Interconversion of Oxo and Imido Ligands at a Dimolybdenum Centre: Molecular and Electronic Structure of $[\{Mo(\eta\text{-}C_5H_4Me)(NPh)(\mu\text{-}NPh)\}_2]$†

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The tetraimido complexes $[\{Mo(\eta\text{-}C_5H_4R)(NR')(\mu\text{-}NR')\}_2]$ (R = Me, R' = Ph or C_6H_4Me-*p*; R = Pr^i, R' = Ph) have been synthesised from the corresponding oxo compounds $[\{Mo(\eta\text{-}C_5H_4R)O(\mu\text{-}O)\}_2]$ and the aryl isocyanates R'NCO. The three mixed imido–oxo derivatives $[Mo_2(\eta\text{-}C_5H_4Me)_2O_{4-x}(NPh)_x]$ (x = 1—3), presumed to be intermediates in the synthesis of the tetraimido derivatives, have been synthesised independently. The imido-oxo compounds react with excess of phenyl isocyanate to give $[\{Mo(\eta\text{-}C_5H_4Me)(NPh)(\mu\text{-}NPh)\}_2]$, for which a single-crystal *X*-ray structure analysis reveals a *trans* disposition of the η-methylcyclopentadienyl ligands and a planar $Mo_2(\mu\text{-}N)_2$ core. A molecular-orbital analysis suggests that each NPh ligand acts as a formal three-electron donor. Hydrolysis of $[\{Mo(\eta\text{-}C_5H_4R)(NPh)(\mu\text{-}NPh)\}_2]$ proceeds *via* a stepwise replacement of the two terminal imido groups to give $[Mo_2(\eta\text{-}C_5H_4R)_2O_{2-x}(NPh)_x(\mu\text{-}NPh)_2]$ (x = 0 or 1). Attempts to replace the bridging imido functionalities of $[\{Mo(\eta\text{-}C_5H_4Me)O(\mu\text{-}NPh)\}_2]$ by oxo ligands proved unsuccessful.

Transition metal complexes containing the isoelectronic oxo (=O) or imido (nitrene) (=NR) ligands have attracted considerable attention mainly as a result of their occurrence in the oxidation, amination, and oxyamination of unsaturated organic compounds.[1] Recently, interest in organometallic imido complexes has focused on their involvement in carbon–hydrogen bond activation.[2,3] The activation of methane by a transient imido complex was recently reported.[3]

Synthetic routes to both metal–oxo and –imido complexes are now well established.[4] One widely adopted strategy for the incorporation of the imido group is the conversion of a transition-metal oxo group (M=O) into the corresponding imido functionality (M=NR) using reagents such as phosphorus imides $R_3P{=}NR$[5] or isocyanates RNCO.[6] The reverse of this reaction, namely the conversion of a transition-metal-bound imido ligand into an oxo moiety, is less common,[7] often occurring with degradation of the complex. Such a process has, however, been implicated recently in the biological nitrogen-fixation process.[8]

We have previously described the synthesis of the tetraimido complex $[\{Mo(\eta\text{-}C_5H_5)(NPh)(\mu\text{-}NPh)\}_2]$ (**1**) by replacement of both the terminal and bridging oxo groups of $[\{Mo(\eta\text{-}C_5H_5)O(\mu\text{-}O)\}_2]$ by reaction with phenyl isocyanate.[9] Compound (**1**) is only sparingly soluble in common organic solvents making it inconvenient for reactivity studies. Here we describe the synthesis of alkyl-substituted cyclopentadienyl analogies of (**1**) and a study of the interconversion of terminal oxo and imido ligands. Part of this work has been communicated previously.[10]

Results and Discussion

Treatment of the tetraoxo complexes $[\{Mo(\eta\text{-}C_5H_4R)O(\mu\text{-}O)\}_2]$ (**2a**; R = Me) and (**2b**; R = Pr^i) with an excess of phenyl isocyanate in refluxing thf (tetrahydrofuran) gave the corresponding tetraimido complexes $[\{Mo(\eta\text{-}C_5H_4R)(NPh)(\mu\text{-}NPh)\}_2]$ (**3**; R = Me) and (**4**; R = Pr^i) as orange, air-stable crystalline solids. The *p*-tolyl analogue $[\{Mo(\eta\text{-}C_5H_4Me)(NC_6H_4Me\text{-}p)(\mu\text{-}NC_6H_4Me\text{-}p)\}_2]$ (**5**) was similarly prepared from (**2a**) and *p*-tolyl isocyanate. Isolated yields were between 20 and 65%. Characterising data for the new compounds are presented in Table 1.

Although conversions of the tetraoxo into tetraimido complexes were shown to be quantitative by ^1H n.m.r. spectroscopy, purification from excess of isocyanate proved difficult. No reaction was observed between tetraoxo complexes and *o*-tolyl isocyanate even upon prolonged thermolysis, presumably due to steric reasons. t-Butyl isocyanate was found to react slowly with $[\{Mo(\eta\text{-}C_5H_4Me)O(\mu\text{-}O)\}_2]$ resulting in a colour change to orange as expected. However, the ^1H n.m.r. spectrum of the reaction mixture indicated a complex mixture of products, none of which could be isolated.

The imido complexes (**3**)—(**5**) are soluble in common organic solvents. The ^1H n.m.r. spectra all displayed complex, but well resolved, resonances in the aromatic region assignable to the terminal and bridging imido ligands. Warming a $[^2H_8]$toluene solution of (**3**) to 100 °C showed no appreciable broadening of resonances attributable to the NPh ligands, implying that interconversion of terminal and bridging groups is not fast on the n.m.r. time-scale. The i.r. spectra of (**3**)—(**5**) showed strong absorptions in the regions 1 263—1 266 and 1 320—1 326 cm^{-1} which may be assigned to the ν(Mo–N–Mo) and ν(M=N) modes respectively.

The tetraimido complex $[\{Mo(\eta\text{-}C_5H_5)(NPh)(\mu\text{-}NPh)\}_2]$ (**1**) was postulated to have a puckered metallacore geometry,[9] by analogy with the parent tetraoxo compound. In order to obtain direct structural evidence, an *X*-ray crystal-structure analysis of $[\{Mo(\eta\text{-}C_5H_4Me)(NPh)(\mu\text{-}NPh)\}_2]$ (**3**) was undertaken. Suitable crystals were grown by slow evaporation of an acetone solution. The molecular structure is shown in Figure 1, selected bond distances and angles in Table 2, and atomic co-ordinates in Table 3.

The metal–metal vector [Mo(1)–Mo(1B) 2.717 5(5) Å] is spanned by two phenylimido ligands, and each molybdenum atom has a pseudo-octahedral geometry. The methylcyclopentadienyl ligands adopt a mutually *trans* disposition, a

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† Di-μ-phenylimido-bis[(η-methylcyclopentadienyl)(phenylimido)-molybdenum] (*Mo–Mo*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: eV ≈ 1.60 × 10^{-19} J.

