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Preliminary communication

A CATIONIC YLIDE COMPLEX OF PLATINUM(II): ITS STRUCTURE AND FORMATION FROM A CHLOROMETHYL-PLATINUM COMPLEX

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Summary

The reactions of *cis*- or *trans*-[$Pt(PPh_3)_2(CH_2Cl)I$] with triphenylphosphine give the ylide complex *cis*-[$Pt(PPh_3)_2(CH_2PPh_3)Cl$]I. The reactions involve a novel migration of Cl from a CH_2 group to Pt. The structure of the cationic ylide complex has been determined by X-ray crystallography.

As a possible route to halomethyl complexes of platinum, we have investigated reactions of some dihalomethanes with zerovalent platinum complexes. The reaction of chloroiodomethane with $Pt(PPh_3)_4$ gave, however, an unexpected product in high yield which we formulated [1] as the cationic ylide complex I.

$$Pt(PPh_3)_4 + CH_2ClI \rightarrow \underset{(I)}{cis[Pt(PPh_3)_2(CH_2PPh_3)Cl]I} \quad (1)$$

Possible mechanisms for the formation of I could involve either the phosphonium salt [Ph_3PCH_2Cl]I or the chloromethyl complex $Pt(PPh_3)_2(CH_2Cl)I$ (II). If II was initially formed, reaction with PPh_3 requires an unusual migration of Cl from CH_2 to Pt in order to give the observed product I. Since we were unable to demonstrate that the phosphonium salt was an intermediate in the reaction, we investigated possible routes to II [2].

We find that $Pt(PPh_3)_2(C_2H_4)$ reacts with CH_2ClI in benzene to give white parallelograms m.p. 220—222°C, which we formulate as *cis*-[$Pt(PPh_3)_2(CH_2Cl)I$] (IIa). Independent of our studies, several halomethyl complexes of platinum(II) have recently been reported. Thus Scherer and Jungmann prepared $Pt(PPh_3)_2(CH_2Cl)Cl$ [3], while Lappert et al. [4] reported the synthesis of

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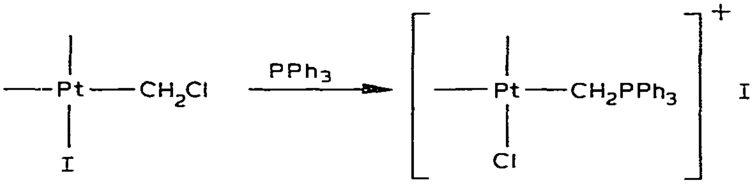
several halomethyl complexes formed by the reaction of $Pt(PPh_3)_2(C_2H_4)$ with dihaloalkanes. The latter workers [4], however report a complicated mixture of products including halogen-scrambled species from the reaction of $Pt(PPh_3)_2(C_2H_4)$ with CH_2ClI.

Using a short reaction time, we find that IIa* is produced in this reaction without the formation of halogen-scrambled products. IIa shows: ν(Pt—I) 190 cm^{-1} (no ν(Pt—Cl) could be detected); ^1H NMR ($CDCl_3$) δ 3.96 ppm, doublet (CH_2) ^3J(PH) 9, ^2J(PtH) 49.1 Hz. A triplet is also observed due to isomerisation of IIa to *trans*-$[Pt(PPh_3)_2(CH_2Cl)I]$ (IIb). ^{31}P NMR ($CDCl_3$) of IIa relative to 85% H_3PO_4 shows two doublets δ 17.57, 14.07 ppm, ^1J(PtP) 4255, 1748 Hz, ^2J(PtPP) 17 Hz. A singlet is observed in the ^{31}P NMR spectrum due to IIb and a minor singlet is seen at δ 6.22 ppm, ^1J(PtP) 3704 Hz due to an unknown species. The isomerisation of IIa to IIb takes place over several hours and was followed by ^1H and ^{31}P NMR. IIb is obtained as lemon yellow needles m.p. 226—228°C on recrystallisation of IIa from CH_2Cl_2/diethyl ether. IIb shows ν(Pt—I) at 189 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.06 ppm, triplet (CH_2) ^3J(PH) 9.2, ^2J(PtH) 49.5 Hz; ^{31}P NMR δ 23.62 ppm, singlet, ^1J(PtP) 3091 Hz.

