Molybdenum(VI) imidodisulfur complexes formed *via* double sulfur–carbon bond cleavage of dithiocarbamates

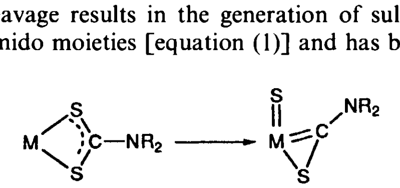
Thérèse A. Coffey, Glyn D. Forster and Graeme Hogarth *

Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK

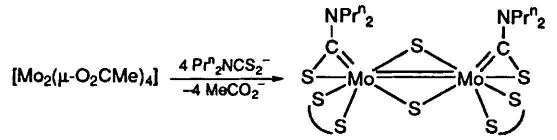
Thermolysis of the bis(oxo) complexes [$MoO_2(S_2CNR'_2)_2$] **1** with organic isocyanates afforded imidodisulfur complexes [$Mo(NR)(\eta^2\text{-}S_2)(S_2CNR'_2)_2$] **2** in moderate yields. Three of the latter, [$Mo(NPh)(\eta^2\text{-}S_2)(S_2CNEt_2)_2$] **2a**, [$Mo(NBu^t)(\eta^2\text{-}S_2)(S_2CNMe_2)_2$] **2j** and [$Mo(NC_6H_3Pr^i{}_2\text{-}2,6)(\eta^2\text{-}S_2)(S_2CNMe_2)_2$] **2k** have been characterised by X-ray crystallography. All contain a distorted pentagonal-bipyramidal metal centre, the disulfur ligand lying in the equatorial plane while the linear imide ligand occupies an axial site. Reaction of **2a** with $P(OEt)_3$ afforded the dinuclear molybdenum(V) complex [$Mo_2O_2(\mu\text{-}NPh)(\mu\text{-}S)(S_2CNEt_2)_2$] **3** which has also been crystallographically characterised. Thermolysis of **2a** with an excess of the activated alkyne dimethyl acetylene dicarboxylate yielded three isomeric insertion products formulated as [$Mo\{SC(R){=}C(R)NPh\}\{\eta^4\text{-}SC(R){=}C(R)C(NEt_2)S\}(S_2CNEt_2)$] **4** and **5** (differing in the relative orientations of sulfur) and [$Mo\{SC(R){=}C(R)NPh\}\{\eta^3\text{-}SC(R){=}C(R)SC(NEt_2)\}(S_2CNEt_2)$] **6** ($R = CO_2Me$). The nature of the sulfur–carbon bond cleavage reaction was investigated in a series of experiments centred around the formation of **2a** which is concomitant with that of [$\{MoO(\mu\text{-}NPh)(S_2CNEt_2)\}_2$] **7a**. Thermolysis of [$MoO_2(S_2CNEt_2)_2$] **1a** alone afforded the known molybdenum(V) complex [$Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(S_2CNEt_2)_2$] and, while addition of PhNCO to [$MoO(\eta^2\text{-}S_2)(S_2CNEt_2)_2$] afforded **2a**, imido substitution was not noted with Bu^tNCO, thus ruling out the general intermediacy of [$MoO(\eta^2\text{-}S_2)(S_2CNEt_2)_2$] in the dithiocarbamate cleavage process. Thermolysis of bis(imido) complexes [$Mo(NR)_2(S_2CNEt_2)_2$] **8** (R = Ph or C_6H_4Me-*o*) did not afford the respective disulfur complexes, however thermolysis of [$MoO(NPh)(S_2CNEt_2)_2$] did give **2a** and **7a**, thus implicating the oxoimidomolybdenum(VI) complexes as key reaction intermediates. These observations allow a general reaction scheme to be formulated.

Dithiocarbamates ($R_2NCS_2^-$) find widespread use in transition-metal chemistry, primarily due to their ability to stabilise metal centres in a wide range of oxidation states.[1] For example, dithiocarbamate-stabilised molybdenum complexes are known for oxidation states ranging from +6, [$MoO_2(S_2CNR_2)_2$],[2] to −1, [$Mo(CO)_4(S_2CNR_2)$]$^-$.[3] One of the major advantages of using the small bite-angle dithiocarbamate moiety as a stabilising chelate ligand is its robust nature, remaining intact under a variety of reaction conditions.

Metal-mediated carbon–sulfur bond cleavage is generally a facile process which has been exploited towards the hydrodesulfurisation of fossil fuels.[4] As the chemistry of the dithiocarbamate ligand develops, it is becoming increasingly apparent that under certain conditions the cleavage of a carbon–sulfur bond of this ligand may become a favourable process. Such a scission process is essentially an oxidative-addition reaction and as such is expected to be prevalent at metal centres in lower oxidation states. A single carbon–sulfur bond cleavage results in the generation of sulfido and thiocarboxamido moieties [equation (1)] and has been noted in a number of instances. The first reaction of this type was reported by Weiss and co-workers[5] in 1972. In an attempt to substitute the carboxylate groups in the molybdenum(II) dimer [$Mo_2(\mu\text{-}O_2CMe)_4$] with dithiocarbamate ligands, reaction with 4 equivalents of [NH_4][$S_2CNPr^n{}_2$] was carried out. The isolated product was, however, the sulfido-bridged molybdenum(IV) dimer [$\{Mo(\mu\text{-}S)(\eta^2\text{-}SCNPr^n{}_2)(S_2CNPr^n{}_2)\}_2$] [equation (2)], a result of oxidative addition of a dithiocarbamate to both metal centres.[5]

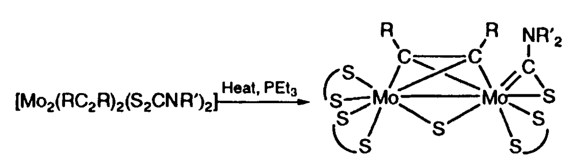


(1)

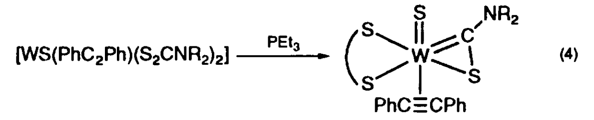


(2)

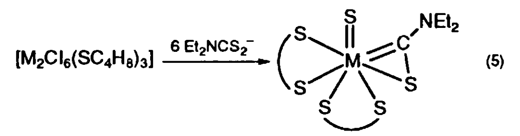
Closely related to the latter reaction is the formation of molybdenum(III) dimers [$Mo_2(\mu\text{-}S)(\mu\text{-}RC_2R)(\eta^2\text{-}SCNR'_2)(S_2CNR'_2)_3$] upon thermolysis of the monomeric molybdenum(II) complex [$Mo(RC_2R)_2(S_2CNR'_2)_2$] in the presence of PEt_3 [equation (3)]. These are formed *via* a single dithiocarbamate cleavage, and while the role of the phosphine is not clear, non-stoichiometric quantities of $Et_3P{=}S$ were produced.[6] The scission process is not limited to binuclear centres. Addition of PEt_3 to the tungsten(IV) sulfido complex [$WS(PhC_2Ph)(S_2CNR_2)_2$] results in sulfur abstraction and dithiocarbamate cleavage to afford [$WS(PhC_2Ph)(\eta^2\text{-}SCNR_2)(S_2CNR_2)$] [equation (4)],[7] while the same complex is isolated as a minor product from the reaction of [$W(CO)(PhC_2Ph)(S_2CNR_2)_2$] with cyclohexene sulfide.[8] The scission process is also not restricted to Group 6 metals. Addition of 6 equivalents of NaS_2CNEt_2 to metal(III) dimers [$M_2Cl_6(SC_4H_8)_3$] (M = Nb or Ta) affords monomeric metal(V) complexes [$MS(\eta^2\text{-}SCNEt_2)(S_2CNEt_2)_2$] in moderate



(3)



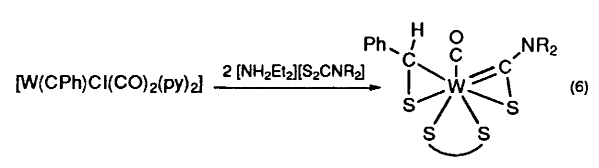
(4)



(5)

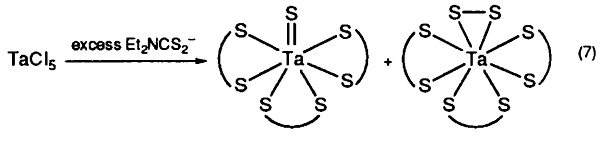
yields [equation (5)]. The authors speculate that the carbon–sulfur bond cleavage may occur at the binuclear centre with later breakdown to monomeric products.[9]

In one instance the sulfide ligand generated upon carbon–sulfur bond cleavage reacts with a metal-bound alkylidyne fragment. Thus, addition of 2 equivalents of $[\mathrm{NH_2Et_2}][\mathrm{S_2CNEt_2}]$ to $[\mathrm{W(CPh)Cl(CO)_2(py)_2}]$ (py = pyridine) affords the thiobenzaldehyde complex $[\mathrm{W(CO)(\eta^2\text{-}SCHPh)(\eta^2\text{-}SCNEt_2)(S_2CNEt_2)}]$ as a result of further carbon–sulfur bond formation and proton abstraction [equation (6)].[10]



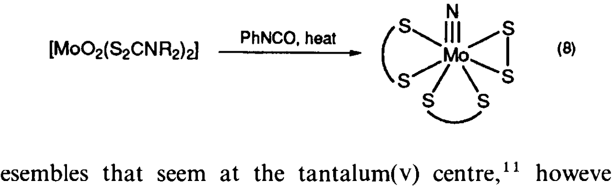
(6)

In the examples quoted above the oxidation state of the metal centre increases upon cleavage of the dithiocarbamate ligand consistent with the view that it is an oxidative-addition process. Addition of an excess of $\mathrm{NaS_2CNEt_2}$ to $\mathrm{TaCl_5}$, however, affords two tantalum(V) products, $[\mathrm{TaS(S_2CNEt_2)_3}]$ and $[\mathrm{Ta(\eta^2\text{-}S_2)(S_2CNEt_2)_3}]$ [equation (7)].[11] In both, the organic moiety formed as a result of carbon–sulfur bond cleavage, is eliminated from the metal co-ordination sphere. The formation of the disulfur complex is intriguing since it suggests that a double carbon–sulfur bond-cleavage process has occurred. However, it has been shown that addition of sulfur or sulfur-containing compounds to the sulfido complex readily affords the disulfur complex.[12]

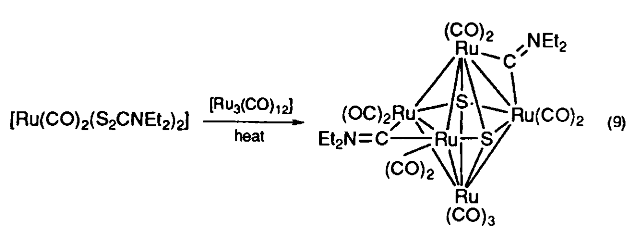


(7)

Recent work by both ourselves[13] and Deeming and Vaish[14] has given further credence to the possibility of a double carbon–sulfur bond cleavage of dithiocarbamates. We have noted that thermolysis of the molybdenum(VI) bis(oxo) complex $[\mathrm{MoO_2(S_2CNEt_2)_2}]$ **1a** in the presence of phenyl isocyanate affords the imidodisulfur complex $[\mathrm{Mo(NPh)(\eta^2\text{-}S_2)(S_2CNEt_2)_2}]$ **2a** [equation (8)].[13] This transformation closely resembles that seem at the tantalum(V) centre,[11] however, in contrast, the monosulfidomolybdenum(VI) complex is unknown. In both instances the fate of the $\mathrm{CNEt_2}$ fragment cleaved from the dithiocarbamate is unknown. Very recently Deeming and Vaish[14] have provided conclusive evidence for the double carbon–sulfur bond cleavage of a dithiocarbamate ligand. Thus, reaction of $[\mathrm{Ru(CO)_2(S_2CNEt_2)_2}]$ with $[\mathrm{Ru_3(CO)_{12}}]$ affords pentanuclear $[\mathrm{Ru_5(CO)_{11}(\mu_4\text{-}S)_2(\mu\text{-}CNEt_2)_2}]$ [equation (9)] in which both the sulfur and aminomethylidyne moieties resulting from the double-scission process are trapped. It is, however, noteworthy that only two of the expected four sulfur atoms are observed in the final product.



