# Desulfurisation and ring opening of cyclic trithiocarbonates at a dimolybdenum centre

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The dimolybdenum alkyne complexes [Mo$_2$(μ-R^{1}C≡CR^1)(CO)$_4$(η-C$_5$H$_5$)$_2$] (R^1 = CO$_2$Me, Ph) react with 1,3-dithiole-2-thiones by cleavage of the C=S bond, ring opening of the resulting carbene and coupling with the alkyne ligand; one of the products, [Mo$_2$(μ-S)(μ-SCR^2=CR^{2}SCCR^{1}CR^1)(η-C$_5$H$_5$)$_2$] (R^1 = R^2 = CO$_2$Me), is structurally characterised.

The chemistry of 1,3-dithiole-2-thiones and related sulfur heterocycles has undergone a massive expansion in the last twenty years following the observation that certain charge-transfer salts of tetrathiafulvalene (TTF) and bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) (and their selenium analogues) exhibit conducting and superconducting properties.[1–3] The coupling of two five-membered 1,3-dithiole rings to form the central double bond is an important step in most TTF syntheses (Scheme 1), and is usually performed with P(OEt)$_3$; however yields can be variable, and the reaction often works better if X = O than if X = S, thus necessitating an extra synthetic step as the thiones are usually more easily available. Some time ago, metal carbonyls, most successfully [Co$_2$(CO)$_8$], were reported to effect desulfurisation and coupling of 1,3-dithiole-2-thiones to the corresponding TTF derivatives, with moderate yields.[4] In some cases, intermediate species were observed but no organometallic products were isolated.[5] We have therefore decided to examine the chemistry of such desulfurisation reactions with the ultimate aim of discovering an efficient, widely applicable reagent to effect thione coupling.
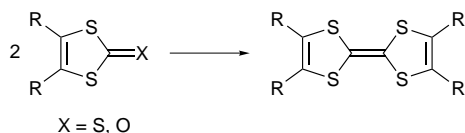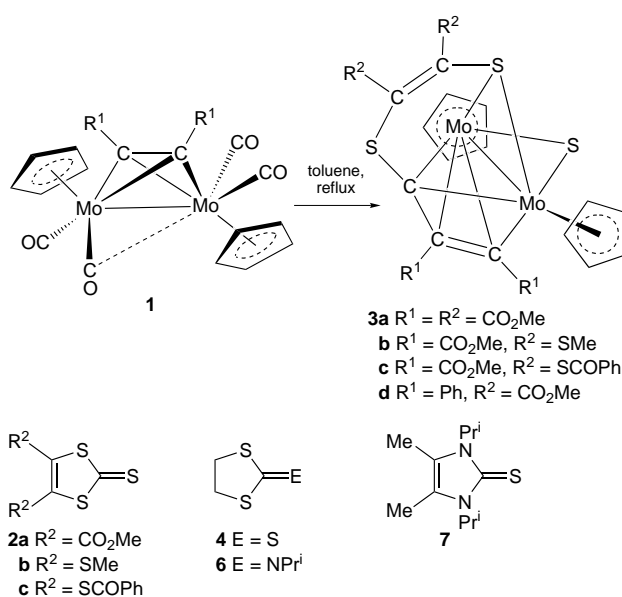

Scheme 1

During our investigation of the chemistry of the alkyne complexes [Mo$_2$(μ-R^{1}C≡CR^1)(CO)$_4$(η-C$_5$H$_5$)$_2$] **1** (R^1 = H, alkyl, aryl, CO$_2$Me, *etc.*), we have shown that their reactions with thiols differ markedly from those of the parent compounds [Mo$_2$(CO)$_n$(η-C$_5$H$_5$)$_2$] (n = 4, 6) in that C–S bond cleavage is a common occurrence, leading to sulfido-bridged complexes.[6,7] Here we demonstrate that cleavage of the C=S bond of 1,3-dithiole-2-thiones is also possible in this system, and moreover that it leads to the construction of novel sulfur-based ligands which incorporate the alkyne bridge.

Reaction of **1** (R^1 = CO$_2$Me) with 1 equiv. of 4,5-bis(carbomethoxy)-1,3-dithiole-2-thione **2a** in refluxing toluene over 5.5 h resulted in the formation of a single green product, **3a**, which was isolated by chromatography in 67% yield (Scheme 2). This complex displayed no metal carbonyl absorptions in its IR spectrum, and mass spectrometry indicated incorporation of one molecule of the heterocycle into the dimolybdenum complex with retention of the alkyne ligand. Its NMR spectra† displayed equivalent C$_5$H$_5$ ligands and four different methyl resonances (two of them coincident in the room-temperature ^{1}H NMR spectrum). Analogous complexes **3b** (R^2 = SMe) and **3c** (R^2 = SCOPh) were formed from **1** and heterocycles **2b** and **2c**

