising data are in Tables 1 and 2. Deprotonation of this salt with dbu gave the neutral platinum(II) *p*-tolylacetylide complex **3h**, for which the CH= hydrogen resonance appeared at δ 4.63 with ^2J(PH) = ^4J(PH) = 4.6 Hz.

We have investigated the co-ordination chemistry of some platinum(0) complexes of the azine diphosphine **I** (Scheme 3). A convenient source of platinum(0) is [Pt(nb)$_3$] {nb = norbornene (bicyclo[2.2.1]hepta-2-ene)}.[7,8] Treatment of [Pt(nb)$_3$] with I under mild conditions *viz.* 30 min at *ca.* 20 °C in benzene solution gave what we formulate as a binuclear platinum(0) complex [Pt$_2$(nb)$_2$(μ-PPh$_2$CH$_2$CBu^t=N–N=CBu^t-CH$_2$PPh$_2$)$_2$] **7a** in 84% yield. This formulation as an 18-atom ring binuclear complex is based on the fact that all the starting diphosphine had been consumed and a single product has been formed, characterised by a *singlet* phosphorus resonance with platinum-195 satellites, ^1J(PtP) = 3663 Hz. Such a coupling constant is typical of platinum(0) complexes of type [Pt(PR$_3$)$_2$(olefin)].[8–11] The elemental analytical and mass spectral data (*m/z* 1706; Experimental section) are in agreement with the formulation as a binuclear species containing the *Z*,*Z*-azine diphosphine ligand. The characteristic of complexes of the type [Pt(PR$_3$)$_2$(olefin)] is that the olefins have less affinity for platinum(0) than do acetylenes, especially acetylenes containing electron-withdrawing groups.[12–15] When we treated **7a** with an excess of dimethyl acetylenedicarboxylate it gave a mixture of two products; the major product was isolated and characterised as **7b**, *i.e.* the strong π-acid ligand MeO$_2$CC≡CCO$_2$Me had simply displaced the norbornene from **7a**. The minor product, showing an AB pattern with a ^2J(PP) value of 6.5 Hz in its ^{31}P-{^{1}H} NMR spectrum, was tentatively formulated as the mononuclear platinum(0) complex **8** containing the nine-membered chelate ring derived from the *E*,*Z* isomer of **I**. When complex **7a** was heated at 75 °C for 3 h in benzene in the presence of a small (catalytic) amount of the diphosphine **I** it lost norbornene and was transformed to the mononuclear platinum(II) hydride **3i**, containing the terdentate dehydroazine backbone. The ν(Pt–H) band occurred at 2120 cm^{-1} and δ_H(PtH) −12.8 with ^1J(PtH) = 1047 and ^2J(PH) = 17.6 and 12.2 Hz.[16–19] Treatment of complex **7a** with MeI at 60 °C caused oxidative addition with loss of norbornene to give the methylplatinum(II) iodide salt **4h**, which with dbu gave the neutral methylplatinum(II) complex **3f**, identical to that described above.

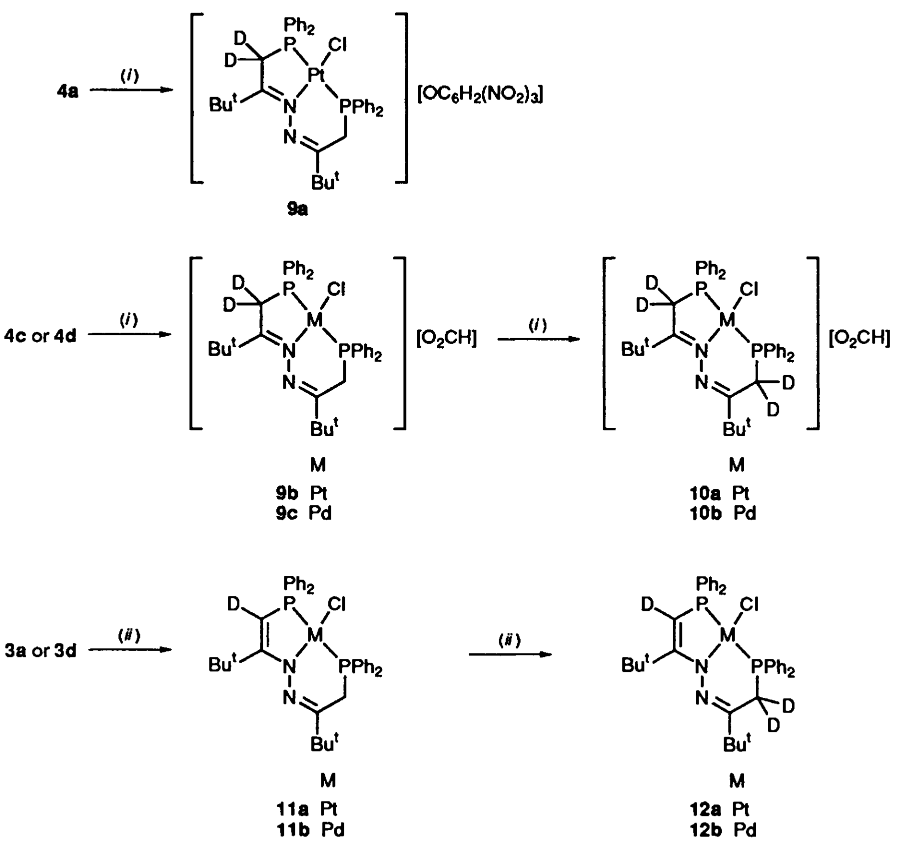


Scheme 2 (*i*) picric acid; (*ii*) base

We have also studied (Scheme 4) the acid- or base-catalysed deuteriation of the azine or dehydroazine backbone of palladium or platinum complexes of type **3** and **4** by NMR spectroscopy. Methods were devised of forming di- or tetra-deuteriated azine backbones and mono- or tri-deuteriated dehydroazine backbones by replacing CH$_2$ or CH= protons with deuterium. The exchanges were followed by ^{1}H and ^{1}H-{^{31}P} NMR spectroscopy *in situ* and the NMR data on the partially deuteriated products in CD$_2$Cl$_2$ or CDCl$_3$ are given in Tables 1 and 2. Treatment of the picrate salt **4a** in CD$_2$Cl$_2$ with D$_2$O for 30 min with intermittant shaking gave **9a** in which both methylene hydrogens in the five-membered chelate ring had been replaced by deuterium, whereas the methylene hydrogens



Scheme 3 nb = norbornene. (*i*) MeO$_2$CC≡CCO$_2$Me; (*ii*) heat; (*iii*) MeI, heat; (*iv*) base



