CHEMISTRY LETTERS, pp. 2447-2450 1992.

Stereoselective Alkylation of Terminal Sulphide in trans-$Mo(S)_2$(syn-Me_8[16]aneS_4) by Alkyl Halides. Preparation and Crystal Structure of trans-{$Mo(SR)(S)$(syn-Me_8[16]aneS_4)}$^+$ (R=Me, $PhCH_2$) Containing Three Distinctive Types of Sulfur Donors

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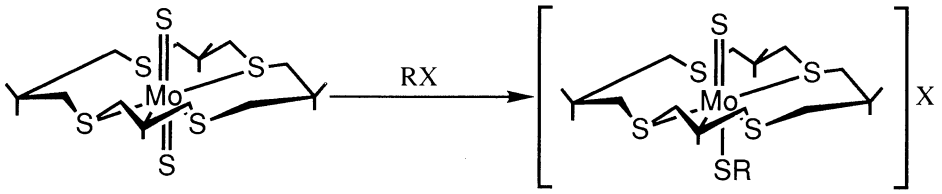
Facile monoalkylation of trans-$Mo(S)_2$(syn-Me_8[16]aneS_4) with MeI and $PhCH_2Br$ proceeds stereoselectively at the terminal sulphide located on the uncongested axial site to give trans-{$Mo(SR)(S)$(syn-Me_8[16]aneS_4)}$^+$ (R=Me, CH_2Ph) containing three different types of sulfur donors; thiolato, terminal sulphido, and thioether ligands; the structure of the methyl thiolate complex was elucidated by an X-ray diffraction study.

Despite the vast chemistry of thiolate complexes of transition metals,[1] their preparative methods are rather restricted to the use of thiolato anions and thiols or their derivatives such as RSSR and $RSSiMe_3$ as the ligand sources.[1a] In view of the ready availability of sulphido complexes and the micro-reversibility of C-S bond cleavage of alkyl thiolato ligands affording sulphides,[2] the alkylation of sulphido functionality may provide useful alternative routes. A few such approaches have been developed for anionic and cationic dinuclear μ-sulphido complexes such as $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$, $[(\eta^5\text{-}C_5H_5Mo)_2(\mu\text{-}S)_4]^{2-}$, and $[(\eta^5\text{-}MeC_5H_4Mo)_2(\mu\text{–}S)(\mu\text{-}SMe)(S_2CH_2)]^+$. [3-6] Direct alkylation, alkenylation, and acetylation of the neutral μ-sulphido complex $(\eta^5\text{-}MeC_5H_4Mo)_2(\mu\text{-}S)_2(S_2CH_2)$ with the corresponding organic halides are also known, but the nucleophilicity of μ-sulphides seems to vary dependent on the coordination environments and the μ-sulphides in $(\eta^5\text{-}MeC_5H_4Mo)_2(\mu\text{-}S)_2(SMe)_2$ failed to react even with MeI.[6] Recently we have prepared trans-$Mo(S)_2$(syn-Me_8[16]aneS_4) (**1**, Me_8[16]aneS_4=3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane).[7] The long Mo=S distances (average 2.238(9) Å) compared to those (2.126-2.129 Å) known for Mo(IV) sulphides [8] may give rise to high nucleophilicity for the terminal sulphides in **1** due to a reduced $p_\pi(S)\rightarrow d_\pi(Mo)$ interaction. Indeed, we have found that the terminal sulphide located at the uncongested axial site in **1** reacts readily and regioselectively with alkyl halides to give trans-{$Mo(SR)(S)$(syn-Me_8[16]aneS_4)}X (**2**, R=$PhCH_2$, X=Br; **3**, R=Me, X=I). As far as we know, the preparation of thiolato complexes from terminal sulphides by alkylation with alkyl halides has no precedent. The compounds **2** and **3** also represent the novel examples of mononuclear MoS_6 species containing three distinctive types of sulfur ligands; thiolate, terminal sulphide, and thioether. To our best knowledge, $[NbS(SCH_2CH_2S)(SCH_2CH_2SCH_2CH_2S)]^-$ may be the sole example for the whole transition elements .[9]

