Bis(η-cyclopentadienyl)imidomolybdenum Compounds†

Malcolm L. H. Green,* Peter C. Konidaris, Despo M. Michaelidou and Philip Mountford
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

The mono(η-cyclopentadienyl)imide compounds $[Mo(\eta\text{-}C_5H_4R)(NR')Cl_2]$ (R, R' = H, R''; Me, Pr^i; Me, R''; or Pr^i, R''; R'' = $C_6H_3Me_2$-2,6) and the new bis(η-cyclopentadienyl)imide compounds $[Mo(\eta\text{-}C_5H_4R)_2(NR')]$ (R, R' = Me, Bu^t; H, Bu^t; H, Pr^i; H, Ph; H, R''; Me, Pr^i; Me, Ph; Me, R''; Pr^i, Bu^t; or Pr^i, R''), $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Pr^i)(NBu^t)]$, $[Mo(\eta^3\text{-}C_9H_7)(\eta\text{-}C_5H_4Pr^i)(NBu^t)]$ and $[Mo(\eta\text{-}C_5H_4Me)_2Me(NBu^t)]X$ (X = I or BF_4) have been prepared. The salt $[Mo(\eta\text{-}C_5H_4Me)(PMe_3)_2(NBu^t)][C_5H_4Me]$ has also been prepared. The crystal structures of the latter and of $[Mo(\eta\text{-}C_5H_5)_2(NBu^t)]$ have been determined.

We and others have been exploring the chemistry of η-cyclopentadienylimide derivatives of molybdenum and tungsten.[1-22] Here we describe the first examples of bis(η-cyclopentadienyl)imide derivatives of molybdenum. A preliminary report of part of this work has been published.[8]

Results and Discussion

The most convenient route to the compounds $[Mo(\eta\text{-}C_5H_4R)_2(NR')]$ is by treatment of $[Mo(\eta\text{-}C_5H_4R)(NR')Cl_2]$ with the corresponding sodium cyclopentadienide salt $Na[C_5H_4R]$. The ten precursor compounds in the class $[Mo(\eta\text{-}C_5H_4R)(NR')Cl_2]$ **1**–**10** used in this study are specified in Scheme 1; **1**–**3**, **5**, **7** and **10** have been described previously. The new compounds **4**, **6**, **8** and **9** have been prepared by the previously described general reaction (1)[7,16] and characterising data are given in Table 1.

$$[Mo(\eta\text{-}C_5H_4R)Cl_4] + 3NR'H_2 \longrightarrow [Mo(\eta\text{-}C_5H_4R)(NR')Cl_2] + 2NR'H_3Cl \quad (1)$$

The precursor compounds **1**–**10** when treated with 2 equivalents of the appropriate sodium cyclopentadienide reagent $Na[C_5H_4R]$ give the corresponding bis(η-cyclopentadienyl)imidomolybdenum compounds $[Mo(\eta\text{-}C_5H_4R)_2(NR')]$ **11**–**20**, respectively, as shown in Scheme 1. The data characterising the new compounds are given in Table 1 and only selected data are discussed below.

In a typical synthesis, treatment of $[Mo(\eta\text{-}C_5H_5)(NBu^t)Cl_2]$ **1** with 2 equivalents of sodium cyclopentadienide gave red crystals of $[Mo(\eta\text{-}C_5H_5)_2(NBu^t)]$ **11** in 46% yield. Similarly, treatment of $[Mo(\eta\text{-}C_5H_4Me)(NBu^t)Cl_2]$ **5** with 2 equivalents of $Na[C_5H_4Me]$ gave low-melting red-purple crystals of $[Mo(\eta\text{-}C_5H_4Me)_2(NBu^t)]$ **15**. The compounds **11** and **15** were prepared in gram quantities and have been studied in greatest detail.

Compound **15** can also be prepared from the previously described[7,16] $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_2H_4)(NBu^t)Cl]$ **21** by treatment with sodium methylcyclopentadienide in thf, followed by photolysis of the mixture using a medium-pressure mercury lamp. Although the yield from this route was 47%, the precursor **21** is not so readily available as **5**. The compound $[Mo(\eta\text{-}C_5H_5)_2(NBu^t)]$ **11** can also be prepared in low yield (6%) by treatment of the compound $[Mo(\eta\text{-}C_5H_4Pr^i)(\eta\text{-}C_2H_4)(NBu^t)Cl]$ **22** with sodium cyclopentadienide in thf, followed by photolysis. This reaction involves exchange of a co-ordinated $\eta\text{-}C_5H_4Pr^i$ group by a $\eta\text{-}C_5H_5$ ligand.

The crystal structure of compound **11** has been determined and is shown in Fig. 1. Comparison of the ^1H NMR spectra of **11** with those of the homologous compounds **12**–**20** clearly indicates that these latter compounds are isostructural with **11**. Further details of the structure of **11**, including a discussion of the interesting features of the $Mo(\eta\text{-}C_5H_5)_2$ moiety [namely unusually long molybdenum–η-cyclopentadienyl ring centroid (Cp) distances and a low Cp–Mo–Cp angle], have been given elsewhere.[7] Related metal–ligand multiply bonded Group 6 bis(η-cyclopentadienyl) complexes of the type $[M(\eta\text{-}C_5R_5)_2E]$ [M = Mo or W; E = O, S or $P(C_6H_2Bu^t_3\text{-}2,4,6)$] have been described previously.[23-27]

The structure of the compound **11** appears to challenge the 18-electron rule. The near linearity of the imide ligand implies formal sp hybridisation at the nitrogen atom, and, in principle, the donation of four electrons to the Mo. This would result in a formally 20-electron compound. Related compounds with a formal electron count greater than 18 include $[Mo(\eta\text{-}C_5H_5)_2R(NO)]$ (R = alkyl)[28-30] and $[V(\eta\text{-}C_5Me_5)(NC_6H_3Me_2\text{-}2,6)]$[31] and both show substantially distorted metal–η-cyclopentadienyl ring interactions. The molecular-orbital calculations which have been used to investigate the bonding in these systems[31,32] suggest that the 'surplus' electrons are located in orbitals that are essentially ligand based, thus avoiding violation of the eighteen-electron rule.

Similar results have been obtained from calculations on the model compound $[Mo(\eta\text{-}C_5H_5)_2(NH)]$, and are supported by photoelectron spectra of the methyl-substituted compound $[Mo(\eta\text{-}C_5H_4Me)_2(NBu^t)]$ **15**.[7,33] Thus the complexes $[Mo(\eta\text{-}C_5H_4R)_2(NR')]$ possess a ligand-based lone pair which is localised more or less equally on the $\eta\text{-}C_5H_4R$ ligand ring carbons *and* on the imide nitrogen atom. Thus neither the $\eta\text{-}C_5H_4R$ ligands nor the NR' imide group in the complexes $[Mo(\eta\text{-}C_5H_4R)_2(NR')]$ act as formal five- or four-electron donor groups respectively and the bis(η-cyclopentadienyl) complexes are thus 18-electron species.

In addition to the vanadium complex, $[V(\eta\text{-}C_5Me_5)_2(NC_6H_3Me_2\text{-}2,6)]$, other complexes have also been shown to possess imide groups that donate fewer electrons to the metal centre than would be expected from a consideration of formal hybridisation at nitrogen. Examples include $[Os(NC_6H_3Pr^i_2\text{-}2,6)_3]$ (three 3.33-electron donor imide groups)[34,35] and $[Mo_2(\eta\text{-}C_5H_4Me)_2(NPh)_2(\mu\text{-}NPh)_2]$ (four three-electron donor imide groups).[6]

The implied weakening of the metal–ring binding in the complexes $[Mo(\eta\text{-}C_5H_4R)_2(NR')]$ by competition for metal acceptor orbitals by the imide ligand has important consequences for the reactivity of these bis(η-cyclopentadienyl)

