

# Complexes of the Bidentate Ligands $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNR}_2$ ( $\text{R} = \text{H}$ or $\text{Me}$ ) and $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CHPh}$ with Palladium and Platinum. X-Ray Crystal Structure of $\text{cis}-[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}_2]^{\dagger}$

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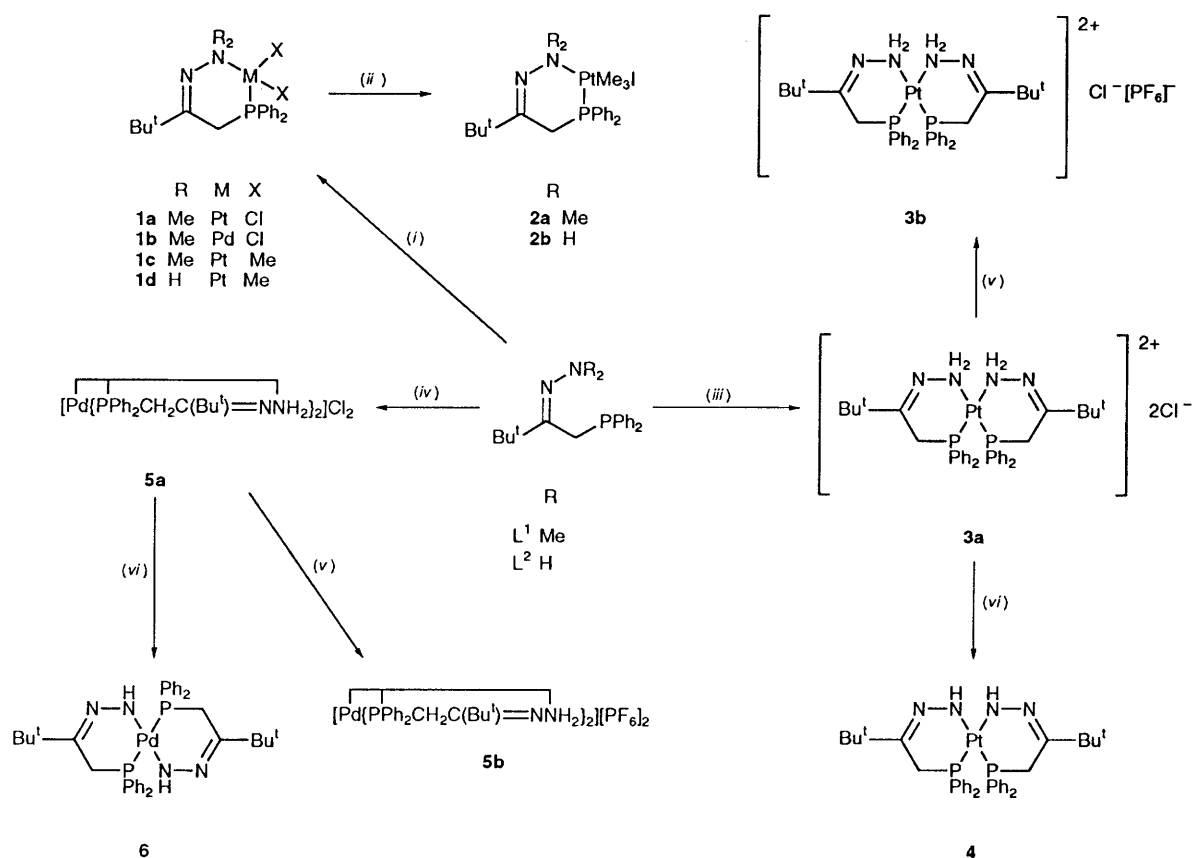
*tert*-Butyl diphenylphosphinomethyl ketone dimethylhydrazone  $\text{L}^1$  reacts with  $[\text{PtCl}_2(\text{cod})]$  ( $\text{cod} =$  cycloocta-1,5-diene) to give the chelate  $[\text{PtCl}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNMe}_2\}]$  with a six-membered chelate ring; the corresponding palladium complex was also prepared. The phosphino dimethylhydrazone  $\text{L}^1$  or the phosphino hydrazone  $\text{L}^2$  also react with  $[\text{PtMe}_2(\text{cod})]$  to give  $[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNR}_2\}]$ , ( $\text{R} = \text{Me}$  or  $\text{H}$ ); these platinum(II) complexes react with methyl iodide to give the corresponding trimethylplatinum(IV) complexes  $[\text{PtMe}_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNR}_2\}]$ . Treatment of  $[\text{PtCl}_2(\text{cod})]$  with 2 equivalents of  $\text{L}^2$  gave the dication  $\text{cis}-[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}_2]^{2+}$  isolated as the chloride or chloride hexafluorophosphate salts. The dicationic dichloride reacted with 2 moles of sodium ethoxide to give the neutral  $\text{cis}-[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}_2]$ . Treatment of  $[\text{PdCl}_2(\text{NCPH})_2]$  with  $\text{L}^2$  gave  $[\text{Pd}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}_2]\text{Cl}_2$ , which with sodium ethoxide gave the neutral  $\text{trans}-[\text{Pd}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}_2]$ . The mixed azine monophosphine  $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CHPh}$   $\text{L}^3$  with  $[\text{PdCl}_2(\text{NCPH})_2]$  gave the chelate complex  $[\text{PdCl}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CHPh}\}]$  and with  $[\text{PtMe}_2(\text{cod})]$  it gave  $[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CHPh}\}]$ . Treatment of  $[\text{PtCl}_2(\text{NCMe})_2]$  with 2 equivalents of  $\text{L}^3$  gave  $\text{trans}-[\text{PtCl}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CHPh}\}_2]$  which on heating gave the dicationic dichloride salt  $\text{cis}-[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CHPh}\}_2]\text{Cl}_2$ . Successive treatments of this salt with 1 mole of sodium methoxide gave  $\text{cis}-[\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CHPh}\}\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CHPh}\}]^+$  and  $\text{cis}-[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CHPh}\}_2]$ . Proton,  $^{13}\text{C}-\{^1\text{H}\}$ ,  $^{31}\text{P}-\{^1\text{H}\}$  NMR and infrared data have been obtained. Crystals of  $\text{cis}-[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}_2]$  are monoclinic, space group  $P2_1/c$ , with  $a = 1261.5(2)$ ,  $b = 1794.6(3)$ ,  $c = 1792.0(4)$  pm and  $Z = 4$ ; final  $R = 0.0451$  for 4088 observed reflections.

In a previous paper we have described the synthesis of *tert*-butyl diphenylphosphinomethyl ketone dimethylhydrazone  $\text{L}^1$  by deprotonating *tert*-butyl methyl ketone dimethylhydrazone with *n*-butyllithium and treating the resultant carbanion with chloro(diphenyl)phosphine.<sup>1</sup> We established that the configuration of this phosphine around the C=N bond as *Z* since, when treated with  $[\text{Mo}(\text{CO})_4(\text{nbdi})]$  ( $\text{nbdi} =$  norbornadiene) under mild conditions (20 °C), it gave  $[\text{Mo}(\text{CO})_4\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNMe}_2\}]$  the crystal structure of which was determined;<sup>1</sup> this showed the presence of a six-membered chelate ring, *i.e.* the configuration around the C=N is *Z*. When heated strongly (180 °C) this six-membered chelate ring complex isomerised to the five-membered chelate ring complex with an *E*-configuration around C=N. We also showed that the phosphino dimethylhydrazone ( $=\text{NNMe}_2$ )  $\text{L}^1$  underwent an exchange reaction with hydrazine in the presence of acetic acid as catalyst to give a phosphino hydrazone ( $=\text{NNH}_2$ )  $\text{L}^2$  which probably also had the *Z*-configuration; we also studied this phosphine as a ligand for chromium, molybdenum and tungsten carbonyls in the zero-valent state. It was of interest to study the behaviour of these hydrazone phosphines,  $\text{L}^1$  and  $\text{L}^2$ , as ligands towards some more electropositive and labile metals *viz.* platinum(II) and palladium(II) and in the present paper we describe the results of this study. For convenience the work is summarised in Scheme 1.

