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Carbon–carbon bond formation upon ligand displacement from bis(chloromethyl)(1,5-cyclooctadiene)platinum(II) with tricyclohexylphosphine. X-ray structure of *trans*-di-μ-chlorobis(2-tricyclohexylphosphonioethyl)-bis(tricyclohexylphosphine)diplatinum(II) bis(hexafluorophosphate)

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Abstract

Treatment of bis(chloromethyl)(1,5-cyclooctadiene)platinum(II) (**3**) with tricyclohexylphosphine gave a product (**4**) which underwent anion exchange with ammonium hexafluorophosphate to give di-μ-chlorobis(2-tricyclohexylphosphonioethyl)bis(tricyclohexylphosphine)diplatinum(II) bis(hexafluorophosphate) (**5**) the structure of which was established by X-ray crystallography. ^{31}P NMR indicates that the dication of **5** exists as a *cis–trans* mixture in solution and that in chloroform **4** has the structure *cis*-dichloro(2-tricyclohexylphosphonioethyl)(tricyclohexylphosphine)platinum(II). In more polar media the latter is in equilibrium with the same *cis–trans* dicationic pair. Crystals of **5** are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions *a* 14.917(2), *b* 14.950(3), *c* 10.476(2) Å, α 96.20(2), β 106.43(2), γ 103.45(1)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations; *R* is 0.033 for 3825 observed reflections. In the solid state **5** exists as a centrosymmetric chlorine-bridged dimer, with square-planar platinum and Pt–P 2.229(2), Pt–Cl 2.402(2) (*trans* to P), 2.450(2) (*trans* to CH_2), Pt–CH_2 2.052(8) Å.

Introduction

We have shown [1,2] that the reaction of diazomethane with certain complexes of platinum(II) and palladium(II) halides gives halomethyl derivatives via methylene

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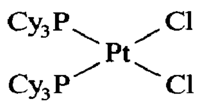
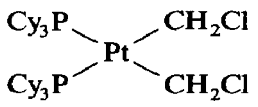
insertion. In the course of this work it was observed [3] that *cis*-dichlorobis(tricyclohexylphosphine)platinum(II) (**1**) (Cy = cyclohexyl) could be recovered quantitatively from treatment with diazomethane, although it promoted rapid conversion of the latter into ethylene. A possible mechanism for this transformation could involve [3] the intermediacy of cis-bis(chloromethyl)bis(tricyclohexylphosphine)platinum(II) (**2**). We therefore attempted to generate **2** by reaction of bis(chloromethyl)(1,5-cyclooctadiene)platinum(II) (**3**) with two molar equivalents of tricyclohexylphosphine.



(**1**)



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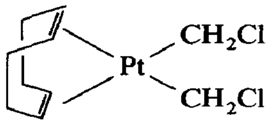

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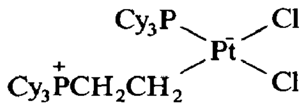
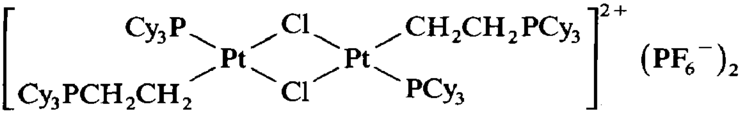


(**4**)



(**5**)

Results and discussion

Reaction of complex **3** and the phosphine in deuteriochloroform under nitrogen was monitored by ^{31}P NMR spectroscopy which showed rapid formation of essentially a single product **4** with δ 26.8 (^3J(P–Pt) 402 Hz) and 18.5 (^1J(P–Pt) 4530 Hz). The latter coupling could be ascribed to a phosphine ligand *trans* to chlorine but the former coupling was not consistent with either a PPt or a PCH_2Pt [4] moiety. Upon opening to air, well-formed crystals were obtained from the reaction solution, but these turned opaque upon washing and were unsuitable for X-ray work. The resulting material redissolved, with some difficulty, in deuteriochloroform to give the same ^{31}P NMR spectrum as indicated above. Dissolution took place much more readily when small quantities of methanol were added. However, a new set of signals, assignable to a major and a minor species (see experimental), appeared. When progressively larger proportions of methanol were added the new signals increased in intensity at the expense of the original ones. Since it was suspected that ionization of chloride might be occurring in the more polar medium, a solution of the compound in methanol was treated with aqueous ammonium hexafluorophosphate to give a crystalline product **5** which proved suitable for X-ray analysis (see below). This revealed that **5** is a chloride-bridged dicationic dimer containing a novel platinum-bonded phosphonioethyl moiety [5*]. A ^{31}P NMR spectrum of this material showed resonances at positions virtually identical with those observed for the two species that built up upon addition of methanol to chloroform solutions of **4**. Presumably, the dication exists as a *cis–trans* mixture in solution. One may then conclude that **4** is monomeric in chloroform but is in equilibrium with the dimeric species in more polar media. Since **4** undergoes no observable decomposition on

