# Conformations of platinacyclohexanes: NMR studies and crystal structures of [Pt(CH$_2$)$_4$CH$_2$(PPhMe$_2$)$_2$] and [PtCH$_2$CH$_2$CMe$_2$CH$_2$CH$_2$(PPhMe$_2$)$_2$]

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(Received October 10th, 1989)

## Abstract

The platinacyclohexanes Pt(CH$_2$CH$_2$CR′R″CH$_2$CH$_2$)(PR$_3$)$_2$] where R$_3$ = Ph$_3$ (**a**) or Me$_2$Ph (**b**) and R′ = R″ = H (**1a,b**), R′ = H, R″ = Me, R$_3$ = Ph$_3$ (**2**), or R′ = R″ = Me (**3a,b**) have been prepared. Variable temperature $^1$H{$^{31}$P} (400 MHz) and $^{13}$C{$^1$H} (100 MHz) NMR studies reveal that ring reversal is rapid even at −150°C. The X-ray crystal structures of compounds **1b** and **3b** have been determined; in **1b** the ring has the half-chair form, while in **3b** it is in the skew conformation.

## Introduction

Conformational analysis of six membered heterocycles is a subject of much interest [1]. The conformations that have been observed can be categorised as chair (**A**), half chair (**B**), boat (**C**), twist boat (**D**) and planar (**E**). The great majority of
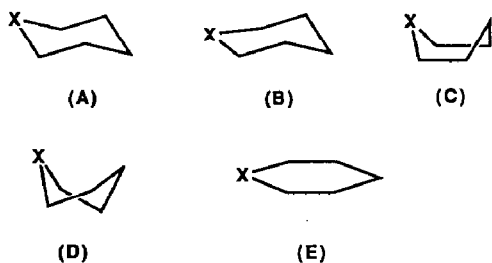


saturated rings adopt the chair conformation **A**, which undergoes a ring inversion (eq. 1) that is often rapid on the NMR timescale at ambient temperatures [1]. This,

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eq 1
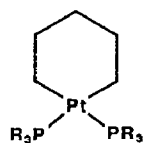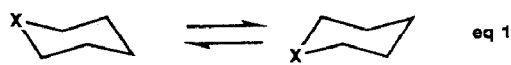
(1a)  PR$_3$ = PPh$_3$     (1a′)  PR$_3$ = PPh$_3$

(1b)  PR$_3$ = PPhMe$_2$
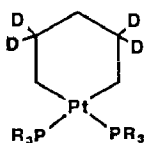
fluxionality can be studied by variable temperature $^1$H NMR spectroscopy for many heterocycles and, from measurement of the coalescence temperature $T_c$ or NMR lineshape analysis, the kinetic parameters for the process can be determined. Generally the free energy of activation $\Delta G^{\neq}$ at $T_c$ falls in the range 25–60 kJ mol$^{-1}$, the precise value depending on the heteroatom and the nature of the substituents on the ring [1]. We report here the first conformational study of six-membered heterocycles in which the heteroatom is a transition metal.

### Results and discussion

The saturated platinacycles **1a,b**, **2** and **3a,b** were made by a modification of the method of Whitesides et al. [2] and characterised by elemental analysis and NMR spectroscopy (Tables 1 and 2).

The variable temperature $^1$H NMR spectra of **1a** were obtained in order to investigate the possibility of observing ring reversal on the NMR timescale. However the spectrum of **1a** at $-150\,^\circ$C and 400 MHz was very complex, and little could be concluded because of overlapping signals and complex $^1$H–$^1$H, $^1$H–$^{31}$P and $^1$H–$^{195}$Pt couplings. To avoid these problems, the tetradeuterio derivative **1a′** was made and its $^1$H{$^{31}$P} NMR spectra measured at low temperatures. It is clear

Table 1

$^{31}$P{$^1$H} NMR $^a$ and $^{195}$Pt{$^1$H} NMR $^b$ data

| Compound | $\delta(^{31}$P$)$ | $^1J$(PtP) | $\delta(^{195}$Pt$)$ |
|---|---|---|---|
| **1a** | 28.3 | 1738 | $-222$ |
| **1b** | $-9.7$ | 1676 | – |
| **1a′** | 28.2 | 1738 | – |
| **2** | 28.3 | 1744 | $-243$ |
| **3a** | 28.6 | 1732 | $-225$ |
| **3b** | $-9.4$ | 1672 | – |

$^a$ Spectra (162 MHz) measured in CDCl$_3$ at $+21\,^\circ$C; chemical shifts ($\delta$) in ppm ($\pm0.1$) to high frequency of 85% H$_3$PO$_4$. $^b$ Spectra (85.6 MHz) measured in CD$_2$Cl$_2$ at $+21\,^\circ$C; chemical shifts ($\pm1$ ppm) to high frequency of $\Xi$(Pt) 21.4 MHz.

