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Regioselective and reversible carbon–nitrogen bond formation: Synthesis, structure and reactivity of ureato-bridged complexes $[Mo_2(NAr)_2(\mu\text{-}X)\{\mu\text{-}ArNC(O)NAr\}(S_2CNR_2)_2]$ (Ar = Ph, *p*-tol; X = S, NAr; R = Me, Et, Pr)

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Reaction of ArNCO with *syn*-$[MoO(\mu\text{-}O)(S_2CNR_2)]_2$ or *syn*-$[MoO(\mu\text{-}NAr)(S_2CNR_2)]_2$ at 110 °C leads to the facile formation of bridging ureato complexes $[Mo_2(NAr)_2(\mu\text{-}NAr)\{\mu\text{-}ArNC(O)NAr\}(S_2CNR_2)_2]$ (Ar = Ph, *p*-tol; R = Me, Et, Pr), formed upon substitution of all oxo ligands and addition of a further equivalent of isocyanate across one of the bridging imido ligands. Related sulfido-bridged complexes $[Mo_2(NAr)_2(\mu\text{-}S)\{\mu\text{-}ArNC(O)NAr\}(S_2CNR_2)_2]$ have been prepared from *syn*-$[Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(S_2CNR_2)_2]$. When reactions with *syn*-$[MoO(\mu\text{-}NAr)(S_2CNEt_2)]_2$ were followed by NMR, intermediates were observed, being formulated as $[Mo_2O(NAr)(\mu\text{-}NAr)\{\mu\text{-}ArNC(O)NAr\}(S_2CNEt_2)_2]$, which at higher temperatures convert to the fully substituted products. A crystallographic study of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNPr_2)_2]$ reveals that the bridging ureato ligand is bound asymmetrically to the dimolybdenum centre—molybdenum–nitrogen bonds *trans* to the terminal imido ligands being significantly elongated with respect to those *cis*—a result of the *trans*-influence of the terminal imido ligands. This *trans*-influence also leads to a *trans*-effect, whereby the exchange of aryl isocyanates can occur in a regioselective manner. This is followed by NMR studies and confirmed by a crystallographic study of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}N\text{-}p\text{-}tol)\{\mu\text{-}p\text{-}tolNC(O)NPh\}(S_2CNEt_2)_2]$—the PhNCO occupying the site *trans* to the terminal imido ligands. Ureato complexes also react with PhNCS, initially forming $[Mo_2(NAr)_2(\mu\text{-}S)\{\mu\text{-}ArNC(O)NAr\}(S_2CNR_2)_2]$, resulting from exchange of the bridging imido ligand for sulfur, together with small amounts of $[Mo_2(NAr)_2(\mu\text{-}S)(\mu\text{-}S_2)(S_2CNEt_2)_2]$, containing bridging sulfide and disulfide ligands. The ureato complexes $[Mo_2(NAr)_2(\mu\text{-}S)\{\mu\text{-}ArNC(O)NAr\}(S_2CNR_2)_2]$ react further with PhNCS to give $[Mo_2(NAr)_2(\mu\text{-}S)_2(S_2CNR_2)_2]_n$ (n = 1, 2), which exist in a dimer–tetramer equilibrium. In order to confirm these results crystallographic studies have been carried out on $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)(\mu\text{-}S_2)(S_2CNEt_2)_2]$ and $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CNPr_2)_2]_2$.

Introduction

Ureato (or ureylene) ligands, $[RNC(O)NR]^{2-}$, are doubly-deprotonated ureas and, while moderately common at mononuclear metal centres (A), they are surprisingly rare at binuclear centres,[1–12] at which binding modes (B–D) have been identified.

As early as 1964, Manuel isolated a product from the reaction of $Fe_3(CO)_{12}$ and PhNCO which was incorrectly formulated as $Fe_2(CO)_6(PhNCO)_2$,[1] but later shown to be the ureato-bridged iron(I) complex, $[Fe_2(CO)_6\{\mu\text{-}PhNC(O)NPh\}]$.[2] Soon after, Dekker and Knox produced the methyl analogue, $[Fe_2(CO)_6\{\mu\text{-}MeNC(O)NMe\}]$ from the reaction of methyl azide with $Fe_2(CO)_9$, and showed that the structure closely resembled the phenyl analogue.[3,4] More recently, Hansert and Vahrenkamp reported the formation of $[Fe_2(CO)_6\{\mu\text{-}NPhC(O)NPh\}]$ from the addition of CO to $[Fe_2(CO)_6(\mu\text{-}PhN_2Ph)]$ under mild conditions.[5] Since this report, Kabir and co-workers have detailed the synthesis of a range of phosphine, $[Fe_2(CO)_5(PPh_3)\{\mu\text{-}PhNC(O)NPh\}]$, $[Fe_2(CO)_4(\mu\text{-dppm})\{\mu\text{-}PhNC(O)NPh\}]$, and phosphite, $[Fe_2(CO)_{6-n}\{P(OMe)_3\}_n\{\mu\text{-}PhNC(O)NPh\}]$ (n = 1, 2) substitution products. These can be formed directly from $[Fe_2(CO)_6\{\mu\text{-}PhNC(O)NPh\}]$ upon addition of the appropriate phosphorus-containing ligand, but are also produced directly from $[Fe_2(CO)_6(\mu\text{-}PhN_2Ph)]$; the latter suggesting that $[Fe_2(CO)_6\{\mu\text{-}PhNC(O)NPh\}]$ is initially produced with phosphorus substitution occurring on this complex and not directly onto $[Fe_2(CO)_6(\mu\text{-}PhN_2Ph)]$.[6]

Somewhat similar ureato-bridged dicobalt complexes are known. Thus, the dicobalt(II) complex, $[Cp_2Co_2\{\mu\text{-}t\text{-}BuNC(O)\text{-}t\text{-}Bu\}]$, is a low yield product of the reaction of $(t\text{-}BuN)_2S$ with $[CpCo(CO)_2]$, an X-ray diffraction study confirming the presence of the ureato-bridge.[7] Casey and co-workers have also reported the preparation of the related complex, $[Cp^*_2Co_2\{\mu\text{-}PhNC(O)NPh\}]$, formed upon addition of PhNCO to $[Cp^*_3Co_3(\mu\text{-}H_3)(\mu\text{-}H)]$ at 55 °C; the IR spectrum displaying a strong band at 1659 cm^{-1} indicative of C=O stretching vibration.[8]

In all the above examples, the metal is in a relatively low oxidation state and the ligand acts in a $\mu\text{-}\eta^1,\eta^1$-manner (C). In contrast in the binuclear titanium complex, $[(Cp_2Ti)_2\{\mu\text{-}PhNC(O)NPh\}]$, reported by Fachinetti and co-workers, a structural analysis shows the diphenylureato ligand bridges the two Cp_2Ti units through both the nitrogen and oxygen atoms (D). Interestingly, the latter is isolated upon thermolysis of trinuclear, $[(Cp_2Ti)_3\{\mu\text{-}PhNC(O)NPh\}]$, which itself contains a rare example of ureato bonding mode (B).[9]

A few years ago we reported the synthesis of the dimolybdenum(V) ureato-bridged complex, $[Mo_2(NPh)_2(\mu\text{-}NPh)\{\mu\text{-}PhNC(O)NPh\}(S_2CNEt_2)_2]$ (**1a**), produced upon refluxing a toluene solution of *syn*-$[MoO(\mu\text{-}NPh)(S_2CNEt_2)]_2$ with excess PhNCO.[10–11] Formation of **1a** involves substitution of both terminal oxo ligands and addition of a further equivalent of isocyanate across a bridging imido ligand. At the time we showed that the latter process was reversible; thermolysis of **1a** in the absence of isocyanate affording *syn*-$[Mo(NPh)(\mu\text{-}NPh)(S_2CNEt_2)]_2$, a process which could be readily reversed upon addition of PhNCO.

At the time, a study of the crystal structure of **1a** suggested that the *trans*-influence of the terminal imido ligands may lead to a *trans*-effect, by way of the regioselective loss of the PhNCO

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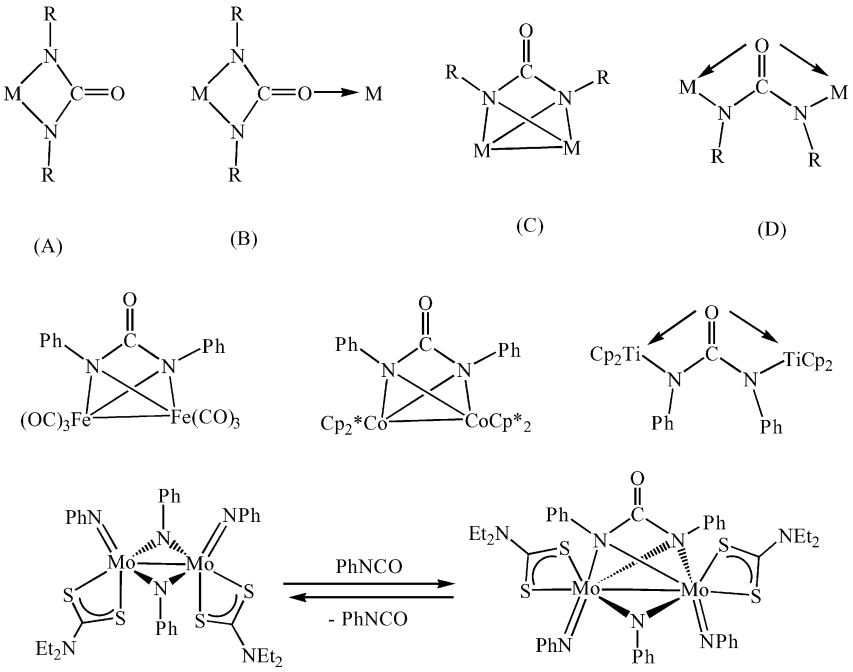


moiety *trans* to these ligands (in preference to that *trans* to the bridging imido group). We have now returned to this area of chemistry and herein demonstrate that this is indeed the case, suggesting that this type of ureato-bridged complex are quite unique in their structure and chemical behaviour.

Results and discussion

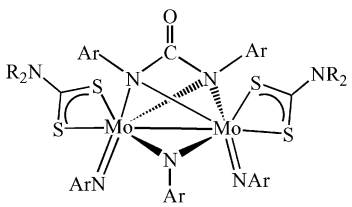
Synthesis of ureato complexes

We have previously prepared the ureato-bridged complexes $[Mo_2(NPh)_2(\mu\text{-}NPh)\{\mu\text{-}PhNC(O)NPh\}(S_2CNEt_2)_2]$ (**1a**) and $[Mo_2(NPh)_2(\mu\text{-}S)\{\mu\text{-}PhNC(O)NPh\}\ (S_2CNEt_2)_2]$ (**2a**) upon thermolysis a slight excess of PhNCO with $[MoO_2(S_2CNEt_2)_2]$ or *syn*-$[MoO(\mu\text{-}O)(S_2CNEt_2)]_2$ and *syn*-$[Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(S_2CNEt_2)_2]$ respectively, followed by purification by column chromatography.[10,11] As it was our intention to monitor reactions of molybdenum(v) ureato complexes by ^{1}H NMR spectroscopy, it was decided that *p*-tolyl ureato complexes would be desirable—the presence of the methyl groups providing a useful spectroscopic handle, while also serving to simplify the complex aromatic region of the spectrum.

The ureato complex $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}N\text{-}p\text{-}tol)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNEt_2)_2]$ (**1b**) was prepared upon refluxing *syn*-$[MoO(\mu\text{-}O)(S_2CNEt_2)]_2$ with approximately five equivalents of *p*-tolylNCO for 24 h in toluene. The dark red–brown **1b** was obtained in 58% yield after purification by column chromatography. A similar reaction of *p*-tolylNCO with *syn*-$[MoO(\mu\text{-}O)(S_2CNPr_2)]_2$ afforded $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}N\text{-}p\text{-}tol)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNPr_2)_2]$ (**1d**) in 12% yield, while thermolysis of *cis*-$[MoO_2(S_2CNMe_2)_2]$ with *p*-tolylNCO gave $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}N\text{-}p\text{-}tol)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNR_2)_2]$ (**1c**) in *ca.* 10% yield. With the latter, the sulfido-bridged ureato complex $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNMe_2)_2]$ (**2c**) was also formed and isolation of pure **1c** was difficult as the two could not be separated by chromatography. Fortunately, crystallisation of the mixture from a dichloromethane–methanol solution gave brown crystals of **1c** and orange crystals of **2c** that could be separated mechanically.

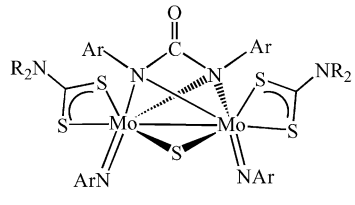
Synthesis of the ureato complexes, $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}N\text{-}p\text{-}tol)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNR_2)_2]$ (**1b–1d**), by the above method is presumed to occur *via* the initial formation of *syn*-$[MoO(\mu\text{-}N\text{-}p\text{-}tol)(S_2CNR_2)]_2$. Indeed, refluxing *syn*-$[MoO(\mu\text{-}N\text{-}p\text{-}tol)(S_2CNEt_2)]_2$ with a further three equivalents of *p*-tolylNCO in toluene for 24 h resulted in the formation of **1b** in 90% yield. In a similar manner, $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNR_2)_2]$ (**2b** and **2d**) were prepared in high yields upon thermolysis of *syn*-$[Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(S_2CNR_2)_2]$ with four equivalents of *p*-tolylNCO in toluene for 24 h. Again, this was the only product recovered after column chromatography. The reaction of *syn*-$[MoO(\mu\text{-}S)(S_2CNEt_2)]_2$ with *p*-tolylNCO was also performed, however, in this instance only the starting material was recovered.

While ureato complexes were successfully synthesized with PhNCO and *p*-tolylNCO, attempts to produce them with the more bulky isocyanates, such as 2,6-dimethylphenylisocyanate, 2,6-diisopropylphenylisocyanate and *o*-tolylNCO proved to be unsuccessful. When the reaction was undertaken with *o*-tolylNCO the previously reported tetraimido complex, $[Mo(N\text{-}o\text{-}tol)(\mu\text{-}N\text{-}o\text{-}tol)(S_2CNEt_2)]_2$, was the only identifiable product.[11]



1

a R = Et, Ar = Ph
b R = Et, Ar = p-tol
c R = Me, Ar = p-tol
d R = Pr, Ar = p-tol



2

a R = Et, Ar = Ph
b R = Et, Ar = p-tol
c R = Me, Ar = p-tol
d R = Pr, Ar = p-tol

With the bulky arylisocyanates, reactions cleanly took place but timescales were long and stable products could not be isolated.

