

Desulfurisation of trithiocarbonates at a dimolybdenum centre: an unexpected insertion into a co-ordinated alkyne

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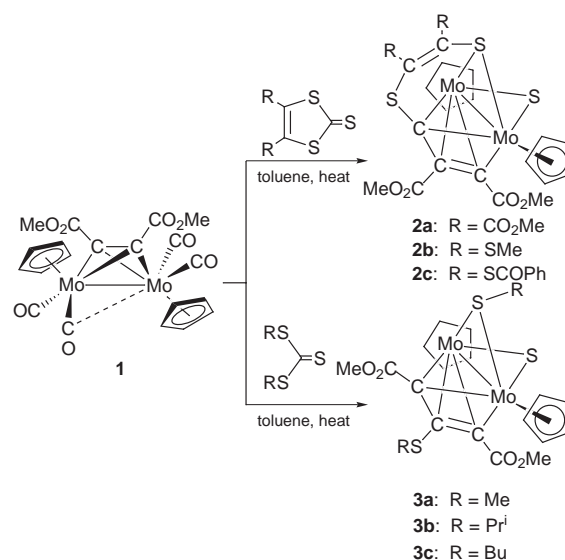
On reaction with the dimolybdenum alkyne complex $[\text{Mo}_2\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$, dialkyl trithiocarbonates $(\text{RS})_2\text{C}=\text{S}$ were dismantled into sulfido ($\mu\text{-S}$), thiolate ($\mu\text{-SR}$) and CSR fragments; remarkably the last of these inserts into the middle of the alkyne to produce a dimetalla-allyl species with a $\mu\text{-C}(\text{CO}_2\text{Me})\text{C}(\text{SR})\text{C}(\text{CO}_2\text{Me})$ ligand.

The desulfurisation of organic molecules is an important process which finds widespread application in organic synthesis and materials chemistry, in particular the formation of tetrathiafulvalenes by phosphite-induced coupling of two sulfur heterocycles.¹ Recently we described the unusual reaction of the dimolybdenum alkyne complex $[\text{Mo}_2\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ **1** with cyclic trithiocarbonates (1,3-dithiole-2-thiones) $\text{S}=\text{CS}_2\text{C}_2\text{R}_2$ ($\text{R} = \text{CO}_2\text{Me}$, SMe or SCOPh) to produce complexes **2**, in which the C=S bond had been cleaved to produce a $\mu\text{-sulfido}$ ligand and a complex organic fragment derived by ring opening of the heterocycle and coupling with the alkyne ligand (Scheme 1).² Subsequently we showed that further reaction of **2** with sulfur produced dithiolene complexes in which the C_2R_2 backbone of the original heterocycle was incorporated into the dithiolene ligand.³ Here we describe the reaction of **1** with acyclic dialkyl trithiocarbonates which sheds further light on the mechanism of the processes involved.

Treatment of **1** with 1 equivalent of the trithiocarbonates $(\text{RS})_2\text{C}=\text{S}$ ($\text{R} = \text{Me}$, Pr^i or Bu) in refluxing toluene for 48 h followed by column chromatography afforded green complexes **3** as the only isolable products (Scheme 1), though yields in general were lower than those of **2**. Spectroscopic characterisation[‡] indicated that **3** had a structure very similar to **2**, though with certain differences. Crystals of **3a** suitable for X-ray diffraction were obtained from dichloromethane and diethyl ether solution.[§] The structure is shown in Fig. 1, with selected bond lengths given in the caption. There are two independent molecules in the unit cell, but the only significant difference between

them lies in the position of C(13), which in one molecule is almost equidistant from the two metal atoms, but in the other is displaced towards one molybdenum; the former molecule is shown in Fig. 1 and the bond lengths quoted refer to this.