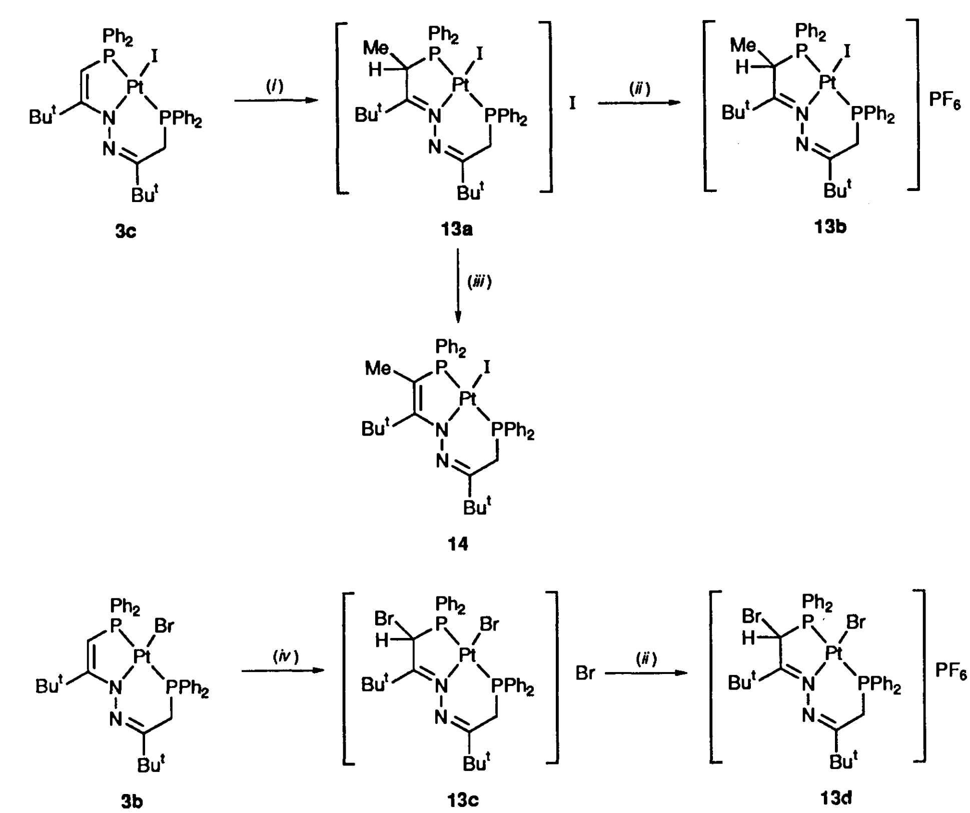
Scheme 4 (*i*) D_2O, H^+; (*ii*) 0.05 mol dm^{-3} NaOD–D_2O

in the six-membered chelate ring showed no detectable replacement. In the presence of a catalytic amount of picric acid the exchange was complete within 5 min. However, the methylene hydrogens in the six-membered chelate ring showed no detectable exchange with deuterium even after 2 weeks in contact with D_2O and a catalytic amount of picric acid. Similarly, the formate salts **4c** (Pt) and **4d** (Pd), prepared *in situ* by adding formic acid to a CD_2Cl_2 solution of **3a** or **3d** respectively, when treated with an excess of D_2O underwent complete exchange of methylene hydrogens in the five-membered chelate ring within 5 min to give dideuteriated complexes **9b** (Pt) and **9c** (Pd) respectively. On prolonged contact with D_2O in this formic acid system the methylene hydrogens in the six-membered ring were completely replaced by deuterium to give tetradeuteriated complexes **10a** (Pt) and **10b** (Pd), respectively. We attribute the difference between the formic acid and picric acid systems to steric hindrance, *i.e.* the very bulky picrate ion does not remove H^+ from the methylene group in the six-membered chelate ring for steric reasons. It seems likely that the strong but very sterically demanding picric acid could be used for selective H/D exchange in other systems controlled by steric factors.

We studied the base-catalysed H/D exchange in complexes of type **3** containing the dehydroazine backbone using NaOD–D_2O. Treatment of a $CDCl_3$ solution of **3a** with NaOD–D_2O with a reaction time of 5 min gave the monodeuterioplatinum(II) complex **11a** in which the CH= proton had been completely replaced to give CD= but the CH_2 protons in the six-membered chelate ring were essentially unchanged; similarly for the corresponding monodeuteriopalladium(II) complex **11b**. Prolonged (36 h) treatment of a $CDCl_3$ solution of **3a** gave the trideuterioplatinum(II) complex **12a**; similarly the palladium(II) complex **3d** gave trideuteriopalladium(II) complex **12b** after a reaction time of 8 h.

The complexes of type **3** containing an ene–hydrazone backbone have an enamine type (C=C–N) moiety. Enamines react with electrophiles in what is a very useful and selective synthetic method in organic chemistry.[20–22] We therefore investigated the tendency of these complexes to be attacked by electrophiles other than the proton, which we have discussed above. The results are summarised in Scheme 5. Treatment of the iodoplatinum(II) complex **3c** with an excess of MeI in chloroform solution for 15 h at 20 °C gave the *C*-methylated platinum(II) iodide salt **13a** in essentially quantitative yield (98%). This iodide salt when treated with NH_4PF_6 gave the corresponding PF_6 salt **13b**. The phosphorus-31 NMR data for complexes **13** are in agreement with those of the platinum(II) salts **4** as discussed above. The carbon-13 NMR spectrum of **13a** showed a doublet resonance at δ 19.6 with $^2J(PC)$ = 3.5 Hz for the CH*Me* carbon. As expected, the methylene hydrogens in the six-membered ring are now non-inequivalent and absorbed at δ 3.64 and 3.91 with $^2J(HH)$ = 13.2 Hz. In the $^1H-\{^{31}P\}$ NMR spectrum the C*H*Me proton appeared as a quartet at δ 4.42 with $^3J(HH)$ = 7.1 Hz, whilst the CH*Me* protons appeared as a doublet at δ 1.89. The iodide salt **13a** was readily deprotonated by dbu to give the neutral platinum(II) complex **14** containing the methylated moiety (MeC=C–N) in 95% yield, for which the MeC= protons appeared as a doublet of doublets at δ 1.91 with $^3J(PH)$ = 10.7 and $^5J(PH)$ = 2.2 Hz. This smooth and quantitative conversion of **3c** into the *C*-methylated complex **13a** is remarkable since the site of attack is quite sterically hindered *i.e.* close to both Bu^t and PPh_2 groups. We suggest that this and related attack by electrophiles could be developed into a useful method of functionalising and derivatising the ligand backbones, including a method of introducing chirality, since the carbon atom attacked in **3c** becomes a chiral centre in complex **13a**.

We have also shown that halogenation of the enamine carbon in a compound of type **3** introduces a halogen into the azine backbone by electrophilic attack. Treatment of the bromoplatinum(II) complex **3b** with 1 equivalent of bromine gives the *C*-brominated bromoplatinum(II) bromide salt **13c** in



Scheme 5 (*i*) MeI; (*ii*) NH_4PF_6; (*iii*) base; (*iv*) Br_2

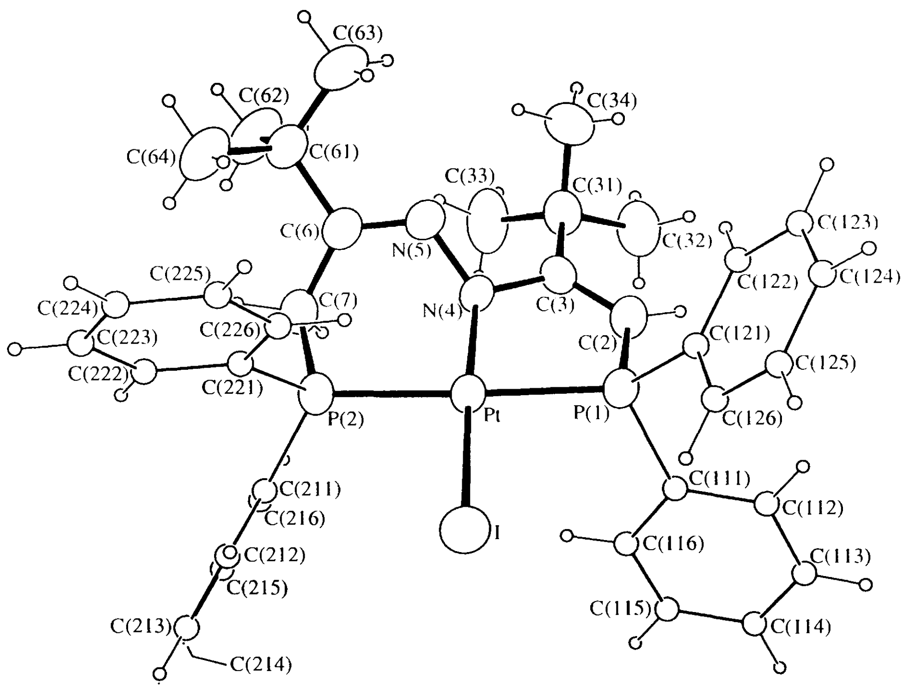


Fig. 1 Crystal structure of complex **3c**. For clarity, hydrogens and phenyl carbon atoms are shown with arbitrarily small radii; all other non-hydrogen atoms are shown at the 50% probability level

good isolated yield (81%). This was also converted into the corresponding PF_6 salt **13d**. The CHBr protons of salts **13c** and **13d** were significantly deshielded by bromine and absorbed at δ 6.15 and 5.77, respectively.

