η-Cyclopentadienylimido Molybdenum Chemistry: Hydrido, Alkyl and η-Allyl Derivatives†

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The following compounds have been prepared and characterized: $[Mo(\eta\text{-}C_5H_4R)Cl_3(NBu^t)]$ (R = H, Me or Pr^i), $[\{MoCl_3(\mu\text{-}Cl)(NBu^t)\}_2]$, *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_4Me)(NBu^t)(\mu\text{-}NBu^t)\}_2]$, $[\{Mo(\eta\text{-}C_5H_4Me)O(\mu\text{-}NBu^t)\}_2]$, $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_2H_4)Me(NBu^t)]$, $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_2H_4)Ph(NBu^t)]$, $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_2H_4)(H \text{ or } D)(NBu^t)]$, $[Mo(\eta\text{-}C_5H_4Me)(PMe_3)Cl(NBu^t)]$, $[Mo(\eta\text{-}C_5H_4Me)(PMe_3)Me(NBu^t)]$, $[Mo(\eta\text{-}C_5H_4Me)(PMe_3)_2(NBu^t)]^+A^-$ (A = Cl or BF_4), $[Mo(\eta\text{-}C_5H_4Me)(PMe_2Ph)Cl(NBu^t)]$, isomers of $[Mo(\eta\text{-}C_5H_4R)(\eta\text{-}C_3H_5)(NBu^t)]$ (R = Me or Pr^i), and $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_2H_4)(\sigma\text{-}C_3H_5)(NBu^t)]$. The crystal structure of $[\{MoCl_3(\mu\text{-}Cl)(NBu^t)\}_2]$ has been determined. These compounds include the first or rare examples of combinations of ligands with the imido group, for example, imido η^3-allyl derivatives.

We have recently described the synthesis and reactions of η-cyclopentadienylimido derivatives of molybdenum and tungsten. In particular, the compounds $[M(\eta\text{-}C_5H_4R)X_2(NR')]$ (M = Mo or W, R = H or alkyl, R′ = alkyl or aryl, X = Cl or Br) were shown to be precursors to an extensive chemistry of η-cyclopentadienylimido transition-metal derivatives.[1] Here we describe further studies in this area; a part of this work has appeared in a communication.[2]

Results and Discussion

Treatment of the previously described[1,2] compounds $[Mo(\eta\text{-}C_5H_4R)Cl_2(NBu^t)]$ (R = H **1**, Pr^i **2** or Me **3**) in dilute dichloromethane solution with chlorine gas affords the d^0 molybdenum(VI) compounds $[Mo(\eta\text{-}C_5H_5)Cl_3(NBu^t)]$ **4**, $[Mo(\eta\text{-}C_5H_4Pr^i)Cl_3(NBu^t)]$ **5** and $[Mo(\eta\text{-}C_5H_4Me)Cl_3(NBu^t)]$ **6**, respectively, in up to 50% yield. High purity of the starting materials and rigorously dried solvents were found to be imperative for successful preparations. The compounds $[M(\eta\text{-}C_5R_5)Cl_3(NBu^t)]$ (R = H, M = Mo **4** or W; R = Me, M = Mo) have been previously and independently prepared by Sundermeyer[3] by a different route, while this work was in progress and the crystal structure of the compound where R = Me, M = Mo determined.[3a] The analytical and spectroscopic data for compounds **5** and **6**, and for all other new compounds described below, are given in Table 1. These data will not be further discussed except where the interpretation is not straightforward. The related oxo compounds $[M(\eta\text{-}C_5Me_5)Cl_3O]$ (M = Mo or W) have been described recently.[4]

Treatment of compound **3** with chlorine gas in *concentrated* dichloromethane solution afforded the red air-sensitive compound $[\{MoCl_3(\mu\text{-}Cl)(NBu^t)\}_2]$ **7** in 35% yield. Cooling a dichloromethane solution to −20 °C gave crystals suitable for X-ray diffraction studies. The molecular structure of **7** is shown in Fig. 1 and is essentially similar to that of the compound $[\{WCl_3(\mu\text{-}Cl)(NC_2Cl_5)\}_2]$.[5] Fractional atomic coordinates for the non-hydrogen atoms of **7** are listed in Table 2 and selected bond lengths and angles for both compounds are compared in Table 3. Both compounds possess a pseudo-octahedral geometry at the metal centre with nearly linear M–N–C linkages. The M–N bond lengths are 1.680(2) (M = Mo) and 1.71(2) Å (M = W) consistent with the imide ligands acting as four-electron donors. Evidence for a *trans* influence of the imide ligand is seen in the metal–bridging chloride bond lengths; the bond *trans* to the imide ligand is 0.27 Å longer than the corresponding *cis* bond.

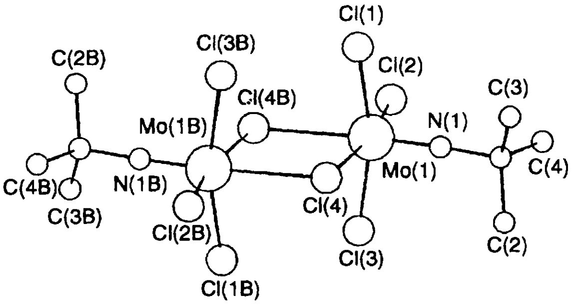

Fig. 1 Molecular structure of $[\{MoCl_3(\mu\text{-}Cl)(NBu^t)\}_2]$ **7**. Hydrogen atoms omitted for clarity

Treatment of $[Mo(\eta\text{-}C_5H_4Me)Cl_2(NBu^t)]$ **3** with 2 equivalents of $LiNHBu^t$ gave a yellow solid comprising a mixture of *cis* and *trans* isomers of the compound $[\{Mo(\eta\text{-}C_5H_4Me)(NBu^t)(\mu\text{-}NBu^t)\}_2]$ **8** and **9**, respectively. These two compounds recrystallised together from toluene solution and sublimed together at *ca.* 100 °C, and could not be separated. The ^1H NMR spectrum of the mixture showed resonances assignable to bridging and terminal *tert*-butylimide ligands on both isomers, and to two $\eta\text{-}C_5H_4Me$ ligands. The assignment of the $\eta\text{-}C_5H_4$ groups for the two isomers was confirmed by selective proton decoupling. The cyclopentadienyl ring proton resonances are virtual triplets, consistent with the presence of a plane of symmetry in both molecules. The $^{13}C\text{-}\{^1H\}$ NMR spectrum is fully consistent with the proposed structures. Compounds **8** and **9** are volatile, and the FAB mass specrum shows a band assignable to parent ion [for $^{96}Mo^{97}Mo$ (16.5 and 9.5%) and $^{95}Mo^{98}Mo$ (15.7 and 23.8%)] at *m/z* 635 and there are further peaks assignable to fragmentation products formed by loss of methyl, *tert*-butyl and *tert*-butylimido groups. On the basis of the data, and by analogy to the structurally characterised dimetallic tetraimido compounds *trans*-$[\{Mo(\eta\text{-}C_5H_4Me)(NPh)(\mu\text{-}NPh)\}_2]$[6] and *cis*-$[\{Cr(\eta\text{-}C_5H_5)(NSiMe_3)(\mu\text{-}NSiMe_3)\}_2]$,[7] we propose the structures for **8** and **9** shown in Scheme 1. Close analogues of **8** and **9**, namely *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_5)(NBu^t)(\mu\text{-}NBu^t)\}_2]$ and the crystal structure of the latter have been reported by Sundermeyer.[3b]

In an attempt to separate compounds **8** and **9** the mixture

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: mmHg ≈ 133 Pa.