The basic structure is indeed very similar to that of **2** and incorporates the now familiar quadruply-bridged Mo^{IV} motif. The two molybdenum atoms are joined by a bond of 2.5605(10) Å, even shorter than the 2.5825(7) Å observed in **2a**, and are bridged symmetrically by the sulfido ligand S(3) and by the methanethiolate sulfur S(1). The methyl substituent on the bridging thiolate group is pointing away from the dimetalla-allyl ligand, whereas in **2** it is constrained to point towards it by the linking chain. The main point of interest however lies in the dimetalla-allyl ligand itself. By analogy with **2** we had expected the carbon atom derived from the trithiocarbonate to be situated at the terminus of this ligand, *i.e.* $\mu\text{-C}(\text{SMe})\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})$. Instead, remarkably, it occupies the central position in a $\mu\text{-C}(\text{CO}_2\text{Me})\text{C}(\text{SMe})=\text{C}(\text{CO}_2\text{Me})$ arrangement. Although in the molecule shown all three carbons of this ligand are equidistant from both metal atoms within experimental error, the bonds from the metals to the central carbon C(13) are much longer than those to the terminal carbons C(11) and C(12). The ¹³C NMR spectrum of **3a** contains three peaks at δ 141.2, 102.7 and 98.0 assigned to the carbons of the dimetalla-allyl ligand. This can be compared with **2a–2c**, where all three peaks occur with very similar shifts in the region δ 108–113. Since the two terminal carbons C(11) and C(12) are



Scheme 1

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[‡] Spectroscopic data (NMR in CDCl₃, all signals are singlets unless otherwise stated). Satisfactory elemental analyses were obtained for all new compounds. **3a**: green solid, 51% yield, m.p. 184–200 °C (decomp). ¹H NMR: δ 5.94 (10 H, C₅H₅), 3.67, 3.53 (both 3 H, CO₂Me), 2.18, 1.97 (both 3 H, SMe). ¹³C NMR (–60 °C): δ 176.3, 175.5 (both CO₂Me), 141.2 (CSMe), 102.7 (CCO₂Me), 99.6 (C₅H₅), 98.0 (CCO₂Me), 52.8, 52.1 (both CO₂Me), 46.3 ($\mu\text{-SMe}$), 13.7 (SMe). MS: m/z 603 (M^+). **3b**: green solid, 24% yield, m.p. 132–133 °C. ¹H NMR: δ 5.92 (10 H, C₅H₅), 3.66 (3 H, CO₂Me), 3.52 (spt, 1 H, $J = 6.6$, CH), 3.49 (3 H, CO₂Me), 1.19 (d, 6 H, $J = 6.6$, Me), 1.09 (d, 6 H, $J = 6.7$, Me), 0.49 (spt, 1 H, $J = 6.7$ Hz, CH). ¹³C NMR: δ 175.3, 174.8 (both CO₂Me), 140.9 (CSP^r), 103.1 (CCO₂Me), 99.2 (C₅H₅), 98.1 (CCO₂Me), 69.3 (CH), 52.1, 51.6 (both CO₂Me), 34.5 (CH), 28.4, 23.8 (both Me). MS: m/z 659 (M^+). **3c**: green oil, 26% yield. ¹H NMR: δ 5.92 (10 H, C₅H₅), 3.66, 3.52 (both 3 H, CO₂Me), 2.70 (t, 2 H, $J = 7.3$, CH₂), 1.81 (t, 2 H, $J = 7.6$, CH₂), 1.55–1.08 (m, 8 H, CH₂), 0.88 (t, 3 H, $J = 7.2$, Me), 0.78 (t, 3 H, $J = 7.2$ Hz, Me). ¹³C NMR: δ 175.3, 174.9 (both CO₂Me), 140.8 (CSBu), 102.9 (CCO₂Me), 99.2 (C₅H₅), 98.7 (CCO₂Me), 63.5 (CH₂), 52.0, 51.5 (both CO₂Me), 37.7, 31.2, 29.7, 21.9, 21.8 (all CH₂), 13.7, 13.6 (both Me). MS: m/z 688 (M^+).