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* Reference number with asterisk indicates a note in the list of references.

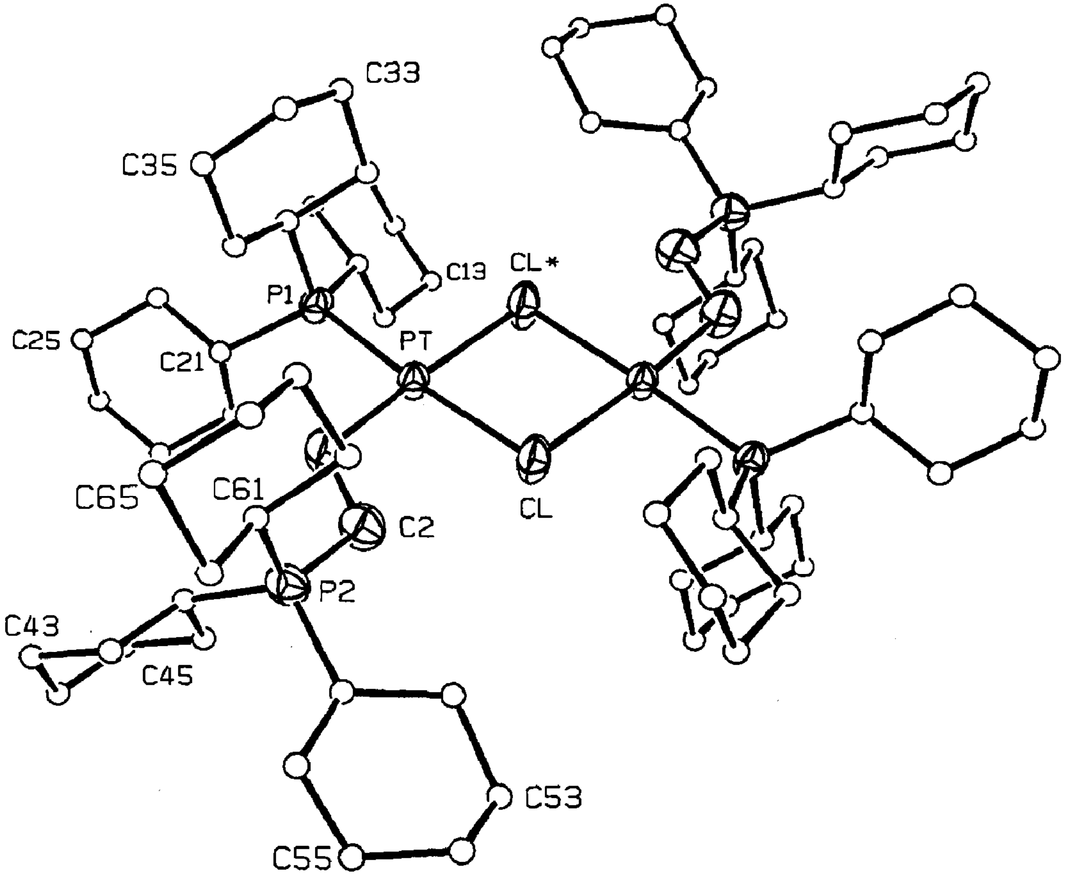
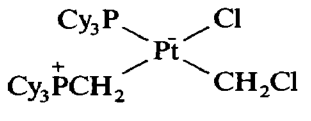


Fig. 1. A view of the di-μ-chlorobis(2-tricyclohexylphosphonioethyl)bis(tricyclohexylphosphine)diplatinum(II) cation. For clarity, cyclohexyl carbon atoms are indicated as spheres of an arbitrary size and only one of the possible orientations of the disordered cyclohexyl rings is shown.

