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Preliminary communication

The interconversion of oxo and imido ligands at a dimolybdenum centre: X-ray crystal structure of $[\mathrm{Mo}(\eta\text{-}C_5H_4\mathrm{Me})(\mathrm{NPh})(\mu\text{-}\mathrm{NPh})]_2$ *

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Abstract

The reversible interconversions of oxo and arylimido ligands and a metathesis reaction between arylimido ligands and arylisocyanates are described. The compound $[\mathrm{Mo}(\eta\text{-}C_5H_4\mathrm{Me})(\mathrm{NPh})(\mu\text{-}\mathrm{NPh})]_2$ contains linear terminal Mo–NPh ligands and a planar $\mathrm{Mo}_2(\mu\text{-N})_2$ fragment.

We have previously described the synthesis of the tetra-imido complex $[\mathrm{Mo}(\eta\text{-}C_5H_5)(\mathrm{NPh})(\mu\text{-}\mathrm{NPh})]_2$ (**1**) by replacement of the terminal and bridging oxo groups of $[\mathrm{Mo}(\eta\text{-}C_5H_5)(\mathrm{O})(\mu\text{-O})]_2$ by reaction with phenylisocyanate [1]:

$$[\mathrm{Mo}(\eta\text{-}C_5H_5)(\mathrm{O})(\mu\text{-O})]_2 + 4\ \mathrm{PhNCO} \rightarrow [\mathrm{Mo}(\eta\text{-}C_5H_5)(\mathrm{NPh})(\mu\text{-}\mathrm{NPh})]_2 + 4\ \mathrm{CO}_2$$

Here we describe the synthesis of alkyl-substituted cyclopentadienyl analogues of **1** and a study of the interconversion of terminal oxo and imido ligands in these compounds.

Results and discussion

Treatment of the tetra-oxo complexes $[\mathrm{Mo}(\eta\text{-}C_5H_4R)(\mathrm{O})(\mu\text{-O})]_2$ [**2a**, R = Me; **2b**, R = Pr^i] with an excess of phenylisocyanate in refluxing THF (tetrahydrofuran) gave the corresponding tetra-imido complexes $[\mathrm{Mo}(\eta\text{-}C_5H_4R)(\mathrm{NPh})(\mu\text{-}\mathrm{NPh})]_2$, [**3**, R = Me; **4**, R = Pr^i] as orange, air-stable, crystalline solids. † The *p*-tolyl analogue $[\mathrm{Mo}(\eta\text{-}C_5H_4\mathrm{Me})(\mathrm{N}\text{-}p\text{-tolyl})(\mu\text{-N}\text{-}p\text{-tolyl})]_2$ (**5**) was similarly prepared from **2a** and *p*-tolylisocyanate. Isolated yields were between 20 and 65%.

The crystal structure of $[\mathrm{Mo}(\eta\text{-}C_5H_4\mathrm{Me})(\mathrm{NPh})(\mu\text{-}\mathrm{NPh})]_2$ (**3**) has been determined ‡ (Fig. 1) and reveals a planar $\mathrm{Mo}_2(\mu\text{-N})_2$ core and a mutually *trans* disposition of the $\eta\text{-}C_5H_4\mathrm{Me}$ rings. Thus the molecular structure of **3** is analogous

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* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

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to that of the mono-imido analogue $[Mo_2(\eta\text{-}C_5H_5)_2(O)_2(\mu\text{-}O)(\mu\text{-}N\text{-}p\text{-tolyl})]$ [2] and is in contrast to the puckered metallacore geometry of the tetra-oxo compound $[Mo(\eta\text{-}C_5H_5)(O)(\mu\text{-}O)]_2$. In the latter complex the $Mo_2(\mu\text{-}O)_2$ core has a dihedral angle of 152° between the two $Mo_2(\mu\text{-}O)$ planes, and a *cis* disposition of the $\eta\text{-}C_5H_5$ ligands [3]. Compound **1** was previously proposed to be structurally analogous to the parent tetra-oxo compound [1]. The terminal imido ligands of **3** are approximately linear [Mo(1)–N(1)–C(10) = 173.6(2)°], a feature indicative of significant $N(p\pi) \rightarrow Mo(d\pi)$ 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]. That the bridging imido moieties also have significant π-donor character is shown by the trigonal geometry about the bridging nitrogen atoms.