Crystal Structure of the Ene–Hydrazone Diphosphine Complex [PtI(PPh₂CH=CBuᵗN–N=CBuᵗCH₂PPh₂)] **3c**.—The crystal structure of complex **3c** is shown in Fig. 1 with selected bond lengths and angles in Table 3. Some features are (*i*) the two 'ene' carbons C(2) and C(3) are separated by 1.344(6) Å, consistent with a C=C double bond, (*ii*) the non-planarity of the six-membered chelate ring, in which the angle between the planes PtP(2)C(7) and N(5)C(6)C(7) is 58.6°, (*iii*) the sum of the three angles at the co-ordinated ene nitrogen N(4) *viz.* 112.0(3), 117.7(2) and 119.3(2) = 349.0° suggests that this nitrogen is

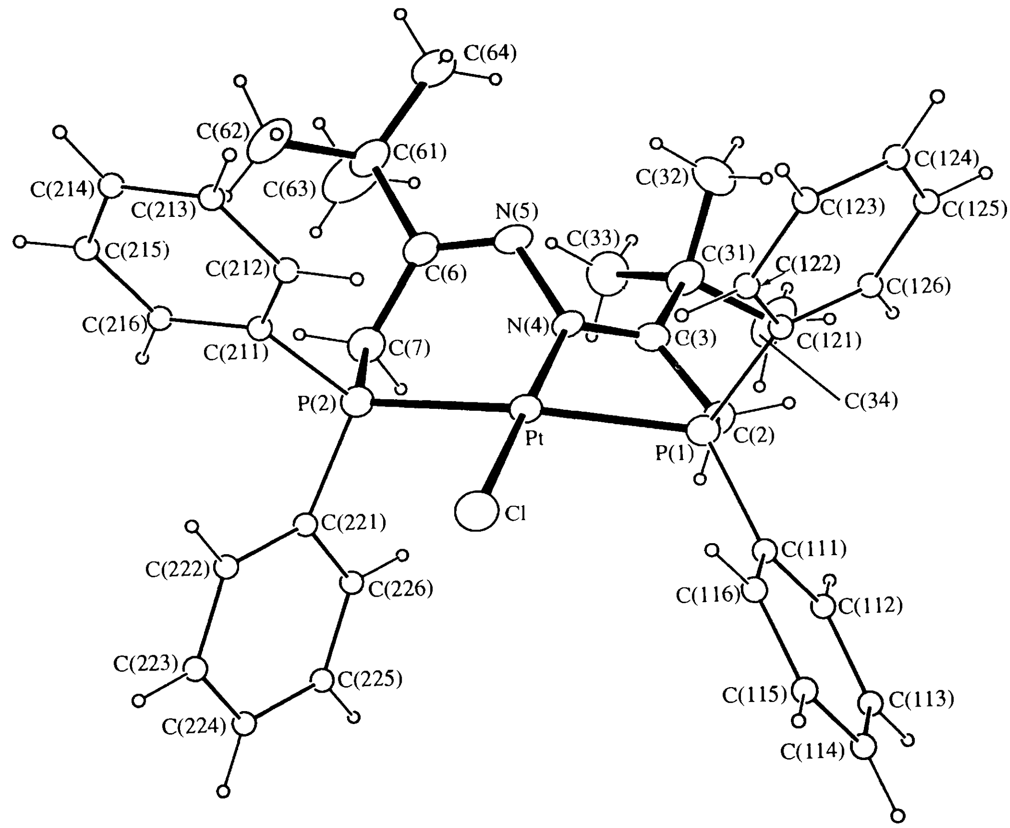


Fig. 2 Crystal structure of complex **4a**. Details as in Fig. 1

Table 3 Selected bond lengths (Å) and angles (°) for compound **3c** with e.s.d.s in parentheses

Pt–P(2)	2.290(1)	Pt–P(1)	2.280(1)
Pt–N(4)	2.062(3)	Pt–I	2.6091(4)
P(1)–C(2)	1.757(4)	P(2)–C(7)	1.827(4)
P(1)–C(111)	1.822(4)	P(2)–C(211)	1.823(5)
P(1)–C(121)	1.822(4)	P(2)–C(221)	1.816(4)
C(2)–C(3)	1.344(6)	C(3)–N(4)	1.413(5)
C(3)–C(31)	1.533(6)	N(4)–N(5)	1.420(4)
N(5)–C(6)	1.282(5)	C(6)–C(7)	1.502(6)
C(6)–C(61)	1.533(6)		
N(4)–Pt–P(1)	83.34(9)	N(4)–Pt–P(2)	89.16(9)
P(1)–Pt–P(2)	170.62(4)	N(4)–Pt–I	117.29(9)
P(1)–Pt–I	94.03(3)	P(2)–Pt–I	93.52(3)
C(2)–P(1)–Pt	99.78(14)	C(7)–P(2)–Pt	105.4(1)
C(3)–C(2)–P(1)	117.9(3)	C(2)–C(3)–N(4)	119.6(4)
C(2)–C(3)–C(31)	121.6(4)	N(4)–C(3)–C(31)	118.7(3)
C(3)–N(4)–N(5)	112.0(3)	C(3)–N(4)–Pt	117.7(2)
N(5)–N(4)–Pt	119.3(2)	C(6)–N(5)–N(4)	117.9(4)
N(5)–C(6)–C(7)	122.9(4)	N(5)–C(6)–C(61)	117.1(4)
C(7)–C(6)–C(61)	119.6(4)	C(6)–C(7)–P(2)	111.8(3)

Table 4 Selected bond lengths (Å) and angles (°) for compound **4a** with e.s.d.s in parentheses

Pt–P(1)	2.290(1)	Pt–P(2)	2.284(1)
Pt–N(4)	2.045(3)	Pt–Cl	2.302(1)
P(1)–C(111)	1.808(3)	P(2)–C(211)	1.808(3)
P(1)–C(121)	1.817(4)	P(2)–C(221)	1.802(3)
P(1)–C(2)	1.823(3)	P(2)–C(7)	1.834(3)
C(2)–C(3)	1.510(4)	C(3)–N(4)	1.312(4)
C(3)–C(31)	1.533(5)	N(4)–N(5)	1.420(4)
N(5)–C(6)	1.288(5)	C(6)–C(7)	1.510(5)
N(4)–Pt–P(2)	91.15(8)	N(4)–Pt–P(1)	80.69(8)
P(2)–Pt–P(1)	165.83(3)	N(4)–Pt–Cl	179.10(8)
P(2)–Pt–Cl	89.64(4)	P(1)–Pt–Cl	98.61(4)
C(2)–P(1)–Pt	96.23(11)	C(7)–P(2)–Pt	104.8(1)
C(3)–C(2)–P(1)	108.0(2)	N(4)–C(3)–C(2)	115.8(3)
N(4)–C(3)–C(31)	124.7(3)	C(2)–C(3)–C(31)	119.5(3)
C(3)–C(31)–C(33)	111.7(3)	C(3)–N(4)–N(5)	116.7(3)
C(3)–N(4)–Pt	122.1(2)	N(5)–N(4)–Pt	120.3(2)
C(6)–N(5)–N(4)	118.7(3)	N(5)–C(6)–C(7)	124.4(3)
N(5)–C(6)–C(61)	116.0(3)	C(7)–C(6)–C(61)	119.5(3)
C(6)–C(61)–C(63)	106.3(3)	C(6)–C(7)–P(2)	110.1(2)

closer to sp^2 than sp^3 hybridised, and (*iv*) the Pt–I distance 2.6091(4) Å is similar to other platinum–iodide distances when iodide is *trans* to nitrogen.[23–25] Other bond lengths and angles are as would be expected.