[§] Crystal data for **3a**: C₁₉H₂₂Mo₂O₄S₃, $M = 602.43$, monoclinic, space group $P2_1/n$ (a non-standard setting of $P2_1/c$, C_{2h}^2 , no. 14), $a = 10.086(3)$, $b = 13.077(3)$, $c = 33.601(7)$ Å, $\beta = 95.00(2)^\circ$, $U = 4415(2)$ Å³, $Z = 4$, Mo-K α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-K}\alpha) = 1.442$ mm⁻¹, $T = 293(2)$ K; 10 070 reflections measured, 7770 independent reflections ($R_{\text{int}} = 0.0331$), $R1 = 0.0406$ for 7765 unique data. CCDC reference number 186/1070. See <http://www.rsc.org/suppdata/dt/1998/2607> for crystallographic files in .cif format.

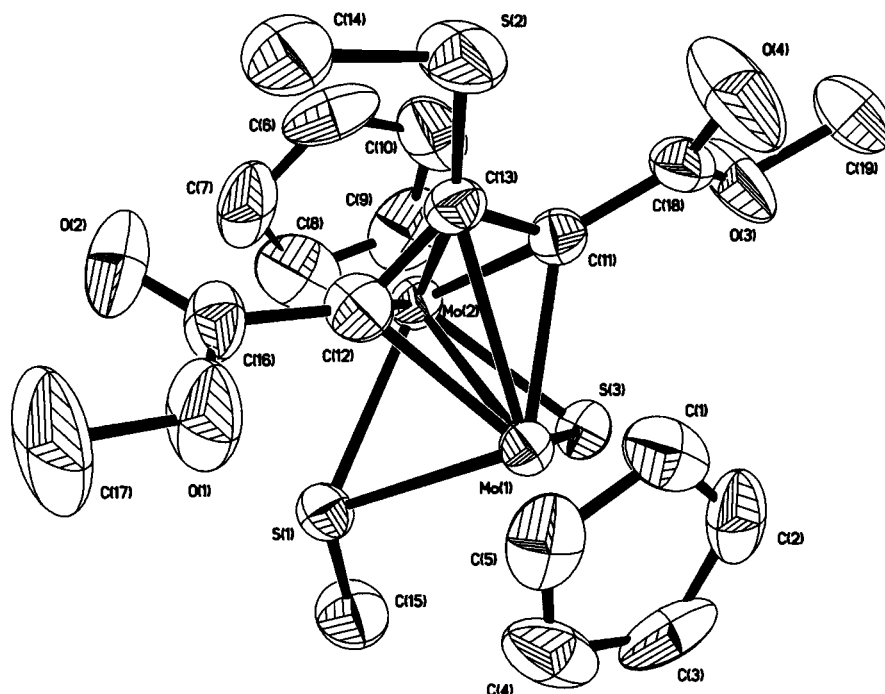
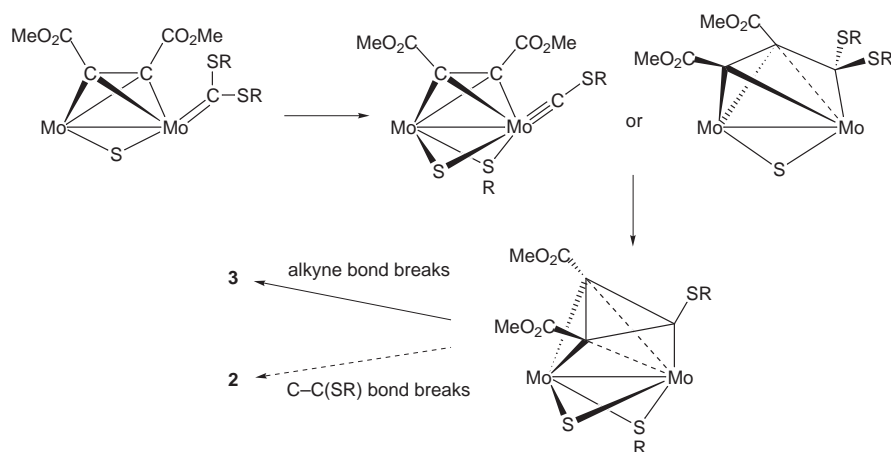


