Imido Ligand Reactivity in Four-co-ordinate Bis(imido) Complexes of Molybdenum(VI)

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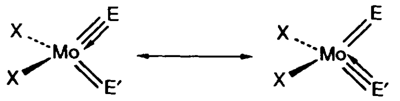
The four-co-ordinate complexes $Mo(NR)_2(OBu^t)_2$ ($R = Bu^t$ or $2,6\text{-}Pr^i{}_2C_6H_3$) undergo imido ligand exchange reactions with benzaldehyde, amines and dioxygen; the reaction of $Mo(NR)_2(OBu^t)_2$ ($R = 2,6\text{-}Pr^i{}_2C_6H_3$) with phenyl isocyanate, however, leads to the formation of a bis(metallacycle) complex.

The reactivity of multiply bonded oxo and imido ligands attached to molybdenum is of considerable interest due to their role in industrially significant oxidation and ammoxidation processes.[1] We were particularly attracted to a study of four-co-ordinate molybdenum derivatives of the type MoE_2X_2 ($E = O$ or NR, X = alkoxide) since in this low-co-ordinate tetrahedral environment a number of factors may contribute to providing unusually reactive oxo and imido groups.



First, in tetrahedral complexes there exists a competition between the two multiply bonded groups for the available metal d_π orbitals, ensuring that one of the ligands can form only a double bond with the metal centre as opposed to the triple-bond interaction usually prevalent in high-oxidation-state oxo and imido complexes.[1a] It has been suggested from calculations on model systems that such a competition between *cis* multiply bonded ligands is likely to lead to enhanced reactivity.[2] Another consequence of the competition is a formal metal electron count of 14, which along with the low co-ordination number ensures a highly acidic, sterically accessible metal environment, allowing for ready interaction with substrate molecules. The only previous report concerning the reactivity of four-co-ordinate molybdenum compounds of this type, by Lai *et al.*,[3] described the reaction of $MoO_2(mes)_2$ ($mes = 2,4,6\text{-}Me_3C_6H_2$) with PhNCO, in which the isocyanate inserts into the Mo–C bond to give *N*-phenyl-2,4,6-trimethylbenzenecarboxamide upon work-up. For the purpose of this study we have chosen ancillary alkoxide ligands in order (*i*) to circumvent ancillary ligand reactivity and (*ii*) to provide a potential model system for an active site of a molybdenum oxide catalyst containing two multiply bonded oxo or imido units.

Bis(imido) compounds of the type $Mo(NR)_2(OBu^t)_2$ (R = Ph or tolyl) have been prepared previously by Chisholm *et al.*[4] *via* treatment of $Mo_2(OBu^t)_6$ with RN_3; they are found to be monomeric in solution but form imido-bridged dimers in the solid state. In order to maintain a mononuclear environment in both the solid state and in solution, we have synthesised the sterically hindered analogues $Mo(NR)_2(OBu^t)_2$ ($R = Bu^t$ or $2,6\text{-}Pr^i{}_2C_6H_3$) and these provide the starting complexes for the chemistry shown in Scheme.1.† The complexes $Mo(NBu^t)_2(OBu^t)_2$ **1** and $Mo(NC_6H_3Pr^i{}_2\text{-}2,6)_2(OBu^t)_2$ **2** may be conveniently prepared in good yield by treatment of $Mo(NBu^t)_2Cl_2$ and $Mo(NC_6H_3Pr^i{}_2\text{-}2,6)_2Cl_2(dme)$ (dme = 1,2-dimethoxyethane) respectively with 2 equivalents of $LiOBu^t$ in Et_2O. The dioxo complex **4** may be obtained by an analogous procedure from MoO_2Cl_2.

