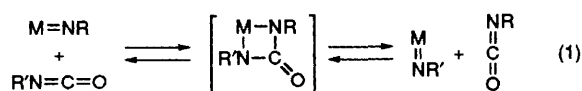# Isocyanate *versus* Isothiocyanate Insertion into Alkoxo and Imido Ligands

Vernon C. Gibson,* [a] Carl Redshaw, [a] William Clegg [b] and Mark R. J. Elsegood [b]

[a] Department of Chemistry, University Science Laboratories, South Road, Durham, UK DH1 3LE
[b] Department of Chemistry, The University, Newcastle upon Tyne, UK NE1 7RU

Room-temperature treatment of Mo(NAr)$_2$(OBu^t)$_2$ **1** (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) with excess PhNCO in pentane affords the bis(carbamate) complex, Mo(NAr)$_2$[NPhC(O)OBu^t]$_2$ **2**, as a result of isocyanate insertion into both of the metal–alkoxide bonds; contrastingly **1** adds PhNCS to one metal–nitrogen bond to give the thioureato-N,N' complex Mo(NAr)[NPhC(S)NAr](OBu^t)$_2$ **3**.

Reactions of imido complexes with isocyanates have been exploited to access new imido derivatives,[1] a process that proceeds *via* cycloaddition of the isocyanate N–C double bond to the M–N multiple bond [eqn. (1)]; in certain cases the intermediate ureato complexes have been isolated.

$$\begin{array}{c} M=NR \\ + \\ R'N=C=O \end{array} \rightleftharpoons \left[\begin{array}{c} M-NR \\ | \quad | \\ R'N-C \diagdown O \end{array} \right] \longrightarrow \begin{array}{c} M \\ \| \\ NR' \end{array} + \begin{array}{c} NR \\ \| \\ C \\ \| \\ O \end{array} \qquad (1)$$

This type of reaction belongs to the important class of metathetical exchange processes involving M=E (E = O, NR, CHR) and substrate multiple bonds.[2] In recent work,[3] we have investigated reactions of isocyanates with four-coordinate complexes of the type [Mo(NR)$_2$(O-Bu^t)$_2$] (R = Bu^t, 2,6-Pr$^i_2$C$_6$H$_3$) in which both imido and alkoxide ligands are attached to the molybdenum centre. In the absence of structural data, and by analogy with previously reported reactivity of isocyanates towards M=NR bonds,[1c,4] the products were formulated as ureato derivatives.[3] However, recent findings by Wilkinson and coworkers,[5] that isocyanates insert preferentially into the mono-anionic amide ligands of [W(NBu^t)$_2$(NHBu^t)$_2$] rather than the dianionic imide linkages prompted us to carry out further investigations on this molybdenum system. Here, we report the unexpected finding that isocyanates insert selectively into the Mo–O bonds of the *tert*-butoxide ligands while isothiocyanate adds reversible to the M–N bond to give a thioureato-N,N' moiety; these transformations are summarised in Scheme 1.† Insertions of organic isocyanates into metal–alkoxide bonds are rare,[6,7] the only structurally characterised examples being M$_2$(O-Bu^t)$_4$[μ-PhNC(O)OR]$_2$ (M = Mo, W; R = Bu^t, Pr^i) reported by Chisholm and coworkers,[7] while thioureato-N,N' complexes have not, to our knowledge, been structurally characterised previously.

The reaction of [Mo(N-2,6-Pr$^i_2$C$_6$H$_3$)$_2$(OBu^t)$_2$] **1** with excess PhNCO proceeds smoothly to give complex **2** as large air-stable, red prisms upon crystallization from a saturated pentane solution at room temp. The molecular structure‡ of **2** is shown in Fig. 1. The molecular geometry is best described as