Table 2

$^{13}C\{^1H\}$ NMR $^a$ data for the platinacycle carbons $^b$

| Compound | $\delta(C^1)$ | $|J(C^1Px)+J(C^1Px')|$ | $^1J(C^1Pt)$ | $\delta(C^2)$ | $^2J(C^2Pt)$ | $\delta(C^3)$ | $^3J(C^3Pt)$ | $\delta(C^4)$ | $^4J(C^4Pt)$ |
|---|---|---|---|---|---|---|---|---|---|
| 1a | 20.3 | 95.9 | 638.7 | 26.7 | 35.8 | 32.9 | 36.2 | – | – |
| 1b | 15.8 | 100.2 | 610.3 | 28.9 | 36.7 | 32.9 | 35.2 | – | – |
| 1a′ | 20.1 | 95.5 | 640.0 | 27.9 | m | 32.8 | 36.6 | – | – |
| 2 | 20.9 | 96.3 | 641.1 | 38.3 | 32.3 | 38.9 | 31.0 | 23.8 | n.r. |
| 3a | 16.4 | 90.7 | 642.6 | 33.5 | 26.8 | 41.7 | n.r. | 29.8 | n.r. |

$^a$ Spectra (100.6 MHz) measured in CDCl$_3$ at +21°C; chemical shifts ($\delta$) in ppm ($\pm$0.1) to high frequency of SiMe$_4$ and coupling constants ($J$) in Hz ($\pm$0.1). n.r. = not resolved; m-complex multiplet. $^b$ The carbons are numbered from platinum: $[Pt(C^1H_2C^2H_2C^3H_2C^3R_2C^2H_2C^1H_2)]$ R = H or C$^4$H$_3$.
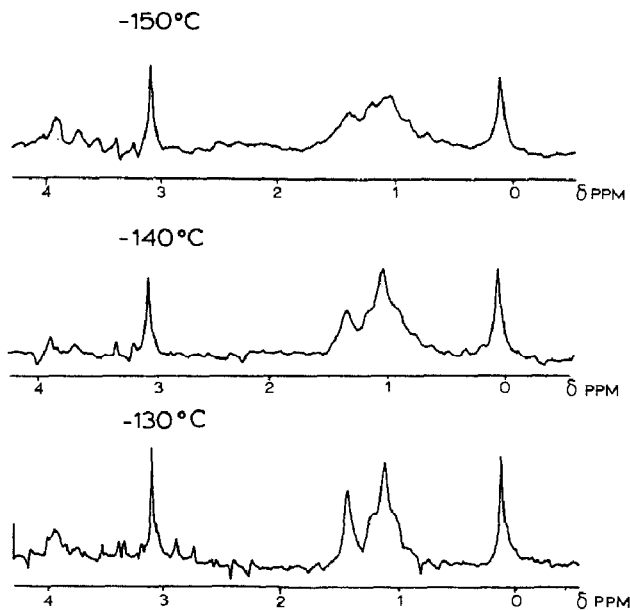
Fig. 1. Low temperature $^1H\{^{31}P\}$ NMR spectra of $[(Ph_3P)_2Pt(CH_2CD_2CH_2CD_2CH_2)]$ (**1a′**) in $CHClF_2$ at 400 MHz.

from Fig. 1 that at $-150\,°C$ and 400 MHz the signals are broadened, but the slow exchange limit could not be reached because of lack of solubility below $-150\,°C$.



(2)  $PR_3 = PPh_3$

(3a)  $PR_3 = PPh_3$

(3b)  $PR_3 = PPhMe_2$
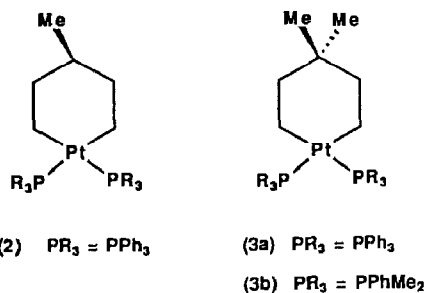
## 4-Substituted platinacyclohexanes

It is well known that the replacement of hydrogens by more bulky substituents on the six membered ring slows down ring reversal because the more severe [1,2]-diaxial interactions raise the activation energy. The 4-methylplatinacyclohexane (2) and 4,4-dimethylplatinacyclohexane (3a,b) were made (see Experimental) and characterised fully (see Tables 1–3).

It was hoped that at low temperatures two $CH_3$ resonances 2 and 3a would be apparent for the axial and equatorial $CH_3$ groups. However, as with the unsubstituted complex 1a, the slow exchange limit was not reached, and at $-150\,°C$ and 400 MHz only slight broadening of the $CH_3$ resonances was observed. More significant line broadening of the $CH_3$ resonances was observed in the $^{13}C\{^1H\}$ NMR spectrum of 3a at $-130\,°C$ and 100.6 MHz, but once again the slow exchange limit was not reached.