Complex **1** was found to react cleanly with 2 equivalents of 2,6-diisopropylaniline in a sealed NMR tube at room temperature to afford the mixed imido species **3** and the bis(arylimido) complex **2** in a 2:1 ratio. The same (equilibrium) mixture was obtained upon treatment of **2** with 2 equivalents of NH_2Bu^t. This reaction is likely to proceed *via* a trigonal-bipyramidal base adduct (Scheme 2), which must then undergo a proton transfer to give a bis(amide) intermediate which we have not been able to observe. Nevertheless, related five-co-ordinate, square-based pyramidal amide[5] and phenoxide[6] compounds of this type are known. Such an exchange of imido groups using amines is unusual and to date has only been observed for imido complexes of the later transition metals.[7] There appears to be a significant difference, however, in the reactivity of these systems towards alcohols: whereas the late transition-metal imides react to give bis(alkoxide) species,[7b] **1** and **2** remain unchanged after warming at 60 °C with excess of Bu^tOH for 2 weeks.

Both complexes **1** and **2** react with excess of benzaldehyde (typically 10 equivalents) at room temperature to afford the oxoimido complexes **5** and **6** along with their Schiff-base by-products. The reaction with **1** proceeds notably faster giving >95% conversion into **5** after 1 week. The subsequent conversion of **5** into **4** is very slow at room temperature (requiring several weeks) but may be accelerated by warming the mixture to 60 °C. Displacement of the second imido ligand is apparently much slower and initially it was thought that this transformation may also be complicated by a back reaction of **4** with the Schiff base generated during the reaction. However, in a separate experiment in which **4** was treated with an excess of RN=CHPh ($R = 2,6\text{-}Pr^i{}_2C_6H_3$ or Bu^t) no reaction was observed during prolonged heating at 100 °C.

Unlike the molybdenum dimer species $[\{Mo(\eta\text{-}C_5H_4Me)(NPh)_2\}_2]$,[8] complexes **1** and **2** do not undergo imido ligand exchange with isocyanates. Treatment of **2** with excess (>2

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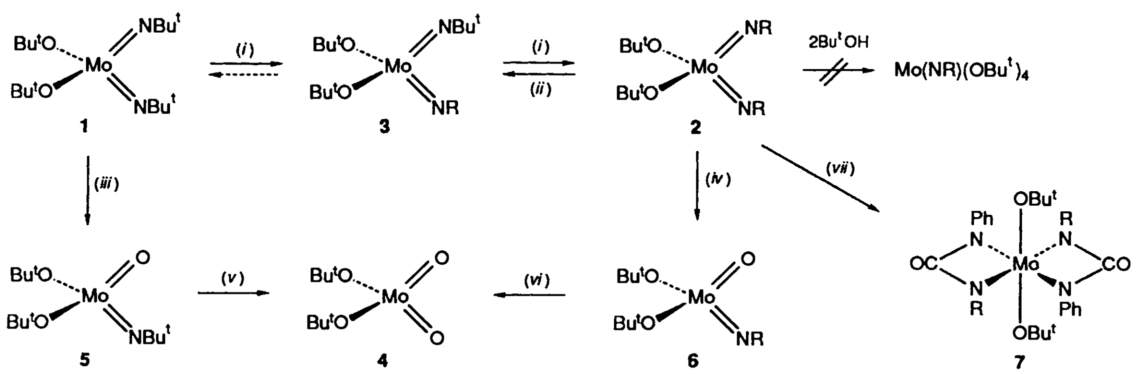
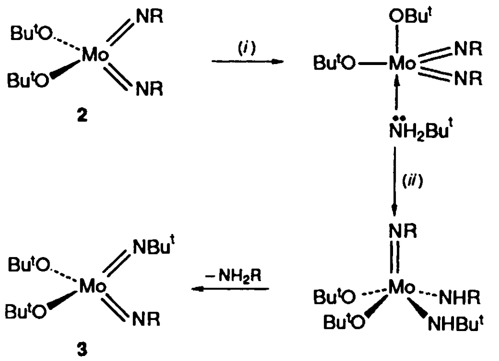
† Satisfactory elemental analyses have been obtained. Selected spectroscopic data: for **1**, ^1H NMR (C_6D_6, 400 MHz, 298 K) δ 1.36 (s, 18 H, NBu^t) and 1.38 (s, 18 H, OBu^t); **2**, ^1H NMR δ 1.19 (d, 24 H, $^3J_{HH}$ 6.8, CH*Me*$_2$), 1.42 (s, 18 H, OBu^t), 3.84 (spt, 4 H, $^3J_{HH}$ 6.8, C*H*Me$_2$), 6.93 (t, 2 H, $^3J_{HH}$ 7.8, H_p) and 7.01 (d, 4 H, $^3J_{HH}$ 7.8 Hz, H_m); **3**, ^1H NMR δ 1.20 (s, 9 H, NBu^t), 1.33 (d, 12 H, $^3J_{HH}$ 6.8, CH*Me*$_2$), 1.39 (s, 18 H, OBu^t) and 3.73 (spt, 2 H, $^3J_{HH}$ 6.8 Hz, C*H*Me$_2$); **4**, ^1H NMR δ 1.15 (s, 18 H, OBu^t); **5**, ^1H NMR δ 1.25 (s, 18 H, OBu^t) and 1.37 (s, 9 H, NBu^t); **6**, ^1H NMR δ 1.26 (s, 18 H, OBu^t), 1.35 (d, 12 H, $^3J_{HH}$ 6.8, CH*Me*$_2$), 4.33 (spt, 2 H, $^3J_{HH}$ 6.8, C*H*Me$_2$), 6.97 (t, 1 H, H_p) and 7.07 (d, 2 H, H_m); **7**, ^1H NMR δ 0.96 [d(br), 12 H, $^3J_{HH}$ 5.6, CH*Me*$_2$], 1.13 [d(br), 12 H, $^3J_{HH}$ 6.4, CH*Me*$_2$], 1.43 (s, 18 H, OBu^t), 3.76 (spt, 4 H, $^3J_{HH}$ 6.4, C*H*Me$_2$), 6.7–7.0 (overlapping multiplets, aryl H) and 7.59 (d, 4 H, $^3J_{HH}$ 7.5 Hz, aryl H); $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 100.6 MHz, 298 K) δ 227.2 (s, CO); IR (Nujol, CsI) 1600 cm^{-1} [ν(CO)].