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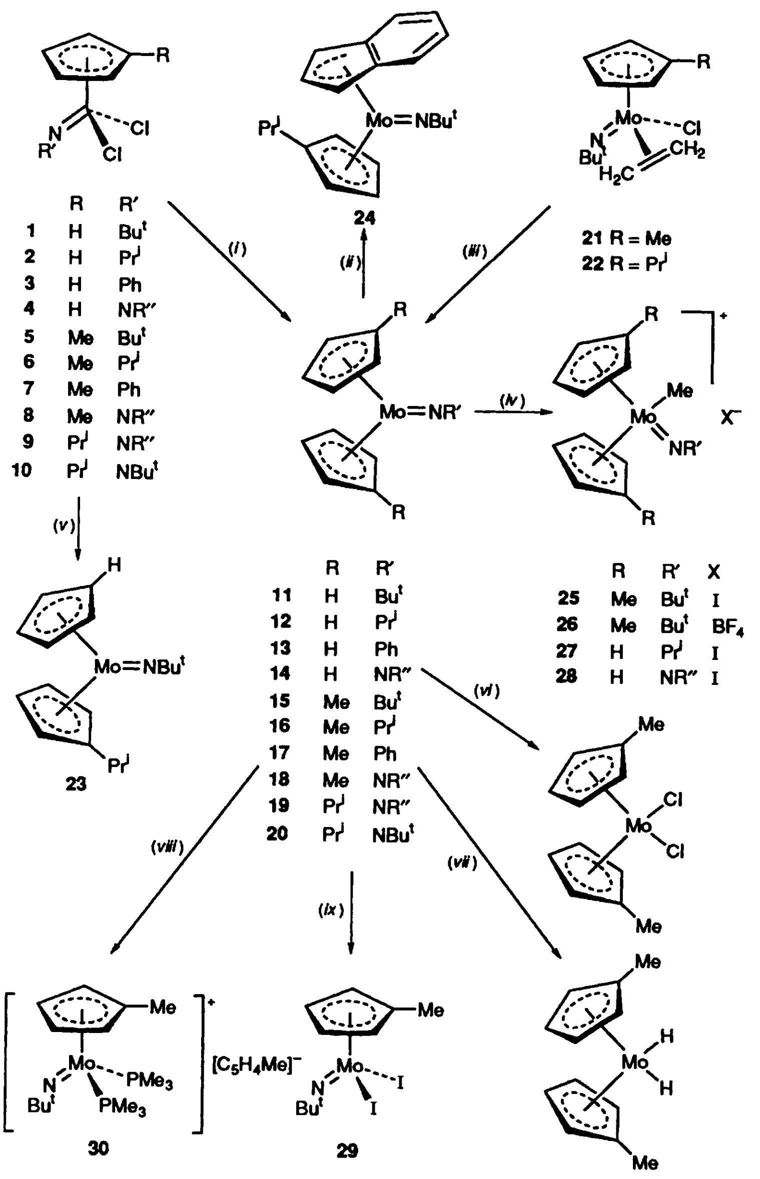
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: mmHg ≈ 133 Pa.



Scheme 1 R'' = $C_6H_3Me_2$-2,6. (*i*) Typically, $Na[C_5H_4R]$ in tetrahydrofuran (thf) at room temperature (r.t.) for 12 h; yields 30–50%; (*ii*) for R = Pr^i, lithium indenide in thf for 1 h, then photolysis for 30 min, 33%; (*iii*) for R' = Pr^i, $Na[C_5H_5]$ in thf at r.t. for 14 h, then photolysis for 1.5 h, 6% **11**; for R = Me, $Na[C_5H_4Me]$ in thf treated as before, 47% **15**; (*iv*) typically, MeI in thf for 10 min–5 h, yields 60–80%; (*v*) for R = Pr^i, R' = NBu^t, $Na[C_5H_5]$ in thf for 2 d, then photolysis for 4 h, 45%; (*vi*) for R = Me, R' = Bu^t, HCl gas for 2 min in thf at −80 °C, 50%; (*vii*) for R = Me, R' = Bu^t, $LiAlH_4$ in thf at r.t. for 14 h, 71%; (*viii*) for R = Me, R' = Bu^t, PMe_3 in thf at r.t. for 5 d, 50%; (*ix*) for R = Me, R' = Bu^t, allyl iodide in thf at r.t. for 2 d, 21%

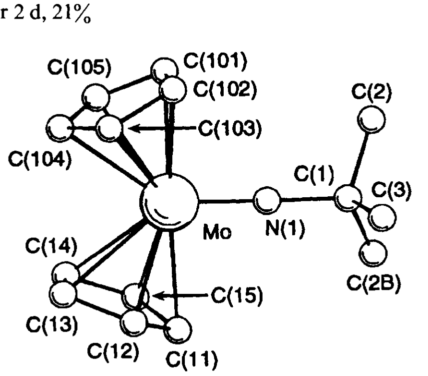


Fig. 1 Crystal structure of $[Mo(\eta\text{-}C_5H_5)_2(NBu^t)]$ **11**. Hydrogen atoms omitted for clarity. Further details given elsewhere[8]

compounds. The formation of the ring-exchanged product **11** is indicative of the inherent substitution lability of the η-cyclopentadienyl rings in this system. Ring exchange has also been demonstrated for the isolated compound **15**. Thus photolysis with 2 equivalents of sodium cyclopentadienide, removal of solvent and extraction of the products with light petroleum yields a mixture of products. The ^1H NMR spectrum of the mixture shows resonances assignable to the starting material **15** and to the doubly ring-exchanged compound **11**.

The cyclic voltammogram of compound **11** displays two irreversible one-electron oxidation waves at −0.49 and −0.19 V relative to the ferrocene–ferrocenium couple. These oxidations are at low potential, and may be tentatively correlated with the low-ionisation-potential bands (assigned to ionisation from the metal d^2 orbital and to the ligand-based lone pair) observed in the gas-phase photoelectron spectrum of **15**.[7]

Treatment of the compound $[Mo(\eta\text{-}C_5H_4Pr^i)(\eta\text{-}C_2H_4)(NBu^t)Cl]$ **22** with 0.9 equivalent of sodium cyclopentadienide in thf, followed by photolysis of the mixture, afforded the mixed-ring compound $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Pr^i)(NBu^t)]$ **23** as a red, extremely air-sensitive oil in 45% yield. This suggests that the