pseudo-octahedral with *cis*-imido groups [N(3)–Mo–N(4) 104.01(9)°] and two chelating (O, N) carbamate ligands (bite angles *ca.* 59°) about the metal centre. The Mo–N(imido) distances are essentially equal, Mo–N(3) 1.754(2) and Mo–N(4) 1.759(2) Å, with Mo–N–C angles of 171.9(2) and 159.1(2)°, respectively. If the carbamate ligands are considered as three-electron donors then an electron count of 18 is achieved with only one of the imido groups acting as a four-electron donor. Contrary to expectation, the Mo–O bond *trans* to the 'linear' imido group is actually shorter [Mo–O(1) 2.304(2) Å] than that *trans* to the 'bent' imido group [Mo–O(3) 2.381(2) Å], a situation mirrored in the M–NH(Bu^t) bonds of the ureato complex [W[N(Bu^t)-C(O)(NHBu^t)]$_2$(NBu^t)$_2$].[5]

In marked contrast, the reaction of **1** with excess PhNCS in pentane gives an air-sensitive brown product **3** the crystal structure of which§ (Fig. 2) shows that the isothiocyanate has preferentially added to the organoimido ligand. The core geometry is best described as a distorted square-based pyramid with the imido ligand occupying the axial position; the distortion results from the restricted bite angle [N–Mo–N 61.98(8)°] of the chelating thioureato-N,N' ligand. To our knowledge, this is the first solid-state structure determination of a metal complex containing a chelating thioureato-N,N' ligand. In the organoimido ligand of **3**, the Mo–N bond length of 1.728(2) Å and the Mo–N–C angle of 178.1(2)° are consistent with a bond order of close to three. The two alkoxide ligands, however, are quite different [Mo–O(2) 1.818(2) Å, Mo–O(2)–C(36) 173.2(2)° *cf.* Mo–O(1) 1.859(2) Å, Mo–O(1)–C(32) 146.0(2)°] reflecting the differing degrees of π donation to the metal:[8] only one alkoxide is required to act as a three-electron donor for an overall 18-electron count. If the thioureato ligand is regarded as a chelating bis(amide) and therefore electronically related to the two alkoxide ligands, lone pair donation from just two of these four ligands would be sufficient to give an 18-electron count. The structural

Ar = 2,6-Pr$^j_2$C$_6$H$_3$
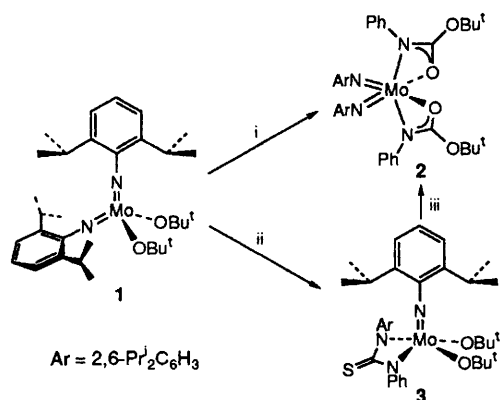
Scheme 1 *Reagents and conditions:* i, excess PhNCO, pentane, room temp., 12 h; ii, excess PhNCS, pentane, room temp., 12 h; iii, excess PhNCO, pentane, room temp., 12 h
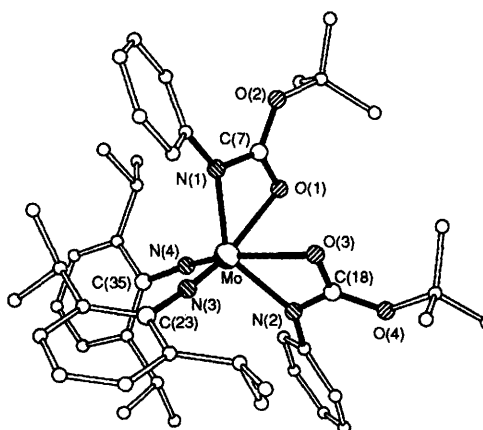
Fig. 1 The molecular structure of **2** with the principal atoms labelled. Important bond lengths and bond angles: Mo–N(1) 2.108(2), Mo–O(1) 2.304(2), Mo–N(2) 2.103(2), Mo–O(3) 2.381(2), Mo–N(3) 1.754(2), Mo–N(4) 1.759(2) Å; N(3)–Mo–N(4) 104.01(9), N(1)–Mo–O(1) 59.59(7), N(2)–Mo–O(3) 58.63(7), Mo–N(3)–C(23) 171.9(2), Mo–N(4)–C(35) 159.1(2)°.
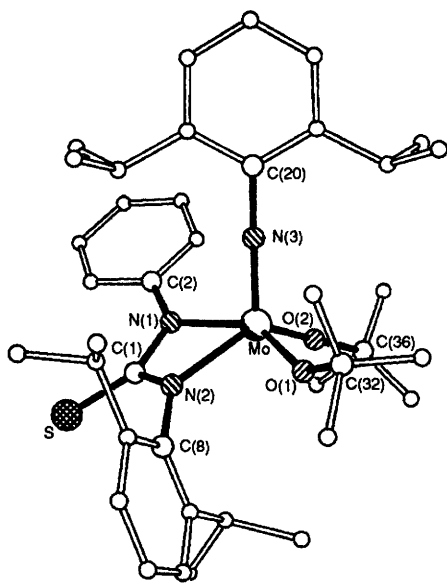
Fig. 2 The molecular structure of **3** with the principal atoms labelled. Important bond lengths and bond angles: Mo–N(1) 2.106(2), Mo–N(2) 2.063(2), Mo–N(3) 1.728(2), Mo–O(1) 1.859(2), Mo–O(2) 1.818(2) Å; N(1)–Mo–N(2) 61.98(8), O(1)–Mo–O(2) 100.46(10), Mo–N(3)–C(20) 178.10(2), Mo–O(1)–C(32) 146.0(2), Mo–O(2)–C(36) 173.2(2)°.

