Crystal Structure of Hexakis(trimethylsilylmethyl)dimolybdenum

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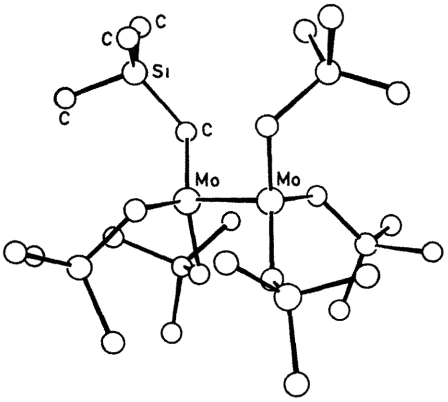
Summary Hexakis(trimethylsilylmethyl)dimolybdenum has a short Mo–Mo bond (2 167 Å) corresponding to a triple bond, similar neopentyl and benzyl derivatives and the isostructural tungsten compound are reported

WE suggested[1] that if the alkene elimination reaction, which is one of the principal modes of decomposition of binary transition-metal alkyls, could be prevented, such alkyls may be stabilized, and trimethylsilylmethyl compounds, which meet the criteria, were prepared

The structure of one of these, hexakis(trimethylsilylmethyl)dimolybdenum,† $Mo_2(CH_2SiMe_3)_6$, is now reported The compound crystallised from light petroleum as yellow, air-sensitive prisms The crystals are monoclinic $a = 31\ 20$, $b = 12\ 457$, $c = 23\ 415$ Å, $\beta = 112° 10'$, $U = 8427$ Å^3, $Z = 8$, $D_c = 1\ 13$ g cm^{-3}, space group *Pc*

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 3475 independent reflections were measured (to $\theta = 35°$) of which 539 were judged to be unobserved The structure was solved by the heavy atom method, although considerable difficulty was experienced in locating the eight independent molybdenum atoms Least-squares refinement, with only molybdenum and silicon atoms anisotropic, has now reached $R = 0\ 043$

The complex exists in the structure in the form of dimeric units as shown in the Figure There are no significant differences between the four crystallographically independent dimers, and the mean values of the most significant bond lengths and angles are quoted in the Table



FIGURE

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† Incorrectly reported[1] as $Mo(CH_2SiMe_3)_4$

TABLE

	No. of independent values	Average bond lengths and bond angles
Mo–Mo	4	2·167 Å
Mo–CH_2	24	2·131 Å
Mo–Mo–CH_2	24	100·6°
Mo–CH_2–Si	24	121·1°

The Mo–Mo bond distance, 2·167 Å, is only slightly longer than that found in tetra-acetatodimolybdenum[2] (2·12 Å). Each molybdenum has a distorted tetrahedral co-ordination and the configuration of the methylene groups in the dimer, which has approximate 32 (D_3) symmetry, is staggered. The Mo–CH_2–Si angle (and possibly the Mo–Mo–CH_2 angle) is probably a consequence of the mutual repulsion of the bulky trimethylsilyl groups rather than of any electronic factor. The Mo–Mo bond can be considered as a multiple bond,[3] *i.e.*, a six-electron triple bond with the d_{z^2} orbitals forming the σ-bond and overlap of two sets of d_{xz} and d_{yz} orbitals of both metal atoms forming π-bonds; since these have cylindrical symmetry there is no restriction on rotation which accords with the staggered configuration found.

The tungsten analogue, obtained from the interaction of WCl_6 and Me_3SiCH_2MgCl is similar and single-crystal photographs show that it is isostructural with the Mo compound: $a = 31·26$, $b = 12·50$, $c = 23·43$ Å, $\beta = 112°$.

The nearest analogue of these structures is $Li_4[Cr_2Me_8]$, $4C_4H_8O$,[4] where the Cr–Cr bond is short (1·980 Å), Cr-Me is 2·199 Å, but the symmetry is D_{4h} like $Re_2Cl_8^{2-}$.

The corresponding benzyl and neopentyl complexes, $M_2(CH_2Ph)_6$, M = Mo and W, and $Mo_2(CH_2CMe_3)_6$ have been made by Grignard reactions. The yellow crystals, whose properties are similar to the trimethylsilylmethyls are stable to *ca.* 130°; the n.m.r. spectra show the expected CH_2, Me, and Ph resonances. No binary transition-metal neopentyls have previously been isolated but studies on manganese dialkyls prepared *in situ* show that the methyl, benzyl, and neopentyl complexes, which cannot readily undergo decomposition by olefin elimination, are the most stable alkyls.[5]

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[4] J. Krausse, G. Marx, and G. Schödl, *J. Organometallic Chem.*, 1970, **21**, 159.
[5] M. Tamura and J. K. Kochi, *J. Organometallic Chem.*, 1971, **29**, 111.