Characterisation of ureato-bridged complexes was made on the basis of IR, FAB mass spectroscopic and ^{1}H NMR data. The IR spectrum all exhibited a strong band at *ca.* 1710 cm^{-1}, assigned to the C=O stretching mode of the ureato ligand. In the mass spectrum, all showed molecular ions, together with a further high mass peak associated with loss of one equivalent of arylisocyanate (see later). The ^{1}H NMR spectra were quite characteristic and that of **1b** (Fig. 1) was studied in some detail in order that reactions of it could be monitored by NMR. In the aromatic region of the spectrum, eight clearly resolved doublets are apparent, those at higher field being associated with the terminal imido ligands. In the region between δ 2.5–2.0, four methyl singlets are seen. That at δ 2.16 is clearly associated with the terminal imido ligands (C). A comparison with the spectra of other ureato complexes described in this paper has also allowed the unambiguous assignment of the remaining three methyl resonances; δ 2.39 to the bridging imido ligand (A), δ 2.34 to the tolyl (B) group *trans* to bridging imido ligand (bottom isocyanate) and δ 2.10 to the tolyl group (D) *trans* to the terminal imido ligands (top isocyanate). Further, a COSY spectrum allowed the aromatic resonances associated with each methyl group to be established (as shown in Fig. 1).

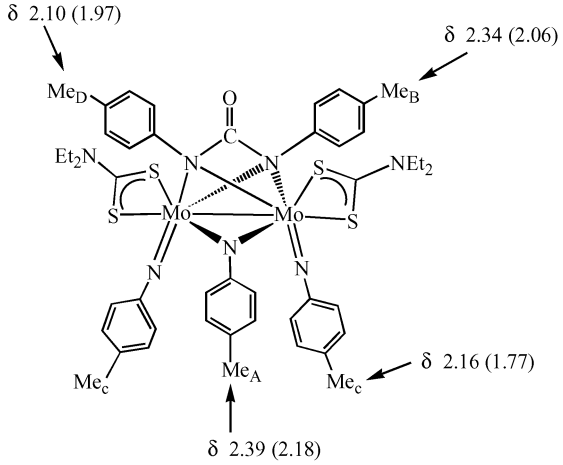


Fig. 1 ^{1}H NMR assignments for **1b** in $CDCl_3$ (and toluene).

We have previously characterised $[Mo_2(NPh)_2(\mu\text{-}NPh)\{\mu\text{-}PhNC(O)NPh\}(S_2CNEt_2)_2]$ (**1a**) crystallographically,[10,11] while Kim and Lee have also crystallographically characterized a THF adduct.[12] The most salient feature of the molecule is the asymmetric nature of the binding to molybdenum of the two nitrogen atoms of the ureato-bridge. Thus, molybdenum–nitrogen bond lengths *trans* to the terminal imido ligands (*av.* 2.387 Å) being around 0.230 Å longer than those *trans* to the bridging imido ligand (*av.* 2.158 Å). In order to confirm that this was a general feature of these ureato-bridged complexes, we obtained a crystal structure of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNPr_2)_2]$ (**2d**), the results of which are summarised in Fig. 2. Importantly, the same feature is seen, molybdenum–nitrogen bonds *trans* to the sulfido-bridge [Mo(1)–N(4) 2.162(3), Mo(2)–N(4) 2.180(2) Å] being on average some 0.173 Å shorter than those *trans* to the terminal imido ligands [Mo(1)–N(3) 2.354(3), Mo(2)–N(3) 2.333(3) Å].

Regioselective isocyanate exchange

We previously noted that thermolysis of $[Mo_2(NPh)_2(\mu\text{-}NPh)\{\mu\text{-}PhNC(O)NPh\}(S_2CNEt_2)_2]$ (**1a**) led, in part, to the loss of one equivalent of PhNCO and formation of the tetraimido complex $[Mo(NPh)(\mu\text{-}NPh)(S_2CNEt_2)]_2$, a process which can be

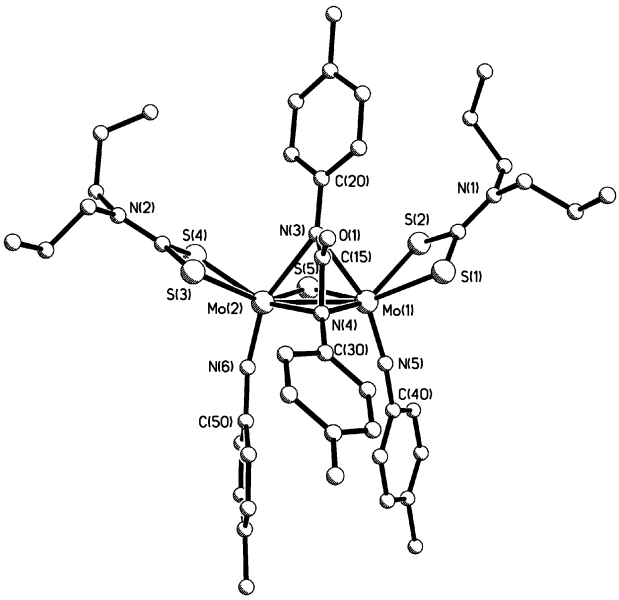
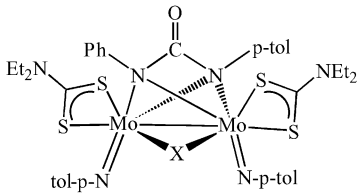


Fig. 2 Molecular structure of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNPr_2)_2]$ (**2d**) with selected bond lengths (Å) and angles (°); Mo(1)–Mo(2) 2.6793(5), Mo(1)–S(5) 2.3509(10), Mo(2)–S(5) 2.3442(10), Mo(1)–N(3) 2.354(3), Mo(2)–N(3) 2.333(3), Mo(1)–N(4) 2.162(3), Mo(2)–N(4) 2.180(2), Mo(1)–N(5) 1.733(3), Mo(2)–N(6) 1.724(3), N(3)–C(15) 1.373(4), N(4)–C(15) 1.436(4), C(15)–O(1) 1.204(4), Mo(1)–S(5)–Mo(2) 69.59(3), Mo(1)–N(3)–Mo(2) 69.72(7), Mo(1)–N(4)–Mo(2) 76.19(8), N(3)–C(15)–N(4) 101.0(3), N(3)–Mo(1)–N(5) 158.44(12), N(3)–Mo(2)–N(6) 151.51(11), N(4)–Mo(1)–N(5) 103.08(12), N(4)–Mo(2)–N(6) 95.05(12), Mo(1)–N(5)–C(40) 168.6(3), Mo(2)–N(6)–C(50) 168.2(2).

reversed upon further addition of isocyanate.[11] The successful isolation of $[Mo(NPh)(\mu\text{-}NPh)(S_2CNEt_2)]_2$ was based on its relative insolubility in toluene, especially when compared to that of **1a**, shifting the equilibrium to the right hand side. Heating **1b** alone in d^8-toluene for 3 h leads to some spectral changes consistent with the generation of small amounts of (presumably) $[Mo(N\text{-}p\text{-}tol)(\mu\text{-}N\text{-}p\text{-}tol)(S_2CNEt_2)]_2$, however, its relative solubility has made it impossible to isolate.

In order to probe further the nature of isocyanate exchange in these ureato complexes we followed the reactions of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}N\text{-}p\text{-}tol)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNEt_2)_2]$ (**1b**) and $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNEt_2)_2]$ (**2b**) with an approximate four-fold excess of PhNCO in d^8-toluene by NMR. The most informative region of the spectra was the methyl signals associated with the *p*-tolyl groups. In both cases, at between 80–90 °C new species developed clearly, concurrent with the generation of one equivalent of *p*-tolylNCO; as seen by the growth of a new resonance at δ 1.92. This was accompanied by the decay of resonances at δ 2.01 (at room temperature but moves to slightly higher field upon heating) in **1b** and at δ 2.06 in **2b**. In the case of **2b**, at the end of the reaction we were able to isolate a small amount of orange precipitate. The ^{1}H NMR spectrum of this in $CDCl_3$ showed two methyl resonances in a 1 : 2 ratio at δ 2.34 and 2.17, clearly showing that one *p*-tolyl group had been lost. When compared to the spectrum of **2b**, which shows three methyl resonances in a 1 : 2 : 1 ratio at δ 2.32, 2.15 and 2.07, it is clear that it is the high-field signal that is lost; *i.e.* that proposed to be associated with the tolyl group (D) (Fig. 1) *trans* to the terminal imido ligands. From the reaction of **1b**, we were also able to isolate the final product as a dark brown solid which showed three methyl singlets in a ^{1}H NMR spectrum run in $CDCl_3$ at δ 2.39, 2.34 and 2.16 in a ratio 1 : 1 : 2. Again comparing this with the spectrum of **1b** in $CDCl_3$ (Fig. 1) which shows four methyl signals in a 1 : 1 : 2 : 1 ratio at δ 2.39, 2.34, 2.16 and 2.10, it is again the high-field signal associated with the tolyl group *trans* to the terminal imido ligands which has disappeared.



3

a X = N-p-tol
b X = S

On the basis of these results it seems clear that it is the *p*-tolylNCO unit *trans* to the terminal imido groups that is exchanged regioselectively in both instances; *i.e.* the *trans*-influence observed in the crystal structures of **1a** and **2d** is translated into a *trans*-effect in these exchange reactions. This suggests that the two products observed are $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}N\text{-}p\text{-tol})\{\mu\text{-}PhNC(O)N\text{-}p\text{-tol}\}(S_2CNEt_2)_2]$ (**3a**) and $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}S)\{\mu\text{-}PhNC(O)N\text{-}p\text{-tol}\}(S_2CNEt_2)_2]$ (**3b**) respectively. Fortunately, we have been able to confirm this with the crystallographic characterisation of **3a**, the results of with are summarised in Fig. 3. The molecular structure closely resembles that of **1a** and **2b**, and importantly it confirms that it is the *p*-tolylNCO *trans* to the terminal imido ligands which is exchanged. As expected, the *trans*-influence of the latter is manifested in the molybdenum–nitrogen bonds; those *trans* to the imido-bridge [Mo(1)–N(3) 2.163(6), Mo(2)–N(3) 2.159(6) Å] being on average some 0.228 Å shorter than those *trans* to the terminal imido ligands [Mo(1)–N(4) 2.394(5), Mo(2)–N(4) 2.383(5) Å].

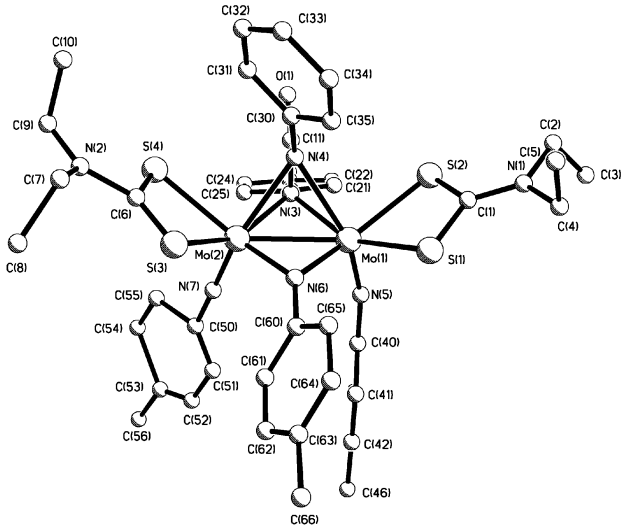
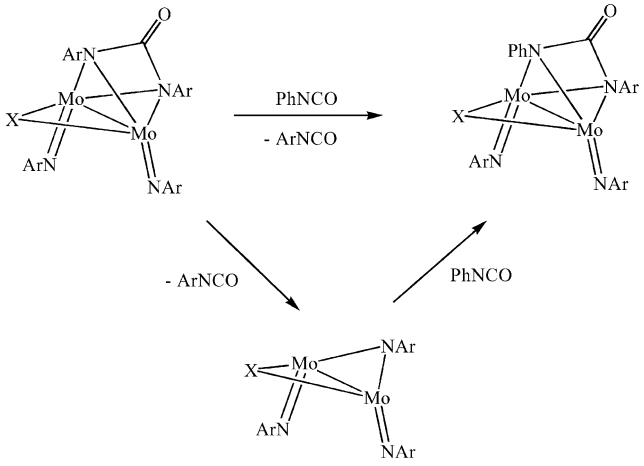


Fig. 3 Molecular structure of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}N\text{-}p\text{-tol})\{\mu\text{-}p\text{-tolNC(O)NPh}\}(S_2CNEt_2)_2]$ (**3a**) with selected bond lengths (Å) and angles (°); Mo(1)–Mo(2) 2.6018(9), Mo(1)–N(3) 2.163(6), Mo(2)–N(3) 2.159(6), Mo(1)–N(4) 2.394(5), Mo(2)–N(4) 2.383(5), Mo(1)–N(5) 1.730(6), Mo(2)–N(7) 1.732(6), N(3)–C(11) 1.451(9), N(4)–C(11) 1.355(9), C(11)–O(1) 1.206(8), Mo(1)–N(3)–Mo(2) 74.03(18), Mo(1)–N(4)–Mo(2) 66.01(14), Mo(1)–N(6)–Mo(2) 82.8(2), N(3)–C(11)–N(4) 101.7(6), Mo(1)–N(5)–C(40) 162.9(5), Mo(2)–N(7)–C(50) 173.7(7).

