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The synthesis and characterization of a platina(IV)cyclopentane complex

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Abstract

The new metallacycle [PtIMe$(CH_2)_4$(dppm)], which contains both methylplatinum and platinacyclopentane groups, has been characterized by multinuclear NMR methods. It exists in solution as an equilibrium mixture of the two possible isomers having the *fac*-[PtC_3] stereochemistry. The chelating $(CH_2)_4$ ligand is shown to exert a significantly higher *trans*-influence than the methyl ligand. Molecular mechanics calculations predict a slight preference for the less symmetrical isomer [Me and one CH_2 group *trans* to dppm] over the more symmetrical isomer [two CH_2 groups *trans* to dppm], in agreement with the experimental observations.

Introduction

Metallacycles are significant as intermediates in several catalytic reactions and so their chemistry has been studied in considerable detail [1–3]. Platinum(IV) complexes containing a 5-membered PtC_4 ring have been studied previously and one such complex has been characterized crystallographically [4,5]. The chemical properties of both platinum(II) and platinum (IV) metallacyclopentanes have also been studied [4,6–8]. This paper describes in detail the characterization of a new complex [PtIMe{$(CH_2)_4$}(dppm)], dppm = $Ph_2PCH_2PPh_2$, which contains both a Pt–Me group and a $Pt(CH_2)_4$ ring and which exists as an equilibrium mixture of two isomers. This allows a direct comparison of the *trans* influences of the methyl group and the CH_2 group of the metallacycle.

Results and discussion

The new complex [PtIMe{$(CH_2)_4$}(dppm)] was prepared by oxidative addition of MeI to the known complex [Pt{$(CH_2)_4$}(dppm)] [9] (eq. 1). It was readily

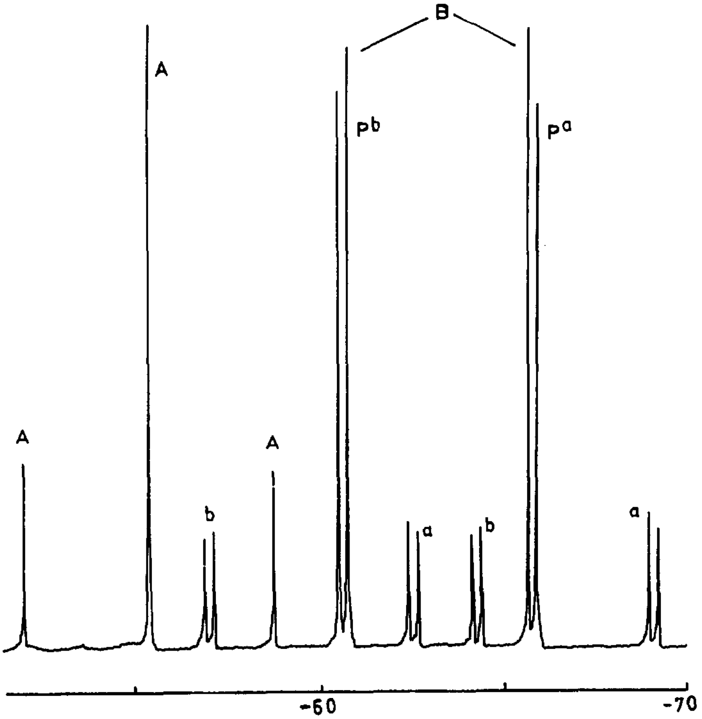
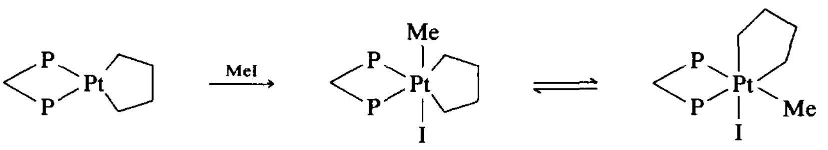


Fig. 1. The ^{31}P NMR spectrum (121 MHz) of an equilibrium mixture of isomers **A** and **B**.