## Results and Discussion

We first attempted to prepare a chelate of  $\text{L}^1$  with platinum dichloride by treating the labile olefin complex  $[\text{PtCl}_2(\text{cod})]$  ( $\text{cod} =$  cycloocta-1,5-diene) with 1 equivalent of the phosphino dimethylhydrazone  $\text{L}^1$  at *ca.* 20 °C. This gave the hoped for chelate complex **1a** in *ca.* 80% yield; preparative details and elemental analytical data for this and other new complexes are in the Experimental section, infrared and  $^{31}\text{P}$  NMR data are in Table 1 and  $^1\text{H}$  data are in Table 2. The complex showed a single resonance in its  $^{31}\text{P}-\{^1\text{H}\}$  NMR spectrum, with satellites due to platinum-195, and the large value of  $^1J(\text{PtP})$  of 4126 Hz is consistent with a phosphorus *trans* to a chloride ligand.<sup>2</sup> The infrared spectrum showed two strong bands, at 340 and 285  $\text{cm}^{-1}$  for the *cis*- $\text{PtCl}_2$  moiety<sup>3</sup> due to  $\nu(\text{Pt}-\text{Cl})$ . The proton NMR data for the  $\text{NMe}_2$  methyls are consistent with the proposed structure for **1a**, having a six-membered chelate ring; the value of  $J(\text{PtNCH}_3)$  of 26.9 Hz is consistent with a three-bond coupling<sup>3,4</sup> and too large for a four-bond coupling, which it would have to be if the chelate ring were five-membered. The carbon-13 data (see Experimental section) are also consistent with the assigned structure. In particular, the low  $\delta_{\text{C}}$  value of  $\delta$  17.9 for the methylene carbon is in agreement with the observed low  $\delta_{\text{C}}$  value of  $\delta$  24.0 for the six-membered  $[\text{Mo}(\text{CO})_4\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNMe}_2\}]$  complex whereas the five-membered  $[\text{Mo}(\text{CO})_4\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{NMe}_2\}]$  complex has a higher  $\delta_{\text{C}}$  value of  $\delta$  42.1. In extensive studies of azine diphosphines acting as terdentates with metals such as Cr, Mo, W, Pd, Pt and Ir, we have found that the methylene carbons in the six-membered rings give lower  $\delta_{\text{C}}$

<sup>†</sup> Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii-xxviii.



**Scheme 1** (i) [PtCl<sub>2</sub>(cod)], [PdCl<sub>2</sub>(NCPH)<sub>2</sub>] or [PtMe<sub>2</sub>(cod)]; (ii) **1c** or **1d** with MeI; (iii) 0.5 equivalent [PtCl<sub>2</sub>(cod)]; (iv) [PdCl<sub>2</sub>(NCPH)<sub>2</sub>]; (v) NH<sub>4</sub>PF<sub>6</sub>; (vi) NaOMe

**Table 1** Infrared and <sup>31</sup>P-<sup>1</sup>H NMR<sup>a</sup> data

Compound	$\nu(\text{C}=\text{N})^b$	$\nu(\text{M}-\text{Cl})^c$	$\nu(\text{N}-\text{H})^c$	$\delta_p$
L <sup>1</sup>	1610m	—	—	-9.7
L <sup>2</sup>	1640w	—	3330m, 3350w	-22.6
L <sup>3</sup>	1585w	—	g	59.1
<b>1a</b>	1640m	285m, 340m	—	16.5 (4126)
<b>1b</b>	1620m	275w, 325w	—	43.2
<b>1c</b>	1610m	—	—	43.2 <sup>d</sup> (2186)
<b>1d</b>	1630m	—	3100w, 3300m	41.5 <sup>d</sup> (2199)
<b>2a</b>	1640w	—	—	7.2 <sup>d</sup> (1217)
<b>2b</b>	1630m	—	3100m, 3300m	7.1 <sup>d</sup> (1215)
<b>3a</b>	1630m	—	3100s, 3350w	36.4 <sup>e</sup> (3600)
<b>3b</b>	1630m	—	3100s, 3350w	36.9 <sup>f</sup> (3607)
<b>4</b>	1595s	—	g	38.4 <sup>h</sup> (3313)
<b>5a</b>	1630m	—	3130s, 3330w	63.3 <sup>e</sup>
<b>5b</b>	1640m	—	3130s, 3330w	64.1 <sup>h</sup>
<b>6</b>	1615m	—	—	-10.1
<b>7a</b>	1600s	280w, 340w	—	49.3
<b>7b</b>	1600s	—	—	31.3 (2136)
<b>8</b>	1630m	340w	—	11.2 (2575)
<b>9a</b>	—	—	—	21.5 <sup>e</sup> (3412)
<b>9b</b>	1620m	—	—	21.7 <sup>f</sup> (3361)
<b>11</b>	1595m	—	—	21.9 <sup>d</sup> (3146)
<b>12a</b> <sup>i</sup>	—	—	—	20.2 <sup>d</sup> (1703)
<b>12b</b> <sup>i</sup>	—	—	—	9.06 <sup>d</sup> (1540)
<b>12c</b> <sup>i</sup>	—	—	—	18.15 (1657)

<sup>a</sup> Recorded at 36.2 MHz, chemical shifts  $\delta$  ( $\pm 0.1$  ppm) relative to 85% H<sub>3</sub>PO<sub>4</sub>, solvent CDCl<sub>3</sub> unless otherwise stated, <sup>1</sup>J(PtP)/Hz in parentheses. <sup>b</sup> As compressed KBr disc. <sup>c</sup> As Nujol mull between polythene plates. <sup>d</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>e</sup> In ethanol with C<sub>6</sub>D<sub>6</sub> as external reference. <sup>f</sup> In (CD<sub>3</sub>)<sub>2</sub>CO. <sup>g</sup> Not observed. <sup>h</sup> In CD<sub>2</sub>Cl<sub>2</sub>. <sup>i</sup>  $\nu(\text{C}=\text{O})$  2040 cm<sup>-1</sup> in C<sub>6</sub>H<sub>6</sub>.

values ( $\delta$  20–25) than the ones in five-membered chelate rings ( $\delta$  40–45).<sup>5,6</sup> Similarly, treatment of [PdCl<sub>2</sub>(NCPH)<sub>2</sub>] with L<sup>1</sup> gave the corresponding palladium dichloride chelate **1b**; characterising data are given in the Experimental section and in Tables 1 and 2. We prepared the chelate complex of PtMe<sub>2</sub> and in Tables 1 and 2. We prepared the chelate complex of PtMe<sub>2</sub> with L<sup>1</sup> i.e. [PtMe<sub>2</sub>{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNMe<sub>2</sub>}] **1c** by displacing cod from [PtMe<sub>2</sub>(cod)] under mild conditions (ca. 20 °C). As would be expected,<sup>2</sup> the value of <sup>1</sup>J(PtP), viz. 2186 Hz was much less than with the corresponding dichloride **1a**. The proton NMR data (Table 2) are consistent with the assigned structure **1c**, e.g. the NMe<sub>2</sub> methyls are equivalent, J(PtH) = 15.9 Hz, consistent with a three-bond coupling.<sup>3,4</sup> We also treated [PtMe<sub>2</sub>(cod)] with the phosphino hydrazone L<sup>2</sup> and obtained the corresponding dimethylplatinum complex **1d**; the characterising data are consistent with a six-membered chelate ring, in particular, the values of <sup>2</sup>J(PtNH<sub>2</sub>) (29.3 Hz) and <sup>3</sup>J(PNH<sub>2</sub>) (6.1 Hz), excluded a five-membered ring chelate.

A characteristic reaction of complexes of the type [PtMe<sub>2</sub>(phosphine)<sub>2</sub>] is the oxidative addition of methyl iodide to give platinum(IV) adducts of the type [PtMe<sub>3</sub>I(phosphine)<sub>2</sub>]<sup>4</sup> and it was of interest to see whether the chelates **1c** or **1d** would react similarly. Treatment of **1c** with an excess of iodomethane gave an adduct **2a** which was fully characterised. The small value of <sup>1</sup>J(PtP) in the <sup>31</sup>P-<sup>1</sup>H NMR spectrum (Table 1) is typical for platinum(IV)<sup>2,7</sup> and the occurrence of three chemically inequivalent platinum methyl resonances in the proton NMR spectrum indicated a *fac*-PtMe<sub>3</sub> arrangement. It is known that in trimethylplatinum(IV) complexes, methyl *trans* to iodine or nitrogen have <sup>2</sup>J(PtCH<sub>3</sub>) = ca. 70 Hz<sup>8</sup> and for methyl *trans* to phosphorus <sup>2</sup>J(PtCH<sub>3</sub>) = ca. 57 Hz.<sup>4</sup> The two *N*-methyls are not equivalent, chemically, excluding a five-membered chelate ring and the values of J(PtNCH<sub>3</sub>) of 11.7 and 8.5 Hz are