Scheme 1 Reagents and conditions: (*i*) 2NH$_2$R, benzene, equilibrium reached after 10 d, room temperature (r.t.) (R = 2,6-Pr$^i_2$C$_6$H$_3$); (*ii*) 2NH$_2$Bu^t, benzene, 10 d, r.t.; (*iii*) 10 PhCHO, benzene, 7 d, r.t., >95% conversion; (*iv*) 10 PhCHO, benzene, 2 weeks, r.t., 12% conversion; (*v*) 10 PhCHO, benzene, 4 weeks, r.t., >95% conversion; (*vi*) 10 PhCHO, benzene, 7 d, 60 °C, 20% conversion; (*vii*) 10 PhNCO, pentane, 19 h, r.t.



Scheme 2 R = 2,6-Pr$^i_2$C$_6$H$_3$. (*i*) NH$_2$Bu^t; (*ii*) proton transfer

equivalents) of phenyl isocyanate in pentane at room temperature rapidly gives a mixture of intermediates which have not yet been identified; monitoring of a sample by ^{1}H NMR spectroscopy shows that RNCO (R = 2,6-Pr$^i_2$C$_6$H$_3$) is not eliminated during this transformation. However, if this mixture is allowed to stand for 24 h at room temperature a single product results, which may be isolated from pentane as red crystals whose spectroscopic data are consistent with the bis(metallacycle) complex **7**. In particular, an IR absorption due to a C=O stretch is observed at 1600 cm^{-1} and the oxygen-bearing carbon atom resonates at δ 227 in the ^{13}C NMR spectrum. Complex **7** is believed to be a bis(ureato-*N*,*N*′) complex, for which a tungsten amide analogue has recently been characterised by Wilkinson and co-workers[9] from a related reaction in which [W(NBu^t)$_2$(HNBu^t)$_2$] was treated with Bu^{t}NCO. We are currently attempting to confirm the structure of **7** through a single-crystal X-ray diffraction study.

Finally, we note that the bis(imido) complex **1** also reacts with dry dioxygen at 60 °C to afford the mixed oxoimido compound **5** followed by a slower transformation to the dioxo species **4**. To our knowledge such exchange reactions of multiply bonded ligands with dioxygen have not been observed previously, but are of considerable relevance to molybdenum-catalysed oxidation processes. These, and related transformations, will form the basis of future investigations.

Acknowledgements

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