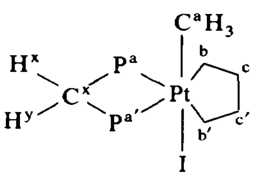
crystallized in analytically pure form but the NMR spectra showed very clearly that it exists as an inseparable mixture of the isomers **A** and **B**, in approximately 1 : 3



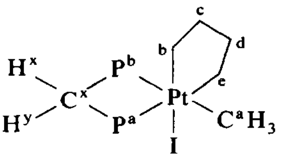
(A) **(B)**

(1)

ratio. The characterization of **A** and **B** required the use of ^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopies and is described below. The spectra are complex but very informative and so are described in detail.



(**A**, minor)



(**B**, major)

The ^{31}P NMR spectrum (Fig. 1) contained three resonances in the range $\delta = -50$ to -65 ppm which is characteristic for chelating dppm and hence proves that there is no monomer–dimer equilibrium as found for some other platinum–dppm com-

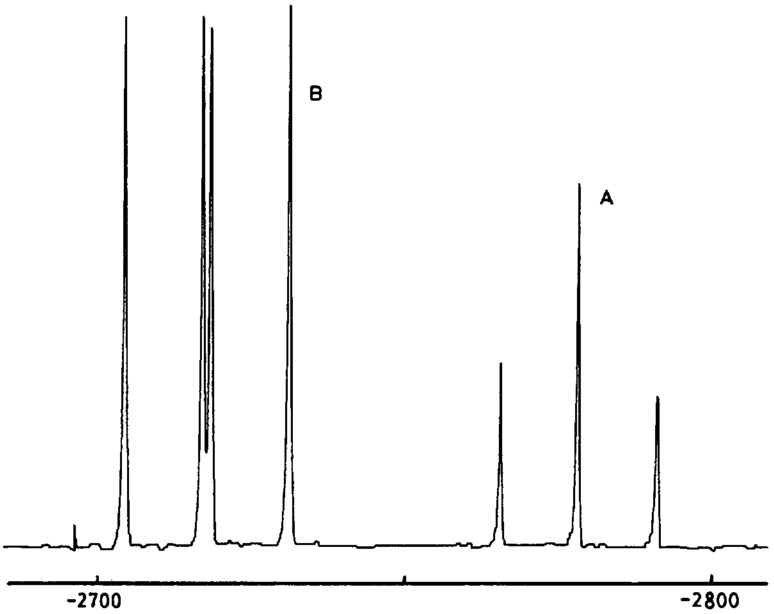


Fig. 2. The ^{195}Pt NMR spectrum (64 MHz) of an equilibrium mixture of isomers **A** and **B**.

plexes [9,10]. Since trialkylplatinum(IV) complexes invariably have the *fac*-PtC_3 stereochemistry [11], the isomers **A** and **B** are the only likely stable complexes. The structures are proved as follows.

The singlet in the ^{31}P NMR spectrum (Fig. 1) is due to isomer **A** and has $^{1}J(PtP) = 824$ Hz. This low value is characteristic of a phosphorus atom *trans* to a carbon donor [10,12]. The two doublets in the ^{31}P NMR spectrum are then due to the non-equivalent phosphorus atoms of isomer **B**. The doublet at $\delta = -65.93$ has $^{1}J(PtP) = 812$ Hz and that at $\delta = -60.76$ has $^{1}J(PtP) = 899$ Hz. The lower $^{1}J(PtP)$ value is assigned as the phosphorus atom P^a which is *trans* to CH_2 whereas the larger value of $^{1}J(PtP)$ belongs to P^b, which is *trans* to CH_3. For comparison, $[PtIMe_3(dppm)]$ and $[PtMe_4(dppm)]$ have $^{1}J(PtP) = 897$ Hz and 936 Hz respectively, similar to the higher value of $^{1}J(PtP)$ for isomer **B**. Thus, noting also the low value of $^{1}J(PtP)$ for isomer **A**, it is clear that the CH_2 group of the metallacycle exerts a significantly stronger *trans* influence than the methyl group [13].

The ^{195}Pt NMR spectrum (Fig. 2) contained a triplet due to isomer **A** [$^{1}J(PtP) =$ 825 Hz] and a doublet of doublets due to **B** [$^{1}J(PtP) = 812$, 899 Hz], exactly as could be predicted from the ^{31}P NMR data described above.