Table 2 Proton NMR data<sup>a</sup>

Compound	$\delta(\text{Bu}^1)$	$\delta(\text{CH}_2)$	Others
L <sup>1</sup>	1.12 (9 H, s)	3.05 [2 H, d, <sup>2</sup> J(PH) 2.9]	2.10 (6 H, s, NMe <sub>2</sub> )
L <sup>2</sup>	0.98 (9 H, s)	3.10 [2 H, d, <sup>2</sup> J(PH) 2.2]	4.75 (2 H, br s, NH <sub>2</sub> )
L <sup>3</sup>	1.22 (9 H, s)	3.52 [2 H, d, <sup>2</sup> J(PH) 3.2]	8.04 (1 H, s, CHPh)
1a	0.74 (9 H, s)	3.20 [2 H, d, <sup>2</sup> J(PH) 13.2, <sup>3</sup> J(PtH) 45.4]	3.55 [6 H, s, <sup>3</sup> J(PtH) 26.9, NMe <sub>2</sub> ]
1b	0.73 (9 H, s)	3.01 [2 H, d, <sup>2</sup> J(PH) 13.9]	3.41 (6 H, s, NMe <sub>2</sub> )
1c	0.63 (9 H, s)	2.80 [2 H, d, <sup>2</sup> J(PH) 10.3, <sup>3</sup> J(PtH) 16.4]	1.10 [3 H, d, <sup>3</sup> J(PH) 8.0, <sup>2</sup> J(PtH) 89.9, PtMe]
1d <sup>b</sup>	0.64 (9 H, s)	2.65 [2 H, d, <sup>2</sup> J(PH) 10.0, <sup>3</sup> J(PtH) 17.6]	1.28 [3 H, d, <sup>3</sup> J(PH) 7.8, <sup>2</sup> J(PtH) 64.9, PtMe]
2a <sup>b</sup>	0.70 (9 H, s)	2.5 (1 H) <sup>c</sup> 3.80 [1 H, dd, <sup>2</sup> J(PH) 11.2, <sup>2</sup> J(HH) 13.6]	2.94 [6 H, s, <sup>3</sup> J(PtH) 15.9, NMe <sub>2</sub> ] 1.20 [3 H, d, <sup>3</sup> J(PH) 7.8, <sup>2</sup> J(PtH) 67.4, PtMe] 1.36 [3 H, d, <sup>3</sup> J(PH) 7.1, <sup>2</sup> J(PtH) 90.8, PtMe]
2b <sup>b</sup>	0.85 (9 H, s)	3.19 [1 H, dd, <sup>2</sup> J(PH) 9.7, <sup>2</sup> J(HH) 13.9] 3.39 [1 H, dd, <sup>2</sup> J(PH) 12.0, <sup>2</sup> J(HH) 14.4]	5.34 [2 H, br d, <sup>3</sup> J(PH) 6.1, <sup>2</sup> J(PtH) 29.3, NH <sub>2</sub> ] 1.09 [3 H, d, <sup>3</sup> J(PH) 7.1, <sup>2</sup> J(PtH) 75.7, PtMe] 1.85 [3 H, d, <sup>3</sup> J(PH) 7.3, <sup>2</sup> J(PtH) 78.1, PtMe] 1.95 [3 H, d, <sup>3</sup> J(PH) 7.6, <sup>2</sup> J(PtH) 56.6, PtMe] 2.51 [3 H, s, <sup>3</sup> J(PtH) 11.7, NMe <sub>2</sub> ] 3.17 [3 H, s, <sup>3</sup> J(PtH) 8.5, NMe <sub>2</sub> ] 1.42 [3 H, d, <sup>3</sup> J(PH) 6.3, <sup>2</sup> J(PtH) 70.3, PtMe] 1.95 [3 H, d, <sup>3</sup> J(PH) 7.3, <sup>2</sup> J(PtH) 73.7, PtMe] 2.03 [3 H, d, <sup>3</sup> J(PH) 8.5, <sup>2</sup> J(PtH) 57.8, PtMe]
3b <sup>d,e</sup>	0.67 (18 H, s)	4.14 [4 H, br d, <sup>2</sup> J(PH) 13.0, <sup>3</sup> J(PtH) 45.0]	5.72 [2 H, br d, <sup>3</sup> J(PH) 5.1, <sup>2</sup> J(PtH) 20.0, NH <sub>2</sub> ]
4 <sup>e,f</sup>	0.56 (18 H, s)	2.96 [4 H, d, <sup>2</sup> J(PH) 12.2, <sup>3</sup> J(PtH) 44.0]	—
5b <sup>b,e</sup>	0.65 (18 H, s)	3.92 (4 H, filled-in d, N = 13.2)	—
6 <sup>e</sup>	0.61 (18 H, s)	2.79 (4 H, vt, N = 11.0)	—
7a	0.87 (9 H, s)	2.66 [1 H, dd, <sup>2</sup> J(PH) 11.5, <sup>2</sup> J(HH) 13.0] 3.19 [1 H, dd, <sup>2</sup> J(PH) 15.0, <sup>2</sup> J(HH) 13.0]	8.25 [1 H, d, <sup>4</sup> J(PH) 1.7, CHPh]
7b <sup>b</sup>	0.79 (9 H, s)	2.28 [1 H, dd, <sup>2</sup> J(PH) 10.7, <sup>2</sup> J(HH) 12.6, <sup>3</sup> J(PtH) 10.3] 3.11 [1 H, dd, <sup>2</sup> J(PH) 10.7, <sup>2</sup> J(HH) 12.6, <sup>3</sup> J(PtH) 18.8]	1.23 [3 H, d, <sup>3</sup> J(PH) 7.8, <sup>2</sup> J(PtH) 70.4, PtMe] 1.53 [3 H, d, <sup>3</sup> J(PH) 7.8, <sup>2</sup> J(PtH) 89.4, PtMe] 8.40 [1 H, d, <sup>4</sup> J(PH) 1.9, <sup>3</sup> J(PtH) 37.0, CHPh]
8 <sup>g</sup>	1.25 (18 H, s)	4.43 [4 H, vt, N = 9.2, <sup>3</sup> J(PtH) 24.9]	—
9b <sup>d,h</sup>	1.18 (18 H, s)	4.71 [2 H, dd, <sup>2</sup> J(PH) 15.4, <sup>2</sup> J(HH) 19.3] 5.15 [2 H, dd, <sup>2</sup> J(PH) 7.8, <sup>2</sup> J(HH) 18.5]	9.10 (2 H, s, CHPh)
11 <sup>b</sup>	1.61 (18 H, s)	—	4.42 [2 H, d, <sup>2</sup> J(PH) 8.8, <sup>3</sup> J(PtH) 22.2, CHP] 8.66 [2 H, d, <sup>4</sup> J(PH) 2.0, CHPh]
12a <sup>b</sup>	1.12 (9 H, s)	3.01 [2 H, d, <sup>2</sup> J(PH) 10.7, <sup>3</sup> J(PtH) 11.8]	0.54 [3 H, d, <sup>3</sup> J(PH) 10.3, <sup>2</sup> J(PtH) 69.6, PtMe] 1.27 [3 H, d, <sup>3</sup> J(PH) 7.3, <sup>2</sup> J(PtH) 74.4, PtMe] 1.59 (6 H, s, NMe <sub>2</sub> )
12b <sup>b</sup>	0.88 (9 H, s)	3.45 [2 H, d, <sup>2</sup> J(PH) 11.2, <sup>3</sup> J(PtH) 21.5]	0.93 [3 H, d, <sup>3</sup> J(PH) 10.3, <sup>2</sup> J(PtH) 70.1, PtMe] 1.56 [3 H, d, <sup>3</sup> J(PH) 7.3, <sup>2</sup> J(PtH) 74.5, PtMe] 5.54 (2 H, br s, NH <sub>2</sub> )
12c	1.18 (9 H, s)	4.07 [2 H, d, <sup>2</sup> J(PH) 11.5, <sup>3</sup> J(PtH) 17.3]	0.25 [3 H, d, <sup>3</sup> J(PH) 10.25, <sup>2</sup> J(PtH) 69.6, PtMe] 0.81 [3 H, d, <sup>3</sup> J(PH) 7.3, <sup>2</sup> J(PtH) 74.7, PtMe] 7.99 (1 H, s, CHPh)