(8)



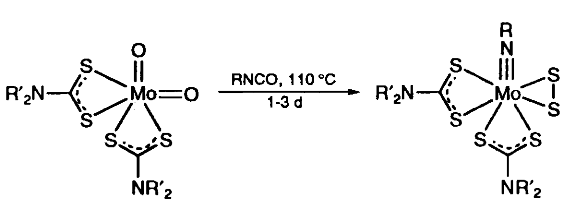
(9)

In this paper we give details of our full studies on the double carbon–sulfur bond cleavage of dithiocarbamates at the molybdenum(VI) centre. While the reactions occur only in moderate yields, the abundance and cheapness of the starting materials allows for the large-scale synthesis of imido-disulfur complexes and aspects of their chemistry have been explored. Further, a number of experiments have been carried out in order to elucidate mechanistic details of the double-scission process. Part of this work has been previously communicated.[13]

Results and Discussion

(*i*) Synthesis of imidodisulfur complexes $[\mathrm{Mo(NR)(\eta^2\text{-}S_2)(S_2CNR'_2)_2}]$ 2

Treatment of the bis(oxo) complex $[\mathrm{MoO_2(S_2CNEt_2)}]$ **1a** with organic isocyanates in refluxing toluene led to the isolation of the corresponding imidodisulfur complexes $[\mathrm{Mo(NR)(\eta^2\text{-}S_2)(S_2CNEt_2)_2}]$ **2a–h** in moderate yield (≈30%) after chromatography (Scheme 1). Recrystallisation was carried out by the slow diffusion of methanol into saturated dichloromethane solutions and all complexes are air and water stable. Their colour varies depending upon the nature of the imido substituent, being purple for aryl and red for alkyl moieties. Characterising ^{1}H NMR and IR data are given in Table 1. All show a weak absorption at ≈550 cm^{-1} in the IR spectrum assigned to vibration of the sulfur–sulfur bond,[15] as well as bands characteristic of the imide ligand at ≈1275 cm^{-1} and the



1a R′ = Et
1b R′ = Me

2a R′ = Et, R = Ph
2b R = *o*-$\mathrm{MeC_6H_4}$
2c R = *p*-$\mathrm{MeC_6H_4}$
2d R = 2,6-$\mathrm{Me_2C_6H_3}$
2e R = 2,6-$\mathrm{Cl_2C_6H_3}$
2f R = 2,6-$\mathrm{Pr^i_2C_6H_3}$
2g R = adamantyl
2h R = $\mathrm{Bu^t}$
2i R′ = Me, R = Ph
2j R = $\mathrm{Bu^t}$
2k R = 2,6-$\mathrm{Pr^i_2C_6H_3}$

Scheme 1

Table 1 Proton NMR and IR data for imidodisulfur complexes **2**

Complex	^{1}H NMR ($CDCl_3$), δ (*J*/Hz)
2a	7.44 (t, 2 H), 7.20 (d, *J* 7.1, 2 H), 7.15 (t, *J* 7.2, 1 H), 4.07–3.52 (m, 8 H), 1.37 (t, *J* 7.1, 3 H), 1.35 (t, *J* 7.1, 3 H), 1.31 (t, *J* 7.2, 3 H), 1.14 (t, *J* 7.2, 3 H)
2b	7.35–7.33 (m, 1 H), 7.03–6.98 (m, 3 H), 3.97–3.51 (m, 8 H), 2.36 (s, 3 H), 1.37 (t, *J* 7.2, 3 H), 1.35 (t, *J* 7.2, 3 H), 1.32 (t, *J* 7.2, 3 H), 1.15 (t, *J* 7.0, 3 H)
2c	7.14 (d, *J* 8.2, 2 H), 6.98 (d, *J* 8.2, 2 H), 3.96–3.50 (m, 8 H), 2.30 (s, 3 H), 1.37 (t, *J* 7.3, 3 H), 1.35 (t, *J* 7.4, 3 H), 1.33 (t, *J* 7.1, 3 H), 1.15 (t, *J* 7.0, 3 H)
2d	6.89 (t, *J* 7.8, 1 H), 6.81 (d, *J* 7.8, 2 H), 4.03–3.50 (m, 8 H), 2.49 (s, 6 H), 1.37 (t, *J* 7.2, 3 H), 1.35 (t, *J* 7.2, 3 H), 1.31 (t, *J* 7.2, 3 H), 1.15 (t, *J* 7.2, 3 H)
2e	7.09 (d, *J* 7.5, 2 H), 6.92 (t, *J* 7.5, 1 H), 4.02–3.47 (m, 8 H), 1.38 (t, *J* 7.3, 3 H), 1.36 (t, *J* 7.2, 3 H), 1.30 (t, *J* 7.2, 3 H), 1.13 (t, *J* 7.0, 3 H)
2f	7.06 (t, *J* 7.0, 1 H), 6.97 (d, *J* 7.0, 2 H), 4.01–3.49 (m, 10 H), 1.37 (t, *J* 7.2, 3 H), 1.36 (t, *J* 7.2, 3 H), 1.28 (t, *J* 7.1, 3 H), 1.20 (d, *J* 7.0, 12 H), 1.14 (t, *J* 7.2, 3 H)
2g	3.95–3.49 (m, 8 H), 1.97 (br s, 3 H), 1.90 (br s, 6 H), 1.58 (br s, 6 H), 1.34 (t, *J* 7.2, 9 H), 1.12 (t, *J* 7.2, 3 H)
2h	3.91–3.49 (m, 8 H), 1.34 (t, *J* 7.2, 3 H), 1.31 (t, *J* 7.2, 6 H), 1.20 (s, 9 H), 1.09 (t, *J* 7.2, 3 H)
2i	7.30–7.15 (m, 5 H), 3.47 (s, 3 H), 3.44 (s, 3 H), 3.39 (s, 3 H), 3.18 (s, 3 H)
2j	3.46 (s, 3 H), 3.42 (s, 3 H), 3.40 (s, 3 H), 3.16 (s, 3 H), 1.27 (s, 9 H)
2k	7.06 (t, *J* 7.2, 1 H), 6.97 (d, *J* 7.2, 2 H), 3.74 (spt, *J* 7.0, 2 H), 3.46 (s, 3 H), 3.44 (s, 3 H), 3.33 (s, 3 H), 3.19 (s, 3 H), 1.20 (d, *J* 6.9, 12 H)
	IR (KBr disc)/cm^{-1}
2a	1522s, 1497s, 1456m, 1435s, 1275s, 1206w, 1146m, 1092w, 1072m, 759m, 682m, 669m, 653m, 522w
2b	1527s, 1505s, 1433s, 1380w, 1354m, 1298m, 1273m, 1207m, 1149m, 1115w, 1096w, 1078m, 1001w, 849m, 763m, 548m
2c	1522s, 1499s, 1456m, 1436m, 1355m, 1297w, 1276s, 1208m, 1148m, 1091w, 1070w, 818m, 552w
2d	1504s, 1459m, 1434s, 1378w, 1355w, 1275s, 1209m, 1150m, 1094w, 1074w, 849w, 772w, 549w
2e	1504s, 1458w, 1430s, 1411w, 1379w, 1351w, 1304w, 1273m, 1207m, 1195w, 1149m, 1072m, 989w, 850w, 794m, 775m, 723m, 548w
2f	1520s, 1491s, 1456m, 1433s, 1378m, 1356m, 1269s, 1209m, 1142m, 1095m, 1073s, 1005m, 798w, 757w, 669w, 554w
2g	1500s, 1457w, 1429m, 1378w, 1354w, 1301w, 1275m, 1230w, 1209m, 1149m, 1094w, 1075w, 999 (br), 848w, 552w
2h	1516s, 1501s, 1458m, 1434s, 1378w, 1357m, 1301w, 1277s, 1227m, 1210m, 1149m, 1093w, 1072w, 1021w, 1001w, 916w, 849w, 669w, 571w, 553w
2i	1536s, 1467m, 1446m, 1392s, 1314m, 1252m, 1211w, 1149s, 1060m, 984m, 754m, 680w, 548w
2j	1539s, 1523s, 1469m, 1445m, 1390s, 1250m, 1221s, 1147s, 1048m, 987m, 577m, 569w, 550m, 445w
2k	1542s, 1516s, 1459m, 1395s, 1254m, 1145m, 1085w, 1052w, 800w, 756m, 669w, 574w, 549w

C=N stretch of the dithiocarbamate ligand at ≈1510 cm^{-1}. The ^{1}H NMR spectra contain four inequivalent methyl resonances, one being shifted upfield with respect to the others. This behaviour has previously been noted for the related oxosulfido complexes $[\mathrm{MoO}(\eta^2\text{-}\mathrm{S}_2)(\mathrm{S_2CNR'_2})_2]$, the shielded signal being assigned to the alkyl group which resides closest to the Mo=O vector.[16] In an attempt to probe the sensitivity of the cleavage process to the substituent on the dithiocarbamate, a number of experiments were carried out with $[\mathrm{MoO_2(S_2CNMe_2)_2}]$ **1b** which yielded the analogous imidodisulfur complexes $[\mathrm{Mo(NR)}(\eta^2\text{-}\mathrm{S}_2)(\mathrm{S_2CNMe_2})_2]$ **2i–k**. The methyl-substituted complexes are less soluble than their ethyl analogues and have simpler ^{1}H NMR spectra, however again one of four inequivalent methyl signals is shifted upfield. Reactions of **1a** with allyl- and isopropyl-isocyanate were also performed and led to the formation of deep red solutions. Attempts to purify these complexes, however, resulted in extensive decomposition. Their relative instability may be due to the increased acidity of the protons on the α-carbon of the imido substituent.[17] A similar reaction of **1a** with PhNCS was performed in order to provide another source of sulfur. As expected, this afforded **2a** but in somewhat lower yield than found with the isocyanate indicating that the source of the disulfur moiety is exclusively the dithiocarbamate ligands.

