

## Synthesis and Conformation of 9,10-Dihydroplatina-anthracenes: Nuclear Magnetic Resonance and X-Ray Crystal Structure Studies†

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The platinacycles [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)L<sub>2</sub>] (**1a**)–(**1h**) [L = PEt<sub>3</sub>, PMe<sub>3</sub>, PMe<sub>2</sub>Ph, PMePh<sub>2</sub>, or PPh<sub>3</sub>; L<sub>2</sub> = cyclo-octa-1,5-diene (cod), Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, or Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>] have been made and characterised by <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>195</sup>Pt n.m.r. spectroscopy. The crystal structure of (**1a**; L = PEt<sub>3</sub>) has been determined, showing that the platinacycle has a boat conformation with a substantial dihedral angle (105.3°) between the aromatic rings. The boat conformation metallacyclic ring in complex (**1a**) is rigid on the n.m.r. time-scale up to at least 100 °C in dimethyl sulphoxide. The platinum(IV) complex [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)I<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (**2**) has been made by oxidative addition of I<sub>2</sub> to (**1a**). Its crystal structure also shows a boat conformation, but the ring is very much flatter (dihedral angle 151.2°), and the octahedral geometry at Pt causes one PEt<sub>3</sub> group to lie beneath the platinacycle. Complex (**2**) is fluxional at ambient temperatures due to rapid ring inversion but this can be frozen out at low temperatures and Δ*G*‡ of 41 kJ mol<sup>-1</sup> estimated for the inversion process at *T*<sub>c</sub>. Mean bond distances are: Pt–P 2.323(10) (**1a**), 2.386(3) (**2**), Pt–I 2.785(20) (**2**), Pt–C 2.05(1) (**1a**), 2.08(1) Å (**2**). Both crystals are monoclinic, space groups *P*2<sub>1</sub>/*n* and *P*2<sub>1</sub>/*c*: (**1a**), *a* = 10.748(2), *b* = 15.259(4), *c* = 14.885(4) Å, and β = 90.77(2)°; (**2**), *a* = 17.375(5), *b* = 9.681(3), *c* = 19.192(5) Å, and β = 120.72(2)°. For (**1a**), *R* = 0.048 for 2 725 observed diffractometer collected reflections [*I*/σ(*I*) > 3.0], and for (**2**), *R* = 0.053 for 3 311 observed reflections.

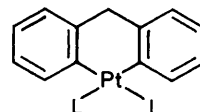
Metallacyclic chemistry is a topic of great interest in organometallic chemistry.<sup>1,2</sup> In comparison to four- and five-membered metallacycles, six-membered metallacycles have been little studied. As part of a general study<sup>3</sup> of the conformations of six-membered metallacycles, we report here our results with unsaturated 9,10-dihydroplatina-anthracenes. Recently 9,10-dihydrometalla-anthracenes have been reported<sup>4</sup> with Hf, Ti, and Co.

### Results and Discussion

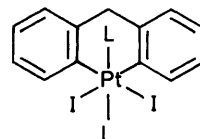
The 9,10-dihydroplatina-anthracenes (**1a**)–(**1e**) are air-stable solids made by treatment of [PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] with 2,2'-dilithiodiphenylmethane, and fully characterised by a combination of elemental analysis and n.m.r. spectroscopy (see Tables 1–4). The X-ray crystal structure of (**1a**) was carried out in order to determine the conformation of the metallacycle.

**X-Ray Crystal Structure of [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (**1a**).**—Selected bond lengths and angles are listed in Table 5 and the numbering scheme for the molecule is shown in Figure 1. In compound (**1a**) the square planar geometry around the platinum atom is slightly distorted. The six-membered ring containing the platinum atom adopts a boat conformation as shown in Figure 1.

The aromatic rings defined by C(1), C(2), C(3), C(4), C(14), C(13) (plane 1) and C(5), C(6), C(7), C(8), C(12), C(11) (plane 2) are inclined at an angle of 105.3°. The molecule thus consists of two separate halves hinged about the axis Pt–C(10). However neither Pt nor C(10) lies precisely on planes 1 and 2, being displaced by 0.13 and 0.23 Å to opposite sides. The trigonal geometries around C(12) and C(13) are also distorted; the angles Pt–C(12)–C(8) and Pt–C(13)–C(1) are 127.4(8)° and 127.5(8)° respectively. The dihedral angle of 110.5° in the PtC<sub>5</sub> ring itself between the planes through atoms Pt, C(10), C(11), C(12) and atoms Pt, C(13), C(14), C(10) signifies a large degree of ring folding and indicates that the boat conformation is



- |                                       |   |
|---------------------------------------|---|
| ( <b>1a</b> ) L = PEt <sub>3</sub>    | ( <b>1e</b> ) L = PPh <sub>3</sub>  |
| ( <b>1b</b> ) L = PMe <sub>3</sub>    | ( <b>1f</b> ) L <sub>2</sub> = Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> (dppe) |
| ( <b>1c</b> ) L = PMe <sub>2</sub> Ph | ( <b>1g</b> ) L <sub>2</sub> = Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> (dppm)                 |
| ( <b>1d</b> ) L = PMePh <sub>2</sub>  | ( <b>1h</b> ) L <sub>2</sub> = C <sub>8</sub> H <sub>12</sub> (cod)                                     |



(**2**) L = PEt<sub>3</sub>

highly puckered. It is the smallest dihedral angle reported for a 9,10-dihydroanthracene compound.