Table 1 Analytical and spectroscopic data

Compound and analysis[a]	NMR[b] and other data
4 [Mo(η-C$_5$H$_5$)(NC$_6$H$_3$Me$_2$-2,6)Cl$_2$] C, 45.0 (44.5); H, 4.0 (4.0); N, 3.9 (4.0) *m/z* 354 (100%), *M*$^+$	
6 [Mo(η-C$_5$H$_4$Me)(NRr^i)Cl$_2$] C, 35.5 (35.7); H, 4.6 (4.7); N, 4.55 (4.6) *m/z* 305 (75%), *M*$^+$	
8 [Mo(η-C$_5$H$_4$Me)(NC$_6$H$_3$Me$_2$-2,6)Cl$_2$] C, 46.3 (46.05); H, 4.55 (4.4); N, 3.7 (3.8) *m/z* 368 (100%), *M*$^+$	
9 [Mo(η-C$_5$H$_4$Pr^i)(NC$_6$H$_3$Me$_2$-2,6)Cl$_2$] C, 49.2 (48.9); H, 5.15 (5.1); N, 3.55 (3.6) *m/z* 397 (3%), *M*$^+$	ESR: *g* = 1.9714 IR (CsI, cm^{-1}): 1586w, 1406w, 1320w, 1032m, 854s, 829m, 779s
11 [Mo(η-C$_5$H$_5$)$_2$(NBu^t)] C, 56.5 (56.6); H, 6.4 (6.4); N, 4.6 (4.7) *m/z* 299 (3%), *M*$^+$	NMR data given elsewhere[8]
12 [Mo(η-C$_5$H$_5$)$_2$(NPr^i)] C, 53.1 (55.1); H, 5.8 (6.05); N, 4.2 (4.95) *m/z* 283 (43%), *M*$^+$	^{1}H: 5.11 (s, 10 H, 2C$_5$H$_5$), 3.46 [spt, 1 H, *J*(H–H), 6.4, C*H*(CH$_3$)$_2$], 0.99 [d, 6 H, *J*(H–H) 6.4, CH(C*H*$_3$)$_2$] ^{13}C-{^{1}H}:[c] 95.0 (s, C$_5$H$_5$), 66.8 [s, *C*H(CH$_3$)$_2$], 24.1 [s, CH(*C*H$_3$)$_2$]
13 [Mo(η-C$_5$H$_5$)$_2$(NPh)] C, 60.35 (60.6); H, 4.8 (4.8); N, 4.0 (4.4) *m/z* 319 (100%), *M*$^+$	^{1}H: 7.10 [t, 2 H, *J*(H–H), 7.8, *m*-H, Ph], 6.72 [t, 1 H, *J*(H–H) 7.3, *p*-H, NPh], 6.64 [d, 2 H, *J*(H–H) 7.6, *o*-H, NPh], 5.06 (s, 10 H, 2C$_5$H$_5$) ^{13}C-{^{1}H}:[c] 160.9 (s, C, NPh), 128.4 (s, CH, NPh), 120.0 (s, CH, NPh), 116.6 (s, CH, NPh), 95.0 (s, C$_5$H$_5$)
14 [Mo(η-C$_5$H$_5$)$_2$(NC$_6$H$_3$Me$_2$-2,6)] C, 62.6 (62.6); H, 5.4 (5.55); N, 4.2 (4.1) *m/z* 347 (97%), *M*$^+$	^{1}H: 7.03 [d, 2 H, *J*(H–H) 7.3, NC$_6$*H*$_3$(CH$_3$)$_2$], 6.73 [t, 1 H, *J*(H–H) 7.5, NC$_6$*H*$_3$(CH$_3$)$_2$], 4.94 (s, 10 H, 2C$_5$H$_5$), 2.37 [s, 6 H, NC$_6$H$_3$(C*H*$_3$)$_2$] ^{13}C:[c] 157.3 [s, C, N*C*$_6$H$_3$(C$_6$H$_3$)$_2$], 122.5 [s, C, N*C*$_6$H$_3$(CH$_3$)$_2$], 120.5 [d, CH, *J*(^{13}C–H) 158, N*C*$_6$H$_3$(CH$_3$)$_2$], 96.1 [d, CH, *J*(^{13}C–H) 176, C$_5$H$_5$], 19.1 [q, CH$_3$, *J*(^{13}C–H) 126, NC$_6$H$_3$(*C*H$_3$)$_2$], one N*C*$_6$H$_3$(CH$_3$)$_2$(CH) signal obscured by C$_6$D$_6$
15 [Mo(η-C$_5$H$_4$Me)$_2$(NBu^t)] C, 58.3 (59.1); H, 6.9 (7.1); N, 4.1 (4.3)	^{1}H (CD$_3$C$_6$D$_5$): 5.17, 4.77 [2 × 2 H, 2 × vt (*J* = 2.3), C$_5$*H*$_4$Me], 1.90 (6 H, s, C$_5$H$_4$*Me*), 1.08 (9 H, s, Bu^t)
16 [Mo(η-C$_5$H$_4$Me)$_2$(NPr^i)][d] *m/z* 327, *M*$^+$; 312, *M*$^+$ − Me; 256, *M*$^+$ − NBu^t	^{1}H: 5.13 [vt, 4 H, *J*(H–H) 2.3, 2MeC$_5$*H*$_4$], 4.96 [vt, 4 H, *J*(H–H) 2.3, 2MeC$_5$*H*$_4$], 3.70 [spt, 1 H, *J*(H–H) 6.4, C*H*(CH$_3$)$_2$], 1.77 (s, 6 H, 2C*H*$_3$C$_5$H$_4$), 1.08 [d, 6 H, *J*(H–H) 6.4, CH(C*H*$_3$)$_2$] ^{13}C:[c] 112.4 (s, C, CH$_3$*C*$_5$H$_4$), 94.7 [d, CH, *J*(^{13}C–H) 172, CH$_3$*C*$_5$H$_4$], 94.0 [d, CH, *J*(^{13}C–H) 173, CH$_3$*C*$_5$H$_4$], 66.3 [d, CH, *J*(^{13}C–H) 133, N*C*H(CH$_3$)$_2$], 24.7 [q, CH$_3$, *J*(^{13}C–H) 128, NCH(*C*H$_3$)$_2$], 16.2 [q, CH$_3$, *J*(^{13}C–H) 127, *C*H$_3$C$_5$H$_4$]
17 [Mo(η-C$_5$H$_4$Me)$_2$(NPh)] C, 61.6 (62.6); H, 5.8 (5.55); N, 3.6 (4.1) *m/z* 346 (24%), *M*$^+$	^{1}H: 7.11 [t, 2 H, *J*(H–H) 7.7, *m*-H, NPh], 6.70 [t, 1 H, *J*(H–H) 7.3, *p*-H, NPh], 6.64 [d, 2 H, *J*(H–H) 7.4, *o*-H, NPh], 5.34 [vt, 4 H, *J*(H–H) 2.1, 2CH$_3$C$_5$*H*$_4$], 4.67 [vt, 4 H, *J*(H–H) 2.3, 2CH$_3$C$_5$*H*$_4$], 1.64 (s, 6 H, 2*C*H$_3$C$_5$H$_4$) ^{13}C-{^{1}H}:[c] 160.2 (s, C, NPh), 128.6 [s, CH, NPh], 119.0 (s, CH, NPh), 115.6 (s, CH, NPh), 115.3 (s, C, CH$_3$*C*$_5$H$_4$), 94.2 (s, CH, CH$_3$*C*$_5$H$_4$), 93.7 (s, CH, CH$_3$*C*$_5$H$_4$), 5.7 (s, *C*H$_3$C$_5$H$_4$)
18 [Mo(η-C$_5$H$_4$Me)$_2$(NC$_6$H$_3$Me$_2$-2,6)] C, 62.4 (64.3); H, 6.1 (6.2); N, 3.8 (3.75) *m/z* 375 (82%), *M*$^+$	^{1}H: 7.05 [d, 2 H, *J*(H–H) 7.4, NC$_6$*H*$_3$(CH$_3$)$_2$], 6.73 [t, 1 H, *J*(H–H) 7.4, NC$_6$*H*$_3$(CH$_3$)$_2$], 5.18 [vt, 4 H, 2CH$_3$C$_5$*H*$_4$], 4.60 (vt, 4 H, CH$_3$C$_5$*H*$_4$), 2.38 [s, 6 H, NC$_6$H$_3$(C*H*$_3$)$_2$], 1.55 (s, 6 H, 2C*H*$_3$C$_5$H$_4$) ^{13}C:[c] 156.7 [s, C, N*C*$_6$H$_3$(CH$_3$)$_2$], 120.5 [s, C, N*C*$_6$H$_3$(CH$_3$)$_2$], 119.6 [d, CH, *J*(^{13}C–H) 157, N*C*$_6$H$_3$(CH$_3$)$_2$], 114.3 [s, C, CH$_3$*C*$_5$H$_4$], 95.4 [d, CH, *J*(^{13}C–H) 175, CH$_3$*C*$_5$H$_4$], 94.6 [d, CH, *J*(^{13}C–H) 175, CH$_3$*C*$_5$H$_4$], 15.2 [q, CH$_3$, *J*(^{13}C–H) 125, NC$_6$H$_3$(*C*H$_3$)$_2$], 9.3 [q, CH$_3$, *J*(^{13}C–H) 127, *C*H$_3$C$_5$H$_4$], one N*C*$_6$H$_3$(CH$_3$)$_2$(CH) signal obscured by C$_6$D$_6$
19 [Mo(η-C$_5$H$_4$Pr^i)$_2$(NC$_6$H$_3$Me$_2$-2,6)] C, 66.4 (67.1); H, 7.2 (7.3); N, 3.25 (3.3) *m/z* 432 (53%), *M*$^+$	^{1}H: 7.04 [d, 2 H, *J*(H–H) 7.4, N(C$_6$*H*$_3$(CH$_3$)$_2$], 6.71 [t, 1 H, *J*(H–H) 7.4, NC$_6$*H*$_3$(CH$_3$)$_2$], 4.89 [vt, 4 H, *J*(H–H) 2.4, 2Pr^{i}C$_5$*H*$_4$], 4.73 [vt, 4 H, *J*(H–H) 2.3, 2Pr^{i}C$_5$*H*$_4$], 2.36 [s, 6 H, NC$_6$H$_3$C*H*$_3$], 2.29 [spt, 2 H, *J*(H–H) 6.9, 2C*H*(CH$_3$)$_2$], 1.10 [d, 12 H, *J*(H–H) 6.8, 2CH(C*H*$_3$)$_2$] ^{13}C:[c] 157.7 [s, C, N*C*$_6$H$_3$(CH$_3$)$_2$], 122.0 [s, C, N*C*$_6$H$_3$(CH$_3$)$_2$], 120.8 (s, C, Pr^i*C*$_5$H$_4$), 119.6 [d, CH, *J*(^{13}C–H) 158, N*C*$_6$H$_3$(CH$_3$)$_2$], 96.4 [d, CH, *J*(^{13}C–H) 165, Pr^i*C*$_5$H$_4$], 94.1 [d, CH, *J*(^{13}C–H) 178, Pr^i*C*$_5$H$_4$], 28.8 [d, CH, *J*(^{13}C–H) 128, *C*H(CH$_3$)$_2$], 23.9 [q, CH$_3$, *J*(^{13}C–H) 126, CH(*C*H$_3$)$_2$] 19.2 [q, CH$_3$, *J*(^{13}C–H) 125, N(*C*H$_3$)$_2$C$_6$H$_3$] ^{13}C-{^{1}H}:[e] 157.4 [s, C, N*C*$_6$H$_3$(CH$_3$)$_2$], 118.6 [d, CH, *J* 158, N*C*$_6$H$_3$(CH$_3$)$_2$], 127.1 [d, CH, *J* 155, N*C*$_6$H$_3$(CH$_3$)$_2$], 122.2 [s, C, N*C*$_6$H$_3$(CH$_3$)$_2$], 120.6 (s, C, Pr^i*C*$_5$H$_4$), 96.6 (d, CH, *J* 174, Pr^i*C*$_5$H$_4$), 93.9 (d, CH, *J* 176, Pr^i*C*$_5$H$_4$), 28.7 [d, CH, *J* 129, *C*H(CH$_3$)$_2$], 23.7 [q, CH$_3$, *J* 126, CH(*C*H$_3$)$_2$], 18.7 [q, CH$_3$, *J* 127, NC$_6$H$_3$*C*H$_3$)$_2$]
20 [Mo(η-C$_5$H$_4$Pr^i)$_2$(NBu^t)]	^{1}H: 5.29 [vt, 4 H, *J*(H–H) 2.5, 2Pr^{i}C$_5$*H*$_4$], 4.30 [vt, 4 H, *J*(H–H) 2.5, 2Pr^{i}C$_5$*H*$_4$], 2.72 [spt, 2 H, *J*(H–H) 6.8, 2C*H*(CH$_3$)$_2$], 1.33 [d, 12 H, *J*(H–H) 6.8, 2CH(C*H*$_3$)$_2$], 1.10 [s, 9 H, C(CH$_3$)$_3$] ^{13}C-{^{1}H}:[c] 116.8 (s, C, Pr^i*C*$_5$H$_4$), 101.1 (s, CH, Pr^i*C*$_5$H$_4$), 91.5 (s, CH, Pr^i*C*$_5$H$_4$), 69.5 [s, *C*(CH$_3$)$_3$], 30.6 [s, C(*C*H$_3$)$_3$], 29.2 [s, *C*H(CH$_3$)$_2$], 5.4 [s, CH(*C*H$_3$)$_2$]
23 [Mo(η-C$_5$H$_5$)(η-C$_5$H$_4$Pr^i)(NBu^t)] C, 59.9 (60.0); H, 7.5 (7.7); N, 4.0 (4.1) *m/z* 341, *M*$^+$; 326, *M*$^+$ − Me; 270, *M*$^+$ − NBu^t	^{1}H: 5.30 [2 H, vt (*J* = 2.3), C$_5$*H*$_4$Pr^i], 5.14 (5 H, s, C$_5$H$_5$), 4.23 [2 H, vt (*J* = 2.3), C$_5$*H*$_4$Pr^i], 2.65 [1 H, spt (*J* = 6.8), C*H*Me$_2$], 1.31 [6 H, d (*J* = 6.8), CH*Me*$_2$], 1.05 (9 H, s, Bu^t) ^{13}C-{^{1}H} DEPT:[c] 101.5 (CH of *C*$_5$H$_4$Pr^i), 95.1 (C$_5$H$_5$), 91.5 (CH of *C*$_5$H$_4$Pr^i), 30.4 (C*Me*$_3$), 29.0 (*C*HMe$_2$), 25.4 (CH*Me*$_2$)
24 [Mo(η^3-C$_9$H$_7$)(η-C$_5$H$_4$Pr^i)(NBu^t)][f] C, 64.6 (64.8); H, 6.9 (7.0); N, 3.5 (3.6) *m/z* 391, *M*$^+$, 376, *M*$^+$ − Me; 320, *M*$^+$ − NBu^t	NMR data given elsewhere[8]
25, **26** [Mo(η-C$_5$H$_4$Me)$_2$Me(NBu^t)]I and BF$_4^-$	
25[g] C, 42.8 (43.7); H, 5.3 (5.6); I, 25.7 (27.1); N, 3.0 (3.0)	**25**, ^{1}H:[e] 6.78, 6.41, 5.67, 5.59 [4 × 2 H, 4 × vq (*J* = 2.3), C$_5$*H*$_4$Me], 2.20 (6 H, s, C$_5$H$_4$*Me*), 1.68 (3 H, s, MoMe), 1.20 (9 H, s, Bu^t) ^{13}C-{^{1}H} DEPT (CD$_2$Cl$_2$): 115.8, 110.0, 108.3, 107.6 (4 × CH of *C*$_5$H$_4$Me), 28.5 (C*Me*$_3$), 14.5 (C$_5$H$_4$*Me*), 10.4 (MoMe)

