Two versatile new routes to dinuclear molybdenum dithiolene complexes

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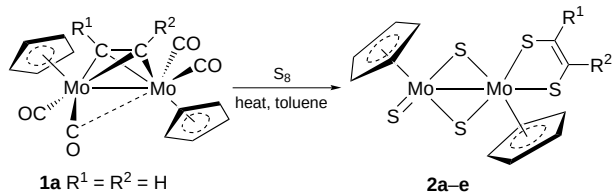
Two routes to the dithiolene complexes [$Mo_2S(\mu\text{-}S)_2(SCR^1{=}CR^2S)(\eta\text{-}C_5H_5)_2$] starting from the complexes [$Mo_2(\mu\text{-alkyne})(CO)_4(\eta\text{-}C_5H_5)_2$] are described; in one case the dithiolene ligand is derived from the alkyne, and in the other from a 1,3-dithiole-2-thione reagent.

A combination of techniques have indicated that the molybdenum atom in the molybdenum cofactor (Moco) common to a range of oxotransferase enzymes is coordinated by a pterin ligand which is bonded through a dithiolene linkage.[1] Recent protein crystallographic studies, however, have shown that in some of these enzymes the metal atom is ligated by one dithiolene ligand whereas in other cases, unexpectedly, two such ligands were present.[2] Molybdenum (and tungsten) dithiolene complexes have been known for many years,[3] and are of continuing interest as model systems for the metal site in the cofactor.

Here, we describe two versatile routes to dimolybdenum complexes containing terminal dithiolene or tetrathiooxalate ligands, both of which start with the alkyne complexes [$Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4(\eta\text{-}C_5H_5)_2$] **1a–e**. We have recently shown that reactions of these compounds with thiols often proceed with C–S bond cleavage to give sulfido-bridged species.[4] In contrast, it is notable that the reactions discussed here involve the formation of C–S bonds as well as their scission.

In the first approach we found that heating a toluene solution of **1** with elemental sulfur for 5 h provided the green dithiolene complexes [$Mo_2S(SCR^1{=}CR^2S)(\mu\text{-}S)_2(\eta\text{-}C_5H_5)_2$] **2a–e** in yields of up to 80% after isolation by column chromatography (Scheme 1). Five representative examples are given but the reaction works equally well with other complexes of type **1**. Complex **2c** and the corresponding oxo species [$Mo_2O(SCH{=}CPhS)(\mu\text{-}S)_2(\eta\text{-}C_5H_5)_2$] **3** have been prepared previously by a different route,[5] but in contrast to this report we find that complexes of type **2** are not particularly air sensitive even in solution, and only slowly convert into the oxo complexes analogous to **3**; small amounts of these were isolated from some reactions.

The dithiolene compounds were characterised spectroscopically (and by comparison with the published values for **2c**, for which our data agree exactly).† In the ^1H NMR spectrum each complex displays two rather widely separated signals for the C_5H_5 rings and appropriate resonances for the substituents R^1 and R^2. In the complexes derived from terminal alkynes, the signal for the CH group appears shifted downfield at δ 8–9. This is a characteristic feature of terminal dithiolene complexes and can be regarded as arising either from the contribution of a dithioglyoxal canonical form[6,7] or the presence of a ring current in the pseudo-aromatic metalladithiolene unit.[8] Interestingly the products all gave high intensity molecular ions in their electron impact mass spectra, but most evidently disintegrated completely when subjected to fast atom bombardment (FAB).



1a $R^1 = R^2 = H$
b $R^1 = H$, $R^2 = Me$
c $R^1 = H$, $R^2 = Ph$
d $R^1 = R^2 = Et$
e $R^1 = R^2 = CO_2Me$

2a–e

Scheme 1

The result of an X-ray crystal structure determination of **2a** is shown in Fig. 1.‡ The molecule is based on a dimolybdenum centre with a metal–metal distance of 2.984(1) Å, which is similar to that of 2.927(1) Å observed in [$Mo_2O(SCH{=}CPhS)(\mu\text{-}S)_2(\eta\text{-}C_5H_5)_2$] **3**.[5] The coordination geometry in the two complexes is also very similar. Thus Mo(1) has a pseudo-tetrahedral coordination (if the C_5H_5 ligand is regarded as occupying one site) whereas Mo(2) is in a square pyramidal environment. The $Mo_2(\mu\text{-}S)_2$ core is not planar: the dihedral angle between the two intersecting Mo_2S planes is 161.3°, whereas in **3** the corresponding angle is 144.6°. This contrasts with related Mo^V dimers with imido ligands, *e.g.* [$Mo_2(NPh)_2(\mu\text{-}NPh)_2(\eta\text{-}C_5H_4Me)_2$] which all contain strictly planar cores.[9]

The bond lengths between Mo(2) and the bridging sulfur atoms are significantly longer than the distances from Mo(1) to the same sulfurs. Together with the rather short S(4)–C(11) and S(5)–C(12) bonds within the dithiolene ligand itself, this could be regarded as evidence for some contribution of the dithioglyoxal canonical form: if the dithiolene ligand is dianionic, each Mo atom is formally Mo^V, but if it is bonded in the dithioglyoxal form, Mo(2) would be formally Mo^{III}. Again an alternative interpretation is that the dithiolene ligand acts as a delocalised 6π pseudo-aromatic system which is a better π-donor than the sulfide ligand on Mo(1).