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† Selected spectroscopic data: IR data, cm^{-1}, CsI. NMR data, ^1H 300 MHz, ^{13}C 75.5 MHz, as δ (ppm) relative to TMS, ^{a} in $[^2H_6]$benzene, ^{b} in $[^2H]$chloroform. Satisfactory microanalyses have been obtained for all the new compounds.

3: ν(Mo=N) 1266, 1322. ^1H NMR: 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] ^{a}. $^{13}C\{^1H\}$: 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] ^{a}.

4: ν(Mo=N) 1265, 1327. ^1H NMR: 0.59 [12 H, d(*J* 7.0), $CH(CH_3)_2$], 2.17 [2 H, sept(*J* 6.9), $CH(CH_3)_2$], 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] ^{a}.

5: ν(Mo=N) 1270, 1322. ^1H: 1.23 [6 H, s, C_5H_4 CH_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] ^{a}.

7: ν(Mo=N) 1263 ν(Mo=O) 885. ^1H: 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] ^{b}.

8: ν(Mo=N) 1263, 1327; ν(Mo=O) 884. ^1H: 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] ^{a}.

9: ν(Mo=N) 1263, 1328; ν(Mo=O) 882. ^1H: 0.75 [6 H, d(*J* 7), CH_3], 1.17 [6 H, d(*J* 7), CH_3], 2.13 [1 H, sept(*J* 6.9), $CH(CH_3)_2$], 2.81 [1 H, sept(*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] ^{b}.

10: ν(Mo=N) 1263; ν(Mo=O) 881. ^1H: 0.99 [12 H, d(*J* 6.9), CH_3], 2.71 [2 H, sept(*J* 6.9), $CH(CH_3)_2$], 5.11 [4H, 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 [4H, t(*J* 7.3), C_6H_5], 8.20 [4 H, d(*J* 7), C_6H_5] ^{a}.

11: ν(Mo=N) 1264, 1324; ν(Mo=S) 474. ^1H: 1.30 [3 H, s, Me], 1.72 [3 H, s, Me], 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, s, 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] ^{a}.

12: ν(Mo=N) 1321, 1265. ^1H: 1.17 [6 H, C_5H_4Me], 1.98 [3 H, C_6H_4Me], 5.15 [4 H, t(*J* 3), C_5H_4Me], 5.84 [4 H, t(*J* 3), C_5H_4Me], 6.70–8.10 [19 H, m, C_6H_5 and C_6H_4] ^{a}.

13: ν(Mo=N) 1326, 1270. ^1H: 1.19 [6 H, C_5H_4Me], 2.07 [6 H, C_6H_4Me], 5.18 [4 H, t(*J* 3), C_5H_4Me], 5.86 [4 H, t(*J* 3), C_5H_4Me], 6.70–8.10 [18 H, m, C_6H_5 and C_6H_4Me] ^{a}.

Crystal data for 3: $C_{36}H_{34}N_4Mo_2$, $M = 714.57$, 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 1533.93 $Å^3$, $Z = 2$, D_c 1.547 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ 8.285 cm^{-1}, $F(000) = 724$, scan mode $\omega - 2\theta$, T 293 K, $2\theta_{max}$ 50°, total data 3759, number of observations 2281, number of variables 195, observations/variables = 11.7, R(merge) = 0.022, $R = 0.024$, $R_w = 0.026$ (unit weights). Data were collected using an Enraf-Nonius CAD4 diffractometer. The structure was solved from Patterson and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined riding on their attached carbon atoms. Crystallographic calculations were carried out by use of the Oxford CRYSTALS package [7].