Table 1 (*contd.*)

Compound and analysis[a]	NMR[b] and other data
26[h] C, 45.95 (47.8); H, 5.95 (6.1); N, 3.2 (3.3)	**26**, ^1H:[e] 6.61, 6.35, 5.60, 5.44 [4 × 2 H, 4 × vq (J = 2.3), C_5H_4Me], 2.18 (6 H, s, C_5H_4Me), 1.67 (3 H, s, MoMe), 1.19 (9 H, s, Bu^t)
27 $[Mo(\eta-C_5H_5)_2Me(NPr^i)]I$ C, 39.2 (39.55); H, 4.9 (4.7); N, 3.1 (3.3)	^1H:[e] 6.35 (s, 10 H, $2C_5H_5$), 4.40 [spt, 1 H, J(H–H) 6.5, $NCH(CH_3)_2$], 1.92 (s, 3 H, MoMe), 1.14 [d, 6 H, J(H–H) 6.4, $NCH(CH_3)_2$] $^{13}C-\{^1H\}$: 112.2 (s, $2C_5H_5$), 74.6 [s, $NCH(CH_3)_2$], 21.5 [s, $NCH(CH_3)_2$], 2.6 (s, MoMe)
28 $[Mo(\eta-C_5H_5)_2Me(NC_6H_3Me_2-2,6)]I$ C, 47.8 (46.8); H, 4.6 (4.55); N, 2.9 (2.9)	^1H:[e] 6.99 [d, 2 H, J(H–H) 7.6, $NC_6H_3(CH_3)_2$], 6.61 [t, 1 H, J(H–H) 7.6, $NC_6H_3(CH_3)_2$], 6.48 (s, 10 H, $2C_5H_5$), 2.27 [s, 6 H, $NC_6H_3(CH_3)_2$], 2.22 (s, 3 H, MoMe)
29 $[Mo(\eta-C_5H_4Me)(NBu^t)I_2]$[i] C, 24.2 (24.0); H, 3.4 (3.2); N, 2.7 (2.8) m/z 502, M^+; 445, $M^+ - Bu^t$; 318, $M^+ - Bu^t - I$; 303, $M^+ - Bu^t - I - Me$	
30 $[Mo(\eta-C_5H_4Me)(PMe_3)_2(NBu^t)][C_5H_4Me]$[j] C, 55.1 (55.3); H, 8.5 (8.65); N, 2.8 (2.9)	^1H:[e] 6.41, 6.34 [2 × 2 H, 2 × vt (J = 2.4), $2C_5H_4Me$], 5.03, 4.57 (2 × 2 H, 2 × br s, $2C_5H_4Me$), 3.09 (3 H, s, C_5H_4Me), 1.72 (3 H, s, C_5H_4Me), 1.29 [18 H, d (J = 9.1), PMe_3], 0.80 (9 H, s, Bu^t) $^{31}P-\{^1H\}$ (C_6D_6):[e] 10.36 (PMe_3)

