Journal of
The Chemical Society,
Chemical Communications

NUMBER 21/1980

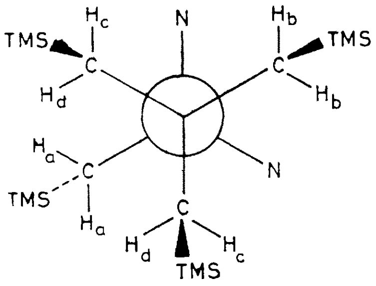
Formation and Stability of 1,1- and 1,2-Bis(dimethylamido)tetrakis-(trimethylsilylmethyl)dimolybdenum(*Mo*≡*Mo*)

By Malcolm H. Chisholm* and Ian P. Rothwell

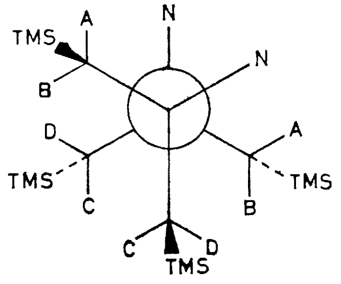
(*Department of Chemistry, Indiana University, Bloomington, Indiana* 47405)

Summary The reaction of hexane solutions of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ with $LiNMe_2$ and $HNMe_2$ gives 1,1- and 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$, respectively, which, once formed, do not isomerize readily.

Addition of anhydrous HBr (2 equiv.) to a toluene solution of $Mo_2(CH_2SiMe_3)_6$[1] at −78 °C yields Me_4Si and 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ (**2**)† which can be purified by crystallization from cold hexane solutions. Addition of anhydrous $NHMe_2$ (>> 2 equiv.) to a hexane solution of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ yields a precipitate of $Me_2NH_2^+Br^-$ and an orange-brown solution of 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ which can be isolated as an analytically and isomerically pure orange-brown liquid by filtration (to remove $Me_2NH_2^+Br^-$) and removal of the solvent under reduced pressure.‡ Addition of $LiNMe_2$ (⩾ 2 equiv.) to a hexane solution of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ yields an orange-brown solution and a fine precipitate of LiBr which can be removed by filtration. Removal of the solvent under reduced pressure yields an orange-brown liquid which is *ca.* 95% 1,1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ (**1**) and 5% 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ (**2**).† This ratio of isomers has not been observed to change with time. Both isomers are air-sensitive and must be handled in dry and oxygen-free atmospheres and solvents. In the mass spectrometer samples of $Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ prepared by both routes gave molecular ions. The substitution pattern, 1,1- *vs.* 1,2-, is readily deduced from ^1H n.m.r. studies.



(1)



(2)

TMS = trimethylsilyl

---

† 1,2- and 1,1- denote the isomers $(Me_3SiCH_2)_2XMoMoX(CH_2SiMe_3)_2$ and $(Me_3SiCH_2)X_2MoMo(CH_2SiMe_3)_3$, respectively.

‡ Standard vacuum-line and Schlenk techniques were used.

For the 1,1-isomer below -40 °C at 220 MHz there are 3 silylmethyl-group resonances in the integral ratio 1 : 1 : 2, as expected for the staggered ethane-like conformation (**1**) The methylene carbons associated with two of the trimethylsilylmethyl-ligands are contained in a plane of symmetry and the methylene protons associated with each give rise to separate singlets, a and b in Figure 1 The methylene protons associated with the other two trimethylsilylmethyl-ligands are diastereotopic and give rise to an AB quartet, c and d in Figure 1 Upon raising the temperature, rotation about the Mo≡Mo bond becomes fast on the n m r time scale The AB quartet and one of the singlets collapse and then coalesce to give at + 95 °C two singlets in the integral ratio 3 : 1

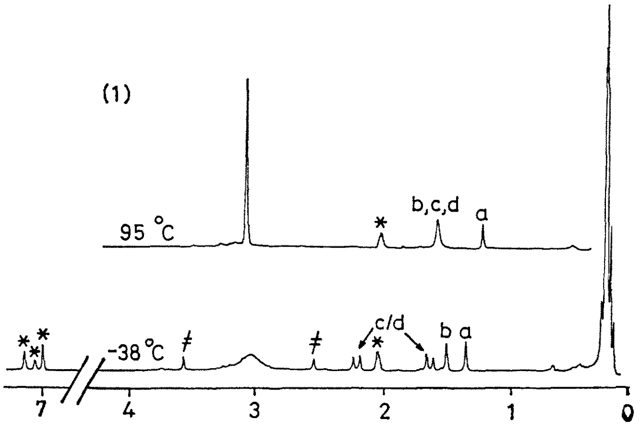


FIGURE 1 ^{1}H N m r spectra of 1 1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ recorded at 220 MHz in [$^2H_8$] toluene$_8$ at -38 °C and at + 95 °C (inset) The *N*-methyl-group signals of 1 2 $Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ are denoted by ‡ proton impurities in the [$^2H_8$] toluene solvent are indicated by *