Table 2 Selected bond lengths (Å) and angles (°) for imidodisulfur complexes

	2a	**2j**	**2k**
Mo–S(1)	2.544(1)	2.527(1)	2.484(1)
Mo–S(2)	2.487(1)	2.464(1)	2.452(1)
Mo–S(3)	2.511(1)	2.509(1)	2.497(2)
Mo–S(4)	2.605(1)	2.636(1)	2.612(1)
Mo–S(5)	2.398(2)	2.399(1)	2.384(2)
Mo–S(6)	2.431(2)	2.421(1)	2.402(1)
Mo–N(3)	1.759(4)	1.713(2)	1.734(3)
S(5)–S(6)	2.033(2)	2.035(2)	2.011(2)
Mo–N(3)–C_{ipso}	165.2(3)	168.7(2)	179.1(3)
Mo–S(5)–S(6)	65.9(1)	65.6(1)	65.6(1)
Mo–S(6)–S(5)	64.3(1)	64.4(1)	64.7(1)
S(5)–Mo–S(6)	49.8(1)	50.0(1)	49.7(1)
N(3)–Mo–S(1)	85.9(1)	89.3(1)	91.5(1)
N(3)–Mo–S(2)	100.6(1)	100.9(1)	102.2(1)
N(3)–Mo–S(3)	94.9(1)	93.0(1)	100.2(1)
N(3)–Mo–S(4)	161.4(1)	160.5(1)	168.1(1)
N(3)–Mo–S(5)	106.3(1)	105.4(1)	100.8(1)
N(3)–Mo–S(6)	100.9(1)	98.5(1)	96.8(1)

(*ii*) Solid-state structure of imidodisulfur complexes 2

In order fully to elucidate the molecular structure of the imidodisulfur complexes, X-ray crystallographic studies were performed on $[\mathrm{Mo(NPh)}(\eta^2\text{-}\mathrm{S}_2)(\mathrm{S_2CNEt_2})_2]$ **2a**, $[\mathrm{Mo(NBu^t)}(\eta^2\text{-}\mathrm{S}_2)(\mathrm{S_2CNMe_2})_2]$ **2j** and $[\mathrm{Mo(NC_6H_3Pr^i{}_2\text{-}2,6)}(\eta^2\text{-}\mathrm{S}_2)(\mathrm{S_2CNMe_2})_2]$ **2k**. The results are summarised in Fig. 1 and Table 2. All show the expected seven-co-ordinate approximately pentagonal-bipyramidal co-ordination geometry of molybdenum. The equatorial sites are composed of the sulfur atoms [S(5) and S(6)] of the disulfur ligand, both sulfur atoms of one of the dithiocarbamate ligands [S(1) and S(2)] and one of the sulfur atom [S(3)] from the second dithiocarbamate, while the second sulfur of the latter [S(4)] and the imido moiety occupy the axial sites. The metal centre is displaced somewhat out of the equatorial plane towards the imide ligand, an effect caused by the *trans* influence of the latter which is also manifested in elongation of the axial sulfur by ≈0.11 Å with respect to those in equatorial sites. The overall geometry is similar to that found in the oxo complex $[\mathrm{MoO}(\eta^2\text{-}\mathrm{S}_2)(\mathrm{S_2CNEt_2})_2]$,[18] the major difference being the degree of elongation of this metal–sulfur contact *trans* to the π-donor ligand, being greater in the oxo [2.663(6) Å] as compared to the imido [**2a** 2.605(1), **2j** 2.636(1), **2k** 2.612(1) Å] complexes. The disulfur ligands are bound approximately symmetrically to the metal centre, the sulfur–sulfur distances [**2a** 2.033(2), **2j** 2.035(2), **2k** 2.011(2) Å] being typical.[19] The geometry at

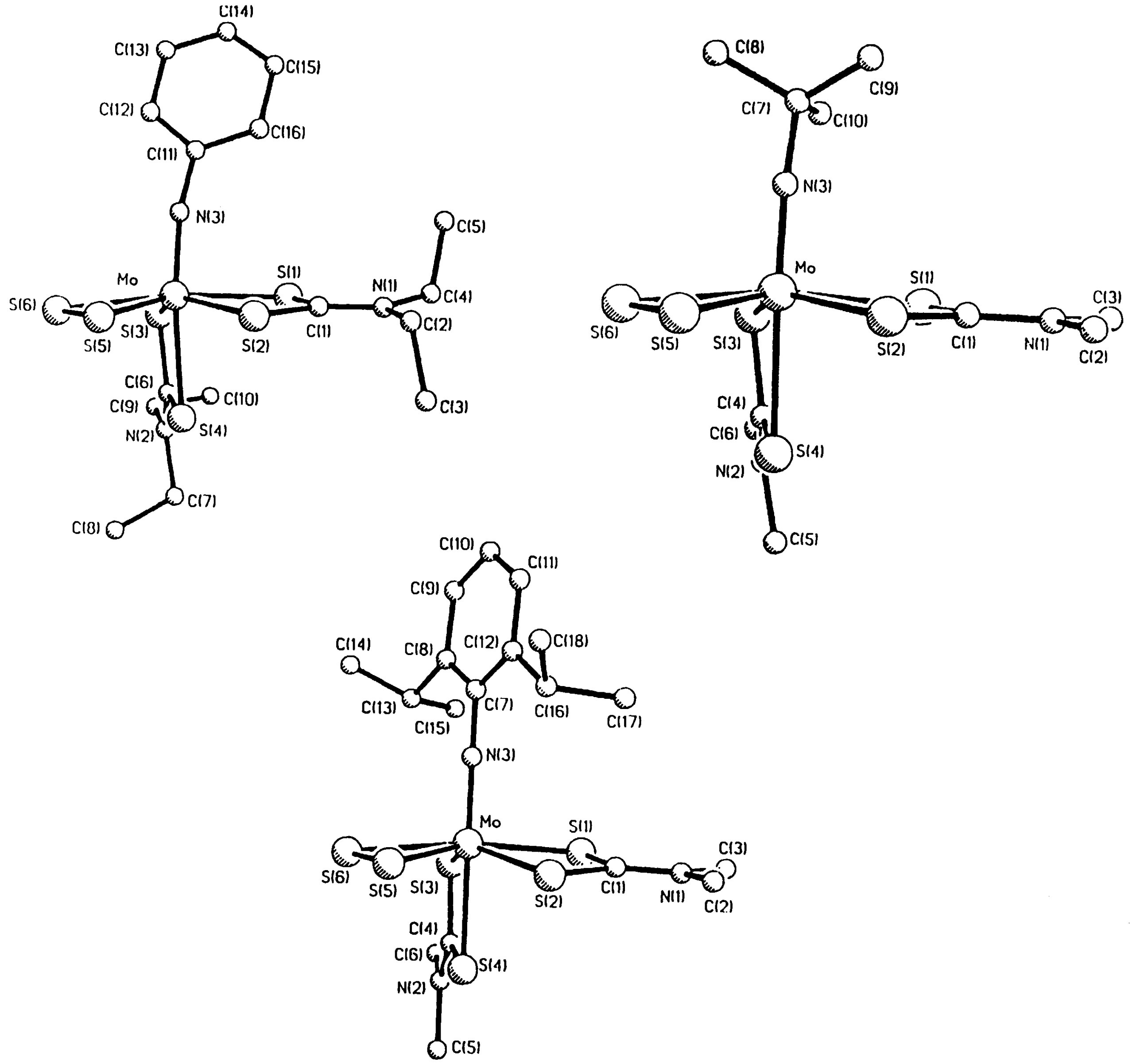
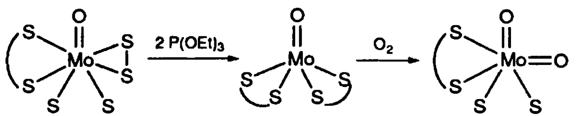


Fig. 1 Molecular structures of imidodisulfur complexes **2a**, **2j** and **2k**

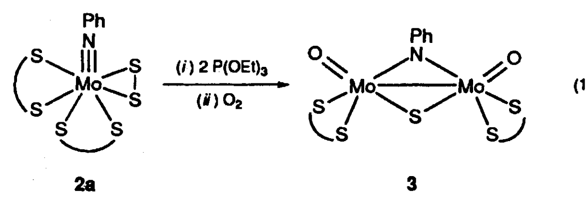
nitrogen is essentially linear [**2a** 165.2(3), **2j** 168.7(2), **2k** 179.1(3)°] and thus the imide ligands are best considered as acting in a four-electron capacity and, in support of this supposition, the metal–nitrogen vector is short [**2a** 1.759(4), **2j** 1.713(2), **2k** 1.734(3) Å]. There is, however, a noteworthy shortening of this vector upon the introduction of more electron-donating substituents, $Bu^t > 2,6\text{-}Pr^i_2C_6H_3 > Ph$, an effect which is mirrored in the consequent lengthening of the *trans* metal–sulfur bond.

(*iii*) Reactivity of the imidodisulfur complex [Mo(NPh)(η^2-S_2)(S_2CNEt_2)$_2$] 2a

In view of the large-scale preparation of imidodisulfur complexes, a number of reactivity studies were performed on [Mo(NPh)(η^2-S_2)(S_2CNEt_2)$_2$] **2a**. Young and co-workers[12] had previously described the desulfurisation of [MoO(η^2-S_2)(S_2CNEt_2)$_2$] by 2 equivalents of $P(OEt)_3$, affording the five-co-ordinated molybdenum(IV) oxide [MoO(η^2-S_2CNEt_2)$_2$], which is rapidly oxidised by air to the bis(oxo) complex [MoO_2(S_2CNEt_2)$_2$] **1a** [equation (10)]. We attempted a similar desulfurisation process with **2a** with the aim of preparing the known oxoimido complex [MoO(NPh)(S_2CNEt_2)$_2$] **11a**.[20] Treatment of **2a** with 2 equivalents of $P(OEt)_3$ resulted in a change from purple to brown, which upon exposure to air, initially turned red and finally afforded an orange solution. Removal of solvent followed by crystallisation from dichloromethane–methanol afforded the dimeric molybdenum(V) complex [Mo_2O_2(μ-NPh)(μ-S)(S_2CNEt_2)$_2$] **3** as a yellow crystalline solid in 60% yield [equation (11)]. The above formulation was in full accord with the spectroscopic and analytical data, however in order fully to elucidate the structure



(10)



(11)

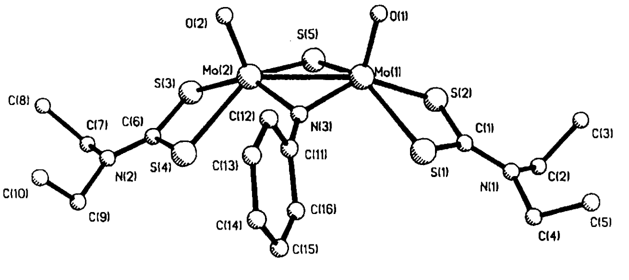


Fig. 2 Molecular structure of complex 3

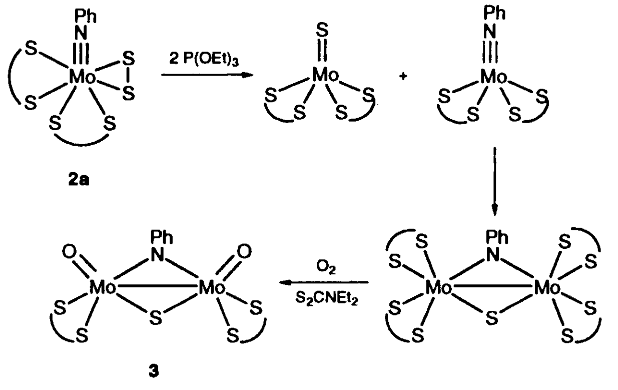
Table 3 Selected bond lengths (Å) and angles (°) for complex 3

Mo(1)–Mo(2)	2.732(1)	Mo(1)–S(1)	2.465(2)
Mo(1)–S(2)	2.481(2)	Mo(1)–S(5)	2.334(2)
Mo(1)–N(3)	1.974(4)	Mo(1)–O(1)	1.681(4)
Mo(2)–S(3)	2.491(2)	Mo(2)–S(4)	2.460(2)
Mo(2)–S(5)	2.315(2)	Mo(2)–N(3)	1.979(5)
Mo(2)–O(2)	1.681(5)	N(3)–C(11)	1.396(6)
S(1)–Mo(1)–S(2)	70.9(1)	Mo(2)–Mo(1)–O(1)	106.1(2)
S(3)–Mo(2)–S(4)	70.8(1)	Mo(1)–Mo(2)–O(2)	106.1(1)
Mo(1)–S(5)–Mo(2)	72.0(1)	Mo(1)–N(3)–Mo(2)	87.4(2)

a crystallographic study was undertaken, the results of which are summarised in Fig. 2 and Table 3.