The <sup>1</sup>H n.m.r. spectrum of compound (**1a**) showed two sharp signals for the CH<sub>2</sub> of the metallacycle indicating that the ring was rigid on the n.m.r. time-scale (see Figure 2). The signal with the larger coupling to platinum was assigned to the equatorial proton on the assumption that this coupling constant is a function of the dihedral angle (*i.e.* a Karplus-type relationship). The <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectrum of (**1a**) was a singlet with <sup>195</sup>Pt

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‡ Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

**Table 1.** Elemental analyses (%)<sup>a</sup>

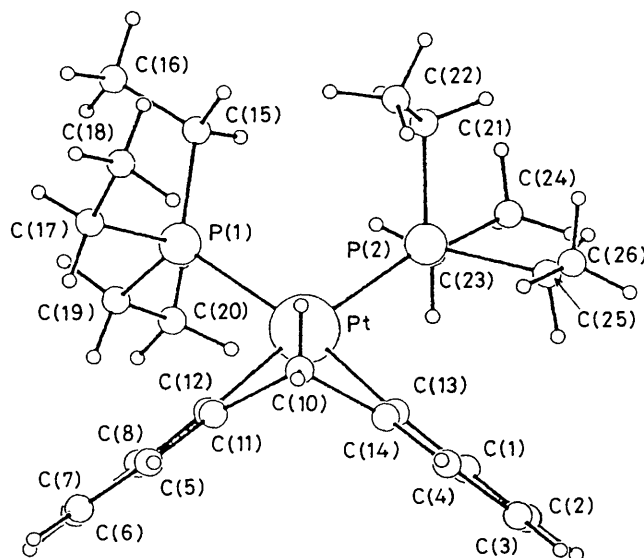
Compound	Analysis	
	C	H
(1a)	50.60 (50.25)	6.65 (6.75)
(1b)	43.90 (44.40)	3.70 (3.50)
(1c)	54.50 (53.65)	4.45 (5.05)
(1e)	66.20 (66.45)	4.70 (4.55)
(1f)	54.70 (53.70)	4.45 (4.70)
(2)	35.55 (35.25)	4.70 (4.75)

<sup>a</sup> Calculated values are given in parentheses.

**Table 2.** <sup>31</sup>P-<sup>1</sup>H<sup>a</sup> and <sup>195</sup>Pt-<sup>1</sup>H<sup>b</sup> n.m.r. data

Compound	δ( <sup>31</sup> P)	<sup>1</sup> J(PtP)	δ( <sup>195</sup> Pt)
(1a)	4.3	1 833	-52.2
(1b)	-26.1	1 779	6.6
(1c)	-13.1	1 845	-30.0
(1d)	3.8	1 856	-28.9
(1e)	22.9	1 890	-29.7
(1g)	44.9	1 818	—
(1h)	-33.1	1 466	—
(2)	-20.0	1 782	847.2
	-17.9 <sup>c</sup>	1 734	
	-18.1	1 779	

<sup>a</sup> Spectra (162 MHz) measured in CDCl<sub>3</sub> at +21 °C. Chemical shifts (δ) in p.p.m. (±0.1) to high frequency of 85% H<sub>3</sub>PO<sub>4</sub>. Coupling constants (*J*) in Hz (±3). <sup>b</sup> Spectra (85.6 MHz) measured in CDCl<sub>3</sub> at ambient temperature. Chemical shift (δ) in p.p.m. to high frequency of Ξ(Pt) 21.4 MHz. <sup>c</sup> At -95 °C in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure 1.** Molecular structure of complex (1a) showing the atomic numbering scheme

satellites and the <sup>13</sup>C-<sup>1</sup>H n.m.r. spectrum showed a single resonance assignable to the CH<sub>2</sub> of the PEt<sub>3</sub> ligands. However there are two <sup>1</sup>H n.m.r. signals associated with the CH<sub>2</sub> of the PEt<sub>3</sub> ligands and correlation spectroscopy (COSY) showed that these were coupled to each other. Hence the CH<sub>2</sub> protons of the PEt<sub>3</sub> are diastereotopic which is consistent with a boat conformation of the ring and provides further evidence that the ring is rigid on the n.m.r. time-scale. The <sup>1</sup>H, <sup>31</sup>P-<sup>1</sup>H, and <sup>13</sup>C-<sup>1</sup>H n.m.r. spectra for the other metallacycles (1b)—(1e) are

similar to those of (1a), showing that the rings are rigid in all of these compounds; two signals are observed in the <sup>1</sup>H and the <sup>13</sup>C-<sup>1</sup>H n.m.r. spectra for the diastereotopic CH<sub>3</sub> groups of the PMe<sub>2</sub>Ph ligands in (1c).

The ring in compound (1a) remained rigid on the n.m.r. time-scale even at 100 °C, as shown by <sup>1</sup>H n.m.r. (90 MHz) spectroscopy in dimethyl sulphoxide (dmsO); above this temperature, decomposition occurred. The behaviour of these metallacycles should be contrasted with that of the parent hydrocarbon 9,10-dihydroanthracene<sup>5</sup> which undergoes rapid ring inversion of the n.m.r. time-scale at -60 °C (60 MHz). The rigidity of the metallacycles is therefore due to the PtL<sub>2</sub> moiety.

The conformation of the ring in (1a) is doubtless influenced by the constraints imposed by the square-planar platinum atom. In addition the phosphine ligands interfere sterically with the peri protons of the aromatic rings. For the metallacycle to invert it must pass through a planar transition state which would necessarily bring the peri protons and ligand protons very close together. It is therefore most likely that this steric hindrance is responsible for the high activation energy to ring inversion. We reasoned that by reducing the steric demands of the ancillary ligands on platinum we could reduce the energy barrier to inversion. Complexes (1f)—(1h) containing less sterically demanding, chelating ligands were made. At ambient temperatures, the dppe complex (1f) was still rigid on the n.m.r. time-scale but the dpmp complex (1g) and the cyclo-octa-1,5-diene(cod) complex (1h) both showed a single ring CH<sub>2</sub> signal, indicating that ring inversion was taking place.

It was of interest to investigate the effect an octahedral metal centre would have on the conformation of the ring. Complex (1a) readily adds I<sub>2</sub> to give the platinum(IV) complex (2) which has been fully characterised (see Tables 1—3).