parameters indicate that one of the *tert*-butoxide ligands, *i.e.* the one displaying significant bending at oxygen, is acting as a one-electron donor. The M–N(amide) bond *trans* to the 'linear' alkoxide is the longer of the two [2.106(2) Å for Mo–N(1) *cf.* 2.063(2) Å for Mo–N(2)], though there is no pyramidalisation at this nitrogen [sum of bond angles at N(1) 359.5°], however, it should be noted that pyramidalisation at the amido nitrogen is not always observed, even at coordinatively saturated metal centres.[9]

Addition of excess PhNCO to **3** in pentane led over 18 h to a red–brown solution, from which red needles were isolated upon cooling of the solution to −20 °C. A unit-cell determination confirmed their identity as **2** and ¹H NMR spectra on the product mixture showed the presence of **2** together with other closely related products, presumed to be derived from loss of ArNCS from **3** and subsequent insertions into the *tert*-butoxide ligands of the phenylimido derivatives. These results indicate that the addition of PhNCS to the imido ligand of **1** is reversible and suggest that the imido ligand may also be the kinetic site of attack by PhNCO. It may also provide an explanation as to why certain oxo complexes do not react cleanly with isocyanates to give imido derivatives when monoanionic ligands are also appended to the metal centre.

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Footnote

† Satisfactory elemental analyses have been obtained. *Selected spectroscopic data* for **2**: see ref. 3. For **3**: ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 1.23 (d, 12H, ³J_HH 7.0 Hz, CH*Me*₂), 1.27 (s, 9H, OC*Me*₃),

1.28 (d, 12H, ³J_HH 7.0 Hz, CH*Me*₂), 1.33 (s, 9H, OC*Me*₃), 4.18 (spt, 4H, ³J_HH 7.0 Hz, C*H*Me₂), 6.96–7.26 (overlapping multiplets, aryl H) and 7.77 (d, ³J_HH 8.6 Hz, aryl H). ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298 K): δ 23.81, 24.66 (s, CH*Me*₂), 28.38, 28.71 (s, *C*HMe₂), 32.27 (s, OC*Me*₃), 80.28, 86.40 (s, O*C*Me₃), 122.6–153.4 (m, br, aryl C). IR (Nujol, CsI): 1584 cm⁻¹ [ν(C=S)].