Crystal Structure of the Picrate Salt $[PtCl(PPh_2CH_2CBu^t{=}N{-}N{=}CBu^tCH_2PPh_2)][OC_6H_2(NO_2)_3\text{-}2,4,6]$ **4a** *containing an Azine Backbone*.—The crystal structure of complex **4a** is shown in Fig. 2 with selected bond lengths and angles in Table 4. Some noteworthy features are (*i*) the angle C(3)–C(2)–P(1) 108.0(2)° contrasts that for the ene–hydrazone complex **3c**, *i.e.* 117.9(3)°, (*ii*) the six-membered chelate ring is also non-planar and the interplanar angle (see above) is 59°, (*iii*) the Pt–Cl distance 2.302(1) Å is similar to other platinum–chloride distances when chloride is *trans* to nitrogen.[26–30] Other bond lengths and angles are normal.

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, NMR spectra using a JEOL FX-90Q (operating frequencies for ^1H and ^{31}P of 89.5 and 36.2 MHz respectively), FX-100 (operating frequencies for ^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 ^{1}H and ^{13}C chemical shifts are relative to tetramethylsilane and ^{31}P shifts to 85% phosphoric acid. Fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec spectrometer with 8 kV acceleration. For the metal complexes *m/z* values are quoted for ^{106}Pd and ^{195}Pt.

[PtCl(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] **3a**.—A mixture of [PtCl$_2$(cod)] (0.60 g, 1.6 mmol) and compound **I** (0.90 g, 1.6 mmol) in CHCl$_3$ (20 cm^3) was heated under reflux for 3 h. An excess of NEt$_3$ (0.5 cm^3) was then added, and the reaction mixture was refluxed for 30 min. The solution was filtered and then concentrated to a low volume (*ca.* 5 cm^3) under reduced pressure. Addition of MeOH (*ca.* 10 cm^3) to the residue gave the chloroplatinum(II) complex **3a** as yellow microcrystals (0.86 g, 68%) (Found: C, 52.95; H, 5.1; Cl, 7.3; N, 3.25. $C_{36}H_{41}ClN_2P_2Pt \cdot 0.25CHCl_3$ requires C, 52.85; H, 5.05; Cl, 7.5; N, 3.4%); ν(Pt–Cl) 340 cm^{-1}; *m/z* 794 (*M* + 1); ^{13}C-{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$): δ 20.4 [1C, d, ^1J(PC) 25.0, CH$_2$], 28.4 (3C, s, C*Me*$_3$), 31.1 (3C, s, C*Me*$_3$), 39.3 (1C, s, *C*Me$_3$), 39.4 [1C, d, ^3J(PC) 12.0, ^3J(PtC) 49, *C*Me$_3$], 78.1 [1C, d, ^1J(PC) 64.4, ^2J(PtC) 35, =CHP], 155.9 [1C, d, ^2J(PC) 3.3, ^2J(PtC) 37, =CN] and 191.8 [1C, d, ^2J(PC) 19.1 Hz, C=N].

[PtBr(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] **3b**.—A solution containing complex **3a** (0.15 g, 0.19 mmol) and LiBr (0.16 g, 1.9 mmol) in acetone (10 cm^3) was put aside for 15 h. The solvent was then removed and the residue extracted into CH$_2$Cl$_2$ (2 × 3 cm^3). Complex **3b** crystallised from CH$_2$Cl$_2$–EtOH as yellow-orange crystals (0.125 g, 78%) (Found: C, 49.95; H, 4.8; N, 3.05. $C_{36}H_{41}BrN_2P_2Pt \cdot 0.1CH_2Cl_2$ requires C, 50.1; H, 4.9; N, 3.3%); *m/z* 839 (*M* + 1).

[PtI(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] **3c**.—A solution containing complex **3a** (0.15 g, 0.19 mmol) and NaI (0.28 g, 1.9 mmol) in acetone (10 cm^3) was put aside for 15 h. The resulting orange crystals of complex **3c** were filtered off, washed with MeOH then with water, and dried. Yield (0.146 g, 87%) (Found: C, 49.95; H, 4.9; N, 3.0. $C_{36}H_{41}IN_2P_2Pt \cdot C_3H_6O$ requires C, 49.65; H, 5.0; N, 2.95%); *m/z* 885 (*M* + 1).

[PdCl(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] **3d**.—A mixture of [PdCl$_2$(NCPh)$_2$] (0.67 g, 1.77 mmol) and compound **I** (1.0 g, 1.77 mmol) in CHCl$_3$ (50 cm^3) was heated under reflux for 1 h. An excess of NEt$_3$ (1.0 cm^3) was added and the resulting dark solution concentrated to low volume (*ca.* 5 cm^3) under reduced pressure. Addition of MeOH (*ca.* 10 cm^3) to the residue gave complex **3d** as purple microcrystals (0.98 g, 78%) (Found: C, 57.25; H, 5.55; Cl, 11.25; N, 3.7. $C_{36}H_{41}ClN_2P_2Pd \cdot 0.75CH_2Cl_2$ requires C, 57.35; H, 5.55; Cl, 11.5; N, 3.65%); ν(Pd–Cl) 335 cm^{-1}; *m/z* 705 (*M* + 1); ^{13}C-{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$): δ 21.8 [1C, d, ^1J(PC) 16.0, CH$_2$], 28.4 (3C, s, C*Me*$_3$), 31.0 (3C, s, C*Me*$_3$), 39.1 [1C, d, ^3J(PC) 1.8, *C*Me$_3$], 40.0 [1C, d, ^3J(PC) 15.7, *C*Me$_3$], 77.4 [1C, d, ^1J(PC) 56.0, =CHP], 157.1 (1C, s, =CN) and 191.4 [1C, dd, ^2J(PC) 23.7, ^4J(PC) 1.5 Hz, C=N].

[PdBr(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] **3e**.—A solution containing complex **3d** (0.20 g, 0.28 mmol) and LiBr (0.12 g, 1.4 mmol) in acetone (10 cm^3) was put aside for 15 h. The resulting dark purple crystals of complex **3e** were filtered off, washed with MeOH and dried. Yield (0.18 g, 83%) (Found: C, 57.3; H, 5.5; N, 3.55. $C_{36}H_{41}BrN_2P_2Pd$ requires C, 57.65; H, 5.5; N, 3.75%); *m/z* 751 (*M* + 1).

[PtMe(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] **3f**.—A solution containing complex **1a** (80 mg, 0.10 mmol) in benzene (1 cm^3) was heated to 75 °C for 5 h. The resulting yellow solution was concentrated to *ca.* 0.3 cm^3 under reduced pressure. Addition of MeOH (1 cm^3) gave the complex **3f** as yellow microcrystals (55 mg, 70%) (Found: C, 57.85; H, 5.7; N, 3.3. $C_{37}H_{44}N_2P_2Pt$ requires C, 57.45; H, 5.7; N, 3.6%); *m/z* 774 (*M* + 1).

[PdMe(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] **3g**.—A solution containing complex **3d** (100 mg, 0.14 mmol) in dry tetrahydrofuran (thf) (2 cm^3) was treated with an excess of MgMeI (0.5 mol dm^{-3}) in diethyl ether (1.0 cm^3). The resulting yellow solution was cooled to −78 °C and the excess of MgMeI was destroyed by the addition of water; the solution was then allowed to warm to room temperature. It was evaporated to dryness in vacuum. The residue was extracted into C$_6$D$_6$ (0.5 cm^3) and the NMR spectra were recorded.