[a] Given as found (calculated) in %. [b] Given as chemical shift (δ) [relative intensity, multiplicity (J in Hz), assignment]. Where required, assignments were confirmed by $^1H-^1H$ and $^1H-^{13}C$ shift correlation experiments. At 300 MHz, in C_6D_6 unless otherwise indicated. vt = virtual triplet. [c] At 75.5 MHz, in C_6D_6. [d] Satisfactory analysis could not be obtained. IR: ν(M=N) 1353 cm^{-1}. [e] In CD_2Cl_2. [f] IR: ν(M=N) 1358 cm^{-1}. Cyclic voltammogram showed two irreversible one-electron oxidations: $E_{ox1} = -0.61$ and $E_{ox2} = -0.37$ V (both recorded in 0.1 mol dm^{-3} NBu_4PF_6 solution in acetonitrile, relative to ferrocene–ferrocenium. [g] IR: ν(M=N) 1366 cm^{-1}. [h] Satisfactory analysis could not be obtained despite repeated efforts, possibly due to trace contamination with sodium tetrafluoroborate. [i] Cyclic voltammogram (recorded in 0.1 mol dm^{-3} NBu_4PF_6 in thf) gave $E_{ox} = +0.18$ and $E_{red} = -1.31$ V relative to ferrocene–ferrocenium. [j] Synthesised by visiting student Mr. Frank Arnold of the Technical University of Munich. IR: ν(M=N) 1359 cm^{-1}.

ring-exchange reaction implicit in the formation of **11** from **22** proceeds *via* **23**. Treatment of the compound **22** with 1.1 equivalents of lithium indenide in thf, followed by photolysis of the mixture, afforded the product $[Mo(\eta^3-C_9H_7)(\eta-C_5H_4Pr^i)(NBu^t)]$ **24** in 33% yield. This compound, a deep violet-purple extremely air-sensitive solid, was isolated by crystallisation from light petroleum at −20 °C.

The ^1H and $^{13}C-\{^1H\}$ NMR spectra of compound **24** show resonances consistent with the proposed structure with an η^3-indenyl ring. Thus the chemical shifts of the indenyl quaternary carbons (δ 135.8) are comparable with those observed for other indenyl complexes in which the $\eta-C_9H_7$ ligand adopts a η^3 geometry.[36,37] The indenyl ligand is known to adopt readily a trihapto co-ordination mode; by doing so here it relieves the electronic congestion at the molybdenum centre and gives a formal eighteen-electron configuration. Compound **24** can thus be considered to be formally analogous to the η^3-allyl compounds $[Mo(\eta-C_5H_4R)(\eta^3-C_3H_5)(NBu^t)]$ (R = Me or Pr^i).[17] The isoelectronic, related mixed η^5-cyclopentadienyl–η^3-indenyl ring cationic molybdenum complex $[Mo(\eta^3-C_9H_7)(\eta-C_5H_4Pr^i)(CO)_2]^+$ has recently been structurally characterised.[38] Compound **24** can be electrochemically oxidised; cyclic voltammetry shows two irreversible one-electron oxidation waves at −0.61 and −0.37 V.

Treatment of compound **15** with an excess of iodomethane in thf afforded orange, air-stable crystals of $[Mo(\eta-C_5H_4Me)_2Me(NBu^t)]I$ **25** which were soluble in water. The structure of the cationic part of **25** is shown in Fig. 2. Further details of the structure determination have been given elsewhere.[8] The crystal structure confirms that overall methylation occurs at the metal, rather than at the nitrogen lone pair. The spectroscopic data for **25** are also consistent with the solid-state structure observed. The ^1H and $^{13}C-\{^1H\}$ distortionless enhancements of polarisation transfer (DEPT) NMR spectra reveal resonances assignable to *tert*-butylimide, diastereotopic methylcyclopentadienyl and metal–methyl ligands.

Treatment of an aqueous solution of compound **25** with 1 equivalent of sodium tetrafluoroborate in water afforded the BF_4^- salt **26** in 66% yield. The ^1H NMR spectrum is closely similar to that of **25**. The compounds $[Mo(\eta-C_5H_5)_2Me(NPr^i)]I$ **27** and $[Mo(\eta-C_5H_5)_2Me(NC_6H_3Me_2-2,6)]I$ **28** have been prepared by treatment of **12** and **14** respectively with iodomethane and the spectroscopic data suggest they are analogues of **25**. The complexes $[Mo(\eta-C_5H_4R)_2Me(NR')]^+$ are closely related to the Group 5 and 6 bis(η-cyclopentadienyl) complexes $[W(\eta-C_5Me_5)_2Me(O)]^+$ {prepared from $[W(\eta-C_5Me_5)_2O]$ and MeI}, $[Ta(\eta-C_5Me_5)_2H(NR)]$ (R = H, Bu^t or Ph), $[Nb(\eta-C_5H_5)_2X(NBu^t)]$ (X = Me, Cl, Br, C_5H_5-κC or CH_2Ph) and $[M(\eta-C_5H_5)(\eta-C_5Me_5)(NBu^t)Cl]$ (M = Nb or Ta).[39–44]

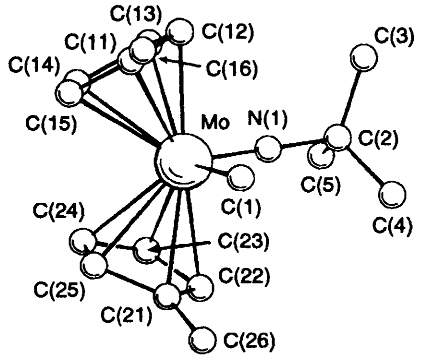


Fig. 2 Crystal structure of the $[Mo(\eta-C_5H_4Me)_2Me(NBu^t)]^+$ cation in compound **25**. Hydrogen atoms omitted for clarity. Further details given elsewhere[8]

In an attempt to co-ordinate an allyl moiety to the metal centre, and possibly induce coupling of the allyl and imide ligands, compound **15** was treated with 1.2 equivalents of allyl iodide in thf. However, only the air-sensitive, paramagnetic (NMR), 17-electron compound $[Mo(\eta-C_5H_4Me)(NBu^t)I_2]$ **29** could be isolated. It is presumably analogous to the structurally characterised compounds of the type $[M(\eta-C_5R_5)(NR')Cl_2]$ (M = V, Nb, Ta, Mo or Re).[16,45–47]

Treatment of compound **15** with trimethylphosphine in a sealed ampoule for 5 d afforded the ionic $[Mo(\eta-C_5H_4Me)(PMe_3)_2(NBu^t)][C_5H_4Me]$ **30**, in *ca.* 70% yield as red, extremely air-sensitive crystals. The crystal structure has been determined and is shown in Fig. 3. Selected bond lengths and angles are given in Table 2 and fractional atomic coordinates for the non-hydrogen atoms in Table 3. We have prepared Cl^- and BF_4^- salts of the cation $[Mo(\eta-C_5H_4Me)(PMe_3)_2(NBu^t)]^+$ recently by an alternative route.[17] The cation $[Mo(\eta-C_5H_4Me)(PMe_3)_2(NBu^t)]^+$ is isolobal with the oxomolybdenum cations $[Mo(\eta-C_5H_5)(PMe_3)_2O]^+$ and $[Mo(\eta-C_5H_5)(dmpe)O]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$, structurally characterised).[48,49] The formation of **30** from **15** and

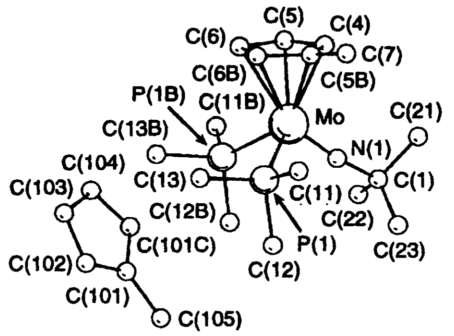


Fig. 3 Crystal structure of $[\mathrm{Mo(\eta\text{-}C_5H_4Me)(PMe_3)_2(NBu^t)}][\mathrm{C_5H_4Me}]$ **30**. Hydrogen atoms omitted for clarity. Atoms labelled 'B' are related to their counterparts by a crystallographic mirror plane at $y = \frac{1}{4}$. Atom C(101C) is related to C(101) by a crystallographic inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

Table 2 Selected bond lengths (Å) and angles (°) for the $[\mathrm{Mo(\eta\text{-}C_5H_4Me)(PMe_3)_2(NBu^t)}]^+$ cation in compound **30** (Cp refers to the computed $\eta\text{-}\mathrm{C_5H_4Me}$ ring carbon centroid)

Mo–N(1)	1.716(9)	Mo–N–C(1)	154.9(5)
Mo–P(1)	2.442(2)	P(1)–Mo–P(1B)	92.8(1)
N–C(1)	1.48(1)	P(1,1B)–Mo–N	95.7(2)
Mo–Cp	2.03	N–Mo–Cp	131.1
		P(1)–Mo–Cp	114.9