Scheme 1 highlights the proposed mode of arylisocyanate exchange. Exclusive loss of the *p*-tolylNCO moiety *trans* to the terminal imido ligands would generate *syn*-$[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}X)(\mu\text{-}N\text{-}p\text{-tol})(S_2CNEt_2)_2]$. It is expected that only a minor structure rearrangement of the Mo_2N_3X core would take place during this process, most notably a slight folding of the $Mo_2(\mu\text{-}X)(\mu\text{-}N\text{-}p\text{-tol})$ unit would be expected since the fold-angle in species of this type is typically 145–165°.[13] Alternative loss of the second *p*-tolylNCO unit of the ureato-bridge would require a much more significant perturbation of the $Mo_2(\mu\text{-}X)(\mu\text{-}N\text{-}p\text{-tol})$ core in opening up from approximately 90° found in the ureato complexes. Addition of the PhNCO to the $Mo_2(\mu\text{-}X)(\mu\text{-}N\text{-}p\text{-tol})$



Scheme 1 Proposed mode of arylisocyanate exchange (dithiocarbamates omitted for clarity).

would then occur exclusively to the more exposed "top" face *i.e.* that containing the sterically non-demanding dithiocarbamate ligands. It should be noted that this is a dissociative pathway and it is easy to rule out an associative pathway since the latter would lead to an inversion of the stereochemistry at the dimolybdenum centre, placing the ureato-bridge in the sterically less favourable site close to the terminal imido ligands.

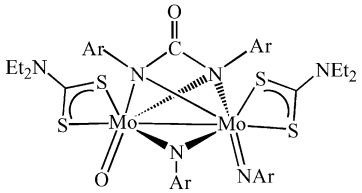
Heating the NMR sample of **3a** and excess PhNCO at 100 °C for 1 h did not result in any further significant changes illustrating the regioselective nature of the isocyanate exchange process. However, heating a toluene solution of **1b** and excess PhNCO for 24 h leads to the formation of a mixture of inseparable ureato-containing species as shown by NMR. Further, the integrated ratio of the eight methylene protons and the methyl groups of the *p*-tolyl moieties suggested that there were now only an average of 3.6 *p*-tolyl groups per molecule, *i.e.* on average four of the five *p*-tolyl groups have been replaced (by phenyl groups). Three major methyl signals were seen in an approximate 1 : 1 : 1 ratio at δ 2.39, 2.34 and 2.15, together with a much smaller resonance at δ 2.11 (*ca.* 15%). This suggests that all three remaining sites have been substituted under these more forcing conditions.

Mode of formation of ureato complexes and characterisation of an intermediate

As mentioned above, formation of the ureato-bridged complexes **1** from *syn*-$[MoO(\mu\text{-}NAr)(S_2CNR_2)]_2$ involves three steps; the substitution of both terminal oxo groups, and addition of an equivalent of isocyanate to one of the bridging imido ligands. In order to further probe these processes, reactions of *syn*-$[MoO(\mu\text{-}NAr)(S_2CNEt_2)]_2$ (Ar = Ph, *p*-tol) with excess arylisocyanates were followed by ^{1}H NMR in d^8-toluene. The presence of excess isocyanate and protio-toluene made changes to the aromatic region of the spectra difficult to follow, but the methyl resonances of both the dithiocarbamate (δ 1.0–0.5) and *p*-tolyl (δ 2.2–1.7) groups provided particularly useful probes.

The reaction of yellow *syn*-$[MoO(\mu\text{-}NPh)(S_2CNEt_2)]_2$ and excess PhNCO in d^8-toluene occurred over 4 h at room temperature to afford an orange solution identified as $[Mo_2O(NPh)(\mu\text{-}NPh)\{\mu\text{-}PhNC(O)NPh\}(S_2CNEt_2)_2]$ (**4a**). This assignment was made initially on the basis of NMR evidence, which clearly showed the addition of two equivalents of PhNCO. The two ends of the molecule are now inequivalent being easily established by the appearance of four triplet resonances between δ 0.7–0.4 associated with the methyl groups of the dithiocarbamate ligands. We were able to prepare **4a** in a bench scale reaction between *syn*-$[MoO(\mu\text{-}NPh)(S_2CNEt_2)]_2$ and two equivalents of PhNCO at room temperature over 72 h. The IR spectrum confirmed the presence of the ureato-bridge [ν(CO) 1709 cm^{-1}]

and the remaining terminal oxo group [ν(MoO) 927 cm^{-1}]. Further, the mass spectrum showed a molecular ion, and in line with all other ureato complexes, a second heavy ion associated with loss of one equivalent of PhNCO. Unfortunately, we have been unable to isolate **4a** pure, all samples produced in this way being seemingly contaminated with isocyanate oligomers (molybdenum–oxo complexes are well-known to facilitate this reaction). Nevertheless, we believe that we have strong evidence for the initial formation of **4a** and importantly, warming the mixture of **4a** and excess PhNCO to 100 °C resulted in the clean and complete conversion to **1a**.



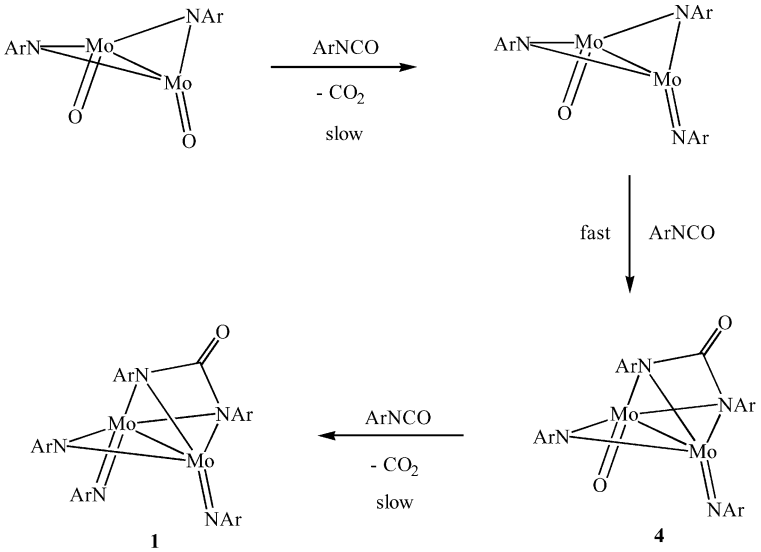
4

a Ar = Ph
b Ar = p-tol

The reaction of *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$ and excess *p*-tolylNCO in d^8-toluene proceeded in a similar manner, although owing to the relative insolubility of *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$ in toluene, no significant reaction was observed until the temperature reached 60 °C. Over about 30 min at this temperature a new species appeared which was characterised as [Mo_2O(N-*p*-tol)(μ-N-*p*-tol){μ-*p*-tolNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**4b**). Seven low-field doublets are clearly seen in the aromatic region of the spectrum (one is obscured) together with four triplet resonances associated with the methyl groups of the dithiocarbamates and four singlets between δ 2.19–1.80 assigned to the four inequivalent tolyl groups. As above, further warming of **4b** at 100 °C resulted in the clean formation of brown **2b** over about 10 min. Unfortunately, the insolubility of *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$ precluded the isolation of a good quality sample of **4b**; after stirring *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$ and two equivalents of *p*-tolylNCO at room temperature for 4 days only starting materials and oligiomeric *p*-tolylNCO were seen.

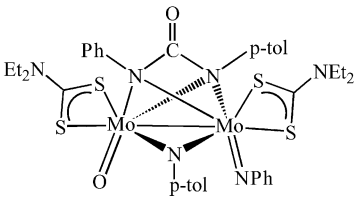
These experiments suggest that the mode of formation of ureato complexes **1** from *syn*-[MoO(μ-NAr)(S_2CNR_2)]$_2$ is as shown in Scheme 2. Initial substitution of one of the terminal oxo groups occurs to afford [Mo_2O(NAr)(μ-NAr)$_2$(S_2CNR_2)$_2$] in a slow, rate-determining, step. This is followed by the rapid addition of a second equivalent of isocyanate to one of the bridging imido ligands affording the isolated intermediates **4a–b**; and in the final step the second terminal oxo group is replaced to give ureato complexes **1**. A key question is why the substitution of terminal oxo ligand results in the facile addition of isocyanate to a bridging imido ligand? We presume that the Mo_2N_2 core in the starting complexes is not electron-rich enough to undergo addition of the isocyanate- or that at this stage the equilibrium between the bound and unbound isocyanate states lies strongly towards the latter. The substitution of oxo for imido ligands by isocyanates is quite well known and in (almost) all cases there is a substantial energy barrier—necessitating the use of higher temperatures.[14] However once this has occurred, the stronger π-donor ability of the imido *versus* the oxo moiety is expected to lead to an increase in the electron density at the metal centre—thus activating it towards isocyanate addition. Clearly, now the equilibrium lies over towards the bound state; that is, the ureato-bridge. Finally, the second oxo ligand is substituted at a slightly higher temperature (possibly due to increased steric constraints) to afford the final fully substituted product.

Following the experiments described above, we decided to investigate two crossover reactions with the aim of gaining more insight into the nature of the isocyanate addition process. Reaction of *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$ and excess PhNCO in d^8-toluene occurred at *ca.* 60 °C, the starting materials being consumed over approximately 20 min at 70 °C. Importantly, spectral changes mirrored those of the two previous experiments and >90% of new resonances were associated with a single complex, showing that the transformation is highly regioselective. We propose that this new product, characterised by the appearance of two new methyl resonances are observed at δ 2.17 and 2.02, is [Mo_2O(NPh)(μ-N-*p*-tol){μ-PhNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**5**). Unfortunately, we cannot unambiguously assign each of the tolyl methyl resonances for **1b** in d^8-toluene as one is obscured by the toluene signal (at *ca.* δ 2.05). However, based on the spectrum of **1b** in $CDCl_3$ (Fig. 1) and the observation of four methyl signals for **1b** in d^8-toluene at δ 2.18 (3H), *ca.* 2.05 (3H), 2.01 (3H) and 1.77 (6H), we favour the assignment of the signal at δ 2.17 to the bridging tolylimido ligand and that at δ 2.02 to one half of the newly created ureato-bridge. We assign the latter to the tolyl group *trans* to the bridging imido ligand. Further warming of **5** and PhNCO at 100 °C resulted in substitution of the second oxo group to afford a single new species (>95%) assigned as [Mo_2(NPh)$_2$(μ-N-*p*-tol){μ-PhNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**6**), and characterized by tolyl methyl resonances at δ 2.18 and 2.04, and two methyl triplets associated with the dithiocarbamate ligands.

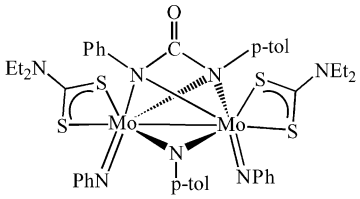


1 **4**

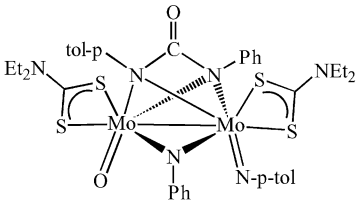
Scheme 2 Proposed mode of formation of ureato-bridges complexes **1** (dithiocarbamates omitted for clarity).



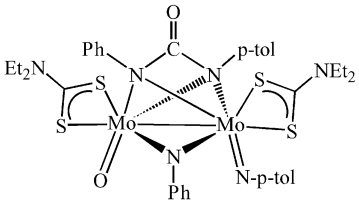
5



6



7a



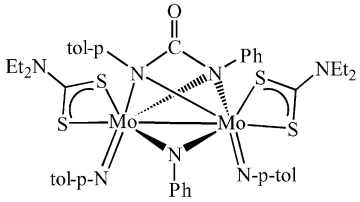
7b

The reaction between *syn*-[MoO(μ-NPh)(S_2CNEt_2)]$_2$ and excess *p*-tolylNCO in d^8-toluene did not proceed with the high level of regioselectivity expected. Upon warming to 70 °C two new species developed in an approximate 2 : 1 ratio. That both were ureato complexes was apparent from the doubling up of all aromatic resonances giving a spectrum, which was impossible to unambiguously assign. Nevertheless, on the basis of its general features and the above experiments we tentatively assign these changes to the formation of two isomers of [Mo_2O(N-*p*-tol)(μ-NPh){μ-PhNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**7a–b**).

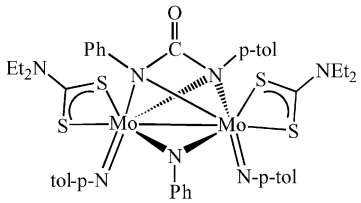
Formation of two isomers is difficult to reconcile with the high regioselectivity observed in all previous transformations of these complexes. Isomer **7a** is the expected product, and formation of **7b** would require the folding of the Mo_2N_2 core upon addition of the isocyanate. It may be that this is possible in this instance and we note that the fold angle of 155.1° in *syn*-[MoO(μ-NPh)(S_2CNEt_2)]$_2$ is significantly less than that of 164.6° found for *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$.[13] Further warming to 100 °C resulted in substitution of the remaining oxo ligand to produce two products in a 1.4 : 1 ratio. The change in ratio suggests that a secondary process is occurring. Heating the final mixture for a further 1 h at 100 °C resulted in no significant further changes to the spectrum. This secondary process may be the isomerisation of **7b–7a** at the more elevated temperatures, however, we favour a second process, namely the exchange of the labile isocyanate *trans* to the terminal imido ligands. In **7a** and **8a** this will have no net effect, however, for **7b** and **8b** it will result in exchange of PhNCO for *p*-tolylNCO; for example, **8b** will react to form **9**. There is some evidence to suggest that this does occur since in the final spectrum there are eight methyl resonances associated with the *p*-tolyl groups having a total integrated intensity of nearly 12 protons (against the expected 9). Thus, we favour the final formation of [Mo_2(N-*p*-tol)$_2$(μ-NPh){μ-PhNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**8a**) and [Mo_2(N-*p*-tol)$_2$(μ-NPh){μ-*p*-tolNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**9**), although we stress that this is speculative.

Reactions of ureato complexes with PhNCS and CS_2

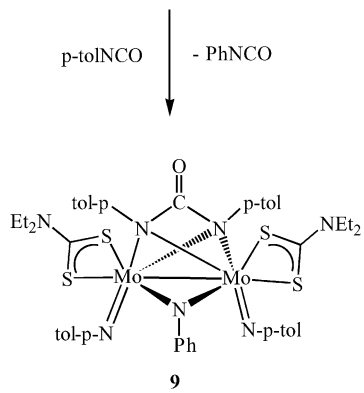
Heating [Mo_2(N-*p*-tol)$_2$(μ-N-*p*-tol){μ-*p*-tolNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**1b**) with an excess of PhNCS for 3 h in toluene led to a colour change from brown to orange. After removal of volatiles under reduced pressure addition of a small amount of dichloromethane gave an orange solution together with a small amount of a green insoluble solid. Chromatography of the



8a

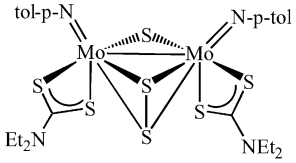


8b



9

soluble fraction led to separation of two bands. These afforded $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNEt_2)_2]$ (**2b**) as an inseparable mixture with what is believed to be two isomers of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}PhNC(O)N\text{-}p\text{-}tol\}(S_2CNEt_2)_2]$ (**10a**) (*ca.* 17%) (see below), and $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)(\mu\text{-}S_2)(S_2CNEt_2)_2]$ (**11**) (20%). When the same reaction was carried out over a slightly longer timescale, again small amounts of impure **2b** and **11** were obtained together with larger amounts of the insoluble green solid, identified as $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CNEt_2)_2]_2$ (**12a**).