**X-Ray Crystal Structure of [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)I<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (2).**—Selected bond lengths and angles are listed in Table 5 and the numbering scheme for the molecule is shown in Figure 3. In the platinum(IV) compound (2) the octahedral geometry around the platinum atom is slightly distorted. It can be seen from Figure 3 that the two iodine ligands are mutually *cis* and the two triethylphosphine ligands are *trans* to each other. The conformation of the six-membered platinumacyclic ring is also a boat, though more flattened than in the platinum(II) compound (1a) (Figure 1). The aromatic rings defined by C(1), C(2), C(3), C(4), C(14), C(13) and C(5), C(6), C(7), C(8), C(12), C(11) (plane 3) are mutually inclined at an angle of 151.2°, close to the dihedral angle of 145° in 9,10-dihydroanthracene. The Pt atom and C(10) are above and below the planes by 0.06 and 0.11 Å. The trigonal geometries around C(12) and C(13) are again distorted, with angles Pt-C(12)-C(11) and Pt-C(13)-C(14) 123.1(13) and 122.6(11)° respectively.

Clearly the positioning of the phosphine above and below the ring leads to the observed flattening. However it is not immediately clear why the phosphine ligands should rearrange to the *trans* positions on oxidative addition of iodine. Possibly the electronic effects are more favourable in this than in either of the other two isomers or it may be that steric interactions between the peri protons on the aromatic rings of the 9,10-dihydroanthracene moiety are minimised when the iodine ligands are *trans* to it.

The boat conformation of the ring in compound (2) renders the ring CH<sub>2</sub> protons inequivalent and also the two phosphine ligands inequivalent. However the <sup>1</sup>H n.m.r. signal for the ring CH<sub>2</sub> is a singlet at ambient temperatures as is the <sup>31</sup>P-<sup>1</sup>H n.m.r. signal for the phosphines; hence ring inversion is rapid on the n.m.r. time-scale at ambient temperatures. At -95 °C two <sup>31</sup>P signals are clearly resolved (see Table 2 for the data) and

Table 3. Proton n.m.r.<sup>a</sup> data

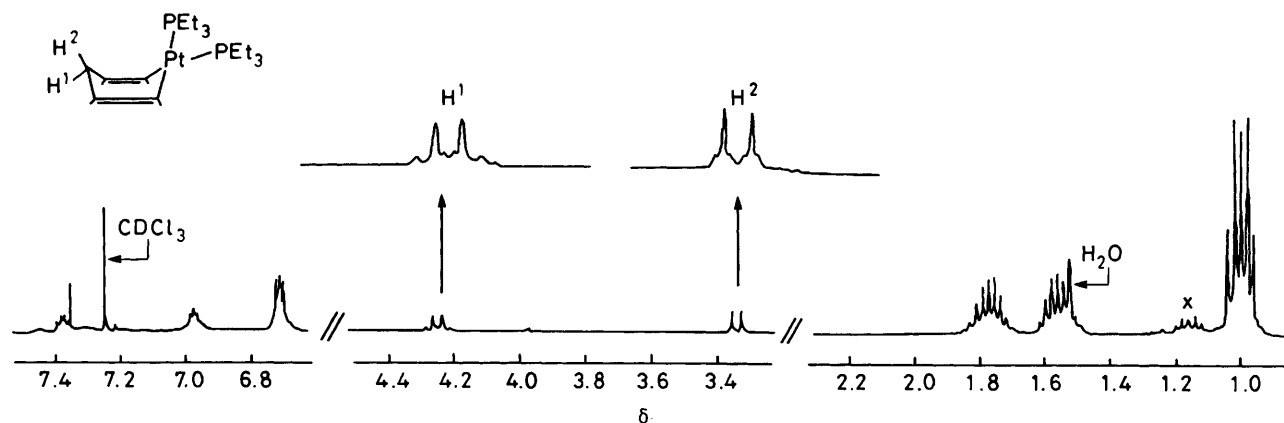
Compound	$\delta(\text{H}^1)$	$^4J(\text{PtH}^1)$	$\delta(\text{H}^2)$	$^4J(\text{PtH}^2)$	$^2J(\text{H}^1\text{H}^2)$	$\delta(\text{H}^3, \text{H}^4, \text{H}^5, \text{H}^6)$	$\delta$ (ligand resonances)
(1a)	4.25	16.4	3.34	5.5	12.36	6.70–6.75 (4 H, m), 6.95 [2 H, m, $J(\text{PtH}) = 18.0$ , $J(\text{PtH}) = 6.2$ ], 7.37 [2 H, m, $J(\text{PtH}) = 57.0$ ]	1.00 [18 H, m, $J(\text{PH}) = 13.2$ ], 1.52 (6 H, m), 1.75 (6 H, m)
(1b)	4.14	16 <sup>b</sup>	3.37	6 <sup>b</sup>	12.50	6.74 (4 H, m), 7.03 (2 H, m), 7.41 [2 H, m, $J(\text{PtH}) = 57.2$ ]	1.34 [18 H, m, $J(\text{PH}) = 7.9$ , $J(\text{PtH}) = 20.1$ ]
(1c)	4.34	16 <sup>b</sup>	3.49	6 <sup>b</sup>	12.54	6.73 (2 H, m), 6.80 (2 H, m) 7.14 [2 H, m, $J(\text{PH}) = 7.3$ , $J(\text{PtH}) = 16.9$ ], 7.30–7.42 (2 H, m)	1.18 [6 H, m, $J(\text{PH}) = 7.8$ , $J(\text{PtH}) = 19.2$ ], 1.46 [6 H, m, $J(\text{PH}) = 7.6$ , $J(\text{PtH}) = 19.2$ ], 7.30–7.42 (6 H, m), 7.61 (4 H, m)
(1d)	4.27	16.4	1.42	6.4	12.62	6.24–6.40 (2 H, m), 6.54–6.68 (2 H, m), 6.78–6.92 (2 H, m), 7.10–7.48 (2 H, m)	1.36 [6 H, m, $J(\text{PH}) = 8.8$ , $J(\text{PtH}) = 19.8$ ], 7.10–7.48 (20 H, m)
(1e)	4.55	15.4	3.49	6 <sup>b</sup>	12.68	6.02 (2 H, m), 6.43 (2 H, m) 6.75 [2 H, m, $J(\text{PtH}) = 64.1$ ], 6.95 [2 H, m, $J(\text{PH}) = 7.3$ , $J(\text{PtH}) = 18.0$ ], 6.95–7.64 (8 H, m)	7.04 (12 H, m), 7.16 (6 H, m), 7.27 (12 H, m)
(1f)	3.85	Not resolved	3.85	Not resolved	—	6.41 (2 H, m), 6.79 (2 H, m), 6.95 (2 H, m), 7.10–7.86 (2 H, m)	2.53 (8 H, br s), 5.31 [4 H, t, $J(\text{PtH}) = 39.1$ ]
(1g)	4.28	Not resolved	3.38	Not resolved	12.50	6.58 (2 H, m), 6.82 (2 H, m), 7.05 (2 H, m), 7.10–7.80 (2 H, m)	2.08 (4 H, m), 7.10–7.86 (20 H, m)
(1h)	4.01	Not resolved	4.01	Not resolved	—	6.76–7.28 (6 H, m), 8.85 [2 H, m, $J(\text{PtH}) = 52.5$ ]	4.35 (2 H, m, $J(\text{PH}) = 9.2$ , $J(\text{PtH}) = 22.4$ ], 7.10–7.80 (20 H, m)
(2)	4.19	9.4 <sup>b</sup>	4.19	9.4 <sup>b</sup>	—	—	0.82 (18 H, m), 2.18 (12 H, m)

