Reversible Insertion of an Isocyanate into an Imido Moiety at a Dimolybdenum Centre. Synthesis and X-Ray Crystal Structure of $[Mo_2(NPh)_2(S_2CNEt_2)_2(\mu\text{-}NPh)\{\mu\text{-}PhNC(O)NPh\}]$

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Thermolysis of $[\{MoO(S_2CNEt_2)(\mu\text{-}NPh)\}_2]$ in the presence of an excess of phenyl isocyanate affords the ureato complex $[Mo_2(NPh)_2(S_2CNEt_2)_2(\mu\text{-}NPh)\{\mu\text{-}PhNC(O)NPh\}]$ **1** as a result of oxo substitution, and insertion of an isocyanate into one of the bridging imido functionalities; heating **1** in toluene results in release of phenyl isocyanate to give the tetraimido complex $[\{Mo(NPh)(S_2CNEt_2)(\mu\text{-}NPh)\}_2]$ **2**, a process which is reversible.

The major impetus driving the current resurgence in interest in transition-metal imido chemistry is the anticipation that such complexes may have applications as amination and oxyamination reagents in organic synthesis. Clearly for such a process to be viable, facile nitrogen–carbon bond formation is required when imido complexes react with organic substrates. To date this seemingly simple reaction has only been noted on a handful of occasions,[1] and generally high-valent metal–imido complexes are inert to such bond-forming reactions. In a number of instances however, attempts to substitute oxo with imido ligands using isocyanates has led to the isolation of ureato complexes, formed seemingly as a consequence of the initially generated imido moiety reacting with a second equivalent of isocyanate.[2] Thus while a number of ureato complexes are known,[2,3] surprisingly this simple nitrogen–carbon bond-formation reaction has not been well characterised at a high-valent metal centre. The transformation is however also important with regard to the use of transition-metal imido complexes in isocyanate metathesis.[4] Such a process requires both facile nitrogen–carbon bond formation and cleavage, however to date neither of these processes has been well characterised at a high-valent metal centre.

Heating a toluene solution of $[\{MoO(S_2CNEt_2)(\mu\text{-}NPh)\}_2]$[5] with excess phenyl isocyanate resulted in the isolation after chromatography of the ureato complex $[Mo_2(NPh)_2(S_2CNEt_2)_2(\mu\text{-}NPh)\{\mu\text{-}PhNC(O)NPh\}]$ **1** in 72% yield.† Characterisation was made on the basis of analytical and spectroscopic data.‡ In order to elucidate the structure fully an X-ray crystallographic study was undertaken the results of which are shown in Fig. 1.§ The molecule consists of two molybdenum(V) centres each bound to a dithiocarbamate ligand and a linear imido moiety [Mo(1)–N(7)–C(71) 175.1(13), Mo(2)–N(6)–C(61) 168.4(15)°]. The short terminal molybdenum–imido distances [Mo(1)–N(7) 1.740(15), Mo(2)–N(6) 1.742(15) Å] are typical,[6] and the dithiocarbamates adopt the expected *cis* configuration. Bridging the molybdenum–molybdenum vector approximately symmetrically is a further imido ligand [Mo(1)–N(3) 1.973(15), Mo(2)–N(3) 1.991(15) Å] and also a diphenylureato ligand. The latter also bridges approximately symmetrically although the molybdenum–nitrogen distances are strongly influenced by the *trans* ligand. Thus those *trans* to the linear imido ligands [Mo(1)–N(5) 2.386(14), Mo(2)–N(5) 2.338(14) Å] are elongated considerably with respect to those *trans* to the bridging imido moiety [Mo(1)–N(4) 2.147(13), Mo(2)–N(4) 2.169(13) Å]. This difference reflects the stronger *trans* influence of the imido ligand in the terminal *versus* the bridging position.

The molecule poses a particular problem in terms of electron

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† Complex **1** was obtained, operating in an inert atmosphere, on refluxing a mixture of $[\{MoO(S_2CNEt_2)(\mu\text{-}NPh)\}_2]$ (1.08 g, 1.59 mmol) and PhNCO (0.38 cm^3, 3.18 mmol) in toluene (75 cm^3) for 3 d. The deep red solution formed was cooled to room temperature and evaporated to dryness under vacuum. The solid residue was absorbed onto alumina and purified by chromatography on deactivated alumina. Elution with dichloromethane–light petroleum (b.p. 40–60 °C) (9:1) afforded a brown band which yielded 1.08 g (72%) of **1**. Recrystallisation was effected upon slow mixing of dichloromethane solutions with methanol. Complex **2** was obtained upon reflux of a toluene solution (75 cm^3) of **1** (1.20 g, 1.23 mmol). Cooling after 2 d afforded an orange microcrystalline precipitate which yielded 0.35 g (33%) of **2** upon washing with light petroleum (b.p. 40–60 °C). Heating a toluene solution of **2** (0.20 g, 0.23 mmol) with PhNCO (0.03 cm^3, 0.25 mmol) resulted in the formation of **1** in 50% yield.