In the ^{1}H NMR spectrum, the methylplatinum and CH_2P_2 resonances were clearly resolved for each isomer **A** and **B**, but the resonances due to the $Pt(CH_2)_4$ ring were broad and not resolved. For each isomer the $CH^xH^yP_2$ resonances occurred as AB multiplets showing that there is no plane of symmetry containing the PtP_2C atoms of the platinum–dppm unit.

The ^{13}C NMR spectrum was more useful for structure determination. The methylplatinum resonance for **A** occurred as a singlet at $\delta = 9.13$ with $^{1}J(PtC) = 682$ Hz; the *cis* coupling $^{2}J(PC)$ was not resolved. In contrast the MePt resonance for **B** occurred as a doublet of doublets at $\delta = 2.58$ with the *trans* coupling $^{2}J(P^bC^a) = 117$

Hz and *cis* coupling $^2J(P^aC^a) = 3$ Hz and with $^1J(PtC) = 584$ Hz. The assignment as CH_3Pt groups was confirmed by recording the DEPT ^{13}C NMR spectrum, which also confirmed that all resonances in the region 25–45 ppm were due to CH_2 groups. The CH_2P_2 resonances occurred as triplets at $\delta = 36.8$ and 39.0 due to isomers **A** and **B** respectively, each with $^1J(PC) = 24$–25 Hz. Three CH_2Pt resonances could be identified by the large couplings $^1J(PtC)$, and appeared as an intense singlet, an intense doublet and a less intense doublet. The intense singlet at $\delta = 40.16$, $^1J(PtC) = 668$ Hz was assigned to C^b of isomer **B** because there is no resolved coupling to ^{31}P, and C^b is the only CH_2Pt group with no *trans* phosphine and hence the only CH_2Pt group for which no large coupling $^2J(PPtC)$ is expected. The more intense doublet at $\delta = 32.65$ ppm, $^2J(PC) = 107$, $^1J(PtC) = 541$ Hz is then assigned as C^e of isomer **B**, with a large *trans* coupling to P^a. This then requires that the less intense (and partly obscured) doublet of doublet resonance at $\delta = 31.30$, $^2J(PC\ \textit{trans}) = 115$, $^2J(PC\ \textit{cis}) = 12$, $^1J(PtC) = 549$ Hz is due to the equivalent CH_2Pt groups of isomer **A**. The β-CH_2 groups of the metallacycle occurred in the narrow range $\delta = 34.9$–35.6 ppm and tentative assignments based on intensity are given in the experimental section.

The above data leave no doubt about the structures of **A** and **B**, but leave two puzzles. Why is **B** more stable than **A** and why do the CH_2 groups of the metallacycle exert a stronger *trans* influence than the methyl group? It has not been possible to grow crystals of **A** and **B** for X-ray structure determination and so molecular mechanics calculations have been carried out to predict if differences in steric hindrance in the isomers might be responsible for the isomer ratio observed. The minimized structures are shown in Fig. 3, and the following structural features are predicted. In each isomer the PtP_2C atoms of the platinum-dppm unit adopt an envelope conformation with the CH_2 flap directed towards the iodide ligand. This leads to the phenyl substituents on the iodide side of the molecule being pseudo-equatorial and those on the opposite side being pseudo-axial. The iodide is the bulkiest ligand and so this conformation minimizes repulsions between the phenyl