11

In order to confirm the identity of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)(\mu\text{-}S_2)(S_2CNEt_2)_2]$ (**11**) it was crystallographically characterised (Fig. 4). The molecule is essentially the same as $[Mo_2(NAr)_2(\mu\text{-}S)(\mu\text{-}S_2)(S_2CNEt_2)_2]$ (Ar = 2,6-*i*-$Pr_2C_6H_3$), previously isolated as a low yield product of the reaction of $[Mo(NAr)_2(S_2CNEt_2)_2]$ with hydrogen sulfide.[15] In **11**, the sulfide and disulfide units are crystallographically disordered, and both sulfur atoms bind approximately symmetrically to the dimolybdenum centre. A feature of the crystal structure of $[Mo_2(NAr)_2(\mu\text{-}S)(\mu\text{-}S_2)(S_2CNEt_2)_2]$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) was the presence of weak intermolecular sulfur–sulfur interactions which are absent in **11**.

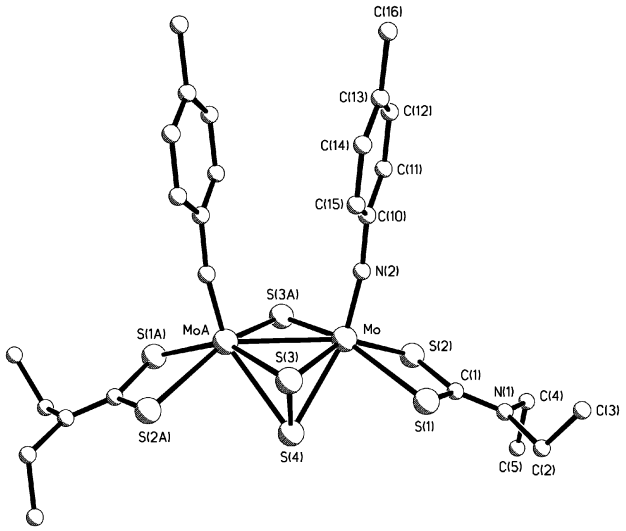


Fig. 4 Molecular structure of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)(\mu\text{-}S_2)(S_2CNEt_2)_2]$ (**11**). The molecule has crystallographically imposed twofold symmetry, atoms labelled "A" being at the equivalent position (1 − *x*, *y*, 0.5 − *z*). Selected bond lengths (Å) and angles (°); Mo–Mo(A) 2.7854(15), Mo–N(2) 1.731(6), Mo–S(3) 2.3750(19), Mo(A)–S(3) 2.387(2), Mo–S(4) 2.528(4), Mo(A)–S(4) 2.618(4), S(3)–S(4) 1.932(4), Mo–S(3)–Mo(A) 71.59(6), Mo–S(4)–Mo(A) 65.51(10), Mo–N(2)–C(10) 169.9(5).

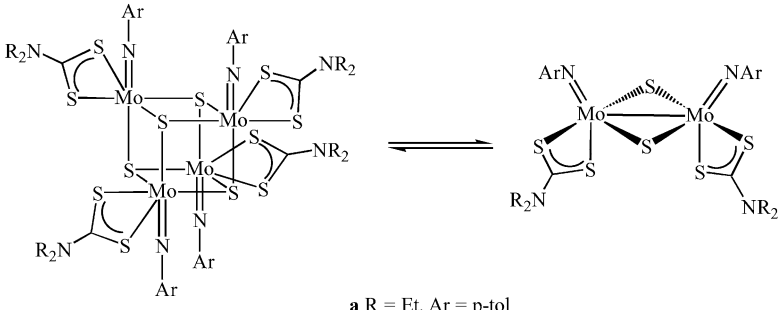
Refluxing **2b** with an excess of PhNCS for 2 h also gave green **12a** upon removal of volatiles, showing that **2b** is the primary product of the reaction of **1b** with PhNCS. This was further confirmed by a ^{1}H NMR study. Thus at around 85 °C in d^8-toluene, **1b** begins to react with PhNCS giving **2b** and one equivalent of *p*-tolylNCO. Complete consumption of **1b** occurred over *ca.* 1 h at this temperature, with formation of **2b** being relatively clean, although small amounts of other products (see below) were noted. Further heating of the solution at 100 °C for 5 h led to consumption of **2b** affording a yellow solution with a green precipitate.

Thermolysis of both **1b** and **2b** with carbon disulfide for extended periods also resulted in the clean generation of green **12a**, although in both cases **11** was notably absent. Heating green insoluble **12a** in toluene affords a clear yellow solution, which on cooling leads to re-precipitation of the insoluble green solid. From this observation we surmise that tetrameric green $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CNEt_2)_2]_2$ (**12a**) is in thermal equilibrium with dimeric yellow $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (**13a**). Wentworth and co-workers have previously noted a similar situation for the analogous complexes $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CN\text{-}i\text{-}Bu_2)_2]_n$ ($n = 1, 2$).[16]

Reaction of **1d** with PhNCS proceeds in a similar manner to that of **1b**, although no disulfide product analogous to **11** was obtained. Chromatography of the soluble fraction afforded an inseparable mixture of **2d** and two isomers of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}PhNC(O)N\text{-}p\text{-}tol\}(S_2CNPr_2)_2]$ (**10b**) (see below), while a green solid which precipitated from the reaction mixture was identified as a mixture of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CNPr_2)_2]_2$ (**12b**) and $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CNPr_2)_2]$ (**13b**). Crystallization from dichloromethane–methanol gave a small number of red crystals identified by crystallography as (**12b**) (Fig. 5). The molecule is almost identical to the di-*iso*-butyldithiocarbamate analogue previously characterised by Wentworth.[16] The two dimeric units are held together by triply-bridging sulfido ligands bound *via* two short [Mo–S(av) 2.373 Å] and one long [Mo–S(av) 2.715 Å] molybdenum–sulfur interactions, values which compare well with those of 2.38 and 2.69 Å found in $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CN\text{-}i\text{-}Bu_2)_2]_n$ ($n = 1, 2$).[16]

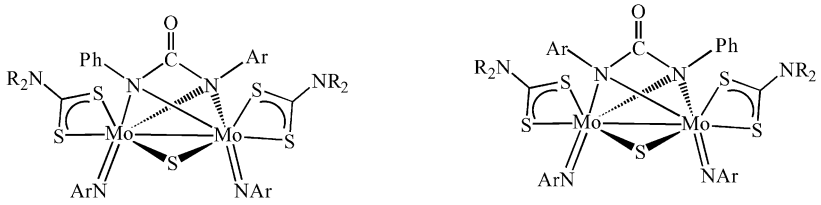
As detailed above, in both the reaction of **1b** and **1d** with PhNCS, one of the products was an inseparable mixture of the sulfido-bridged ureato complexes $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNR_2)_2]$ (**2b** and **2d**) with two other species, believed to be isomers of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}PhNC(O)N\text{-}p\text{-}tol\}(S_2CNR_2)_2]$ (**10a–b**). We have designated these as *cis* and *trans*-relating to the relative positions of the *N*-tolyl group of the ureato ligand and those occupying the terminal sites.

While similar features were seen for the diethyl and dipropyl complexes, only the latter is discussed fully. The ^{1}H NMR spectrum clearly showed the presence of **2d** together with two further complexes. For example, the aromatic region was quite complex, but significantly there were three low-field doublets all of similar intensities, one being assigned to **2d**. In the tolylmethyl region of the spectrum, six singlets were observed, in three pairs being associated with the two ureato and the terminal



12 **13**

a R = Et, Ar = p-tol
b R = Pr, Ar = p-tol



10

cis *trans*

a R = Et, Ar = p-tol
b R = Pr, Ar = p-tol

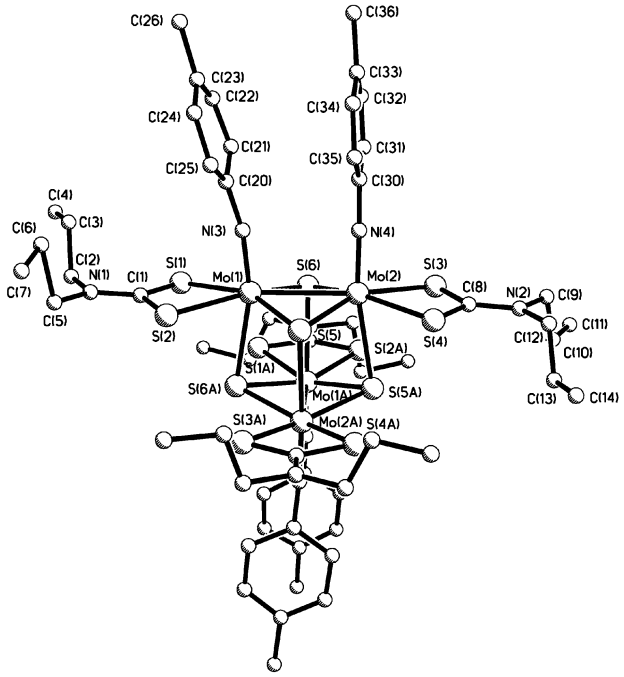
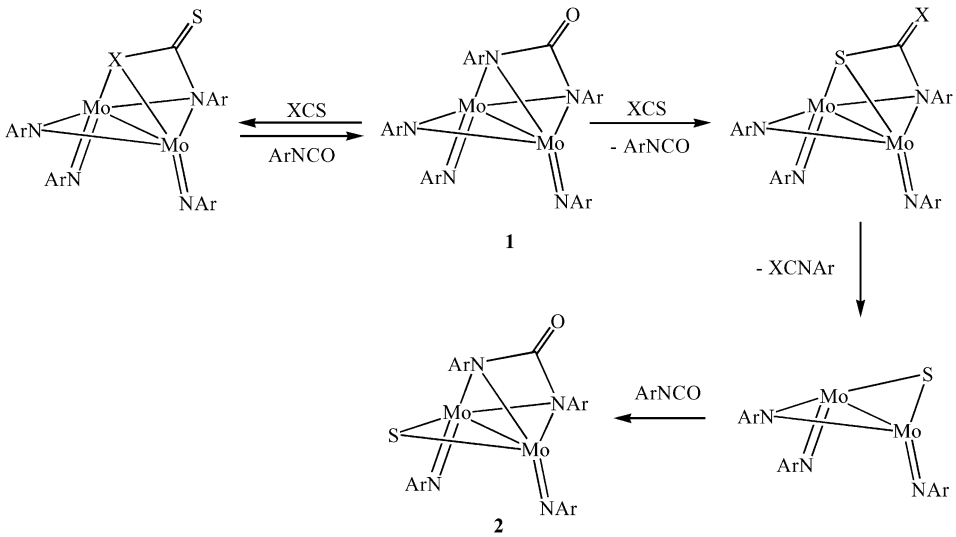


Fig. 5 Molecular structure of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CNPr_2)_2]_2$ (**12b**). The molecule has crystallographically imposed twofold symmetry, atoms labelled "A" being at the equivalent position (x, y, $-z$). Selected bond lengths (Å) and angles (°); Mo(1)–Mo(2) 2.8694(5), Mo(1)–N(3) 1.724(3), Mo(2)–N(4) 1.726(4), Mo(1)–S(5) 2.3741(12), Mo(2)–S(5) 2.3732(12), Mo(2A)–S(5) 2.7368(11), Mo(1)–S(6) 2.3732(12), Mo(2)–S(6) 2.3733(12), Mo(1A)–S(6) 2.6923(11), Mo(1)–S(5)–Mo(2) 74.37(4), Mo(1)–S(6)–Mo(2) 74.33(4), Mo(1)–N(3) C(20) 168.1(3), Mo(2)–N(4)–C(30) 175.6(4).

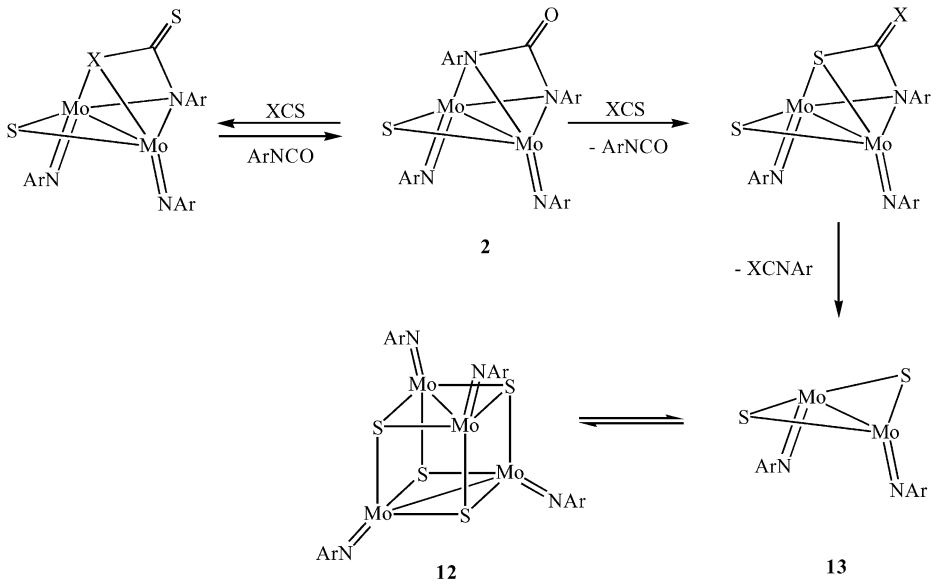
imido sites. Close scrutiny of the relative integrated intensities of the dithiocarbamate and these resonances showed that rather than the expected 12 protons for pure **2d**, there were only 9.7 protons—suggesting some incorporation of phenyl groups. The combined integral of the peaks associated with the terminal imido ligands at δ 2.14 and 2.13 (C) was approximately 6 protons, showing that all products contained these groups. In contrast, those at δ 2.32 and 2.31 associated with the tolyl group *trans* to the imido bridge (B) integrated to only 1.6 protons, and at δ 2.08 and 2.07 assigned to the tolyl group *trans* to the terminal imido ligands (D) to 2.1 protons (Fig. 1). This suggests that the inseparable mixture contains both **2d** and two isomers of $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}PhNC(O)N\text{-}p\text{-}tol\}(S_2CNPr_2)_2]$ (**10b**). This is substantiated by the FAB mass spectrum which shows ions at both 1026 and 1012 associated with **2d** and **10b**, respectively, together with their respective arylisocyanate loss peaks at 890 and 876. While we cannot unambiguously assign all the resonances in the spectrum to *cis* and *trans* isomers of **10b** we can assign some. Thus, since tolyl-methyl resonances at δ 2.31, 2.14 and 2.07 are associated with **2d**, then that at δ 2.32 must be associated with *cis*-**10b** and that at δ 2.08 with *trans*-**10b**. On this basis we can surmise that the ratio of *cis* : *trans* **10b** is approximately 1.3 : 1.