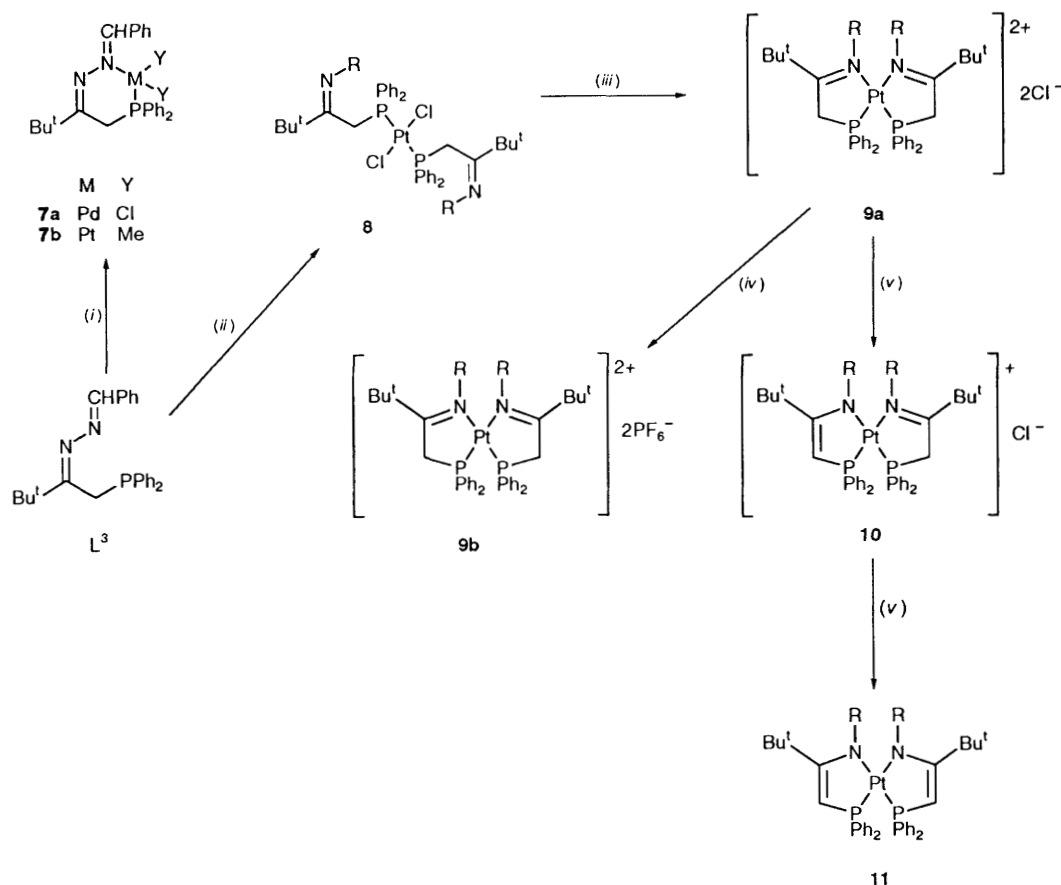
<sup>a</sup> Recorded at 100 MHz, chemical shifts  $\delta$  ( $\pm 0.01$  ppm) relative to SiMe<sub>4</sub>, solvent CDCl<sub>3</sub> unless otherwise stated, coupling constants  $J$  in Hz; s = singlet, d = doublet, vt = virtual triplet and br = broad. <sup>b</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>c</sup> Obscured by the NMe<sub>2</sub> signal. <sup>d</sup> In (CD<sub>3</sub>)<sub>2</sub>CO. <sup>e</sup> NH resonance not observed. <sup>f</sup> In CD<sub>2</sub>Cl<sub>2</sub>. <sup>g</sup> CHPh obscured by the aromatic protons. <sup>h</sup> Recorded at  $-50$  °C. N = <sup>4</sup>J(PH) + <sup>2</sup>J(PH).

consistent with a three-bond coupling in a platinum(IV) complex.<sup>4</sup>

When we treated [PtCl<sub>2</sub>(cod)] with 1 equivalent of the phosphino hydrazone L<sup>2</sup> in dichloromethane solution in an attempt to make the chelate [PtCl<sub>2</sub>{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>1</sup>)=NNH<sub>2</sub>}] we obtained a mixture of two platinum–phosphine complexes, the more intense resonances occurring at  $\delta_p$  37.9 with <sup>1</sup>J(PtP) = 3796 Hz and the less intense at  $\delta_p$  33.6 with <sup>1</sup>J(PtP) = 4143 Hz; the proportions of the two complexes being ca. 3:1. Subsequently, when we treated [PtCl<sub>2</sub>(cod)] with 2 equivalents of L<sup>2</sup> we produced the complex with  $\delta_p$  37.9, <sup>1</sup>J(PtP) 3796 Hz, exclusively and identified it as the *cis*-bis(chelate) dication chloride salt **3a** (see below). The minor product with  $\delta_p$  33.6, <sup>1</sup>J(PtP) = 4143 Hz was probably the chelate dichloride [PtCl<sub>2</sub>{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>1</sup>)=NNH<sub>2</sub>}] but we were unable to isolate this pure or characterise it. When we treated [PtCl<sub>2</sub>(cod)] with 2 equivalents of L<sup>2</sup> in dichloromethane we prepared the bis(chelate) dication, isolated as its dichloride salt [Pt{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>1</sup>)=NNH<sub>2</sub>}<sub>2</sub>]Cl<sub>2</sub>, **3a**, characterised by elemental analysis (Experimental section) and <sup>31</sup>P NMR data

(Table 1). The dication was also isolated as the mixed chloride/hexafluorophosphate salt [Pt{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>1</sup>)=NNH<sub>2</sub>}<sub>2</sub>]-Cl[PF<sub>6</sub>]**3b**, which was similarly characterised; the large value of <sup>1</sup>J(PtP) of 3607 Hz excludes the *trans* stereochemistry, but is consistent with phosphorus being *trans* to a more electronegative ligand such as nitrogen.<sup>9,10</sup>

We anticipated that the bis(chelate) dication should have NH<sub>2</sub> groups which could be deprotonated with base. We therefore treated the dication dichloride salt **3a** with 2 equivalents of sodium ethoxide in ethanol. This gave the hoped for neutral complex *cis*-[Pt{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>1</sup>)NNH}]<sub>2</sub> **4**, the crystal structure of which was determined and is discussed below. This neutral complex was also characterised by elemental analysis and by its infrared spectrum for which the value of  $\nu(\text{C}=\text{N})$  of 1595 cm<sup>-1</sup> was significantly less than the value for the free ligand or for the values for the complexes **1–3** (Table 1). The value of <sup>1</sup>J(PtP) of 3313 Hz (Table 1) is in agreement with a *cis* geometry. The <sup>1</sup>H NMR data are also in agreement with the assigned structure for **4** although we could not observe the NH resonance which was presumably too broad



**Scheme 2** R = -N=CHPh. (i) [PdCl<sub>2</sub>(NCPh)<sub>2</sub>] or [PtMe<sub>2</sub>(cod)]; (ii) [PtCl<sub>2</sub>(NCMe)<sub>2</sub>]; (iii) reflux in ethanol for 4 h; (iv) NH<sub>4</sub>PF<sub>6</sub>; (v) 1 mole equivalent of NaOMe

because of quadrupole relaxation or chemical exchange effects, or it might be obscured by the aromatic proton signals.<sup>10</sup>

Treatment of [PdCl<sub>2</sub>(NCPh)<sub>2</sub>] with 2 equivalents of L<sup>2</sup> gave the bis(chelate) dication  $cis\text{-}[\text{Pd}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}_2]^{2+}$ , isolated as the dichloride **5a**, and the bis(hexafluorophosphate) **5b**, salts. The <sup>1</sup>H NMR pattern of the methylene hydrogens in both cases consisted of a second order or 'filled-in' doublet with  $N = {}^4J(\text{PH}) + {}^2J(\text{PH}) = 13.2$  Hz. We tentatively assign these to have *cis* geometry.<sup>11,12</sup> We also treated the dicationic dichloride salt **5a** with 2 moles of sodium ethoxide in ethanol in order to effect deprotonation. An orange product was obtained, which appeared to be essentially pure from the phosphorus-31 and proton NMR spectra although it was too unstable to prepare a sample pure enough for elemental analysis. However, the phosphorus-31 NMR spectrum showed a singlet resonance at  $\delta_p$  59.1 and the proton NMR spectrum showed a well-defined 'virtual triplet' pattern for the CH<sub>2</sub> protons with  $N = {}^2J(\text{PH}) + {}^4J(\text{PH}) = 11.0$  Hz, suggesting that the phosphorus atoms were mutually *trans*. The fast atom bombardment (FAB) mass spectrum showed a parent molecular ion at  $m/z = 701$ , in agreement with  $M^+$ .