Table 3

$^1$H NMR data $^a$ for the platinacycle hydrogens $^b$

| | $\delta(H^1)$ | $J(PtH^1)$ | $\delta(H^2)$ | $\delta(H^3)$ | $\delta(H^4)$ |
|---|---|---|---|---|---|
| 1a$^c$ | 1.20 | 80.0 | 1.42 | 1.52 | |
| 1b | broad multiplet 1.10–1.72 | | | | |
| 1a$'$ | 1.27 | 79.0 | – | 1.50 | |
| 2 | broad multiplet 0.82–1.84 | | 0.74 | | |
| 3a$^d$ | broad multiplet 1.22–1.79 | | 0.84 | | |
| 3b | broad multiplet 0.94–1.76 | | 0.82 | | |

$^a$ Spectra (220 MHz) measured in CDCl$_3$ at +21°C. Chemical shifts in ppm ($\pm$0.01) to high frequency of SiMe$_4$ and coupling constants in Hz 9$\pm$0.1). $^b$ The hydrogens are numbered as follows: PtCH$_2^1$CH$_2^2$CH$^3$(CH$_3^4$).

Table 4

Bond distances (Å) and bond angles (°) for the platinacyclohexane [(PMe$_2$Ph)$_2$Pt(CH$_2$)$_5$] (1b)

*Bond distances*

| | | | |
|---|---|---|---|
| Pt–P(1) | 2.289(3) | Pt–P(2) | 2.268(4) |
| Pt–C(1) | 2.195(16) | Pt–C(5) | 2.097(34) |
| P(1)–C(11) | 1.798(10) | P(1)–C(12) | 1.826(19) |
| P(1)–C(13) | 1.832(10) | P(2)–C(21) | 1.809(11) |
| P(2)–C(22) | 1.826(18) | P(2)–C(23) | 1.827(10) |
| C(1)–C(2) | 1.258(28) | C(2)–C(3) | 1.443(44) |
| C(3)–C(4) | 1.516(33) | C(4)–C(5) | 1.226(31) |
| C(13)–C(14) | 1.380(16) | C(13)–C(18) | 1.374(15) |
| C(14)–C(15) | 1.375(16) | C(15)–C(16) | 1.360(19) |
| C(16)–C(17) | 1.364(20) | C(17)–C(18) | 1.360(14) |
| C(23)–C(24) | 1.391(14) | C(23)–C(28) | 1.386(15) |
| C(24)–C(25) | 1.365(16) | C(25)–C(26) | 1.340(16) |
| C(26)–C(27) | 1.342(17) | C(27)–C(28) | 1.384(18) |

*Bond angles*

| | | | |
|---|---|---|---|
| P(1)–Pt–P(2) | 98.1(1) | P(1)–Pt–C(1) | 167.0(4) |
| P(2)–Pt–C(1) | 91.3(5) | P(1)–Pt–C(5) | 86.6(9) |
| P(2)–Pt–C(5) | 170.5(7) | C(1)–Pt–C(5) | 85.5(11) |
| Pt–P(1)–C(12) | 114.4(4) | Pt–P(1)–C(11) | 122.4(5) |
| C(11)–P(1)–C(13) | 102.5(4) | Pt–P(1)–C(13) | 113.7(4) |
| Pt–P(2)–C(21) | 114.9(6) | C(12)–P(1)–C(13) | 102.1(6) |
| Pt–P(2)–C(23) | 117.6(4) | Pt–P(2)–C(22) | 116.1(5) |
| C(22)–P(2)–C(23) | 99.3(7) | C(21)–P(2)–C(23) | 104.2(5) |
| C(1)–C(2)–C(3) | 123.2(23) | Pt–C(1)–C(2) | 121.8(20) |
| Pt–C(5)–C(4) | 128.6(23) | C(2)–C(3)–C(4) | 129.2(17) |
| C(13)–C(14)–C(15) | 118.7(11) | C(3)–C(4)–C(5) | 116.9(29) |
| P(1)–C(13)–C(18) | 119.3(8) | P(1)–C(13)–C(14) | 122.1(8) |
| C(13)–C(14)–C(15) | 118.7(11) | C(14)–C(13)–C(18) | 118.5(9) |
| C(15)–C(16)–C(17) | 117.1(11) | C(14)–C(15)–C(16) | 123.0(13) |
| C(13)–C(18)–C(17) | 120.9(11) | C(16)–C(17)–C(18) | 121.6(11) |
| P(2)–C(23)–C(28) | 123.7(8) | P(2)–C(23)–C(24) | 118.4(7) |
| C(23)–C(24)–C(25) | 120.7(10) | C(24)–C(23)–C(28) | 117.9(10) |
| C(25)–C(26)–C(27) | 119.6(12) | C(24)–C(25)–C(26) | 121.0(10) |
| C(23)–C(28)–C(27) | 118.9(10) | C(26)–C(27)–(C28) | 122.0(11) |

The anomalously low activation energies [3] for ring reversal in **1a** and **3a** prompted us to determine the conformation of these rings in the solid by X-ray crystallography; we were unable to obtain suitable crystals of **1a** and **3a**, but crystals of the closely related complexes **1b** and **3b** were readily grown.