Table 1. Analytical and spectroscopic data for the new compounds

Compound, colour, and analysis[a] (%)	Selected i.r. data (cm^{-1})	N.m.r. data[b]
(**3**) $[\{Mo(\eta-C_5H_4Me)(NPh)(\mu-NPh)\}_2]$ C, 60.6 (60.5); H, 4.7 (4.8); N, 7.9 (7.8) Orange	ν(M=N) 1 266, 1 322	^{1}H: 1.15 (6 H, s, CH_3), 5.15 [4 H, vt (*J* 1.7), C_5H_4], 5.83 [4 H, vt(*J* 1.5), C_5H_4], 6.76 [2 H, t(*J* 7.3), C_6H_5], 6.92 [4 H, d(*J* 6.8), C_6H_5], 6.94—7.1 (6 H, m, C_6H_5), 7.50 [4 H, t(*J* 7), C_6H_5], 7.95 [4 H, d(*J* 7.7), C_6H_5][c] $^{13}C-\{^{1}H\}$: 13.3 (CH_3), 101.3 (C_5H_4), 102.5 (C_5H_4), 121.6 (C_6H_5), 123.1 (C_6H_5), 123.4 (C_6H_5), 125.6 (C_6H_5), 158.8 (C_6H_5), 165.5 (C_6H_5)[c]
(**4**) $[\{Mo(\eta-C_5H_4Pr^i)(NPh)(\mu-NPh)\}_2]$ C, 62.0 (62.3); H, 5.3 (5.5); N, 7.2 (7.3) Orange	ν(M=N) 1 265, 1 327	^{1}H: 0.59 [12 H, d(*J* 7.0), CH_3], 2.17 [2 H, spt (*J* 6.9), CH_3], 5.46 [4 H, vt(*J* 2.5), C_5H_4], 5.68 [4 H, vt(*J* 2.5), C_5H_4], 6.77 [2 H, t(*J* 7), C_6H_5], 6.89—7.15 (10 H, m, C_6H_5), 7.53 [4 H, t(*J* 7.5), C_6H_5], 8.03 [4 H, d(*J* 7.3), C_6H_5][c]
(**5**) $[\{Mo(\eta-C_5H_4Me)(NC_6H_4Me\text{-}p)(\mu-NC_6H_4Me\text{-}p)\}_2]$ C, 61.9 (62.3); H, 5.7 (5.6); N, 7.1 (7.3) Orange	ν(M=N) 1 270, 1 322	^{1}H: 1.23 (6 H, s, $C_5H_4CH_3$), 2.08 (6 H, s, $C_6H_4CH_3$), 2.41 (6 H, s, $C_6H_4CH_3$), 5.22 [4 H, vt(*J* 2.4), C_5H_4], 5.86 [4 H, vt(*J* 2.5), C_5H_4], 6.83—6.95 (8 H, m, C_6H_4), 7.32 [4 H, d(*J* 8), C_6H_4], 7.94 [4 H, d(*J* 7.6), C_6H_4][c]
(**7**) $[\{Mo(\eta-C_5H_4Me)O(\mu-NPh)\}_2]$ C, 50.9 (51.1); H, 4.3 (4.3); N, 5.0 (5.0) Yellow	ν(M=N) 1 263 ν(M=O) 885	^{1}H: 1.77 (6 H, s, CH_3), 5.52 [4 H, vt(*J* 2.5), C_5H_4], 5.76 [4 H, vt(*J* 2.5), C_5H_4], 7.27 [2 H, t(*J* 3.5), C_6H_5], 7.58 [4 H, t(*J* 8.2), C_6H_5], 7.95 [4 H, dd(*J* 7 and 1), C_6H_5][d]
(**8**) $[Mo_2(\eta-C_5H_4Me)_2O(NPh)(\mu-NPh)_2]$ C, 57.4 (56.3); H, 4.6 (4.5); N, 6.7 (6.6) Yellow	ν(M=N) 1 263, 1 327 ν(M=O) 884	^{1}H: 1.29 (3 H, s, CH_3), 1.59 (3 H, s, CH_3), 5.15 [2 H, vt(*J* 2.5), C_5H_4], 5.21 [2 H, vt(*J* 2.5), C_5H_4], 5.62 [2 H, vt(*J* 2.4), C_5H_4], 5.78 [2 H, vt(*J* 2.5), C_5H_4], 6.7—7.2 (7 H, m, C_6H_5), 7.46 [4 H, t(*J* 7.9), C_6H_5], 8.04 [4 H, d(*J* 7.6), C_6H_5][c]
(**9**) $[Mo_2(\eta-C_5H_4Pr^i)_2O(NPh)(\mu-NPh)_2]$ C. 58.5 (58.7); H, 5.3 (5.3); N, 5.9 (6.0) Yellow	ν(M=N) 1 263, 1 328 ν(M=O) 882	^{1}H: 0.75 [6 H, d(*J* 7), CH_3], 1.17 [6 H, d(*J* 7), CH_3], 2.13 [1 H, spt(*J* 6.9), $CH(CH_3)_2$], 2.81 [1 H, spt(*J* 6.8), $CH(CH_3)_2$], 4.75 [2 H, vt(*J* 2.4), C_5H_4], 5.56 [2 H, vt(*J* 2.4), C_5H_4], 6.00 [2 H, vt(*J* 2.5), C_5H_4], 6.09 [2 H, vt(*J* 2.4), C_5H_4], 6.60 [2 H, d(*J* 7), C_6H_5], 6.74 [1 H, t(*J* 7.3), C_6H_5], 7.16 (4 H, m, C_6H_5), 7.51 [4 H, t(*J* 7.2), C_6H_5], 7.83 [4 H, t(*J* 7.5), C_6H_5][d]
(**10**) $[\{Mo(\eta-C_5H_4Pr^i)O(\mu-NPh)\}_2]$ C, 53.7 (54.2); H, 5.3 (5.2); N, 4.4 (4.5) Yellow	ν(M=N) 1263 ν(M=O) 881	^{1}H: 0.99 [12 H, d(*J* 6.9), CH_3], 2.71 [2 H, spt(*J* 6.9), $CH(CH_3)_2$], 5.11 [4 H, vt(*J* 2.5), C_5H_4], 5.79 [4 H, vt(*J* 2.5), C_5H_4], 7.10 [2 H, vt(*J* 7), C_6H_5], 7.47 [4 H, t(*J* 7.3), C_6H_5], 8.20 [4 H, d(*J* 7), C_6H_5][c]
(**11**) $[Mo_2(\eta-C_5H_4Me)_2S(NPh)(\mu-NPh)_2]$ C, 55.5 (55.0); H, 4.6 (4.4); N, 6.4 (6.4); S, 4.7 (4.9) Red	ν(M=N) 1 264, 1 324 ν(M=S) 474	^{1}H: 1.30 (3 H, s, CH_3), 1.72 (3 H, s, CH_3), 5.05 [2 H, vt(*J* 2), C_5H_4Me], 5.18 [2 H, vt(*J* 2), C_5H_4Me], 5.26 [2 H, vt(*J* 2), C_5H_4Me], 5.80 [2 H, vt(*J* 2), C_5H_4Me], 6.75 [1 H, t(*J* 7), C_6H_5], 6.79 [2 H, d(*J* 7), C_6H_5], 6.97 [2 H, t(*J* 7), C_6H_5], 7.11 [2 H, t(*J* 7), C_6H_5], 7.46 [4 H, t(*J* 7), C_6H_5], 8.16 [4 H, d(*J* 7), C_6H_5][c]

