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Preliminary communication

SILYLHEXACARBONYLVANADIUM: A VOLATILE SEVEN-COORDINATE DERIVATIVE OF VANADIUM(I)

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Summary

Reaction of sodium or thallium(I) hexacarbonylvanadate(−1) with iodosilane gives silylhexacarbonylvanadium as an orange solid, volatile at room teperature; its IR spectrum is consistent with a structure of C_{3v} symmetry.

Although the seven-coordinate complexes $PPh_3AuV(CO)_6$ [1, 2] and $Ph_3SnV(CO)_6$ [2] have been obtained from $V(CO)_6^-$ and the corresponding chlorides, such reactions are relatively rare, and in particular recent work [3] has shown that hexacarbonylvanadate(−1) does not undergo similar reactions with other halides such as CF_3COCl or CH_3I.

We now report that iodosilane reacts readily at low temperatures with TlV(CO [4] in 2-methylbutane, or with diglyme-free $NaV(CO)_6$ in diethyl ether (eq. 1), to give $SiH_3V(CO)_6$ as an orange solid, volatile in vacuo at 273 K [Found: Si,

$$SiH_3I + MV(CO)_6 \rightarrow SiH_3V(CO)_6 + MI \quad (M = Na, Tl) \tag{1}$$

11.8; H, 1.1; V, 19.2. $C_6H_3O_6SiV$ calcd.: Si, 11.2; H, 1.2; V, 20.4%. B.p. (est.): 440—460 K]. This is the first definite example of a molecular compound in which silicon is bonded to a metal of the vanadium group.

Decomposition occurred even in the gas phase at room temperature, giving $(SiH_3)_2O$, $V(CO)_6$, and an involatile yellow solid; disiloxane has been observed previously as a relatively minor decomposition product of other silylmetal carbonyls [5], but the present case is unusual in that essentially all silyl groups are removed as $(SiH_3)_2O$, implying that $V—CO \rightarrow SiH_3$ interactions are particularly significant. The silicon—vanadium bond was cleaved readily by HCl or water in the gas phase (eq. 2). The general reactivity of silyl—metal bonds in $SiH_3M(CO)_n$

$$SiH_3V(CO)_6 + HX \rightarrow SiH_3X + \tfrac{1}{2}H_2 + V(CO)_6 \quad (X = Cl, O/2) \tag{2}$$

derivatives therefore appears to decrease in the order: Si—V > Si—Co [5] >

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Si—Fe [6] > Si—Mn [7] > Si—Re [8]. As with $SiH_3Co(CO)_4$ [9], trimethylamine gave an involatile adduct, $SiH_3V(CO)_6 \cdot xNMe_3$ (where x is probably 2), formulated as $[SiH_3 \cdot xNMe_3]^+ [V(CO)_6]^-$ on the basis of its IR spectrum (ν(CO) 1842 cm^{-1}, δ(VCO) 651 cm^{-1}, perfluorokerosene mull).

The gas-phase IR spectrum of $SiH_3V(CO)_6$ (but not that of $SiD_3V(CO)_6$) showed a weak absorption at 2147 cm^{-1}, assigned as the SiH stretching frequency. Bands of medium intensity at 906 and 633 cm^{-1} are assigned to SiH_3 and VCO deformations respectively. The pattern of carbonyl stretching absorptions (2088m, 2026m, 1990vs, 1959s cm^{-1}) is consistent with that expected for a face-capped octahedral arrangement in which the silyl group occupies the capping position (C_{3v}), but structures of lower symmetry such as the face-capped trigonal prism or edge-capped octahedron cannot be entirely ruled out.

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