The ^{1}H n m r spectrum of 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ recorded at -43 °C and 220 MHz is shown in Figure 2 This is consistent with that expected for a low-temperature limiting spectrum of the *gauche*-rotamer (**2**) There are two types of trimethylsilylmethyl-ligands and for each the methylene protons are diastereotopic, there are two *N*-methyl-resonances corresponding to proximal and distal methyl-groups [2] Upon raising the temperature, rotations about the Mo–N bonds and the Mo≡Mo bond become rapid on the n m r time-scale until, at +120 °C, a high-temperature limiting spectrum is approached having a single *N*-methyl-resonance, a single silylmethyl-resonance and an AB quartet for the methylene protons The rotation about the Mo≡Mo bond could be either *gauche* ⇌ *gauche′* (enantiomerization) or *gauche*(*g*) ⇌ *anti*(*a*) ⇌ *gauche′*(*g*) In the absence of a significant equilibrium concentration of the *anti*-rotamer these can not be distinguished, though on steric grounds the latter ($g \rightleftharpoons a \rightleftharpoons g'$) seems more likely to be the threshold mechanism for rotation about the M≡Mo bond

Though a number of ethane-like d^3-d^3 (M≡M) dimers of the general formula $M_2X_2Y_4$, where M = Mo and W, have been characterized previously,[3,4] this is the first observation that substitution at these dimetal centres can lead to either a 1,1- or a 1,2-substituted product Stability with respect to isomerization implies a substantial kinetic barrier to alkyl-group transfer between the molybdenum atoms in the ethane-like products, though alkyl-group transfer must occur in the formation of the 1,1-isomer The further reactions of these isomers promise to be interesting For example, addition of Bu^{t}OH to 1,1- and 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ yields 1,1- and 1,2-$Mo_2(OBu^t)_2(CH_2SiMe_3)_4$,

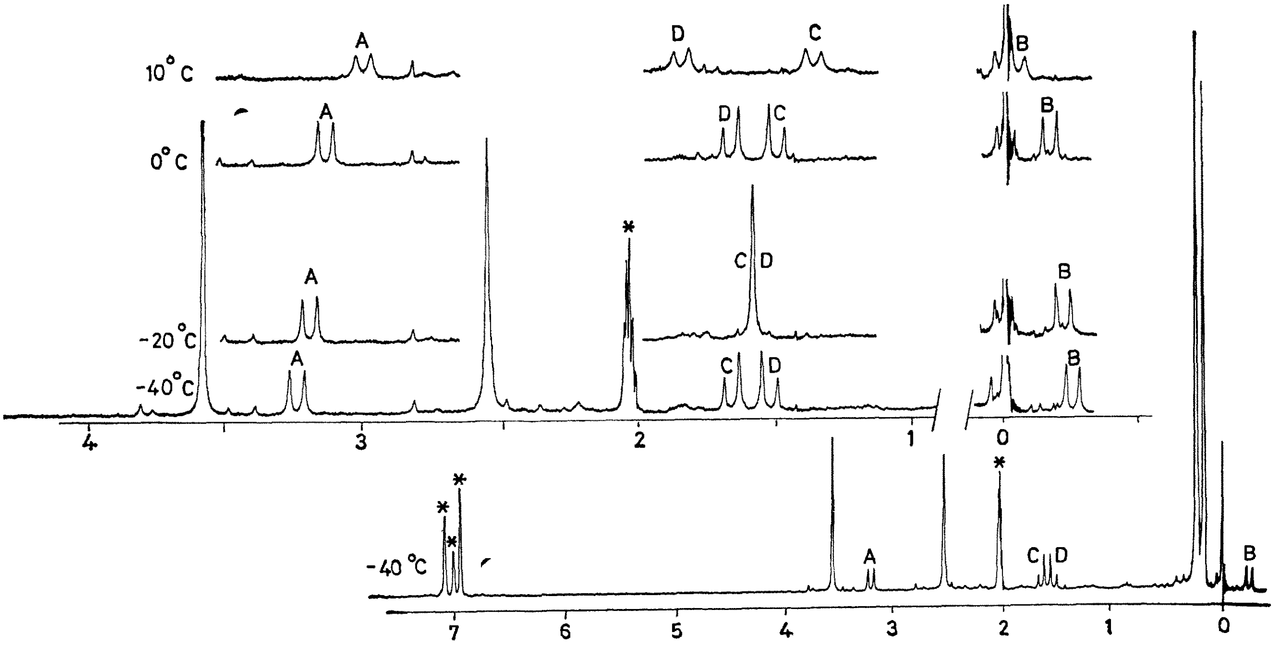


FIGURE 2 ^{1}H N m r spectrum of *gauche*-1 2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ recorded at 220 MHz in [$^2H_8$]toluene at -40 °C The insets show a scale expansion of the methylene proton resonances over the temperature range -40 to +10 °C An absolute assignment of the methylene protons signals A, B, C, D with those labelled accordingly in (**2**) is not possible respectively, whereas with CO_2 (1 atmos., 25 °C) the 1,1-isomer yields $(Me_3SiCH_2)(Me_2N)(Me_2NCO_2)MoMo(CH_2SiMe_3)_3$ while the 1,2-isomer does not react.

We thank the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society for financial support.

(*Received*, 26*th June* 1980; *Com.* 696.)

[1] F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1971, 1079.
[2] M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, and L. W. Shive, *J. Am. Chem. Soc.*, 1976, **98**, 4469.
[3] M. H. Chisholm and F. A. Cotton, *Acc. Chem. Res.*, 1978, **11**, 356.
[4] M. H. Chisholm, *Transition Met. Chem.*, 1978, **3**, 321.