Alkyne addition across imido and sulfido moieties: molecular structure of the 1-thio-2-iminoene complex [Mo{η²-PhNC(R)= C(R)S}{η¹,η³-SC(R)=C(R)C(NEt₂)S}(S₂CNEt₂)] (R = CO₂Me)

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Thermolysis of [Mo(η²-S₂)(NPh)(S₂CNEt₂)₂] with dimethyl acetylenedicarboxylate afforded the crystallographically characterised 1-thio-2-iminoene complex [Mo{η²-PhNC(R)=C(R)S}{η¹,η³-SC(R)=C(R)C(NEt₂)S}-(S₂CNEt₂)] (R = CO₂Me), resulting from alkyne addition across sulfido and phenylimido moieties and further insertion of alkyne into the sulfur–carbon bond of a dithiocarbamate ligand.

Complexes containing the 1,2-dithiolene ligand have attracted widespread attention primarily due to their ability to form extended π systems resulting from delocalisation of electrons between the metal and ligand.[1] In this context, their electronic structures have provoked a great deal of controversy, the dithiolene formulation being the most apt description when bound to low-valent metal centres, while a 1,2-dithiolato form is preferred at high-valent centres. Similarly, a wide range of complexes containing the isoelectronic α-diimine ligand have also been prepared, although here the neutral diimine formulation appears generally to be the best ligand description.[2]

Somewhat surprisingly, given the extensive chemistry of 1,2-dithiolene and α-diimine ligands, hybrid 1-thio-2-iminoene complexes are relatively rare and appear to be limited specifically to the 2-aminobenzenethiolate ligand. Complexes of this type include [Ni(HNC₆H₄S)₂],[3] [Mo(HNC₆H₄S)₂(S₂CNEt₂)],[4] [Mo(HNC₆H₄S)₃],[5] [Co(η-C₅H₅)(HNC₆H₄S)],[6] [Tc(HNC₆-H₄S)₃],[7] [TcO(HNC₆H₄S)₂]⁻ [8] and [Re(HNC₆H₄S)₃].[9] This limitation to the benzene backbone is a consequence of the use of commercially available 2-aminobenzenethiol as the ligand precursor. While a number of synthetic methods have been adopted towards the synthesis of 1,2-dithiolene complexes, one often used is the addition of activated alkynes across two sulfido moieties[10] or the sulfur–sulfur bond of a disulfide ligand.[11,12] Potentially, this approach could be modified to produce 1-thio-2-iminoene complexes *via* alkyne addition across sulfido and imido moieties, however to date this has not been achieved.

Dithiocarbamate is widely employed in transition-metal chemistry as a stable ligand which is capable of supporting metal centres in a wide range of oxidation states.[13] There are, however, an increasing number of examples in which the ligand is found to act in a non-innocent fashion, generally resulting from the cleavage of one or both carbon–sulfur bonds.[14,15] Recently, Young *et al.*[12] described novel transformations of a dithiocarbamate ligand in [MoO(η²-S₂)(S₂CNR′₂)₂] (R′ = Me or Et) upon reaction with the activated alkyne dimethyl acetylenedicarboxylate (dmad). At elevated temperatures, two 1,2-dithiolato complexes, [Mo{η²-SC(R)=C(R)S}{η³-C(NR′₂)SC-(R)=C(R)S}(S₂CNR′₂)] and [Mo{η²-SC(R)=C(R)S}{η¹,η³-SC(R)=C(R)C(NR′₂)S}(S₂CNR′₂)] (R = CO₂Me), were formed. Both result from addition of alkyne across a disulfide ligand and also *via* insertion of further alkyne into a sulfur–carbon bond of the dithiocarbamate. This latter process was termed 'melding' and affords novel new bidentate ligands at the molybdenum(VI) centre. We recently reported a novel route to a wide range of imidodisulfido complexes [Mo(η²-S₂)(NR)-(S₂CNEt₂)₂].[15] During our attempts to use imido complexes in carbon–nitrogen bond-formation reactions, and prompted by the report of Young *et al.*[12] detailed above, we investigated the
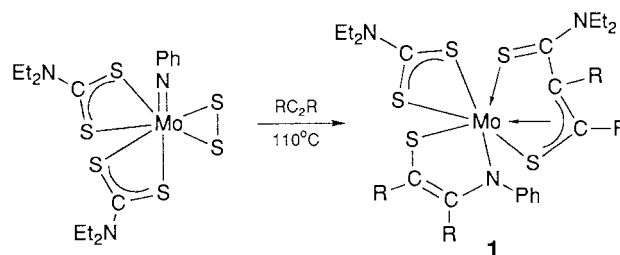
Scheme 1

reaction of [Mo(η²-S₂)(NPh)(S₂CNEt₂)₂] with dmad. In a recent paper[15] we briefly described that this gave a mixture of products, the major component of which was the 1-thio-2-iminoene complex [Mo{η²-PhNC(R)=C(R)S}{η¹,η³-SC(R)=C(R)C(NEt₂)S}(S₂CNEt₂)] **1** (R = CO₂Me). Since such complexes have not previously been reported, we sought to substantiate this formulation and herein report further details of this reaction together with the crystal structure of **1**.