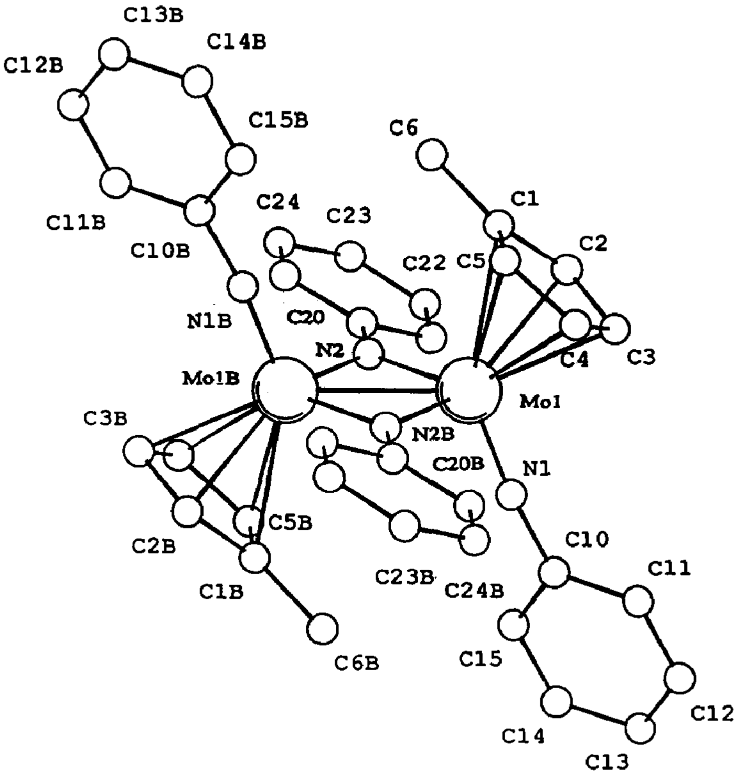
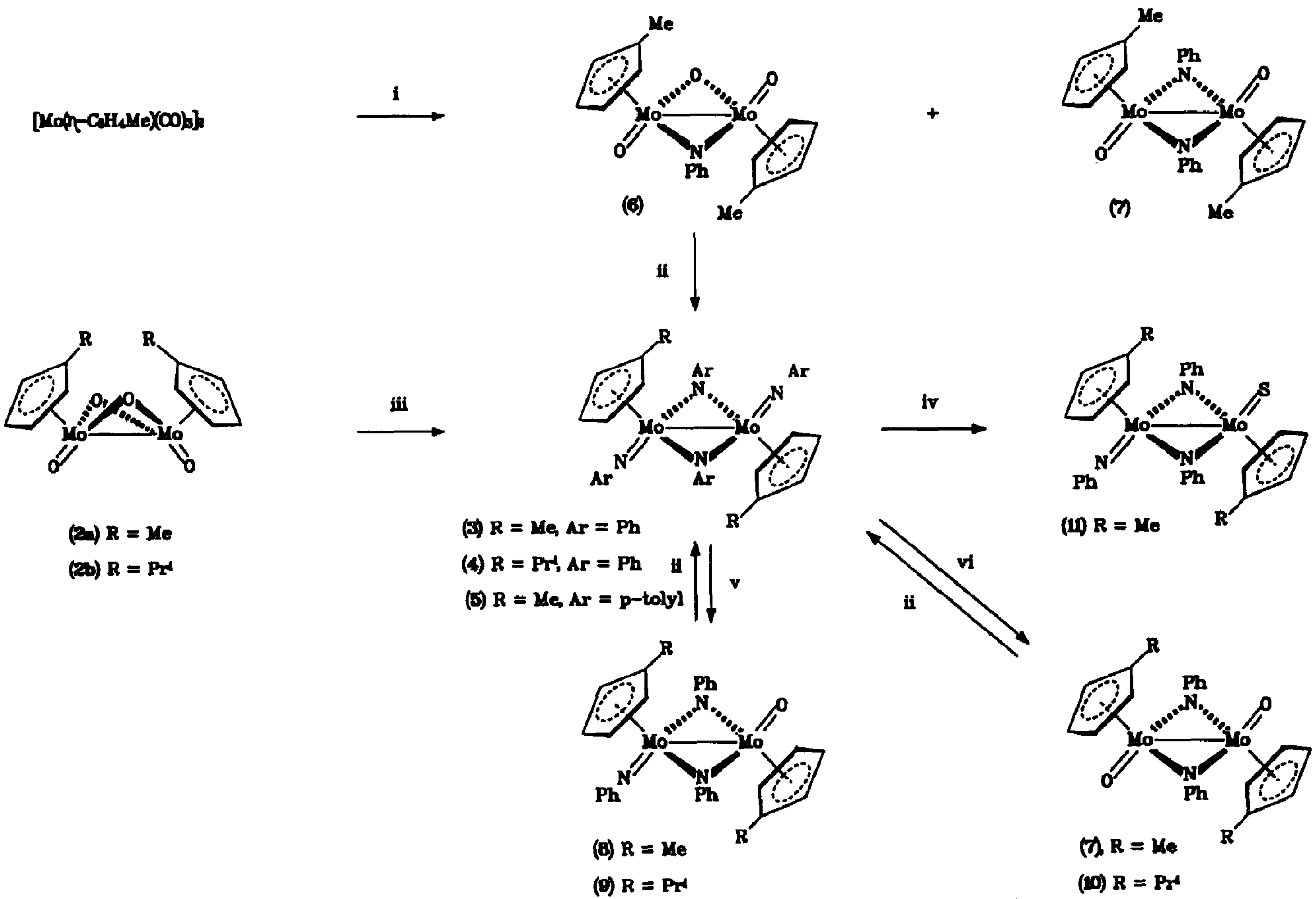