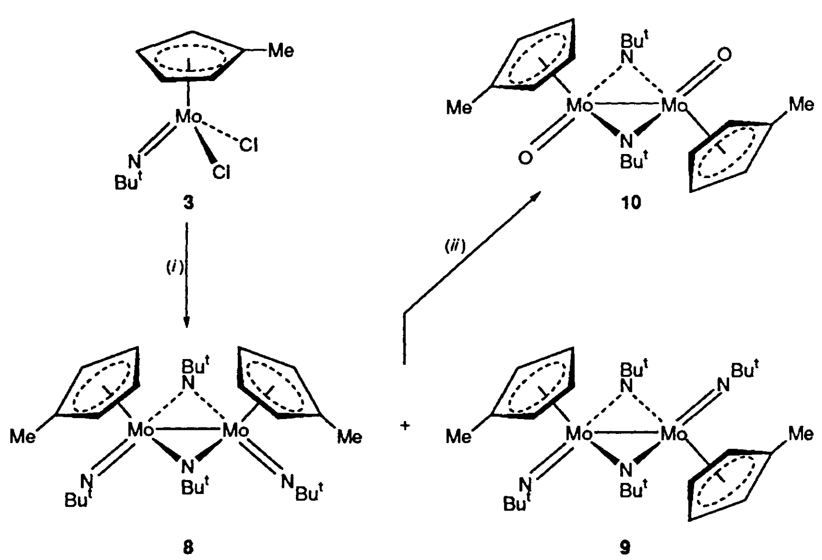
Table 1 Analytical and spectroscopic data