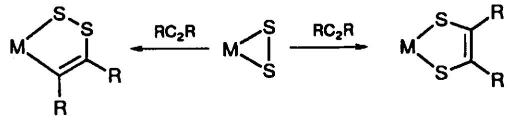
The molecule displays the expected *cis* configuration of dithiocarbamate ligands and puckered $Mo_2(\mu\text{-}X)_2$ core geometry,[21] while each metal centre also carries a terminal oxo moiety [Mo(1)–O(1) 1.681(4), Mo(2)–O(2) 1.681(5) Å]. The dimolybdenum centre is bridged approximately symmetrically by both sulfide [Mo(1)–S(5) 2.334(2), Mo(2)–S(5) 2.315(2) Å] and phenylimide ligands [Mo(1)–N(3) 1.974(4), Mo(2)–N(3) 1.979(5) Å], the latter being trigonal planar at nitrogen. The molybdenum–molybdenum distance at 2.732(1) Å is within the range of a single bond. The intermetallic distance in such complexes appears to be controlled by the nature of the bridging ligands, and the bond length in 3 is intermediate between those found in $[\{MoS(\mu\text{-}S)(S_2CNEt_2)\}_2]$ [2.801(2) Å][22] and $[\{Mo(NC_6H_4Me\text{-}o)(\mu\text{-}NC_6H_4Me\text{-}o)(S_2CNEt_2)\}_2]$ [2.633(1) Å].[23] The methyl groups on the dithiocarbamate ligands are not in the expected 'up–down' configuration but rather are in an 'up–up' arrangement.[24] The reason for this becomes clear when the packing of the molecules is considered since they pack closely into layers, an effect that would not be possible for the 'up–down' configuration of methyl groups, and suggesting that the observed 'up–up' configuration is a result of crystal-packing forces.

While the mode of formation of complex 3 is not clear, a plausible mechanism is shown in Scheme 2. Since 3 contains both sulfido and imido moieties, this suggests that sulfur and imido abstraction from 2a by the phosphite may be competitive processes, leading to the formation of both the expected five-coordinate complex $[Mo(NPh)(S_2CNEt_2)_2]$, and also $[MoS(S_2CNEt_2)_2]$, resulting from sulfur and imido abstraction. Reaction between these two molybdenum(IV) fragments (which must be more favourable than either dimerisation reaction) would afford dimeric $[Mo_2(\mu\text{-}NPh)(\mu\text{-}S)(S_2CNEt_2)_4]$. The related tungsten(IV) dimer $[\{W(\mu\text{-}S)(S_2CNEt_2)_2\}_2]$ is known and indeed is reported to be air sensitive in solution.[25] Applying the latter criterion, exposure of the molybdenum(IV) dimer to air would result in oxidation of molybdenum centres to afford the observed product 3 as a result of dithiocarbamate loss (probably as tetraethylthiuram disulfide).

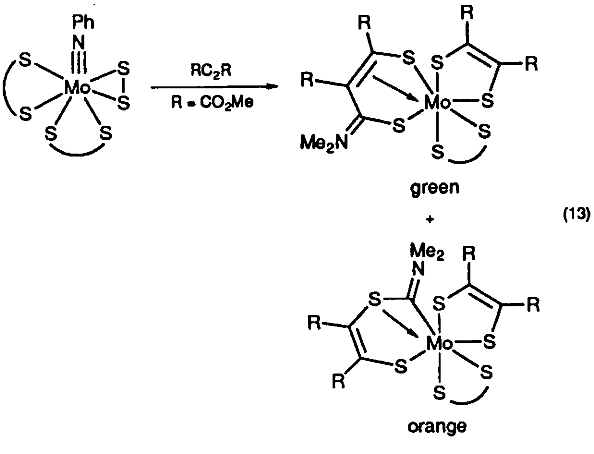


Scheme 2

Activated alkynes such as dimethylacetylene dicarboxylate (dmad) are known to insert into the sulfur–sulfur or metal–sulfur bond of disulfur complexes affording dithiolene[26] and vinyl disulfide[27] complexes respectively [equation (12)]. Recently Young *et al.*[28] have reported that reaction of the oxodisulfur complex $[MoO(\eta^2\text{-}S_2)(S_2CNMe_2)_2]$ with dmad affords two isomeric dithiolate complexes, namely orange $[Mo\{SC(R){=}C(R)S\}\{\eta^3\text{-}SC(R){=}C(R)SC(NMe_2)\}(S_2CNMe_2)]$ and green $[Mo\{SC(R){=}C(R)S\}\{\eta^3\text{-}SC(R){=}C(R)C(NMe_2)S\}(S_2CNMe_2)]$ [equation (13), R = CO_2Me]. They result from oxo loss, alkyne insertion into the sulfur–sulfur bond, and the novel insertion of the alkyne into a dithiocarbamate ligand.



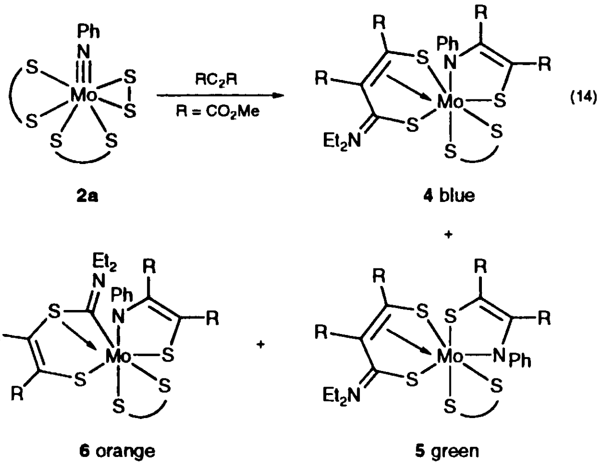
(12)



(13)

Thermolysis of a toluene solution of complex 2a and a slight excess of dmad led to the isolation of three products after column chromatography, tentatively formulated as blue 4 and green 5 isomers of the formula $[Mo\{SC(R){=}C(R)NPh\}\{\eta^4\text{-}SC(R){=}C(R)C(NEt_2)S\}(S_2CNEt_2)]$ (R = CO_2Me) which differ with respect to the relative orientations of the ligands about the octahedral molybdenum(VI) centre, and an orange isomer $[Mo\{SC(R){=}C(R)NPh\}\{\eta^3\text{-}SC(R){=}C(R)SC(NEt_2)\}(S_2CNEt_2)]$ 6 [equation (14)].

The blue complex 4 was characterised on the basis of analytical and spectroscopic data as well as a preliminary X-ray crystallographic study. Refinement proved problematic due to a disorder in the dithiocarbamate ligand and some poor thermal parameters associated with the phenyl ring and the CO_2Me groups, however it provided strong evidence for the formulation given. Characterisation of the green isomer 5 proved more problematic due to difficulties in obtaining pure samples free of isomeric 4. Both the spectroscopic data and the colour of 5 strongly suggest that it is an isomer of 4. While three further geometrical isomers are possible which we cannot distinguish, we favour the structure shown in which it differs in



the orientation of the ligand formed upon alkyne insertion into the dithiocarbamate. The nature of the orange complex **6** is less clear. The ^{1}H NMR spectrum shows four methyl resonances associated with the alkyne while integration of the aromatic region indicates that the NPh moiety is retained. We believe that **6** is also an isomer of **4** and **5**, which differs in the mode of insertion of the alkyne into the dithiocarbamate. Thus, the orange complex described by Young and co-workers is that in which the alkyne bridges across the two sulfur atoms of the cleaved dithiocarbamate and on the basis of the similar colours we tentatively assign the structure shown to **6**.

The reaction of complex **2a** then with dmad closely resembles that of the oxosulfido complex $[\mathrm{MoO}(\eta^2\text{-S}_2)(\mathrm{S_2CNMe_2})_2]$ in that in all cases alkyne insertion occurs into the dithiocarbamate and across isoelectronic S and/or NPh moieties. The noteworthy difference between the two reactions is the retainment of the imido fragment in all products derived from **2a**, while in contrast the π-donor (oxo) ligand is always eliminated. The reason for this is not immediately apparent but may be a consequence of the strong molybdenum–nitrogen bond.

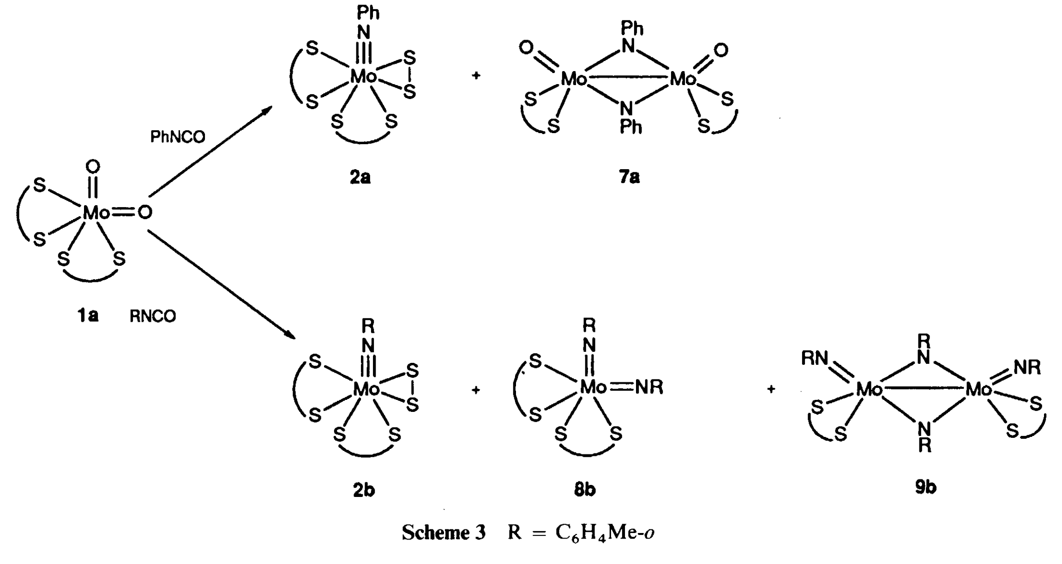
The oxidation of disulfur ligands by mild oxidants to generate S_2O and S_2O_2 is a well documented process which has been studied extensively at iridium(III) centres.[29] Treatment of complex **2a** with 1 or 2 equivalents of 2-chloroperoxybenzoic acid at room temperature led to a change from blue to green. In both cases a green solid was isolated after work-up and shown by ^{1}H NMR spectroscopy to be a complex mixture of products. Attempts at purification by column chromatography led only to extensive decomposition and the formation of small amounts of $[\mathrm{Mo_2O_2}(\mu\text{-NPh})(\mu\text{-S})(\mathrm{S_2CNEt_2})_2]$ **3** (≈5%). A recent report relating to the oxidation of the molybdenum(V) disulfur complex $[\mathrm{Mo}(\eta^2\text{-S}_2)(\mathrm{S_2CNEt_2})_3]$ suggests that oxidation is only controlled to afford the S_2O complex at low temperatures, while at room temperature low yields of the latter and decomposition products including $[\{\mathrm{MoO}(\mu\text{-S})(\mathrm{S_2CNEt_2})\}_2]$ result.[30]