<sup>a</sup> Spectra (400 MHz) measured in [<sup>2</sup>H<sub>6</sub>]benzene at +21 °C. Chemical shifts ( $\delta$ ) are in p.p.m. ( $\pm 0.01$ ) to high frequency of SiMe<sub>4</sub> and coupling constants ( $J$ ) are in Hz ( $\pm 0.1$ ). Multiplicities: s = singlet, t = virtual triplet, and m = multiplet. <sup>b</sup> Not fully resolved.

**Table 4.**  $^{13}\text{C}\{-^1\text{H}\}$  N.m.r.\* data for the metallacycle carbons

Compound	$\delta(\text{C}^1)$	$^1J(\text{C}^1\text{Pt})$	$^2J(\text{C}^1\text{P})$	$\delta(\text{C}^2-\text{C}^6)$	$\delta(\text{C}^7)$	$^3J(\text{C}^7\text{Pt})$
(1a)	161.5	806.5	116.7	121.5 (s), 123.3 [t, $J(\text{CPT}) = 60.9$ ], 125.3 [t, $J(\text{CPT}) = 34.8$ ], 137.3 [t, $J(\text{CPT}) = 7.4$ Hz], 147.5 (s)	51.6	138.4
(1b)	159.9	799.9	120.7	122.1 (s), 123.3 [t, $J(\text{CPT}) = 60.3$ ], 125.4 [t, $J(\text{CPT}) = 34.3$ ], 138.1 [t, $J(\text{CPT}) = 8.90$ ], 146.8 (s)	51.8	136.6
(1c)	159.7	813.7	119.4	122.2 (s), 123.5 [t, $J(\text{CPT}) = 60.5$ ], 125.5 [t, $J(\text{CPT}) = 34.2$ ], 138.3 (br, s), 146.29 (s)	52.0	135.0
(1d)	159.7	812.9	119.9	122.2 (s), 123.5 [t, $J(\text{CPT}) = 59.9$ ], 125.4 [t, $J(\text{CPT}) = 34.6$ ], 138.3 [t, $J(\text{CPT}) = 9.8$ ], 146.3 (s)	51.9	137.5
(1e)	159.0	850.3	114.4	121.4 (s), 123.7 [t, $J(\text{CPT}) = 66.2$ ], 124.8 [t, $J(\text{CPT}) = 37.9$ ], 139.2 [t, $J(\text{CPT}) = 9.9$ ], 145.4 (br m)	52.1	138.1
(1f)	153.6	Not resolved	—	124.2 (s), 125.7 [t, $J(\text{CPT}) = 65.5$ ], 126.5 [t, $J(\text{CPT}) = 49.2$ ], 134.6 (s), 142.3 (s)	51.1	144.8
(2)	146.1	Not resolved	—	125.9 [t, $J(\text{CPT}) = 45.9$ ], 126.4 (s), 128.2 [t, $J(\text{CPT}) = 33.8$ ], 137.0 (s), 143.7 (s)	50.3	61.1

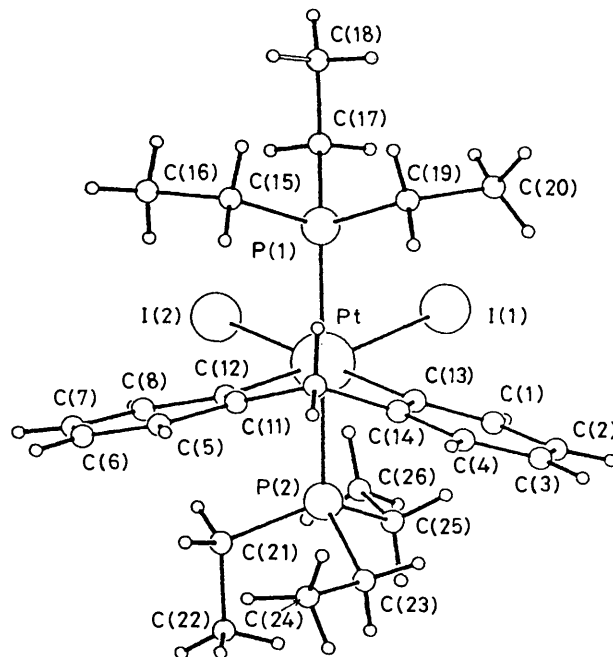
\* Spectra (100.6 MHz) measured in  $\text{CDCl}_3$  at ambient temperature. Chemical shifts ( $\delta$ ) in p.p.m. ( $\pm 0.1$ ) relative to  $\text{SiMe}_4$ . Coupling constants ( $J$ ) in Hz ( $\pm 0.1$ ).