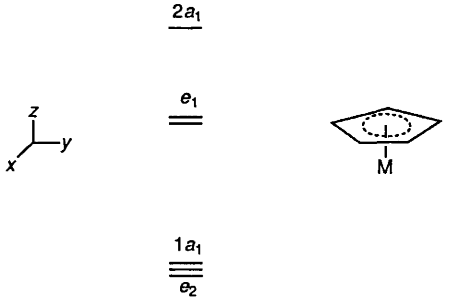
[a] Calculated values in parentheses. [b] Given as: chemical shift (δ), [relative intensity, multiplicity (*J* in Hz), and assignment] where s = singlet, d = doublet, t = triplet, vt = virtual triplet, dd = doublet of doublets, m = multiplet, spt = septet, br s = broad signal. [c] In $[^{2}H_6]$benzene. [d] In $[^{2}H]$chloroform.

feature which contrasts sharply with the *cis* disposition of the cyclopentadienyl ligands of the isoelectronic oxo complex $[\{Mo(\eta-C_5H_5)O(\mu-O)\}_2]$.[11] Furthermore, the $Mo_2(\mu-N)_2$ core is planar, the maximum deviation from planarity being 0.02 Å, whereas the $Mo_2(\mu-O)_2$ core of $[\{Mo(\eta-C_5H_5)O(\mu-O)\}_2]$ is puckered with a dihedral angle of 152° between the two $Mo_2(\mu-O)$ planes. Substitution of even a single μ-O ligand by μ-NR as in $[Mo_2(\eta-C_5H_5)_2O_2(\mu-O)(\mu-NC_6H_4Me\text{-}p)]$[12] leads to the adoption of a planar $Mo_2(\mu-O)(\mu-N)$ core with a *trans* disposition of the $\eta-C_5H_5$ rings. Molecular-orbital calculations by Bursten and Cayton[13] on the complex $[\{Mo(\eta-C_5H_5)O(\mu-O)\}_2]$ have shown that, for a *cis* arrangement of the $\eta-C_5H_5$ rings, folding the μ-O ligands towards the rings is required to maximise Mo/μ-O overlap. However, for a bulky bridging group such as NR (R = aryl), such a folding could lead to increasingly significant steric interactions favouring the *trans*-planar geometry observed.

The Mo–Mo distance of 2.717 5(5) Å in (**3**) is somewhat longer than those of the complexes $[\{Mo(\eta-C_5H_5)O(\mu-O)\}_2]$ [2.602(1) Å][11] and $[Mo_2(\eta-C_5H_5)_2O_2(\mu-O)(\mu-NC_6H_4Me\text{-}p)]$ [2.649(5) Å],[12] an observation which may be attributable to coulombic and/or π-donor effects. The terminal imido ligands of (**3**) are approximately linear [Mo(1)–N(1)–C(10) 173.6(2)°], a feature indicative of significant $N(p_\pi) \longrightarrow Mo(d_\pi)$ interactions. The Mo(1)–N(1) distance of 1.763(3) Å is, however, the longest reported to date for a linear imido ligand bound to molybdenum.[4] The compound $[Mo(NPh)_2(S_2CNEt_2)_2]$ has a bent imido group [Mo–N–R 139.4(4)°] for which the M–N distance is 1.789(4) Å.[14] Thus it appears that there is only partial π donation in the terminal N–Mo bonds of (**3**). The Mo(1)–N(2) distance of 1.975(2) Å is somewhat longer than Mo(1)–N(1) as expected. That the bridging imido moieties also have significant π-donor character is shown by the trigonal geometry about the bridging nitrogen atoms.

Molecular-orbital Description of $[\{Mo(\eta-C_5H_4Me)(NPh)(\mu-NPh)\}_2]$.—The molecular structure of complex (**3**) poses a dilemma within the framework of formal electron-counting procedures. The planar $Mo_2(\mu-N)_2$ core, together with the essentially linear terminal imido ligands [Mo(1)–N(1)–C(10) 173.6(2)°], require that each NPh ligand acts as a formal four-electron donor. Adding the four imido ligands to a metal–metal singly bonded $Mo_2(\eta-C_5H_4Me)_2$ core gives a formal twenty-electron valence-electron count around each Mo atom. However, this apparent violation of the effective atomic number (e.a.n.) rule may be rationalised using simple symmetry-based molecular-orbital arguments supplemented by extended-Hückel calculations.

A convenient starting point for the analysis is a fragment approach based on a $Mo_2(\eta\text{-}C_5H_4Me)_2/(NPh)_4$ partitioning of the molecule. The frontier orbitals of the $M(\eta\text{-}C_5H_5)$ fragment have been discussed at length elsewhere and their basic ordering is shown below with orbital labels appropriate to C_{5v} symmetry.[15]



At relatively high energy is an a_1 orbital ($2a_1$) composed mainly of metal s and p atomic orbital character with variable contribution from d_{z^2}. The e_1 set are a mixture of metal d_{yz}, d_{xz} and p_x, p_y. The lower set of orbitals ($1a_1$ and e_2) arise primarily from metal d_{z^2}, $d_{x^2-y^2}$, and d_{xy} and would be the t_{2g} set of non-bonding orbitals of an octahedral metal complex. For M = Mo these orbitals house the remaining five metal-based electrons. At lower energy still (not shown above) are three metal–ring bonding orbitals (one of a_1 and a degenerate set of e_1 symmetry) which accommodate the six π electrons of the $\eta\text{-}C_5H_5^-$ ligand. These orbitals will be relatively unperturbed by any further bonding interations of $M(\eta\text{-}C_5H_5)$.

When two $Mo_2(\eta\text{-}C_5H_4Me)$ fragments are united in a *trans*-$Mo_2(\eta\text{-}C_5H_4Me)_2$ unit, the six frontier orbitals ($1a_1$, e_2, e_1, and $2a_1$) combine to give twelve fragment molecular orbitals, of which only eleven need be considered in metal–nitrogen bonding. This is because the out-of-phase combination (transforming as b_u under C_{2h} symmetry) of the $2a_1$ orbitals of $Mo(\eta\text{-}C_5H_4Me)$ will be high energy and will remain essentially non-bonding in any further interactions of $Mo_2(\eta\text{-}C_5H_4Me)_2$. Under the idealised C_{2h} symmetry of *trans*-$Mo_2(\eta\text{-}C_5H_4Me)_2$, the eleven remaining metal-based orbitals transform as $4a_g + 2a_u + 3b_u + 2b_g$ and will contain the ten d^5–d^5 electrons.