Table 3 Fractional atomic coordinates for $[\mathrm{Mo(\eta\text{-}C_5H_4Me)(PMe_3)_2(NBu^t)}][\mathrm{C_5H_4Me}]$ **30**

Atom	*x*	*y*	*z*
Mo	0.264 87(9)	0.250 0	0.945 76(8)
P(1)	0.309 6(2)	0.151 6(1)	0.781 2(2)
N	0.469(1)	0.254 6(1)	1.088(1)
C(1)	0.627(2)	0.276 0(5)	1.223(1)
C(4)	0.100(2)	0.250 0	1.094(1)
C(5)	0.054(1)	0.311 3(3)	1.008(1)
C(6)	−0.032 1(8)	0.289 7(5)	0.850(1)
C(7)	0.058(2)	0.389 4(5)	1.071(2)
C(11)	0.280(2)	0.058 4(3)	0.837(1)
C(12)	0.524(1)	0.150 6(9)	0.778(2)
C(13)	0.178(1)	0.148 0(5)	0.575 2(6)
C(21)	0.577(2)	0.273 8(8)	1.369(1)
C(22)	0.695(2)	0.353 6(7)	1.200(2)
C(101)	0.544 8(5)	0.473 3(1)	0.468 1(4)
C(102)	0.418(1)	0.442 4(3)	0.322 7(5)
C(103)	0.250 0(9)	0.477 0(5)	0.296 4(7)
C(104)	0.273 2(5)	0.529 3(4)	0.426(1)
C(105)	0.733 3(9)	0.451 2(6)	0.543(1)

$\mathrm{PMe_3}$ under such mild conditions also supports the view that the metal–η-cyclopentadienyl ring bonding in the bis(η-cyclopentadienyl) complexes **11**–**20** is weakened by the imide ligand.

Removal of the imide ligand may be effected by treatment of, for example, compound **15** in thf at −80 °C with hydrogen chloride gas giving $[\mathrm{Mo(\eta\text{-}C_5H_4Me)_2Cl_2}]$[24,50] in 50% yield. Treatment of compound **15** with an excess of lithium aluminium hydride in diethyl ether again led to cleavage of the metal–nitrogen bond and formation of the dihydride $[\mathrm{Mo(\eta\text{-}C_5H_4Me)_2H_2}]$,[50] in 71% yield.

Conclusion

We have demonstrated the facile synthesis of the first bis(η-cyclopentadienyl)molybdenum imide complexes, $[\mathrm{Mo(\eta\text{-}C_5H_4R)_2(NR')}]$, and their mixed-ring analogues. Preliminary studies have shown that the metal–η-cyclopentadienyl ring bonding in these complexes is weakened by strong π donation from the imide nitrogen atom. These complexes promise to demonstrate an interesting reaction chemistry and further studies are in progress.

Experimental

Where necessary, reactions were performed under an inert atmosphere of dinitrogen using a dual nitrogen/vacuum line. Reactions were performed in Schlenk vessels, sealed at the B24 cone by rubber Suba-Seals, or glass caps. Liquids were transferred through stainless-steel cannulae (diameter 0.5–2 mm) by an excess of dinitrogen pressure. 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) or Kieselguhr.

Toluene was distilled from over sodium, tetrahydrofuran from over potassium, and diethyl ether and light petroleum (b.p. 40–60 °C) from over sodium–potassium alloy. Distillation was conducted under dinitrogen. Dried solvents were stored over activated molecular sieves (4 Å) in flame-dried Young's ampoules. Solvents were degassed prior to use by repeated pumping and admission of dinitrogen. Deuteriated solvents were stored over molecular sieves (4 Å) for 1 week prior to use. Microanalyses were either obtained from the microanalytical department of this department, or from Analytische Laboratorien, Engelskirchen, Germany.

Infrared spectra were recorded on either Mattson 'Polaris' Fourier-transform, Perkin-Elmer 1710 Fourier-transform or Perkin-Elmer 457 grating spectrometers. Samples were prepared as pressed CsI discs unless otherwise stated. The NMR spectra were recorded on a Bruker AM 300 instrument, ^{1}H at 300, ^{31}P at 121.6 and ^{13}C at 75.5 MHz. They were referenced internally by using the residual protio solvent resonance, solvent resonance (^{13}C) or by using the standard Brüker software SR command (for ^{31}P, relative to trimethyl phosphate in $\mathrm{D_2O}$). Mass spectra were either measured on an AEI MS 302 spectrometer or obtained by Dr. Ballantine at the SERC facility at the University of Swansea (for FAB) ESR spectra on a Varian E 109 instrument. Cyclic voltammograms were measured using an Oxford Instruments potentiostat connected to a Rikadenki XY recorder.

The compounds $[\mathrm{Mo(\eta\text{-}C_5H_4R)Cl_4}]$ (R = H, Me or $\mathrm{Pr^i}$),[51] $[\mathrm{Mo(\eta\text{-}C_5H_4R)(NR')Cl_2}]$ (R, R′ = H, $\mathrm{Bu^t}$; H, $\mathrm{Bu^t}$; H, Ph; Me, $\mathrm{Bu^t}$; Me, Ph; or $\mathrm{Pr^i}$, $\mathrm{Bu^t}$),[16] and $[\mathrm{Mo(\eta\text{-}C_5H_4R)(\eta\text{-}C_2H_4)(NBu^t)Cl}]$ (R = Me or $\mathrm{Pr^i}$)[16] were prepared as described previously.

Preparations.—$[\mathrm{Mo(\eta\text{-}C_5H_5)(NC_6H_3Me_2\text{-}2,6)Cl_2}]$ **4**. 2,6-Dimethylaniline (3.77 cm^3, 31 mmol) in toluene (10 cm^3) was added slowly to a stirred suspension of $[\mathrm{Mo(\eta\text{-}C_5H_5)Cl_4}]$ (3.10 g, 10 mmol) in toluene (150 cm^3). It was stirred for 90 min and the resulting red-brown mixture filtered through a Kieselguhr frit to give a clear brown solution and a brown solid which remained on the frit. The volume of the solution was reduced to 30 cm^3 under partial vacuum. Cooling to 0 °C overnight produced $[\mathrm{Mo(\eta\text{-}C_5H_5)(NC_6H_3Me_2\text{-}2,6)Cl_2}]$ as a dark brown powder which was isolated and dried *in vacuo*. Yield 0.33 g, 8.3%.

$[\mathrm{Mo(\eta\text{-}C_5H_4Me)(NPr^i)Cl_2}]$ **6**. A red suspension of $[\mathrm{Mo(\eta\text{-}C_5H_4Me)Cl_4}]$ (3.38 g, 10.7 mmol) in thf (150 cm^3) was cooled to −50 °C and isopropylamine (1.89 g, 2.72 cm^3, 32.1 mmol) added giving a brown solution. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. It was filtered through Kieselguhr and the volume reduced to 50 cm^3. After cooling to −80 °C for 3 h a solid separated. Light petroleum (70 cm^3) was added while keeping the reaction mixture at that temperature and the solution was then decanted, leaving a light brown solid which was washed once with light petroleum (50 cm^3). Recrystallisation from toluene at -25 °C gave $[Mo(\eta\text{-}C_5H_4Me)(NPr^i)Cl_2]$ as a light brown crystalline solid. Yield 1.80 g, 55%.

$[Mo(\eta\text{-}C_5H_4Me)(NC_6H_3Me_2\text{-}2,6)Cl_2]$ **8**. 2,6-Dimethylaniline (2.33 cm^3, 19.0 mmol) in toluene (6 cm^3) was added slowly to a stirred suspension of $[Mo(\eta\text{-}C_5H_4Me)Cl_4]$ (2.0 g, 6.3 mmol) in toluene (15 cm^3). The resulting brown-red reaction mixture was stirred for 12 h and subsequently filtered through a Kieselguhr frit to give a clear red-brown solution and a brown solid which remained on the frit. The volume of the solution was reduced to 30 cm^3 under reduced pressure. Cooling to -20 °C overnight produced $[Mo(\eta\text{-}C_5H_4Me)(NC_6H_3Me_2\text{-}2,6)Cl_2]$ (220 mg) as a brown crystalline solid, which was isolated by decantation and washed twice with cold toluene (10 cm^3) and once with light petroleum. A further 0.80 g was isolated from the mother-liquor. Yield 1.0 g, 43%.

