Silicon, a Ligand Atom of Exceptionally High *trans*-Effect

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A CONSIDERABLE number of platinous complexes of the types $[PtCl(MR_3)(PR'_3)_2]$ and $[Pt(MR_3)_2(PR'_3)_2]$ (M = C, Ge, or Sn; R = H, alkyl, aryl, or Cl; R′ = alkyl or aryl) are known, but only one silicon derivative, *trans*-$[PtCl(SiMe_3)(PEt_3)_2]$, which was obtained only recently.[1] It is hydrolytically unstable and attempts to obtain $[Pt(SiMe_3)_2(PEt_3)_2]$ failed.

We find that some aromatic silylplatinous derivatives are quite stable and they have interesting properties which throw light on the instability of their aliphatic analogues. The reaction of $LiSiMePh_2$ in tetrahydrofuran with *cis*-$[PtCl_2(PMe_2Ph)_2]$ (I) gives $[Pt(SiMePh_2)_2(PMe_2Ph)_2]$ (II) in beautiful yellow crystals, quite stable in air and in organic solvents. This reacts with hydrogen

TABLE

Compound	m.p. °c.	μ(Pt–X) cm.$^{-1}$ (X = Cl or Br)
cis-[$PtCl_2L_2$]*	190—191	289, 309†
[$Pt(SiMePh_2)_2L_2$]	124—126	
trans-[$PtCl(SiMePh_2)L_2$]	153—155	242‡
trans-[$PtBr(SiMePh_2)L_2$]	181—182	158‡
trans-[$PtHClL_2$]	102—104	282†
[$Pt(GeMePh_2)_2L_2$]	169—171	
trans-[$PtCl(GeMePh_2)L_2$]	156—158	248†

* L = PMe_2Ph
† In Polythene disc.
‡ In Nujol mull (measured by Dr. R. H. Cragg)

chloride (1 mol.) in benzene to give a monosilyl derivative (III).

$$\text{(II)} \xrightarrow{\text{HCl}} \textit{trans}\text{-}[PtCl(SiMePh_2)(PMe_2Ph)_2] \ \text{(III)} + SiHMePh_2$$

which is colourless and also stable in air and in solution. The other possible cleavage products [$PtH(SiMePh_2)(PMe_2Ph)_2$] and $SiClMePh_2$ were not detected. A second mole of hydrogen chloride cleaves (III) in the opposite sense. The platinum(II) hydrido-product is new and has ν(Pt–H) at 2205 cm.$^{-1}$ (Nujol mull).

$$\text{(III)} + HCl \quad [PtHCl(PMe_2Ph)_2] + SiClMePh_2$$

From the reaction of (I) with one mole of $LiSiMePh_2$ at room temperature only (II) and some unchanged (I) have been isolated, but there was considerable oily residue.

The bromide corresponding to (III), and the germanium analogue of (II) and thence of (III) were prepared to ensure the correct assignment of infrared spectral bands to ν(Pt–Cl) and ν(Pt–Br). These are given in the Table. On the basis of arguments put foward in ref. 2, the exceptionally low values of ν(Pt–Cl) and ν(Pt–Br) suggest that silicon has the greatest *trans*-effect of inductive origin ever observed, much greater even than cyanide ion, hydride ion, or methyl, and germanium appears to have a similarly high *trans*-effect. The trichlorostannyl radical in platinous complexes has a strong *trans*-effect but its origin appears to be mesomeric rather than inductive.[3] Since the *trans*-effect of silicon is inductive in origin, it should be just as pronounced relatively in octahedral and other less polarisable transition-metal complexes as in platinous complexes.

That silicon has an exceptionally strong *trans*-effect is consistent with the little that is known of silylplatinum chemistry. The aliphatic silyl ligands should have a greater inductive *trans*-effect than the aromatic. This could account for the instability of the bis(trimethylsilyl)platinum(II) complex and the hydrolytic instability of the chloro(trimethylsilyl) analogue. The high *trans*-effect also accounts for the different sense of addition of HCl to the Pt–Si bonds in (II) and in (III).

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[1] F. Glockling and K. A. Hooton, *Chem. Comm.*, 1966, 218.
[2] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 724; and references therein.
[3] R. V. Lindsey, G. W. Parshall, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658; G. W. Parshall *ibid.*, 1966, **88**, 704.