

Crystal Structure of Bis- μ -(trimethylsilylmethylidyne)tetrakis-(trimethylsilylmethyl)diniobium(v). A New Type of Carbon Bridging Group

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Summary X-Ray structural studies have shown that the new complexes $M_2(CSiMe_3)_2(CH_2SiMe_3)_4$ ($M = Nb, Ta$) contain $CSiMe_3$ bridging groups which form part of a four-membered quasi-aromatic $\overline{M-C-M-C}$ ring.

IN CONTINUATION of studies ^{1,2} on the preparation of stable transition-metal alkyls we have obtained niobium and tantalum compounds of stoichiometry $M_2(CSiMe_3)_2(CH_2SiMe_3)_4$ by the interaction of trimethylsilylmethylmagnesium chloride with the respective metal pentahalides in ether. Bis- μ -(trimethylsilylmethylidyne)tetrakis(trimethylsilylmethyl)diniobium(v) crystallises from light petroleum as reddish brown elongated prisms, m.p. 152°, which are air-sensitive. The crystals are triclinic, with unit-cell

dimensions $a = 19.540$, $b = 11.014$, $c = 12.155$ Å, $\alpha = 115.91$, $\beta = 110.14$, $\gamma = 103.76^\circ$, $U = 1961.8$ Å³, $Z = 2$, $D_c = 1.19$ g cm⁻³, space group $P\bar{1}$.

Three-dimensional X-ray data were collected on a Siemens four-circle diffractometer from a crystal sealed under nitrogen in a Lindemann tube. Using Cu- K_α radiation a total of 3396 independent reflections were measured (to $\theta = 50^\circ$), of which 114 were judged to be unobserved. The structure was solved by Patterson and Fourier methods, and least-squares refinement has now reached $R = 0.052$ with an absorption correction still to be applied.

The complex has a dimeric molecular structure, with $\bar{1}$ symmetry, shown in the Figure. The two crystallographically independent dimers have no significant differences

between them and mean values of the more important bond lengths and angles are quoted in the Table. In the dimer

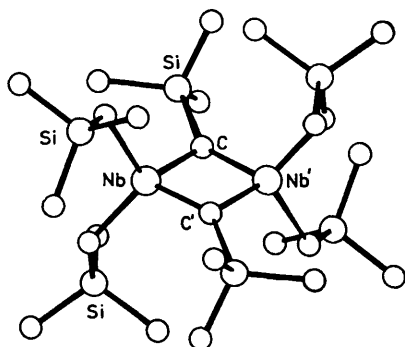


FIGURE. The molecular structure of $\text{Nb}_2(\text{CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$. Primed atoms are related to unprimed atoms by a centre of symmetry inside the ring.

TABLE. Interatomic distances (Å) and angles (degrees) are the average of two independent values unless otherwise stated.

Nb-C	1.995(9)	Nb...Nb'	..	2.897(2)
Nb'-C	1.954(9)	C...C'	..	2.684(13)
Nb-CH ₂	2.160(9)	Si-C	1.860(13)
(mean of 4)		(mean of 24)		
C-Nb-C'	85.6(4)	Nb-C-Si	119.8(6)
Nb-C-Nb'	94.4(4)	Nb'-C-Si	142.4(5)

each niobium atom is joined to another niobium atom by two bridging CSiMe_3 groups and the distorted tetrahedral co-ordination about each metal atom is completed by two terminal CH_2SiMe_3 groups. The Nb-CH₂ bond length of

2.160 Å may be compared with Mo-CH₂ of 2.131 Å in $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$ ² and Cr-CH₃ of 2.199 Å found in $\text{Li}_4[\text{Cr}_2\text{Me}_6]$, $4\text{C}_4\text{H}_8\text{O}^3$.

The mean value of the Nb-C (bridging) distance is 1.974 Å. However, because of the asymmetry at the bridging carbon where the two Nb-C-Si angles are appreciably different the slight difference between the two Nb-C (bridging) distances may possibly be real (see Table). There is a little buckling at the bridging carbon atom such that it is *ca.* 0.2 Å out of the plane Nb, Nb', Si. These distortions may well be the result of mutual repulsion of the bulky ligand groups.

There are several reasons for believing that there is no hydrogen attached to the bridging carbon. (1) The n.m.r. spectrum shows only resonances due to two types of methyl group (at τ 9.54 and 9.79 for Nb) and one methylene group (τ 8.5) in ratios corresponding to $\text{Me}_3\text{SiCH}_2:\text{Me}_3\text{Si}$ of 2:1. (2) No trace of hydrogen could be seen on a difference Fourier while all other hydrogen atoms were easily locatable. (3) The Nb-C bridging bonds evidently have multiple, *i.e.* 1.5, bond character. The quasi-aromatic nature of the Nb-C-Nb-C ring can explain the diamagnetism of the complex without the necessity of invoking metal-metal bonding.

Single-crystal photographs show that the tantalum analogue, orange, m.p. 170°, is isostructural with the niobium complex. The unit-cell dimensions are $a = 19.49$, $b = 11.19$, $c = 12.29$ Å, $\alpha = 116.0$, $\beta = 110.3$, $\gamma = 103.5^\circ$ and the intensity distribution is very similar.

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