Treatment of **1** with an excess of $PhCH_2Br$ in benzene for 10 h at room temperature and recrystallization of the precipitates from CH_2Cl_2 and ether gave **2** as brick red crystals quantitatively. A similar alkylation of the terminal sulphide with MeI took place more readily and was completed in 1.5 h affording **3** as brick red crystals. In both cases the S-alkylation of the crown thioether was not observed. An attempt to prepare the PhS analogue



1

2 ; R=$PhCH_2$, X=Br

3 ; R=Me, X=I

through arylation with PhI failed even under more forced conditions (80 °C, 12 h in toluene). The cationic character of **3** was confirmed by anion exchange with $NaBPh_4$ to give the corresponding salt. The FAB MS spectrum (m/e, 3-nitrobenzylalcohol) of **2** and **3** shows the respective parent peak at 661 and 585. The presence of terminal sulphide was confirmed by the observation of a strong ν(Mo=S) band (**2**, 486; **3**, 484 cm^{-1}). The ^1H NMR spectra of **2** and **3** indicate that a syn-conformation of Me_8[16]aneS_4 in **1** is retained throughout the alkylation and only one geometrical isomer was produced stereoselectively among two possible diastereomers.[10] The relative position of terminal sulphido and MeS ligands at the two stereochemically different axial sites was determined unequivocally by the X-ray diffraction study of **3** (Fig. 1).[11]

The geometry about the Mo atom shows a slight pyramidal distortion from a regular octahedral coordination sphere with the syn-Me_8[16]aneS_4 ligand at the equatorial sites. The terminal sulphide occupies the congested axial site surrounded by the ring carbon atoms, while the methyl thiolate coordinates at the opposite uncongested site. From the trend of increasing p_π-donor ability of three sulfur donors, terminal sulphide>thiolate>thioether, the terminal sulphide and one of four thioethers are expected to be mutually in trans as observed in the Nb complex.[9] Therefore, the rather unusual trans disposition of the terminal sulphido and thiolato ligands may be rationallized by the tight coordination of the quadridentate crown thioether encircling the equatorial plane. The Mo-S distances range from the short Mo=S length (2.140(5) Å) to the long Mo-S(thioether) separations (average 2.459(5) Å). The shrinkage of the Mo=S bond compared to those (average 2.238(9) Å) found in **1** [7] is reflected in the higher ν(Mo=S) frequency than that (436 cm^{-1}) of **1** and is consistent with the weak p_π-donor ability of thiolato ligand compared to that of terminal sulfide and the cationic character of **3** as well. The pyramidal distortion of the Mo atom also facilitates the $p_\pi(S) \rightarrow d_\pi(Mo)$ donation; the Mo atom is displaced by 0.195(9) Å from the equatorial 4S plane toward the terminal sulphide, which is more extensive than the corresponding displacement (0.031(5) Å) of **1**. The S atoms of the crown thioether in **3** is nearly coplanar with the maximaum deviation from the least squares 4S plane of 0.009(4) Å. This stereoelectronic effect and strong π-donor ability of the terminal sulphide would in turn reduce π-interaction between the Mo atom and the thiolato S atom. Indeed, the Mo-SMe distance (2.440(6) Å) is significantly longer than those (2.31-2.36 Å) observed for octahedral Mo(IV) thiolato complexes.[12] The Mo-S (thioether) lengths are similar to those (average 2.483 (8) Å) observed for **1**.[7]

Why does the alkylation of the terminal sulphide take place specifically at the uncongested site ? Steric reasoning is excluded since the protonation of **1** with HX (X=OTf, BF_4) also proceeds regioselectively at the same terminal sulphide.[13] In view of the similarity of the Mo=S separations (2.245(8) and 2.232(9) Å) in **1**, their nucleophilicities would not differ so much as to achieve the complete discrimination. Here it is worth noting that the uncongested axial site surrounded by four lone pair orbitals of the macrocycle seems to be more