Spectral features of the diethyldithiocarbamate complexes, **2b** and **10a**, show similar features. The ratio of the low-field aromatic doublets at *ca.* 1 : 1 : 2 (**2b**) suggests that this sample contains a greater amount of **2b**. This is also reflected in the overall integral of the tolyl-methyl resonances at 10.8 (*versus* the expected 12). This comprises a 2.3 : 6 : 2.5 ratio (B : C : D) suggesting that the ratio of *cis* : *trans* **10a** is nearer 1.1 : 1.

From these results a picture emerges of the reactions of **1** with PhNCS and CS_2. The first isolated product is **2**, which is possibly produced as shown in Scheme 3. With PhNCS,



Scheme 3 Proposed mode of formation of **2** from **1** and PhNCS or CS_2.



Scheme 4 Proposed mode of formation of **12–13** from **2**.

substitution of the *trans*-activated isocyanate could produce isomeric products, with either the sulfur or nitrogen being metal bound. The latter mimics the reactivity of the isocyanates, but if the isocyanate is more strongly bound than the isothiocyanate then the equilibrium will lie towards the former. In the second orientation, to which carbon disulfide is limited, sulfur is metal bound. Molybdenum(v) is well known to be chalcogenophilic and thus such an orientation is expected to be favourable. Loss of ArNCX would then afford the sulfido-bridged complex $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-S})(\mu\text{-N-}p\text{-tol})(S_2CNEt_2)_2]$ to which the released isocyanate can bind to give **2**.

Formation of the sulfido-bridged complexes $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-S})_2(S_2CNR_2)_2]_n$ ($n = 1, 2$) (**12–13**) presumably arise from **2** *via* a similar process as summarised in Scheme 4.

It is noteworthy that in both transformations described in Schemes 3–4, when PhNCS is used the by-product is the carbodiimide, PhNCN-*p*-tol. We have not been able to isolate this but note that **1b** does not react with CyNCNCy even upon prolonged thermolysis.

Exchange of the aryl-substituents of the ureato-bridged sulfido complexes leading to the formation of isomers of **10a–b** was quite unexpected—yet reproducible with different dithiocarbamate substituents. Scheme 5 attempts to account for this. Exchange of *p*-tolylNCO for PhNCS as shown would be reversible and have no resultant effect. However, if a competing pathway involved loss of *p*-tolylNCS then this would result in the formation of a new complex, $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-NPh})(\mu\text{-S})(S_2CNR_2)_2]$. This could then undergo further addition of *p*-tolylNCO to afford the observed product; isomers perhaps resulting from a relaxation of the puckered Mo_2NS core to a preferred flatter arrangement.

The precise mode of formation of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-S})(\mu\text{-S}_2)(S_2CNEt_2)_2]$ (**11**) remains unclear, and a related dipropyldithiocarbamate product was not seen. It is certainly formed directly from **1b** and PhNCS although it was not identified from either the reaction of **2b** with PhNCS or **1b** with carbon disulfide. This suggests that it is not a sulfur addition product of **13a** and may arise directly from **1b**.

Summary. It is clear from this work that ureato complexes $[Mo_2(NAr)_2(\mu\text{-X})\{\mu\text{-ArNC(O)NAr}\}(S_2CNR_2)_2]$ (X = S, NAr) (**1–2**) display chemical behaviour quite unlike any other bridging ureato complexes previously studied. This seems to result from the *trans*-influence of the terminal imido ligands. The latter leads directly to the asymmetric binding of the ureato ligand, which in turn accounts for the regioselective exchange of one arylisocyanate for another. Transformations with sulfur-containing heterocummulenes are more complex and lead to the formation of a number of sulfido-bridged species, which nevertheless can be rationalised in terms of the labile nature of isocyanate addition–elimination from the ureato ligand.

Experimental

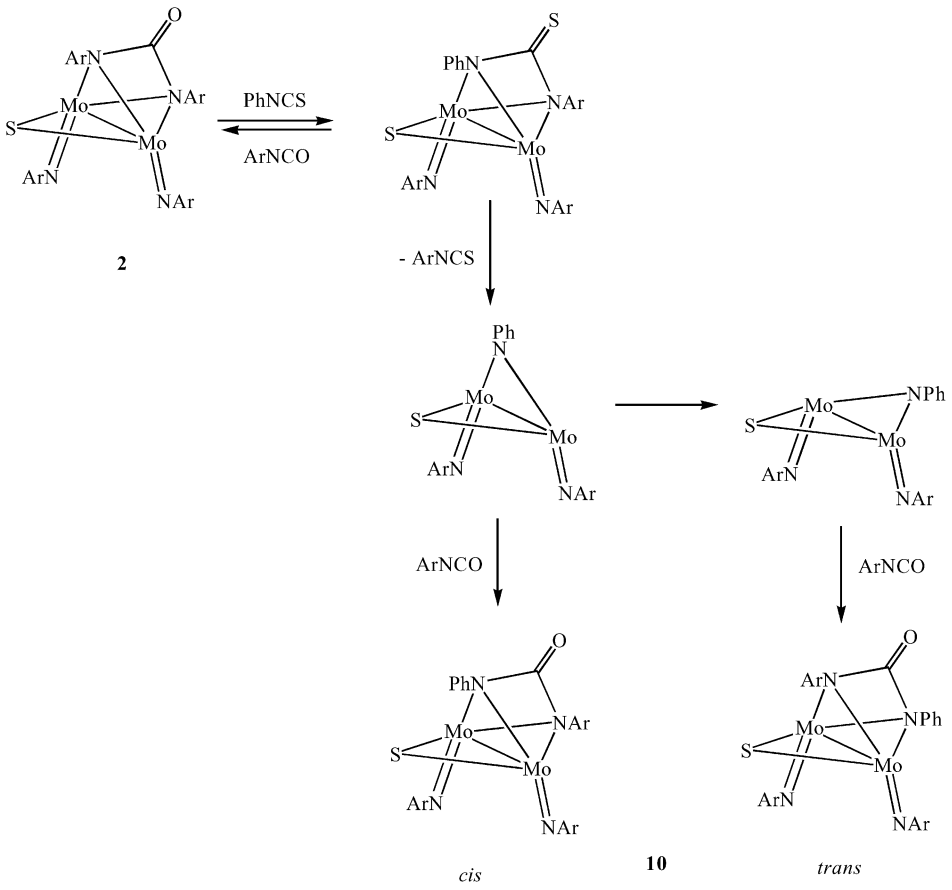
All reactions were carried out under an inert atmosphere unless otherwise stated. Molybdenum complexes, $[MoO_2(S_2CNR_2)_2]$,[17] *syn*-$[MoO(\mu\text{-O})(S_2CNR_2)]_2$,[18] *syn*-$[Mo_2O_2(\mu\text{-O})(\mu\text{-S})(S_2CNR_2)_2]$[18] and *syn*-$[MoO(\mu\text{-S})(S_2CNR_2)]_2$[18] were prepared by literature methods. All isocyanates and isothiocyanates were used as supplied. Chromatography was carried out in air on deactivated (6% w/w water) alumina columns.

Synthesis of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-N-}p\text{-tol})\{\mu\text{-N-}p\text{-tolC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (1b)

syn-$[MoO(\mu\text{-O})(S_2CNEt_2)]_2$ (0.56 g, 1.01 mmol) was dissolved in toluene (50 ml) and *p*-tolylNCO (0.64 ml, 5.03 mmol) was added and the mixture was refluxed for 24 h. After removal of volatiles a very dark product was obtained. This was absorbed onto alumina and passed down a chromatography column. Elution with 40% dichloromethane in petrol gave a small unidentified yellow band. Elution with 70% dichloromethane in petrol resulted in a dark red–brown product identified as $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-N-}p\text{-tol})\{\mu\text{-N-}p\text{-tolC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (**1b**) (0.62 g, 58%). IR (KBr) ν/cm^{-1} 1703s, 1660m, 1596w, 1509vs, 1493s, 1445w, 1437m, 1320m, 1274m, 1255m, 1205w, 1148w, 1075w, 993w, 919w, 816m; ^1H ($CDCl_3$) δ 7.79 (d, *J* 8.2, 2H, Ar), 7.39 (d, *J* 8.2, 2H, Ar), 7.10 (d, *J* 8.2, 2H, Ar), 7.05 (d, *J* 8.1, 2H, Ar), 7.02 (d, *J* 8.3, 2H, Ar), 6.63 (d, *J* 8.3, 2H, Ar), 6.59 (d, *J* 8.1, 4H Ar), 6.34 (d, *J* 8.2, 4H Ar), 3.88 (m, 4H, CH_2), 3.65 (sextet, *J* 7.1, 2H, CH_2), 3.55 (sextet, *J* 7.1, 2H, CH_2), 2.39 (s, 3H, Me), 2.34 (s, 3H, Me), 2.16 (s, 6H, Me), 2.10 (s, 3H, Me), 1.23 (t, *J* 7.1, 6H, Me), 1.00 (t, *J* 7.1, 6H Me); mass spectrum (FAB), *m/z* 1044 (M^+), 909 (M − *p*-tolNCO); Anal. Calc. for $Mo_2C_{46}H_{55}O_1S_4N_7$ C, 53.03, H, 5.28, N 9.41; Found C, 51.97, H, 5.27, N, 9.20. Complex **1b** was also prepared in 90% yield upon refluxing a toluene solution of *syn*-$[MoO(\mu\text{-N-}p\text{-tol})(S_2CNEt_2)]_2$ and 3.5 equivalents of *p*-tolylNCO for 1 h.

Synthesis of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-S})\{\mu\text{-N-}p\text{-tolC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (2b)

syn-$[Mo_2O_2(\mu\text{-S})(\mu\text{-O})(S_2CNEt_2)_2]$ (0.20 g, 0.35 mmol) was dissolved in toluene (*ca.*50 ml) and *p*-tolylNCO (0.18 ml,



Scheme 5 Possible route to the formation of mixed-substituent sulfido-bridged ureato complexes **10**.

1.41 mmol) was added and the mixture was refluxed for 24 h. After removal of volatiles an orange–red product was obtained. This was absorbed onto alumina and passed down a chromatography column. Elution with 90% dichloromethane in petrol gave a red–orange product, identified as $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}S)\{\mu\text{-}N\text{-}p\text{-tolC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (**2b**) (0.37 g, 84%). IR (KBr) ν/cm^{-1} 1703s, 1654m, 1636w, 1563vw, 1511vs, 1460w, 1437m, 1315m, 1275m, 1251m, 1205w, 1148w, 1079w, 918w, 815m; $^1H(CDCl_3)$ δ 7.74 (d, *J* 8.2, 2H, Ar), 7.04 (d, *J* 8.2, 2H, Ar), 6.91 (d, 2H, *J* 8.3, Ar), 6.67 (d, *J* 8.3, 2H, Ar), 6.57 (d, 8.2, 4H, Ar), 6.46 (d, *J* 8.2, 4H, Ar), 3.98 (m, 4H, CH_2), 3.60 (m, 4H, CH_2), 2.32 (s, 3H, Me), 2.15 (s, 6H, Me), 2.07 (s, 3H, Me), 1.29 (t, *J* 7.1, 6H, Me), 1.05 (t, *J* 7.1, 6H, Me); mass spectrum (FAB), *m*/*z* 970 (M^+), 835 (M − *p*-tolNCO); Anal. Calc. for $Mo_2C_{39}H_{48}O_1S_5N_6$ C, 48.34, H, 4.96, N 8.68, S 16.52; Found C, 48.93, H, 4.78, N, 8.68, S, 17.19.