[Pt(C≡CC$_6$H$_4$Me-*p*)(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] **3h**.—An excess of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) (30 μl) was added to a solution of complex **4g** (25 mg, 0.022 mmol) in CHCl$_3$ (0.5 cm^3). The solvent was then removed and residue triturated with MeOH to give the required product **3h** as yellow microcrystals (16 mg, 80%) (Found: C, 61.0; H, 5.15; N, 3.15. $C_{45}H_{48}N_2P_2Pt \cdot 0.1CHCl_3$ requires C, 61.15; H, 5.45; N, 3.15%); *m/z* 874 (*M* + 1).

[PtH(PPh$_2$CH=CBu^{t}N–N=CBu^{t}CH$_2$PPh$_2$)] **3i**.—A solution containing complex **7a** (50 mg, 0.029 mmol) and compound **I** (5 mg, 0.009 mmol) in benzene (1.5 cm^3) was heated to 75 °C for 3 h. The resulting yellow solution was concentrated to low volume (*ca.* 0.3 cm^3) under reduced pressure. Addition of MeOH (1 cm^3) gave complex **3i** as yellow microcrystals (32 mg, 72%) (Found: C, 56.9; H, 5.3; N, 3.7. $C_{36}H_{42}N_2P_2Pt$ requires C, 56.9; H, 5.55; N, 3.7%); ν(Pt–H) 2120 cm^{-1}; *m/z* 760 (*M* + 1).

[PtCl(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)][OC$_6$H$_2$-(NO$_2$)$_3$-2,4,6] **4a**.—Picric acid (45 mg, 0.19 mmol) was added to a solution of complex **3a** (0.15 g, 0.19 mmol) in CH$_2$Cl$_2$ (4 cm^3). The resulting yellow solution was concentrated to low volume (*ca.* 0.3 cm^3) under reduced pressure. Addition of MeOH (*ca.* 0.5 cm^3) to the residue gave the picrate salt **4a** as yellow microcrystals (0.18 g, 96%) (Found: C, 49.1; H, 4.25; Cl, 3.6; N, 6.75. $C_{42}H_{44}ClN_5O_7P_2Pt$ requires C, 49.3; H, 4.35; Cl, 3.45; N, 6.85%); ν(Pt–Cl) 340 cm^{-1}; *m/z* 794 [*M* − OC$_6$H$_2$(NO$_2$)$_3$-2,4,6].

[PdCl(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)][OC$_6$H$_2$-(NO$_2$)$_3$-2,4,6] **4b**.—Complex **4b** was prepared from **3d** in a similar manner to the analogous platinum complex **4a**, in 86% yield (Found: C, 52.25; H, 4.45; Cl, 6.1; N, 7.25. $C_{42}H_{44}ClN_5O_7P_2Pd \cdot 0.4CH_2Cl_2$ requires C, 52.55; H, 4.65; Cl, 6.6; N, 7.25%); ν(Pd–Cl) 335 cm^{-1}; *m/z* 705 [*M* − OC$_6$H$_2$(NO$_2$)$_3$]; ^{13}C-{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$): δ 23.9 [1C, dd, ^1J(PC) 16.0, ^3J(PC) 2.5, CH$_2$ of six-membered ring], 26.9 (3C, s, C*Me*$_3$), 27.9 (3C, s, C*Me*$_3$), 40.8 [1C, d, ^3J(PC) 1.7, *C*Me$_3$], 41.4 [1C, dd, ^1J(PC) 25.7, ^3J(PC) 2.1, CH$_2$ of five-membered ring], 41.8 [1C, d, ^3J(PC) 5.4, *C*Me$_3$], 175.5 (1C, s, C=N) and 189.5 [1C, dd, *J*(PC) 5.8 Hz, 1.7, C=N].

[PtCl(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)][O$_2$CH] **4c**.—Complex **4c** was prepared *in situ* by the addition of an excess of formic acid (20 μl) to a solution of **3a** (25 mg, 0.031 mmol) in CD$_2$Cl$_2$ (0.4 cm^3).

[PdCl(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)][O$_2$CH] **4d**.—Complex **4d** was prepared *in situ* by the addition of an excess of formic acid (8 μl) to a solution of **3d** (20 mg, 0.028 mmol) in CD$_2$Cl$_2$ (0.4 cm^3).

[PdCl(PPh$_2$CH$_2$CBu^t=N–N=CBu^{t}CH$_2$PPh$_2$)][O$_3$SC$_{10}$-H$_{15}$O] **4e**.—(1*S*)-(+)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-methanesulfonic acid (21 mg, 0.085 mmol) was added to a solution of complex **3d** (60 mg, 0.085 mmol) in CHCl$_3$ (1.5 cm^3). The resulting yellow solution was concentrated to low volume (*ca.* 0.2 cm^3) under reduced pressure. Addition of ether (*ca.* 1 cm^3) to the residue gave the sulfonate salt **4e** as yellow microcrystals (73 mg, 91%); ν(Pd–Cl) 340 cm^{-1}; *m*/*z* 705 [*M* − $O_3SC_{10}H_{15}O$] (Found: C, 57.8; H, 6.0; N, 2.6. $C_{46}H_{56}ClN_2O_4P_2PdS{\cdot}0.25CHCl_3$ requires C, 57.45; H, 5.85; N, 2.9%).

[$PtMe(PPh_2CH_2CBu^t$=N–N=$CBu^tCH_2PPh_2)][OC_6H_2(NO_2)_3$-2,4,6] **4f**.—Picric acid (9 mg, 0.039 mmol) was added to a solution of complex **1a** (30 mg, 0.038 mmol) in C_6H_6 (1.5 cm^3). After gas evolution had ceased the resulting yellow solution was concentrated to low volume (*ca.* 0.2 cm^3) under reduced pressure. Addition of EtOH (*ca.* 0.5 cm^3) to the residue gave the picrate salt **4f** as yellow microcrystals (31 mg, 82%) (Found: C, 51.7; H, 4.55; N, 6.85. $C_{43}H_{47}N_5O_7P_2Pt$ requires C, 51.5; H, 4.7; N, 7.0%); *m*/*z* 744 [*M* − $OC_6H_2(NO_2)_3$].

[$Pt(C{\equiv}CC_6H_4Me$-*p*)($PPh_2CH_2CBu^t$=N–N=$CBu^tCH_2PPh_2)][OC_6H_2(NO_2)_3$-2,4,6] **4g**.—Picric acid (34 mg, 0.148 mmol) was added to a solution containing [$Pt(C{\equiv}CC_6H_4Me$-*p*)$_2$(cod)] (80 mg, 0.148 mmol) and compound **I** (85 mg, 0.148 mmol) in C_6H_6 (2 cm^3). After 1 h the resulting yellow solution was concentrated to low volume (*ca.* 0.3 cm^3) under reduced pressure. Addition of ether (*ca.* 2 cm^3) to the residue gave the picrate salt **4g** as yellow microcrystals (60 mg, 36%) (Found: C, 55.8; H, 4.5; N, 6.5. $C_{51}H_{51}N_5O_7P_2Pt$ requires C, 55.55; H, 4.65; N, 6.35%); *m*/*z* 874 [*M* − $OC_6H_2(NO_2)_3$].

