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Asymmetrical Cleavage of Halide-Bridged Platinum Dimers

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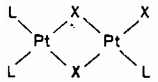
The reaction between PMe_2Ph and $[Pt_2Cl_4(PMe_2Ph)_2]$ at –60 °C appears to proceed mainly by consecutive attack of two phosphine molecules at the same platinum atom of the dimer to produce $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2PH)]^-$.

Results and Discussion

Bridge cleavage reactions of dimeric platinum compounds by ligands, L′, are oft-used reactions of considerable synthetic value (eqn. 1).



$$+ \ 2L' \longrightarrow 2\ [PtX_2LL'] \qquad (1)$$

The rate law for the nucleophilic attack [1] resembles that for ligand replacement reactions of monomeric platinum compounds, and the geometry of the products generally depends on the relative *trans* effects of the terminal ligands L and X [2]. Many cases are known, however, where the products are not those expected from the simple application of (1). For example, subsequent isomerisation [2] or disproportionation [3] of the products can occur, particularly if excess free ligand is present in solution. We report here the discovery of unexpected products from the reactions of PMe_2Ph and $[Pt_2Cl_4(PMe_2Ph)_2]$, which appear to result from the operation of a novel reaction pathway.

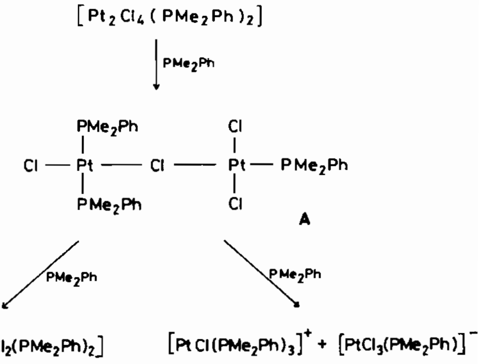
When one molar equivalent of liquid PMe_2Ph was added to solutions of $[Pt_2Cl_4(PMe_2Ph)_2]$ in $CDCl_3$ at room temperature the products (from ^{31}P NMR examination) were a 1:1 mixture of *cis*- and *trans*-$[PtCl_2(PMe_2Ph)_2]$, as well as unreacted dimer (50%). It seemed unlikely that the expected *trans* compound would isomerise under these conditions, since the presence of unreacted dimer ensured that no free phosphine catalyst would be present [4]. When the reaction was repeated and examined at –60 °C, 85% of the products were the ions $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2Ph)]^-$, with the remaining 15% consisting of *cis*- and *trans*-$[PtCl_2(PMe_2Ph)_2]$. The product mixture remained unchanged at –60 °C for several hours, but at room temperature the ionic complexes disappeared, being replaced by more $[PtCl_2(PMe_2Ph)_2]$ (eqn. 2). The cation $[PtCl(PMe_2Ph)_3]^+$ is known to form *cis*-$[PtCl_2(PMe_2Ph)_2]$ exclusively by Cl^- attack [5], and nucleophilic attack of PMe_2Ph on the anion would expected to yield *trans*-$[PtCl_2(PMe_2Ph)_2]$ from *trans* effect considerations.

$$[Pt_2Cl_4(PMe_2Ph)_2] \xrightarrow[-60\ ^\circ C]{2PMe_2Ph} [PtCl(PMe_2Ph)_3]^+ + [PtCl_3(PMe_2Ph)]^- \xrightarrow{20\ ^\circ C} cis\text{-}[PtCl_2(PMe_2Ph)_2] + trans\text{-}PtCl_2(PMe_2Ph)_2] \qquad (2)$$

The cation could have been formed by the action of a local excess of PMe_2Ph on primary reaction products $[PtCl_2(PMe_2Ph)_2]$ [5] before mixing was complete (3), and the halide released would subsequently react with more dimer (4) [6]. The product ratio of the low temperature reactions was unaltered, however, when solutions of the phosphine were added to the dimer, or when the two solutions were rapidly mixed using a tangentially arranged two-jet glass mixing apparatus

$$[PtCl_2(PMe_2Ph)_2] + PMe_2Ph \rightarrow [PtCl(PMe_2Ph)_3]Cl \qquad (3)$$

$$[Pt_2Cl_4(PMe_2Ph)_2] + 2Cl^- \rightarrow 2[PtCl_3(PMe_2Ph)]^- \qquad (4)$$



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and capillary leading directly to the NMR tube (the whole assembly being maintained at –60 °C). We propose, therefore, that the ionic species are produced as a result of a second phosphine molecule attacking the same platinum atom of the dimer as the first one, at the stage of singly bridged intermediate A. This reaction leads directly to cation and anion, and can operate alongside or instead of the well-authenticated symmetrical attack (Scheme). Singly bridged intermediates, A, are known to have appreciably lifetimes [1, 7]. If solvent participated in the cleavages (the usual two-term rate laws apply [1]), there is no reason why these pathways, too, should not result in ionic products.

It should be noted that from the similar reactions between PBu_3 and $[Pt_2Cl_4(PBu_3)_2]$ we failed to detect any ionic products under any conditions. It therefore seems that the nature of the ligands involved exerts a marked effect on the course of these reactions.

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