We have prepared and described the crystalline mixed azine monophosphine L<sup>3</sup>,<sup>1</sup> formed by condensing benzaldehyde with the phosphino hydrazone, L<sup>2</sup>. This azine monophosphine probably has the *Z,E*-configuration; for comparison purposes the infrared and NMR data are given in Tables 1 and 2. The coordination chemistry of this ligand has been summarised in Scheme 2. Treatment of *trans*-[PdCl<sub>2</sub>(NCPh)<sub>2</sub>] with L<sup>3</sup> in dichloromethane at 20 °C gave the required chelated palladium dichloride complex **7a** in over 90% yield. We formulate this as having a six-membered chelate ring, *i.e.* with the *Z*-configuration around CH<sub>2</sub>C(Bu<sup>t</sup>)=N-N since it was formed under mild conditions and in the proton NMR spectrum

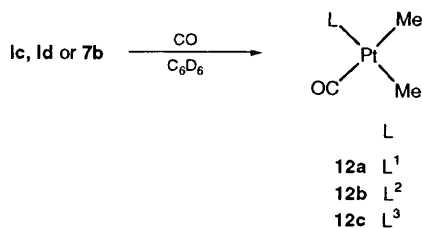
coupling between phosphorus and =CHPh was observed [<sup>4</sup>J(PH) = 1.7 Hz]. The six-membered chelate ring structure is also supported by the carbon-13 NMR data (see Experimental section). We also prepared the dimethylplatinum complex with this ligand and formulate this with a six-membered chelate ring, as in **7b**; in this case the values of <sup>4</sup>J(PCHPh) = 1.9 Hz and <sup>3</sup>J(PtCHPh) = 37.0 Hz exclude the five-membered chelate ring.

Treatment of *trans*-[PtCl<sub>2</sub>(NCMe)<sub>2</sub>] with 2 equivalents of the mixed azine phosphine L<sup>3</sup> at 20 °C gave a bis(phosphine) complex which we formulate as the dichloride **8** with *trans* monodentate phosphines. Electric conductivity measurements in acetone solution showed this complex to be a non-electrolyte (specific molar conductivity,  $\Lambda_m = 1.95 \times 10^{-2} \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ ).<sup>13</sup> The coupling constant of phosphorus to platinum [<sup>1</sup>J(PtP) = 2575 Hz] is typical of mutually *trans* phosphines co-ordinated to platinum(II).<sup>2</sup> Additionally, in the proton NMR spectrum, the CH<sub>2</sub> protons gave a virtual triplet with  $N = {}^2J(\text{PH}) + {}^4J(\text{PH}) = 9.2$  Hz, with satellites due to platinum-195 coupling, <sup>3</sup>J(PtCH<sub>2</sub>) = 24.9 Hz, typical of mutually *trans* phosphines.<sup>12</sup>

When *trans*-[PtCl<sub>2</sub>(NCMe)<sub>2</sub>] was heated with 2 equivalents of L<sup>3</sup> in ethanol-dichloromethane for 4 h, the hoped for dichloro salt **9a** was formed (Table 1), and was isolated as the bis(hexafluorophosphate) salt **9b**. Electric conductivity measurements in acetone solution showed this complex to be a 2:1 electrolyte (specific molar conductivity,  $\Lambda_m = 0.2 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ ).<sup>13</sup> The coupling constant of phosphorus to platinum-195 of 3361 Hz is consistent with the phosphorus atoms being co-ordinated mutually *cis* and is much too high for mutually *trans* co-ordination.<sup>2,9</sup> We found that at *ca.* 20 °C the resonance of the methylene protons (CH<sub>2</sub>P) of **9b** was broad, and at -50 °C, an ABX pattern was observed but coupling to platinum was not

resolved. The broadness was possibly due to exchange or a fluxional process. When we treated a methanol solution of **9a** with 1 mole equivalent of sodium methoxide a product was formed which showed an AB phosphorus pattern with satellites [ $\delta(P_A)$  17.2,  $^1J(PtP_A) = 3363$  and  $\delta(P_B)$  31.5,  $^1J(PtP_B) = 3363$ ,  $^2J(P_AP_B) = 11$  Hz], which we suggest was due to the monodeprotonated complex **10**. When we treated **10** with 1 mole equivalent of sodium methoxide we obtained the orange neutral complex  $cis-[Pt\{PPh_2CH=C(Bu^i)N=N=CHPh\}_2]$  **11** with  $\delta_p$  21.9 and  $^1J(PtP) = 3146$  Hz was obtained. In the proton NMR spectrum of **11**, the methine proton showed a doublet at  $\delta_H$  4.42,  $^2J(PH) = 8.8$  Hz, with satellites,  $^3J(PtH) = 22.2$  Hz (Table 2). As expected complex **11** was found to be a non-electrolyte in acetone (specific molar conductivity,  $\Lambda_m = 6.1 \times 10^{-3} \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ ).<sup>13</sup>

We have also studied the action of carbon monoxide on the three dimethylplatinum complexes **1c**, **1d** and **7b** (Scheme 3). When carbon monoxide was bubbled through a solution of **1c** in  $C_6D_6$  at 20 °C the  $^{31}P\{-^1H\}$  NMR spectrum due to **1c** disappeared and was replaced by a singlet with satellites,  $\delta_p$  20.2,  $^1J(PtP) = 1703$  Hz. Moreover, the solution showed a strong infrared absorption at 2040  $cm^{-1}$  typical of carbon monoxide co-ordinated to platinum(II).<sup>14</sup> The product proved to be too soluble to isolate but was further characterised by its proton NMR spectrum (Table 2). We formulate the complex as **12a** with the ligand  $L^1$  being monodentate through phosphorus. The other two chelates **1d** and **7b** reacted similarly and were similarly characterised as **12b** and **12c**, respectively, data in Tables 1 and 2.



Scheme 3

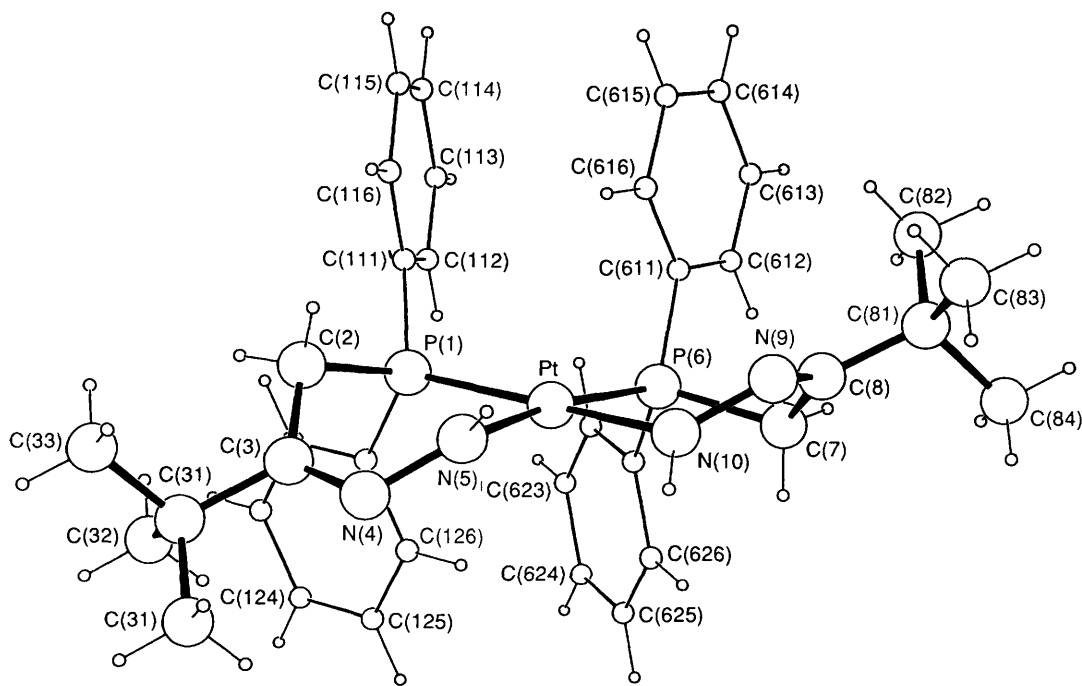
**Crystal Structure of  $cis-[Pt\{PPh_2CH_2C(Bu^i)=NNH\}_2]$  **4**.**—The crystal structure of complex **4** is shown in Fig. 1, with selected bond lengths and angles in Table 3 and atom coordinates in Table 4. As can be seen from the figure and Table 3, the arrangement around the platinum is strictly planar, the phosphorus atoms are *cis* to each other as are the nitrogens and the six-membered chelate rings are puckered. The bond lengths and angles are not unusual.