Consider now the frontier orbitals of the four NPh ligands. Each nitrogen atom may be considered to be *sp*-hybridised giving a total of eight p orbitals and eight *sp* hybrids, four of which will be used in N–Ph σ bonding. The four remaining *sp* hybrid orbitals transform as $2a_g + 1a_u + 1b_u$, and the eight p orbitals as $1a_g + 1a_u + 3b_g + 3b_u$, under the local C_{2h} symmetry of the $(NPh)_4$ fragment.

The solution to the electron-counting anomaly now becomes clear. The eleven orbitals of $Mo_2(\eta\text{-}C_5H_4Me)_2$ that are available for interaction with the $(NPh)_4$ fragment transform as $4a_g + 2a_u + 3b_u + 2\mathrm{b}_g$, whereas the twelve orbitals offered by the $(NPh)_4$ fragment transform as $3a_g + 2a_u + 4b_u + 3b_g$. Hence a metal-based a_g orbital and two ligand-based orbitals (one b_u and one b_g) have no partners and will be non-bonding with respect to metal–nitrogen interactions.

The metal-based a_g orbital will contain the d^1–d^1 electron pair of the $[Mo_2]^{10+}$ dimer. The twelve orbitals of the four imido ligands (now formally considering each one as NPh^{2-}) contain twenty-four electrons, but only twenty of these may contribute towards the formal valence count of the two metal atoms since two of the orbitals are metal–nitrogen non-bonding. For the whole complex there are therefore six filled $Mo(\eta\text{-}C_5H_4Me)$ bonding orbitals [from the two $a_1 + e_1$ sets of $Mo_2(\eta\text{-}C_5H_4Me)_2$], ten filled Mo–NPh bonding orbitals ($3a_g + 2a_u + 3b_u + 2b_g$), and one filled metal-based orbital of a_g symmetry. Summing the occupancies up over the two metal atoms gives a total of thirty-four valence-shell electrons, the requisite number for two metal atoms united by a metal–metal single bond and with individual valence-shell electron counts of eighteen electrons.

The conclusions worked out through the group theoretical analysis presented above have been supplemented by extended-

Table 2. Selected bond lengths (Å) and angles (°) for compound (**3**) with estimated standard deviations in parentheses. Cp_{cent} refers to the computed centroid of the $\eta\text{-}C_5H_4Me$ ring

Mo(1)–Mo(1B)	2.717 5 5)	Mo(1)–N(1)	1.763(3)
Mo(1)–N(2)	1.975(2)	Mo(1)–N(2B)	1.964(2)
Mo(1)–C(1)	2.485(3)	Mo(1)–C(2)	2.386(3)
Mo(1)–C(3)	2.345(4)	Mo(1)–C(4)	2.349(4)
Mo(1)–C(5)	2.442(4)	N(1)–C(10)	1.380(4)
N(2)–C(20)	1.390(4)	C(1)–C(2)	1.422(5)
C(1)–C(5)	1.397(5)	C(1)–C(6)	1.516(5)
C(2)–C(3)	1.392(5)	C(3)–C(4)	1.408(6)
C(4)–C(5)	1.400(6)	C(10)–C(11)	1.387(5)
C(10)–C(15)	1.388(5)	C(11)–C(12)	1.379(5)
C(12)–C(13)	1.360(6)	C(13)–C(14)	1.373(6)
C(14)–C(15)	1.370(5)	C(20)–C(21)	1.398(4)
C(20)–C(25)	1.394(5)	C(21)–C(22)	1.380(5)
C(22)–C(23)	1.366(6)	C(23)–C(24)	1.374(6)
C(24)–C(25)	1.384(5)	Mo(1)–Cp_{cent}	2.084
N(1)–Mo(1)–Mo(1B)	112.32(9)	N(2)–Mo(1)–Mo(1B)	46.21(7)
N(2)–Mo(1)–N(1)	105.7(1)	N(2)–Mo(1)–Mo(1B)	46.56(7)
N(2)–Mo(1B)–N(1B)	104.7(1)	N(2)–Mo(1)–N(2B)	92.8(1)
C(10)–N(1)–Mo(1)	173.6(2)	Mo(1)–N(2)–Mo(1B)	87.2(1)
C(20)–N(2)–Mo(1)	135.3(2)	C(20)–N(2)–Mo(1B)	137.3(2)
Cp_{cent}–Mo(1)–Mo(1B)	124.89	Cp_{cent}–Mo(1)–N(1)	122.78
Cp_{cent}–Mo(1)–N(2)	112.52	Cp_{cent}–Mo(1)–N(2B)	113.97

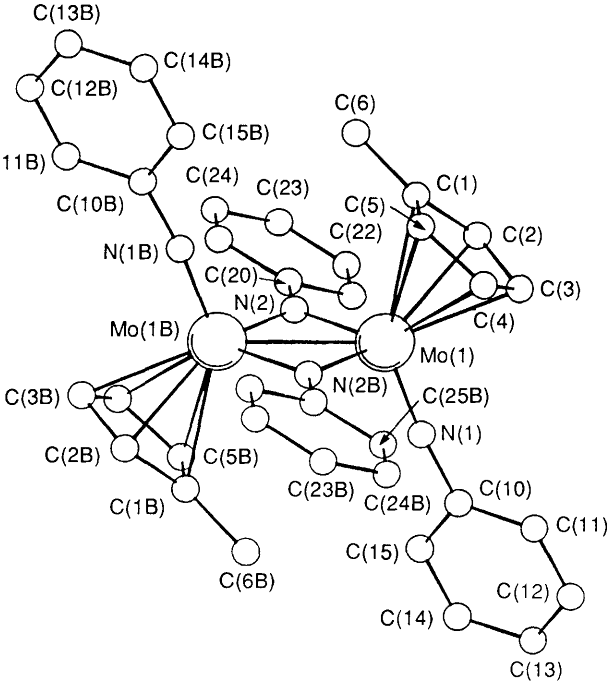


Figure 1. Molecular structure of complex (**3**) viewed very nearly perpendicular to the Mo–Mo bond. Hydrogen atoms omitted for clarity. The molecule lies across a crystallographic inversion centre. Atoms labelled B are related to their counterparts by the symmetry operator $-x$, $-y$, $-z$