‡ *Crystal data* for **2**: C₄₆H₆₂MoN₄O₄, *M* = 830.9, orthorhombic, space group *Pccn*, *a* = 19.315(4), *b* = 39.716(8), *c* = 11.478(2) Å, *U* = 8805(3) Å³, *Z* = 8, *D*_c = 1.254 g cm⁻³, *F*(000) = 3520. 9226 reflections were measured on a Stoe-Siemens diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, 2θ < 50°, μ = 0.343 mm⁻¹) with ω–θ scans and on-line profile fitting.[10] Data were corrected for absorption by a semi-empirical method from ψ-scan data.[11] Structure solution was by direct methods,[11] refinement by full-matrix least-squares analysis on *F*² for all 7735 independent reflections (*R*_int = 0.0160).[12] *R*_w = {Σ[*w*(*F*₀² − *F*_c²)²]/Σ[*w*(*F*₀²)²]}¼ = 0.1001 for all data, conventional *R* [on *F* values for 5763 reflections with *F*² > 2σ(*F*²)] = 0.0286, goodness of fit = 1.068 on *F*² for 510 refined parameters. All non-H atoms were refined with anisotropic displacement parameters, H-atoms were constrained. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *Crystal data* for **3**: C₃₉H₅₇MoN₃O₂S, *M* = 727.9, triclinic, space group *P*1̄, *a* = 10.628(5), *b* = 13.404(6), *c* = 13.911(6) Å, α = 96.63(5), β = 98.69(4), γ = 100.32(4)°, *U* = 1906(2) Å³, *Z* = 2, *D*_c = 1.268 g cm⁻³, *F*(000) = 772, μ(Mo-Kα) = 0.434 mm⁻¹. Experimental details are as for **2** except as follows: 8383 reflections measured using ω–θ scans by the conventional background–peak–background method; 6153 independent data, *R*_int = 0.0268. The structure was solved by Patterson synthesis. Disorder was successfully modelled in one *tert*-butyl group. *R*_w = 0.0837 for all data, conventional *R* = 0.0268 [for 5770 reflections with *F*² > 2σ(*F*²)], goodness of fit = 1.130 on *F*² for 454 parameters.

References

1 (a) M. L. H. Green, G. Hogarth, P. C. Konidaris and P. Mountford, *J. Chem. Soc., Dalton Trans*, 1990, 3781; (b) G. D. Forster and G. Hogarth, *J. Chem. Soc., Dalton Trans.*, 1993, 2539; (c) G.Hogarth and P. C. Konidaris, *J. Organomet. Chem.*, 1990, **399**, 149.

2 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York, 1988.

3 M. Jolly, J. P. Mitchell and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 1329.

4 D. S. Glueck, J. X. Wu, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 2041; R. I. Michelman, R. A. Anderson and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 5100; P. Legzdins, E. C. Phillips, S. J. Rettig, J. Trotter, J. E. Velthew and V. C. Yee, *Organometallics*, 1992, **11**, 3104; W. H. Leung, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 2791.

5 H. W. Lam, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1993, 781.

6 P. Braunstein and D. Nobel, *Chem. Rev.*, 1989, **89**, 1927.

7 M. H. Chisholm, F. A. Cotton, K. Folting, J. C. Huffman, A. L. Raterman and E. S. Shamshoum, *Inorg. Chem.*, 1984, **23**, 4423.

8 Chisholm and coworkers have noted a correlation between M–OR bond distances and M–O–C angles: See ref. 7.

9 M. D. Fryzuk, K. Joshi and S. J. Rettig, *Polyhedron*, 1989, **8**, 2291; M. D. Fryzuk, K. Joshi and R. K. Chadra, *J. Am. Chem. Soc.*, 1989, **111**, 4498; J. Feldman and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 1991, 1042.

10 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

11 G. M. Sheldrick, SHELXTL/PC Manual, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1990.

12 G. M. Sheldrick, SHELXL-93, program for crystal structure refinement, University of Göttingen, 1993.