(*iv*) Sulfur–carbon bond cleavage and imido substitution processes

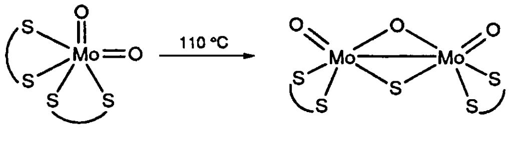
While in all cases, reaction of organic isocyanates with $[\mathrm{MoO_2}(\mathrm{S_2CNEt_2})_2]$ **1a** affords imidodisulfur complexes $[\mathrm{Mo(NR)}(\eta^2\text{-S}_2)(\mathrm{S_2CNEt_2})_2]$ **2**, other products are formed dependent upon the nature of the substituent group. In all instances, however, imido-containing dimolybdenum(V) complexes of the type $[\{\mathrm{MoX}(\mu\text{-X})(\mathrm{S_2CNEt_2})\}_2]$ (X = O, S or NR) are also formed,[24] indicating that reduction of the molybdenum(VI) centre can occur with imido incorporation. For aryl isocyanates containing substituents in the 2 and/or 6 positions of the ring a third product, namely the bis(imido) complex $[\mathrm{Mo(NR)_2}(\mathrm{S_2CNEt_2})_2]$ **8**, also results from the double substitution of oxo for imido moieties.[31] In order then to gain more insight into the nature of the cleavage process, a number of experiments were carried out based primarily on the reaction with phenyl isocyanate in which the dimeric molybdenum(V) complex $[\{\mathrm{MoO}(\mu\text{-NPh})(\mathrm{S_2CNEt_2})\}_2]$ **7**[13] was the only other isolated product, but also on the reaction with *o*-tolyl isocyanate which yielded both $[\{\mathrm{Mo(NC_6H_4Me}\text{-}o)(\mu\text{-NC_6H_4Me}\text{-}o)(\mathrm{S_2CNEt_2})\}_2]$ **9b**[23,24] and $[\mathrm{Mo(NC_6H_4Me}\text{-}o)_2(\mathrm{S_2CNEt_2})_2]$ **8b**[32] as minor products (Scheme 3).

Our first investigation was aimed at trying to ascertain whether the cleavage process took place before or after imido incorporation. We strongly favoured the latter since all products from all reactions contained at least one imide ligand. Thermolysis of $[\mathrm{MoO_2}(\mathrm{S_2CNEt_2})_2]$ **1a** alone was carried out, anticipating that products such as $[\mathrm{MoO}(\eta^2\text{-S}_2)(\mathrm{S_2CNEt_2})_2]$ **10** and $[\{\mathrm{MoO}(\mu\text{-O})(\mathrm{S_2CNEt_2})\}_2]$ would be suggestive of sulfur–carbon bond cleavage prior to oxo substitution. Heating **1a** in toluene for 2 d led to the gradual development of a purple colouration which might be associated with the known oxo-bridged molybdenum(V) dimer $[\mathrm{Mo_2O_2}(\mu\text{-O})(\mathrm{S_2CNEt_2})_2]$.[21] Chromatography resulted in elution of a number of bands from which the only identifiable product was $[\mathrm{Mo_2O_2}(\mu\text{-O})(\mu\text{-S})(\mathrm{S_2CNEt_2})_2]$[33] formed in 49% yield [equation (15)]. Critically **10** was not formed.

In order further to probe the intermediacy of complex **10**, reaction with phenyl isocyanate was carried out and led to the formation of **2a** in 90% yield. A similar thermolysis of **10** with Bu^{t}NCO, however, did not lead to any significant reaction even



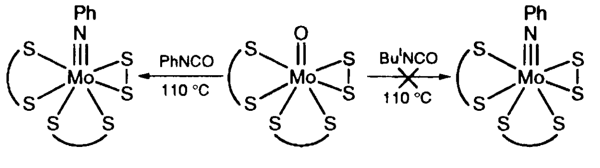
Scheme 3 R = C_6H_4Me-*o*



(15)

1a

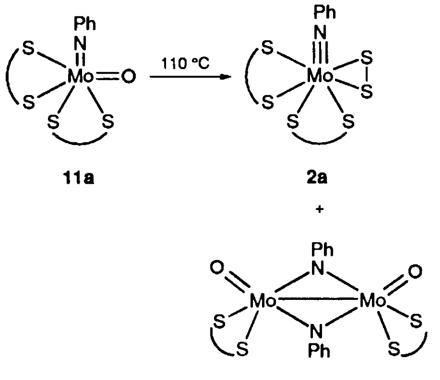
after 3 d, again ruling out the formation of **10** (a result of the double sulfur–carbon cleavage process) followed by oxo substitution as a process *general* to all isocyanates [equation (16)].



(16)

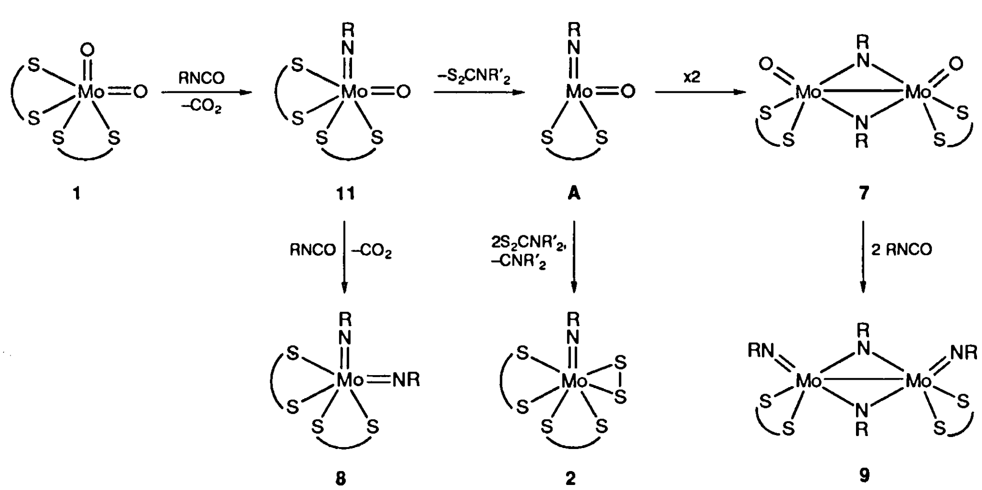
2a **10** **2h**

From the experiments described above it is concluded that the major reaction pathway is one in which oxo substitution occurs prior to sulfur–carbon bond cleavage. Most obvious intermediates in the process then are the mono- and bis-substituted complexes [MoO(NR)(S$_2$CNEt$_2$)$_2$] **11** and [Mo(NR)$_2$(S$_2$CNEt$_2$)$_2$] **8** respectively. The latter are found for substituted aryl isocyanates, for example with 2,6-X$_2$C$_6$H$_3$NCO (X = Me, Pr^i or Cl) they constitute the major product isolated.[31,32] While with phenyl isocyanate the known bis(imido) complex [Mo(NPh)$_2$(S$_2$CNEt$_2$)$_2$] **8a**[20] was not observed, as previously stated, low yields of [Mo(NC$_6$H$_4$Me-*o*)$_2$(S$_2$CNEt$_2$)$_2$] **8b** were formed from the reaction with *o*-tolyl isocyanate. The intermediacy of a bis(imido) complex appeared particularly likely in the reaction with *o*-tolyl isocyanate since here the second product [{Mo(NC$_6$H$_4$Me-*o*)(μ-NC$_6$H$_4$Me-*o*)(S$_2$CNEt$_2$)}$_2$][23,24] also contains an imido to dithiocarbamate ratio of 2 : 1. Heating **8b** in [^{2}H$_8$]toluene in a sealed NMR tube, however, led to no appreciable change even after periods of up to 5 d. Indeed **8a** was also found to be stable under these conditions (provided that exclusion of air is rigorous) thus ruling out the possibility of double oxo substitution prior to dithiocarbamate degradation. The remaining plausible intermediate is then monosubstituted [MoO(NR)(S$_2$CNEt$_2$)$_2$] **11**. We have previously postulated [MoO(NPh)(S$_2$CNEt$_2$)$_2$] **11a** as an intermediate in the reaction with phenyl isocyanate on the basis that both products formed have a molybdenum to imido ratio of 1 : 1.[13] In order to check this hypothesis, **11a** was heated in [^{2}H$_8$]toluene in a sealed NMR tube whilst monitoring by ^{1}H NMR spectroscopy. At reflux a change from yellow to green was observed and the complexity of the spectrum changed dramatically with resonances assigned to both [Mo(NPh)(η^2-S$_2$)(S$_2$CNEt$_2$)$_2$] **2a** and [{MoO(μ-NPh)(S$_2$CNEt$_2$)}$_2$] **7a** appearing, such that after 16 h **11a** had been completely consumed [equation (17)]. The oxoimido complex **11a** is then clearly an intermediate in the formation of both disulfur and molybdenum(v) complexes upon reaction of [MoO$_2$(S$_2$CNEt$_2$)$_2$] **1a**. In light of this finding a plausible reaction pathway is shown in Scheme 4. Initial oxo substitution of [MoO$_2$(S$_2$CNEt$_2$)$_2$] **1a** affords the respective oxoimido complex [MoO(NR)(S$_2$CNEt$_2$)$_2$] **11** as might be expected. Under the reaction conditions employed, namely toluene reflux, the latter is not stable and undergoes dithiocarbamate loss to form a co-ordinatively unsaturated molybdenum(v) complex [MoO(NR)(S$_2$CNEt$_2$)] **A** which rapidly undergoes dimerisation to imido-bridged [{MoO(NR)(S$_2$CNEt$_2$)}$_2$] **7**. That the imide and not the oxide ligands occupy the bridging sites is expected on the basis of the better π-donor capability of the latter and has previously been observed in related cyclopentadienyl-stabilised complexes.[34] In support of the supposition that dithiocarbamate is lost, small amounts of tetraethylthiuram disulfide, formed upon dimerisation, were isolated from the thermolysis reactions. The dithiocarbamate released could react further with **11** resulting in oxo substitution, a process which is well documented at molybdenum(vi) centres.[35] The cleavage process then could occur at this stage, the Et$_2$NC fragment being extruded from the molecule. The fate of the latter is unknown and no evidence was found for formation of the alkyne Et$_2$NC≡CNEt$_2$. It should, however, be noted that the latter is likely to be highly reactive under the reaction conditions employed. A further possible pathway towards the formation of the disulfur complex cannot be discounted, namely that the disulfur moiety



11a **2a** (17)

7a



Scheme 4

originates from the tetraethylthiuram disulfide. Such an extrusion process is, however, not generally associated with disulfides, sulfur–sulfur bond cleavage predominating over sulfur–carbon bond scission.