Table 3. Fractional atomic co-ordinates for compound (**3**) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.028 07(2)	0.125 73(3)	0.467 42(2)
N(1)	0.186 1(2)	0.171 6(3)	0.510 7(2)
N(2)	0.029 1(2)	−0.069 6(3)	0.423 7(2)
C(1)	−0.152 6(3)	0.154 8(4)	0.332 4(2)
C(2)	−0.045 3(4)	0.224 5(4)	0.317 6(2)
C(3)	−0.013 9(4)	0.333 0(4)	0.381 2(3)
C(4)	−0.096 7(5)	0.328 1(4)	0.439 1(3)
C(5)	−0.181 9(4)	0.219 6(5)	0.408 0(3)
C(6)	−0.217 9(4)	0.030 1(5)	0.278 7(3)
C(10)	0.306 7(3)	0.221 4(3)	0.539 2(2)
C(11)	0.330 5(3)	0.363 4(4)	0.554 2(2)
C(12)	0.451 8(4)	0.410 9(4)	0.582 2(3)
C(13)	0.549 2(4)	0.319 6(5)	0.595 7(3)
C(14)	0.526 8(4)	0.178 6(5)	0.582 0(3)
C(15)	0.407 0(3)	0.129 5(4)	0.554 1(2)
C(20)	0.064 7(3)	−0.135 5(3)	0.351 4(2)
C(21)	0.147 5(3)	−0.072 1(4)	0.306 7(2)
C(22)	0.178 3(4)	−0.137 3(5)	0.233 1(3)
C(23)	0.130 0(4)	−0.265 6(5)	0.202 9(3)
C(24)	0.050 5(4)	−0.331 3(5)	0.247 1(3)
C(25)	0.018 4(3)	−0.267 7(4)	0.321 0(2)

Table 4. Parameters used in the extended-Hückel calculation

Atom	Orbital	H_{ii}/eV	ζ_1
Mo	4*d*	−11.11	4.54*
	5*s*	−9.38	1.96
	5*p*	−5.27	1.90
N	2*s*	−23.91	1.95
	2*p*	−10.91	1.95
C	2*s*	−21.40	1.63
	2*p*	−11.40	1.63
H	1*s*	−13.60	1.30

* ζ_2 = 1.90, $C_1 = C_2$ = 0.5899, where C_1, C_2 are the coefficients used for the double-ζ expansion.

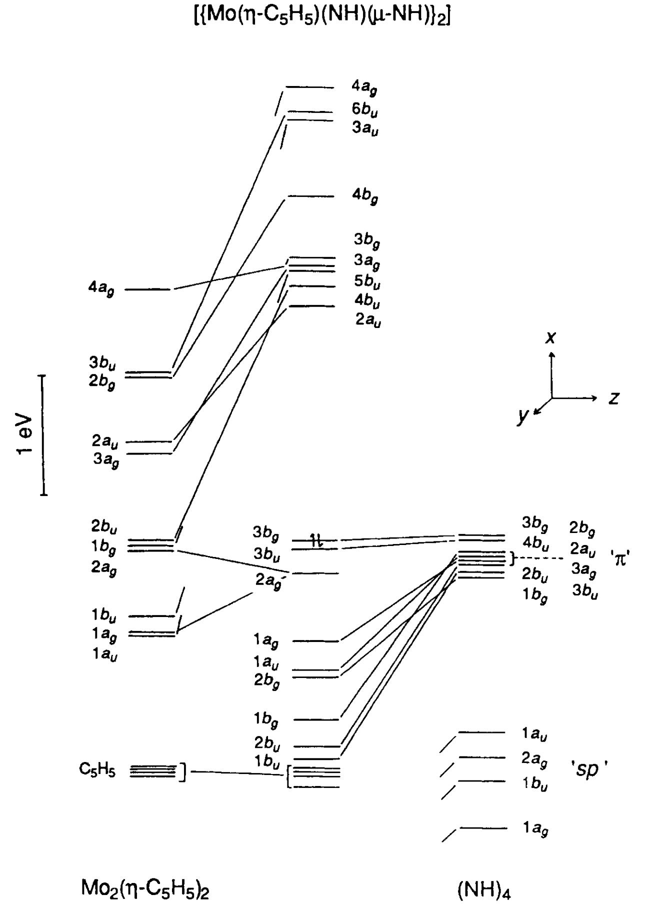


Figure 2. Frontier molecular-orbital diagram for [{Mo(η-C_5H_5)(NH)-(μ-NH)}$_2$]

Hückel calculations[16] on the model complex [{Mo(η-C_5H_5)(NH)(μ-NH)}$_2$] with structural parameters based on those found for (**3**) idealised to C_{2h} symmetry.

Figure 2 shows the assembly of a computed orbital diagram from *trans*-Mo_2(η-C_5H_5)$_2$ and a (NH)$_4$ fragment. The fragment orbitals were computed using Mo and N H_{ii} functions obtained by charge iteration on the whole complex. The values for the H_{ii} functions and orbital exponents are listed in Table 4. The parameters for C and H are the standard ones.

For *trans*-Mo_2(η-C_5H_5)$_2$ there are eleven orbitals in the valence region as predicted from the qualitative analysis presented earlier. There are two groups of three ($1a_u$, $1a_g$, $1b_u$ and $2a_g$, $1b_g$, $2b_u$) and two groups of two ($3a_g$, $2a_u$ and $2b_g$, $3b_u$) orbitals derived from the $1a_1 + e_2$ and e_1 sets respectively of the two Mo(η-C_5H_5) units. At higher energy there is a fourth orbital of a_g symmetry, formally the in-phase combination of the two $2a_1$ orbitals of Mo(η-C_5H_5). Notably there is a large (3.3 eV) computed separation between $4a_g$ and the next orbital higher in energy.

The twelve nitrogen-based orbitals of the (NH)$_4$ fragment separate out into a cluster of four orbitals ($1a_g$, $1b_u$, $2a_g$, $1a_u$) at lower energy which contain predominantly a mixture of nitrogen *s* and *p* character, and eight orbitals ($1b_g$ to $3b_g$) at slightly higher energy which essentially have nitrogen *p* character only.

Consider now the molecular-orbital ordering of the resultant complex [{Mo(η-C_5H_5)(NH)(μ-NH)}$_2$] shown at centre in Figure 2. The six levels $1b_u$ to $1a_g$ are metal–nitrogen bonding combinations. The contribution from the four nitrogen *sp*-hybrid orbitals ($1a_g$ to $1a_u$) in these levels is negligible. The high-energy orbitals ($2a_u$ and above) are metal–ligand antibonding combinations. At intermediate energy between the metal–ligand bonding and antibonding manifolds are found a group of three orbitals that are Mo_2(η-C_5H_5)$_2$/(NH)$_4$ non-bonding in character. The sizeable gap (1.9 eV) between the highest occupied and lowest unoccupied molecular orbitals (h.o.m.o.–l.u.m.o.) is indicative of a stable complex for the present electron count. Contour diagrams of the $3b_g$, $3b_u$, and $2a_g$ orbital wavefunctions are shown in Figure 3.

Orbitals $3b_g$ and $3b_u$ are nitrogen-based and contain approximately equivalent contributions from the terminal and bridging imido ligands. Accordingly one electron per imido ligand is not used in metal–ligand π bonding and so each NPh ligand in (**3**) acts as a three-electron donor. The metal-based orbital $2a_g$ is metal–ligand non-bonding and σ/δ in character, thus representing a weak (in terms of metal–metal overlap population) metal–metal single bond in accord with electron-counting procedures.