‡ Complexes **1** and **2** were characterised by elemental analyses and IR and NMR (^{1}H and ^{13}C) spectroscopy. Selected data for **1**: ^{1}H NMR (CDCl$_3$) δ 7.88 (d, 2 H, *J* 7.2), 7.41 (d, 2 H, *J* 7.4), 7.30 (t, 4 H, *J* 7.2), 7.15 (t, 2 H, *J* 7.3), 7.08 (d, 2 H, *J* 7.4), 6.96 (t, 2 H, *J* 7.4), 6.86 (t, 2 H, *J* 7.3), 6.81–6.73 (m, 4 H), 6.66 (t, 1 H, *J* 7.3), 6.38 (d, 4 H, *J* 7.3), 3.84 (m, 4 H, CH$_2$), 3.65 (sxt, 2 H, *J* 7.2, CH$_2$), 3.52 (sxt, 2 H, *J* 7.1, CH$_2$), 1.20 (t, 6 H, *J* 7.2, Me) and 0.98 (t, 6 H, *J* 7.2, Me); IR (KBr) 1710s, 1696s, 1583m, 1580m, 1512vs, 1474s, 1439s, 1355m, 1318s, 1274s, 1252s, 1205m, 1149m, 1072m, 1023m, 754s and 687s cm^{-1}. Selected data for **2**: ^{1}H NMR (CDCl$_3$) δ 8.12 (d, 4 H, *J* 7.3), 7.52 (t, 4 H, *J* 7.4), 7.20 (t, 2 H, *J* 7.2), 7.13 (t, 4 H, *J* 7.4), 6.74 (t, 2 H, *J* 7.4), 6.67 (d, 4 H, *J* 7.4), 3.68 (q, 8 H, *J* 7.2, CH$_2$) and 1.18 (t, 12 H, *J* 7.2, Me); IR (KBr) 1578m, 1516s, 1474s, 1436m, 1354w, 1309m, 1274m, 1262m, 1201w, 1149m, 1067m, 1023w, 996w, 975w, 767m, 754s, 695m, 686m, 668m and 486w cm^{-1}. Satisfactory elemental analyses were obtained for both **1** and **2**.

§ Crystal data for **1**·MeOH. $C_{49}H_{42}Mo_2N_7O_4S_4$, $M = 1004.10$, orthorhombic, space group $P2_12_12_1$, $a = 11.852(5)$, $b = 17.782(7)$, $c = 22.518(6)$ Å, $U = 4745(3)$ Å^3, $Z = 4$, $T = 292$ K, $D_c = 1.40$ g cm^{-3}, $F(000) = 2056$, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 7.24 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.52 × 0.42 × 0.30 mm mounted on a Nicolet R3mV diffractometer, by the $\bar{\omega}$–2θ scan technique ($5 \leqslant 2\theta \leqslant 50°$). From 4816 measured data (3317 unique measurements), 2757 with $I \geqslant 3\sigma(I)$ were considered observed. The structure was solved by direct methods and refined by full-matrix least squares to *R* and *R'* values of 0.076 and 0.081. Structure solution utilised the SHELXTL PLUS program package[7] on a MicroVax II computer. Only molybdenum and sulfur 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 quantity minimised was $\Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|[w^{-1} = \sigma^2(F) + 0.003\,578F^2]$. The methanol was disordered over two sites which were refined with 50% occupancy. Three standards showed a drop in intensity of 20% during data collection. 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.*, 1993, Issue 1, pp. xxiii–xxviii.

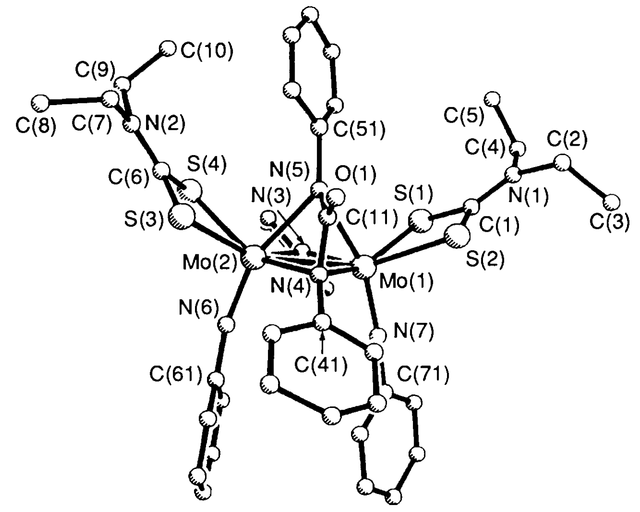
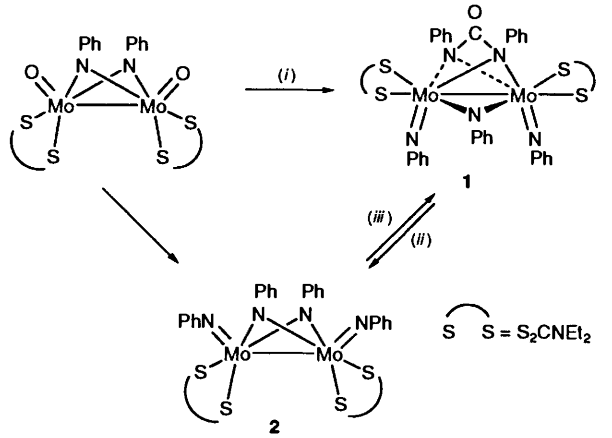