While reaction of *p*-tolyl isocyanate occurs in an exactly analogous fashion to that with phenyl isocyanate, with *o*-tolyl isocyanate the molybdenum(V) complex isolated is not $[\{MoO(\mu\text{-}NC_6H_4Me\text{-}o)(S_2CNEt_2)\}_2]$ **7b** but $[\{Mo(NC_6H_4Me\text{-}o)(\mu\text{-}NC_6H_4Me\text{-}o)(S_2CNEt_2)\}_2]$ **9b**. The former, however, reacts very rapidly with isocyanate to give the latter[24] and thus an oxoimido intermediate is plausible in this instance. With 2,6-disubstituted aryl isocyanates the major reaction product along with the disulfur complexes is the bis(imido) species $[Mo(NR)_2(S_2CNEt_2)_2]$ **8**, with dimeric molybdenum(V) complexes being formed in only very low yields.[24,32] Here we suggest that either the respective oxoimido complexes $[MoO(NR)(S_2CNEt_2)_2]$ **11** are more stable to dithiocarbamate loss or, as seems more likely, the second oxo-substitution process is more rapid and competes effectively with reduction *via* dithiocarbamate loss.

Experimental

General comments

Techniques and instrumentation were as previously described,[24] $[MoO_2(S_2CNR'_2)_2]$ **1** (R' = Et or Me)[2] and $[MoO(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ **10**[16] were prepared by literature routes while new syntheses of $[Mo(NR)_2(S_2CNEt_2)_2]$ **8** (R = Ph or C_6H_4Me-*o*) and $[MoO(NPh)(S_2CNEt_2)_2]$ **11a** will be reported in a separate publication.[32]

Synthesis of imidodisulfur complexes $[Mo(NR)(\eta^2\text{-}S_2)(S_2CNR'_2)_2]$ 2

All reactions were carried out in an analogous fashion. Full details are given for the preparation of complex **2a**. Analytical data for all imidodisulfur complexes are given in Table 4.

The complex $[MoO_2(S_2CNEt_2)_2]$ **1a** (1.13 g, 2.66 mmol) was dissolved in toluene (100 cm^3) and phenyl isocyanate (0.25 cm^3, 2.66 mmol) was added *via* a degassed syringe. The solution was refluxed for 3 d, after which time volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A yellow band, identified as $(Et_2NCSS)_2$ by comparison of its IR spectrum with that of an authentic sample, was obtained after elution with 20% dichloromethane in light petroleum (b.p. 40–60 °C). A purple band was obtained after eluting with 40% dichloromethane in light petroleum which afforded $[Mo(NPh)(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ **2a** (0.33 g, 23%) as a purple solid. $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$); δ 204.6, 203.6 (S_2CN), 154.2 (C_{ipso} of Ph), 128.3 (Ph), 127.6 (*p*-H of Ph), 126.9 (Ph), 45.6, 45.1, 44.6, 44.0 (CH_2), 12.8, 12.6, 12.4, 12.1 (CH_3). Further elution with 90% dichloromethane in light petroleum gave a yellow band which afforded $[\{MoO(\mu\text{-}NPh)(S_2CNEt_2)_2\}_2]$ **7a** (0.74 g, 76%) as a bright yellow solid. An analogous reaction with phenyl isothiocyanate afforded **2a** (15%) and **7a** (55%).

Complex 2b. Dichloromethane (25%) in light petroleum afforded orange $[\{Mo(NC_6H_4Me\text{-}o)(\mu\text{-}NC_6H_4Me\text{-}o)(S_2CNEt_2)\}_2]$ **9b** (34%), 40% dichloromethane in light petroleum gave purple $[Mo(NC_6H_4Me\text{-}o)(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ **2b** (24%), while a minor brown band shown by NMR spectroscopy to be $[Mo(NC_6H_4Me\text{-}o)_2(S_2CNEt_2)_2]$ **8b** decomposed on passage down the column.

Complex 2c. Dichloromethane (40%) in light petroleum afforded purple $[Mo(NC_6H_4Me\text{-}p)(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ **2c** (24%). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 204.7, 203.7 (S_2CN), 138.3, 128.9, 126.9 (C_6H_4), 45.6, 45.1, 44.6, 43.9 (CH_2), 21.64 ($CH_3C_6H_4$), 12.8, 12.6, 12.4, 12.1 (CH_2CH_3). Further elution with 5% methanol in dichloromethane gave yellow $[\{MoO(\mu\text{-}NC_6H_4Me\text{-}p)(S_2CNEt_2)\}_2]$ **7c** (50%).

Table 4 Analytical data for imidodisulfur complexes **2** with calculated values in parentheses

	Analysis (%)			
Complex	C	H	N	S
2a	34.60 (35.10)	4.60 (4.60)	7.55 (7.65)	33.95 (35.10)
2b	36.25 (36.35)	4.65 (4.85)	7.30 (7.45)	32.30 (33.40)
2c	36.45 (36.35)	5.10 (4.85)	7.25 (7.45)	32.65 (33.40)
2d	37.30 (37.55)	5.50 (5.05)	7.15 (7.30)	32.65 (33.40)
2e	31.25 (31.35)	3.40 (3.75)	6.70 (6.80)	30.70 (31.10)
2f	41.80 (41.85)	6.15 (5.85)	6.50 (6.65)	30.30 (30.45)
2g	39.50 (39.65)	5.70 (5.80)	6.70 (6.95)	31.35 (31.75)
2h	31.45 (31.85)	5.15 (5.55)	7.75 (7.95)	35.50 (36.45)
2i	28.80 (29.30)	3.45 (3.50)	8.20 (8.55)	38.00 (39.15)
2j	25.25 (25.45)	4.30 (4.50)	8.50 (8.90)	40.60 (40.80)
2k	37.45 (37.55)	4.90 (5.10)	7.05 (7.30)	32.85 (33.40)

Complex 2d. Dichloromethane (20%) in light petroleum afforded brown $[Mo(NC_6H_3Me_2\text{-}2,6)_2(S_2CNEt_2)_2]$ **8d** (26%), 25% dichloromethane in light petroleum gave orange $[Mo_2O(NC_6H_3Me_2\text{-}2,6)(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (4%) and with 40% dichloromethane in light petroleum red-brown $[Mo(NC_6H_3Me_2\text{-}2,6)(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ **2d** (22%) was isolated. $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 204.9, 203.8 (S_2CN), 141.3, 127.7, 127.5 (C_6H_3), 45.5, 45.0, 44.6, 44.0 (CH_2), 19.4 ($CH_3C_6H_3$), 12.9, 12.7, 12.5, 12.1 (CH_2CH_3).

Complex 2e. Dichloromethane (20%) in light petroleum gave brown $[Mo(NC_6H_3Cl_2\text{-}2,6)_2(S_2CNEt_2)_2]$ **8e** (14%) and red-brown $[Mo(NC_6H_3Cl_2\text{-}2,6)(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ **2e** (9%) was obtained upon elution with 40% dichloromethane in light petroleum (Found: Cl, 11.90. Calc. for $C_{16}H_{23}Cl_2MoN_3S_6$: Cl, 11.35%).

Complex 2f. Dichloromethane (20%) in light petroleum gave brown $[Mo(NC_6H_3Pr^i_2\text{-}2,6)_2(S_2CNEt_2)_2]$ **8f** (27%) and 40% dichloromethane in light petroleum gave purple $[Mo(NC_6H_3Pr^i_2\text{-}2,6)(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ **2f** (24%).

Complex 2g. Dichloromethane (40%) in light petroleum gave a mixture of yellow $[Mo_2O(NC_{10}H_{15})(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (32%) and red $[Mo(NC_{10}H_{15})(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ **2g** (31%) separated by fractional crystallisation from dichloromethane–methanol solutions.

Complex 2h. Dichloromethane (60%) in light petroleum gave a mixture of yellow $[Mo_2O(NBu^t)(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (10%) and red $[Mo(NBu^t)(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ **2h** (18%) which were separated by fractional crystallisation from dichloromethane–methanol solutions.

Complex 2i. Dichloromethane (40%) in light petroleum gave purple $[Mo(NPh)(\eta^2\text{-}S_2)(S_2CNMe_2)_2]$ **2i** (21%). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 206.1, 205.0 (S_2CN), 154.5, 128.4, 127.9, 127.2 (Ph), 40.8, 40.5, 39.2, 38.6 (Me). Further elution with 1% methanol in dichloromethane gave yellow $[\{MoO(\mu\text{-}NPh)(S_2CNMe_2)\}_2]$ **7i** (49%).

Complex 2j. Dichloromethane (50%) in light petroleum gave a mixture of red $[Mo(NBu^t)(\eta^2\text{-}S_2)(S_2CNMe_2)_2]$ **2j** (15%) and yellow $[Mo_2O(NBu^t)(\mu\text{-}S)_2(S_2CNMe_2)_2]$ (50%) separated by fractional crystallisation from dichloromethane–methanol solutions.

Complex 2k. Dichloromethane (20%) in light petroleum gave

Table 5 Crystallographic data

	2a	**2j**	**2k**	**3**
Formula	$C_{16}H_{25}MoN_3S_6$	$C_{10}H_{21}MoN_3S_6$	$C_{18}H_{29}MoN_3S_6$	$C_{16}H_{25}Mo_2N_3O_2S_5$
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	10.4357(23)	8.2321(9)	9.4708(28)	8.8589(16)
b/Å	9.9631(22)	9.0581(7)	17.9944(42)	8.9404(20)
c/Å	23.4058(68)	13.4021(14)	14.5049(19)	16.5833(37)
α/°		95.437(7)		87.310(18)
β/°	98.630(21)	94.171(8)	94.624(11)	74.430(18)
γ/°		101.548(7)		86.880(16)
U/Å^3	2405.99	972.89	2461.18	1262.65
Z	4	2	4	2
F(000)	1120	480	1184	644
D_c/g cm^{-3}	1.51	1.61	1.55	1.69
Crystal size/mm	0.68 × 0.40 × 0.40	0.50 × 0.30 × 0.25	0.60 × 0.30 × 0.30	0.24 × 0.20 × 0.10
μ(Mo-Kα)/cm^{-1}	10.40	12.70	10.20	13.85
Orientation reflections	30, $14 \leqslant 2\theta \leqslant 28$	36, $22 \leqslant 2\theta \leqslant 32$	28, $22 \leqslant 2\theta \leqslant 30$	28, $17 \leqslant 2\theta \leqslant 27$
Data measured	4761	3817	4974	4811
Unique data	4717	3694	4815	4725
No. unique with $I \geqslant 3.0\sigma(I)$	3268	3238	3728	3558
No. parameters	235	181	253	253
R^a	0.039	0.0297	0.0365	0.036
R'^b	0.041	0.0391	0.0473	0.038
$10^6 g^b$	239	2293	6521	433
Largest shift/e.s.d., final cycle	0.001	0.002	0.001	0.002
Largest peak/e Å^{-3}	0.52	0.28	0.40	0.58

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|$; $w^{-1} = \sigma^2(F) + gF^2$.