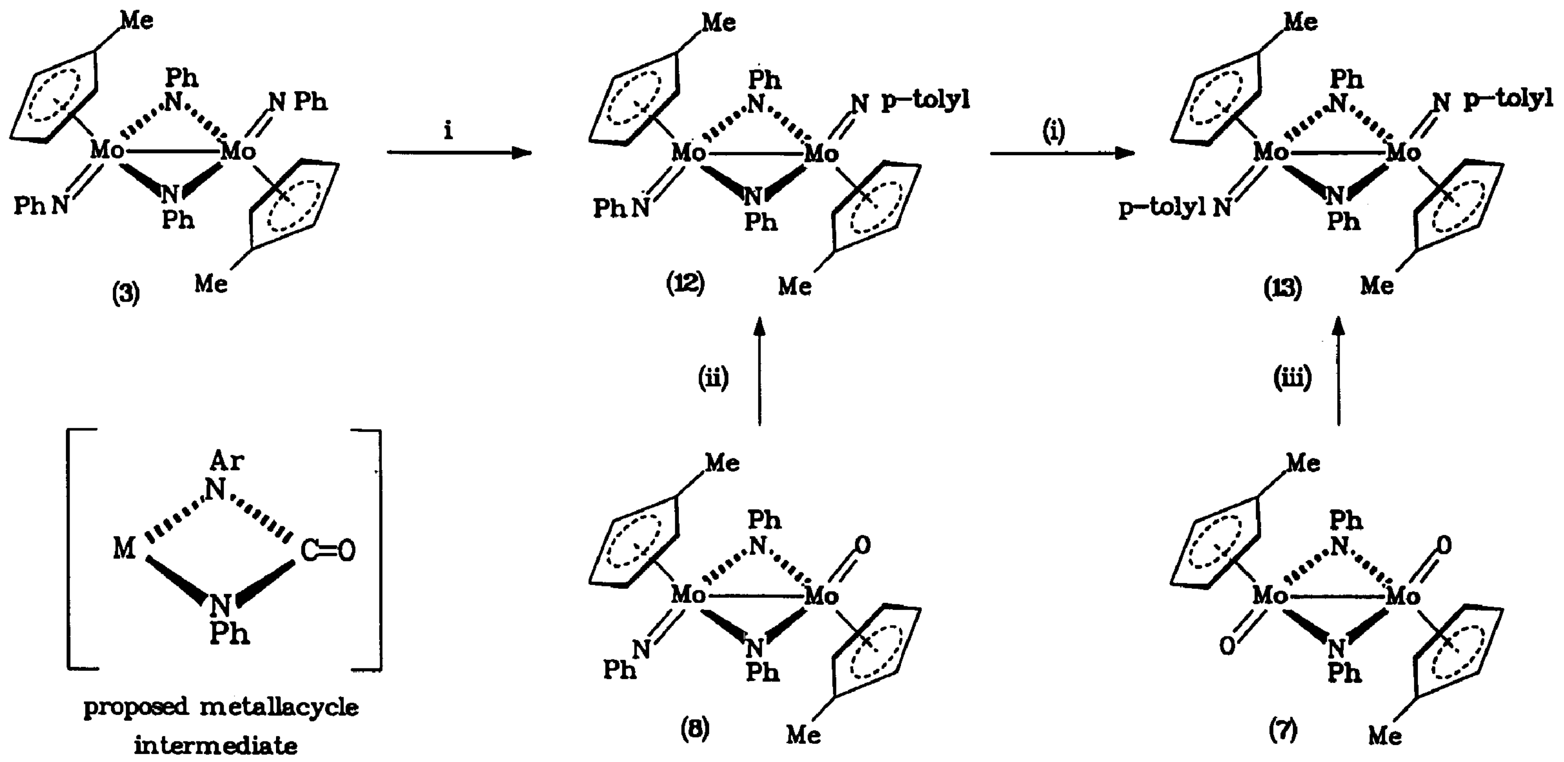
Fig. 1. Molecular structure of 3 viewed very nearly perpendicular to the Mo–Mo bond. Hydrogen atoms omitted for clarity. The molecule lies across a crystallographic inversion centre with atoms labelled "B" related to their counterparts by the symmetry operator [$-x$, $-y$, $-z$]. Selected bond lengths (Å) and angles (°) as follows: Mo(1)–Mo(1B) 2.7175(5), Mo(1)–N(1) 1.763(3), Mo(1)–N(2) 1.975(2), Mo(1)–N(2B) 1.964(2), Mo(1)–Cp_{cent} 2.01; Mo(1B)–Mo(1)–N(1) 112.32(9), Mo(1B)–Mo(1)–Cp_{cent} 124.89, Mo(1)–N(2)–C(20) 135.3(2), Mo(1)–N(1)–C(10) 173.6(2), where Cp_{cent} refers to the computed η-C_5H_4Me ring centroid.

