

Silylmanganese Pentacarbonyl; the Nature of Adducts of Silyl Compounds with Tertiary Amines

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ALTHOUGH two descriptions of the preparation of $\text{Ph}_3\text{SiMn}(\text{CO})_5$ have appeared,^{1,2} almost nothing is known about the chemistry of the Si-Mn bond. We now report on the parent compound, silylmanganese carbonyl, $\text{SiH}_3\text{Mn}(\text{CO})_5$ [m.p., 25.5° ; b.p. (extrapolated), 134°]. It is prepared analogously to silylcobalt carbonyl,³ and is generally less reactive, especially towards protic reagents. Carbonyl insertion into the Si-Mn bond has not been observed.

Tertiary amines such as trimethylamine and pyridine give rise to rather weak 1:2 (acceptor:base) adducts, while 2,2'-bipyridyl gives a weak 1:1 adduct. Typical infrared absorptions in the carbonyl stretching region are given in the Table.

Much stronger adducts of similar stoichiometries are formed between $\text{SiH}_3\text{Co}(\text{CO})_4$ and these amines; their $\nu(\text{CO})$ absorptions are also given. It will be seen that all the adducts appear to contain the carbonylmetallate anion in the solid state, and can be formulated as $(\text{SiH}_3, 2\text{B})^+ [\text{M}(\text{CO})_n]^-$. There has been considerable speculation regarding the nature of adducts⁶ such as $\text{SiH}_3\text{I}, 2\text{B}$; it has

seemed probable (but not completely certain) that they could best be formulated as ionic species with five-co-ordinate silicon, *viz.*, $(\text{SiH}_3, 2\text{B})^+\text{I}^-$, rather than as six-co-ordinate molecular adducts.⁷ This conclusion is now strengthened.

TABLE

Carbonyl stretching frequencies of $\text{SiH}_3\text{-Mn}$ and $\text{SiH}_3\text{-Co}$ derivatives

Compound	$\nu(\text{CO})$ cm. ⁻¹
$\text{SiH}_3\text{Mn}(\text{CO})_5$ (g)	2106,* 2021*
$\text{SiH}_3\text{Mn}(\text{CO})_5, 2\text{C}_5\text{H}_5\text{N}$ (s)	1860
$\text{SiH}_3\text{Mn}(\text{CO})_5, 2\text{NMe}_3$ (s)	1860
$\text{Mn}(\text{CO})_5^-$ † (ref. 4)	1898, 1864
$\text{SiH}_3\text{Co}(\text{CO})_4$ (g)	2106,* 2051,* 2026*
$\text{SiH}_3\text{Co}(\text{CO})_4, 2\text{C}_5\text{H}_5\text{N}$ (s)	1882
$\text{SiH}_3\text{Co}(\text{CO})_4, 2\text{NMe}_3$ (s)	1870
$\text{Co}(\text{CO})_4^-$ † (ref. 5)	1883, 1861 sh

* Centre of multiplet. † Sodium salt in tetrahydrofuran solution.

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