{derived from methylation or acylation of [NEt$_4$]$_2$[Zn(dmit)$_2$] respectively[2]} in comparable yields. Ethylene trithiocarbonate **4** also reacts with **1** to produce a similar complex, formulated as [Mo$_2$(μ-S)(μ-SCH$_2$CH$_2$SCCR^{1}CR^1)(η-C$_5$H$_5$)$_2$] **5**, showing that a saturated group linking the two sulfur atoms can be tolerated. Non-cyclic trithiocarbonates such as (BuS)$_2$C=S react with **1** over a longer time period to give closely related complexes, which will be described elsewhere.[8]

The result of an X-ray crystal structure determination of **3a** is shown in Fig. 1.‡ The two molybdenum atoms, which are linked by a rather short bond of 2.5825(7) Å, are bridged virtually symmetrically by the sulfur atom S(3), which has arisen through C=S bond cleavage of the thione group. The other bridging ligand is formed by ring opening of the five-membered heterocycle and linking of the original thione carbon to the alkyne; it is bonded through the bridging sulfur atom S(1) and through carbon atoms C(11)–C(13). This latter portion bridges the two metals in an allyl-type coordination, σ-bound to Mo(2) and π-bound to Mo(1). The observation of only one C$_5$H$_5$ resonance in the ^{1}H NMR spectrum of **3a** at both room temperature and low temperature (218 K) implies that there is a rapid fluxional process which interchanges the σ, π coordination modes of the allyl portion of the bridging ligand.

The newly assembled ligand is formally tetraanionic, with the result that the two molybdenum atoms are both formally Mo^{IV}. Indeed, the molecular geometry is strongly reminiscent of that found in the quadruply bridged Mo^{IV} compounds [Mo$_2$(μ-S)$_2$(μ-SMe)$_2$(η-C$_5$H$_5$)$_2$][9] and [Mo$_2$(μ-S)$_2$(μ-SPr^i)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$].[10] Thus, the atoms Mo(1), Mo(2), S(1) and C(11) form a plane (maximum deviation 0.0000 Å) which within experimental error intersects at an angle of 90° with the plane formed by Mo(1), Mo(2), S(3) and C(13) (maximum deviation 0.0176 Å).
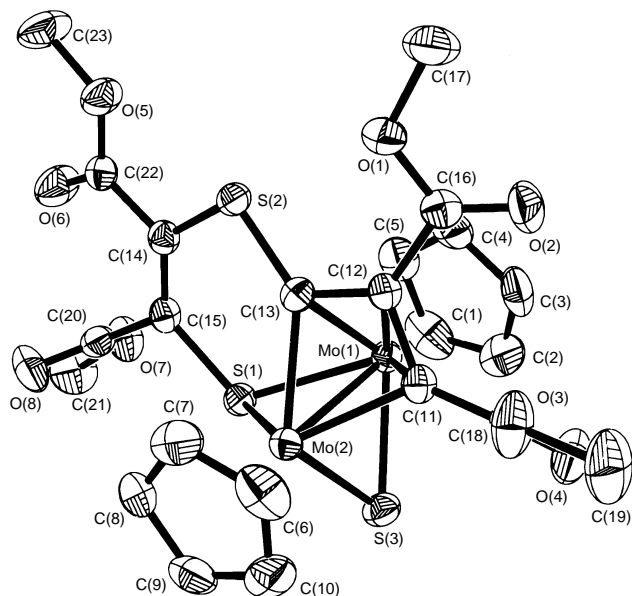

Scheme 2

Fig. 1 Molecular structure of complex **3a** in the crystal. Selected bond lengths (Å): Mo(1)–Mo(2) 2.5825(7), Mo(1)–S(3) 2.343(2), Mo(2)–S(3) 2.325(2), Mo(1)–S(1) 2.4594(14), Mo(2)–S(1) 2.471(2), Mo(1)–C(11) 2.176(5), Mo(1)–C(12) 2.360(5), Mo(1)–C(13) 2.223(5), Mo(2)–C(11) 2.162(5), Mo(2)–C(13) 2.200(5), C(11)–C(12) 1.416(7), C(12)–C(13) 1.415(7), C(14)–C(15) 1.349(7).

