Synthesis and Structure of a Dimolybdenum Alkylidyne-Hydride

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The compound $Mo_2(OAr)_2(CH_2SiMe_3)_4$ (OAr = 2,6-dimethylphenoxide) undergoes the smooth loss of one equivalent of Me_4Si in the presence of pyridine (py) to form an alkylidyne-hydride compound, $Mo_2(\mu\text{-}H)(\mu\text{-}CSiMe_3)(CH_2SiMe_3)_2(OAr)_2(py)_2$; both compounds have been structurally characterised by *X*-ray crystallography.

The formation of alkylidene and alkylidyne groups by α-hydrogen abstraction from early transition metal alkyl compounds has been well documented and extensively studied by Schrock and co-workers.[1] An interesting feature typical of reduced metal alkylidene compounds is the large values of $M{=}C_\alpha{-}C_\beta$ angles typically found,[2] and this has been interpreted as being due to the partial transfer of the α-hydride to the metal.[3] In some cases the resulting alkylidyne-hydride can be isolated and in one case an equilibrium was shown to be present between the alkylidene and alkylidyne-hydride complex.[4] It has been proposed that such an equilibrium is an important step in Ziegler–Natta polymerization of olefins,[5a] and recent work by Green on titanium alkyls has shown the presence, in electron deficient compounds, of strong interactions between the metal and either α-CH[5b] or β-CH bonds.[5c] Studies of the synthesis or reactivity of alkylidene- or alkylidyne-hydrides are hence of considerable current interest. During our studies of early transition metal aryloxide chemistry we have isolated an alkylidyne-hydride compound of dimolybdenum. Of particular interest is that the compound is formed by the addition of an α-CH bond of an alkylidene group to a metal–metal bond.

Treatment of the compound $Mo_2Br_2(CH_2SiMe_3)_4$[6] with excess of LiOAr (OAr = 2,6-dimethylphenoxide) in hydrocarbon solvents leads on work-up to good yields of $Mo_2(OAr)_2(CH_2SiMe_3)_4$ (**1**) as deep-red crystals from hexane. In contrast with the analogous t-butoxide $Mo_2(OBu^t)_2(CH_2SiMe_3)_4$,[6] which can be sublimed at 80 °C with little decomposition, (**1**) slowly darkens in solution at 25 °C with the generation of Me_4Si as identified by ^1H n.m.r. spectroscopy. Sealed n.m.r. sample solutions of (**1**) in C_6D_6 solvent are completely decomposed after 2 h at 60 °C, only Me_4Si and a black precipitate being formed. Structural analysis of (**1**)† (Figure 1) shows

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† *Crystal data* for compound (**1**) (at −169 °C) $Mo_2(OC_6H_3Me_2)_2(CH_2SiMe_3)_4$: triclinic, space group *P*1, $a = 12.091(6)$, $b = 10.839(5)$, $c = 10.384(5)$ Å, $\alpha = 120.06(2)$, $\beta = 120.65(2)$, $\gamma = 74.96(3)°$, $D_c = 1.284$ g cm^{-3}, $Z = 1$. The structure was solved by a combination of Patterson and Fourier techniques using 2657 unique intensities collected on an automated diffractometer using Mo-K_α radiation for $6 \leqslant 2\theta \leqslant 45°$. All hydrogen atoms were located and refined isotropically. Final refinement utilized anisotropic thermal parameters for non-hydrogen atoms and converged to $R(F) = 0.0437$ and $R_w(F) = 0.0410$.

Crystal data for compound (**2**) (at −168 °C) $Mo_2(H)(CSiMe_3)(py)_2(OC_6H_3Me_2)_2(CH_2SiMe_3)_2\cdot C_7H_8$: orthorhombic, space group $P2_1nb$, $a = 13.424(6)$, $b = 21.452(10)$, $c = 16.892(7)$ Å, $D_c = 1.291$ g cm^{-3}, $Z = 4$. The structure was solved by a combination of Patterson, direct, and Fourier techniques using 3357 unique intensities collected on an automated diffractometer using Mo-K_α radiation for $6 \leqslant 2\theta \leqslant 45°$. All hydrogen atoms were located in a difference Fourier phased on the non-hydrogen parameters and were included in the final full-matrix least squares refinement, converging to $R(F) = 0.0514$ and $R_w(F) = 0.0470$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

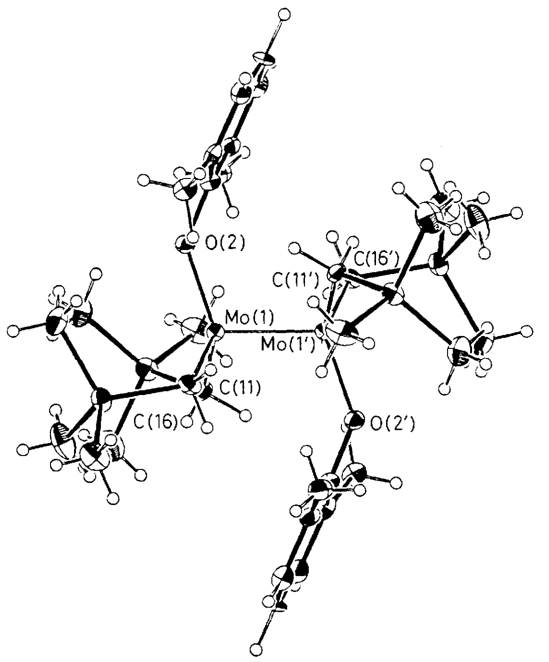


Figure 1. A view of the $Mo_2(OC_6H_3Me_2)_2(CH_2SiMe_3)_4$ molecule (**1**) giving the atom numbering scheme used. Some pertinent bond distances and angles are: Mo(1)–Mo(1′) 2.218(2), Mo(1)–O(2) 1.910(4), Mo(1)–C(11) 2.090(7), Mo(1)–C(16) 2.112(6) Å; Mo(1′)–Mo(1)–O(2) 108.6, Mo(1′)–Mo(1)–C(11) 101.5, Mo(1′)–Mo(1)–C(16) 100.6(2), O(2)–Mo(1)–C(11) 118.6(2), O(2)–Mo(1)–C(16) 114.7(2), C(11)–Mo(1)–C(16) 110.3(3)°.