Fig. 1 Molecular structure of **1**. Important bond lengths (Å) and angles (°) include: Mo(1)–Mo(2) 2.625(3), Mo(1)–N(3) 1.973(15), Mo(2)–N(3) 1.991(15), Mo(1)–N(7) 1.740(15), Mo(2)–N(6) 1.742(15), Mo(1)–N(4) 2.147(13), Mo(2)–N(4) 2.169(13), Mo(1)–N(5) 2.386(14), Mo(2)–N(5) 2.338(14), N(4)–C(11) 1.420(20), N(5)–C(11) 1.386(22), C(11)–O(1) 1.211(20); Mo(1)–N(7)–C(71) 175.1(13), Mo(2)–N(6)–C(61) 168.4(15), Mo(1)–N(3)–Mo(2) 82.9(6), Mo(1)–N(4)–Mo(2) 74.9(2), Mo(1)–N(5)–Mo(2) 67.5(4), N(4)–C(11)–N(5) 101.3(13)

counting. Thus considering both the terminal and bridging imido ligands as four-electron donor ligands and the bridging ureato as a six-electron donor, then the metal centres achieve an 18-electron count in the absence of any metal–metal bonding. The short molybdenum–molybdenum contact [Mo(1)–Mo(2) 2.625(3) Å] and diamagnetic nature of **1** suggests however that some direct or through ligand interaction of metal centres is present. An alternative explanation may be that each terminal imido ligand is acting as a three-electron donor, the remaining pair of electrons occupying a molecular orbital that is mainly nitrogen based. This has been shown to be the case for a number of similar molybdenum(V) imido dimers,[8] and we favour this explanation here.

Complex **1** is apparently formed as a result of the insertion of phenyl isocyanate into a bridging imido ligand of the tetraimido complex $[\{Mo(NPh)(S_2CNEt_2)(\mu\text{-}NPh)\}_2]$ **2**, itself formed *via* oxo substitution. In the presence of isocyanate however **2** was not isolated from the reaction. Heating a toluene solution of **1** in the absence of isocyanate resulted upon cooling in the deposition of orange crystals characterised as the tetraimido complex **2** in 33% yield.† Complex **2** is related to the well known tetraoxo dimer $[\{MoO(S_2CNEt_2)(\mu\text{-}O)\}_2]$ shown to contain a *cis* arrangement of dithiocarbamate ligands and a puckered core geometry.[9] In light of the arrangement of these ligands in **1**, we assume that a similar *cis*, puckered configuration is adopted by **2**. Addition of phenyl isocyanate to **2** results in the rapid and quantitative formation of **1** thus showing that the process is reversible (Scheme 1). We can now see quite clearly how the addition of the isocyanate to the bridging imido ligand takes place. The isocyanate [comprising C(11) and N(4)] approaches the bis(imido) complex perpendicular to the metal–metal vector, and orientated such that the electropositive carbon approaches the nucleophilic bridging imido ligand. The enhanced reactivity of the bridging *versus* terminal imido moieties is in contrast to that found in the related organometallic complexes $[\{Mo(C_5H_4R)(NPh)(\mu\text{-}NPh)\}_2]$ (R = Me or Pr^i) in which reactions were found to occur exclusively at the terminal sites.[8,10] Well defined addition of an isocyanate to an imido ligand has only previously been observed in low-valent, highly reactive imido complexes. Thus $[Ir(C_5Me_5)(NBu^t)]$ readily inserts Bu^{t}NCO to form the ureato complex $[Ir(C_5Me_5)\{Bu^tNC(O)Bu^t\}]$,[11] while a similar reaction occurs for $[Os(NBu^t)(\eta^6\text{-}MeC_6H_4Pr^i\text{-}p)]$.[12] We are currently investigating the reactivity of **2** towards a variety of unsaturated organic substrates, and also exploring the synthetic utility of the isocyanate insertion reaction. Initial studies suggest that a range of isocyanates insert into **2**, and that the carbonyl group in **1** is easily functionalised.



Scheme 1 (*i*), excess PhNCO (110 °C); (*ii*), 110 °C; (*iii*), PhNCO (110 °C)

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