**Figure 2.** Proton n.m.r. spectrum of complex (1a): x = unidentified impurity

from an estimate of the coalescence temperature the activation energy  $\Delta G^\ddagger$  for inversion can be estimated to be  $41 \text{ kJ mol}^{-1}$ ; this can be compared with  $\Delta G^\ddagger > 70 \text{ kJ mol}^{-1}$  for the platinum(II) complex (1a) and  $\Delta G^\ddagger < 30 \text{ kJ mol}^{-1}$  for the parent dihydroanthracene.<sup>6</sup>

It was of interest to see if a platina-anthracene related to the recently reported<sup>7</sup> rhenaphenanthrene or osmabenzene<sup>8</sup> could be generated from complex (1a). However, all our attempts to abstract a hydrogen from (1a) as  $\text{H}^+$  [by treating (1a) with  $\text{NEt}_3$ ,  $\text{LiN}(\text{SiMe}_3)_2$ , or  $\text{LiBu}^+$ ] or as  $\text{H}^-$  [by treating (1a) with  $\text{Ph}_3\text{CBF}_4$ ] failed. It was possible that this failure was due to the steric interactions making planarity for the metallacycle highly energetic (see above). It was hoped that the platinum(IV) complex (2), which has a much flatter ring, would not have such problems and that elimination of HI would be energetically favourable. However our attempts to deprotonate (2) with a range of bases [ $\text{NEt}_3$ , proton sponge, or  $\text{LiN}(\text{SiMe}_3)_2$ ] lead to reductive elimination of  $\text{I}_2$ , and (1a) was the sole product detected by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy.

Finally it is interesting to contrast the effect of platinum(II) on the conformational mobility of six-membered rings. We previously reported<sup>3</sup> very low energy barriers to ring inversion of saturated platinacyclohexanes whereas in this paper we report extremely high energy barriers to ring inversion of unsaturated platinacyclohexadienes.

**Figure 3.** Molecular structure of complex (2) showing the atomic numbering scheme

**Table 5.** Bond distances (Å) and bond angles (°)**(a) [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (1a)**

Pt-P(1)	2.323(3)	Pt-P(2)	2.303(3)	C(11)-C(10)	1.531(17)	C(10)-C(14)	1.512(14)
Pt-C(12)	2.062(11)	Pt-C(13)	2.038(11)	C(14)-C(4)	1.348(17)	C(14)-C(13)	1.415(15)
P(1)-C(15)	1.801(11)	P(1)-C(17)	1.799(13)	C(4)-C(3)	1.374(20)	C(3)-C(2)	1.363(19)
P(1)-C(19)	1.810(12)	P(2)-C(21)	1.835(13)	C(2)-C(1)	1.380(18)	C(1)-C(13)	1.399(15)
P(2)-C(23)	1.797(15)	P(2)-C(25)	1.825(11)	C(15)-C(16)	1.523(20)	C(17)-C(18)	1.510(19)
C(12)-C(8)	1.378(17)	C(12)-C(11)	1.384(15)	C(19)-C(20)	1.498(16)	C(21)-C(22)	1.476(22)
C(8)-C(7)	1.384(18)	C(7)-C(6)	1.355(19)	C(23)-C(24)	1.500(23)	C(25)-C(26)	1.519(16)
C(6)-C(5)	1.360(19)	C(5)-C(11)	1.382(17)				
P(1)-Pt-P(2)	98.8(1)	P(1)-Pt-C(12)	88.1(3)	C(6)-C(5)-C(11)	120.1(11)	C(12)-C(11)-C(5)	121.3(11)
P(2)-Pt-C(12)	172.5(3)	P(1)-Pt-C(13)	168.7(3)	C(12)-C(11)-C(10)	117.6(10)	C(5)-C(11)-C(10)	120.7(10)
P(2)-Pt-C(13)	91.6(3)	C(12)-Pt-C(13)	81.3(4)	C(11)-C(10)-C(14)	107.5(9)	C(10)-C(14)-C(4)	122.1(11)
Pt-P(1)-C(15)	112.7(4)	Pt-P(1)-C(17)	114.1(4)	C(10)-C(14)-C(13)	116.0(10)	C(4)-C(14)-C(13)	121.9(11)
C(15)-P(1)-C(17)	102.2(6)	Pt-P(1)-C(19)	121.6(4)	C(14)-C(4)-C(3)	121.1(12)	C(4)-C(3)-C(2)	119.3(12)
C(15)-P(1)-C(19)	102.5(5)	C(17)-P(1)-C(19)	101.3(5)	C(3)-C(2)-C(1)	120.2(12)	C(2)-C(1)-C(13)	122.1(11)
Pt-P(2)-C(21)	112.0(5)	Pt-P(2)-C(23)	116.4(5)	Pt-C(13)-C(14)	117.4(7)	Pt-C(13)-C(1)	127.5(8)
C(21)-P(2)-C(23)	105.6(7)	Pt-P(2)-C(25)	119.8(4)	C(14)-C(13)-C(1)	115.1(10)	P(1)-C(15)-C(16)	113.9(9)
C(21)-P(2)-C(25)	100.0(6)	C(23)-P(2)-C(25)	100.9(6)	P(1)-C(17)-C(18)	115.1(10)	P(1)-C(19)-C(20)	118.8(9)
Pt-C(12)-C(8)	127.4(8)	Pt-C(12)-C(11)	116.2(8)	P(2)-C(21)-C(22)	122.5(12)	P(2)-C(23)-C(24)	114.5(11)
C(8)-C(12)-C(11)	116.4(10)	C(12)-C(8)-C(7)	122.5(11)	P(2)-C(25)-C(26)	115.4(8)		
C(8)-C(7)-C(6)	119.2(12)	C(7)-C(6)-C(5)	120.2(12)				

**(b) [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)I<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (2)**