### X-ray crystal structures of 1b and 3b

Selected bond lengths and angles with numbering scheme based on **1b** and **3b** are listed in Tables 4 and 5, and information on deviations from planes in Table 6. For platinacyclohexane **1b**, only the major positions (see Experimental) of the ring carbons are considered. In this compound, the square planar geometry around the

Table 5

Bond distances (Å) and bond angles (°) for the platinacyclohexane $[(PMe_2Ph)_2Pt(CH_2CH_2C(CH_3)_2\text{-}CH_2CH_2)]$ (**3b**)

| Bond distances | | | |
|---|---|---|---|
| Pt–P(1) | 2.290(3) | Pt–P(2) | 2.273(3) |
| Pt–C(5) | 2.089(13) | Pt–C(1) | 2.102(13) |
| P(1)–C(13) | 1.833(10) | P(1)–C(11) | 1.822(18) |
| P(1)–C(12) | 1.809(13) | P(2)–C(22) | 1.818(16) |
| P(2)–C(21) | 1.824(12) | P(2)–C(23) | 1.834(11) |
| C(23)–C(24) | 1.363(17) | C(23)–C(28) | 1.391(14) |
| C(24)–C(25) | 1.396(21) | C(25)–C(26) | 1.368(19) |
| C(26)–C(27) | 1.380(22) | C(27)–C(28) | 1.384(17) |
| C(13)–C(14) | 1.360(18) | C(13)–C(18) | 1.371(17) |
| C(14)–C(15) | 1.385(23) | C(15)–C(16) | 1.308(26) |
| C(16)–C(17) | 1.388(26) | C(17)–C(18) | 1.368(17) |
| C(4)–C(33) | 1.483(18) | C(5)–C(4) | 1.498(18) |
| C(2)–C(1) | 1.548(26) | C(2)–C(3) | 1.503(21) |
| C(3)–C(2) | 1.503(21) | C(3)–C(4) | 1.483(18) |
| C(3)–C(32) | 1.505(39) | C(3)–C(31) | 1.420(33) |
| Bond angles | | | |
| P(1)–Pt–P(2) | 97.9(1) | P(1)–Pt–C(5) | 87.4(4) |
| P(2)–Pt–C(5) | 174.6(4) | P(1)–Pt–C(1) | 172.0(5) |
| P(2)–Pt–C(1) | 88.5(4) | C(5)–Pt–C(1) | 86.3(5) |
| Pt(1)–P(1)–C(13) | 114.4(4) | Pt–P(1)–C(11) | 114.2(4) |
| C(13)–P(1)–C(11) | 101.9(6) | Pt–P(1)–C(12) | 121.4(5) |
| C(13)–P(1)–C(12) | 102.1(5) | C(11)–P(1)–C(12) | 100.2(7) |
| Pt–P(2)–C(21) | 118.3(4) | Pt–P(2)–C(22) | 114.6(6) |
| C(21)–P(2)–C(22) | 99.7(7) | Pt–P(2)–C(23) | 118.6(4) |
| C(22)–P(2)–C(23) | 98.4(7) | C(21)–P(2)–C(23) | 104.3(5) |
| P(2)–C(23)–C(24) | 122.9(8) | P(2)–C(23)–C(28) | 117.5(9) |
| C(24)–C(23)–C(28) | 119.4(11) | C(23)–C(24)–C(25) | 119.7(11) |
| C(24)–C(25)–C(26) | 120.6(14) | C(25)–C(26)–C(27) | 120.3(13) |
| C(26)–C(27)–C(28) | 118.9(11) | C(23)–C(28)–C(27) | 121.1(12) |
| P(1)–C(13)–C(14) | 121.8(10) | C(13)–C(14)–C(15) | 119.8(15) |
| C(14)–C(13)–C(18) | 118.3(11) | C(13)–C(14)–C(15) | 122.1(15) |
| C(14)–C(15)–C(16) | 117.2(16) | C(15)–C(16)–C(17) | 123.7(15) |
| C(16)–C(17)–C(18) | 177.7(13) | C(13)–C(18)–C(17) | 120.6(13) |
| Pt–C(5)–C(4) | 114.9(12) | C(5)–C(4)–C(3) | 119.6(11) |
| C(3)–C(2)–C(1) | 109.7(14) | C(4)–C(3)–C(2) | 115.3(11) |
| C(4)–C(3)–C(31) | 115.9(15) | C(2)–C(3)–C(31) | 111.4(19) |
| C(4)–C(3)–C(32) | 109.2(16) | C(2)–C(3)–C(32) | 102.8(16) |
| C(31)–C(3)–C(32) | 100.1(19) | Pt–C(1)–C(2) | 119.2(13) |

Table 6

Deviations (Å) from mean planes (defined by starred atoms; e.s.d.'s ± 0.05 Å)