Results and Discussion

As previously described,[15] thermolysis of [Mo(η²-S₂)(NPh)-(S₂CNEt₂)₂] with an excess of dmad in toluene affords bright blue [Mo{η²-PhNC(R)=C(R)S}{η¹,η³-SC(R)=C(R)C(NEt₂)-S}(S₂CNEt₂)] **1** (R = CO₂Me) in approximately 40% yield after chromatography (Scheme 1). In our earlier report, a further green product was thought to be an isomer of **1**, however we now believe that the latter is a mixture of **1** and an as yet unidentified yellow product which does not contain an NPh group. Slow diffusion of methanol into a saturated dichloromethane solution of **1** afforded small blue crystals suitable for X-ray crystallography, the results of which are summarised in Fig. 1 and Table 1.

The molecule consists of a highly distorted eight-co-ordinate molybdenum centre ligated by three chelating ligands *via* five sulfur, one nitrogen and two carbon atoms. One of the dithiocarbamates remains intact and bond lengths and angles are within the expected ranges. An equivalent of alkyne has inserted into a carbon–sulfur bond of the second dithiocarbamate ligand to give a novel, 3-diethylamino-1,2-bis-(methoxycarbonyl)-3-thioxoprop-1-ene-1-thiolate ligand. This is bound to molybdenum *via* an heteroallylic-type interaction [Mo–S(4) 2.3729(10), Mo–C(43) 2.184(3), Mo–C(42) 2.312(3) Å] and also through a further sulfur atom [Mo–S(3) 2.5582(10) Å]. It is analogous to the related *N,N*-dimethyl ligand crystallographically characterised by Young *et al.*[12] in [Mo{η²-SC-(R)=C(R)S}{η¹,η³-SC(R)=C(R)C(NMe₂)S}(S₂CNMe₂)] (R =
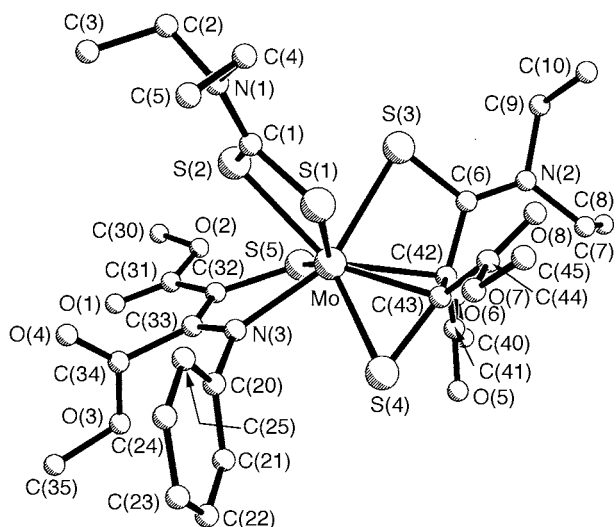
Fig. 1 Molecular structure of complex **1**

CO₂Me) and bond lengths and angles do not vary significantly between the two.

The third chelating ligand is formed *via* addition of alkyne across the sulfur and phenylimido moieties, the fate of the second sulfur atom being unknown. The new 1-thio-2-iminoene ligand binds to the molybdenum centre with a bite angle of 79.49(8)° and both molybdenum–sulfur [Mo–S(5) 2.3382(9) Å] and molybdenum–nitrogen bonds [Mo–N(3) 2.125(3) Å] are relatively short, being indicative of some multiple-bond character. Indeed the former lies close to those found in Young's related dithiolato complexes [average Mo–S 2.340(3) Å][12] indicating that the thiolato (**I**) rather than a thiolene (**II**) formulation is more apt. The Mo–N bond is, however, considerably longer than those found in the related molybdenum(v) [average Mo–N 2.001(2) Å][4] and molybdenum(vi) [average Mo–N 1.997(8) Å][5] 2-aminobenzenethiolate ligands, while the Mo–S bond is somewhat shorter. Indeed, the difference between these two bond lengths (△) in **1** of 0.213 Å is significantly less than found for the 2-aminobenzenethiolate ligand at Mo^VI (△ 0.421 Å),[5] Mo^V (△ 0.371 Å),[4] Tc^VI (△ 0.35 Å)[7] and Co^III (△ 0.349 Å),[6] but comparable to that at Tc^V (△ 0.21 Å).[8] The reason for this difference is not immediately apparent, but may in some part be due to the relatively bulky phenyl group at nitrogen in **1** and/or the *trans* influence of the melded ligand. An imino formulation **I** is, however, supported by the approximate planarity of the Mo–S(5)–C(32)–C(33)–N(3) ring [maximum deviation 0.15 Å by S(5)], the planar nature of N(3) and the short carbon–carbon bond [C(32)–C(33) 1.367(5) Å]. The latter is close to values of 1.33(1) and 1.343(5) Å found by Young in the related dithiolato complexes and is indicative of substantial double-bond character. The phenyl substituent lies approximately at right angles to the latter which may be a result of adverse steric interactions with the methyl ester bound to C(33). This is further manifested in the ¹H NMR spectrum with the appearance of a complex multiplet in the aromatic region even at 50 °C, which, while difficult to interpret precisely, is clearly indicative of the inequivalence of all phenylic protons, and presumably results from the restricted rotation about the carbon–nitrogen bond.

