

Preliminary communication

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

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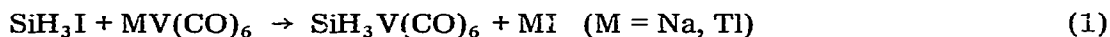
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Summary

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

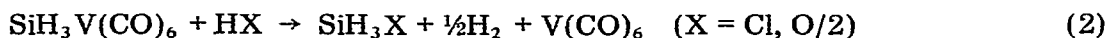
Although the seven-coordinate complexes  $PPh_3AuV(CO)_6$  [1, 2] and  $Ph_3SnV(CO)_6$  [2] have been obtained from  $V(CO)_6^-$  and the corresponding chlorides, such reactions are relatively rare, and in particular recent work [3] has shown that hexacarbonylvanadate(-1) does not undergo similar reactions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

We now report that iodosilane reacts readily at low temperatures with  $TiV(CO)_4$  [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,



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  $SiH_3M(CO)_n$



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  $\text{SiH}_3\text{Co}(\text{CO})_4$  [9], trimethylamine gave an involatile adduct,  $\text{SiH}_3\text{V}(\text{CO})_6 \cdot x\text{NMe}_3$  (where  $x$  is probably 2), formulated as  $[\text{SiH}_3 \cdot x\text{NMe}_3]^+ [\text{V}(\text{CO})_6]^-$  on the basis of its IR spectrum ( $\nu(\text{CO})$   $1842\text{ cm}^{-1}$ ,  $\delta(\text{VCO})$   $651\text{ cm}^{-1}$ , perfluorokerosene mull).

The gas-phase IR spectrum of  $\text{SiH}_3\text{V}(\text{CO})_6$  (but not that of  $\text{SiD}_3\text{V}(\text{CO})_6$ ) showed a weak absorption at  $2147\text{ cm}^{-1}$ , assigned as the SiH stretching frequency. Bands of medium intensity at  $906$  and  $633\text{ cm}^{-1}$  are assigned to SiH<sub>3</sub> and VCO deformations respectively. The pattern of carbonyl stretching absorptions ( $2088\text{m}$ ,  $2026\text{m}$ ,  $1990\text{vs}$ ,  $1959\text{s cm}^{-1}$ ) 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.

## References

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