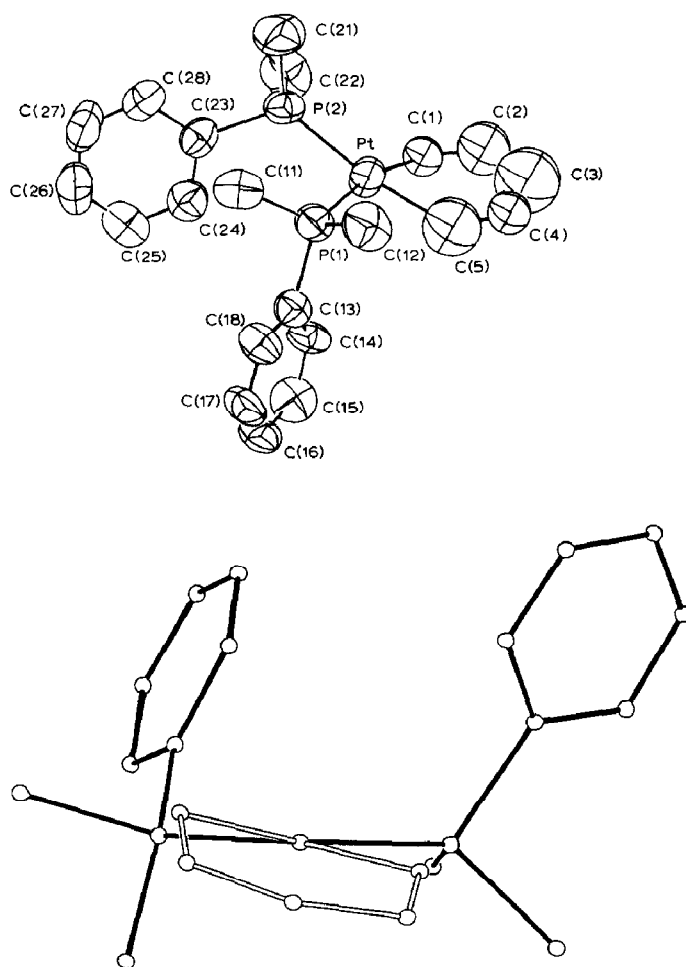| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Compound 1b* | | | | | | | |
| *Pt | 0.00 | *P(1) | 0.00 | *P(2) | 0.00 | C(1) | −0.34 |
| C(2) | 0.26 | C(3) | 0.71 | C(4) | 0.87 | C(5) | 0.30 |
| Pt | 0.75 | *C(1) | 0.00 | *C(2) | 0.00 | C(3) | 0.15 |
| *C(4) | 0.00 | *C(5) | 0.00 | | | | |
| *Compound 3b* | | | | | | | |
| *Pt | 0.00 | *P(1) | 0.00 | *P(2) | 0.00 | C(1) | 0.17 |
| C(2) | −0.76 | C(3) | −0.20 | C(4) | 0.76 | C(5) | 0.04 |
| *Pt | 0.00 | *C(1) | 0.00 | C(2) | −0.55 | C(3) | 0.37 |
| C(4) | −0.81 | *C(5) | 0.00 | | | | |



Fig. 2. The molecule of [(PhMe$_2$P)$_2$Pt(CH$_2$)$_5$] (**1b**): (a) showing the atomic numbering scheme (50% probability ellipsoids); the major ring component only is shown; (b) an end view of the platinacyclohexane ring.
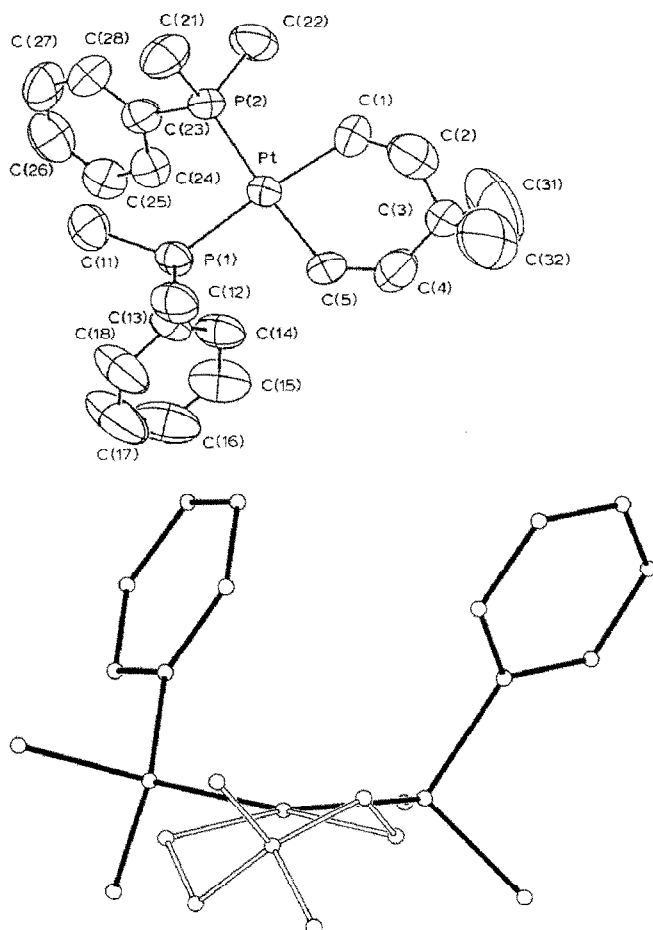
Fig. 3. The molecule of [(PhMe$_2$P)$_2$Pt(CH$_2$CH$_2$CMe$_2$CH$_2$CH$_2$)] (**3b**): (a) showing the atomic numbering scheme (50% probability ellipsoids); (b) an end view of the platinacyclohexane ring.

platinum atom is somewhat distorted (see Fig. 2). This is seen in the displacement of the ring carbon atoms from the plane defined by [Pt, P(1), P(2)] where C(1) is 0.34(5) Å to one side and C(5), 0.30(5) Å to the other. However, C(1), C(2), C(4) and C(5) are themselves coplanar, with the platinum atom below this plane (0.75 Å) and C(3) slightly above it (0.15 Å). This identifies the conformation of the ring as a half chair.