### 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 were recorded using a JEOL FX-90Q spectrometer (operating frequencies for  $^1H$  and  $^{31}P$  of 89.5 and 36.2 MHz, respectively), a JEOL FX-100 spectrometer (operating frequencies for  $^1H$  and  $^{31}P$  of 99.5 and 40.25 MHz, respectively) or a Bruker AM400 spectrometer (operating frequencies for  $^1H$ ,  $^{31}P$  and  $^{13}C$  of 400.13, 161.9 and 100.6 MHz, respectively;  $^1H$  and  $^{13}C$  chemical shifts are relative to tetramethylsilane and  $^{31}P$  shifts are

**Table 3** Selected bond lengths (pm) and angles (°) for complex **4** with estimated standard deviations (e.s.d.s) in parentheses

P(1)–Pt	224.2(4)	P(6)–Pt	223.4(5)
N(5)–Pt	207.8(10)	N(10)–Pt	206.3(11)
C(2)–P(1)	183.1(11)	C(7)–P(6)	184.7(11)
C(3)–C(2)	150.1(16)	C(8)–C(7)	150.1(16)
C(31)–C(3)	154.7(15)	C(81)–C(8)	151.3(16)
N(4)–C(3)	129.7(13)	N(9)–C(8)	128.0(14)
N(5)–N(4)	139.0(12)	N(10)–N(9)	140.7(12)
P(6)–Pt–P(1)	100.2(2)	N(10)–Pt–N(5)	81.8(4)
N(5)–Pt–P(1)	89.0(4)	N(10)–Pt–P(6)	89.2(3)
N(10)–Pt–P(1)	170.2(3)	P(6)–Pt–N(5)	170.1(3)
C(2)–P(1)–Pt	106.3(4)	C(7)–P(6)–Pt	107.8(4)
C(3)–C(2)–P(1)	113.0(7)	C(8)–C(7)–P(6)	113.3(8)
N(4)–C(3)–C(2)	121.3(10)	N(9)–C(8)–C(7)	123.4(10)
N(5)–N(4)–C(3)	119.7(10)	N(10)–N(9)–C(8)	119.7(10)
N(4)–N(5)–Pt	125.0(8)	N(9)–N(10)–Pt	125.7(7)



**Fig. 1** Crystal structure of  $cis-[Pt\{PPh_2CH_2C(Bu^i)=NNH\}_2]$  **4**

**Table 4** Fractional non-hydrogen atomic coordinates ( $\times 10^4$ ) for compound **4** with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Pt	663.3(3)	444.0(2)	2018.0(2)	C(611)	2695(4)	1750(3)	1966(3)
P(1)	233(2)	1196(1)	2850(2)	C(612)	3069(4)	2333(3)	1622(3)
C(111)	1410(5)	1794(3)	3539(4)	C(613)	4178(4)	2644(3)	2058(3)
C(112)	1475(5)	2534(3)	3322(4)	C(614)	4913(4)	2373(3)	2840(3)
C(113)	2452(5)	2966(3)	3798(4)	C(615)	4538(4)	1791(3)	3184(3)
C(114)	3363(5)	2658(3)	4490(4)	C(616)	3429(4)	1479(3)	2747(3)
C(115)	3297(5)	1918(3)	4707(4)	C(621)	263(5)	2021(3)	836(3)
C(116)	2321(5)	1487(3)	4232(4)	C(622)	361(5)	2733(3)	1173(3)
C(121)	-1037(4)	1803(3)	2397(3)	C(623)	-527(5)	3256(3)	793(3)
C(122)	-1302(4)	2349(3)	2845(3)	C(624)	-1512(5)	3067(3)	76(3)
C(123)	-2357(4)	2739(3)	2481(3)	C(625)	-1610(5)	2356(3)	-262(3)
C(124)	-3147(4)	2584(3)	1670(3)	C(626)	-723(5)	1833(3)	119(3)
C(125)	-2882(4)	2037(3)	1222(3)	C(7)	1542(9)	794(6)	560(6)
C(126)	-1827(4)	1647(3)	1586(3)	C(8)	2289(9)	109(6)	856(6)
C(2)	-106(9)	585(6)	3538(6)	C(81)	3331(10)	23(6)	654(7)
C(3)	-1074(9)	44(5)	3081(6)	C(82)	4273(9)	645(6)	1124(7)
C(31)	-2163(8)	9(5)	3267(5)	C(83)	3932(11)	-748(7)	934(8)
C(32)	-2717(10)	757(6)	3194(8)	C(84)	2926(11)	125(7)	-281(7)
C(33)	-1759(10)	-224(7)	4166(6)	N(9)	2055(7)	-427(5)	1233(5)
C(34)	-3018(10)	-575(6)	2697(8)	N(10)	1049(7)	-391(5)	1383(5)
N(4)	-985(7)	-437(5)	2569(5)	C(1S)	6874(13)	4494(8)	1364(9)
N(5)	22(8)	-451(5)	2435(6)	C(1S)	5663(4)	4476(2)	1619(3)
P(6)	1309(2)	1282(1)	1385(2)	C(2S)	6399(5)	4439(3)	296(3)

relative to 85% phosphoric acid. Mass spectra were recorded on an VG Autospec mass spectrometer with 8 kV acceleration.

The ligands  $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNR}_2$  ( $\text{R} = \text{Me}$  L<sup>1</sup> or H L<sup>2</sup>) and  $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}=\text{N}=\text{CHPh}$  L<sup>3</sup> were prepared according to our published procedure.<sup>1</sup>  $^{13}\text{C}\{-^1\text{H}\}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ): L<sup>1</sup>  $\delta_c$  177.1 (1 C, s, C=N), 141.6 [2 C, d,  $^1J(\text{PC})$  16.9,  $C_{\text{ipso}}$ ], 132.4 [4 C, d,  $^2J(\text{PC})$  20.1,  $C_{\text{ortho}}$ ], 128.1 [4 C, d,  $^3J(\text{PC})$  7.0,  $C_{\text{meta}}$ ], 128.1 (2 C, s,  $C_{\text{para}}$ ), 45.8 (2 C, s,  $\text{NMe}_2$ ), 38.4 (1 C, s,  $\text{CMe}_3$ ), 29.0 [1 C, d,  $^1J(\text{PC})$  21.6 Hz,  $\text{CH}_2$ ] and 28.3 (3 C, s,  $\text{CMe}_3$ ); L<sup>2</sup>  $\delta_c$  156.6 (1 C, s, C=N), 137.6 [2 C, d,  $^1J(\text{PC})$  14.9,  $C_{\text{ipso}}$ ], 132.8 [4 C, d,  $^2J(\text{PC})$  19.7,  $C_{\text{ortho}}$ ], 129.0 (2 C, s,  $C_{\text{para}}$ ), 128.5 [4 C, d,  $^3J(\text{PC})$  7.0,  $C_{\text{meta}}$ ], 38.1 [1 C, d,  $^3J(\text{PC})$  1.4,  $\text{CMe}_3$ ], 28.6 (3 C, s,  $\text{CMe}_3$ ) and 26.2 [1 C, d,  $^1J(\text{PC})$  22.7 Hz,  $\text{CH}_2$ ]; L<sup>3</sup>  $\delta_c$  175.6 [1 C, d,  $^2J(\text{PC})$  4.4,  $\text{Bu}^t\text{C}=\text{N}$ ], 157.3 [1 C, d,  $^5J(\text{PC})$  1.6,  $\text{HC}=\text{N}$ ], 139.1 [2 C, d,  $^1J(\text{PC})$  17.3,  $C_{\text{ipso}}$ ], 134.6 [1 C, s,  $\text{C}^1$  of  $\text{CHPh}$ ], 133.0 [4 C, d,  $^2J(\text{PC})$  20.4,  $C_{\text{ortho}}$ ], 131.4 (1 C, s,  $\text{CHPh}$ ), 131.3 (1 C, s,  $\text{CHPh}$ ), 130.8 (1 C, s,  $\text{CHPh}$ ), 130.7 (1 C, s,  $\text{CHPh}$ ), 130.1 (1 C, s,  $\text{C}^4$  of  $\text{CHPh}$ ), 128.6 (2 C, s,  $C_{\text{para}}$ ), 128.3 [4 C, d,  $^3J(\text{PC})$  6.7,  $C_{\text{meta}}$ ], 38.7 (1 C, s,  $\text{CMe}_3$ ), 28.9 [1 C, d,  $^1J(\text{PC})$  22.5,  $\text{CH}_2$ ] and 28.1 [3 C, d,  $^4J(\text{PC})$  1.9 Hz,  $\text{CMe}_3$ ].