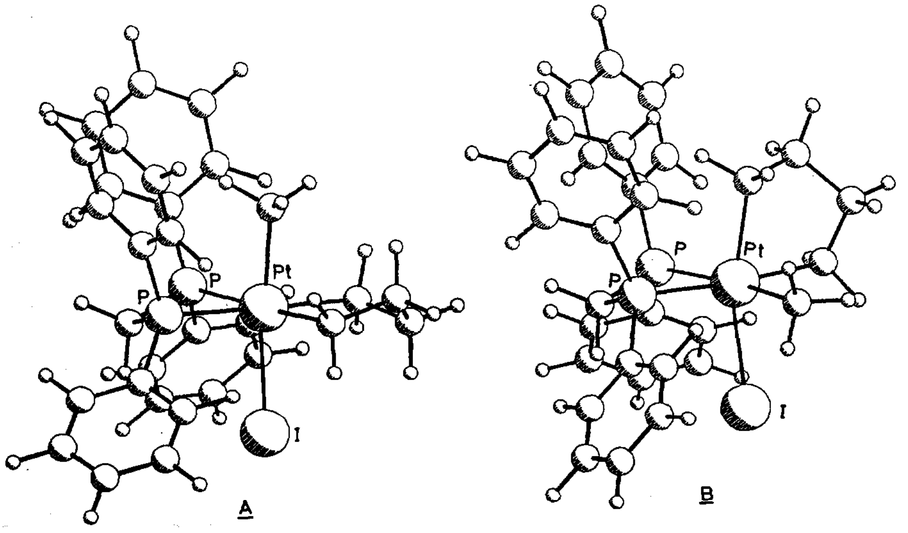


Fig. 3. The predicted structures of isomers **A** and **B** based on molecular mechanics calculations.

groups and the axial ligands. Each isomer is predicted to have a puckered PtC$_4$ ring, very similar to that established crystallographically for [PtI$_2${(CH$_2$)$_4$}(PMe$_2$Ph)$_2$] [5]. Structure **B** is calculated to be more stable than **A**, but by only 0.2 kcal mol^{-1}, which is at the limits of accuracy of the program and so may not be significant. The main difference was in the calculated van der Waals interactions and so suggests that **B** is very slightly less sterically hindered than **A**. Statistical factors favour **B** over **A** in a 2 : 1 ratio and so, if **B** is more stable than **A** by 0.2 kcal mol^{-1}, an equilibrium constant [**B**]/[**A**] ~ 2.8 can be predicted, in good agreement with the observed value of ~ 3. No significant bond angle differences are predicted by the molecular mechanics calculations and so the higher *trans* influence of the CH$_2$ groups of the metallacycle compared to the CH$_3$ group is probably due to electronic effects only, with no significant contribution from geometrical distortions.

Experimental

^{1}H NMR spectra were recorded on a Varian XL-200 NMR spectrometer. ^{31}P, ^{195}Pt and ^{13}C NMR spectra were recorded on a Varian XL-300 NMR spectrometer. References were TMS(^{1}H), H$_3$PO$_4$(^{31}P), aqueous K$_2$[PtCl$_4$](^{195}Pt), and TMS(^{13}C). All the chemical shifts and coupling constants are in ppm and Hz, respectively. [Pt(CH$_2$)$_4$(dppm)] was prepared by the published method [9] and was used without further purification. [PtIMe$_3$(dppm)] was prepared by the reported method [12]. Microanalysis was carried out by Alfred Bernhardt Laboratories. Molecular mechanics calculations were carried out using the programme PCMODEL, distributed by Serena Software Ltd.

[PtIMe(CH$_2$)$_4$(dppm)]