Compound and analysis (%)	NMR data[a]
5 $[Mo(\eta\text{-}C_5H_4Pr^i)Cl_3(NBu^t)]$ C, 38.2 (37.9); H, 5.3 (5.3); N, 3.6 (3.7)	^1H:[b] 5.81 (2 H, br m, $C_5\mathit{H}_4Pr^i$), 5.77 (2 H, br m, $C_5\mathit{H}_4Pr^i$), 3.22 (1 H, br m, $C\mathit{H}Me_2$), 1.10 (9 H, s, Bu^t), 0.95 (6 H, d, J = 7, $CH\mathit{Me}_2$)
6 $[Mo(\eta\text{-}C_5H_4Me)Cl_3(NBu^t)]$ C, 35.2 (34.1); H, 4.9 (4.6); N, 4.0 (4.0)	^1H:[b] 6.66 (2 H, br m, $C_5\mathit{H}_4Me$), 6.31 (2 H, br m, $C_5\mathit{H}_4Me$), 2.47 (3 H, s, $C_5H_4\mathit{Me}$), 1.56 (9 H, s, Bu^t)
7 $[\{MoCl_3(\mu\text{-}Cl)(NBu^t)\}_2]$ C, 15.5 (15.5); H, 3.0 (2.9); N, 4.4 (4.5)	^1H:[b] 1.90 (s, Bu^t) $^{13}C\text{-}\{^1H\}$ DEPT:[b] 27.8 (Bu^t)
8, **9** *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_4Me)(NBu^t)(\mu\text{-}NBu^t)\}_2]$[c] C, 52.7 (53.0); H, 8.1 (7.9); N, 8.7 (8.8)	**8**, ^1H:[b] 6.09 (4 H, virtual t, J = 2.3, $C_5\mathit{H}_4Me$), 5.03 (4 H, virtual t, J = 2.3, $C_5\mathit{H}_4Me$), 2.19 (6 H, s, $C_5H_4\mathit{Me}$), 1.89 (18 H, s, $\mu\text{-}NBu^t$), 0.93 (18 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$:[b,d] 104.1, 99.4 (2CH of C_5H_4Me), 35.8($\mu\text{-}NC\mathit{Me}_3$), 32.0 ($C\mathit{Me}_3$), 17.0 ($C_5H_4\mathit{Me}$) **9**, ^1H:[b] 5.60 (8 H, br m, $C_5\mathit{H}_4Me$), 1.94 (6 H, s, $C_5H_4\mathit{Me}$), 1.80 (18 H, s, $\mu\text{-}NBu^t$), 1.02 (18 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$:[b,d] 102.5, 100.1 (2CH of C_5H_4Me), 35.8 ($\mu\text{-}NC\mathit{Me}_3$), 31.8 ($C\mathit{Me}_3$), 16.0 ($C_5H_4\mathit{Me}$)
10 $[\{Mo(\eta\text{-}C_5H_4Me)O(\mu\text{-}NBu^t)\}_2]$[e] C, 45.5 (45.8); H, 6.1 (6.15); N, 5.2 (5.3)	^1H:[b] 6.37, 4.37 (2 × 4 H, 2 × virtual t, $C_5\mathit{H}_4Me$), 2.22 (6 H, s, $C_5H_4\mathit{Me}$), 1.77 (18 H, s, Bu^t)
12 $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_2H_4)Me(NBu^t)]$ C, 53.6 (54.0); H, 8.1 (8.0); N, 4.75 (4.8)	^1H:[b] 5.30, 5.26, 4.90, 4.72 (4 × 1 H, 4 × virtual q, J = 2.5, $C_5\mathit{H}_4Me$), 2.35, 1.98, 1.82 (3 × 1 H, 3 × m, C_2H_4), 1.51 (3 H, s, $C_5H_4\mathit{Me}$), 1.26 (3 H, s, MoMe), 1.12 (1 H, m, C_2H_4), 0.89 (9 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$ DEPT:[b] 100.8, 100.1, 96.2, 95.0 (4CH of C_5H_4Me), 39.0, 28.0 ($2C_2H_4$), 29.6 ($C\mathit{Me}_3$), 13.5 ($C_5H_4\mathit{Me}$), −0.8 (MoMe)
14 $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_2H_4)Ph(NBu^t)]$ C, 63.2 (60.5),[f] H, 6.8 (6.9); N, 3.5 (4.15)	^1H:[b] 7.74 (2 H, d, J = 6.8), *o*-H of Ph, 7.46 (1 H, d, J = 6.8, *p*-H of Ph), 7.32–7.10 (2 H, partially obscured m, *m*-H of Ph), 5.17 (5 H, s, C_5H_5), 2.63, 2.39, 2.07 (3 × 1 H, 3 × m, C_2H_4), 1.41 (1 H, m, C_2H_4), 0.86 (9 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$ DEPT:[b,d] 142, 129, 127, 126, 122 (C_6H_5), 99.8 (C_5H_5), 45.14 (overlapping $2C_2H_4$), 29.6 ($C\mathit{Me}_3$)
15, **15d** $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_2H_4)(H\text{ or }D)(NBu^t)]$ C, 47.9 (52.4);[g] H, 7.2 (7.7); N, 5.1 (5.1)	**15**, ^1H:[b] 5.19, 5.16, 5.06, 5.01 (4 × 1 H, 4 × br m, $C_5\mathit{H}_4Me$), 2.38, 1.98 (2 × 1 H, 2 × m, C_2H_4), 1.46 (3 H, s, $C_5H_4\mathit{Me}$), 1.24 [2 H, overlapping 2 × m, C_2H_4), 0.95 (9 H, s, Bu^t), 0.08 (1 H, br s, MoH) $^{13}C\text{-}\{^1H\}$ DEPT:[b] 96, 95, 92, 89 (4 × CH of C_5H_4Me), 31 ($C\mathit{Me}_3$), 24, 18 ($2C_2H_4$), 14 ($C_5H_4\mathit{Me}$) **15d**, ^1H:[b] identical to that of **15** ^2H (C_6H_6): 2.26, 1.87 (2 × 1 D, 2 × br m, $C_2H_nD_{4\text{-}n}$), 1.18 (2 D, br m, $C_2H_nD_{4\text{-}n}$), 0.07 (1 D, br s, MoD)
16 $[Mo(\eta\text{-}C_5H_4Me)(PMe_3)Cl(NBu^t)]$[h] C, 43.4 (43.65); H, 6.9 (7.0); N, 3.85 (3.9)	^1H:[b] 5.52, 5.47, 4.06, 3.96 (4 × 1 H, 4 × virtual q, J = 2.0, $C_5\mathit{H}_4Me$), 1.74 (3 H, s, $C_5H_4\mathit{Me}$), 1.30 (9 H, s, Bu^t), 1.11 (9 H, d, $^2J_{HP}$ = 9.2, PMe_3) $^{13}C\text{-}\{^1H\}$ DEPT:[b] 99.6, 87.2, 86.5, 81.8 (4CH of C_5H_4Me), 31.2 ($C\mathit{Me}_3$), 19.6 (d, $^1J_{CP}$ = 27.3, PMe_3), 15.4 ($C_5H_4\mathit{Me}$) $^{31}P\text{-}\{^1H\}$:[b] 12.9 (PMe_3)
17 $[Mo(\eta\text{-}C_5H_4Me)(PMe_3)Me(NBu^t)]$[i] C, 48.8 (49.85); H, 8.1 (8.4); N, 4.3 (4.15)	^1H:[b] 5.18, 5.12, 4.52, 3.86 (4 × 1 H, 4 × br m, $C_5\mathit{H}_4Me$), 1.72 (3 H, s, $C_5H_4\mathit{Me}$), 1.29 (9 H, s, Bu^t), 1.09 (9 H, d, $^2J_{HP}$ = 8.1, PMe_3), 0.38 (3 H, d, $^2J_{HP}$ = 5.9, MoMe) $^{13}C\text{-}\{^1H\}$ DEPT:[b] 96.7, 84.3, 84.0, 83.6 (4CH of C_5H_4Me), 32 ($C\mathit{Me}_3$), 29.6 ($C_5H_4\mathit{Me}$), 21.4 (d, $^1J_{CP}$ = 24.3, PMe_3), MoMe not observed $^{31}P\text{-}\{^1H\}$:[b] 19.4 (PMe_3)
18 or **19** $[Mo(\eta\text{-}C_5H_4Me)(PMe_3)_2(NBu^t)]^+\ Cl^-$ or BF_4^- **18**: C, 43.4 (44.3);[k] H, 7.7 (7.9); N, 3.1 (3.2) **19**: C, 39.5 (38.9); H, 7.7 (7.1); N, 2.85 (2.8)	**18**, ^1H:[j] 5.56, 4.93 (2 × 2 H, 2 × br m, $C_5\mathit{H}_4Me$), 2.10 (3 H, s, $C_5H_4\mathit{Me}$), 1.63 (18 H, d, $^2J_{HP}$ = 8.6, PMe_3), 1.28 (9 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$ DEPT:[j] 95.1, 94.6 (2CH of C_5H_4Me), 31.7 ($C\mathit{Me}_3$), 24.0 (five-line pattern, apparent J_{CP} = 13, PMe_3), 16.1 ($C_5H_4\mathit{Me}$) $^{31}P\text{-}\{^1H\}$:[b] 11.3 (PMe_3)
21 $[Mo(\eta\text{-}C_5H_4Me)(PMe_2Ph)Cl(NBu^t)]$[l]	^1H:[b] 7.56 (2 H, m, C_6H_5), 7.09 (3 H, m, C_6H_5), 5.49, 5.29, 4.03, 3.94 (4 × 1 H, 4 × m, $C_5\mathit{H}_4Me$), 1.71 (3 H, s, $C_5H_4\mathit{Me}$), 1.62 (3 H, d, $^2J_{HP}$ = 9, PMe), 1.41 (3 H, d, $^2J_{HP}$ = 8, PMe), 1.29 (9 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$ DEPT:[b] 130.8, 129.4, 128.3 (3CH of C_6H_5), 101.6, 87.7, 87.3, 84.0 (4CH of C_5H_4Me), 31.0 ($C\mathit{Me}_3$), 20.3 (d, $^1J_{CP}$ = 27.2. PMe), 16.5 (d, $^1J_{CP}$ = 27.2, PMe), 15.3 ($C_5H_4\mathit{Me}$) $^{31}P\text{-}\{^1H\}$:[b] 24.18 (PMe_2Ph)
23, **24** $[Mo(\eta\text{-}C_5H_4Pr^i)(\eta\text{-}C_3H_5)(NBu^t)]$[m] C, 56.9 (57.1); H, 7.7 (8.0); N, 4.3 (4.4)	**23**, ^1H:[b] 5.46, 4.51 (2 × 2 H, 2 × virtual t, J = 2.4, $C_5\mathit{H}_4Pr^i$), 3.98 [2 H, m, $(C\mathit{H}_aH_b)_2CH$], 2.95 [1 H, m, $(CH_2)_2C\mathit{H}$], 2.43 (1 H, spt, J = 6.9, $C\mathit{H}Me_2$), 1.24 [6 H, d, J = 6.9, $CH\mathit{Me}_2$), 0.92 (9 H, s, Bu^t), 0.45 [2 H, m, $(CH_a\mathit{H}_b)_2CH$] $^{13}C\text{-}\{^1H\}$ DEPT:[b] 93.1, 90.4 (2CH of $\mathit{C}_5H_4Pr^i$), 78.4 [$(CH_2)_2\mathit{C}H$], 43.6 [$(\mathit{C}H_2)_2CH$], 30.7 ($C\mathit{Me}_3$), 28 [$(CH_3)_2\mathit{C}H$], 24.8 ($CH\mathit{Me}_2$) **24**, ^1H:[b] 4.84, 4.41 (2 × 2 H, 2 × virtual t, J = 2.2, $C_5\mathit{H}_4Pr^i$), 3.13 [2 H, m, $(C\mathit{H}_aH_b)_2CH$], 2.33 (1 H, spt, J = 6.9, $C\mathit{H}Me_2$), 2.05 [2 H, m $(CH_a\mathit{H}_b)_2CH$], 1.53 [1 H, m, $(CH_2)_2C\mathit{H}$], 1.17 (6 H, d, J = 6.9, $CH\mathit{Me}_2$), 1.02 (9 H, s, Bu^t)

Table 1 (*continued*)

Compound and analysis (%)	NMR data[a]
25, **26** $[\mathrm{Mo}(\eta\text{-}C_5H_4Me)(\eta\text{-}C_3H_5)(NBu^t)]$[n] C, 48.65 (54.4); H, 6.7 (7.4); N, 4.3 (4.9)	**25**, See ref. 2 **26**, ^1H:[b] 5.22, 4.61 (2 × 2 H, 2 × virtual t, J = 2.3, C_5H_4Me), 3.03 [2 H, m $(CH_aH_b)_2CH$], 2.15 [2 H, m $(CH_aH_b)_2CH$], 1.54 [1 H, m $(CH_2)_2CH$], 1.15 (3 H, s, Me), 1.03 (9 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$ DEPT:[b] 93.2, 84.1 (2CH of C_5H_4Me), 73.6 [$(CH_2)_2CH$], 36.5 [$(CH_2)_2CH$], 30.7 (CMe_3), 13.8 (C_5H_4Me)