The geometries of the terminal and bridging PhN ligands suggest that they act as four-electron donors, which would give a formal 20 valence electron count to each molybdenum atom in 3. This apparent violation of the EAN rule may be rationalised by use of simple symmetry-based molecular orbital arguments supplemented by extended Hückel molecular orbital calculations. Thus two of the twelve frontier orbitals of the $(NPh)_4$ fragment (one b_u and one b_g under the idealised C_{2h} symmetry of 3) are essentially non-bonding with respect to $Mo_2(\eta$-$C_5H_4Me)_2/(NPh)_4$ interactions. In the complex 3 these two orbitals house four electrons, and so each NPh ligand acts only as a three-electron donor, giving a formal 18 valence electron count to each molybdenum atom.

We supposed that the conversion of **2a** to **3** proceeded via a stepwise replacement of each oxo ligand by arylimido. Therefore, we set out to isolate and characterise these presumed intermediates. ^1H NMR spectroscopic studies of the reaction between **2a** and one equivalent of PhNCO gave no evidence of mixed oxo-imido compounds. However, the reverse reaction, namely replacement of imido groups by oxo ligands, was readily achieved for the two terminal imido ligands by simple hydrolysis. Thus, hydrolysis of 3 with wet chloroform gave yellow, crystalline **8**.



Scheme 1. (i) $PhNO_2$, toluene reflux, N_2 purge, 3 h; (ii) PhNCO, THF, 70 °C, 2d; (iii) ArNCO, THF, 70 °C, 5 d; (iv) H_2S, toluene, r.t., 10 d; (v) wet $CHCl_3$, r.t., 2 d; (vi) acetone/dil. HCl(aq), r.t., 5 min.