In summary, the extended-Hückel calculations support the qualitative conclusions reached by the symmetry analysis presented earlier. The indication that each NPh ligand acts as a three-electron donor acounts for the relatively long terminal Mo–N bond length, and also for the planarity of the Mo_2(μ-N)$_2$ core and the linear terminal NPh ligands.

We were interested to investigate the structures of the intermediates in the presumed stepwise replacement of the four oxo groups in complex (**2**) by the NR groups in (**3**)—(**5**). However, treatment of (**2a**) or (**2b**) with 1 equivalent of PhNCO

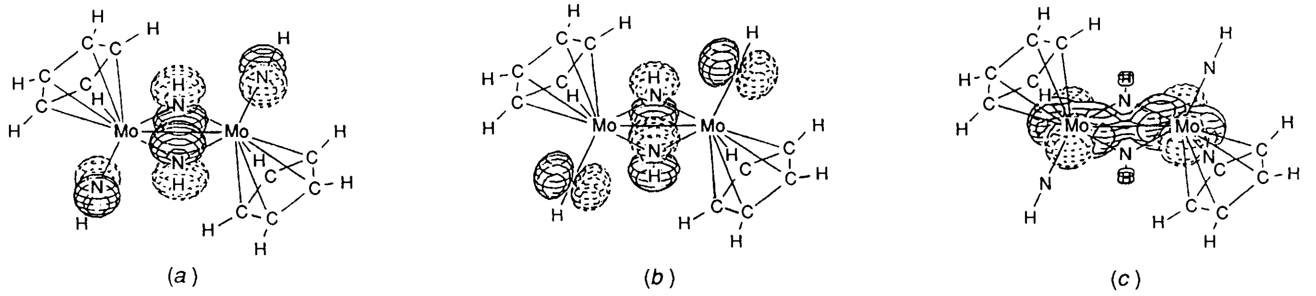


Figure 3. Contour diagrams of the $3b_g$ (*a*), $3b_u$ (*b*), and $2a_g$ (*c*) orbital wavefunctions of $[\{Mo(\eta\text{-}C_5H_5)(NH)(\mu\text{-}NH)\}_2]$

gave a complex mixture of at least three compounds, including unreacted (**2**) and the tetraimido species (**3**) and (**4**) respectively.

Alper *et al.*,[12] have previously reported that the binuclear complexes $[\{Mo(\eta\text{-}C_5H_4R)(CO)_3\}_2]$ (R = H or Me) react with various nitrobenzenes to give the mixed oxo–imido complexes $[Mo_2(\eta\text{-}C_5H_4R)_2O_2(\mu\text{-}O)(\mu\text{-}NR')]$ (R′ = aryl). In our hands, the reaction of $[\{Mo(\eta\text{-}C_5H_4Me)(CO)_3\}_2]$ with 1 equivalent of nitrobenzene led, after chromatography, to the isolation of three products. These were the expected monoimido species $[Mo_2(\eta\text{-}C_5H_4Me)_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ (**6**), the bis(oxo)-bis(imido) complex $[\{Mo(\eta\text{-}C_5H_4Me)O(\mu\text{-}NPh)\}_2]$ (**7**), and a further, as yet uncharacterised, product. The yields of (**6**) and (**7**) varied between 10 and 15%, while in the presence of 2 equivalents of nitrobenzene (**7**) was the major product. The data in Table 1 suggest that (**7**) has the structure given in the Scheme. In particular, the presence of the terminal Mo=O group is shown by the characteristic band at 885 cm^{-1} assignable to ν(Mo=O) and the band at 1 263 cm^{-1} assignable to ν(Mo–N–Mo).

When the tetraimido complex (**3**) was chromatographed on deactivated alumina, a gradual colour change from orange to yellow was observed during elution. The ^1H n.m.r. spectrum of the eluted products showed a mixture of two complexes identified as (**7**) and the mono-oxo compound $[Mo_2(\eta\text{-}C_5H_4Me)_2O(NPh)(\mu\text{-}NPh)_2]$ (**8**). The ratio of (**7**) and (**8**) varied with the rate of elution. When the partial hydrolysis reaction of (**3**) in wet C_6D_6 was monitored by ^1H n.m.r. spectroscopy it was converted fully into (**8**) after 24 h. Then, the spectrum of the bis(oxo) compound (**7**) began to appear. In wet $CDCl_3$ the hydrolysis reactions proceeded somewhat faster but were still clean giving (**8**) after *ca.* 1 h and (**7**) after 1 d. The spectra showed that aniline was also formed stoicheiometrically during the reaction. A pure sample of yellow complex (**8**) was obtained upon dissolution of (**3**) in wet chloroform for 1 h followed by recrystallisation. Similarly, treatment of the isopropyl derivative $[\{Mo(\eta\text{-}C_5H_4Pr^i)(NPh)(\mu\text{-}NPh)\}_2]$ (**4**) with wet chloroform yielded the corresponding mono- and bis-oxo complexes $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2O(NPh)(\mu\text{-}NPh)_2]$ (**9**) and $[\{Mo(\eta\text{-}C_5H_4Pr^i)O(\mu\text{-}NPh)\}_2]$ (**10**) respectively.

Addition of water to an acetone solution of (**3**) gave only a 75% conversion into the mono-oxo complex (**8**) over 2 h. However, addition of small amounts of dilute hydrochloric acid to (**3**) in acetone resulted in an immediate colour change from orange to yellow and the bis(oxo) compound (**7**) could be isolated from the reaction mixture in 90% yield. A similar stepwise hydrolysis of terminal imido ligands has been reported for a sulphido-stabilised dimolybdenum centre.[17]

Treatment of the mixed oxo–imido complexes (**6**), (**7**), or (**8**) with an excess of phenyl isocyanate gave the tetraimido complex (**3**) in smooth high-yield reactions. This is consistent with their occurrence as intermediates on the reaction pathway from the tetraoxo to the corresponding tetraimido complex, as shown in the Scheme.

While the terminal imido ligands of complex (**3**) are readily hydrolysed giving oxo groups, the bridging imido ligands are resistant to hydrolysis. Thus, $[\{Mo(\eta\text{-}C_5H_4Me)O(\mu\text{-}NPh)\}_2]$ (**7**) was indefinitely stable in water. Addition of aqueous hydrochloric acid to an acetone solution of (**7**), however, resulted in an immediate colour change from yellow to red, a transformation which was found to be pH-dependent. Thus, upon dilution, the solution gradually became lighter and, after the addition of an excess of water, (**7**) was recovered quantitatively. Hence it appears that simple reversible protonation of the complex occurs rather than hydrolysis. The nature of the products of this reaction is currently under investigation.