[a] Given as: chemical shift (δ) [relative intensity, multiplicity, J/Hz, assignment]. Where required, assignments were confirmed by ^1H–^1H and ^1H–^{13}C shift correlation experiments. [b] In C_6D_6. [c] As a mixture of *cis* and *trans* isomers. IR: ν(Mo=N) 1352 and 1231 cm^{-1}. FAB mass spectrum: the characteristic isotope pattern was observed; data for the peak corresponding to the $^{96}Mo^{97}Mo$ and $^{95}Mo^{98}Mo$ isotope pairs (16.5, 9.5 and 15.7, 23.8% abundance respectively) are m/z 635 (M^+), 620 (M^+ − Me), 578 (M^+ − Bu^t) and 564 (M^+ − NBu^t) [d] Assignments confirmed by a ^{13}C–^1H shift correlation experiment. [e] IR: ν 1262 (Mo=N), 885 cm^{-1} (Mo=O). FAB mass spectrum: m/z 525 (M^+), 510 (M^+ − Me), 468 (M^+ − Bu^t) and 454 (M^+ − NBu^t). [f] The extreme sensitivity of the compound prevented isolation of an analytically pure sample. [g] Satisfactory analysis could not be obtained due to the sensitivity of the compound. IR: ν(Mo=N) 1355 cm^{-1}. [h] IR: ν 1294 (Mo=N), 390 cm^{-1} (Mo–Cl). The characteristic mass spectral isotope pattern was observed; data for the peak corresponding to $^{98}Mo^{35}Cl$ are m/z 359 (M^+), 283 (M^+ − PMe_3), 226 (M^+ − PMe_3 − Bu^t) and 212 (M^+ − PMe_3 − NBu^t). [i] Satisfactory analysis could not be obtained due to the sensitivity of the compound. Mass spectral data corresponding to ^{98}Mo: m/z 339 (M^+), 324 (M^+ − Me) and 309 (M^+ − 2Me). [j] In CD_2Cl_2. [k] Satisfactory analysis could not be obtained due to failure to crystallise the compound. IR: ν(Mo=N) 1357 cm^{-1}. [l] Satisfactory analysis could not be obtained due to failure to crystallise or otherwise purify the compound, which has been partially characterised by NMR and mass spectral data alone. Mass spectrum: m/z 422 (M^+) and 284 (M^+ − PMe_2Ph). [m] A mixture of isomers, see text. NMR assignments confirmed by a ^1H–^1H shift correlation experiment. The characteristic mass spectral isotope pattern was observed; data corresponding to ^{98}Mo are m/z 317 (M^+) and 219 (M^+ − Bu^t − C_3H_5). [n] A mixture of isomers, see text. Satisfactory analysis could not be obtained due to the extreme sensitivity of the compounds.



Scheme 1 (*i*) $LiNHBu^t$ in toluene at 70 °C for 14 h, yield 27%; (*ii*) chromatography on an alumina column, 8%

Table 2 Fractional atomic coordinates for non-hydrogen atoms of $[\{MoCl_3(\mu\text{-}Cl)(NBu^t)\}_2]$ **7** with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Mo(1)	0.190 90(2)	0.042 09(1)	0.061 81(3)
Cl(1)	0.244 58(8)	−0.028 60(5)	−0.229 2(1)
Cl(2)	0.355 43(9)	−0.025 33(6)	0.254 4(1)
Cl(3)	0.089 02(8)	0.091 19(5)	0.353 4(1)
Cl(4)	−0.019 23(7)	0.088 06(4)	−0.121 0(1)
N(1)	0.279 4(2)	0.127 9(2)	0.008 1(4)
C(1)	0.352 4(3)	0.203 4(2)	−0.036 5(5)
C(2)	0.263 8(4)	0.273 9(2)	0.039 9(6)
C(3)	0.369 2(4)	0.207 0(3)	−0.267 0(6)
C(4)	0.496 8(4)	0.198 6(2)	0.080 8(6)

Table 3 Comparison of selected bond length (Å) and angle (°) data

	$[\{MoCl_3(\mu\text{-}Cl)\text{-}(NBu^t)\}_2]$ **7**	$[\{WCl_3(\mu\text{-}Cl)\text{-}(NC_2Cl_5)\}_2]$[5]
M–N	1.680(2)	1.71(2)
$M–Cl_{ax}$	2.294(1), 2.310(1)	2.29*
$M–Cl_{eq}$	2.290(1)	2.25*
$M–(\mu\text{-}Cl_{cis})$	2.456(1)	2.44(1)
$M–(\mu\text{-}Cl_{trans})$	2.727(1)	2.70(1)
M–N–C	178.3(2)	177(2)

* E.s.d. not reported in ref. 5.

was chromatographed on alumina. Elution with light petroleum followed by thf afforded a yellow band, from which a yellow microcrystalline solid **10** was isolated in low yield (8%). The analytical and NMR and FAB mass spectra were consistent with the formulation $[\{Mo(\eta\text{-}C_5H_4Me)O(\mu\text{-}NBu^t)\}_2]$ **10**. Only one of its possible *cis* and *trans* isomers was present, and it is assumed to be the *trans* by analogy with the related arylimido compound $[\{Mo(\eta\text{-}C_5H_4Me)O(\mu\text{-}NPh)\}_2]$,[6] which has been structurally characterised.[8] The latter was also synthesised by hydrolysis during column chromatography of the parent tetraarylimido compound, namely $[\{Mo(\eta\text{-}C_5H_4Me)(NPh)(\mu\text{-}NPh)\}_2]$.

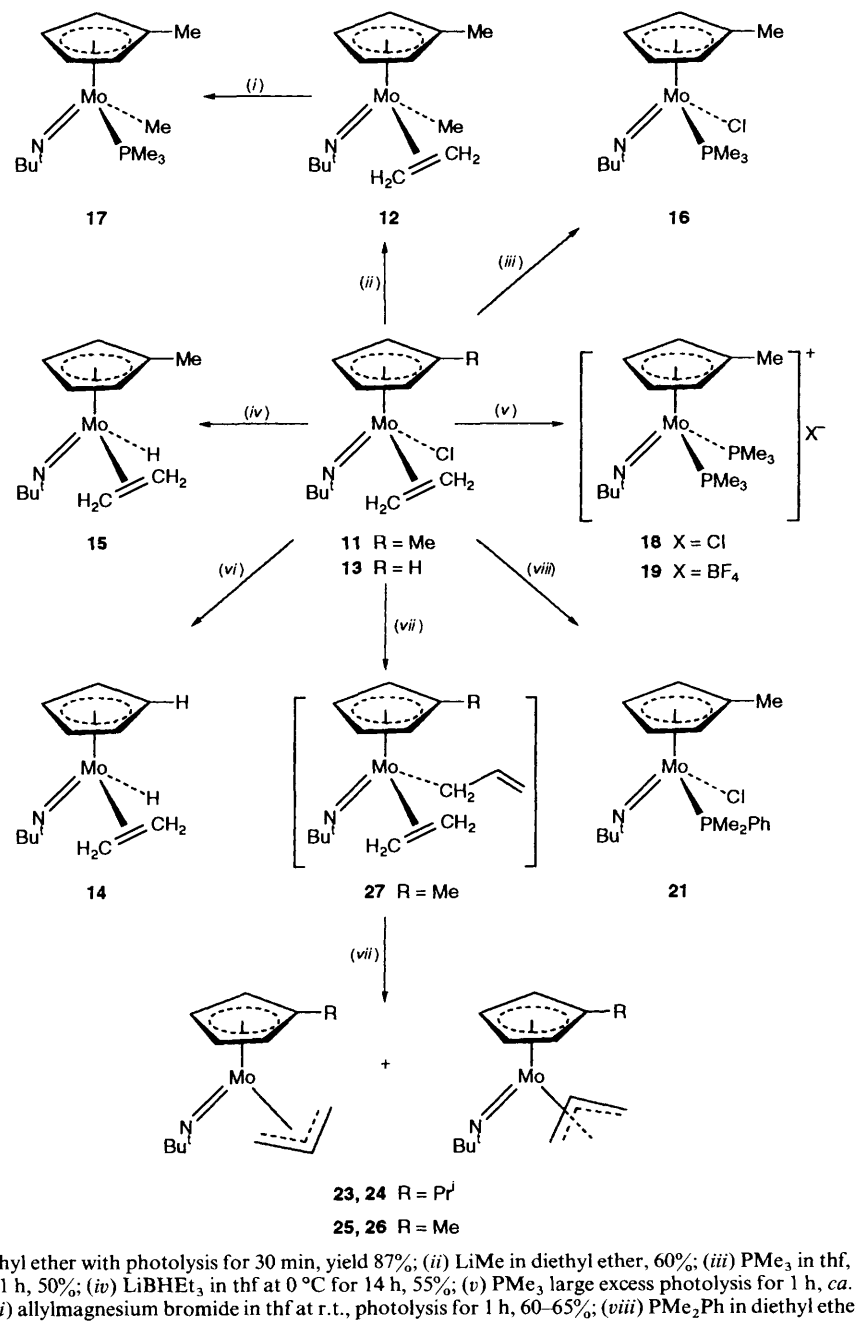
By analogy with the formation of the compounds **8** and **9** from **3** and $LiNHBu^t$, the reaction of $[Mo(\eta\text{-}C_5H_4Me)Cl_2\text{-}$