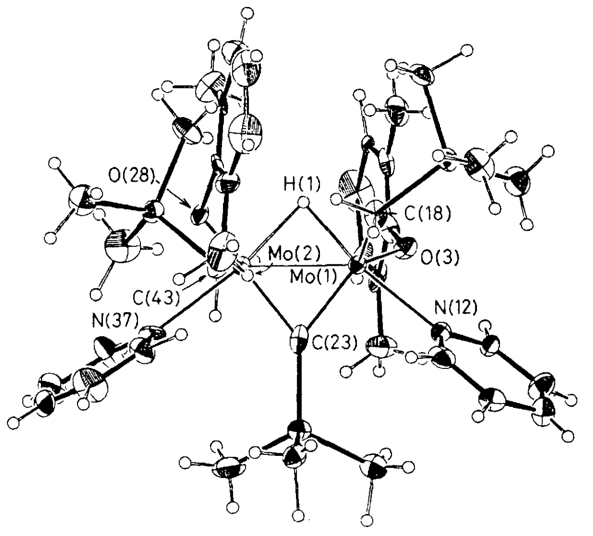
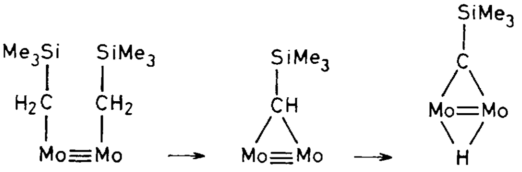


Figure 2. A view of the $Mo_2(H)(CSiMe_3)(OC_6H_3Me_2)_2(py)_2(CH_2SiMe_3)_2$ molecule (**2**) giving the numbering scheme used. Some pertinent bond distances and angles are: Mo(1)–Mo(2) 2.380(2), Mo(1)–C(23) 1.959(11), Mo(2)–C(23) 1.950(11), Mo(1)–H(1) 1.75(9), Mo(2)–H(1) 1.86(9), Mo–N(av.) 2.303, Mo–O(av.) 1.957, Mo–C(av.) 2.145 Å; Mo(1)–C(23)–Mo(2) 75.0(4), Mo(1)–H(1)–Mo(2) 82(3)°.



Scheme 1

that the aryloxide ligands exert much more steric pressure on the alkyl co-ligands than might have been predicted. The preferred conformation is adopted in which the plane of the aryl ring lies perpendicular to the Mo≡Mo triple bond, an effect we have rationalized in terms of maximizing the π-bonding between the oxygen atom and the electron deficient molybdenum atom (using the d_{xy} or $d_{x^2-y^2}$ orbitals on Mo). This slightly greater steric pressure is reflected in a closing up of the R–Mo–R angle to 110.3(3)° in (**1**) from 112.3(5)° in the t-butoxide.[6] We hence believe the instability of (**1**) to be due to this extra steric pressure causing α-hydride abstraction to be induced leading to ill defined products.

However, when solutions of (**1**) are thermolysed in the presence of added pyridine (py), one equivalent of Me_4Si is generated along with a dark green solution, from which dark crystals of a product (**2**) can be isolated. Compound (**2**) was identified by an *X*-ray structure analysis to be of formula $Mo_2(\mu\text{-}H)(\mu\text{-}CSiMe_3)(OAr)_2(CH_2SiMe_3)_2(py)_2$ and an ORTEP view is shown in Figure 2.[†] ^{1}H N.m.r. spectra of (**2**) are consistent with the formula except that we have at present been unable to identify the position of the M–H resonance. The overall geometry about the di-metal centre is of two trigonal bipyramids about each molybdenum sharing a common edge occupied by the bridging hydride and alkylidyne groups. The other ligands are symmetrically bound leading to approximate C_2 symmetry with the pyridine ligands arranged *trans* to the bridging hydride group. Counting the alkylidyne as a tri-anion and the hydride as a mono-anion, one calculates that the molecule contains an Mo_2^{8+} core, and the molybdenum–molybdenum distance of 2.380(2) Å is consistent with a double bond (d^2–d^2, $\sigma^2\pi^2$) being present.[7] The distances to the bridging carbon atom (1.95 Å average) are consistent with the formulation of this as an alkylidyne group, and compare with the terminal alkyl distances of 2.14 Å (average).

The isolation and structure of this compound raised a number of questions. The conversion of (**1**) into (**2**) involves loss of one equivalent of Me_4Si by α-hydride abstraction. We envisage the pathway of conversion as involving two important steps (Scheme 1). The first step, α-hydride abstraction, must take place *across* the metal–metal bond. The second step then involves the addition of the resulting alkylidene group's α-CH bond to the Mo≡Mo triple bond to generate the alkylidyne-hydride.

This raises the possibility that an α-hydride abstraction across the metal–metal bond is a general reaction for such systems. We note that the reported conversion of $Mo_2Br_2(CH_2SiMe_3)_4$ into the bisalkylidene $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$ on addition of PMe_3[8] could occur either by α-hydride abstraction at each metal (similar to known mononuclear chemistry) or involve double abstraction across the metal–metal bond.

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