Our second approach is shown in Scheme 2. We recently reported that alkyne complex **1e** reacted 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 to

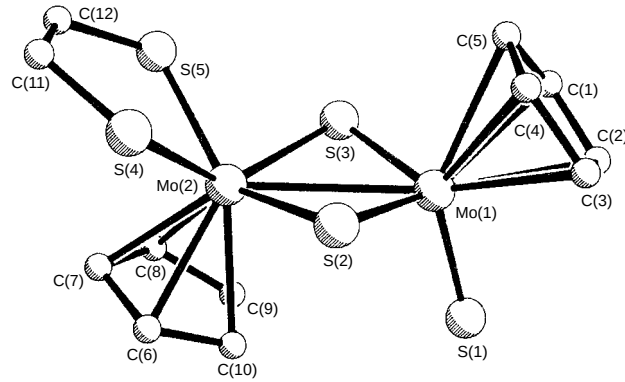
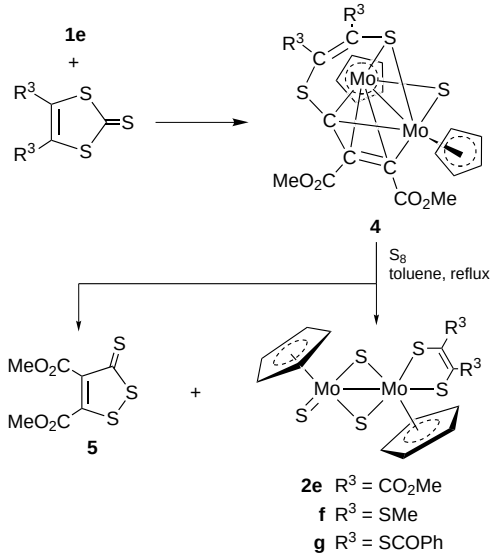


Fig. 1 Molecular structure of complex **2a** in the crystal. Selected bond lengths (Å): Mo(1)–Mo(2) 2.984(1), Mo(1)–S(1) 2.154(1), Mo(1)–S(2) 2.263(1), Mo(1)–S(3) 2.263(1), Mo(2)–S(2) 2.406(1), Mo(2)–S(3) 2.398(1), Mo(2)–S(4) 2.387(1), Mo(2)–S(5) 2.384(1), S(4)–C(11) 1.708(5), S(5)–C(12) 1.705(4), C(11)–C(12) 1.348(7).



Scheme 2

produce complexes of type **4** (R^3 = CO_2Me, SMe, SCOPh).[10] Remarkably, we have now discovered that these compounds also react rapidly (2 h) with elemental sulfur in boiling toluene to give dithiolene complexes **2e**–**g**, in which the dithiolene ligand originates from the backbone of the original thione rather than the alkyne. Compounds **2f** and **2g** are rare examples of dialkyl- and diacyl-tetrathiooxalate (or ethenetetrathiolate) complexes respectively.

The alkyne ligand is recovered in the form of the interesting new sulfur heterocycle **5**, a hitherto inaccessible derivative of the important 1,2-dithiole-3-thione ring system.[11] Indeed, in the case of R^3 = CO_2Me, the reaction represents an elaborate isomerisation of the 1,3-dithiole-2-thione ring. The mechanism presumably involves insertion of three sulfur atoms into the Mo–C bonds of the bridging ligand of **4**, cleavage of the μ-C–S bond to afford the dithiolene ligand, and reductive elimination of the organic by-product **5**. It is notable that this process reforms the thione unit which is cleaved during the formation of **4**.

In summary, the two synthetic routes described here are complementary: simple dithiolene ligands are easily accessed from the appropriate alkyne by the first method, whereas in the second case the availability of convenient synthetic procedures for a large number of requisite thiones, which are readily made by alkylation or acylation of $[NEt_4]_2[Zn(C_3S_5)_2]$, should enable the introduction of a wide variety of more complex substituents including functionalised derivatives such as crown ethers, macrocycles, *etc*. Moreover, compounds containing the 1,2-dithiole-3-thione ring system have been studied for their pharmaceutical properties, particularly as anticancer agents. We are currently exploiting this methodology to synthesize a representative range of dithiolene complexes and heterocycles for further investigation.

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Notes and References

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† *Selected spectroscopic data*: (NMR in $CDCl_3$, all signals are singlets unless otherwise stated). Satisfactory elemental analyses were obtained for all new compounds.