(NPh)][1] with LiNHPh gave yellow-orange crystals which the ^{1}H NMR spectrum showed to be the known[6] *trans*-[{Mo(η-C_5H_4Me)(NPh)(μ-NPh)}$_2$], in 50% yield.

Treatment of the previously reported[1] compound [Mo(η-C_5H_4Me)(η-C_2H_4)Cl(NBu^t)] **11** with methyllithium in diethyl ether yielded the air- and light-sensitive methyl derivative [Mo(η-C_5H_4Me)(η-C_2H_4)Me(NBu^t)] **12**, as a yellow oil, in *ca.* 60% yield. The ^{13}C-{^{1}H} distortionless enhancement by polarisation transfer (DEPT) NMR spectrum showed a resonance at δ −0.8 assignable to the metal-bound methyl carbon. Photolysis gave ethene (detected by ^{1}H NMR spectroscopy), and intractable products.

Similarly, treatment of the compound [Mo(η-C_5H_5)(η-C_2H_4)Cl(NBu^t)][1] **13** with phenyllithium in diethyl ether afforded the phenyl derivative [Mo(η-C_5H_5)(η-C_2H_4)Ph(NBu^t)] **14**, in *ca.* 25% yield. Compound **14** is extremely air- and moderately light-sensitive; it is soluble in light petroleum, and can be sublimed at (60 °C, 10^{-2} mmHg). The extreme air sensitivity of the compound precluded satisfactory analysis. The ^{1}H and ^{13}C-{^{1}H} DEPT NMR spectra are consistent with the proposed structure, assuming that rotation about the metal–carbon bond of the phenyl group is rapid on the ^{1}H NMR time-scale (three CH resonances for the Ph group) but slow on the ^{13}C time-scale (five CH resonances for the Ph group).

Treatment of compound **11** with lithium triethylhydroborate gave an extremely air-sensitive blue solid [Mo(η-C_5H_4Me)(η-C_2H_4)H(NBu^t)] **15**. The compound was soluble in light petroleum. All attempts to crystallise it failed and sublimation led to partial decomposition. The isolation of a pure sample was not achieved. The ^{1}H NMR spectrum shows resonances assignable to *tert*-butylimido, olefin, and diastereotopic methylcyclopentadienyl groups and a broad resonance at δ 0.08 may be assigned to a Mo–H group. No magnetisation transfer between the hydride peak and the olefinic resonances was observed at room temperature, and heating the sample to 351 K showed no evidence for fluxionality. The ^{13}C-{^{1}H} DEPT NMR spectrum was consistent with the proposed structure (Scheme 2). Treatment of **11** with lithium deuteriotriethylborate afforded the monodeuterio compound [Mo(η-C_5H_4Me)(η-C_2-



Scheme 2 (*i*) PMe$_3$ in diethyl ether with photolysis for 30 min, yield 87%; (*ii*) LiMe in diethyl ether, 60%; (*iii*) PMe$_3$ in thf, photolysis with medium-pressure mercury lamp for 1 h, 50%; (*iv*) LiBHEt$_3$ in thf at 0 °C for 14 h, 55%; (*v*) PMe$_3$ large excess photolysis for 1 h, *ca.* 20%; (*vi*) LiPh in diethyl ether for 2 h at r.t., 25%; (*vii*) allylmagnesium bromide in thf at r.t., photolysis for 1 h, 60–65%; (*viii*) PMe$_2$Ph in diethyl ether, photolysis for 1 h, 45%

$H_4)D(NBu^t)]$ **15d**. The ^1H NMR spectrum featured all of the resonances evident in the spectrum of **15**, indicating that scrambling of deuterium had occurred between the hydride and olefinic hydrogens. This was confirmed by the ^2H NMR spectrum which revealed resonances at chemical shifts identical to those for the ^1H NMR spectrum for the ethylene and hydride groups.

Photolysis of the compound $[Mo(\eta-C_5H_4Me)(\eta-C_2H_4)Cl(NBu^t)]$ **11** in the presence of 1 equivalent of trimethylphosphine gave the compound $[Mo(\eta-C_5H_4Me)(PMe_3)Cl(NBu^t)]$ **16** as a deep red, extremely air-sensitive oil which can be distilled *in vacuo* at 65 °C in *ca.* 50% yield. Similarly, photolysis of the compound $[Mo(\eta-C_5H_4Me)(\eta-C_2H_4)Me(NBu^t)]$ **12** in the presence of trimethylphosphine resulted in substitution of the η-ethene group giving the methyl derivative $[Mo(\eta-C_5H_4Me)(PMe_3)Me(NBu^t)]$ **17**, in 87% yield. Photolysis of **11** in the presence of a large excess (*ca.* 30 equivalents) of trimethylphosphine resulted in displacement of both olefin and chloride ligands and the formation of the bis(phosphine) compound $[Mo(\eta-C_5H_5Me)(PMe_3)_2(NBu^t)]Cl$ **18** which precipitated from the reaction mixture as a pink, air-sensitive solid. Addition of sodium tetrafluoroborate to an aqueous solution of **18** gave red microcrystals of $[Mo(\eta-C_5H_4Me)(PMe_3)_2(NBu^t)]BF_4\cdot 0.5H_2O$ **19**. The cation of **18** and **19** has been crystallographically characterised previously, in the salt $[Mo(\eta-C_5H_4Me)(PMe_3)_2(NBu^t)]^+[C_5H_4Me]^-$ **20**,[9] and the ^1H and ^{31}P NMR spectra of the methylcyclopentadienide salt **20** have bands assignable to the cation which are closely similar to those for **18**.

Photolysis of compound **11** in the presence of 1 equivalent of dimethylphenylphosphine gave $[Mo(\eta-C_5H_4Me)(PMe_2Ph)Cl(NBu^t)]$ **21** as an extremely air-sensitive red oily solid in *ca.* 45% yield. The product was soluble in light petroleum but could not be crystallised. It has been characterised by spectroscopic data only. The EI mass spectrum shows a peak assignable to the molecular ion at *m/z* 422 (for ^{98}Mo) and one at *m/z* 284 assignable to the fragmentation product formed by loss of dimethylphenylphosphine.