The oxidation state of the molybdenum centre in complex **1**

Table 1 Bond lengths (Å) and angles (°) in complex **1**

Mo–S(1)	2.5414(11)	Mo–S(2)	2.5507(11)
Mo–S(3)	2.5582(10)	Mo–S(4)	2.3729(10)
Mo–S(5)	2.3382(9)	Mo–N(3)	2.125(3)
Mo–C(42)	2.312(3)	Mo–C(43)	2.184(3)
S(1)–C(1)	1.704(5)	S(2)–C(1)	1.717(5)
C(1)–N(1)	1.334(7)	S(3)–C(6)	1.699(4)
C(6)–N(2)	1.308(4)	C(6)–C(42)	1.493(5)
C(42)–C(43)	1.446(4)	C(43)–S(4)	1.735(3)
N(3)–C(33)	1.349(5)	C(32)–C(33)	1.367(5)
S(5)–C(32)	1.737(4)	N(3)–C(20)	1.447(5)
C(20)–C(21)	1.372(7)	C(21)–C(22)	1.392(7)
C(22)–C(23)	1.347(11)	C(23)–C(24)	1.366(11)
C(24)–C(25)	1.408(9)	C(25)–C(20)	1.392(7)
S(1)–Mo–S(2)	68.23(4)	S(3)–Mo–S(4)	125.13(3)
S(5)–Mo–N(3)	79.49(8)	Mo–N(3)–C(33)	118.9(2)
N(3)–C(33)–C(32)	119.8(3)	C(33)–C(32)–S(5)	117.1(3)
Mo–S(5)–C(32)	99.87(13)		

is not clear, however based on its diamagnetism and the effective oxidation of sulfido and imido centres upon alkyne addition a +4 formulation appears most probable.

In conclusion, complex **1** represents the first example of a non-benzene 1-thio-2-iminoene complex which is formed *via* the novel addition of an alkyne across sulfido and imido moieties. Structural data and physical properties suggest that this hybrid ligand is more akin to a 1,2-dithiolato than an α-diimine ligand.

Experimental

Complex **1** was prepared as previously described.[15] Small blue well formed crystals were grown upon slow diffusion of methanol into a saturated dichloromethane solution at room temperature. A single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-Kα radiation (λ = 0.710 73 Å). The lattice parameters were identified by application of the automatic indexing routine of the diffractometer to the positions of a number of reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure reflections in the range 5 ≤ 2θ ≤ 50°. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorenz-polarisation effects and empirically for absorption. The unique data with $I \geqslant 2.0\sigma(I)$ were used to solve and refine the structure. The structure was solved by direct methods and developed by using alternative cycles of least-squares refinement (based on F^2) and Fourier-difference synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ Å²). Final Fourier-difference maps were featureless and contained no peaks greater than 1.00 e Å⁻³. Structure solution used the SHELXTL PLUS program package[16] on a micro Vax II computer. The methyl carbons on the dithiocarbamate ligand were disordered over two sites with equal occupancies, C(3)/C(3a) and C(5)/C(5a). Important crystallographic parameters; triclinic, space group $P\bar{1}$, $a = 10.7178(17)$, $b = 12.8823(14)$, $c = 12.9820(21)$ Å, α = 96.38(1), β = 95.03(1), γ = 91.37(1)°, $U = 1773.4(4)$ Å³, $Z = 2$, $D_c = 1.50$ g cm⁻³, $F(000) = 824$, μ(Mo-Kα) = 6.90 cm⁻¹, crystal dimensions 0.62 × 0.48 × 0.21 mm, $R(R') = 0.041(0.045)$ for the 5168 unique reflections and 406 variables, 0.049(0.056) for all 6173 data.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors,

Acknowledgements

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