Synthesis of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-N-}p\text{-tol})\{\mu\text{-}p\text{-tolNC(O)N-}p\text{-tol}\}(S_2CNMe_2)_2]$ (1c) and $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-S})\{\mu\text{-}p\text{-tolNC(O)N-}p\text{-tol}\}(S_2CNMe_2)_2]$ (2c)

$[MoO_2(S_2CNMe_2)]$ (1.31 g, 3.56 mmol) was dissolved in toluene (50 ml) and *p*-tolylNCO (1.60 ml, 12.86 mmol) was added and the mixture was refluxed for 24 h. After removal of volatiles a very dark product was obtained. This was absorbed onto alumina and passed down a chromatography column. Elution with 30% dichloromethane in light petroleum afforded a purple band which yielded $[MoS_2(N\text{-}p\text{-tol})(S_2CNMe_2)_2]$ (0.40 g, 22%).[19] Elution with 50% dichloromethane in light petroleum gave a red–orange product, identified as a mixture of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-N-}p\text{-tol})\{\mu\text{-}p\text{-tolNC(O)N-}p\text{-tol}\}(S_2CNMe_2)_2]$ (**1c**) and $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-S})\{\mu\text{-}p\text{-tolNC(O)N-}p\text{-tol}\}(S_2CNMe_2)_2]$ (**2c**) (combined yield 0.25 g, *ca.* 15%). While these complexes could not be separated by chromatography, crystallisation of the mixture from dichloromethane and methanol afforded crystals of two types, namely brown crystals of **1c** and orange crystals of **2c** that could be separated mechanically. For $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-N-}p\text{-tol})\{\mu\text{-N-}p\text{-tolC(O)N-}p\text{-tol}\}(S_2CNMe_2)_2]$ (**1c**): IR (KBr) ν/cm^{-1} 1700s, 1686m, 1654m, 1623w, 1542m, 1507m, 1492s, 1395m, 1321m, 1260m, 1249m, 1103m, 1018w, 987w, 919w, 814m; ^1H $(CDCl_3)$ δ 7.78 (d, *J* 8.2, 2H, Ar), 7.36 (d, *J* 8.2, 2H, Ar), 7.15 (d, *J* 8.2, 2H, Ar), 7.06 (d, 2H, *J* 8.2, Ar), 6.75 (d, *J* 8.3, 2H, Ar), 6.57 (d, 8.1, 4H, Ar), 6.31 (d, *J* 8.1, 4H, Ar), 3.34 (s, 6H, Me), 3.22 (s, 6H, Me), 2.39 (s, 3H, Me), 2.33 (s, 3H, Me), 2.16 (s, 6H, Me), 2.14 (s, 3H, Me); mass spectrum (FAB), *m*/*z* 986 (M^+), 852 (M − *p*-tolNCO); Anal. Calc. for $Mo_2C_{42}H_{47}O_1S_4N_7.0.5CH_2Cl_2$ C, 49.63, H, 4.67, N 9.53, S 12.46; Found C, 49.37, H, 4.53, N, 9.42, S, 12.92. For $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-S})\{\mu\text{-N-}p\text{-tolC(O)N-}p\text{-tol}\}(S_2CNMe_2)_2]$ (**2c**): IR (KBr) ν/cm^{-1} 1705s, 1532s, 1507vs, 1491s, 1394s, 1315s, 1267w, 1248s, 1140m, 1013w, 982m, 922m, 816s; ^1H $(CDCl_3)$ δ 7.75 (d, *J* 8.2, 2H, Ar), 7.05 (d, 2H, *J* 8.2, Ar), 6.94 (d, *J* 8.3, 2H, Ar), 6.73 (d, 8.3, 2H, Ar), 6.57 (d, *J* 8.1, 4H, Ar), 6.46 (d, *J* 8.1, 4H, Ar), 3.38 (s, 6H, Me), 3.20 (s, 6H, Me), 2.34 (s, 3H, Me), 2.16 (s, 6H, Me), 2.13 (s, 3H, Me); mass spectrum (FAB), *m*/*z* 913 (M^+), 780 (M − *p*-tolNCO); Anal. Calc. for $Mo_2C_{42}H_{35}O_1S_5N_6$ C, 46.05, H, 4.39, N, 9.21, S 17.54; Found C, 45.48, H, 4.84, N, 8.10, S, 17.83.

Synthesis of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-N-}p\text{-tol})\{\mu\text{-}p\text{-tol-NC(O)N-}p\text{-tol}\}(S_2CNPr_2)_2]$ (1d)

syn-$[MoO(\mu\text{-O})(S_2CNPr_2)]_2$ (1.56 g, 2.57 mmol) was dissolved in toluene (50 ml), *p*-tolylNCO (1.60 ml, 12.86 mmol) was added and the mixture was refluxed for 24 h. After removal of volatiles a very dark product was obtained. This was absorbed onto alumina and passed down a chromatography column. Elution with 35% dichloromethane in petrol gave an unidentified brown product. Elution with 70% dichloromethane in petrol resulted

in a brown product identified as $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}N\text{-}p\text{-tol})\{\mu\text{-}p\text{-tol-NC(O)N-}p\text{-tol}\}(S_2CNPr_2)_2]$ (**1d**) (0.34 g, 12%). IR (KBr) ν/cm^{-1} 1703s, 1635br, 1501vs, 1441s, 1373w, 1319m, 1248s, 1145m, 1001w, 1030w, 987w, 912w, 812m; ^1H ($CDCl_3$) δ 7.67 (d, J 8.2, 2H, Ar), 7.31(d, J 8.2, 2H, Ar), 7.04 (d, J 8.2, 2H, Ar), 6.96 (d, 2H, J 8.2, Ar), 6.88 (d, J 8.3, 2H, Ar), 6.58 (d, J 8.1, 2H, Ar), 6.48 (d, J 8.1, 4H, Ar), 6.21 (d, J 8.1, 4H, Ar), 3.77 – 3.66 (m, 4H, NCH_2), 3.44 – 3.32 (m, 4H, NCH_2), 2.35 (s, 3H, Me), 2.30 (s, 3H, Me), 2.13 (s, 6H, Me), 2.07 (s, 3H, Me), 1.61 (m, 4H, CH_2), 1.41 – 1.24 (m, 4H, CH_2), 0.81 (t, J 7.4, 6H, Me), 0.70 (t, J 7.4, 6H, Me); mass spectrum (FAB), m/z 1098 (M^+), 966 ($M^+ - p$-tolNCO); Anal. Calc. for $Mo_2C_{50}H_{63}O_1S_4N_7$ C, 54.69, H, 5.74, N 8.93, S 11.67; Found C, 53.94, H, 5.75, N, 8.56, S, 10.87.

Synthesis of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}S)\{\mu\text{-}N\text{-}p\text{-tolC(O)N-}p\text{-tol}\}(S_2CNPr_2)_2]$ (2d)

syn-$[Mo_2O_2(\mu\text{-}S)(\mu\text{-}O)(S_2CNPr_2)_2]$ (0.093 g, 0.15 mmol) was dissolved in toluene (*ca.* 50 ml), *p*-tolylNCO (0.10 ml, 0.75 mmol) was added and the mixture was refluxed for 24 h. After removal of volatiles an orange–red product was obtained. This was absorbed onto alumina and passed down a chromatography column. Elution with 40% dichloromethane in petrol gave a red–orange product, identified as $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}S)\{\mu\text{-}N\text{-}p\text{-tolC(O)N-}p\text{-tol}\}(S_2CNPr_2)_2]$ (**2d**) (0.12 g, 79%). IR (KBr) ν/cm^{-1} 1703s, 1506vs, 1433m, 1367w, 1315m, 1246s, 1194w, 1146m, 1089w, 993w, 920w, 814m; $^1H(CDCl_3)$ δ 7.73 (d, J 8.3, 2H, Ar), 7.02 (d, J 8.0, 2H, Ar), 6.88 (d, 2H, J 8.4, Ar), 6.64 (d, J 8.2, 2H, Ar), 6.56 (d, 8.2, 4H, Ar), 6.44 (d, J 8.2, 4H, Ar), 3.89 (m, 4H, NCH_2), 3.46 (m, 4H, NCH_2), 2.31 (s, 3H, Me), 2.14 (s, 6H, Me), 2.07 (s, 3H, Me), 1.74 (m, 4H, CH_2), 1.46 (m, 4H, CH_2), 0.92 (t, J 7.4, 6H, Me), 0.82 (t, J 7.4, 6H, Me); mass spectrum (FAB), m/z 1026 (M^+), 893 ($M - p$-tolNCO); Anal. Calc. for $Mo_2C_{43}H_{56}O_1S_5N_6$ C, 50.39, H, 5.47, N 8.20; Found C, 50.15, H, 5.56, N, 8.03.

Synthesis of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}N\text{-}p\text{-tol})\{\mu\text{-PhNC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (3a)

In an NMR tube, $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}N\text{-}p\text{-tol})\{\mu\text{-}p\text{-tolNC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (**1b**) (10 mg) was dissolved in *ca.* 2 ml of d^8-toluene and the ^1H NMR spectrum was recorded. ^1H NMR (d^8-toluene) δ 8.18 (d, J 8.2, 2H, Ar), 7.85 (d, J 8.2, 2H, Ar), 7.51 (d, J 8.2, 2H, Ar), 7.09 (d, J 8.2, 2H, Ar), 6.84 (d, J 8.2, 2H, Ar), 6.70 (d, J 8.2, 2H, Ar), 6.60 (d, J 8.2, 4H, Ar), 6.33 (d, J 8.2, 4H, Ar), 3.21 (m, 4H, CH_2), 2.94 (sextet, J 6.8, 2H, CH_2), 2.82 (sextet, J 6.8, 2H, CH_2), 2.18 (s, 3H, Me), *ca.* 2.05 (s, 3H, Me, obscured), 2.01 (s, 3H, Me), 1.77 (s, 6H, Me), 0.67 (t, J 7.1, 6H, Me), 0.50 (t, J 7.1, 6H, Me). The three singlet resonances observed for the methyl groups of the tolyl substituents at room temperature (a fourth being obscured by the toluene) at δ 2.18 (3H), 2.01 (3H) and 1.77 (6H) were monitored throughout the reaction. About four-fold excess of PhNCO was added which resulted in no significant change to the spectrum. The solution was slowly warmed and at 65 °C a new resonance at δ 1.92 began to develop with concomitant reduction of the resonance at 2.01. After approximately 50 min the ratio of these two peaks was *ca.* 5 : 1 and warming to 90 °C resulted in the virtual disappearance of the resonance at δ 2.01. In a separate experiment the resonance at δ 1.92 was shown to be associated with *p*-tolylNCO. Upon cooling back to room temperature four resonances were clearly observed at δ 2.16 (3H), 2.01 (3H), 1.90 (3H) and 1.76 (6H). Further heating of the solution at 100 °C in an oil bath for 18 h did not lead to any significant change. Hexane was layered onto the dark brown toluene solution and over *ca.* 2 weeks small dark red needles developed. These were removed and dried to afford $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}N\text{-}p\text{-tol})\{\mu\text{-PhNC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (**3a**). ^1H ($CDCl_3$) δ 7.78 (d, J 8.2, 2H, Ar), 7.39 (d, J 8.2, 2H, Ar), 7.14 (d, J 8.2, 2H, Ph), 7.11 (d, J 8.2, 2H, Ar), 7.05 (d, J 8.2, 2H, Ar), 6.88 (t, J 8.3, 2H, Ph), 6.67 (t, J 7.3, 1H, Ph), 6.58 (d, J 8.1, 4H, Ar), 6.32 (d, J 8.2, 4H, Ar), 3.85 (m, 4H, CH_2), 3.65 (sextet, J 6.8, 2H, CH_2), 3.54 (sextet, J 6.8, 2H, CH_2), 2.39 (s, 3H, Me), 2.34 (s, 3H, Me), 2.16 (s, 6H, Me), 1.22 (t, J 7.1, 6H, Me), 1.00 (t, J 7.1, 6H, Me); Anal. Calc. for $Mo_2C_{45}H_{53}O_1S_4N_7$ C, 52.58, H, 5.16, N 9.54, S 12.46; Found C, 51.94, H, 5.08, N, 9.37, S, 11.89.

Synthesis of $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}S)\{\mu\text{-PhNC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (3b)

In an NMR tube, $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}S)\{\mu\text{-}p\text{-tolNC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (**2b**) (10 mg) was partially dissolved in *ca.* 2 ml of d^8-toluene and the ^1H NMR spectrum was recorded. ^1H NMR (d^8-toluene) δ 8.20 (d, J 8.2, 2H, Ar), 7.53 (d, J 8.4, 2H, Ar), 7.11–6.88 (obscured), 6.86 (d, J 8.1, 2H, Ar), 6.67 (d, J 8.2, 4H, Ar), 6.28 (d, J 8.0, 4H, Ar), 3.28 (sextet, J 6.8, 2H, CH_2), 3.23 (sextet, J 6.8, 2H, CH_2), 2.88 (sextet, J 6.8, 2H, CH_2), 2.80 (sextet, J 6.8, 2H, CH_2), 2.06 (s, 3H, Me), 1.97 (s, 3H, Me), 1.74 (s, 6H, Me), 0.67 (t, J 7.2, 6H, Me), 0.53 (t, J 7.2, 6H, Me). About four-fold excess of PhNCO was added which resulted in no significant change to the spectrum. The solution was slowly warmed to 80 °C and significant spectral changes took place. After heating for 20 min at 90 °C the clean formation of a new product was apparent together with the formation of one equivalent of *p*-tolylNCO (δ 1.89, s). This has been identified as $[Mo_2(N\text{-}p\text{-tol})_2(\mu\text{-}S)\{\mu\text{-PhNC(O)N-}p\text{-tol}\}(S_2CNEt_2)_2]$ (**3b**). ^1H NMR (d^8-toluene) δ 8.12 (d, J 8.1, 2H, Ar), 7.47 (d, J 8.0, 2H, Ar), 7.26 (d, J 7.8, 4H, Ar), 7.05–6.52 (obscured), 6.23 (d, J 8.1, 4H, Ar), 3.29 (sextet, J 6.8, 2H, CH_2), 3.21 (sextet, J 6.8, 2H, CH_2), 2.75 (m, 4H, CH_2), 1.98 (s, 3H, Me), 1.71 (s, 6H, Me), 0.65 (t, J 7.1, 6H, Me), 0.53 (t, J 7.1, 6H, Me). After standing for a few days, a small amount of yellow solid was deposited in the NMR tube. All liquids were decanted from the tube and the solid was dried under vacuum in the tube. Redissolution of the solid in $CDCl_3$ allowed a cleaner spectrum to be obtained. ^1H NMR ($CDCl_3$) δ 7.81 (d, J 8.2, 2H, Ar), 7.34 (d, J 7.7, 2H, Ph), 7.32 (d, J 8.2, 2H, Ar), 6.91 (t, J 8.3, 2H, Ph), 6.73 (t, J 7.4, 1H, Ph), 6.59 (d, J 8.2, 4H, Ar), 6.50 (d, J 8.2, 4H, Ar), 3.97 (sextet, J 7.1, 2H, CH_2), 3.91 (sextet, J 7.1, 2H, CH_2), 3.53 (septet, J 6.8, 4H, CH_2), 2.34 (s, 3H, Me), 2.17 (s, 6H, Me), 1.26 (t, J 7.2, 6H, Me), 1.05 (t, J 7.2, 6H, Me).