Table 6 Atomic coordinates (× 10^4) for complex **2a**

Atom	x	y	z
Mo	2 032(1)	8 203(1)	3 924(1)
S(1)	4 023(1)	6 701(1)	4 104(1)
S(2)	3 300(1)	8 644(1)	4 893(1)
S(3)	1 407(1)	6 406(1)	3 183(1)
S(4)	966(1)	6 172(1)	4 373(1)
S(5)	696(1)	9 761(1)	4 348(1)
S(6)	−161(1)	8 972(2)	3 585(1)
N(1)	5 562(4)	7 297(4)	5 109(2)
N(2)	294(4)	4 240(4)	3 577(2)
N(3)	2 915(4)	9 156(4)	3 485(2)
C(1)	4 468(4)	7 509(4)	4 752(2)
C(2)	5 835(5)	7 953(5)	5 676(2)
C(3)	5 408(6)	7 106(6)	6 146(3)
C(4)	6 562(5)	6 414(6)	4 934(3)
C(5)	7 497(6)	7 175(7)	4 623(3)
C(6)	802(4)	5 444(5)	3 700(2)
C(7)	−203(6)	3 408(5)	4 022(2)
C(8)	−1 628(7)	3 370(9)	3 959(3)
C(9)	212(5)	3 634(5)	3 000(2)
C(10)	1 344(6)	2 765(7)	2 937(3)
C(11)	3 777(5)	9 595(5)	3 130(2)
C(12)	3 334(6)	10 118(6)	2 589(3)
C(13)	4 180(8)	10 596(8)	2 239(3)
C(14)	5 470(10)	10 525(9)	2 436(4)
C(15)	5 965(7)	10 023(8)	2 974(4)
C(16)	5 099(6)	9 543(6)	3 321(3)

Table 7 Atomic coordinates (× 10^4) for complex **2j**

Atom	x	y	z
Mo	1 508(1)	6 811(1)	2 306(1)
S(1)	−802(1)	8 303(1)	2 278(1)
S(2)	578(2)	7 127(1)	565(1)
S(3)	1 707(1)	7 943(1)	4 111(1)
S(4)	3 337(1)	9 558(1)	2 595(1)
S(5)	3 529(1)	5 864(1)	1 350(1)
S(6)	4 025(1)	5 996(1)	2 870(1)
N(1)	−2 055(5)	8 494(4)	414(3)
N(2)	3 240(3)	10 812(3)	4 481(2)
N(3)	103(3)	5 246(3)	2 500(2)
C(1)	−919(5)	8 041(4)	998(3)
C(2)	−2 042(8)	8 236(6)	−684(3)
C(3)	−3 285(6)	9 251(6)	802(5)
C(4)	2 832(4)	9 609(4)	3 807(2)
C(5)	4 111(5)	12 238(4)	4 223(3)
C(6)	2 749(5)	10 809(5)	5 502(3)
C(7)	−1 176(4)	4 125(4)	2 817(3)
C(8)	−409(8)	2 827(5)	3 078(5)
C(9)	−2 529(6)	3 665(6)	1 944(4)
C(10)	−1 854(5)	4 853(5)	3 732(3)

brown [Mo($NC_6H_3Pr^i{}_2$-2,6)$_2$(S_2CNMe_2)$_2$] **8k** (33%) while 40% dichloromethane in light petroleum gave purple [Mo($NC_6H_3Pr^i{}_2$-2,6)(η^2-S_2)(S_2CNMe_2)$_2$] **2k** (12%).

Crystals of complexes **2a**, **2j** and **2k** grown *via* slow diffusion of methanol in dichloromethane solutions proved suitable for X-ray crystallography.

Reactions of [Mo(NPh)(η^2-S_2)(S_2CNEt_2)$_2$] 2a

(*i*) With P(OEt)$_3$ and air. Complex **2a** (0.36 g, 0.58 mmol) was dissolved in dichloromethane (50 cm^3) and to this was added P(OEt)$_3$ (0.30 cm^3, 1.8 mmol) *via* a degassed syringe. The solution was stirred for 5 h after which time it turned from purple to brown. It was then exposed to the atmosphere and stirred for 24 h during which time it went red and finally yellow. Volatiles were removed at reduced pressure to yield a brown-yellow solid which was washed thoroughly with light petroleum. Crystallisation upon diffusion of methanol into a dichloromethane solution afforded [Mo_2O_2(μ-S)(μ-NPh)(S_2CNEt_2)$_2$] **3** (0.35 g, 60%) as a yellow crystalline solid. Crystals grown in this manner were suitable for X-ray crystallography. The reaction was repeated using a similar amount of material but changing the procedure by adding a dichloromethane solution of **2a** to a dichloromethane solution of P(OEt)$_3$ in the initial step. This method also afforded a similar yield of **3**. NMR ($CDCl_3$): ^{1}H, δ 7.42 (t, 2 H, *J* 7.4, *m*-H of Ph), 7.20 (t, 1 H, *J* 7.3, *p*-H of Ph), 7.14 (d, 2 H, *J* 7.2, *o*-H of Ph), 4.07–3.76 (m, 8 H, CH_2), 1.38 (t, 6 H, *J* 7.2, Me) and 1.31 (t, 6 H, *J* 7.2 Hz, Me): ^{13}C-{^{1}H}, δ 204.5 (S_2CN), 164.5 (C_{ipso} of Ph), 128.0, 125.0 (Ph), 124.7 (*p*-C of Ph), 46.4, 46.1 (CH_2), 12.6, 12.5 (CH_3). IR ($\tilde{\nu}$/cm^{-1}): 1530s, 1479m, 1457m, 1440m, 1380m, 1353m, 1279s, 1201m, 1151m, 1084m, 953s, 941s, 843w, 772m and 691m (Found: C, 29.65; H, 3.85; N, 6.35; S, 24.65.

Table 8 Atomic coordinates (× 10^4) for complex **2k**

Atom	*x*	*y*	*z*
Mo	7 506(1)	4 385(1)	2 263(1)
S(1)	9 673(1)	3 645(1)	2 698(1)
S(2)	9 002(1)	4 305(1)	963(1)
S(3)	6 774(1)	3 616(1)	3 577(1)
S(4)	6 451(1)	3 105(1)	1 703(1)
S(5)	6 050(1)	4 974(1)	1 059(1)
S(6)	5 068(1)	4 761(1)	2 209(1)
N(1)	11 494(3)	3 645(2)	1 402(3)
N(2)	5 590(5)	2 329(2)	3 120(5)
N(3)	8 203(3)	5 154(2)	2 861(2)
C(1)	10 253(4)	3 837(2)	1 649(3)
C(2)	12 006(6)	3 864(3)	543(3)
C(3)	12 440(5)	3 199(3)	2 012(4)
C(4)	6 202(5)	2 940(2)	2 812(4)
C(5)	5 043(7)	1 761(3)	2 448(8)
C(6)	5 429(9)	2 185(4)	4 071(6)
C(7)	8 748(4)	5 756(2)	3 347(3)
C(8)	8 315(4)	5 910(2)	4 231(3)
C(9)	8 948(5)	6 498(3)	4 705(3)
C(10)	9 974(6)	6 918(3)	4 344(3)
C(11)	10 362(5)	6 767(2)	3 473(3)
C(12)	9 772(4)	6 192(2)	2 950(3)
C(13)	7 244(5)	5 442(3)	4 658(3)
C(14)	6 202(7)	5 883(5)	5 151(5)
C(15)	7 975(7)	4 898(4)	5 304(4)
C(16)	10 228(4)	6 029(2)	2 006(3)
C(17)	11 571(6)	5 589(3)	2 070(4)
C(18)	10 402(7)	6 733(3)	1 428(3)

Table 9 Atomic coordinates (× 10^4) for complex **3**

Atom	*x*	*y*	*z*
Mo(1)	3 080(1)	3 556(1)	3 350(1)
Mo(2)	1 799(1)	5 698(1)	2 472(1)
S(1)	5 809(2)	3 279(2)	3 449(1)
S(2)	3 073(2)	3 227(2)	4 845(1)
S(3)	55(2)	7 989(2)	2 822(1)
S(4)	3 143(2)	7 874(2)	1 695(1)
S(5)	769(2)	4 992(2)	3 865(1)
N(1)	5 980(6)	2 642(5)	5 026(3)
N(2)	1 179(6)	10 305(5)	1 775(3)
N(3)	3 955(5)	4 848(5)	2 354(3)
O(1)	2 638(5)	1 897(4)	3 056(3)
O(2)	1 010(5)	4 771(4)	1 837(3)
C(1)	5 084(6)	2 967(5)	4 519(3)
C(2)	5 307(8)	2 504(7)	5 940(4)
C(3)	4 858(11)	941(8)	6 248(5)
C(4)	7 706(7)	2 569(7)	4 711(4)
C(5)	8 455(10)	1 112(10)	4 733(7)
C(6)	1 408(7)	8 932(6)	2 047(3)
C(7)	−289(9)	11 182(7)	2 105(5)
C(8)	−1 351(12)	11 224(13)	1 550(6)
C(9)	2 439(10)	11 058(7)	1 135(5)
C(10)	2 590(13)	10 625(10)	269(5)
C(11)	5 364(7)	5 022(6)	1 737(3)
C(12)	5 578(9)	4 344(9)	974(4)
C(13)	6 911(12)	4 589(12)	332(5)
C(14)	8 021(10)	5 455(12)	422(6)
C(15)	7 880(9)	6 097(10)	1 178(5)
C(16)	6 547(8)	5 887(8)	1 843(4)

Calc. for $C_{16}H_{25}Mo_2N_3O_2S_5$: C, 29.85; H, 3.90; N, 6.50; S, 24.90%).

***(ii)* With dmad.** Complex **2a** (0.25 g, 0.46 mmol) was dissolved in toluene (50 cm^3), dmad (0.08 cm^3, 0.56 mmol) was added *via* a degassed syringe and the solution was refluxed for 20 h after which time the solution had changed from purple to green. Volatiles were removed under reduced pressure, and the resulting green solid was absorbed onto alumina and passed down a chromatography column. Elution with 20% dichloromethane in light petroleum afforded orange [Mo{SC(R)=C(R)NPh}{η^3-SC(R)=C(R)SC(NEt$_2$)}(S_2CNEt_2)] **6** (R = CO_2Me) (0.03 g, 8%). Further elution with 40% dichloromethane in light petroleum afforded blue [Mo{SC(R)=C(R)NPh}{η^4-SC(R)=C(R)C(NEt$_2$)S}(S_2CNEt_2)] **4** (0.10 g, 27%) and elution with 80% dichloromethane in light petroleum afforded green [Mo{SC(R)=C(R)NPh}{η^4-SC(R)=C(R)-C(NEt$_2$)S}(S_2CNEt_2)] **5** (0.06 g, 16%). Crystals of **4** were obtained by slow diffusion of light petroleum into a dichloromethane solution. Attempts to recrystallise **5** and **6** by various methods met with failure.

Complex **4**. ^1H NMR ($CDCl_3$): δ 7.36–7.06 (m, 5 H, Ph), 3.94–3.39 (m, 8 H, CH_2), 3.82 (s, 3 H, OMe), 3.71 (s, 3 H, OMe), 3.69 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 1.42 (t, 3 H, *J* 7.2, Me), 1.41 (t, 3 H, *J* 7.2, Me), 1.26 (t, 3 H, *J* 7.2, Me) and 1.24 (t, 3 H, *J* 7.2 Hz, Me). IR ($\tilde{\nu}$/cm^{-1}): 1731m, 1718s, 1701m, 1685s, 1559m, 1510m, 1473w, 1457w, 1433m, 1357w, 1337m, 1264s, 1246m, 1223s, 1198m, 1153m, 1079m, 850w, 753w, 748w and 700w (Found: C, 41.45; H, 4.60; N, 4.55; S, 19.10. Calc. for $C_{38}H_{37}MoN_3O_8S_5$: C, 42.05; H, 4.65; N, 5.25; S, 20.05%). Crystallographic data: a = 10.7037(43), b = 12.9533(33), c = 13.0390(48) Å, α = 96.483(26), β = 94.488(31), γ = 91.013(28); U = 1790.11(1.10) Å^3. Attempts to elucidate the structure were only partially successful. While most of the molecule refined reasonably, a disorder in one of the dithiocarbamate ligands and unacceptable thermal parameters on the phenyl ring made full refinement impossible. The gross molecular structure is, however, clearly as shown.

