A General Method for the Preparation of Silyl Derivatives of Platinum(II)

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SEVERAL groups of workers have for some time unsuccessfully sought a general method of preparing compounds containing Pt–Si bonds. We recently described the preparation of a few such compounds as stable crystalline material, by treating the complex $[PtCl_2(PMe_2Ph)_2]$ with the reagent $MePh_2SiLi$.[1] We have since used the reaction to prepare the stable crystalline isosteric derivative $[Pt(SiMe_2Ph)_2(PMePh_2)_2]$, but the reaction generally gives noncrystallizable oils.

The first and less useful method originated in a study of the reaction of *trans*-$[PtCl(SiMePh_2)(PMe_2Ph)_2]$ with hydrogen, which was found to lead to equilibrium (1).

$$[PtCl(SiMePh_2)(PMe_2Ph)_2] + H_2 \rightleftarrows [PtHCl(PMe_2Ph)_2] + HSiMePh_2 \qquad (1)$$

As would be expected from this, silicon hydrides, R_3SiH, react readily with the compound $[PtHCl(PMe_2Ph)_2]$ in an open system with evolution of hydrogen, to form the complexes $[PtCl(SiR_3)(PMe_2Ph)_2]$. Several such complexes have been thus obtained as beautiful white crystals, though in some cases they are contaminated with a lower-melting impurity. Germanium hydrides undergo the analogous reaction, but triphenylstannane has so far given only intractable products.

The ease of reaction with silicon hydrides is very dependent on the lability of the hydrogen attached to the platinum; thus the wholly aliphatic chlorohydride $[PtHCl(PEt_3)_2]$ has not so far been induced to undergo the reaction, and the wholly aromatic complex $[PtHCl(PPh_3)_2]$ appears to undergo only slow chlorination when treated with trichlorosilane.[2]

The second method (Reaction 2) has the advantages of using the more readily available dichloroplatinum complexes as starting materials and yielding purer products, but again the ease of reaction depends very much on the type of phosphine attached to the platinum. Aromatic phosphine complexes react readily in boiling benzene to give good yields, but with purely aliphatic phosphine complexes boiling xylene must be used as the reaction medium (with tributylamine to remove the hydrogen chloride), and even then yields are very small or, in some cases, zero.

$$cis\text{-}[PtCl_2(PMe_2Ph_2] + R_3SiH + NEt_3 \rightarrow trans\text{-}[PtCl(SiR_3))PMe_2Ph)_2] + Et_3NHCl \qquad (2)$$

Some of the compounds obtained are listed below.

Compound ($L = PMe_2Ph$)	m.p. (°C)
$[PtCl(SiCl_3)L_2]$	125—127
$[PtCl(SiMePh_2)L_2]$	153—155
$[PtCl\{Si(C_6H_4Cl\text{-}p)_3\}L_2]$	168—170
$[PtCl\{Si(C_6H_4{\cdot}CH_3\text{-}p)_3\}L_2]$	176—179
$[PtCl\{Si(C_6H_4{\cdot}CF_3\text{-}m)_3\}L_2]$	180—182
$[PtCl\{Ge(C_6H_5)_3\}L_2]$	170—172

The Pt–Cl stretching frequency in the compounds prepared is very sensitive to the nature of the substituents on the silicon; *e.g.*, ν(Pt–Cl) is at 242 cm.$^{-1}$ for the compound $[PtCl(SiMePh_2)(PMe_2Ph)_2]$ and at 274 cm.$^{-1}$ for the compound $[PtCl(SiCl_3)(PMe_2Ph)_2]$. This effect is being studied for any light it may throw on the *trans*-effect.

The reactions described here promise to be of considerable utility for preparation of Si–Pt compounds.

(*Received, May 8th,* 1967; *Com.* 435.)

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[1] J. Chatt, C. Eaborn, and S. Ibekwe, *Chem. Comm.*, **1966**, 700.
[2] M. C. Baird, *J. Inorg. Nuclear Chem.*, 1967, **29**, 367.