Room temperature reaction of *syn*-$[MoO(\mu\text{-NPh})(S_2CNEt_2)]_2$ with PhNCO-identification of $[Mo_2O(NPh)(\mu\text{-NPh})\{\mu\text{-PhNC(O)NPh}\}(S_2CNEt_2)_2]$ (4a)

Toluene-d^8 was added to *syn*-$[MoO(\mu\text{-NPh})(S_2CNEt_2)]_2$ (*ca.* 10 mg) in an NMR tube. This gave a pale yellow solution with a significant amount of insolubles. The ^1H NMR showed the dissolved material to be a *ca.* 17 : 1 mixture of *syn* and *anti* isomers. An excess of PhNCO was added and after 1 h a significant number of smaller new resonances had appeared. After 4 h the solution was now bright orange and resonances associated with *syn*-$[MoO(\mu\text{-NPh})(S_2CNEt_2)]_2$ had disappeared (although those due to the *anti* isomer were still apparent). Some precipitate remained although this took on an orange appearance. The orange material is characterised as $[Mo_2O(NPh)(\mu\text{-NPh})\{\mu\text{-PhNC(O)NPh}\}(S_2CNEt_2)_2]$ (**4a**). ^1H NMR (d^8-toluene) δ 8.37 (d, J 7.6, 2H, Ph), 7.92 (d, J 7.5, 2H, Ph), 7.39 (d, J 7.7, 2H, Ph), 7.30 (t, J 8.0, 2H, Ph), 7.05–6.50 (obscured), 3.20 (sextet, 2H, J 6.8, CH_2), 3.04 (m, 4H, CH_2), 2.83 (sextet, J 6.8, 2H, CH_2), 0.73 (t, J 7.2 3H, Me), 0.60 (t, J 7.1, 3H, Me), 0.51 (t, J 7.1, 3H, Me), 0.44 (t, J 7.2, 3H, Me). Upon heating to 100 °C, clean conversion into **1a** occurred with dissolution of all solid materials.

In order to get more data on **4a** a bench scale reaction was carried out. *syn*-$[MoO(\mu\text{-NPh})(S_2CNEt_2)]_2$ (0.12 g, 0.17 mmol) was placed in a Schlenk tube and degassed toluene (*ca.* 50 ml) and PhNCO (0.04 ml, 0.38 mmol) were added. The mixture was stirred for 72 h by which time a red solution was obtained. This was filtered and volatiles removed under reduced pressure

resulting in isolation of **4a** as an orange–red powder (0.12 g, 80%) slightly contaminated with oligomers of PhNCO. IR (KBr) ν/cm^{-1} 1709s, 1658s, 1591s, 1515vs, 1479s, 1441s, 1385w, 1315m, 1265s, 1200w, 1145w, 1078m, 1026m, 927m, 756m, 686m; ^{1}H NMR ($CDCl_3$) δ 7.95 (d, J 7.6, 2H, Ph), 7.48 (d, J 7.6, 2H, Ph), 7.43 (t, J 8.2, 2H, Ph), 7.25 (t, J 7.6, 2H, Ph), 7.20 (t, J 7.9, 1H, Ph), 7.14 (m, 2H, Ph), 7.04 (t, J 7.3, 1H, Ph), 6.97 – 6.91 (obscured), 6.74 (m, 1H, Ph), 6.68 (d, J 7.5, 2H, Ph), 3.89–3.78 (m, 4H, CH_2), 3.73–3.51 (m, 4H, CH_2), 1.26 (t, J 7.1, 3H, Me), 1.24 (t, J 7.1, 3H, Me, 1.07 (t, J 7.1, 3H, Me), 1.02 (t, J 7.1, 3H, Me); Mass spectrum (FAB), m/z 897 (M^+), 779 (M^+ – PhNCO). All attempts to isolate a pure sample of **4a** failed, with crystals of *anti*-[MoO(μ-NPh)(S_2CNEt_2)]$_2$ being deposited from chloroform solutions after extended periods,[13] NMR also showing the formation of *syn*-[MoO(μ-NPh)(S_2CNEt_2)]$_2$ and aniline.

Reaction of *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$ with *p*-tolylNCO followed by NMR-identification of [Mo_2O(N-*p*-tol)(μ-N-*p*-tol){μ-*p*-tolNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (4b)

In a similar fashion to that described above, the reaction of *p*-tolylNCO and *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$ (*ca.* 10 mg) was carried out in d^8-toluene. The insolubility of *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$, however, meant that no significant reaction was observed until the sample was heated to 60 °C. At this temperature, after about 30 min the solution became orange and a new species was seen tentatively characterised as [Mo_2O(N-*p*-tol)(μ-N-*p*-tol){μ-*p*-tolNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**4b**). ^{1}H NMR (d^8-toluene) δ 8.32 (d, J 8.2, 2H, Ar), 7.86 (d, J 8.2, 2H, Ar), 7.34 (d, J 8.2, 2H, Ar), 7.14 (d, J 8.1, 2H, Ar), 6.88 (d, J 8.2, 2H, Ar), 6.76 (d, J 8.2, 2H, Ar), 6.42 (d, J 8.2, 2H, Ar), one doublet obscured, 3.22 (m, 2H, CH_2), 3.05 (m, 4H, CH_2), 2.84 (m, 2H, CH_2), 2.19 (s, 3H, Me), 2.05 (s, 3H, Me), 2.00 (s, 3H, Me), 1.80 (s, 3H, Me), 0.74 (t, J 7.2, 3H, Me), 0.61 (t, J 7.1, 3H, Me), 0.52 (t, J 7.1, 3H, Me), 0.46 (t, J 7.2, 3H, Me). Upon heating to 100 °C, over 10 min clean conversion to **1b** occurred with complete dissolution of all insolubles.

Reaction of *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$ with PhNCO followed by NMR

In a similar fashion to that described above, the reaction of PhNCO and sparingly soluble *syn*-[MoO(μ-N-*p*-tol)(S_2CNEt_2)]$_2$ (*ca.* 10 mg) was carried out in d^8-toluene. Upon warming to 60 °C significant spectral changes were observed, while at 70 °C the starting material was consumed over approximately 20 min (the tube was shaken a few times in order to aid dissolution) with the formation of a bright orange solution. By NMR this contained *ca.* 90% of a single new species tentatively assigned as [Mo_2O(NPh)(μ-N-*p*-tol){μ-PhNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**5**). ^{1}H NMR (d^8-toluene) δ 8.29 (d, J 8.3, 2H, Ar), 7.83 (d, J 8.2, 2H, Ar), 7.41 (d, J 7.8, 2H, Ar), 7.35 (d, J 7.8, 2H, Ar), 7.11–6.54 (obscured), 3.19 (sextet, J 7.0, 2H, CH_2), 3.01 (m, 4H, CH_2), 2.80 (sextet, J 7.0, 2H, CH_2), 2.17 (s, 3H, Me), 2.02 (s, 3H, Me), 0.72 (t, J 7.2, 3H, Me), 0.58 (t, J 7.2, 3H, Me), 0.51 (t, J 7.2, 3H, Me), 0.44 (t, J 7.2, 3H, Me). Some minor peaks were seen which may be associated with a second isomer of *ca.* 10% composition most notably at δ 2.16 (s), 2.13 (s), 0.69 (t, J 7.2), 0.62 (t, J 7.2), 0.52 (t, J 7.2) all others being obscured. Upon warming to 100 °C, further spectral changes were apparent and after 1 h the solution turned dark brown. By NMR this contained *ca.* 95% of a single new species tentatively assigned as [Mo_2(NPh)$_2$(μ-N-*p*-tol){μ-PhNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**6**). ^{1}H NMR (d^8-toluene) δ 8.19 (d, J 8.2, 2H, Ar), 7.84 (d, J 8.2, 2H, Ar), 7.60 (d, J 7.7, 2H, Ar), 7.37 (d, J 7.9, 2H, Ar), 7.09 (d, J 7.7, 2H, Ar), 7.07–6.50 (obscured), 3.25 (m, 4H, CH_2), 2.95 (sextet, J 6.8, 2H, CH_2), 2.84 (sextet, J 6.8, 2H, CH_2), 2.18 (s, 3H, Me), 2.04 (s, 3H, Me), 0.71 (t, J 7.2, 6H, Me), 0.55 (t, J 7.2, 6H, Me).

Reaction of *syn*-[MoO(μ-NPh)(S_2CNEt_2)]$_2$ with *p*-tolylNCO followed by NMR

In a similar fashion to that described above, the reaction of *p*-tolylNCO and *syn*-[MoO(μ-NPh)(S_2CNEt_2)]$_2$ (*ca.* 10 mg) was carried out in d^8-toluene. Upon warming to 70 °C significant spectral changes were observed, being similar to those described above, but with a clear doubling of all the new resonances. The spectrum was too complex to fully assign but in line with the above experiments we ascribe these changes to the formation of a mixture of [Mo_2O(N-*p*-tol)(μ-NPh){μ-PhNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**7a–b**) in an approximate 2 : 1 ratio *e.g.* δ 8.40 (d, J 7.5, Ar, minor), 8.34 (d, J 8.1, Ar, major). Further warming to 100 °C resulted in the loss of these peaks with the concomitant development of new resonances attributed to the formation of [Mo_2(N-*p*-tol)$_2$(μ-NPh){μ-PhNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**8a**) and [Mo_2(N-*p*-tol)$_2$(μ-NPh){μ-*p*-tolNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**9**) in a 1.4 : 1 ratio (major isomer remains unclear). ^{1}H NMR (d^8-toluene) δ 8.22 (d, J 7.6, 2H, Ar, minor), 8.11 (d, J 8.2, 2H, Ar, major), 7.88 (d, J 7.6, 2H, Ar, minor), 7.76 (d, J 8.2, 2H, Ar, major), 7.40 (d, J 8.2, 2H, Ar, major), 7.27 (d, J 7.6, 2H, Ar, minor), 7.18 (d, J 8.3, 2H, Ar, major), 7.07 (d, J 7.9, 2H, Ar, minor), 6.87 (t, J 8.2, 2H, Ph, minor), 6.85 (t, J 8.2, 2H, Ph, major), 6.75 – 6.50 (obscured), 6.41 (d, J 7.8, 2H, Ar, major), 6.39 (d, J 7.7, 2H, Ar, minor), 3.37 (m, 4H, CH_2, major + minor), 3.23 (m, 2H, CH_2, major + minor), 3.12 (m, 2H, CH_2, major + minor), 2.19 (s, 3H, Me, minor), 2.09 (s, 3H, Me, major), 2.06 (s, 3H, Me, minor), 2.01 (s, 3H, Me, minor), 1.86 (s, 6H, Me, major), 1.85 (s, 6H, Me, minor), 0.81 (t, J 7.2, 6H, Me, major), 0.80 (t, J 7.2, 6H, Me, minor), 0.67 (t, J 7.2, 6H, Me, major), 0.66 (t, J 7.2, 6H, Me, minor).

Reactions of [Mo_2(N-*p*-tol)$_2$(μ-X){μ-*p*-tolNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (X = N-*p*-tol, S) (1b–2b) with PhNCS and CS_2

A mixture of [Mo_2(N-*p*-tol)$_2$(μ-N-*p*-tol){μ-*p*-tolNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**1b**) (0.06 g, 0.06 mmol) and PhNCS (0.08 ml, 0.74 mmol) in toluene (*ca.* 50 ml) was refluxed for 3 h. This led to the formation of a green precipitate in an orange solution. After separation of the precipitate, volatiles were removed under reduced pressure to give an orange–brown oily product. This was absorbed onto alumina and passed down a chromatography column. Elution with 50% dichloromethane in petrol resulted in isolation of an orange band shown identified as [Mo_2(N-*p*-tol)$_2$(μ-S)(μ-S_2)(S_2CNEt_2)$_2$] (**11**) (0.01 g, 20%). IR (KBr) ν/cm^{-1} 1511vs, 1437s, 1381m, 1354m, 1318m, 1274s, 1204m, 1148m, 1070w, 987w, 912vw, 846vw, 815m, 778w: ^{1}H ($CDCl_3$) δ 6.62 (d, J 8.4, 2H, Ar), 6.58 (d, J 8.4, 2H, Ar), 3.99 (m, 4H, CH_2), 3.84 (sextet, J 6.9, 2H, CH_2), 3.80 (sextet, J 6.9, 2H, CH_2), 2.14 (s, 6H, Me), 1.35 (d, J 7.1, 6H, Me), 1.34 (t, J 7.1, 6H, Me); mass spectrum (FAB) m/z 796 (M^+).

Elution with 60% dichloromethane in petrol afforded an inseparable mixture of (**2b**) and two isomers of [Mo_2(N-*p*-tol)$_2$(μ-S){μ-PhNC(O)N-*p*-tol}(S_2CNEt_2)$_2$] (**10a**) (0.01 g, *ca.* 17%). IR (KBr) ν/cm^{-1} 1702s, 1653m, 1634m, 1590m, 1511vs, 1504sh, 1493s, 1439m, 1383w, 1313m, 1261s, 1204w, 1146m, 1097s, 1021s, 806s; ^{1}H ($CDCl_3$) δ 7.88 (d, J 8.4, Ar), 7.75 (d, J 8.6, Ar), 7.74 (d, J 8.2, Ar, **2b**), 7.24 (d, J 8.0, Ar), 7.16 (t, J 7.8, Ph), 7.05 (d, J 8.4, Ar), 7.04 (d, J 8.2, Ar, **2b**), 6.92 (d, J 8.4, Ar), 6.91 (d, J 8.3, Ar, **2b**), 6.87 (t, J 8.3, Ph), 6.68 (d, J 8.4, Ar), 6.67 (d, J 8.3, Ar, **2b**), 6.57 (d, J 8.2, Ar, **2b**), 6.56 (d, J 8.2, Ar), 6.47 (d, J 8.3, Ar), 6.46 (d, J 8.2, Ar, **2b**), 6.43 (d, J 8.2, Ar), 3.95 (m, NCH_2), 3.55 (m, NCH_2), 2.33 (s, Me), 2.32 (s, Me, **2b**), 2.15 (s, Me, **2b**), 2.14 (s, Me), 2.08 (s, Me), 2.07 (s, Me, **2b**), 1.293 (t, J 7.1, Me, **2b**), 1.290 (t, J 7.4, Me), 1.06 (t, J 7.4, Me), 1.05 (t, J 7.1, Me, **2b**), 0.801 (t, J 7.4, Me); Anal. Calc. for $Mo_2C_{38}H_{46}O_1S_5N_6$ C, 48.07, H, 4.89, N 8.74; Found C, 47.75, H, 4.85, N, 8.40.