[Pt(CH$_2$)$_4$(dppm)] (870 mg, 1.37 mmol) was dissolved in CH$_3$I (3 mL). The solution was allowed to stand for 48 h followed by evaporation of the solvent to give an off-white powder. Crystallization from CH$_2$Cl$_2$/hexane resulted in a white powder. Yield 85%, m.p. 173–175 °C (decomposed). Anal. Found: C, 46.11; H, 4.15; I, 15.99. C$_{30}$H$_{33}$IP$_2$Pt calc.: C, 46.33; H, 4.25; I, 16.34%. NMR data: ^{31}P, isomer **A**: $\delta = -55.40$ [s, ^{1}J(PPt) = 824, P]; isomer **B**: $\delta = -65.93$ [d, ^{1}J(P^{a}Pt) = 812, ^{2}J(P^{a}P^{b}) = 32.5, P^{a}], −60.76 [d, ^{1}J(P^{b}Pt) = 899, ^{2}J(P^{b}P^{a}) = 32.5, P^{b}]; ^{195}Pt, isomer **A**: $\delta = -2779$ [t, ^{1}J(PtP) = 825, Pt]; isomer **B**: $\delta = -2718$ [dd, ^{1}J(P^{a}Pt) = 812, ^{1}J(P^{b}Pt) = 899, Pt]; ^{13}C, isomer **A**: $\delta = 9.13$ [s, ^{1}J(C^{a}Pt) = 682, C^{a} *trans* to I], 31.30 [dd, ^{1}J(C^{b}Pt) = 549, ^{2}J(C^{b}P$^{a\prime}$) = 115, ^{2}J(C^{b}P^{a}) = 12, C^{b}], 35.40 [s, C^{c}], 36.77 [t, ^{1}J(CP) = 24, C^{x} of dppm ligand]; isomer **B**: $\delta = 2.58$ [dd, ^{1}J(C^{a}Pt) = 584, ^{2}J(C^{a}P^{b}) = 117, ^{2}J(C^{a}P^{a}) = 3, C^{a}], 40.16 [s, ^{1}J(C^{b}Pt) = 668, C^{b}], 32.65 [d, ^{1}J(C^{e}Pt) = 541, ^{2}J(C^{e}P^{a}) = 107, C^{e}], 35.60 [s, C^{c}], 35.52 [s, C^{d}], 39.0 [t, ^{1}J(C^{x}P) = 25, C^{x}); ^{1}H, isomer **A**: $\delta = 0.77$ [t, ^{2}J(H^{a}Pt) = 68, ^{3}J(H^{a}P) = 8, H^{a}), 0.55–4 [broad, ring protons], 5.85 [m, ^{2}J(H^{x}H^{y}) = 15, ^{2}J(H^{x}P) = 8, ^{3}J(H^{x}Pt) = 14.5, 1 H^{x}], 4.59 [m, ^{2}J(H^{y}P^{a}) = 11, 1 H^{y}]; isomer **B**: $\delta = 1.66$ [dd, ^{2}J(H^{a}Pt) = 65, ^{3}J(H^{a}P^{a}P^{b}) = 8, 3 H^{a}], 0.55–4 [broad, ring protons], 5.62 [m, ^{2}J(H^{x}H^{y}) = 15, ^{2}J(H^{x}P^{a}P^{b}) = 8, ^{3}J(H^{x}Pt) = 14.5, 1 H^{x}], 4.57 [m, ^{2}J(H^{y}H^{x}) = 15, ^{2}J(H^{y}P^{a}) = 11, ^{2}J(H^{y}P^{b}) = 11, 1 H^{y}].

For comparison unpublished NMR data for (PtIMe$_3$(dppm)] and [PtMe$_4$(dppm)] are given.

[PtIMe$_3$(dppm)]. ^{13}C, $\delta = 1.25$ [dd, ^{2}J(C^{a}P^{a}) = 8.6, ^{2}J(C^{a}P$^{a\prime}$) = 127.2, ^{1}J(C^{a}Pt) = 530, 2 C^{a} *trans* to P], 10.49 (s, ^{1}J(C^{b}Pt) = 622, 1 C^{b} *trans* to I], 37.27 [t,

${}^{1}J(C^{x}P) = 25.4$, 1 $C^{x}P_2$]; ${}^{31}P$, $\delta = -63.7$ [s, ${}^{1}J(PtP) = 897$]; ${}^{195}Pt$, $\delta = -2323$ [t, ${}^{1}J(PtP) = 897$].

[PtMe₄(dppm)]. ${}^{13}C$, $\delta = -6.11$ [t, ${}^{2}J(C^{b}P) = 4.3$, ${}^{1}J(C^{b}Pt) = 401.3$, 2 C^{b} *trans* to C], 1.52 [dd, ${}^{2}J(C^{a}P^{a}) = 6.7$, ${}^{2}J(C^{a}P^{a\prime}) = 133$, ${}^{1}J(CPt) = 567.4$, 2 C^{a} *trans* to P], 39.98 [t, ${}^{1}J(C^{x}P) = 24.0$, 1 C^{x}]; ${}^{31}P$, -65.9 [s, ${}^{1}J(PtP) = 936$]; ${}^{195}Pt$, $\delta = -2643$ [t, ${}^{1}J(PtP) = 936$].

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