$[Mo(\eta\text{-}C_5H_4Pr^i)(NC_6H_3Me_2\text{-}2,6)Cl_2]$ **9**. 2,6-Dimethylaniline (3.39 cm^3, 27.6 mmol) was added slowly to a stirred red suspension of $[Mo(\eta\text{-}C_5H_4Pr^i)Cl_4]$ (3.17 g, 9.2 mmol) in toluene (150 cm^3). The resulting red-brown reaction mixture was stirred for 12 h and subsequently filtered through a Kieselguhr frit to give a clear red-brown solution and a brown solid which remained on the frit. The solvent was removed under reduced pressure to give a red oil. Light petroleum (200 cm^3) was added at a temperature of -80 °C, causing $[Mo(\eta\text{-}C_5H_4Pr^i)(NC_6H_3Me_2\text{-}2,6)Cl_2]$ to separate from the red oil as a brown solid. This was isolated, washed with light petroleum and dried *in vacuo*. Yield 1.6 g, 44%.

$[Mo(\eta\text{-}C_5H_5)_2(NBu^t)]$ **11**. *Method* (*a*). A brown solution of $[Mo(\eta\text{-}C_5H_5)(NBu^t)Cl_2]$ **1** (0.22 g, 0.73 mmol) in thf (50 cm^3) was added at room temperature to a colourless solution of sodium cyclopentadienide (0.14 mg, 1.55 mmol) in thf (50 cm^3). The colour immediately became deep red. The reaction mixture was allowed to stir overnight after which the solvent was removed under reduced pressure and the residue extracted into light petroleum (100 cm^3). The volume was reduced to 10 cm^3 and the solution cooled to -80 °C to give $[Mo(\eta\text{-}C_5H_5)_2(NBu^t)]$ which was isolated as a red solid and dried *in vacuo*. Yield 100 mg, 46%.

Method (*b*). The compound $[Mo(\eta\text{-}C_5H_4Pr^i)(\eta\text{-}C_2H_4)(NBu^t)Cl]$ **22** (1.93 g, 5.72 mmol) in thf (100 cm^3) was treated with sodium cyclopentadienide (0.97 g, 11 mmol) in thf (100 cm^3) dropwise over 30 min with stirring. The mixture was stirred for 14 h, then photolysed for 1.5 h. The initially orange-yellow solution became deep red-purple. Solvent was removed under reduced pressure and the residual red solid extracted with light petroleum (50 cm^3). The extract was cooled to -80 °C yielding a red solid which was filtered off and recrystallised from light petroleum at -80 °C. Yield *ca.* 0.10 g, 6%.

$[Mo(\eta\text{-}C_5H_5)_2(NPr^i)]$ **12**. A green-brown solution of $[Mo(\eta\text{-}C_5H_5)(NPr^i)Cl_2]$ (0.10 g, 0.35 mmol) in thf (50 cm^3) was added at room temperature to a colourless solution of $Na[C_5H_5]$ (0.4 g, 4.5 mmol) in thf (70 cm^3). The mixture immediately became deep red. It was allowed to stir overnight after which the solvent was removed under reduced pressure and the residue extracted into light petroleum (100 cm^3). The volume was reduced to 20 cm^3 and the solution allowed to cool overnight to -80 °C to give red crystals of $[Mo(\eta\text{-}C_5H_5)_2(NPr^i)]$ which were isolated and dried *in vacuo*. Yield 80 mg, 81%.

$[Mo(\eta\text{-}C_5H_5)_2(NPh)]$ **13**. A brown solution of $[Mo(\eta\text{-}C_5H_5)(NPh)Cl_2]$ **3** (0.5 g, 2 mmol) in thf (70 cm^3) was added at room temperature to a colourless solution of $Na[C_5H_5]$ (0.7 g, 8 mmol) in thf (70 cm^3). The solution became deeper brown. The reaction mixture was allowed to stir overnight after which the solvent was removed under reduced pressure and the residue extracted into toluene (100 cm^3). The volume was reduced to 10 cm^3 and light petroleum (30 cm^3) was added. The solution was allowed to cool to -80 °C overnight to give $[Mo(\eta\text{-}C_5H_5)_2(NPh)]$ as a brown crystalline solid which was isolated *in vacuo*. Yield 0.24 g, 49%.

$[Mo(\eta\text{-}C_5H_5)_2(NC_6H_3Me_2\text{-}2,6)]$ **14**. A brown solution of $[Mo(\eta\text{-}C_5H_5)(NC_6H_3Me_2\text{-}2,6)Cl_2]$ **4** (0.585 g, 1.67 mmol) in thf (70 cm^3) was added at room temperature to a colourless solution of $Na[C_5H_5]$ (0.350 g, 3.4 mmol) in thf (50 cm^3). The solution became deeper brown. It was allowed to stir for 12 h after which the solvent was removed under reduced pressure and the residue extracted into light petroleum (100 cm^3). The volume was reduced to 20 cm^3 and the solution allowed to cool to -80 °C to afford $[Mo(\eta\text{-}C_5H_5)_2(NC_6H_3Me_2\text{-}2,6)]$ as a brown crystalline solid which was isolated and dried *in vacuo*. Yield 150 mg, 26%.

$[Mo(\eta\text{-}C_5H_4Me)_2(NBu^t)]$ **15**. *Method* (*a*). This preparation was performed in a similar fashion to that described above in method (*a*) for $[Mo(\eta\text{-}C_5H_5)_2(NBu^t)]$. The compound $[Mo(\eta\text{-}C_5H_4Me)_2(NBu^t)]$ **15** was isolated as a red oil by cooling the petroleum solution to -80 °C overnight.

Method (*b*). The compound $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_2H_4)(NBu^t)Cl]$ **21** (4.07 g, 0.013 mol) in thf (100 cm^3) was treated with $Na[C_5H_4Me]$ (1.42 g, 0.014 mol) in thf (50 cm^3). Then as for method (*b*) of $[Mo(\eta\text{-}C_5H_5)_2(MBu^t)]$ above. The extract was cooled to -80 °C and orange crystals separated which were filtered off, washed with cold light petroleum (3 cm^3), and dried *in vacuo*. Yield 1.0 g. The combined washings were concentrated and cooled to -80 °C, producing a second crop (1.0 g). Total yield 2.0 g, 47%.

$[Mo(\eta\text{-}C_5H_4Me)_2(NPr^i)]$ **16**. A green-brown solution of $[Mo(\eta\text{-}C_5H_4Me)(NPr^i)Cl_2]$ **6** (0.3 g, 1.3 mmol) in thf (50 cm^3) was added at room temperature to a colourless solution of $Na[C_5H_4Me]\cdot thf$ (0.7 g, 4.02 mmol) in thf (50 cm^3). The solution became red. It was allowed to stir overnight after which the solvent was removed under reduced pressure and the residue extracted into light petroleum (100 cm^3). The volume was reduced and the solution cooled to -80 °C overnight. No solid could be obtained *via* crystallisation, therefore the solvent was removed under reduced pressure to afford a pure red oil from which solvent was removed *in vacuo*.

$[Mo(\eta\text{-}C_5H_4Me)_2(NPh)]$ **17**. A brown solution of $[Mo(\eta\text{-}C_5H_4Me)(NPh)Cl_2]$ **7** (0.5 g, 1.5 mmol) in thf (70 cm^3) was added at room temperature to a colourless solution of $Na[C_5H_4Me]$ (0.7 g, 6.8 mmol) in thf (70 cm^3). The solution became red-brown. It was allowed to stir overnight, after which the solvent was removed under reduced pressure and the residue extracted into light petroleum (100 cm^3) and filtered. The solvent was removed under reduced pressure and the remaining brown solid sublimed in high vacuum at 80 °C to give $[Mo(\eta\text{-}C_5H_4Me)_2(NPh)]$ as a brown solid. Yield 0.20 g, 39%.