**Preparations of Complexes.**— $[\text{PtCl}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNMe}_2\}]$  **1a**. A solution of  $[\text{PtCl}_2(\text{cod})]$  (60 mg, 0.16 mmol) and the phosphino dimethylhydrazone L<sup>1</sup> (53 mg, 0.16 mmol) in dichloromethane (1.5  $\text{cm}^3$ ) was put aside for 1 h at ca. 20 °C. The solvent was then removed under reduced pressure and methanol added to the residue gave the required product **1a** as a pale yellow microcrystalline solid. Yield 74 mg, 78% (Found: C, 39.55; H, 4.5; N, 4.5.  $\text{C}_{20}\text{H}_{27}\text{Cl}_2\text{N}_2\text{Ppt}\cdot 0.25\text{CH}_2\text{Cl}_2$  requires C, 39.65; H, 4.5; N, 4.55%).  $^{13}\text{C}\{-^1\text{H}\}$  NMR (25.2 MHz,  $\text{CDCl}_3$ ):  $\delta_c$  170.1 (1 C, s, C=N), 134.2 [4 C, d,  $^2J(\text{PC})$  10.8,  $^3J(\text{PtC})$  22,  $C_{\text{ortho}}$ ], 132.5 [2 C, d,  $^4J(\text{PC})$  2.7,  $C_{\text{para}}$ ], 128.8 [4 C, d,  $^3J(\text{PC})$  11.8,  $C_{\text{meta}}$ ], 126.8 [2 C, d,  $^1J(\text{PC})$  60.5,  $C_{\text{ipso}}$ ], 55.6 [2 C, s,  $^2J(\text{PtC})$  14.7,  $\text{NMe}_2$ ], 40.9 [1 C, d,  $^3J(\text{PC})$  1.7,  $\text{CMe}_3$ ], 26.9 (3 C, s,  $\text{CMe}_3$ ) and 17.9 [1 C, d,  $^1J(\text{PC})$  24.0,  $^2J(\text{PtC})$  6.6 Hz,  $\text{CH}_2$ ].

The dichloropalladium analogue **1b** was prepared similarly from  $[\text{PdCl}_2(\text{NCPH}_2)]$  and L<sup>1</sup> in 89% yield (Found: C, 46.65; H, 5.3; Cl, 15.55; N, 5.55.  $\text{C}_{20}\text{H}_{27}\text{Cl}_2\text{N}_2\text{Ppd}\cdot 0.15\text{CH}_2\text{Cl}_2$  requires C, 46.85; H, 5.3; Cl, 15.8; N, 5.4%).

$[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNMe}_2\}]$  **1c**. A solution of  $[\text{PtMe}_2(\text{cod})]$  (50 mg, 0.15 mmol) and the phosphino dimethylhydrazone L<sup>1</sup> (50 mg, 0.15 mmol) in benzene (3  $\text{cm}^3$ ) was put

aside for 1 h. The dimethylplatinum complex **1c** crystallized out as a white solid after 1 h and was collected. Yield: 45 mg, 55%. (Found: C, 47.75; H, 6.2; N, 5.0.  $\text{C}_{22}\text{H}_{33}\text{N}_2\text{Ppt}$  requires C, 47.90; H, 6.0; N, 5.1%).

The dimethylplatinum complex **1d** was prepared in a similar manner from equimolar amounts of the phosphino hydrazone L<sup>2</sup> and  $[\text{PtMe}_2(\text{cod})]$ . Yield 40% (Found: C, 46.05; H, 5.55; N, 5.35.  $\text{C}_{20}\text{H}_{29}\text{N}_2\text{Ppt}$  requires C, 45.9; H, 5.60; N, 5.35%).  $^{13}\text{C}\{-^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta_c$  169.5 (1 C, s, C=N), 134.1 [4 C, d,  $^2J(\text{PC})$  12.0,  $C_{\text{ortho}}$ ], 133.1 [2 C, d,  $^1J(\text{PC})$  39.0,  $C_{\text{ipso}}$ ], 130.1 [2 C, d,  $^4J(\text{PC})$  1.8,  $C_{\text{para}}$ ], 128.3 [4 C, d,  $^3J(\text{PC})$  7.2,  $C_{\text{meta}}$ ], 53.0 (2 C, s,  $\text{NMe}_2$ ), 40.7 [1 C, d,  $^2J(\text{PC})$  2.3,  $\text{CMe}_3$ ], 27.8 (3 C, s,  $\text{CMe}_3$ ), 21.3 [1 C, d,  $^1J(\text{PC})$  16.7,  $\text{CH}_2$ ], 16.0 [1 C, d,  $^1J(\text{PC})$  117.7,  $\text{PtMe}$  *trans* to P] and -21.9 [1 C, d,  $^1J(\text{PC})$  3.9 Hz,  $\text{PtMe}$ , *cis* to P].

$[\text{PtMe}_3\text{I}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNMe}_2\}]$  **2a**. An excess of iodomethane (0.1  $\text{cm}^3$ ) was added to a solution of the dimethylplatinum complex **1c** (38 mg, 0.07 mmol) in benzene (1.0  $\text{cm}^3$ ). The solvent was then removed, trituration of the resultant yellow oil with methanol gave the required complex **2a** as a white microcrystalline solid. Yield: 37 mg, 77% (Found: C, 40.4; H, 5.25; N, 4.05.  $\text{C}_{23}\text{H}_{36}\text{IN}_2\text{Ppt}\cdot 0.1\text{C}_6\text{H}_6$  requires C, 40.4; H, 5.25; N, 4.0%).

$[\text{PtMe}_3\text{I}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}]$  **2b**. Iodomethane (0.5  $\text{cm}^3$ ) was added to a solution of the dimethylplatinum complex **1d** (80 mg, 0.15 mmol) in benzene (2  $\text{cm}^3$ ). The reaction mixture was put aside for 1.5 h, filtered, and the solvent was removed under reduced pressure. Addition of methanol to the residue gave the required complex **2b** as colourless prisms (71 mg, 70%) (Found: C, 38.3; H, 4.85; N, 4.35.  $\text{C}_{21}\text{H}_{32}\text{IN}_2\text{Ppt}$  requires C, 37.9; H, 4.85; N, 4.20%).

*cis*- $[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}_2]\text{Cl}_2$  **3a**. The complex  $[\text{PtCl}_2(\text{cod})]$  (125 mg, 0.33 mmol) was added to a stirred solution of the phosphino hydrazone L<sup>2</sup> (200 mg, 0.67 mmol) in dichloromethane. After 30 min, the required product **3a** was formed in the reaction mixture as a white solid. This was filtered off, and washed with dichloromethane. Yield: 200 mg, 70% (Found: C, 48.9; H, 5.6; N, 6.15.  $\text{C}_{36}\text{H}_{46}\text{Cl}_2\text{N}_4\text{P}_2\text{Pt}\cdot 0.35\text{CH}_2\text{Cl}_2$  requires C, 48.9; H, 5.3; N, 6.25%).

*cis*- $[\text{Pt}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2\}_2]\text{Cl}[\text{PF}_6]$  **3b**. This complex was prepared by addition of a solution of ammonium hexafluorophosphate(v) in methanol to **3a** in methanol in 64% yield (Found: C, 43.85; H, 4.9; Cl, 4.15; N, 5.55.  $\text{C}_{36}\text{H}_{46}$

$\text{ClF}_6\text{N}_4\text{P}_3\text{Pt}\cdot 0.15\text{CH}_2\text{Cl}_2$  requires C, 44.05; H, 4.8; Cl, 4.65; N, 5.7%.

*cis*-[Pt{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNH<sub>2</sub>}<sub>2</sub>] **4**. The complex [PtCl<sub>2</sub>-(cod)] (120 mg, 0.32 mmol) was added to the phosphino hydrazone L<sup>2</sup> (200 mg, 0.67 mmol) in dichloromethane (5 cm<sup>3</sup>). A white solid was obtained which was filtered off, dried and then dissolved in hot ethanol (4 cm<sup>3</sup>). Sodium ethoxide solution (1.2 cm<sup>3</sup>, 0.48 mol dm<sup>-3</sup> in ethanol, 0.58 mmol) was added. After 1.5 h, the solvent was reduced to a low volume under reduced pressure. The required product **4** was obtained as a pale yellow solid. Yield 205 mg, 81% (Found: C, 54.55; H, 5.65; N, 7.05. C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>P<sub>2</sub>Pt requires C, 54.75; H, 5.65; N, 7.10%).

[Pd{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNH<sub>2</sub>}<sub>2</sub>]Cl<sub>2</sub> **5a**. A mixture of the phosphino hydrazone L<sup>2</sup> (200 mg, 0.5 mmol) and [PdCl<sub>2</sub>-(NCPH<sub>2</sub>)] (95 mg, 0.25 mmol) in dichloromethane (3 cm<sup>3</sup>) was put aside at room temperature for 1 h. Complex **5a** was obtained as a white solid, which was filtered off and washed with a little dichloromethane. Yield 183 mg, 95% (Found: C, 52.65; H, 6.0; N, 7.05. C<sub>36</sub>H<sub>46</sub>Cl<sub>2</sub>N<sub>4</sub>P<sub>2</sub>Pd·0.75CH<sub>2</sub>Cl<sub>2</sub> requires C, 52.70; H, 5.7; N, 7.0%).