[$PtMe(PPh_2CH_2CBu^t$=N–N=$CBu^tCH_2PPh_2)$]I **4h**.—An excess of MeI (0.5 cm^3) was added to a solution containing [$Pt(nb)_3$] (80 mg, 0.16 mmol) and compound **I** (95 mg, 0.16 mmol) in C_6H_6 (*ca.* 1.5 cm^3), and the reaction mixture then heated to 60 °C for 2 h. The resulting white precipitate of complex **4h** was collected and dried. Yield (65 mg, 45%) (Found: C, 49.2; H, 4.95; N, 3.05. $C_{37}H_{45}IN_2P_2Pt$ requires C, 49.3; H, 5.05; N, 3.1%).

fac-[$PtMe_3(PPh_2CH_2CBu^t$=N–N=$CBu^tCH_2PPh_2)]PF_6$ **5**.—A solution containing complex **1a** (50 mg, 0.98 mmol) and MeI (0.2 cm^3) in benzene (1 cm^3) was put aside for 45 min. The solvent was then removed and the residue redissolved in hot EtOH (*ca.* 1 cm^3). Addition of a solution of NH_4PF_6 in EtOH gave complex **5** as white microcrystals (52 mg, 87%) (Found: C, 48.9; H, 5.55; N, 3.1. $C_{39}H_{51}F_6N_2P_3Pt$ requires C, 49.3; H, 5.4; N, 2.9%); *m*/*z* 804 (*M* − PF_6) and 774 (*M* − PF_6 − C_2H_6); ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2): δ −12.1 [1C, t, ^2J(PC) 3.0, ^1J(PtC) 602, PtMe *trans* to N], 9.7 [1C, dd, ^2J(PC) 110.7, 4.8, ^1J(PtC) 495, PtMe *trans* to P], 11.5 [1C, dd, ^2J(PC) 104.9, 5.3, ^1J(PtC) 510, PtMe *trans* to P], 24.5 [1C, d, ^1J(PC) 17.6, CH_2], 27.7 (3C, s, C*Me*$_3$), 28.4 (3C, s, C*Me*$_3$), 40.1 [1C, d, ^3J(PC) 2.2, *C*Me$_3$], 40.8 [1C, d, ^3J(PC) 4.0, *C*Me$_3$], 41.9 [1C, d, ^1J(PC) 36.1, ^2J(PtC) 11.7, CH_2], 174.1 [1C, d, ^2J(PC) 2.6, C=N] and 180.6 [1C, d, ^2J(PC) 3.0 Hz, C=N].

fac-[$PtMe_3(PPh_2CH$=CBu^tN–N=$CBu^tCH_2PPh_2)$] **6**.—An excess of dbu (20 μl) was added to a solution of complex **5** (30 mg, 0.031 mmol) in $CHCl_3$ (*ca.* 1 cm^3). After 30 min the solvent was removed and the residue triturated with MeOH to give the neutral trimethyl complex **6** as yellow microcrystals (19 mg, 79%) (Found: C, 57.35; H, 6.05; N, 3.25. $C_{39}H_{50}N_2P_2Pt{\cdot}0.1CHCl_3$ requires C, 57.55; H, 6.2; N, 3.45%); *m*/*z* 804 (*M* + 1) and 774 (*M* + 1 − C_2H_6).

[$Pt_2(nb)_2$(μ-$PPh_2CH_2CBu^t$=N–N=$CBu^tCH_2PPh_2)_2$] **7a**.—A solution containing [$Pt(nb)_3$] (0.47 g, 0.98 mmol) and compound **I** (0.56 g, 0.99 mmol) in benzene (10 cm^3) was put aside for 30 min. It was then concentrated to low volume (*ca.* 1 cm^3) under reduced pressure. Addition of EtOH (*ca.* 2 cm^3) to the residue gave complex **7a** as off-white microcrystals (0.65 g, 84%) (Found: C, 60.15; H, 6.0; N, 3.1. $C_{86}H_{104}N_4P_4Pt_2$ requires C, 60.45; H, 6.15; N, 3.3%); *m*/*z* 1706 (M^+).

[$Pt_2(MeO_2CC{\equiv}CCO_2Me)_2$(μ-$PPh_2CH_2CBu^t$=N–N=$CBu^tCH_2PPh_2)_2$] **7b**.—An excess of dimethyl acetylenedicarboxylate (40 μl) was added to a solution containing complex **7a** (50 mg, 0.029 mmol) in C_6H_6 (*ca.* 1.5 cm^3). After 30 min the solution was concentrated to low volume (*ca.* 0.2 cm^3) under reduced pressure. Addition of EtOH (*ca.* 0.5 cm^3) to the residue gave complex **7b** as white microcrystals (29 mg, 56%) (Found: C, 58.8; H, 5.55; N, 2.75. $C_{42}H_{48}N_2O_4P_2Pt{\cdot}C_6H_6$ requires C, 58.8; H, 5.55; N, 2.85%).

[$PtCl(PPh_2CD_2CBu^t$=N–N=$CBu^tCH_2PPh_2)][OC_6H_2(NO_2)_3$-2,4,6] **9a**.—Complex **9a** was prepared *in situ* by the addition of D_2O (30 μl) to a solution of **4a** (25 mg, 0.031 mmol) in CD_2Cl_2 (0.4 cm^3), after a reaction time of 30 min.

[$PtCl(PPh_2CD_2CBu^t$=N–N=$CBu^tCH_2PPh_2)][O_2CH]$ **9b**.—Complex **9b** was prepared *in situ* by the addition of D_2O (30 μl) to a solution containing formic acid (20 μl) and **3a** (25 mg, 0.031 mmol) in CD_2Cl_2 (0.4 cm^3), after a reaction time of 5 min.

[$PdCl(PPh_2CD_2CBu^t$=N–N=$CBu^tCH_2PPh_2)][O_2CH]$ **9c**.—Complex **9c** was prepared *in situ* by the addition of D_2O (30 μl) to a solution containing formic acid (8 μl) and **3d** (20 mg, 0.028 mmol) in CD_2Cl_2 (0.4 cm^3), after a reaction time of 5 min.

[$PtCl(PPh_2CD_2CBu^t$=N–N=$CBu^tCD_2PPh_2)][O_2CH]$ **10a**.—Complex **10a** was prepared *in situ* by the addition of D_2O (30 μl) to a solution containing formic acid (20 μl) and **3a** (25 mg, 0.031 mmol) in CD_2Cl_2 (0.4 cm^3), after a reaction time of 2 d.

[$PdCl(PPh_2CD_2CBu^t$=N–N=$CBu^tCD_2PPh_2)][O_2CH]$ **10b**.—Complex **10b** was prepared *in situ* by the addition of D_2O (30 μl) to a solution containing formic acid (8 μl) and **3d** (20 mg, 0.028 mmol) in CD_2Cl_2 (0.4 cm^3), after a reaction time of 24 h.

[$PtCl(PPh_2CD$=CBu^tN–N=$CBu^tCH_2PPh_2)$] **11a**.—Complex **11a** was prepared *in situ* by the addition of a solution of NaOD (0.05 mol dm^{-3}) in D_2O (15 μl) to a solution of **3a** (25 mg, 0.031 mmol) in $CDCl_3$ (0.4 cm^3), after a reaction time of 5 min.

[$PdCl(PPh_2CD$=CBu^tN–N=$CBu^tCH_2PPh_2)$] **11b**.—Complex **11b** was prepared *in situ* by the addition of a solution of NaOD (0.05 mol dm^{-3}) in D_2O (15 μl) to a solution of **3d** (25 mg, 0.035 mmol) in $CDCl_3$ (0.4 cm^3), after a reaction time of 5 min.

[$PtCl(PPh_2CD$=CBu^tN–N=$CBu^tCD_2PPh_2)$] **12a**.—Complex **12a** was prepared *in situ* by the addition of a solution of NaOD (0.05 mol dm^{-3}) in D_2O (15 μl) to a solution of **3a** (25 mg, 0.031 mmol) in $CDCl_3$ (0.4 cm^3), after a reaction time of 36 h.