Scheme 2. Further metathesis reactions: *p*-tolylisocyanate in THF at 70 ° C. (i) for 4 weeks, > 98%. (ii) for 24 h, 80%. (iii) for 48 h, 83%.

Similarly, treatment of the isopropyl derivative [Mo(η-$C_5H_4Pr^i$)(NPh)(μ-NPh)]$_2$ (**4**) with wet chloroform yielded the corresponding mono- and bis-oxo complexes [Mo_2(η-$C_5H_4Pr^i$)$_2$(O)(NPh)(μ-NPh)$_2$] (**9**) and [Mo(η-$C_5H_4Pr^i$)(O)(μ-NPh)]$_2$ (**10**), respectively. Addition of water to an acetone solution of **3** resulted after two hours in only a 75% conversion into the mono-oxo complex **8**. However, addition of small amounts of dilute hydrochloric acid to **3** in acetone caused an immediate colour change from orange to yellow and the bis-oxo compound **7** was isolated in 90% yield.

Alper and co-workers [2] have previously reported that the binuclear complexes [Mo(η-C_5H_4R)(CO)$_3$]$_2$ (R = H, Me) react with various nitroarenes to give the mixed oxo-imido complexes [Mo_2(η-C_5H_4R)$_2$(O)$_2$(μ-O)(μ-NAr)]. We found that treatment of [Mo(η-C_5H_4Me)(CO)$_3$]$_2$ with one equivalent of nitrobenzene gave both the mono-imido species [Mo_2(η-C_5H_4Me)$_2$(O)$_2$(μ-O)(μ-NPh)] (**6**) and the bis-oxo-bis-imido complex [Mo(η-C_5H_4Me)(O)(μ-NPh)]$_2$ (**7**). The IR data (ν(Mo=O) 885 cm^{-1}) suggest that **7** has a terminal oxo group, as shown in Scheme 1.

In support of the proposal that they are intermediates in the conversion of **2a** to **3**, we found that treatment of the mixed oxo-imido complexes **6**, **7**, or **8** with an excess of phenylisocyanate gave **3** in smooth high yield reactions.

While the terminal imido ligands of **3** are readily hydrolysed to give oxo groups, the bridging imido ligands are resistant to hydrolysis. Thus, [Mo(η-C_5H_4Me)(O)(μ-NPh)]$_2$ (**7**) was indefinitely stable in water. Complex **3** reacted slowly with hydrogen sulphide during ten days to give red crystals of [Mo_2(η-C_5H_4Me)$_2$(S)(NPh)(μ-NPh)$_2$] (**11**) in 62% yield.

Heating the complex **3** with an excess of *p*-tolylisocyanate results in the stepwise exchange of terminal imido ligands yielding first [Mo_2(η-C_5H_4Me)$_2$(N-*p*-tolyl)(NPh)(μ-NPh)$_2$] (**12**) and then [Mo(η-C_5H_4Me)(N-*p*-tolyl)(μ-NPh)]$_2$ (**13**). Conversion of **3** to **13** was complete after eight weeks at 70 °C (^{1}H NMR). Prolonged thermolysis of the reaction mixture did not cause substitution of the bridging phenylimido ligands. We propose that the metathesis between the terminal imido ligands and arylisocyanates proceeds via a metallacyclic intermediate (Scheme 2), and note that structurally analogous metallacyclic compounds have been isolated [5,6].

Pure samples of **12** and **13** could not be isolated from the reaction mixtures owing to contamination by isocyanate oligomers formed during the reaction. However, pure **12** and **13** were prepared separately in high yields by treatment of the mono- and bis-oxo compounds [Mo_2(η-C_5H_4Me)$_2$(O)(NPh)(μ-NPh)$_2$] (**8**) and [Mo(η-C_5H_4Me)(O)(μ-NPh)]$_2$ (**7**), respectively, with an excess of *p*-tolylisocyanate.

The new reactions and structures proposed for the new compounds are shown in the schemes.

In conclusion, selective interconversion of oxo and imido ligands has been observed with bridging imido groups more resistant to hydrolysis or metathesis than terminal arylimido groups.

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