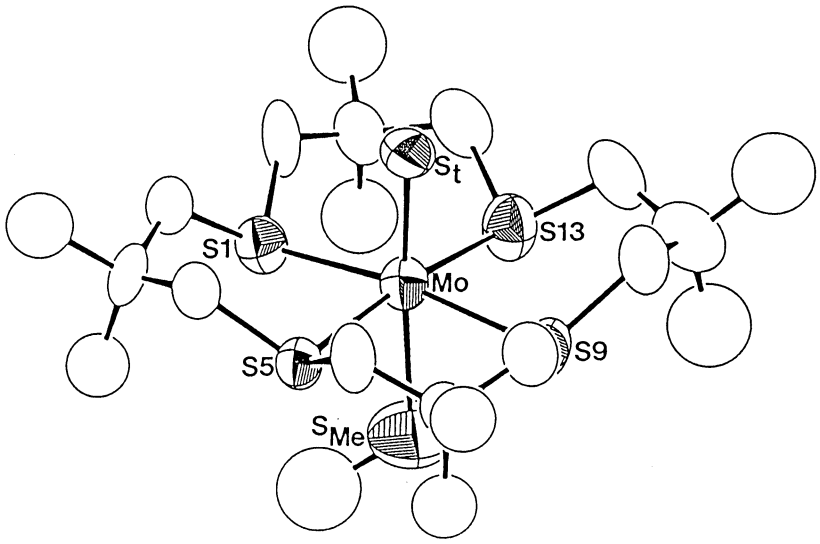


Fig. 1. Molecular structure of the cation of **3** showing 50% thermal ellipsoid. Selected bond lengths (Å) and angles (deg) are: Mo-S(1) 2.448(5), Mo-S(5) 2.452(5), Mo-S(9) 2.463(5), Mo-S(13) 2.474(5); S(1)-Mo-S(5) 88.1(2), S(1)-Mo-S(9) 170.5(2), S(1)-Mo-S(13) 91.3(2), S(5)-Mo-S(9) 91.0(2), S(5)-Mo-S(13) 171.4, S(9)-Mo-S(13) 88.2(2), S_t-Mo-S_{Me} 176.6(2)

electron rich than the opposite congested site. Therefore, it is reasonable to conclude that the stereoselective alkylation occurs due to the different electronic environment.

Further alkylation of the terminal sulfide in **2** and **3** with alkyl halides does not proceed, probably due to the low nucleophilicity as deduced from the short Mo=S separation and high ν(Mo=S) frequencies compared to the respective values of **1**.

This work was partly supported by a Grand-in-Aid for Scientific Research from the Japanese Ministry of Education, Sciences, and Culture (No. 02804050).

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10) ^{1}H NMR data for **2** ($CDCl_3$): δ1.38 (s, C*Me*), 1.42(s, C*Me*), 3.05 (d, *J* 11.4 Hz, SC*H*$_2$CMe$_2$), 3.77 (d, *J* 11.4 Hz, SC*H*$_2$CMe$_2$), 3.62 (s, SC*H*$_2$Ph), 7.00-7.20 (m, Ph). For **3** ($CDCl_3$): δ1,36 (s, C*Me*), 1.39 (s, C*Me*), 2.03 (s, S*Me*), 3.08 (d, *J* 11.4 Hz, SC*H*$_2$), 3.71 (d, *J* 11.4 Hz, SC*H*$_2$).

11) Crystal Data for the BPh_4 salt of **3**: $C_{45}H_{63}BS_6Mo \cdot 1/2C_6H_5CH_3 \cdot 1/4CH_2Cl_2$, monoclinic, space group $P2_1/a$, a=19.870(14), b=20.925(12), c=24.092(16) Å, β=91.25(5)°, U=10015(19) Å^3, Z=8, D_c=1.287 g cm^{-3}, μ(Mo-$K\alpha$)=5.53 cm^{-1}. The structure was solved by the Patterson method and the difference Fourier procedures, and refined by full-matrix least-squares methods to R (R_w)=0.054 (0.052) for 3905 independent significant reflections [$I > 6\sigma(I)$]. There are two crystallographically independent cations and BPh_4 anions, which are essentially similar. In each cation the C atom of the SMe group is disordered over two sites, the relative occupancies are 0.67 and 0.33.

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(Received September 28, 1992)