Complex **5**. ^1H NMR ($CDCl_3$): δ 7.26–7.06 (m, 5 H, Ph), 3.92 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 3.95–3.30 (m, 8 H, CH_2), 1.24–1.21 (m, 6 H, 2 Me), 1.13 (t, 3 H, *J* 7.3, Me) and 1.05 (t, 3 H, *J* 7.3 Hz, Me). IR ($\tilde{\nu}$/cm^{-1}): 1725 (br), 1430 (br), 1360 (br), 1300m, 1270m, 1200 (br), 1070 (br), 755m and 701m.

Complex **6**. ^1H NMR ($CDCl_3$): δ 7.51–7.05 (m, 5 H, Ph), 3.96 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 4.09–3.33 (m, 8 H, CH_2) and 1.15–1.13 (m, 12 H, Me). IR ($\tilde{\nu}$/cm^{-1}): 1721 (br), 1510 (br), 1340 (br), 1265m, 1220 (br), 1101 (br), 750m and 700m.

***(iii)* With 3-chloroperoxybenzoic acid.** To a dichloromethane (50 cm^3) solution of complex **2a** (0.25 g, 0.45 mmol) was added a dichloromethane solution of 3-chloroperoxybenzoic acid [acquired as a 50% mixture with 3-chlorobenzoic acid (0.16 g, 0.46 mmol)]. An immediate change from purple to green was observed, and the solution stirred for 30 min. Volatiles were then removed at reduced pressure, affording a green solid which was washed with ether (3 × 70 cm^3). The ^1H NMR spectrum of this solid indicated the presence of more than one complex. Attempts to purify this mixture by recrystallisation of a refrigerated solution, prepared by dissolving the solid in the minimum volume of dichloromethane (10 cm^3), and adding to this light petroleum (3 cm^3), met with failure. Purification was then attempted *via* the use of column chromatography. The green solid quickly decomposed on the column affording a yellow complex that became stuck on the column. A small amount of a yellow complex was obtained after elution with 90% dichloromethane in light petroleum, and was identified as [Mo_2O_2(μ-S)(μ-NPh)(S_2CNEt_2)$_2$] (0.01 g, 7%). ^1H NMR ($CDCl_3$): δ 7.41 (t, 2 H, *J* 7.1 Hz), 7.21–7.11 (m, 3 H), 4.11–3.70 (m, 8 H) and 1.40–1.20 (m, 12 H).

Thermolysis of [$MoO_2(S_2CNEt_2)_2$] 1a

A toluene (100 cm^3) solution of complex **1a** (1.82 g, 4.29 mmol) was refluxed in a round-bottom flask for 3 d. Volatiles were removed under reduced pressure and the resultant oily brown solid was absorbed onto alumina and passed down a chromatography column. Elution with 70% dichloromethane in light petroleum gave a yellow band identified as [Mo_2O_2(μ-S)(μ-O)(S_2CNEt_2)$_2$] (1.21 g, 49%) by elemental analysis and comparison of the IR spectrum with literature values.

Reactions of [MoO(η^2-S_2)(S_2CNEt_2)$_2$] **10** with isocyanates

To a solution of complex **10** (0.19 g, 0.41 mol) in toluene (50 cm^3) was added phenyl isocyanate (0.05 cm^3, 0.42 mmol) *via* a degassed syringe and the resulting solution was refluxed for 20 h. Volatiles were removed at reduced pressure and the products purified by chromatography, yielding **2a** (0.20 g, 90%) while further elution with 90% dichloromethane in light petroleum afforded yellow [{MoO(μ-S)(S_2CNEt_2)}$_2$] (0.01 g, 9%). A similar reaction with *tert*-butyl isocyanate also resulted in formation of small amounts of [{MoO(μ-S)(S_2CNEt_2)}$_2$] and recovery of **10** (*ca.* 90%).

Thermolysis of [Mo(NR)$_2$(S_2CNEt_2)$_2$] **8**

A [$^2H_8$]toluene solution of complex **8a** (20 mg, 0.03 mmol) was sealed in an NMR tube and warmed to 110 °C while monitoring by ^{1}H NMR spectroscopy. No new resonances were observed even after maintaining this temperature for 3 d. A similar experiment was perfomed on **8b** and again no new resonances were observed.

Thermolysis of [MoO(NPh)(S_2CNEt_2)$_2$] **11a**

A [$^2H_8$]toluene solution of complex **11a** (17 mg, 0.03 mmol) sealed in an NMR tube and warmed to 110 °C while monitoring by ^{1}H NMR spectroscopy. New resonances developed over a few hours concomitant with a gradual green colouration of the yellow solution. After *ca.* 16 h the resonances assigned to **11a** had disappeared and a number of new ones were apparent, some of which were assigned to **2a** and **7a**. The spectrum was, however, quite complex and we were not able to ascertain the relative proportions of the latter.

Crystal structure determinations

Details of the crystal structure analysis of complex **2a** have been communicated previously.[13] Crystals were mounted on a glass fibre. 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) at 19 ± 1 °C. The lattice vectors 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. For **2j**, **2k** and **3** the ω–2θ technique was used to measure reflections in the range $5 \leqslant 2\theta \leqslant 50°$ while for **2a** the ω technique was used. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. ,The data were corrected for Lorentz and polarisation effects, and empirically for absorption. The unique data with $I \geqslant 3.0\sigma(I)$ were used to solve and refine the structures.

The structures were solved by direct methods and developed by using alternating cycles of least-squares refinement and Fourier-difference synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 Å^2). Structure solution used the SHELXTL PLUS[36] program package on a microVax II computer. The final R and R' values together with residual electron-density levels and other important crystallographic parameters are given in Table 5. Atomic coordinates for **2a**, **2j**, **2k** and **3** are listed in Tables 6–9 respectively.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

This work was supported by grants from the SERC (studentships to T. A. C. and G. D. F.), the Nuffield Foundation, the Royal Society and the University of London Central Research Fund.

References

1 A. M. Bond and R. L. Martin, *Coord. Chem. Rev.*, 1984, **54**, 23.
2 F. W. Moore and M. L. Larson, *Inorg. Chem.*, 1967, **6**, 998.
3 B. T. Zhuang, L. R. Huang, L. J. He, Y. Yang and J. X. Lu, *Inorg. Chim. Acta*, 1988, **45**, 225.
4 U. Riaz, O. Curnow and M. D. Curtis, *J. Am. Chem. Soc.*, 1991, **113**, 1416 and refs. therein.
5 L. Ricard, J. Estienne and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 1972, 906; *Inorg. Chem.*, 1973, **9**, 2182.
6 R. S. Herrick, S. Nieter-Burgmayer and J. L. Templeton, *J. Am. Chem. Soc.*, 1983, **105**, 2599.
7 D. C. Brower, T. L. Tonker, J. R. Morrow, D. S. Rivers and J. L. Templeton, *Organometallics*, 1986, **5**, 1093.
8 J. R. Morrow, T. L. Tonker and J. L. Templeton, *Organometallics*, 1985, **4**, 745.
9 P. F. Gilletti, D. A. Femec, F. I. Keen and T. M. Brown, *Organometallics*, 1992, **31**, 4008.
10 A. Mayr, G. A. McDermott, A. M. Dorries and A. K. Holder, *J. Am. Chem. Soc.*, 1986, **108**, 310.
11 P. R. Heckley, D. G. Holah and D. Brown, *Can. J. Chem.*, 1971, **49**, 1151; M. G. B. Drew, D. M. Williams and D. A. Rice, *Inorg. Chim. Acta*, 1984, **89**, L19.
12 X. F. Yan, B. L. Fox, E. R. T. Tiekink and C. G. Young, *J. Chem. Soc., Dalton Trans.*, 1994, 1765.
13 T. A. Coffey, G. D. Forster and G. Hogarth, *J. Chem. Soc., Chem. Commun.*, 1993, 1524.
14 A. J. Deeming and R. Vaish, *J. Organomet. Chem.*, 1993, **460**, C8.
15 J. L. Migot, J. Sala-Pala and J. E. Guerchais, *J. Organomet. Chem.*, 1983, **243**, 427; A. Müller, W. O. Nolte and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 279.
16 X. F. Yan and C. G. Young, *Aust. J. Chem.*, 1991, **44**, 361.
17 R. A. Henderson, S. K. Ibrahim and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 1993, 392.
18 J. Dirand-Colin, M. Schappacher, L. Ricard and R. Weiss, *J. Less-Common Met.*, 1977, **54**, 91.
19 A. Müller and W. Jagermann, *Inorg. Chem.*, 1979, **18**, 2631.
20 E. A. Maatta and R. A. D. Wentworth, *Inorg. Chem.*, 1979, **18**, 2409.
21 L. Ricard, C. Martin, R. West and R. Weiss, *Inorg. Chem.*, 1975, **14**, 2300.
22 A. Müller, R. G. Bhattacharyya, N. Mohan and B. Pfefferkorn, *Z. Anorg. Allg. Chem.*, 1979, **454**, 118.
23 G. D. Forster and G. Hogarth, *Polyhedron*, 1995, **14**, 1401.
24 T. A. Coffey, G. D. Forster and G. Hogarth, *J. Chem. Soc., Dalton Trans.*, 1995, 2337.
25 C. G. Young, M. A. Bruck and J. H. Enemark, *Inorg. Chem.*, 1992, **31**, 593.
26 D. Coucouvanis, A. Hadjikyriacou, M. Draganjac and M. G. Kanatzidis, *Polyhedron*, 1986, **5**, 349.
27 T. R. Halbert, W. H. Pan and E. I. Stiefel, *J. Am. Chem. Soc.*, 1983, **105**, 5476.
28 C. G. Young, X. F. Yan, B. L. Fox and E. R. T. Tiekink, *J. Chem. Soc., Chem. Commun.*, 1994, 2579.
29 J. E. Hoots, T. B. Rauchfuss and S. R. Wilson, *J. Chem. Soc., Chem. Commun.*, 1983, 1226; G. Schmid and G. Ritter, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 645; M. Herberhold, B. Schmidkonz, M. L. Ziegler and T. Zahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 515.
30 M. A. Halcrow, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1994, **33**, 3639.
31 T. A. Coffey, G. D. Forster, G. Hogarth and A. Sella, *Polyhedron*, 1993, **12**, 2741.
32 T. A. Coffey, G. D. Forster and G. Hogarth, unpublished work.
33 F. A. Schultz, V. R. Ott, D. S. Rolinson, D. C. Bravard, J. W. McDonald and W. E. Newton, *Inorg. Chem.*, 1978, **17**, 1758.
34 M. L. H. Green, G. Hogarth, P. C. Konidaris and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1990, 3781; J. Fletcher, G. Hogarth and D. A. Tocher, *J. Organomet. Chem.*, 1991, **403**, 345; **405**, 207.
35 J. Dirand, L. Ricard and R. Weiss, *Transition Met. Chem.*, 1975, **1**, 2.
36 G. M. Sheldrick, SHELXTL PLUS, program package for structure solution and refinement, version 4.2, Siemens Analytical Instruments Inc., Madison, WI, 1990.

Received 2nd August 1995; *Paper* 5/05173H