[$PdCl(PPh_2CD$=CBu^tN–N=$CBu^tCD_2PPh_2)$] **12b**.—Complex **12b** was prepared *in situ* by the addition of a solution of NaOD (0.05 mol dm^{-3}) in D_2O (15 μl) to a solution of **3d** (25 mg, 0.035 mmol) in $CDCl_3$ (0.4 cm^3), after a reaction time of 8 h.

[$PtI(PPh_2CHMeCBu^t$=N–N=$CBu^tCH_2PPh_2)$]I **13a**.—A solution containing complex **3c** (140 mg, 0.16 mmol) and MeI (1 cm^3) in $CHCl_3$ (6 cm^3) was stirred for 15 h. The resulting yellow solution was concentrated to low volume (*ca.* 0.5 cm^3) under reduced pressure. Addition of hexane (*ca.* 1 cm^3) to the residue gave the iodo salt **13a** as yellow microcrystals (160 mg, 98%) (Found: C, 42.45; H, 4.5; N, 2.55. $C_{37}H_{44}I_2N_2P_2Pt{\cdot}0.25CHCl_3$ requires C, 42.3; H, 4.2; N, 2.65%); *m*/*z* 1026 (*M* − 1) and 900 (*M* − I); ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2): δ 19.6 [1C, d,

Table 5 Crystallographic data for compounds **3c** and **4a** [a]

	3c	**4a**
Formula	$C_{36}H_{41}IN_2P_2Pt{\cdot}CH_2Cl_2$	$C_{42}H_{44}ClN_5O_7P_2Pt$
M	970.56 [b]	1023.30
Crystal dimensions/mm	0.72 × 0.34 × 0.30	0.60 × 0.19 × 0.11
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	10.3114(7)	9.126(2)
b/Å	26.234(2)	12.206(2)
c/Å	14.2296(7)	19.421(5)
α/°		89.93(2)
β/°	96.107(5)	85.51(2)
γ/°		75.69(2)
U/Å^3	3827.4(4)	2089.4(8)
Z	4	2
D_c/g cm^{-3}	1.684	1.627
F(000)	1896	1028
μ/mm^{-1}	4.724	3.554
Maximum, minimum transmission factors	0.5946, 0.3561	0.8356, 0.5621
T/K	290	160
$\theta_{min}, \theta_{max}$/°	4.0, 50.0	4.0, 55.0
Minimum, maximum scan speeds/° min^{-1}	1.0, 8.0	c
Scan width/° + α-doublet splitting	1.05	c
No. of data collected	8816	9982
No. of unique data, n	6735	9572
No. of observed data [d]	5329	8729
R_{int} [e]	0.0230	
R_{sig} [f]	0.0324	0.0339
ρ_{max}, ρ_{min}/e Å^{-3}	0.69, −0.77	1.38, −0.91
Δ/σ_{max}	0.012	0.001
wR_2 [g]	0.0652	0.0644
R_1 [h]	0.0432	0.0351
Weighting parameters x, y [i]	0.0349, 1.7804	0.0194, 4.5188
No. of parameters, p	425	529
Goodness of fit [j]	1.044	1.077

[a] Common to both structures: Mo-Kα radiation, λ = 0.710 69 Å. [b] Includes CH_2Cl_2 solvate. [c] Each scan divided into 30 steps, scan width and step size calculated from a learnt profile. [d] Criterion for observed reflection, $|F_o| > 4.0\sigma(|F_o|)$, used only in calculation of R_1. [e] $\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$. [f] $\Sigma[\sigma(F_o^2)]/\Sigma F_o^2$. [g] $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [h] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [i] Weighting scheme used, $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. [j] $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{\frac{1}{2}}$.

^2J(PC) 3.5, CH*Me*], 23.7 [1C, dd, ^1J(PC) 22.2, ^3J(PC) 2.0, CH_2], 26.9 (3C, s, C*Me*$_3$), 28.5 (3C, s, C*Me*$_3$), 41.1 [1C, d, ^3J(PC) 1.9, *C*Me_3], 41.2 [1C, d, ^3J(PC) 4.8, *C*Me_3], 47.2 [1C, d, ^1J(PC) 31.1, *C*HMe], 176.1 (1C, s, C=N) and 193.6 [1C, d, ^2J(PC) 5.2 Hz, C=N].

[PtI($PPh_2CHMeCBu^t$=N–N=$CBu^tCH_2PPh_2$)]PF_6 **13b**.—A solution of NH_4PF_6 (20 mg) in MeOH (*ca.* 0.5 cm^3) was added to a solution containing complex **13a** (35 mg, 0.034 mmol) in MeOH (*ca.* 1 cm^3). The PF_6 salt **13b** deposited as white microcrystals (28 mg, 80%) (Found: C, 42.3; H, 4.15; N, 2.5. $C_{37}H_{44}F_6IN_2P_3Pt$ requires C, 42.55; H, 4.25; N, 2.7%); m/z 900 ($M - PF_6$).

[PtBr($PPh_2CHBrCBu^t$=N–N=$CBu^tCH_2PPh_2$)]Br **13c**.—A solution of bromine (0.047 mmol) in CCl_4 was added to a solution of complex **3b** (40 mg, 0.047 mmol) in CH_2Cl_2. After 15 min the resulting pale yellow solution was concentrated to low volume (*ca.* 0.5 cm^3) under reduced pressure. Addition of hexane (*ca.* 1 cm^3) to the residue gave the bromide salt **13c** as yellow microcrystals (38 mg, 81%) (Found: C, 39.65; H, 3.8; N, 2.45. $C_{36}H_{41}Br_3N_2P_2Pt{\cdot}CH_2Cl_2$ requires C, 41.0; H, 4.0; N, 2.6%).

[PtBr($PPh_2CHBrCBu^t$=N–N=$CBu^tCH_2PPh_2$)]PF_6 **13d**.—A solution of bromine (0.081 mmol) in CCl_4 was added to a solution of complex **3b** (68 mg, 0.081 mmol) in CH_2Cl_2. After 15 min the solvent was removed and residue redissolved in MeOH (*ca.* 1.5 cm^3). Addition of a solution of NH_4PF_6 (40 mg) in MeOH (1 cm^3) gave the PF_6 salt **13d** as off-white microcrystals (81 mg, 94%) (Found: C, 40.55; H, 3.95; N, 2.55. $C_{36}H_{41}Br_2F_6N_2P_3Pt$ requires C, 40.65; H, 3.85; N, 2.6%); m/z 918 ($M - PF_6$) and 838 ($M - PF_6 - Br$).

[PtI(PPh_2CMe=CBu^tN–N=$CBu^tCH_2PPh_2$)] **14**.—An excess of dbu (25 μl) was added to a solution of complex **13a** (100 mg, 0.02 mmol) in $CHCl_3$ (*ca.* 2 cm^3). After 30 min the solvent was removed and the residue triturated with MeOH to give the neutral complex **14** as orange microcrystals (84 mg, 95%) (Found: C, 48.05; H, 5.05; N, 2.95. $C_{37}H_{43}IN_2P_2Pt{\cdot}0.2CHCl_3$ requires C, 48.35; H, 4.7; N, 3.0%); m/z 900 ($M + 1$); ^{13}C-{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 16.1 [1C, d, ^2J(PC) 2.7, =C*Me*], 22.7 [1C, d, ^1J(PC) 23.7, CH_2], 28.4 (3C, s, C*Me*$_3$), 30.1 (3C, s, C*Me*$_3$), 38.5 [1C, d, ^3J(PC) 2.4, *C*Me_3], 40.6 [1C, d, ^3J(PC) 14.6, *C*Me_3], 100.1 [1C, d, ^1J(PC) 55.8, =CP], 158.2 [1C, d, ^2J(PC) 5.0, =CN] and 184.7 [1C, d, ^2J(PC) 21.1 Hz, C=N].