Treatment of the compound $[Mo(\eta-C_5H_4Pr^i)(\eta-C_2H_4)Cl(NBu^t)]$ **22**[1] with 1 equivalent of allylmagnesium chloride in tetrahydrofuran, followed by photolysis of the reaction mixture, yielded two isomers of $[Mo(\eta-C_5H_4Pr^i)(\eta-C_3H_5)(NBu^t)]$ **23** and **24**, in *ca.* 65% yield. The relative proportions of the two isomers varied unpredictably, the ratios of **23**:**24** being in the range 60:40 to 80:20. The mixture is an extremely air-sensitive red oil soluble in light petroleum which could be distilled at 30 °C and 10^{-2} mmHg as an analytically pure mixture of the isomers (presumably *endo* and *exo*). The EI mass spectrum of the mixture of **23** and **24** showed a peak at *m/z* 317 assignable to the molecular ion (for ^{98}Mo) and one at 219 *m/z* due to loss of Bu^t and η-allyl moieties. The ^1H and $^{13}C-\{^1H\}$ DEPT NMR spectra showed resonances assignable to *tert*-butylimido, η-allyl, and isopropylcyclopentadienyl (AA'BB' ring proton system) groups (Table 1).

Treatment of compound **11** with 1.2 equivalents of allylmagnesium chloride in thf, followed by photolysis of the reaction mixture, yielded the two isomers $[Mo(\eta-C_5H_4Me)(\eta-C_3H_5)(NBu^t)]$ **25** and **26**, in *ca.* 70% yield. The relative proportions of **25**:**26** varied between *ca.* 60:40 and 90:10. The isomeric mixture was an extremely air-sensitive red oil, soluble in light petroleum. Microanalysis of a distilled sample of the product was unsatisfactory and the mixture has been characterised by spectroscopic data alone. The EI mass spectrum of the mixture shows a peak at *m/z* 289 assignable to the expected molecular ion. The ^1H NMR spectrum shows two sets of resonances attributable to *tert*-butylimido, methylcyclopentadienyl (AA'BB' system for the ring protons) and η-allyl moieties, and the data are consistent with the presence of two isomers which differ in either an *endo* or *exo* orientation of the η-allyl group. Nuclear Overhauser effect (NOE) difference spectroscopy failed to detect through-space interaction between any of the protons of the allyl moiety and protons on the other ligands. Thus it was not possible to assign the two sets of resonances to particular configurations of the molecule. The variable proportions of each isomer formed suggest that the isomer ratio is kinetically controlled. Prolonged photolysis of the mixture (12 h) did not alter the relative proportions of isomers. Examination of the mixture of **11** and allylmagnesium chloride at an intermediate stage of the reaction (before photolysis) showed evidence for the σ-allyl species $[Mo(\eta-C_5H_4Me)(\eta-C_2H_4)(\sigma-C_3H_5)(NBu^t)]$ **27**. This compound could not be separated from **25** and **26** and was characterised by ^1H NMR spectroscopy.[2] Photolysis of a mixture containing **25**–**27** gave rise to a mixture of **25**, **26** and free ethene (according to ^1H NMR spectroscopy).

The structures proposed for the new compounds are shown in the Schemes 1 and 2. To our knowledge there have been no previous reports of examples of isolated molybdenum–imide–allyl complexes akin to **23**,**24** and **25**,**26**. A σ-allyl tris(imido) rhenium complex $[Re(\sigma-C_3H_5)(NBu^t)_3]$ has been reported by Hermann *et al.*[10] A molybdenum–allylimide complex $[Mo(NCH_2CH{=}CH_2)Cl_3(PPh_3)_2]$ has also been described.[11]

The ammoxidation of propylene is a major industrial process.[12] Despite considerable effort the precise details of the mechanism remain obscure. One of the most widely accepted models is that proposed by Grasselli and Burrington,[13] which postulates initial chemisorption of propene on co-ordinatively unsaturated bis(terminal imido)molybdenum centres, followed by formation of an imidoallyl complex, which then undergoes C–N bond formation to yield a N-allyl species (the immediate precursor of acrylonitrile). However, there is evidence which argues against the necessary intermediacy of terminal imido species; in particular, ammoxidation occurs readily using an antimonate catalyst, in which bridging imide ligands are thought to be present.[14] In a model study the formation of a carbon–nitrogen bond has been observed in a homogeneous system by the trapping of benzyl radicals by $[Mo(Me_3SiO)_2(NBu^t)_2]$ subsequently giving $PhCH{=}NBu^t$.[15] We have studied the thermolysis of **23**–**26** and their reactions with trimethylphosphine but have found no evidence for formation of products with C–N bonds.

Experimental

All reactions were performed under an inert atmosphere of dinitrogen using a dual nitrogen/vacuum line. Filtration was achieved either by using such cannulae modified to take a paper- or glass-filter at one end, or by use of a glass frit covered with a bed of oven-dried Celite (Koch-Light). Chromatography was performed on columns of deactivated alumina (6% w/w water) made up in light petroleum (b.p. 40–60 °C) under dinitrogen.

Toluene and diglyme (2,5,8-trioxanonane) were distilled over sodium, tetrahydrofuran and benzene over potassium, diethyl ether and light petroleum over sodium–potassium alloy, dichloromethane over phosphorus pentaoxide and acetonitrile over calcium hydride. Chlorobenzene was dried over activated molecular sieves (4 Å). Dried solvents were stored over activated molecular sieves (4 Å) in flame-dried Young's ampoules, deuteriated solents over such sieves for 1 week prior to use. Microanalyses were either obtained from the microanalytical department of this laboratory, or from Analytische Laboratorien, Engleskirchen, Germany.

Infrared spectra were recorded on Mattson Polaris FTIR, Perkin-Elmer 1710 FTIR, or Perkin-Elmer 457 grating spectrometers. Samples were prepared as pressed CsI discs unless otherwise stated. The NMR spectra were recorded on a Bruker A.M. 300 instrument, ^1H at 300.13 MHz, ^{31}P at 121.6 MHz, ^2H at 46.07 MHz, and ^{13}C at 75.5 MHz. They were referenced internally by using the residual protio solvent resonance (or residual deuterio solvent for ^2H), or by using the instrument's internal calibration system (for ^{31}P). Mass spectra were either measured on an AEI MS 302 spectrometer or were obtained by Dr. Ballantine at the SERC facility at the University of Swansea (for FAB); ESR spectra were recorded on a Varian E 109 instrument.

The compounds [Mo(η-C_5H_4R)Cl_2(NBu^t)] (R = H, Pr^i or Me) and [Mo(η-C_5H_4R)(η-C_2H_4)Cl(NBu^t)] (R = H or Me) were prepared as described previously.[1]

(tert-*Butylimido*)*trichloro*(η-*cyclopentadienyl*)*molybdenum* **4**.—(*tert*-Butylimido)dichloro(η-cyclopentadienyl)molybdenum (1.0 g, 3.3 mmol) in dichloromethane (50 cm^3) was treated with a slow stream of chlorine gas purging for 5 min. The initially yellow-brown solution became reddish yellow and a small quantity of white solid formed. The solution was filtered, solvent was removed under reduced pressure and the yellow solid washed with light petroleum (10 cm^3) and extracted into dichloromethane. The red solution was concentrated and cooled to −20 °C for 1 week. Orange crystals formed which were filtered off and dried *in vacuo*. On removal of the mother-liquor the crystals became yellow, presumably due to elimination of solvent of crystallisation. Attempts to dry them under a stream of nitrogen also led to solvent elimination. Yield 200 mg (18%) [Found (Calc.): C, 31.9 (31.9); H, 4.3 (4.2); N, 4.1 (4.1)%]. The NMR data were the same as those published.[3a]

(tert-*Butylimido*)*trichloro*(η-*isopropylcyclopentadienyl*)*molybdenum* **5**.—(*tert*-Butylimido)dichloro(η-isopropylcyclopentadienyl)molybdenum (500 mg, 1.58 mmol) in dichloromethane (50 cm^3) was treated with a slow stream of chlorine gas purging for 5 min. The initially dark red-brown solution rapidly became reddish yellow. Solvent was removed under reduced pressure and the red oily residue was extracted with chlorobenzene (50 cm^3). Cooling to −20 °C yielded pale yellow microcrystals which were filtered off and dried *in vacuo*. Yield, *ca*. 300 mg (50%).