In the 4,4-dimethylplatinacyclohexane **3b** the square planar geometry around the platinum atom is less distorted than in **1b** (Fig. 3). This can again be seen from the displacement of the ring carbons from the plane defined by [Pt, P(1), P(2)] where C(1) is 0.17(5) Å to one side and C(5) is 0.04(5) Å to the other. The conformation of the platinacyclohexane ring is skew, with the ring twisted about C(2) and C(4). The twisting is not symmetrical; C(4) is displaced 0.81 Å above the plane defined by [Pt, C(1), C(5)] and C(2) 0.55 Å below it. The effect of this twisting of the ring is probably to alleviate the non bonded interactions between the hydrogens on C(2) and C(4) and the methyl groups on C(3). Unlike the partial disorder found in **1b**, the substituted platinacyclohexane **3b** is ordered in the crystal. However, the methyl groups have large thermal parameters in directions tangential to the ring (see Fig. 3).

Table 7

Comparison of dihedral angles ( ° ) for the platinacyclohexane rings in **1b** and **3b**

|  | **1b** | **3b** |
| --- | --- | --- |
| Pt–C(1)–C(2)–C(3) | 29.3 | 69.1 |
| C(1)–C(2)–C(3)–C(4) | −15.6 | −47.3 |
| C(2)–C(3)–C(4)–C(5) | 16.5 | −20.5 |
| C(3)–C(4)–C(5)–Pt | −35.6 | 66.8 |
| C(4)–C(5)–Pt–C(1) | 38.7 | −36.4 |
| C(5)–Pt–C(1)–C(2) | −32.8 | −24.1 |

These are probably dynamic in origin, rather than arising from disorder, because the thermal parameters of the ring atoms show no unusual features.

The presence of the methyl groups causes a change in the conformation of the platinacyclohexane ring from a half chair in **1b** to skew in **3b**. A significant feature is the higher degree of puckering in the platinacyclohexane ring in **3b** than in **1b**. This puckering is evident if the torsion angles Pt–C(1)–C(2)–C(3), C(2)–C(3)–C(4)–C(5) and C(3)–C(4)–C(5)–Pt in **3b** are compared with those in **1b** (see Table 7). However, both are flattened with respect to cyclohexane itself, for which the torsional angles in the ring are 56°.

The crystal structure of **1b** therefore shows that the presence of the square planar platinum atom in the six membered ring leads to a highly flattened conformation, and this may account for the anomalously low barrier to ring reversal. If the conformation of the rings in solution are assumed to be similar to the solid state, the X-ray structures suggest that the dimethyl substituted metallacycle **3b** would be more rigid, though this effect could not be clearly detected by low temperature NMR studies.

## Experimental

1,5-dibromo-3,3-dimethylpentane, 1,5-dibromo-3-methylpentane and 1,5-dibromo-2,2,4,4-tetradeuteriopentane were made by published methods. The metallacycles were made by a modification of the method of Whitesides et al. [2].

*Preparation of [(Ph$_3$P)$_2$Pt(CH$_2$CD$_2$CH$_2$CD$_2$CH$_2$)] (1a′)*

To a stirred suspension of [PtCl$_2$(1,5-cod)] (0.374 g, 1.0 mmol) in diethyl ether (25 cm$^3$) at −50°C was added dropwise a freshly prepared solution of BrMgCH$_2$CD$_2$CH$_2$CD$_2$CH$_2$MgBr in THF (5.0 cm$^3$, 0.45 M, 2.25 mmol). The mixture was allowed to warm to 0°C during 30 min and then recooled to −50°C, and a further aliquot of the Grignard reagent was added (5.0 cm$^3$, 2.25 mmol). The mixture was then allowed to warm to 0°C over 45 min to give a pale yellow clear solution, which was again recooled to −50°C. A solution of Ph$_3$P (0.524 g, 2.0 mmol) in diethyl ether (5 cm$^3$) was added dropwise during 5 min, then ethanol (10 cm$^3$) was added and the solution concentrated to 10 cm$^3$ under reduced pressure. The off-white solid was then filtered off and washed with ethanol (10 cm$^3$) and diethyl ether (2 × 10 cm$^3$). The product was purified by slow evaporation of a dichloromethane/ethanol solution. Yield 0.79 g, 87%. Anal. Found: C, 62.52; H,

5.73. $C_{41}H_{36}D_4P_2Pt$ calcd.: C, 62.04; H, 5.59%. The following were made similarly (yields in brackets):

**1a** (75%): Found: C, 62.97; H, 5.21. $C_{41}H_{40}P_2Pt$ calcd.: C, 62.35; H, 5.07%.
**1b** (10%): Found, C. 45.87; H, 6.01. $C_{21}H_{32}P_2Pt$ calcd.: C, 46.58; H, 5.96%.
**2** (65%): Found: C, 60.75; H, 4.98. $C_{43}H_{43}ClP_2Pt$ (0.5 $CH_2Cl_2$) calcd.: C, 60.30; H, 5.08%.
**3a** (71%): Found: C, 61.52; H, 5.73. $C_{43}H_{44}P_2Pt$ calcd.: C, 63.15; H, 5.38%.