Single-crystal X-Ray Diffraction Analysis.—All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode and (for compound **3c**) using as an on-line profile fitting method.[31] Crystal data are listed in Table 5 together with details of data collection and structure refinement. Both data sets were corrected for absorption semiempirically using azimuthal ψ scans.

Each structure was solved by heavy-atom methods using SHELXS 86[32] and refined by full-matrix least squares (based on F^2) using SHELXL 93.[33] Refinement was essentially the same for the two compounds in that all non-hydrogen atoms

Table 6 Non-hydrogen atom coordinates ($\times 10^4$) for compound **3c** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	1195.65(14)	1708.43(6)	525.88(10)	C(225)	−709(5)	2229(3)	4182(3)
I	−1155.2(3)	2020.48(13)	−57.7(2)	C(226)	120(5)	2363(2)	3510(3)
P(1)	1410.1(10)	1248.4(4)	−807.9(7)	C(2)	3075(4)	1093(2)	−612(3)
C(111)	1215(4)	1598(2)	−1920(3)	C(3)	3688(4)	1170(2)	258(3)
C(112)	934(5)	1354(2)	−2785(3)	C(31)	5107(4)	1005(2)	518(3)
C(113)	966(5)	1628(2)	−3615(3)	C(32)	5810(5)	940(2)	−383(4)
C(114)	1291(5)	2130(2)	−3589(3)	C(33)	5874(5)	1408(3)	1136(4)
C(115)	1557(5)	2374(2)	−2744(4)	C(34)	5140(6)	490(2)	1030(4)
C(116)	1504(5)	2114(2)	−1908(3)	N(4)	3045(3)	1436.5(13)	937(2)
C(121)	486(4)	664(2)	−1065(3)	N(5)	3331(3)	1230.2(14)	1858(2)
C(122)	1099(5)	191(2)	−955(3)	C(6)	3260(4)	1528(2)	2564(3)
C(123)	395(6)	−254(2)	−1148(4)	C(61)	3654(5)	1307(2)	3551(3)
C(124)	−907(6)	−231(2)	−1454(4)	C(62)	4967(5)	1545(3)	3923(4)
C(125)	−1535(5)	232(2)	−1560(4)	C(63)	3775(7)	728(2)	3517(4)
C(126)	−842(4)	681(2)	−1361(3)	C(64)	2645(5)	1444(2)	4229(3)
P(2)	1334.9(10)	2200.6(4)	1862.3(7)	C(7)	2969(4)	2087(2)	2457(3)
C(211)	1213(4)	2891(2)	1739(3)	C(1s)	2843(50)	98(17)	6127(35)
C(212)	6(5)	3127(2)	1730(4)	C(2s)	1639(37)	−266(12)	5027(21)
C(213)	−98(6)	3651(2)	1666(4)	C(3s)	1892(57)	86(17)	5900(36)
C(214)	996(6)	3941(2)	1595(4)	C(4s)	703(84)	−223(27)	−5256(52)
C(215)	2192(6)	3715(2)	1588(4)	C(5s)	430(39)	−22(14)	−3810(27)
C(216)	2314(5)	3189(2)	1668(4)	C(6s)	2960(48)	−90(22)	−4179(40)
C(221)	218(4)	2053(2)	2729(3)	C(7s)	2985(18)	89(6)	−3103(12)
C(222)	−513(5)	1610(2)	2637(3)	C(8s)	2275(31)	11(11)	−3305(22)
C(223)	−1323(5)	1476(3)	3302(4)	C(9s)	1133(85)	41(29)	−4490(58)
C(224)	−1416(6)	1791(3)	4074(4)	C(10s)	2607(19)	−340(7)	−4772(13)

Table 7 Non-hydrogen atom coordinates ($\times 10^4$) for compound **4a** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	2053.79(15)	3169.76(11)	1764.97(7)	C(3)	948(4)	2597(3)	3159(2)
Cl	3286.0(10)	2861.2(7)	676.3(4)	C(31)	85(4)	2724(3)	3875(2)
P(1)	1802.3(10)	1375.2(7)	1971.2(4)	C(32)	−1631(4)	2949(4)	3790(2)
C(111)	3229(4)	139(3)	1648(2)	C(33)	421(5)	3677(3)	4307(2)
C(112)	4016(4)	−651(3)	2091(2)	C(34)	552(6)	1625(3)	4288(2)
C(113)	5108(5)	−1597(3)	1814(2)	N(4)	938(3)	3427(2)	2728.5(14)
C(114)	5381(4)	−1754(3)	1108(2)	N(5)	−102(3)	4479(2)	2908.7(14)
C(115)	4583(5)	−976(3)	667(2)	C(6)	384(4)	5383(3)	2890(2)
C(116)	3512(4)	−28(3)	937(2)	C(61)	−785(5)	6482(3)	3121(2)
C(121)	−20(4)	1127(3)	1802(2)	C(62)	−2375(5)	6295(4)	3225(3)
C(122)	−820(4)	550(3)	2249(2)	C(63)	−302(7)	6848(4)	3808(2)
C(123)	−2224(5)	420(4)	2091(2)	C(64)	−789(5)	7416(3)	2602(2)
C(124)	−2819(5)	831(4)	1480(3)	C(7)	2013(4)	5408(3)	2702(2)
C(125)	−2017(6)	1378(5)	1030(3)	C(1a)	4840(4)	2287(3)	4195(2)
C(126)	−625(5)	1541(4)	1192(2)	O(1)	4263(3)	2420(2)	3634.1(14)
P(2)	2586.5(10)	4900.0(7)	1809.3(4)	C(2a)	4693(4)	3169(3)	4718(2)
C(211)	1669(4)	6028(3)	1268(2)	N(2)	3909(4)	4322(3)	4564(2)
C(212)	1908(4)	7112(3)	1330(2)	O(21)	3185(3)	4937(2)	5038(2)
C(213)	1041(5)	8003(3)	985(2)	O(22)	4050(4)	4644(2)	3967(2)
C(214)	−60(5)	7825(3)	577(2)	C(3a)	5269(4)	3019(3)	5353(2)
C(215)	−250(5)	6749(4)	487(2)	C(4a)	6187(4)	1972(3)	5504(2)
C(216)	607(4)	5848(3)	834(2)	N(4)	6865(4)	1824(3)	6156(2)
C(221)	4600(4)	4767(3)	1676(2)	O(41)	6437(4)	2577(2)	6604.4(14)
C(222)	5239(4)	5143(3)	1078(2)	O(42)	7856(4)	953(2)	6239(2)
C(223)	6804(5)	4932(4)	956(2)	C(5a)	6478(4)	1071(3)	5032(2)
C(224)	7721(5)	4339(4)	1435(3)	C(6a)	5776(4)	1222(3)	4425(2)
C(225)	7101(5)	3941(4)	2026(2)	N(6)	6085(5)	240(3)	3957(2)
C(226)	5545(4)	4158(4)	2153(2)	O(61)	5069(4)	78(3)	3631(2)
C(2)	1870(4)	1445(3)	2905(2)	O(62)	7385(5)	−372(3)	3906(2)

were refined with anisotropic displacement parameters. The asymmetric unit of **3c** contained a molecule of CH_2Cl_2 which proved to be so badly disordered that it could only be allowed for by refining difference-map peaks of highest electron density as partial-occupancy carbon atoms. Geometrical restraints were applied to the phenyl groups such that each group remained flat with overall C_{2v} symmetry. All hydrogen atoms were constrained in calculated positions (C–H 0.93, 0.97 and 0.96 Å for phenyl, methylene and methyl hydrogen atoms respectively) and were assigned a fixed isotropic thermal parameter of $n(U_{eq})$ of the parent carbon atom where n was 1.5 for methyl hydrogens and 1.2 for all others. The ORTEP[34] diagrams of **3c** and the cation of **4a** are given in Figs. 1 and 2 respectively, atomic coordinates in Tables 6 and 7.

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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