(tert-*Butylimido*)*trichloro*(η-*methylcyclopentadienyl*)*molybdenum* **6**.—(*tert*-Butylimido)dichloro(η-methylcyclopentadienyl)molybdenum (500 mg, 1.45 mmol) in dichloromethane (100 cm^3) was treated with chlorine for 1 min. The initially deep red-brown solution rapidly became pale yellow. Solvent was removed under reduced pressure and the yellow solid was extracted with toluene (50 cm^3). The yellow extract was cooled to −20 °C. Yellow microcrystals formed and were filtered off, washed with light petroleum (5 cm^3) and dried *in vacuo*. Yield *ca*. 100 mg (18%).

Di-μ-*chloro*-*bis*[(tert-*butylimido*)*trichloromolybdenum*] **7**.—(*tert*-Butylimido)dichloro(η-methylcyclopentadienyl)molybdenum (1.5 g, 4.73 mmol) in dichloromethane (20 cm^3) was treated with a slow stream of chlorine gas by purging for 30 s. The initially red-brown solution became deep red and red microcrystals formed. The solution was filtered and the red filtrate cooled to −20 °C. Red crystals formed which were filtered off, washed with cold dichloromethane (1 cm^3) and dried *in vacuo*. Yield *ca*. 500 mg (35%).

Di-μ-tert-*butylimido*-*bis*[(tert-*butylimido*)(η-*methylcyclopentadienyl*)*molybdenum*] (Mo–Mo) **8** (cis) *and* **9** (trans).—(*tert*-butylimido)dichloro(η-methylcyclopentadienyl)molybdenum (550 mg, 1.73 mmol) in toluene (50 cm^3) was treated with LiNHBu^t (280 mg, 3.58 mmol) in toluene (50 cm^3) at 70 °C for 14 h. The initially dark red-brown solution became yellow and a white precipitate formed. The solution was filtered, solvent was removed under reduced pressure and the yellowish residue was extracted with light petroleum (50 cm^3). The yellow extract was cooled to −20 °C. Brown crystals formed which were filtered off, washed with cold light petroleum (3 × 3 cm^3) and dried *in vacuo*. Yield 150 mg (27%). Final purification was effected by sublimation (10^{-2} mmHg, *ca*. 100 °C) yielding a yellow solid. Separation of the two isomers could not be achieved.

Di-μ-tert-*butylimido*-*bis*[(η-*methylcyclopentadienyl*)*oxomolybdenum*] (Mo–Mo) **10**.—(*tert*-Butylimido)dichloro(η-methylcyclopentadienyl)molybdenum (505 mg, 1.59 mmol) in toluene (25 cm^3) was treated with LiNHBu^t (255 mg, 3.26 mmol) in toluene (50 cm^3) at 50 °C for 24 h. The initially red-brown solution became yellow and a white precipitate formed. The solution was decanted, solvent was removed under reduced pressure and the greenish yellow solid extracted with light petroleum (50 cm^3). The solution was concentrated and chromatographed on an alumina column. Elution with light petroleum produced red and yellow bands on the column. However, the material appeared to hydrolyse whilst still on the column and a yellow band was eluted with thf. Solvent was removed under reduced pressure yielding compound **10** as yellow microcrystals which were washed with light petroleum (5 cm^3) and dried *in vacuo*. Yield 35 mg (8%).

Di-μ-*phenylimido*-*bis*[η-*methylcyclopentadienyl*)(*phenylimido*)*molybdenum*](Mo–Mo).—Dichloro(η-methylcyclopentadienyl)(phenylimido)molybdenum (0.43 g, 1.28 mmol) in toluene (50 cm^3) was treated with LiNHPh (0.25 g, 2.53 mmol) in toluene–thf (1 : 1, 50 cm^3) at 60 °C for 24 h. The initially red-brown solution became deep yellow. Solvent was removed under reduced pressure and the dark yellow solid washed with light petroleum (50 cm^3) and extracted with toluene (50 cm^3). The extract was cooled to −20 °C. Orange crystals formed which were filtered off, washed with cold toluene (2 × 1 cm^3), light petroleum (5 cm^3) and dried *in vacuo*. Yield *ca*. 250 mg (50%). The product was identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[6]

(tert-*Butylimido*)(η-*ethene*)*methyl*(η-*methylcyclopentadienyl*)*molybdenum* **12**.—(*tert*-Butylimido)chloro(η-ethene)(η-methylcyclopentadienyl)molybdenum (60 mg, 0.19 mmol) in diethyl ether (50 cm^3) was treated with methyllithium (0.15 cm^3 of a 1.4 mol dm^{-3} solution in diethyl ether, 1 equivalent) in diethyl ether (20 cm^3) with stirring. The initially yellow solution rapidly became green and a white precipitate formed. The solvent was removed under reduced pressure and the greenish yellow solid was extracted with light petroleum (50 cm^3). Solvent was removed under reduced pressure and the product purified by sublimation (10^{-2} mmHg, 40 °C) to yield a yellow, viscous, highly air- and moderately light-sensitive oil. Yield *ca*. 40 mg (60%).

(tert-*Butylimido*)(η-*cyclopentadienyl*)(η-*ethene*)*phenylmolybdenum* **14**.—(*tert*-Butylimido)chloro(η-cyclopentadienyl)(η-ethene)molybdenum (110 mg, 0.37 mmol) in diethyl ether (30 cm^3) was treated with phenyllithium (0.37 cm^3 of a 1.9 mol dm^{-3} solution, 0.37 mmol) in diethyl ether. The mixture was stirred for 2 h at room temperature (r.t.). The initially yellow-orange solution darkened and a pale precipitate formed. The solution was filtered and the solvent removed under reduced pressure yielding a dark yellow oily solid. The product was extracted with light petroleum (30 cm^3) and solvent was removed under reduced pressure. Sublimation (10^{-2} mmHg, *ca*. 100 °C) yielded a red, oily solid. Yield *ca*. 30 mg (25%). The extreme sensitivity of the compound prevented isolation of an analytically pure sample.

(tert-*Butylimido*)(η-*ethene*)*hydrido*(η-*methylcyclopentadienyl*)*molybdenum* **15**.—(*tert*-Butylimido)chloro(η-ethene)(η-methylcyclopentadienyl)molybdenum (200 mg, 0.65 mmol) in thf (50 cm^3) was treated with LiBHEt$_3$ (0.65 cm^3 of a 1.0 mol dm^{-3} solution in thf, 0.65 mmol) at 0 °C with stirring. The mixture was stirred for 14 h. The initially orange solution became deep blue. Solvent was removed under reduced pressure yielding an *extremely* air- and water-sensitive blue oily solid. Extraction with light petroleum yielded a dark blue solution. However, crystallisation could not be induced. Final purification was attempted by sublimation (15 °C, 10^{-2} mmHg), accompanied by some decomposition. Yield *ca.* 100 mg (55%).