Fig. 1 Molecular structure of one of the two independent molecules of complex **3a** in the crystal (50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å): Mo(1)–Mo(2) 2.5605(10), Mo(1)–S(1) 2.476(2), Mo(2)–S(1) 2.466(2), Mo(1)–S(3) 2.318(2), Mo(2)–S(3) 2.322(2), Mo(1)–C(11) 2.173(5), Mo(2)–C(11) 2.152(5), Mo(1)–C(12) 2.204(6), Mo(2)–C(12) 2.203(6), Mo(1)–C(13) 2.564(5), Mo(2)–C(13) 2.594(6), C(11)–C(13) 1.429(7), C(12)–C(13) 1.393(8)



Scheme 2

in very similar environments, we assign the low field ^{13}C NMR signal to the central CSMe feature.

In the molecule shown C(13) is within bonding distance of both metals, but in the second molecule there is one short distance, Mo(1A)–C(13A) [2.509(6) Å] and one which is much longer, Mo(2A)–C(13A) [2.645 Å]. As in complex **2**, the observation of equivalent $\eta\text{-C}_5\text{H}_5$ ligands in the NMR spectra of **3**, even at low temperature, implies that a fluxional process is occurring in solution in which the central carbon of the dimetalla-allyl ligand is flipping back and forth between the two metal atoms, rendering them equivalent. The observation of two molecules in the unit cell which differ only in the position of C(13) (and its associated substituent) provides additional evidence that this trajectory is plausible, since the energy difference between these two positions is evidently small.

In our previous paper we hypothesized that the first step of the reaction mechanism was loss of a CO ligand, co-ordination of the thione group and cleavage of the C=S bond to give a dithiocarbene.² This was followed by coupling of the carbene carbon to the alkyne and cleavage of one of the C–S bonds.

Obviously this mechanism is inadequate to explain the formation of **3**, though it may still be correct for **2**. We now propose that, after carbene formation, cleavage of the C–S bond occurs either before or after coupling with the alkyne, leading ultimately to the formation of a three-membered ring (Scheme 2). Cleavage of the C–C bond of the alkyne would then provide the observed product **3**. Positioning of the CSR group in the centre of the dimetalla-allyl fragment is not possible in the case of **2** because it is anchored to the thiolate bridge through the spacer group, but this mechanism could still account for the formation of **2** by scission of one of the two C(CO₂Me)–C(SR) bonds of the three-membered ring.

The apparent insertion of carbyne ligands into the centre of an alkyne is not without precedent. For example, treatment of $[\text{WFe}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me})(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ with C_2Ph_2 gave two dimetalla-allyl complexes, one of which was $[\text{WFe}\{\mu\text{-CPhC}(\text{C}_6\text{H}_4\text{Me})\text{CPh}\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ with a rearranged chain.⁴ Moreover the compound $[\text{W}_2(\mu\text{-CSiMe}_3)(\mu\text{-CMe-CMeSiMe}_3)(\text{CH}_2\text{SiMe}_3)_4]$, reported by Chisholm *et al.*, was found to undergo a fluxional process in which the substituents of

the bridging ligand changed places, *i.e.* CMeCMeCSiMe₃ interconverted with CMeC(SiMe₃)CMe, for which a similar three-membered ring intermediate was proposed.⁵ Other examples involving dimetalla-allyl ligands are known on trinuclear metal centres.⁶

Further studies on the reactivity of the unusual species **2** and **3** are currently in progress in our laboratory.

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