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

By B. J. AYLETT and J. M. CAMPBELL
(Chemistry Department, Westfield College, London, N.W.3.)

ALTHOUGH two descriptions of the preparation of $Ph_3SiMn(CO)_5$ 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, $SiH_3Mn(CO)_5$ [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 stoicheiometries are formed between $SiH_3Co(CO)_4$ and these amines; their ν(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 $(SiH_3, 2B)^+ [M(CO)_n]^-$. There has been considerable speculation regarding the nature of adducts[6] such as $SiH_3I,2B$; it has seemed probable (but not completely certain) that they could best be formulated as ionic species with five-co-ordinate silicon, *viz.*, $(SiH_3,2B)^+I^-$, rather than as six-co-ordinate molecular adducts.[7] This conclusion is now strengthened.

TABLE

Carbonyl stretching frequencies of SiH_3–Mn *and* SiH_3–Co *derivatives*

Compound	ν(CO) cm.$^{-1}$
$SiH_3Mn(CO)_5$ (g)	2106,* 2021*
$SiH_3Mn(CO)_5$, $2C_5H_5N$ (s)	1860
$SiH_3Mn(CO)_5$, $2NMe_3$ (s)	1860
$Mn(CO)_5^-$ † (ref. 4)	1898, 1864
$SiH_3Co(CO)_4$ (g)	2106,* 2051,* 2026*
$SiH_3Co(CO)_4$,$2C_5H_5N$ (s)	1882
$SiH_3Co(CO)_4$, $2NMe_3$ (s)	1870
$Co(CO)_4^-$ † (ref. 5)	1883, 1861 sh

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

(*Received, January* 10*th*, 1967; *Com.* 030.)

---

[1] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.
[2] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2217.
[3] B. J. Aylett and J. M. Campbell, *Chem. Comm.*, 1965, 217.
[4] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1962, **1**, 933.
[5] W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Amer. Chem. Soc.*, 1965, **87**, 2563.
[6] E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon, Oxford, 1963.
[7] B. J. Aylett and R. A. Sinclair, *Chem. and Ind.*, 1965, 301; H. J. Campbell-Ferguson and E. A. V. Ebsworth, *ibid.*, p. 301; H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1966, 1508.