(tert-*Butylimido*)*deuterido*(η-*ethene*)(η-*methylcyclopentadienyl*)*molybdenum* **15d**.—(*tert*-Butylimido)chloro(η-ethene)(η-methylcyclopentadienyl)molybdenum (100 mg, 0.33 mmol) in thf (50 cm^3) was treated with $LiBDEt_3$ (0.35 cm^3 of 1.0 mol dm^{-3} solution in thf, 0.35 mmol). The initially orange solution rapidly became blue-green. Solvent was removed under reduced pressure affording a blue solid, which was extracted with light petroleum (50 cm^3). Solvent was removed under reduced pressure yielding a blue oily solid. Yield *ca.* 50 mg (55%).

(tert-*Butylimido*)*chloro*(η-*methylcyclopentadienyl*)(*trimethylphosphine*)*molybdenum* **16**.—(*tert*-Butylimido)chloro(η-ethene)(η-methylcyclopentadienyl)molybdenum (50 mg, 0.16 mmol) in thf (30 cm^3) was treated with trimethylphosphine (20 µl, 0.19 mmol). The mixture was photolysed for 1 h. The initially yellow-orange solution became deep red. Volatiles were removed under reduced pressure and the product sublimed (10^{-2} mmHg, 130 °C) as a red oily solid. Yield *ca.* 30 mg (50%).

(tert-*Butylimido*)*methyl*(η-*methylcyclopentadienyl*)(*trimethylphosphine*)*molybdenum* **17**.—(*tert*-Butylimido)(η-ethene)methyl(η-methylcyclopentadienyl)molybdenum (*ca.* 50 mg, 0.17 mmol, freshly prepared and sublimed) in diethyl ether (30 cm^3) was treated with trimethylphosphine (20 µl, 0.19 mmol) and the mixture was photolysed for 30 min. The initially yellow-orange solution became dark red. Solvent was removed under reduced pressue and the residue sublimed (10^{-2} mmHg, 60 °C) as a red oil. Yield *ca.* 50 mg (87%).

(tert-*Butylimido*)(η-*methylcyclopentadienyl*)*bis*(*trimethylphosphine*)*molybdenum Chloride* **18** *and Tetrafluoroborate* **19**.—(*tert*-Butylimido)chloro(η-ethene)(η-methylcyclopentadienyl)molybdenum (100 mg, 0.32 mmol) in diethyl ether (40 cm^3) was treated with trimethylphosphine (*ca.* 1 cm^3, 10 mmol). The mixture was photolysed for 1 h. The initially yellow-orange solution became colourless and a pink precipitate formed. Volatiles were removed under reduced pressure yielding a pink solid **18**, which was extracted into dichloromethane, forming a red solution. The solution was concentrated under reduced pressure and cooled giving a red solid. However, all attempts to induce crystallisation failed. The product in water was treated with aqueous sodium tetrafluoroborate. Red microcrystals of **19** formed which were filtered off, washed with water (1 cm^3) and dried *in vacuo*. Yield *ca.* 20%.

(tert-*Butylimido*)*chloro*(*dimethylphenylphosphine*)(η-*methylcyclopentadienyl*)*molybdenum* **21**.—(*tert*-Butylimido)chloro(η-ethene)(η-methylcyclopentadienyl)molybdenum (50 mg, 0.16 mmol) in diethyl ether (50 cm^3) was treated with dimethylphenylphosphine (40 µl, 0.4 mmol). The mixture was photolysed for 1 h. Solvent was removed under reduced pressure. Partial crystallisation occurred; however, all attempts to recrystallise the product (which could not be sublimed) failed. Yield *ca.* 30 mg (45%).

Isomers of (η-*Allyl*)(tert-*butylimido*)(η-*isopropylcyclopentadienyl*)*molybdenum* **23** *and* **24**.—(*tert*-Butylimido)chloro(η-ethene)(η-isopropylcyclopentadienyl)molybdenum (250 mg, 0.74 mmol) in thf (50 cm^3) was treated with allylmagnesium bromide (0.62 cm^3 of a 1.2 mol dm^{-3} solution in thf, 0.74 mmol). The mixture was photolysed for 1 h and the initially yellow-orange solution became deep red. Volatiles were removed under reduced pressure and the residue was extracted with light petroleum. Filtration, removal of solvent under reduced pressure and sublimation (10^{-2} mmHg, 40 °C) afforded the product as a red oil, consisting of a mixture of two isomers (*ca.* 2:1). Yield *ca.* 150 mg (65%).

(η-*Allyl*)(tert-*butylimido*)(η-*methylcyclopentadienyl*)*molybdenum* **25** *and* **26** *and* (σ-*Allyl*)(tert-*butylimido*)(η-*ethene*)(η-*methylcyclopentadienyl*)*molybdenum* **27**.—(*tert*-Butylimido)chloro(η-ethene)(η-methylcyclopentadienyl)molybdenum (250 mg, 0.81 mmol) in thf (50 cm^3) was treated with allylmagnesium chloride (0.5 cm^3 of a 2 mol dm^{-3} solution in thf, 1 mmol). The mixture was refluxed for 15 min. The initially yellow-orange solution became dark red. Solvent was removed under reduced pressure and the red solid extracted with light petroleum (50 cm^3). Solvent was removed under reduced pressure and the products sublimed (10^{-2} mmHg, 30 °C) as a red oil, being a *ca.* 1:1 mixture of compound **27** and isomers **25** and **26**. The isomers were formed in variable proportions (NMR spectroscopy). Yield *ca.* 150 mg (64%). An analytically pure mixture of the isomers was obtained in *ca.* 70% yield by photolysing the above reaction mixture for 30 min followed by distillation.

Crystal Structure Determination of $[\{MoCl_3(\mu\text{-}Cl)(NBu^t)\}_2]$ **7**.—*Crystal data.* $C_8H_{18}Cl_8Mo_2N_2$, $M = 617.75$, crystal size = 0.2 × 0.4 × 0.4 mm, monoclinic, space group $P2_1/n$, $a = 9.698(2)$, $b = 16.269(2)$, $c = 6.540(2)$ Å, $\beta = 91.29(2)°$, $U = 1031.6$ Å^3, $Z = 2$, $D_c = 1.99$, $\mu = 22.28$ cm^{-1}, $F(000) = 600$, Mo-Kα ($\lambda = 0.710\,69$ Å), $2 < 2\theta < 52°$, scan mode ω–2θ, total unique data 2019, observations [$I > 3\sigma(I)$] 1661, variables 92, observations/variables 18.1, Chebyshev parameters 9.66, −6.11, 7.14, $R_{merge} = 0.031$, $R = 0.024$, $R' = 0.028$.

A crystal of compound **7** was sealed in a Lindemann glass capillary under N_2 and transferred to the goniometer head of an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters were calculated from the setting angles of 25 reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The data were corrected for Lorentz and polarisation effects and an empirical absorption correction[16] based on azimuthal scan data was applied. Equivalent reflections were merged and systematically absent reflections rejected. The tungsten atom positions were determined by direct methods. Subsequent Fourier-difference syntheses revealed the positions of all other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in estimated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (1.3 × the equivalent isotropic thermal parameter of the carbon atom to which they were bonded) and refined riding their supporting carbon atoms. A Chebyshev weighting scheme[17] was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter[18]) in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS suite[19] on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Neutral atom scattering factors were taken from the usual sources.[20]

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

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