Complex (**3**) also reacts slowly with hydrogen sulphide over 10 d to give a red solution. Subsequent chromatography of the reaction mixture gave red crystals of $[Mo_2(\eta\text{-}C_5H_4Me)_2S(NPh)(\mu\text{-}NPh)_2]$ (**11**) in 62% yield.

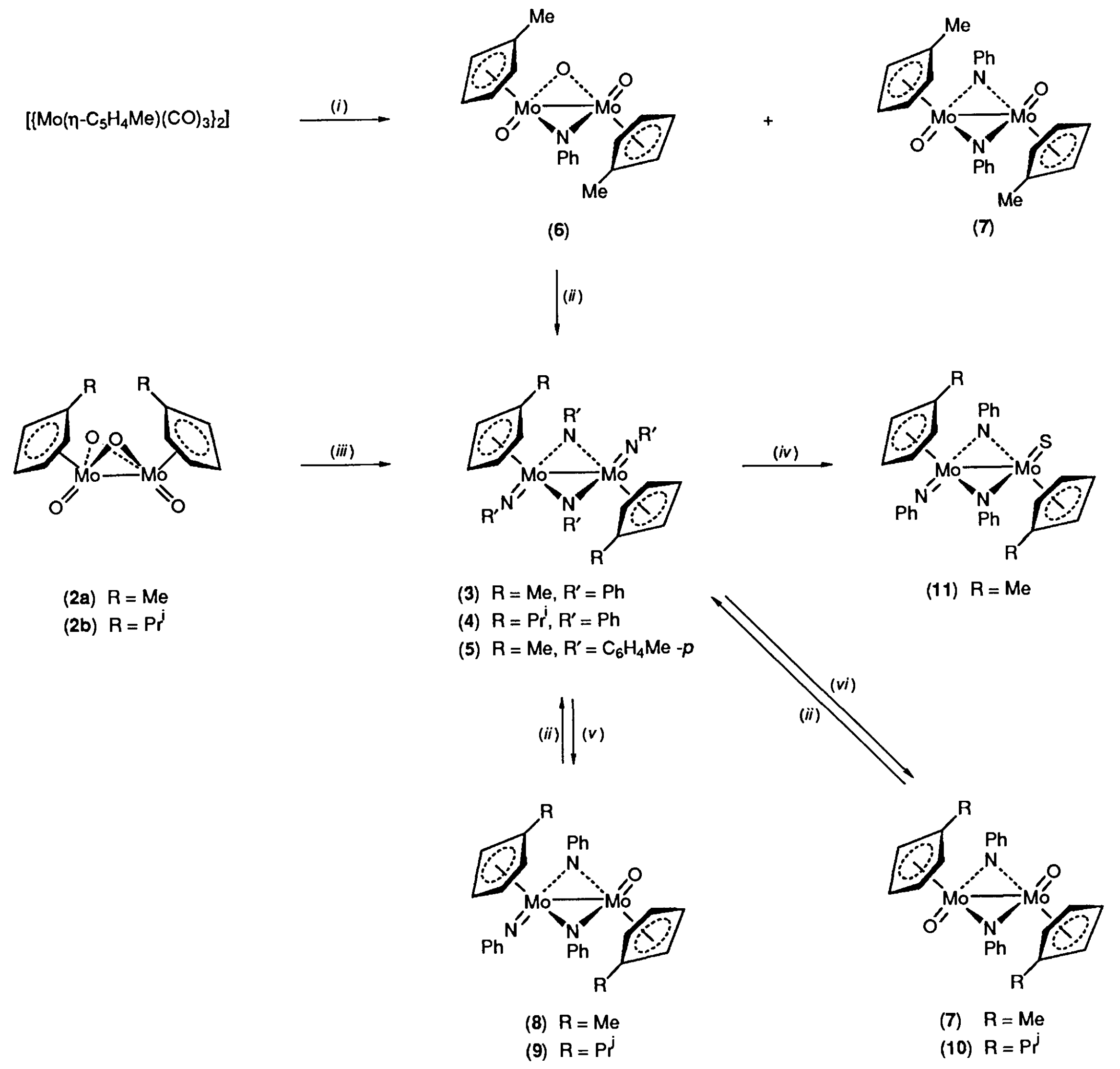
Experimental

All reactions were carried out under a nitrogen atmosphere using pre-dried solvents unless otherwise stated. N.m.r. spectra were recorded on a Bruker AM300 spectrometer (^1H, 300; ^{13}C, 75.43 MHz), i.r. spectra as CsI discs on a Perkin-Elmer 1710 Fourier-transform spectrometer. Chromatography was carried out on columns of deactivated neutral alumina (6% w/w water). The compounds $[\{Mo(\eta\text{-}C_5H_4R)O(\mu\text{-}O)\}_2]$ were prepared as described.[18]

Preparations.—$[\{Mo(\eta\text{-}C_5H_4R)(NR)(\mu\text{-}NR)\}_2]$ (**3**)—(**5**). A thf solution (50 cm^3) of $[\{Mo(\eta\text{-}C_5H_4Me)O(\mu\text{-}O)\}_2]$ (1.02 g, 2.46 mmol) and phenyl isocyanate (5 cm^3, 0.046 mol) was refluxed at 70 °C for 5 d in a sealed Young's ampoule. The initially dark red solution became yellow. The mixture was filtered, concentrated under reduced pressure, and cooled to −80 °C. Orange crystals of $[\{Mo(\eta\text{-}C_5H_4Me)(NPh)(\mu\text{-}NPh)\}_2]$ (**3**) (0.55 g, 29%) formed which were washed with ice-cold thf and dried under reduced pressure. Higher yields (62%) of isolated product were obtained by filtering the reaction mixture, removing all solvent and excess of isocyanate, and washing the residue with acetone (30 cm^3). Crystals suitable for *X*-ray diffraction were grown by slow evaporation of an acetone solution. Complexes (**4**) and (**5**) were synthesised in a similar fashion in 12 and 10% yields respectively.

$[Mo_2(\eta\text{-}C_5H_4R)_2O(NPh)(\mu\text{-}NPh)_2]$, (**8**) *and* (**9**). The tetraimido complex $[\{Mo(\eta\text{-}C_5H_4Me)(NPh)(\mu\text{-}NPh)\}_2]$ (**3**) (0.1 g, 0.14 mmol) was dissolved in wet chloroform (10 cm^3). After 2 d at room temperature (r.t.) the colour changed from orange to yellow. The solvent was removed under reduced pressure. Crystallisation of the residue from light petroleum (b.p. 40—60 °C) gave yellow microcrystalline $[Mo_2(\eta\text{-}C_5H_4Me)_2O(NPh)(\mu\text{-}NPh)_2]$ (**8**) (66 mg, 74%). Compound (**9**) was prepared from (**4**) in a similar manner in >95% yield.