The green precipitate was washed with hexane and dried to afford [Mo_2(N-*p*-tol)$_2$(μ-S)$_2$(S_2CNEt_2)$_2$]$_n$ (**12a–13a**) (0.01 g, 22%). This was better prepared as detailed below. Thermolysis

of a toluene solution of **2b** (0.09 g, 0.09 mmol) and PhNCS (0.11 ml, 0.82 mmol) resulted in the deposition of a large amount of green precipitate. This was isolated, washed with hexane and dried to yield (**12a–13a**) (0.04 g, 56%). The complexes show poor solubility in all common organic solvents. Addition of warm chloroform resulted in the dissolution of a small amount of material giving a yellow solution. Heating in toluene resulted in the complete dissolution to give a golden yellow solution from which a green solid was precipitated upon cooling. When the solution was tepid it took on a red appearance. ^{1}H ($CDCl_3$) δ 6.46 (s, 8H, Ar), 3.91 (dectet, J 7.1, 8H, CH_2), 2.05 (s, 6H, Me), 1.88 (t, J 7.1, 12H, Me); ^{1}H (DMSO) δ 6.84 (d, J 8.3, 4H, Ar, tetramer), 6.77 (d, J 8.3, 4H, Ar, tetramer), 6.58 (d, J 8.2, 4H, Ar, dimer), 6.84 (d, J 8.3, 4H, Ar, tetramer), 6.46 (d, J 8.3, 4H, Ar, tetramer), 6.42 (d, J 8.3, 4H, Ar, tetramer), 6.25 (d, J 8.3, 4H, Ar, dimer), 4.03 – 3.86 (m, 8H, CH_2, dimer + tetramer), 2.10 (s, 6H, Me, tetramer), 2.07 (s, 6H, Me, tetramer), 2.03 (s, 6H, Me, dimer), 1.87 (s, 6H, Me, tetramer), 1.82 (s, 6H, Me, tetramer), 1.31 (t, J 7.2, 12H, tetramer), 1.25 (t, J 7.2, 12H, dimer), 1.15 (t, J 7.2, 12H, tetramer) ratio dimer : tetramer at room temperature *ca.* 12 : 1; mass spectrum (FAB) m/z 763 (M^+); IR (KBr) ν/cm^{-1} 1700w, 1559w, 1491vs, 1450w, 1428s, 1376w, 1356w, 1331m, 1274s, 1209m, 1141m, 1079w, 993w, 813m; Anal. Calc. for $Mo_4C_{48}H_{68}S_{12}N_8.CH_2Cl_2$ C, 36.54, H, 4.35, N 6.96, S 23.87; Found C, 36.69, H, 4.31, N, 6.89, S, 23.96.

Complex **1b** (10 mg) was dissolved in *ca.* 2 ml of d^8-toluene and the ^{1}H NMR spectrum was recorded (see above). An excess of PhNCS was added and the sample warmed to 85 °C at which point new resonances began to appear. After heating for *ca.* 30 min, all **1b** was consumed and a clear orange solution was formed. NMR revealed that one equivalent of *p*-tolylNCO was generated (δ 1.92, s) together with a number of new species one of which **2b** accounted for *ca.* 80% of the material. ^{1}H NMR (d^8-toluene) δ 8.07 (d, J 8.2, 2H, Ar), 7.39 (d, J 8.2, 2H, Ar), 7.23 (d, J 8.2, 2H, Ar), 7.12 (d, J 8.2, 2H, Ar), 6.98–6.50 (obscured), 6.31 (d, J 8.2, 4H, Ar), 6.21 (d, J 8.2, 2H, Ar), 3.51–2.96 (m, 8H, CH_2), 1.98 (s, 3H, Me), 1.78 (s, 6H, Me), 1.75 (s, 3H, Me), 0.75 (t, J 7.2, 6H, Me), 0.64 (t, J 7.2, 6H, Me). Further heating of the solution at 100 °C for 2 h gave a clear yellow–green solution from which **11** was noticeably absent. After a further 5 h at 100 °C, copious amounts of green precipitate were deposited making the acquisition of good quality NMR spectra impossible.

Thermolysis of toluene solutions of **1b** and excess CS_2 resulted in the formation of **2b** and **12a–13a**. Precise amounts of each varied depending on the amount of CS_2 used and the reaction time—with longer reaction times (>3 h) leading to the formation of more **12a–13a**. Likewise, heating a toluene solution of **2b** and a 10 fold excess of CS_2 overnight resulted in the formation of **12a–13a** in 73% yield.

Reaction of [Mo$_2$(N-*p*-tol)$_2$(μ-N-*p*-tol){μ-*p*-tol-NC(O)N-*p*-tol}(S$_2$CNPr$_2$)$_2$] (1d) with PhNCS

Heating a toluene solution (50 ml) of **1d** (0.129 g, 0.12 mmol) with PhNCS (0.16 ml, 1.34 mmol) for 3 h resulted in a colour change from brown to orange. Removal of volatiles gave an orange–red solid. This was absorbed onto alumina and passed down a chromatography column. Elution with 40% dichloromethane in light petroleum gave a yellow band which afforded an orange solid (0.03 g, *ca.* 27%) identified as an inseparable mixture of [Mo$_2$(N-*p*-tol)$_2$(μ-S){μ-*p*-tol-NC(O)N-*p*-tol}(S$_2$CNPr$_2$)$_2$] (**2d**) and isomers of [Mo$_2$(N-*p*-tol)$_2$(μ-S){μ-PhNC(O)N-*p*-tol}(S$_2$CNPr$_2$)$_2$] (**10b**). IR (KBr) ν/cm^{-1} 1712s, 1593w, 1508vs, 1493s, 1433m, 1371w, 1311s, 1244s, 1192w, 1146m, 1104w, 993w, 816m; ^{1}H ($CDCl_3$) δ 7.86 (d, J 8.0, Ar), 7.74 (d, J 8.2, Ar), 7.73 (d, J 8.3, Ar, **2d**), 7.23 (d, J 8.1, Ar), 7.16 (t, J 7.5, Ph), 7.03 (d, J 8.0, Ar, **2d**), 7.02 (t, J 8.4, Ph), 6.89 (d, J 8.4, Ar), 6.88 (d, J 8.4, Ar, **2d**), 6.84 (t, J 8.3, Ph), 6.65 (d, J 8.4, Ar), 6.64 (d, J 8.2, Ar, **2d**), 6.56 (d, J 8.2, Ar, **2d**), 6.55 (d, J 8.2, Ar), 6.44 (d, J 8.2, Ar, **2d**), 6.43 (d, J 8.3, Ar), 6.42 (d, J 8.2, Ar), 3.87 (m, NCH_2), 3.45 (m, NCH_2), 2.32 (s, Me), 2.31 (s, Me, **2d**), 2.14 (s, Me, **2d**), 2.13 (s, Me), 2.08 (s, Me), 2.07 (s, Me, **2d**), 1.72 (m, CH_2), 1.23 (m, CH_2), 0.93 (t, J 7.4, Me, **2d**), 0.92 (t, J 7.4, Me), 0.819 (t, J 7.4, Me), 0.816 (t, J 7.4, Me, **2d**), 0.801 (t, J 7.4, Me); mass spectrum (FAB), m/z 1024 (M_A^+), 1012 (M_B^+), 890 (M_A^+ – *p*-tolNCO + M_B^+ – PhNCO); Anal. Calc. for $Mo_2C_{42}H_{55}O_1S_5N_6$ C, 49.85, H, 5.44, N 8.31; Found C, 49.37, H, 5.41, N, 8.03.

Further elution with 40% dichloromethane in light petroleum gave a yellow–green band which afforded a mixture of [Mo$_2$(N-*p*-tol)$_2$(μ-S)$_2$(S$_2$CNPr$_2$)$_2$]$_2$ (**12b**) and [Mo$_2$(N-*p*-tol)$_2$(μ-S)$_2$(S$_2$CNPr$_2$)$_2$] (**13b**) (0.44 g, 43%). Red crystals grown from a dichloromethane–methanol mixture were analysed crystallographically. Upon addition of chloroform a yellow solution was generated, shown by NMR to be **13b**. IR (KBr) ν/cm^{-1} 1655m, 1635m, 1487s, 1460m, 1424m, 1382w, 1308w, 1242m, 1196vw, 1144m, 1099m, 102ovw, 986w, 811m; ^{1}H NMR ($CDCl_3$) δ 6.51 (s, 8H, Ar), 3.92–3.81 (m, 8H, NCH_2), 2.10 (s, 6H, Me), 1.89–1.77 (m, 8H, CH_2), 1.01 (t, J 7.4, 12H, Me); mass spectrum (FAB), m/z 819 (M^+); Anal. Calc. for $Mo_2C_{28}H_{42}S_6N_4$ C, 41.08, H, 5.13, N 6.85; Found C, 41.55, H, 5.42, N, 6.77.

X-Ray data collection and solution

For all complexes, a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. For [Mo$_2$(N-*p*-tol)$_2$(μ-S)(μ-S$_2$)(S$_2$CNEt$_2$)$_2$] (**11**) data collection was made on an automated Nicolet R3mV four-circle diffractometer equipped with Mo-K$_\alpha$ radiation (λ = 0.710 73 Å) at 293 ± 2 K. 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 $\omega - 2\theta$ technique was used to measure reflections and three standard reflections (re-measured every 97 scans) showed no significant loss in intensity during data collection. The data was corrected for Lorenz and polarisation effects and unique data with $I \geq 2\sigma(I)$ were used to solve and refine the structure. This was solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. 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 sulfide and disulfide units were disordered and this was modelled by fixing the occupancy of S(4) at 50%. Structure solution used SHELXTL PLUS program package on an IBM PC.

For [Mo$_2$(N-*p*-tol)$_2$(μ-S){μ-*p*-tolNC(O)N-*p*-tol}(S$_2$CNPr$_2$)$_2$] (**2d**), [Mo$_2$(N-*p*-tol)$_2$(μ-N-*p*-tol){μ-*p*-tolNC(O)NPh}(S$_2$CNEt$_2$)$_2$] (**3a**) and [Mo$_2$(N-*p*-tol)$_2$(μ-S)$_2$(S$_2$CNPr$_2$)$_2$]$_2$ (**12b**) data collection was made on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 ± 2 K (**2d** and **12b**) and at 150 ± 2 K (**3a**). Data reduction was carried out with SAINT+ and absorption correction applied using the program SADABS. Structures were solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically except for atom C(7) in **12b** which had a large isotropic thermal parameter. In **3a**, some of the carbon atoms of one of the phenyl groups [C(50)–C(55)] were disordered over two positions which shared two atoms [C(50) and C(53)]. This was successfully modeled using 50% occupancy for sites C(51)/C(81), C(52/C82), C(54)/C(84) and C(55)–C(85). Hydrogens were generally placed in calculated positions (riding model). Structure solution used the SHELXTL PLUS V6.10 program package.

CCDC reference numbers 253354–253357.

See http://www.rsc.org/suppdata/dt/b4/b417234p/ for crystallographic data in CIF or other electronic format.

Crystallographic data for $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)\{\mu\text{-}p\text{-}tolNC(O)N\text{-}p\text{-}tol\}(S_2CNPr_2)_2]$ (**2d**); orange block, dimensions 0.12 × 0.10 × 0.09 mm, triclinic, space group $P\bar{1}$, $a = 12.9948(9)$, $b = 13.0247(9)$, $c = 16.4809(11)$ Å, $\alpha = 88.154(1)$, $\beta = 69.828(1)$, $\gamma = 65.095(1)°$, $V = 2353.8(3)$ Å^3, $Z = 2$, $F(000) = 1054$, $d_{calc} = 1.445$ g cm^{-3}, $\mu = 0.794$ mm^{-1}, $T_{max}/T_{min} = 0.932/0.911$. 20955 reflections were collected, 10851 unique [R(int) = 0.0219] of which 7712 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0486$, $wR_2 = 0.1102$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0728$, $wR_2 = 0.1126$ (all data), for 521 parameters.

Crystallographic data for $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}N\text{-}p\text{-}tol)\{\mu\text{-}p\text{-}tolNC(O)NPh\}(S_2CNEt_2)_2]$ (**3a**); red needle, dimensions 0.15 × 0.08 × 0.02 mm, monoclinic, space group $C2/c$, $a = 35.949(2)$, $b = 16.1750(11)$, $c = 17.8306(12)$ Å, $\beta = 112.957(1)°$, $V = 9546.8(11)$ Å^3, $Z = 8$, $F(000) = 4184$, $d_{calc} = 1.424$ g cm^{-3}, $\mu = 0.741$ mm^{-1}, $T_{max}/T_{min} = 0.985/0.897$. 29627 reflections were collected, 11157 unique [R(int) = 0.0723] of which 5984 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0804$, $wR_2 = 0.1942$ [$I > 2.0\sigma(I)$] and $R_1 = 0.1573$, $wR_2 = 0.2296$ (all data), for 576 parameters.

Crystallographic data for $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)(\mu\text{-}S_2)(S_2CNEt_2)_2]$ (**11**); orange block, dimensions 0.42 × 0.27 × 0.25 mm, monoclinic, space group $C2/c$, $a = 18.516(4)$, $b = 12.012(2)$, $c = 14.994(3)$ Å, $\beta = 90.13(3)°$, $V = 3334.9(11)$ Å^3, $Z = 4$, $F(000) = 1608$, $d_{calc} = 1.583$ g cm^{-3}, $\mu = 1.211$ mm^{-1}, $T_{max}/T_{min} = 0.988/0.741$. 2980 reflections were collected, 2886 unique [R(int) = 0.0231] of which 2104 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0539$, $wR_2 = 0.1147$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0776$, $wR_2 = 0.1319$ (all data), for 172 parameters.

Crystallographic data for $[Mo_2(N\text{-}p\text{-}tol)_2(\mu\text{-}S)_2(S_2CNPr_2)_2]_2$ (**12b**); red block, dimensions 0.12 × 0.11 × 0.10 mm, tetragonal, space group $P4_32_12$, $a = b = 12.4558(5)$, $c = 49.648(3)$ Å, $V = 7702.8(6)$ Å^3, $Z = 4$, $F(000) = 1672$, $d_{calc} = 1.412$ g cm^{-3}, $\mu = 0.999$ mm^{-1}, $T_{max}/T_{min} = 0.907/0.890$. 68980 reflections were collected, 9229 unique [R(int) = 0.0501] of which 7565 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0472$, $wR_2 = 0.1000$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0625$, $wR_2 = 0.1057$ (all data), for 356 parameters.

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