2a: yield 64%. mp 196–198 °C. ^{1}H NMR δ 8.37 (2 H, CH), 6.00 (5 H, C_5H_5), 5.38 (5 H, C_5H_5); ^{13}C NMR δ 149.5 (CH), 103.7 (C_5H_5), 100.1 (C_5H_5); MS *m*/*z* 508 (M^+), 482 ($M - C_2H_2^+$). The dithiolene complexes **2a**–**f** all show peaks at *m*/*z* 450, 418, 386, 353 and 323 ($Mo_2S_{4-n}Cp_2^+$, n = 0–4) in the EI mass spectrum.

2b: yield 54%. mp 234 °C (decomp.). ^{1}H NMR δ 8.00 (1 H, CH), 6.00 (s, 5 H, C_5H_5), 5.40 (5 H, C_5H_5), 2.80 (3 H, Me); ^{13}C NMR δ 163.0 (CMe), 145.6 (CH), 103.6 (C_5H_5), 100.1 (C_5H_5), 23.4 (Me). MS *m*/*z* 522 (M^+), 482 ($M - HC_2Me^+$).

2d: yield 70%. mp 232–233 °C. ^{1}H NMR δ 6.00 (5 H, C_5H_5), 5.35 (5 H, C_5H_5), 3.10 (dq, *J* 7 Hz, 2 H, 1 H of CH_2), 2.85 (dq, *J* 7 Hz, 2 H, 1 H of CH_2), 1.55 (t, *J* 7 Hz, 6 H, Me); ^{13}C NMR δ 163.2 (CEt), 103.6 (C_5H_5), 100.0 (C_5H_5), 29.8 (CH_2), 16.6 (Me); MS *m*/*z* 564 (M^+), 532 ($M - S^+$), 482 ($M - C_2Et_2^+$).

2e: yield 80%. mp > 250 °C. ^{1}H NMR δ 6.00 (5 H, C_5H_5), 5.50 (5 H, C_5H_5), 3.87 (s, 6 H, Me); ^{13}C NMR δ 165.1 (CO_2Me), 154.7 (CCO_2Me), 103.8 (C_5H_5), 100.9 (C_5H_5), 53.0 (Me); MS *m*/*z* 624 (M^+), 592 ($M - S^+$), 482 [$M - C_2(CO_2Me)_2^+$].

2f: yield 66%. mp 230 °C (decomp.). ^{1}H NMR δ 6.02 (5 H, C_5H_5), 5.40 (5 H, C_5H_5), 2.70 (6 H, Me); ^{13}C NMR δ 153.6 (*C*SMe), 103.7 (C_5H_5), 100.2 (C_5H_5), 19.3 (Me); MS *m*/*z* 600 (M^+).

2g: yield 58%. mp 214 °C. ^{1}H NMR δ 8.03–7.43 (m, 10 H, Ph), 6.03 (5 H, C_5H_5), 5.84 (5 H, C_5H_5); ^{13}C NMR 189.4 (COPh), 151.4 (*C*SCOPh), 136.4 (C_{ipso}), 133.8–127.7 (m, Ph), 103.7 (C_5H_5), 101.4 (C_5H_5); FAB MS *m*/*z* 780 (M^+).

5: Yield 70%. mp 93–94 °C. ^{1}H NMR δ 3.97 (3 H, Me), 3.95 (3 H, Me); ^{13}C NMR δ 210.4 (C=S), 162.7, 159.4 (both CO_2Me), 156.1, 146.2 (both CCO_2Me), 54.4, 53.7 (both Me); MS *m*/*z* 250 (M^+).

‡ *Crystal data* for **2a**: $C_{12}H_{12}Mo_2S_5$, M = 508.40, monoclinic, space group *C*2/*c* (no. 15), a = 22.2528(29), b = 11.0848(21), c = 12.9379(26) Å, β = 105.933(15)°, U = 3068.7(9) Å^3, F(000) = 1984, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 22.34 cm^{-1}, Z = 8, D_c = 2.20 g cm^{-3}.

Room temperature X-ray data were collected on a Nicolet R3mV diffractometer. A total of 3937 reflections (3779 unique) were measured in the range $5 < 2\theta < 50°$ by the ω–2θ scan technique, all of which were corrected for Lorentz and polarisation effects and for absorption by analysis of ψ-scans (minimum and maximum transmission coefficients 0.806 and 0.913); 2634 data with $I \geqslant 3.0\sigma(I)$ were used in the refinement. The structure was solved by direct methods and developed by alternating cycles of least squares refinement and difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 Å^2). The last cycle of least squares refinement included 172 parameters for 2497 variables. The final R values were R = 0.035 and R_w = 0.042 and the final difference Fourier map contained no peaks > 1.00 e Å^{-3}. The structure was solved using the SHELXTL PLUS program package[12] on a Micro Vax II computer. CCDC 182/722.

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