

A Volatile Silicon-Transition-metal Compound

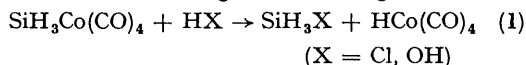
By B. J. AYLETT and J. M. CAMPBELL

(Chemistry Department, Westfield College, Hampstead, London, N.W.3.)

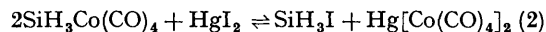
MOLECULAR compounds in which silicon is linked to transition metals are little known. The organo-substituted derivatives $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiMe}_3$ ¹ and $\text{Ph}_3\text{SiMn}(\text{CO})_5$ ² have been reported, and it has also been proposed³ that a product of the reaction between dicobalt octacarbonyl and tetravinylsilane is a compound of composition $\text{Co}_3(\text{CO})_9\text{Si}(\text{CH}:\text{CH}_2)$ which presumably contains Co-Si bonds. Very recently, Chalk and Harrod⁴ have described the preparation of various $\text{R}_3\text{SiCo}(\text{CO})_4$ compounds by the reaction of R_3SiH with dicobalt octacarbonyl. We now report the preparation and some properties of a simple volatile compound, silylcobalt carbonyl, $\text{SiH}_3\text{Co}(\text{CO})_4$.

Iodosilane reacted readily at low temperatures with a solution containing $[\text{Co}(\text{CO})_4]^-$ in dimethyl or diethyl ether. Fractionation *in vacuo* yielded a yellow liquid, m.p. -53.5° , b.p. (extrap.) 112° , (Found: Si, 13.8; H, 1.44; Co, 29.0%; ratio CO/Co, 4.00; *M*, 202.3. $\text{SiH}_3\text{Co}(\text{CO})_4$ requires Si, 13.9; H, 1.49; Co, 29.2%; CO/Co, 4.00; *M*, 202.0). Saturated vapour pressures in the range $22-90^\circ$ defined the equation; $\log p$ (mm.) = $-1754/T + 7.432$; decomposition was marked above 85° . Heating to 100° for $\frac{1}{2}$ hr. yielded some unchanged material (30%), hydrogen, carbon monoxide, silane, cobalt carbonyl hydride, and a dark brown

solid residue. Treatment with protic reagents produced the following initial cleavage:



while alkaline hydrolysis led to evolution of all the hydrogen (free from carbon monoxide). Bromine caused complete breakdown to SiBr_4 , HBr , CO , COBr_2 , and CoBr_2 . It was further shown that the equilibrium:



lies well to the right.

The value of the Si-H stretching frequency (2175 cm.^{-1}) and the position of equilibrium in (2) are consistent with a low effective electronegativity for the $\text{Co}(\text{CO})_4$ group and the presence of $d\pi-d\pi$ interaction in the Co-Si bond. The methyl analogue decomposes above -30° ,⁵ and it is tempting to attribute this difference in thermal stability to lack of π -bonding capability in the methyl case.

Experiments now in progress indicate that similar compounds may be formed by other later transition-metals, and that disubstituted derivatives such as $\text{SiH}_2[\text{Co}(\text{CO})_4]_2$ behave analogously.

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³ S. F. A. Kettle and I. A. Khan, *Proc. Chem. Soc.*, 1962, 82.

⁴ A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1965, **87**, 1133.

⁵ W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, 1958, **13b**, 192.