

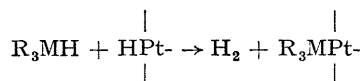
Some Platinum-substituted Silyl and Germyl Halides

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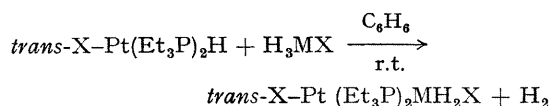
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Summary Compounds of the formula *trans*-XPt(Et₃P)₂MH₂Y have been prepared (M = Si or Ge; X, Y = Cl, Br or I); treatment of *trans*-ClPt(Et₃P)₂SiH₂Cl with GeH₃Cl gives SiH₃Cl and *trans*-ClPt(Et₃P)₂GeH₂Cl.

PLATINUM HYDRIDES react with silanes or germanes to eliminate hydrogen and give platinum-silyl or -germyl compounds:^{1,2}



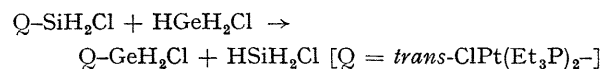
We find that substituted silanes and germanes of general formula MH₃X (M = Si or Ge; X = Cl, Br, or I) react with *trans*-XPt(Et₃P)₂H to give platinum-silyl or -germyl compounds with halogen bound to silicon or germanium:



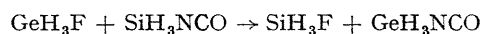
The products are white or pale yellow crystalline compounds which are readily hydrolysed; the germanium derivatives are less thermally stable than their silicon analogues. They have been characterized spectroscopically and by analysis. We have also prepared *trans*-X-Pt(Et₃P)₂MH₃ by similar methods.

If MH₃X is treated with *trans*-Y-Pt(Et₃P)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(Et₃P)₂SiH₂Cl, is formed from SiH₃Cl and *trans*-I-Pt(Et₃P)₂H or from SiH₃I and *trans*-Cl-Pt(Et₃P)₂H. A similar exchange occurs between SiH₃Br and *trans*-(Et₃P)₂PtCl₂, giving SiH₃Cl and *trans*-(Et₃P)₂PtBr₂, while a slow side-reaction gives SiH₂Cl₂ and *trans*-BrPt(Et₃P)₂SiH₂Cl.

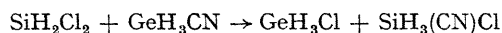
The compound *trans*-ClPt(Et₃P)₂SiH₂Cl reacts with GeH₃Cl in benzene at room temperature to give a number of products; among these, *trans*-ClPt(Et₃P)₂GeH₂Cl is formed initially, though it decomposes slowly at room temperature. Silyl chloride is also produced. The formation of these compounds implies a formal exchange of a Pt-Si with a Ge-H bond:



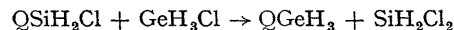
This exchange is unusual. It is superficially like other exchange reactions between silyl and germyl compounds,^{3,4} e.g.



In those systems, however, the GeH₃ and the SiH₃ 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:



The occurrence of such a reaction in this system would lead to the formation of SiH₂Cl₂ and *trans*-ClPt(Et₃P)₂GeH₃:



No *trans*-ClPt(Et₃P)₂GeH₃ was detected among the products of the reaction; dichlorosilane was formed slowly, presumably by a different mechanism.

The formation of *trans*-ClPt(Et₃P)₂GeH₂Cl could occur via addition of a GeH bond of GeH₃Cl to the Pt-SiH₂Cl species, giving an octahedral platinum complex as intermediate.

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