We propose that the initial step in the reaction is loss of a CO ligand and coordination of the heterocycle followed by cleavage of the C=S bond to produce the sulfido ligand and a coordinated dithiocarbene; coupling of the carbene ligand to the alkyne and ring opening by cleavage of one C–S bond would give the observed product. Dithiolium carbenes such as those derived from **2a–c** are pseudo-aromatic and thought to be relatively stable: they can be trapped in the reactions of CS_2 with activated alkynes[11] and can also be stabilised at a variety of metal centres.[12] Moreover formation of dithiocarbene ligands by desulfurisation of trithiocarbonates, including **4**, has previously been observed in reactions with iron carbonyls,[13] and an example of thioketone C=S bond cleavage at an alkoxide-ligated dimolybdenum centre leading to a bridging sulfido ligand and a terminal diarylcarbene has recently been reported.[14]

Further experiments to delineate the scope of the reaction have shown that all three sulfur atoms of the trithiocarbonate group appear to be necessary for successful product formation. Thus, neither the related 2-imino-1,3-dithiole **6** nor the tetraalkyl imidazole 2-thione **7** gave any tractable product. Changing the alkyne ligand in complex **1** also has a detrimental effect: so far only $[Mo_2(\mu\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ has given an analogous complex $[Mo_2(\mu\text{-}S)\{\mu\text{-}SC(CO_2Me)=C(CO_2Me)\text{-}SCCPhCPh\}(\eta\text{-}C_5H_5)_2]$ **3d** on treatment with **2a**.

Further studies on the reactivity of these novel compounds are currently in progress.

Footnotes

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† *Spectroscopic data* (NMR in CDCl$_3$, all signals are singlets unless otherwise stated). Satisfactory elemental analyses were obtained for all new compounds.

3a: mp 200–203 °C. ¹H NMR δ 5.75 (10 H, C$_5$H$_5$), 3.88 (3 H, Me), 3.87 (6 H, 2 × Me), 3.60 (3 H, Me); ¹³C NMR δ 173.4, 168.5, 164.1, 161.5 (all *C*O$_2$Me), 134.5, 132.6 (both C*C*O$_2$Me), 112.9, 111.4 (2 *C*CO$_2$Me), 108.4 (µ-C), 99.8 (C$_5$H$_5$), 53.3, 53.2, 52.8, 52.2 (all Me); MS *m/z* 715 (M⁺), 572. **3b**: mp 200–202 °C. ¹H NMR δ 5.78 (10 H, C$_5$H$_5$), 3.85, 3.58 (both 3 H, OMe), 2.52, 2.48 (both 3 H, SMe); ¹³C NMR δ 174.0, 161.9 (both CO$_2$Me),

137.0, 124.3 (both *C*SMe), 110.7, 110.4 (both *C*CO$_2$Me), 109.9 (µ-C), 99.7 (C$_5$H$_5$), 52.6, 52.0 (both OMe), 20.2, 19.8 (both SMe); MS *m/z* 691 (M⁺), 572. **3c**: mp 168–170 °C. ¹H NMR δ 7.96–7.37 (m, 10 H, Ph), 5.94 (10 H, C$_5$H$_5$), 3.85, 3.60 (both 3 H, Me); ¹³C NMR δ 189.3, 188.1 (both COPh), 173.8, 161.5 (both *C*O$_2$Me), 136.4–127.6 (m, Ph), 136.2, 125.4 (both *C*SCOPh), 112.1, 110.7, 110.2 (2 *C*CO$_2$Me + µ-C), 100.2 (C$_5$H$_5$), 52.7, 52.1 (both Me); MS *m/z* 871 (M⁺), 573. **5**: mp 172–173 °C. ¹H NMR δ 6.03 (10 H, C$_5$H$_5$), 3.75, 3.48 (both 3 H, Me), 2.72, 2.29 (both m, 2 H, CH$_2$); ¹³C NMR δ 174.5, 162 3 (both *C*O$_2$Me), 123.1, 111.4 (both *C*CO$_2$Me), 104.6 (µ-C), 99.7 (C$_5$H$_5$), 52.2, 51.7 (both Me), 35.9, 29.8 (both CH$_2$); MS *m/z* 601 (M⁺), 573.

‡ *Crystal data* for **3a**: C$_{23}$H$_{22}$Mo$_2$O$_8$S$_3$, M = 714.47, monoclinic, space group P2$_1$/c (C$_{2h}^5$, no. 14), a = 17.994(4), b = 8.4820(10), c = 16.713(4) Å, β = 98.97(3)°, U = 2519.6(9) Å³, $F(000)$ = 1424, Mo-Kα radiation ($\overline{\lambda}$ = 0.71073 Å), μ(Mo-Kα) = 1.291 mm⁻¹, Z = 4, D_c = 1.883 g cm⁻³.

Three-dimensional, room-temperature X-ray data were collected in the range 3.5 < 2θ < 50° on a Siemens P4 diffractometer by the ω-scan method. Of the 5513 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by the analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.486 and 0.908), 3605 independent reflections exceeded the significance level $|F|/\sigma(|F|)$ > 4.0. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0393 (wR_2 = 0.1625 for all 4377 unique data, 325 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.775 and 0.827 e A⁻³. A weighting scheme w = 1/[$\sigma^2(F_o^2)$ + $(0.0748P)^2$ + 0.00P] where P = $(F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93[15] as implemented on the Viglen 486dx computer. CCDC 182/493.

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