*Crystal structure analysis of 1b and 3b [(PMe$_2$Ph)$_2$Pt(CH$_2$CH$_2$C(CH$_3$)$_2$CH$_2$CH$_2$]*

For both compounds, data were collected with a Syntex $P2_1$ four circle diffractometer for $2\theta$ in the range 3–50°C. 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

Table 8

Crystal data and data collection conditions

| Compound | [(PMe$_2$Ph)$_2$Pt(CH$_2$)$_5$] (**1b**) | [(PMe$_2$Ph)$_2$Pt(CH$_2$CH$_2$C(CH$_3$)$_2$CH$_2$CH$_2$)] (**3b**) |
|---|---|---|
| Formula | $C_{21}H_{32}P_2Pt$ | $C_{23}H_{36}P_2Pt$ |
| Crystal system | Triclinic | Triclinic |
| Systematic absences | None | None |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 9.669(3) | 9.615(4) |
| $b$ (Å) | 9.956(2) | 10.097(3) |
| $c$ (Å) | 13.712(4) | 13.835(6) |
| $\alpha$ (°) | 68.97(2) | 71.06(3) |
| $\beta$ (°) | 70.40(2) | 74.22(3) |
| $\gamma$ (°) | 64.35(2) | 73.87(3) |
| $U$ (Å$^3$) | 1084.8(5) | 1195.7(8) |
| $Dc$ (gcm$^{-3}$) | 1.66 | 1.58 |
| $Dm$ (gcm$^{-3}$) | 1.53 | 1.44 |
| $Z$ | 2 | 2 |
| $\mu$(Mo-$K_\alpha$) (cm$^{-1}$) | 66.8 | 60.6 |
| Crystal size (mm) | 0.10×0.20×0.63 | 0.44×0.43×0.81 |
| Max. transmission factor | 0.63 | 0.47 |
| Min. transmission factor | 0.43 | 0.19 |
| Scan range about $K_{\alpha1} - K_{\alpha2}$ (°) | −1.0/+1.0 | −1.1/+1.1 |
| Reflections collected | 3845 | 4216 |
| Reflections observed $[I/\sigma(I) \geqslant 3.0]$ | 2721 | 3252 |
| No. of parameters | 221 | 247 |
| Weighting constant: g | 0.00003 | 0.00078 |
| $R$(final) | 0.0545 | 0.0500 |
| $R_w$(final) | 0.0471 | 0.0523 |
| Max. on final difference Fourier | 1.8 | 3.0 |
| Min. on final difference Fourier | −1.8 | −1.5 |
| Max. $\delta/\sigma$ (final cycle) | 0.32 | 0.48 |

Table 9

Atom coordinates ($\times 10^4$) and isotropic thermal parameters (Å$^2 \times 10^3$) for **1b** and **3b**

