Some Platinum-substituted Silyl and Germyl Halides

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Summary Compounds of the formula *trans*-$XPt(Et_3P)_2MH_2Y$ have been prepared (M = Si or Ge; X, Y = Cl, Br or I); treatment of *trans*-$ClPt(Et_3P)_2SiH_2Cl$ with GeH_3Cl gives SiH_3Cl and *trans*-$ClPt(Et_3P)_2GeH_2Cl$.

PLATINUM HYDRIDES react with silanes or germanes to eliminate hydrogen and give platinum–silyl or –germyl compounds:[1,2]

$$R_3MH + H\underset{|}{\overset{|}{Pt}}- \rightarrow H_2 + R_3M\underset{|}{\overset{|}{Pt}}-$$

We find that substituted silanes and germanes of general formula MH_3X (M = Si or Ge; X = Cl, Br, or I) react with *trans*-$XPt(Et_3P)_2H$ to give platinum–silyl or –germyl compounds with halogen bound to silicon or germanium:

$$trans\text{-}X\text{–}Pt(Et_3P)_2H + H_3MX \xrightarrow[\text{r.t.}]{C_6H_6} trans\text{-}X\text{–}Pt\,(Et_3P)_2MH_2X + H_2$$

The products are white or pale yellow crystalline compounds which are readily hydrolysed; the germanium derivatives are less thermally stable than their silicon analogues. They have been characterized spectroscopically and by analysis. We have also prepared *trans*-$X\text{–}Pt(Et_3P)_2MH_3$ by similar methods.

If MH_3X is treated with *trans*-$Y\text{–}Pt(Et_3P)_2H$ (X = Cl, Br, or I; Y = Cl, Br, or I; X ≠ Y), halogen exchange leads to the formation of the product in which the heavier halogen is bound to platinum; thus the same product, identified spectroscopically as *trans*-$IPt(Et_3P)_2SiH_2Cl$, is formed from SiH_3Cl and *trans*-$I\text{–}Pt(Et_3P)_2H$ or from SiH_3I and *trans*-$Cl\text{–}Pt(Et_3P)_2H$. A similar exchange occurs between SiH_3Br and *trans*-$(Et_3P)_2PtCl_2$, giving SiH_3Cl and *trans*-$(Et_3P)_2PtBr_2$, while a slow side-reaction gives SiH_2Cl_2 and *trans*-$BrPt(Et_3P)_2SiH_2Cl$.

The compound *trans*-$ClPt(Et_3P)_2SiH_2Cl$ reacts with GeH_3Cl in benzene at room temperature to give a number of products; among these, *trans*-$ClPt(Et_3P)_2GeH_2Cl$ is formed initially, though it decomposes slowly at room temperature. Silyl chloride is also produced. The formation of these compounds implies a formal exchange of a Pt–Si with a Ge–H bond:

$$\begin{aligned}&Q\text{–}SiH_2Cl + HGeH_2Cl \rightarrow\\ &\qquad Q\text{–}GeH_2Cl + HSiH_2Cl\ [Q = trans\text{-}ClPt(Et_3P)_2\text{–}]\end{aligned}$$

This exchange is unusual. It is superficially like other exchange reactions between silyl and germyl compounds,[3,4] *e.g.*

$$GeH_3F + SiH_3NCO \rightarrow SiH_3F + GeH_3NCO$$

In those systems, however, the GeH_3 and the SiH_3 groups are transferred intact. Treatment of a disubstituted silane with a germyl compound also leads to exchange,[5] but once more there is no change in the number of GeH and of SiH bonds:

$$SiH_2Cl_2 + GeH_3CN \rightarrow GeH_3Cl + SiH_3(CN)Cl$$

The occurrence of such a reaction in this system would lead to the formation of SiH_2Cl_2 and trans-$ClPt(Et_3P)_2GeH_3$:

$$QSiH_2Cl + GeH_3Cl \rightarrow QGeH_3 + SiH_2Cl_2$$

No *trans*-$ClPt(Et_3P)_2GeH_3$ was detected among the products of the reaction; dichlorosilane was formed slowly, presumably by a different mechanism.

The formation of *trans*-$ClPt(Et_3P)_2GeH_2Cl$ could occur *via* addition of a GeH bond of GeH_3Cl to the Pt–SiH_2Cl species, giving an octahedral platinum complex as intermediate.

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