[Pd{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNH<sub>2</sub>}<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **5b**. Complex **5b** was prepared by the addition of a methanolic solution of ammonium hexafluorophosphate(v) to a solution of **5a** in hot methanol. The required salt was obtained as a pale yellow solid in 60% yield (Found: C, 44.0; H, 4.8; N, 6.05. C<sub>36</sub>H<sub>46</sub>F<sub>12</sub>N<sub>4</sub>P<sub>4</sub>Pd requires C, 43.6; H, 4.7; N, 5.65%).

*trans*-[Pd{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNH<sub>2</sub>}<sub>2</sub>] **6**. A solution of the palladium salt **5a** (80 mg, 0.20 mmol) in ethanol (1.5 cm<sup>3</sup>) was treated with a solution of sodium ethoxide (0.48 mol dm<sup>-3</sup> in ethanol, 0.45 cm<sup>3</sup>, 0.21 mmol) to give the required compound **6** as an orange solid. Yield 80 mg, 57%; *m/z* 701 (*M*<sup>+</sup>). The complex decomposed on attempted recrystallization.

[PdCl<sub>2</sub>{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N=N=CHPh}] **7a**. A solution of the azine monophosphine L<sup>3</sup> (60 mg, 0.16 mmol) and [PdCl<sub>2</sub>(NCPH<sub>2</sub>)] (59 mg, 0.15 mmol) in dichloromethane was put aside for 30 min. The solvent was then removed under reduced pressure and methanol added to the residue; this gave the required palladium complex **7a** as a yellow microcrystalline solid. Yield 79 mg, 91% (Found: C, 50.7; H, 4.75; N, 5.05. C<sub>25</sub>H<sub>27</sub>Cl<sub>2</sub>N<sub>2</sub>N<sub>2</sub>PPd·1.5CH<sub>2</sub>Cl<sub>2</sub> requires C, 50.5; H, 4.7; N, 4.6%). <sup>13</sup>C-<sup>1</sup>H NMR (100.6 MHz, CDCl<sub>3</sub>): δ<sub>c</sub> 175.8 (1 C, s, Bu<sup>t</sup>C=N), 162.8 [1 C, <sup>3</sup>J(PC) 3.3, HC=N], 134.8 [2 C, d, <sup>2</sup>J(PC) 12.1, *C*<sub>ortho</sub>], 133.8 (1 C, s, *C*<sub>para</sub>), 133.4 [2 C, d, <sup>1</sup>J(PC) 57.8, *C*<sub>ipso</sub>], 132.7 (1 C, s, CHPh), 132.7 (1 C, s, CHPh), 132.6 (1 C, s, CHPh), 132.5 (1 C, s, CHPh), 132.3 [2 C, d, <sup>2</sup>J(PC) 9.9, *C*<sub>ortho</sub>], 131.3 (1 C, s, *C*<sub>para</sub>), 129.9 (1 C, s, C<sup>4</sup> of CHPh), 129.4 [2 C, d, <sup>3</sup>J(PC) 11.2, *C*<sub>meta</sub>], 128.9 [2 C, d, <sup>3</sup>J(PC) 10.2, *C*<sub>meta</sub>], 128.8 (1 C, s, CHPh), 39.3 [1 C, d, <sup>3</sup>J(PC) 1.9, CMe<sub>3</sub>], 27.0 (3 C, s, CMe<sub>3</sub>) and 25.2 [1 C, d, <sup>1</sup>J(PC) 25.3 Hz, CH<sub>2</sub>] (*C*<sup>1</sup> of CHPh was obscured).

[PtMe<sub>2</sub>{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N=N=CHPh}] **7b**.—A solution of the azine monophosphine L<sup>3</sup> (120 mg, 0.31 mmol) and [PtMe<sub>2</sub>(cod)] (100 mg, 0.30 mmol) in degassed benzene (2 cm<sup>3</sup>) was put aside for 2 h. The solvent was then removed under reduced pressure and methanol added to the residue to give the required compound **7b** as a yellow solid. Yield 130 mg, 71% (Found: C, 51.85; H, 5.7; N, 4.25. C<sub>27</sub>H<sub>33</sub>N<sub>2</sub>PPT·1.5CH<sub>3</sub>OH requires C, 51.9; H, 5.95; N, 4.25%).

*trans*-[PtCl<sub>2</sub>{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N=N=CHPh}] **8**. A solution of the azine monophosphine L<sup>3</sup> (90 mg, 0.23 mmol) and [PtCl<sub>2</sub>(NCMe)<sub>2</sub>] (40 mg, 0.11 mmol) in dichloromethane (2 cm<sup>3</sup>) was stirred for 1 h, until a clear solution was obtained. The solvent was then removed under reduced pressure and the residue triturated with methanol to give the required product **8** as a white solid. Yield 52 mg, 43% (Found: C, 54.25; H, 4.85; N, 4.95. C<sub>50</sub>H<sub>54</sub>Cl<sub>2</sub>N<sub>4</sub>P<sub>2</sub>Pt·1.1CH<sub>2</sub>Cl<sub>2</sub> requires C, 54.2; H, 5.00; N, 4.95%).

*cis*-[Pt{PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=N=N=CHPh}]<sub>2</sub>[PF<sub>6</sub>]<sub>2</sub> **9b**. A solution of the azine monophosphine L<sup>3</sup> (90 mg, 0.23 mmol) in

ethanol (2 cm<sup>3</sup>) was added to a suspension of [PtCl<sub>2</sub>(NCMe)<sub>2</sub>] (40 mg, 0.11 mmol) in dichloromethane (1 cm<sup>3</sup>). The reaction mixture was then refluxed under a nitrogen atmosphere for 4 h after which, a saturated solution of ammonium hexafluorophosphate(v) in methanol was then added to precipitate the required product **9b** as a white solid (76 mg, 53%) (Found: C, 44.85; H, 3.9; N, 4.4. C<sub>50</sub>H<sub>54</sub>F<sub>12</sub>N<sub>4</sub>P<sub>2</sub>Pt·1.4CH<sub>2</sub>Cl<sub>2</sub> requires C, 44.85; H, 4.1; N, 4.1%).

*cis*-[Pt{PPh<sub>2</sub>CH=C(Bu<sup>t</sup>)=N=CHPh}]<sub>2</sub> **11**. The complex [PtCl<sub>2</sub>(CNMe)<sub>2</sub>] (40 mg, 0.11 mmol) and the azine monophosphine L<sup>3</sup> (90 mg, 0.23 mmol) were dissolved in dichloromethane (1.5 cm<sup>3</sup>). Ethanol (1 cm<sup>3</sup>) was then added and the reaction mixture was refluxed for 3.5 h to give a pale yellow solution. Sodium methoxide (0.673 mol dm<sup>-3</sup> in methanol, 0.34 cm<sup>3</sup>, 0.23 mmol) was then added, the resultant dark red solution filtered, and the solvents removed under reduced pressure. The required product **11** was obtained as an orange solid. Yield 43 mg, 40% (Found: C, 59.85; H, 5.25; N, 5.4. C<sub>50</sub>H<sub>52</sub>N<sub>4</sub>P<sub>2</sub>Pt·0.6CH<sub>2</sub>Cl<sub>2</sub> requires C, 59.80; H, 5.25; N, 5.5%).

*Single-crystal X-Ray Diffraction Analysis of Complex 4*.—All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω-θ scan mode using graphite-monochromated Mo-Kα X-radiation (λ = 71.069 pm). The data set was corrected for absorption using azimuthal ψ-scans.

The structure was determined by standard heavy-atom methods and was refined by full-matrix least squares using SHELX 76.<sup>15</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters and the phenyl groups were treated as rigid bodies with idealised 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* = [σ<sup>2</sup>(*F*<sub>o</sub>) + 0.0004(*F*<sub>o</sub>)<sup>2</sup>]<sup>-1</sup> was used. Final non-hydrogen atomic coordinates are given in Table 4. An ORTEP<sup>16</sup> diagram of the molecular structure of **4** is given in Fig. 1.

*Crystal data*. C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>P<sub>2</sub>Pt·CH<sub>2</sub>Cl<sub>2</sub>, 0.65 × 0.5 × 0.45 mm, *M* = 874.73 (includes solvent molecule), monoclinic, space group P2<sub>1</sub>/c, *a* = 1261.5(2), *b* = 1794.6(3), *c* = 1792.0(4) pm, *U* = 3.6675(12) nm<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.58 Mg m<sup>-3</sup>, μ = 39.08 cm<sup>-1</sup>, *F*(000) = 1752.

*Data collection*. 4.0 < 2θ < 50.0°, 6843 data collected, 4088 with *I* > 2.0σ(*I*) considered observed, *T* = 200 K.

*Structure refinement*. Number of parameters = 381, *R* = 0.0451, *R*' = 0.0443.

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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