| **1b** | | | | | **3b** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| atom | x | y | z | U | atom | x | y | z | U |
| Pt | 3636.5(5) | 770.2(5) | 3011.4(5) | 76(1)[a] | Pt | 3818.7(4) | 381.1(4) | 3129.0(3) | 55(1)[a] |
| P(1) | 6253(3) | 270(3) | 2788(2) | 61(2)[a] | P(1) | 6320(3) | 94(3) | 2925(2) | 55(1)[a] |
| P(2) | 3821(3) | -1598(3) | 3052(2) | 58(2)[a] | P(2) | 3793(3) | -1846(3) | 3091(2) | 56(1)[a] |
| C(1) | 1144(17) | 1732(18) | 2945(13) | 66(5) | C(1) | 1496(14) | 817(14) | 3457(13) | 96(7)[a] |
| C(2) | 137(27) | 2667(26) | 3482(19) | 125(8) | C(2) | 640(18) | 2013(19) | 3999(16) | 142(12)[a] |
| C(3) | 497(22) | 3716(21) | 3776(17) | 190(8) | C(3) | 833(13) | 3448(13) | 3263(12) | 83(6)[a] |
| C(4) | 2082(20) | 3695(21) | 3758(15) | 82(6) | C(4) | 2372(15) | 3545(14) | 2715(13) | 103(8)[a] |
| C(5) | 3237(34) | 2896(30) | 3232(24) | 153(12) | C(5) | 3633(13) | 2482(11) | 3153(12) | 83(6)[a] |
| C(101) | 1239(34) | 1195(33) | 3813(24) | 55(9) | C(11) | 6863(15) | 783(15) | 3801(10) | 83(7)[a] |
| C(201) | 389(55) | 2098(55) | 4173(38) | 129(16) | C(12) | 7521(14) | -1662(15) | 3108(12) | 92(7)[a] |
| C(401) | 2046(57) | 4122(54) | 2754(38) | 124(16) | C(13) | 7220(11) | 1062(12) | 1644(9) | 62(5)[a] |
| C(501) | 3230(22) | 3181(21) | 2661(16) | 13(5) | C(14) | 8696(15) | 1030(12) | 1404(12) | 119(9)[a] |
| C(11) | 7682(12) | -1652(12) | 2948(9) | 76(7)[a] | C(15) | 9397(19) | 1695(25) | 419(15) | 156(13)[a] |
| C(12) | 6702(16) | 908(16) | 3701(10) | 95(9)[a] | C(16) | 8559(21) | 2501(22) | -246(12) | 133(11)[a] |
| C(13) | 7117(12) | 1279(11) | 1478(8) | 56(6)[a] | C(17) | 7035(18) | 2662(18) | -34(10) | 100(8)[a] |
| C(14) | 8681(12) | 1117(13) | 1194(9) | 74(7)[a] | C(18) | 6386(14) | 1902(14) | 917(9) | 75(6)[a] |
| C(15) | 9250(15) | 1889(15) | 188(11) | 86(8)[a] | C(21) | 3970(18) | -3229(15) | 4313(10) | 91(7)[a] |
| C(16) | 8338(16) | 2823(15) | -538(10) | 85(8)[a] | C(22) | 2136(13) | -2130(15) | 2863(11) | 84(7)[a] |
| C(17) | 6783(14) | 3010(14) | -224(9) | 84(8)[a] | C(23) | 5151(12) | -2621(12) | 2097(8) | 61(5)[a] |
| C(18) | 6181(13) | 2245(12) | 757(7) | 65(6)[a] | C(24) | 5616(15) | -4060(13) | 2221(10) | 79(6)[a] |
| C(21) | 4043(18) | -3009(14) | 4318(9) | 105(10)[a] | C(25) | 6604(16) | -4573(16) | 1412(13) | 103(8)[a] |
| C(22) | 2155(14) | -1777(17) | 2831(11) | 99(9)[a] | C(26) | 7095(15) | -3646(18) | 489(1) | 97(8)[a] |
| C(23) | 5386(12) | -2566(11) | 2068(9) | 59(6)[a] | C(27) | 6612(13) | -2187(14) | 345(10) | 77(6)[a] |
| C(24) | 5799(12) | -1673(13) | 1052(9) | 71(7)[a] | C(28) | 5634(12) | -1683(14) | 1150(9) | 70(5)[a] |
| C(25) | 6908(12) | -2346(14) | 272(9) | 78(7)[a] | C(31) | -249(24) | 4012(37) | 2629(23) | 258(21)[a] |
| C(26) | 7629(14) | -3877(14) | 466(11) | 96(8)[a] | C(32) | 292(26) | 4423(29) | 3971(26) | 219(20)[a] |
| C(27) | 7232(15) | -4767(14) | 1433(12) | 113(9)[a] | | | | | |
| C(28) | 6118(15) | -4150(13) | 2254(10) | 90(8)[a] | | | | | |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalised $U_{ij}$ tensor.

cell dimensions and standard deviations were obtained by least squared fit to 15 high angle reflections. Refinement used the observed reflections $(I/\sigma(I) \geqslant 3.0)$ corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method. Details for each compound are given in Table 8.

Heavy atoms were located by Patterson methods and the remaining lighter atoms by successive Fourier synthesis. In general, anisotropic temperature factors were used for all atoms except hydrogens which were inserted at fixed positions and not refined ($U$ 0.07 Å$^2$). Methyl groups were treated as rigid $CH_3$ 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. Weighting scheme of the form $w = 1/(\sigma^2(F) + gF^2)$ was applied. Computing used SHELXTL [4] on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors were taken from the International Tables [5]. Atomic coordinates are in Table 9 *.

Suitable crystals (yellow irregular plates) of $[(PMe_2Ph)_2Pt(CH_2)_5]$ (**1b**) were obtained by recrystallisation from dichloromethane/methanol 2/1 v/v. In the structure determination, anisotropic temperature factors were used for all non-H atoms apart from those of the pentamethylene ring. It was found that four of the carbon atoms of the ring were disordered, each having a major and a minor position. Their linked occupancies were refined as a single population parameter which converged to 0.664 and 0.336 for the major and minor components, respectively.

Colourless flaky crystals of $[(PMe_2Ph)_2Pt(CH_2CH_2C(CH_3)_2CH_2CH_2)]$ (**3b**) were obtained from dichloromethane/methanol 2/1 v/v. The crystals had a strong tendency to grow with satellites attached, and several crystals had to be examined to find a suitable single crystal. The one selected contained one principal component with a satellite giving approximately 3% of the diffraction intensity of the main crystal, and this was ignored.

## Acknowledgements

## References

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* Anisotropic thermal parameters, full bond lengths and angles (for **1b**), and H-atom coordinates have been deposited with the Cambridge Crystallographic Data Centre. In both structures all significant peaks on the final difference Fourier syntheses were near the Pt atoms.