To test if II is a reasonable intermediate in the formation of I, we have investigated the reactions of IIa and IIb with PPh_3 in both benzene and tetrahydrofuran. The product of these reactions is found to be I (eq. 2).

$$\underset{\text{(IIa or IIb)}}{Pt(PPh_3)_2(CH_2Cl)I} + PPh_3 \rightarrow \underset{\text{(I)}}{cis\text{-}[Pt(PPh_3)_2(CH_2PPh_3)Cl]I} \qquad (2)$$

We have previously reported the reactions of some MCH_2Cl complexes with PPh_3 to yield $[MCH_2PPh_3]^+ Cl^-$ species [5] and others have also shown that some halomethyl complexes react with tertiary phosphines to give ylide complexes [4,6,7]. The novelty of the reaction in eq. 2 is the specific formation of I in over 70% yield which involves the migration of Cl from carbon to platinum with loss of I^- from the coordination sphere of the metal (eq. 3).



(3)

The formation of an isomer of I or any other compound with a Pt—I bond is not observed.

To confirm the presence of the ylide ligand and the stereochemistry of complex I, we have determined its structure by X-ray crystallography.

Crystal data: $C_{55}H_{47}ClIP_3Pt \cdot CH_2Cl_2$ monoclinic, space group $P2_1/n$, a 13.886(7), b 20.267(10), c 18.239(9) Å, β 96.51(2)°; the number of observed reflections was 3542 (using Mo-K_α radiation); R 7.1%. We have also determined the structure of the complex *cis*-$[Pt(PPh_3)_2(CH_2PPh_3)I]I$, which is found to be isomorphous with I.

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*Satisfactory microanalyses have been obtained for all new compounds.

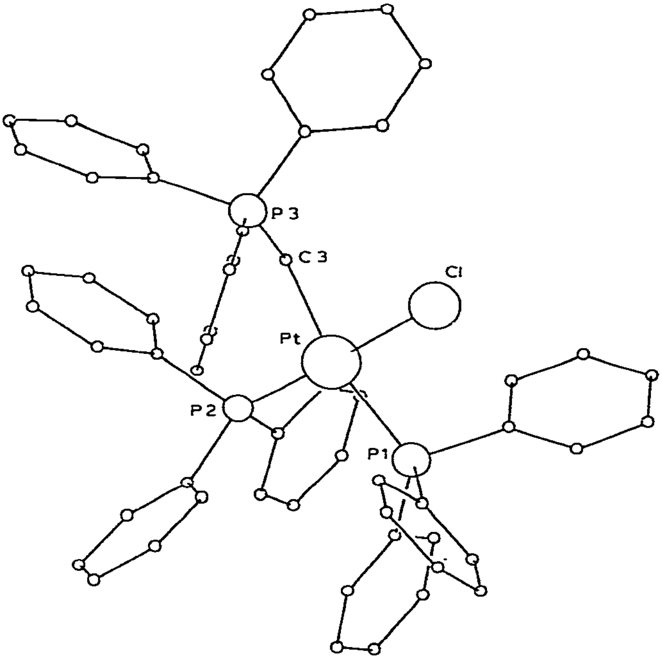

Fig. 1. The molecular structure of *cis*-[Pt$(PPh_3)_2(CH_2PPh_3)$Cl] I. Bond lengths: Pt—C(3), 2.12(2); P(3)—C(3), 1.80(2); Pt—Cl, 2.40(0); Pt—P(1), 2.33(1); Pt—P(2), 2.35(1) Å. Bond angles: Cl—Pt—C(3), 86.9(5); C(3)—Pt—P(2), 91.8(5), P(3)—C(3)—Pt, 121.8(10); P(2)—Pt—P(1), 97.0(2); P(1)—Pt—Cl, 85.1(2)°

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