Pt-I(1)	2.755(1)	Pt-I(2)	2.814(1)	C(6)-C(5)	1.327(20)	C(5)-C(11)	1.415(26)
Pt-P(1)	2.381(3)	Pt-P(2)	2.391(3)	C(11)-C(10)	1.533(27)	C(10)-C(14)	1.469(22)
Pt-C(12)	2.093(15)	Pt-C(13)	2.078(14)	C(14)-C(4)	1.502(25)	C(14)-C(13)	1.424(17)
P(1)-C(15)	1.817(19)	P(1)-C(17)	1.804(15)	C(4)-C(3)	1.346(27)	C(3)-C(2)	1.328(23)
P(1)-C(19)	1.826(16)	P(2)-C(21)	1.821(16)	C(2)-C(1)	1.426(24)	C(1)-C(13)	1.426(21)
P(2)-C(23)	1.837(17)	P(2)-C(25)	1.821(19)	C(15)-C(16)	1.490(28)	C(17)-C(18)	1.496(19)
C(12)-C(8)	1.366(26)	C(12)-C(11)	1.380(17)	C(19)-C(20)	1.535(28)	C(21)-C(22)	1.544(20)
C(8)-C(7)	1.381(24)	C(7)-C(6)	1.368(23)	C(23)-C(24)	1.528(24)	C(25)-C(26)	1.614(25)
I(1)-Pt-I(2)	81.9(10)	I(1)-Pt-P(1)	90.6(10)	Pt-C(12)-C(11)	123.1(13)	C(8)-C(12)-C(11)	117.5(15)
I(2)-Pt-P(1)	87.4(10)	I(1)-Pt-P(2)	90.3(10)	C(12)-C(8)-C(7)	121.9(14)	C(8)-C(7)-C(6)	120.6(17)
I(2)-Pt-P(2)	94.3(10)	P(1)-Pt-P(2)	178.2(10)	C(7)-C(6)-C(5)	118.4(18)	C(6)-C(5)-C(11)	122.3(15)
I(1)-Pt-C(12)	173.2(4)	I(2)-Pt-C(12)	92.3(4)	C(12)-C(11)-C(5)	119.2(17)	C(12)-C(11)-C(10)	124.1(15)
P(1)-Pt-C(12)	92.7(3)	P(2)-Pt-C(12)	86.6(3)	C(5)-C(11)-C(10)	116.4(12)	C(11)-C(10)-C(14)	117.8(11)
I(1)-Pt-C(13)	94.0(4)	I(2)-Pt-C(13)	175.5(4)	C(10)-C(14)-C(4)	119.3(12)	C(10)-C(14)-C(13)	124.6(14)
P(1)-Pt-C(13)	90.7(3)	P(2)-Pt-C(13)	87.6(3)	C(4)-C(14)-C(13)	116.1(14)	C(14)-C(4)-C(3)	124.0(13)
C(12)-Pt-C(13)	91.9(6)	Pt-P(1)-C(15)	116.1(4)	C(4)-C(3)-C(2)	119.1(17)	C(3)-C(2)-C(1)	121.4(16)
Pt-P(1)-C(17)	116.1(4)	C(15)-P(1)-C(17)	101.4(8)	C(2)-C(1)-C(13)	122.5(12)	Pt-C(13)-C(14)	122.6(11)
Pt-P(1)-C(19)	115.1(6)	C(15)-P(1)-C(19)	101.5(8)	Pt-C(13)-C(1)	120.5(9)	C(14)-C(13)-C(1)	116.7(13)
C(17)-P(1)-C(19)	104.7(7)	Pt-P(2)-C(21)	115.8(6)	P(1)-C(15)-C(16)	118.2(10)	P(1)-C(17)-C(18)	116.1(10)
Pt-P(2)-C(23)	116.3(4)	C(21)-P(2)-C(23)	102.8(7)	P(1)-C(19)-C(20)	115.7(10)	P(2)-C(21)-C(22)	114.3(14)
Pt-P(2)-C(25)	115.5(4)	C(21)-P(2)-C(25)	105.3(8)	P(2)-C(23)-C(24)	114.8(14)	P(2)-C(25)-C(26)	116.1(16)
C(23)-P(2)-C(25)	98.9(8)	Pt-C(12)-C(8)	119.2(10)				

**Experimental**

2,2'-Dichlorodiphenylmethane was synthesised by reduction<sup>9</sup> of 2,2'-dichlorodiphenylmethanol.<sup>10</sup>

**Preparations.**—2,2'-Dilithiodiphenylmethane. Lithium flakes (4.0 g, 0.57 mol) were suspended in diethyl ether (75 cm<sup>3</sup>) in a flask (1 000 cm<sup>3</sup>) filled with argon. The flask was fitted with a mechanical stirrer and dropping funnel and cooled to 0 °C. A solution of 2,2'-dichlorodiphenylmethane (10.80 g, 0.046 mol) in diethyl ether (125 cm<sup>3</sup>) was added dropwise over a period of 1 h. The resulting orange suspension was then stirred for 24 h. The reaction mixture was filtered free of the excess of lithium metal. The organolithium concentration was determined by a modification of the double titration method of Gilman and Haubein:<sup>11</sup> separate aliquots were quenched with water and successively with 1,2-dibromoethane and water, and titrated against 0.05 mol dm<sup>-3</sup> hydrochloric acid.

[Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (1a). A solution of 2,2'-dilithiodiphenylmethane (5 cm<sup>3</sup>, 0.22 mol dm<sup>-3</sup> in diethyl-ether,

1.10 mmol) was added dropwise to a stirred suspension of [PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (0.374 g, 1.0 mmol) in benzene (25 cm<sup>3</sup>). The reaction mixture was then stirred for 2 h during which time the suspension had turned bright orange. Water (20 cm<sup>3</sup>) was then added and the two layers separated. The organic layer was dried over MgSO<sub>4</sub> and then filtered. Removal of the solvent by evaporation under reduced pressure followed by addition of diethyl ether (40 cm<sup>3</sup>) gave the orange solid product. Recrystallisation from benzene-methanol (1:1 v/v) gave a white air-stable crystalline solid. Yield 0.44 g, 74%. The compound [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (1e) was made similarly in 62% yield.

[Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PMe<sub>3</sub>)<sub>2</sub>] (1b). A solution of 2,2'-dilithiodiphenylmethane (11 cm<sup>3</sup>, 0.22 mol dm<sup>-3</sup> in diethyl ether, 2.2 mmol) was added dropwise to a stirred suspension of [PtCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (0.90 g, 1.82 mmol) in benzene (40 cm<sup>3</sup>) cooled to 0 °C. The reaction mixture was then stirred for 2 h and allowed to warm to ambient temperature. The bright yellow mixture was again cooled to 0 °C, water (25 cm<sup>3</sup>) added, and the two layers

Table 6. Crystal data and data collection conditions

Compound	[Pt(C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )(PEt <sub>3</sub> ) <sub>2</sub> ]	[Pt(C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )I <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> ]
Formula	C <sub>25</sub> H <sub>40</sub> P <sub>2</sub> Pt	C <sub>25</sub> H <sub>40</sub> I <sub>2</sub> P <sub>2</sub> Pt
Crystal system	Monoclinic	Monoclinic
Systematic absences	<i>h</i> 0 <i>l</i> ; <i>h</i> + <i>l</i> = 2 <i>n</i> + 1 0 <i>k</i> 0; <i>k</i> = 2 <i>n</i> + 1	<i>h</i> 0 <i>l</i> , <i>l</i> = 2 <i>n</i> + 1 0 <i>k</i> 0, <i>k</i> = 2 <i>n</i> + 1
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	10.748(2)	17.375(5)
<i>b</i> /Å	15.259(4)	9.681(3)
<i>c</i> /Å	14.885(4)	19.192(5)
β/°	90.77(2)	120.72(2)
<i>U</i> /Å <sup>3</sup>	2 440.9(10)	2 775.4(13)
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.60	2.04
<i>D<sub>m</sub></i> /g cm <sup>-3</sup>	1.53	1.44
<i>Z</i>	4	4
μ(Mo-K <sub>α</sub> )/cm <sup>-1</sup>	61.79	76.41
<i>F</i> (000)	1 191.73	1 615.73
Crystal size/cm	0.043 × 0.033 × 0.048	—
Max. and min. transmission factors	0.61, 0.21	—
Scan range about <i>K</i> <sub>α1</sub> - <i>K</i> <sub>α2</sub> /°	-1.05/+1.05	-1.1/+1.1
Reflections collected	4 768	5 415
Reflections observed [ <i>I</i> /σ( <i>I</i> ) ≥ 3.0]	2 725	3 311
Weighting constant: <i>g</i>	0.0079	0.002 92
No. of parameters	271	289
<i>R</i>	0.0476	0.0533
<i>R'</i>	0.0550	0.0581
Max. and min. on final difference Fourier/e Å <sup>-3</sup>	2.53, -1.95	2.83, -2.12
Max. δ/σ (final cycle)	0.38	0.107

separated. The organic layer was dried over MgSO<sub>4</sub> and then filtered. Removal of the solvent by evaporation under reduced pressure followed by addition of diethyl ether (40 cm<sup>3</sup>) gave the pale brown solid product. Recrystallisation from benzene-methanol (1:1 v/v) gave a white air-stable crystalline solid. Yield 0.59 g, 63%. The following were made similarly: [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (1c) (56%) and [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PMePh)<sub>2</sub>] (1d) (49%).

[Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(cod)] (1b). A solution of 2,2'-dilithiodiphenylmethane (9.0 cm<sup>3</sup>, 0.27 mol dm<sup>-3</sup> in diethyl ether, 2.4 mmol) was added dropwise to a stirred suspension of [PtCl<sub>2</sub>(cod)] (0.8 g, 2.14 mmol) in diethyl ether (40 cm<sup>3</sup>) cooled to -78 °C. The mixture was then stirred for 2 h. Methanol (20 cm<sup>3</sup>) was then added and the mixture allowed to warm to ambient temperature over 30 min. The volume was reduced to 10 cm<sup>3</sup> by evaporation under reduced pressure. The yellow solid product was filtered off, washed with methanol (25 cm<sup>3</sup>) and diethyl ether (30 cm<sup>3</sup>), and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. Yield 1.2 g, 84%.

[Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(dppm)] (1g). A solution of bis(diphenylphosphino)methane (0.115 g, 0.30 mmol) in dichloromethane (10 cm<sup>3</sup>) was added to a stirred solution of [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(cod)] (0.150 g, 0.32 mmol) in dichloromethane (25 cm<sup>3</sup>). The mixture was then stirred for 1 h. The solvent was removed by evaporation under reduced pressure. The residue was triturated with diethyl ether (40 cm<sup>3</sup>) to give the pale yellow solid product. Recrystallisation from benzene-ethanol (1:1 v/v) gave a white solid. Yield 0.20 g, 93%. The compound [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(dppe)] (1f) was made similarly in 92% yield.

[Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)I<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (2). A solution of iodine (2.08 cm<sup>3</sup>, 0.079 mol dm<sup>-3</sup> in benzene, 0.165 mmol) diluted with dichloromethane (15 cm<sup>3</sup>) was added dropwise over 4 h to a stirred solution of [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (0.10 g, 0.167 mmol) in dichloromethane (40 cm<sup>3</sup>) cooled to -50 °C under argon. The mixture was then stirred for a further 2 h at -50 °C. The solvent was then removed by evaporation under reduced pressure. Addition of ethanol (40 cm<sup>3</sup>) gave the yellow

solid product which was filtered off and washed with ethanol (15 cm<sup>3</sup>). Recrystallisation from benzene-methanol (1:1 v/v) gave a yellow air-stable crystalline solid. Yield 0.132 g, 93%.