$[\{Mo(\eta\text{-}C_5H_4R)O(\mu\text{-}NPh)\}_2]$, (**7**) *and* (**10**). A solution of complex (**3**) (0.2 g, 0.30 mmol) in acetone (30 cm^3) was treated



Scheme. (*i*) $PhNO_2$, toluene reflux, nitrogen purge, 3 h; (*ii*) PhNCO, thf, 70 °C, 6 d; (*iii*) R′NCO, thf, 70 °C, 5 d; (*iv*) H_2S, toluene, r.t., 10 d; (*v*) wet $CHCl_3$, r.t., 2 d; (*vi*) acetone–dilute HCl(aq), r.t., 5 min

with hydrochloric acid (0.5 cm^3 of a 10 mol dm^{-3} solution) in a dropwise manner. The initial orange solution became red. Addition of water (*ca.* 5 cm^3) turned the solution yellow. The acetone was removed under reduced pressure giving a yellow solid which was separated and washed with water. The residue was chromatographed on deactivated alumina. Eluting with dichloromethane–light petroleum (b.p. 40–60 °C) (1:1) gave a yellow band which afforded 120 mg (76%) of [{Mo(η-C_5H_4Me)O(μ-NPh)}$_2$] (**7**) as a yellow solid. Recrystallisation was effected from an acetone solution at −40 °C. Compound (**10**) was prepared from (**4**) in an analogous manner in 83% yield.

[Mo_2(η-C_5H_4Me)$_2O_2$(μ-O)(μ-NPh)], (**6**). The procedure was essentially similar to that previously described.[12] A toluene solution (100 cm^3) of [{Mo(η-C_5H_4Me)(CO)$_3$}$_2$] (0.85 g, 2.36 mmol) was refluxed for 3 h while purging with dinitrogen. After cooling to r.t., nitrobenzene (0.25 cm^3, 2.43 mmol) was added and the red mixture was stirred for 12 h and became yellow. The volatiles were removed under reduced pressure. Chromatography of the residue on deactivated alumina and eluting with light petroleum (b.p. 40—60 °C) gave a red band. This was shown to contain the starting material. Further elution with diethyl ether–light petroleum (b.p. 40—60 °C) (1:1) gave yellow-orange [Mo_2(η-C_5H_4Me)$_2O_2$(η-O)(μ-NPh)] (**6**) (100 mg, 12%). Further elution with diethyl ether yielded yellow [{Mo(η-C_5H_4Me)O(μ-NPh)}$_2$] (**7**) (180 mg, 19%).

[Mo_2(η-C_5H_4Me)$_2$S(NPh)(μ-NPh)$_2$], (**11**). A thf solution (30 cm^3) of [{Mo(η-C_5H_4Me)(NPh)(μ-NPh)}$_2$] (**3**) (130 mg, 0.18 mmol) was purged periodically with H_2S over a period of 10 d resulting in a colour change from orange to red. The volatiles were removed under reduced pressure. Chromatography of the resulting red solid, eluting with dichloromethane–light petroleum (b.p. 40—60 °C) (1:1), gave a red band. The solvent was removed under reduced pressure and the residue was recrystallised from light petroleum (b.p. 40—60 °C) giving [Mo_2(η-C_5H_4Me)$_2$S(NPh)(μ-NPh)$_2$] (**11**), yield 74 mg (62%).

Reactions of Mixed Imido–Oxo Complexes [Mo_2(η-C_5H_4Me)$_2O_{4-x}$(NPh)$_x$] x = 1—3, *with Phenyl Isocyanate*.—A thf solution (30 cm^3) of complex (**6**) (130 mg, 0.27 mmol) was treated with phenyl isocyanate (0.3 cm^3, 2.80 mmol) at 70 °C for 6 d in a sealed Young's ampoule. The yellow solution became orange. Solvent was removed under reduced pressure and (**3**) identified as the sole organometallic product by ^{1}H n.m.r. spectroscopy. The reactions of (**7**) and (**8**) proceeded in a similar fashion over periods of 2 and 1 d respectively giving (**3**).

Reactions of [{Mo(η-C_5H_4Me)O(μ-O)}$_2$] *with t-butyl isocyanate.*—A thf solution (30 cm^3) of [{Mo(η-C_5H_4Me)O(μ-O)}$_2$] (0.34 g, 0.82 mmol) was treated with t-butyl isocyanate (5 cm^3, 0.04 mol) at 70 °C for 7 d. The solvent and excess of isocyanate were removed under reduced pressure. Proton n.m.r. spectroscopy of the residue revealed a complex mixture of products, and the reaction was not investigated further.

With o-*tolyl isocyanate.* A thf solution (40 cm^3) of ({Mo(η-C_5H_4Me)O(μ-O)}$_2$] (0.65 g, 1.38 mmol) was treated with *o*-tolyl isocyanate (2 cm^3, 17 mmol) at 70 °C for 7 d. The ^1H n.m.r. spectrum of the reaction mixture showed only the presence of starting materials.

Crystal Structure Determination of Compound (**3**).—*Crystal data.* $C_{36}H_{34}Mo_2N_4$, $M = 714.57$, crystal size = 0.15 × 0.22 × 0.22 mm, monoclinic, space group $P2_1/n$, $a = 11.066(2)$, $b = 9.542(2)$, $c = 14.987(2)$, $\beta = 104.24(2)°$, $U = 1533.92$ Å^3, $Z = 2$, $D_c = 1.547$ g cm^{-3}, μ(Mo-K_α) = 8.285 cm^{-1}, $F(000) = 724$.

Scan mode ω—2θ, $T = 293$ K, $2\theta_{max.} = 50°$, total data = 3 759, number of observations = 2 281, variables = 195, observations/variables = 11.7, R(merge) = 0.022, $R = 0.024$, $R' = 0.026$ (unit weights).

Structure solution and refinement. An orange crystal of complex (**3**) was sealed in a glass capillary and transferred to the goniometer head of an Enraf-Nonius CAD4F diffractometer. Cell dimensions were obtained by least-squares methods from the positions of 25 carefully centred reflections. Data were collected using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). During data collection three intensity-control reflections were measured every 3 600 s of *X*-ray exposure time, and three orientation controls were checked every 250 reflections.

Lorentz and polarisation corrections were applied, together with an empirical absorption correction.[19] Equivalent reflections were merged, and only those for which $I > 3\sigma(I)$ [where $\sigma(I)$ is the standard deviation based on counting statistics] were included in subsequent refinement cycles.

The heavy-atom position was located from a Patterson synthesis, and the locations of non-hydrogen atoms determined from subsequent difference syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms could not be reliably located and were placed in calculated positions (C–H 0.99 Å) and refined riding on their attached carbons with common isotropic thermal parameters.

Corrections for anomalous dispersion and isotropic extinction [20] were made in the final stages of refinement. Bond lengths and angles (excluding H atoms) and final positional parameters are given in Tables 2 and 3 respectively. All calculations were performed on a VAX 11/750 computer in the Chemical Crystallography Laboratory, Oxford using the Oxford CRYSTALS system,[21] and plotted using the SNOOPI package. Atomic scattering factors and anomalous dispersion coefficients were taken from the usual sources.[22]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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