standing in chloroform solution over several days it cannot be a key intermediate in the formation of ethylene from diazomethane in the presence of **1**. Several pathways incorporating a C–C bond forming step may be envisaged for the formation of **4** from **3**. Further studies are being directed towards distinguishing among these possibilities. However, the ^{31}P NMR spectrum of a freshly prepared benzene-d_6 solution of **3** and tricyclohexylphosphine (ca. 1/1 mole ratio) showed i.a. a resonance at δ 19.39 (^1J(P–Pt) 1904 Hz), ascribable to **2**, along with resonances arising from **4**. The former resonance disappeared on standing while the latter resonances built up. Taking into account the reported [4] formation of ylids in related reactions, we suggest that **4** may be formed by a route of the type outlined in eq. 1.



$$\mathbf{3} \longrightarrow \mathbf{2} \longrightarrow \begin{array}{c} Cy_3P \quad\quad Cl \\ \overset{-}{Pt} \\ Cy_3\overset{+}{P}CH_2 \quad\quad CH_2Cl \end{array} \longrightarrow \mathbf{4} \qquad (1)$$

The X-ray structure analysis of **5** shows that the crystals contain centrosymmetric chlorine-bridged cation dimers (Fig. 1) [6] and PF_6^- anions. The Pt coordination is planar and approximately square, and each Pt atom bears a $Cy_3P^+CH_2CH_2$ group. The conformation of the $PtCH_2CH_2P$ moiety is *anti* (torsion angle 165.5(4)°). The

Table 1

Principal dimensions

Bond lengths (Å)		Bond angles (°)	
Pt-Cl1	2.402(2)	Cl1-Pt-Cl1*	79.49(7)
Pt-Cl1*	2.450(2)	Cl1-Pt-P1	174.10(6)
Pt-P1	2.229(2)	Cl1-Pt-C1	94.7(3)
Pt-C1	2.052(8)	Cl1*-Pt-P1	94.76(7)
P1-C11	1.857(6)	Cl1*-Pt-C1	173.1(3)
P1-C21	1.866(9)	P1-Pt-C1	91.2(3)
P1-C31	1.847(9)	Pt-Cl1-Pt*	100.51(7)
P2-C2	1.818(8)	Pt-P1-C11	107.8(3)
P2-C41	1.821(10)	Pt-P1-C21	116.3(3)
P2-C51	1.841(11)	Pt-P1-C31	113.0(3)
P2-C61	1.817(12)	C11-P1-C21	110.0(4)
C1-C2	1.506(12)	C11-P1-C31	104.3(3)
		C21-P1-C31	104.8(4)
		C2-P2-C41	109.0(4)
		C2-P2-C51	106.7(5)
		C2-P2-C61	109.6(4)
		C41-P2-C51	110.7(4)
		C41-P2-C61	108.9(5)
		C51-P2-C61	112.0(5)
		Pt-C1-C2	114.9(7)
		P2-C2-C1	117.3(7)

[a] The * refers to equivalent position: $-x, -y, -z$.

Pt_2Cl_2 ring is planar (by space group symmetry) and the Pt–Cl bond lengths (Table 1) differ as expected, with Pt–Cl *trans* to P (2.402(2) Å) significantly shorter than that *trans* to CH_2 (2.450(2) Å). The cyclohexane rings all adopt chair conformations (but two of them are severely disordered in the crystal lattice). There are no untoward inter-ion contacts.

Experimental

Hydrogen-1 and phosphorus-31 NMR spectra were obtained on a Bruker WH-400 spectrometer for solutions in deuteriochloroform using internal tetramethylsilane and external 85% H_3PO_4, respectively, as reference standards.