*X-Ray Crystal Structure Analysis of [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (1a) and [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)I<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (2).*—For both compounds data were collected with a Syntex *P*2<sub>1</sub> four-circle diffractometer for 2θ in the range 3–50°. Background intensities were measured at each end of the scan for 0.25 s of the scan time. Three standard reflections, monitored every 200 reflections, showed slight changes during data collection; the data were rescaled to correct for this. The density was measured by flotation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Refinement used the observed reflections [*I*/σ(*I*) ≥ 3.0] corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method. Details for each compound are given in Table 6.

Heavy atoms were located by Patterson methods and the remaining lighter atoms by successive Fourier synthesis. In general, anisotropic thermal parameters were used for all atoms except hydrogens which were inserted at fixed positions and not refined (*U* = 0.07 Å<sup>2</sup>). Methyl groups were treated as rigid CH<sub>3</sub> units with their initial orientation taken from the H-atom peaks on a difference Fourier synthesis. Final refinement of *F* was by cascaded least-squares methods. A weighting scheme of the form *W* = 1/[σ<sup>2</sup>(*F*) + *gF*<sup>2</sup>] was applied. Computing used SHELXTL<sup>12</sup> on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 13. Atomic co-ordinates are in Table 7.

Suitable crystals of compound [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PEt<sub>3</sub>)<sub>2</sub>] were obtained by recrystallisation from benzene-methanol (1:1 v/v). The crystals formed were irregularly shaped colourless plates. Orange-red plate crystals of compound [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)I<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] were obtained by recrystallisation from benzene-methanol (1:1 v/v). For [Pt(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)I<sub>2</sub>-

**Table 7.** Atom co-ordinates ( $\times 10^4$ )

Atom	x	y	z	Atom	x	y	z
<b>(a) For complex (1a)</b>				<b>(b) For complex (2)</b>			
Pt	868.2(4)	6 997.2(2)	5 853.5(3)	Pt	2 526.1(3)	7 240.1(5)	5 072.0(3)
P(1)	944(3)	7 832(2)	4 550(2)	I(1)	2 617.7(8)	5 234.3(11)	4 098.7(7)
P(2)	2 424(3)	6 010(2)	5 536(2)	I(2)	2 524.2(8)	4 911.5(11)	5 948.5(7)
C(1)	313(11)	5 618(7)	7 320(8)	P(1)	4 115(2)	7 247(4)	5 908(2)
C(2)	261(12)	5 331(8)	8 198(9)	P(2)	932(2)	7 308(4)	4 222(2)
C(3)	511(14)	5 894(9)	8 888(9)	C(1)	2 409(8)	8 635(14)	3 590(8)
C(4)	811(13)	6 749(10)	8 699(9)	C(2)	2 499(9)	9 696(17)	3 121(9)
C(5)	-996(13)	8 914(7)	7 438(8)	C(3)	2 703(10)	10 984(17)	3 394(8)
C(6)	-2 095(13)	9 088(8)	7 010(9)	C(4)	2 869(9)	11 275(14)	4 144(11)
C(7)	-2 442(12)	8 621(8)	6 274(9)	C(5)	2 442(10)	10 822(15)	6 432(10)
C(8)	-1 628(12)	8 009(7)	5 927(8)	C(6)	2 073(10)	10 343(18)	6 842(9)
C(10)	966(11)	8 007(6)	7 627(8)	C(7)	1 837(9)	8 978(15)	6 759(7)
C(11)	-195(11)	8 292(7)	7 095(7)	C(8)	1 966(9)	8 131(15)	6 249(8)
C(12)	-480(11)	7 842(7)	6 312(7)	C(10)	3 094(9)	10 641(14)	5 533(9)
C(13)	646(10)	6 478(7)	7 103(7)	C(11)	2 595(9)	9 974(12)	5 914(9)
C(14)	820(11)	7 045(7)	7 846(7)	C(12)	2 369(8)	8 594(13)	5 841(7)
C(15)	893(12)	8 992(7)	4 769(8)	C(13)	2 580(8)	8 865(12)	4 391(7)
C(16)	2 014(15)	9 334(8)	5 298(10)	C(14)	2 837(8)	10 227(14)	4 706(8)
C(17)	-371(12)	7 682(8)	3 806(8)	C(15)	4 718(9)	8 250(14)	5 539(9)
C(18)	-525(16)	6 767(9)	3 435(12)	C(16)	4 720(11)	7 743(16)	4 807(11)
C(19)	2 223(11)	7 740(7)	3 777(7)	C(17)	4 660(9)	5 590(15)	6 086(9)
C(20)	2 207(13)	8 292(8)	2 945(8)	C(18)	5 658(9)	5 596(18)	6 613(10)
C(21)	1 995(15)	5 283(9)	4 600(8)	C(19)	4 548(10)	7 980(15)	6 918(8)
C(22)	2 746(18)	4 549(10)	4 343(11)	C(20)	4 439(13)	7 076(17)	7 519(10)
C(23)	3 907(13)	6 466(10)	5 249(10)	C(21)	530(9)	7 309(16)	3 136(8)
C(24)	4 295(16)	7 240(11)	5 807(12)	C(22)	-529(11)	7 310(19)	2 607(10)
C(25)	2 891(12)	5 199(7)	6 376(7)	C(23)	366(9)	8 800(15)	4 353(9)
C(26)	3 468(14)	5 569(8)	7 232(7)	C(24)	538(10)	10 177(17)	4 066(11)
				C(25)	328(10)	5 931(15)	4 386(10)
				C(26)	342(12)	4 439(16)	4 018(12)

( $\text{PET}_3$ )<sub>2</sub>] the refinement did not include correction for absorption effects, because the crystal was lost before its dimensions were recorded. In both structures the only substantial peaks on the final difference Fourier syntheses were close to Pt.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

### Acknowledgements

We would like to thank the S.E.R.C. for an Earmarked Studentship (to K. H. B.) and Johnson Matthey plc for a generous loan of platinum salts.

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Received 12th June 1989; Paper 9/02460C