Reaction of bis(chloromethyl)(1,5-cyclooctadiene)platinum(II) (3) with tricyclohexylphosphine

Complex **3** (35 mg) and tricyclohexylphosphine (24.5 mg) were placed in an NMR tube and dissolved in deuteriochloroform under nitrogen. A ^{31}P NMR spectrum was run immediately and showed the presence of largely a single product **4** with δ 26.8 (^3J(P–Pt) 402 Hz) and 18.5 (^1J(P–Pt) 4530 Hz). After standing in the dark for 4 days the solution gave an identical spectrum. The tube was then opened and the solution transferred to another container, whereupon colorless rods crystallized out quite rapidly. The opaque material obtained by washing these crystals with dichloromethane/hexane (1/1) was much more soluble in methanol than in chloroform. A ^{31}P NMR spectrum of this material in deuteriochloroform showed only the resonances for **4** (reported above). When progressively larger proportions of methanol were added to this solution new signals appeared for a major (δ 27.4 (^3J(P–Pt) 386 Hz) and 21.9 (^1J(P–Pt) 4635 Hz)) and a minor species (δ 27.4 and 23.1). The ^{1}H NMR spectrum of **4** is complex, but three downfield multiplets are resolved, δ 2.82(PCH_2CH$_2$Pt), 2.37(PtPCH) and 2.18(CH$_2$PCH); a ^{1}H-COSY experiment located the PCH$_2$CH_2Pt resonance at δ 1.36 within a set of overlapping multiplets.

Preparation of di-μ-chlorobis(2-tricyclohexylphosphonioethyl)bis(tricyclohexylphosphine)diplatinum(II) bis(hexafluorophosphate (5)

A concentrated aqueous solution of ammonium hexafluorophosphate (12 mg) was added to complex **4** (45 mg) in methanol. Upon evaporation of most of the methanol, colorless crystals of **5** started to form and one was chosen for X-ray structure analysis. These crystals had m.p. 202–208 ° C (softening and gas evolution from 188 ° C); ^{31}P NMR (CDCl$_3$): major isomer, δ 27.9 (^3J(P–Pt) 350 Hz) and 21.8 (^1J(P–Pt) 4655 Hz); minor isomer, δ 28.0 (^3J(P–Pt) 350 Hz) and 23.1 (^1J(P–Pt) 4650 Hz).

Crystal structure analysis

Crystal data and details of the refinement for **5** are collected in Table 2. Accurate cell parameters were determined by least-squares calculations based on the angular settings for 25 automatically centred reflections using an Enraf–Nonius CAD4 diffractometer. Data were corrected for Lorentz, polarisation and absorption effects. The coordinates of the Pt and Cl atoms were obtained from analysis of the three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. One of the PF$_6$ groups lies on

Table 2

Crystal and refinement data for **5**

Formula	$[C_{74}H_{136}Cl_2Pt_2]^{2+}\cdot 2(PF_6^-)$
F.W.	1900.8
Crystal class	triclinic
Space Group	$P\bar{1}$
Crystal dimensions (mm)	0.08 × 0.20 × 0.33
a (Å)	14.917(2)
b (Å)	14.950(3)
c (Å)	10.476(2)
α (°)	96.20(2)
β (°)	106.43(2)
γ (°)	103.45(1)
V (Å^3)	2141(2)
D_c (g cm^{-3})	1.47
Z	1
F(000)	968
μ (cm^{-1})	35.3
Total number of independent reflections	4586
Number of reflections with $I > 3\sigma(I)$	3825
$2\theta_{max}$ (°)	42
Final R	0.033
Final wR	0.045

an inversion centre and the other has the phosphorus in a general position, but disordered over two adjacent sites with the fluorine atoms totally disordered about them. Two of the six cyclohexyl rings (rings 5 and 6) in the asymmetric unit are disordered (over at least two sites) essentially by rotation about the appropriate C1...C4 axis. Refinement [7] was by full-matrix least-squares calculations, initially with isotropic, then with anisotropic vibration parameters (for the atoms which were not disordered). Difference maps were computed at intermediate stages in the refinement and revealed maxima in positions expected for the hydrogen atoms of the non-disordered carbon atoms; these were then allowed for in geometrically idealised positions and included in the final rounds of calculations but not refined. The possibility that the space group was the non-centrosymmetric *P*1 system was considered but was rejected for the reasons outlined by Marsh [8]. Scattering factors used in the structure-factor calculations and the anomalous dispersion correction data were taken from the literature [9]. Final difference maps had many small peaks (< 1 e$Å^{-3}$) in the volume around the disordered P atoms (in the volume where the disordered fluorine atoms could be expected) but no clear sets of octahedra could be discerned. A table of fractional coordinates, the structure factor listings, calculated hydrogen coordinates, lists of molecular dimensions and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre and are also available from one of the authors (G.F.) on request.

Acknowledgement

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