$[Mo(\eta\text{-}C_5H_4Me)_2(NC_6H_3Me_2\text{-}2,6)]$ **18**. A brown solution of $[Mo(\eta\text{-}C_5H_4Me)(NC_6H_3Me_2\text{-}2,6)Cl_2]$ **8** (0.590 g, 1.62 mmol) in thf (50 cm^3) was added at room temperature to a colourless solution of $Na[C_5H_4Me]\cdot thf$ (0.750 g, 4.3 mmol) in thf (100 cm^3). The solution became deeper brown. It was allowed to stir for 24 h after which the solvent was removed under reduced pressure and the residue extracted into light petroleum (200 cm^3). The volume was reduced to 30 cm^3 and the solution allowed to cool to -80 °C overnight to give brown crystalline needles of $[Mo(\eta\text{-}C_5H_4Me)_2(NC_6H_3Me_2\text{-}2,6)]$ which were isolated and washed with cold light petroleum and dried *in vacuo*. Yield 0.380 g, 62%.

$[Mo(\eta\text{-}C_5H_4Pr^i)_2(NC_6H_3Me_2\text{-}2,6)]$ **19**. A brown solution of $[Mo(\eta\text{-}C_5H_4Pr^i)(NC_6H_3Me_2\text{-}2,6)Cl_2]$ **9** (0.583 g, 1.48 mmol) in thf (75 cm^3) was added at room temperature to a colourless solution of $Na[C_5H_4Pr^i]\cdot thf$ (0.650 g, 3.2 mmol) in thf (50 cm^3). The solution became deeper brown. It was allowed to stir for 48 h after which the solvent was removed under reduced pressure and the residue extracted into light petroleum (100 cm^3). The volume was reduced to 20 cm^3 and the solution allowed to cool to -80 °C overnight to give dark brown needles of $[Mo(\eta\text{-}C_5H_4Pr^i)_2(NC_6H_3Me_2\text{-}2,6)]$. Yield 0.335 g, 50%.

$[Mo(\eta\text{-}C_5H_4Pr^i)_2(NBu^t)]$ **20**. Treatment of $[Mo(\eta\text{-}C_5H_4Pr^i)(NBu^t)Cl_2]$ **10** (*ca.* 0.2 g) with $Na[C_5H_4Pr^i]$ (*ca.* 0.6 g) in thf (50 cm^3) gave a red solution. The solvent was removed under reduced pressure and the solid extracted into light petroleum.

A red sticky solid was isolated by crystallisation. Sublimation of this afforded an oil which was identified as $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})_2(\mathrm{NBu^t})]$ by $^1\mathrm{H}$ NMR spectroscopy only.

$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{NBu^t})]$ **23**. The compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\eta\text{-}\mathrm{C_2H_4})(\mathrm{NBu^t})\mathrm{Cl}]$ **22** (1.1 g, 3.25 mmol) in thf (50 $\mathrm{cm^3}$) was treated with sodium cyclopentadienide (0.25 g, 2.84 mmol) in thf (50 $\mathrm{cm^3}$). The mixture was stirred for 2 d, then photolysed for 4 h. The initially orange-yellow solution became deep red. Solvent was removed under reduced pressure yielding a red solid. Extraction with light petroleum (50 $\mathrm{cm^3}$) afforded a deep red-purple solution. Removal of solvent under reduced pressure yielded a red oil (m.p. *ca.* r.t.). Final purification was effected by sublimation [10^{-2} mmHg (*ca.* 1.33 Pa), *ca.* 60 °C]. Yield *ca.* 0.50 g, 45%.

$[\mathrm{Mo}(\eta^3\text{-}\mathrm{C_9H_7})(\eta\text{-}\mathrm{C_5H_4Pr^i})(\mathrm{NBu^t})]$ **24**. The compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Pr^i})(\eta\text{-}\mathrm{C_2H_4})(\mathrm{NBu^t})\mathrm{Cl}]$ **22** (200 mg, 0.59 mmol) in thf (30 $\mathrm{cm^3}$) was treated with lithium indenide (80 mg, 0.66 mmol) in thf (50 $\mathrm{cm^3}$). The mixture was stirred for 1 h, then photolysed for 30 min. The initially orange-yellow solution became deep violet-purple. Solvent was removed under reduced pressure and the deep purple residue extracted with light petroleum (30 $\mathrm{cm^3}$). The extract was concentrated and cooled to −20 °C. Crystals formed which were filtered off, washed with cold light petroleum (2 × 1 $\mathrm{cm^3}$) and dried *in vacuo*. Yield 75 mg, 33%.

$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})_2\mathrm{Me}(\mathrm{NBu^t})]\mathrm{I}$ **25** *and* $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})_2\mathrm{Me}(\mathrm{NBu^t})][\mathrm{BF_4}]$ **26**. The compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})_2(\mathrm{NBu^t})]$ **15** (0.20 g, 0.61 mmol) in thf (50 $\mathrm{cm^3}$) was treated with iodomethane (0.1 $\mathrm{cm^3}$, 1.6 mmol) in thf (50 $\mathrm{cm^3}$) over 3 min. The initial deep red-purple solution rapidly became yellow-orange and yellow-orange air-stable crystals of **25** formed. These were filtered off, washed with thf (0.5 $\mathrm{cm^3}$) and dried *in vacuo*. Yield 0.175 g, 60%.

A solution of the compound **25** (0.10 g, 0.21 mmol) in water (50 $\mathrm{cm^3}$) was treated with sodium tetrafluoroborate (23 mg, 0.21 mmol) in water (50 $\mathrm{cm^3}$). The solution was slowly concentrated under reduced pressure, affording orange needle crystals of **26** which were filtered off, washed with cold water (2 × 3 $\mathrm{cm^3}$), cold thf (1 $\mathrm{cm^3}$), and light petroleum (5 $\mathrm{cm^3}$), and dried *in vacuo*. Yield *ca.* 60 mg, 66%.

$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Me}(\mathrm{NPr^i})]\mathrm{I}$ **27**. A red solution of $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{NPr^i})]$ **12** (0.1 g) in thf (25 $\mathrm{cm^3}$) was treated with an excess of MeI. An orange precipitate formed immediately. After further stirring for 5 min, the solvent and excess of MeI were removed under reduced pressure and the orange product was washed three times with light petroleum and dried *in vacuo*. Yield *ca.* 80%.

$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Me}(\mathrm{NC_6H_3Me_2}\text{-}2,6)]\mathrm{I}$ **28**. The compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{NC_6H_3Me_2}\text{-}2,6)]$ **14** (0.1 g) was dissolved in thf (25 $\mathrm{cm^3}$) giving a brown solution and an excess of MeI was added. The solution was stirred for 5 h during which time some precipitate appeared. The solvent and excess of MeI were then removed under reduced pressure to give $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Me}(\mathrm{NC_6H_3Me_2}\text{-}2,6)]\mathrm{I}$ as a brown-orange powder which was washed three times with light petroleum and dried *in vacuo*. Yield *ca.* 80%.

$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})(\mathrm{NBu^t})\mathrm{I_2}]$ **29**. The compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})_2(\mathrm{NBu^t})]$ **15** (0.30 g, 0.92 mmol) in thf (50 $\mathrm{cm^3}$) was treated with allyl iodide (0.1 $\mathrm{cm^3}$, 1.10 mmol). The mixture was stirred for 2 d. The initially deep red-purple solution became burgundy red. Solvent was removed under reduced pressure yielding a red oily solid. This was extracted with light petroleum (75 $\mathrm{cm^3}$) and the solution cooled to −20 °C. Deep red, very air-sensitive crystals formed which were filtered off, washed with cold light petroleum (1 $\mathrm{cm^3}$), and dried *in vacuo*. Yield *ca.* 0.10 g, 21%. Final purification was effected by sublimation (10^{-2} mmHg, *ca.* 50 °C).

$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})(\mathrm{PMe_3})_2(\mathrm{NBu^t})][\mathrm{C_5H_4Me}]$ **30**. The compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})_2(\mathrm{NBu^t})]$ **15** (0.10 g, 0.30 mmol) was treated with trimethylphosphine (*ca.* 2 $\mathrm{cm^3}$) at r.t. in a sealed ampoule for 5 d. Red crystals were obtained and dried by evaporation of solvent in an inert atmosphere. Yield *ca.* 75 mg, 50%.

Reactions of $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})_2(\mathrm{NBu^t})]$ **15**.—*With lithium aluminium hydride. Compound* **15** (70 mg, 0.22 mmol) in diethyl ether (50 $\mathrm{cm^3}$) was treated with lithium aluminium hydride (0.20 g, 5.2 mmol) in diethyl ether (40 $\mathrm{cm^3}$). The mixture was stirred for 14 h. The initially purple suspension became grey. Solvent was removed under reduced pressure and the grey solid extracted with light petroleum (2 × 50 $\mathrm{cm^3}$). Concentration and cooling the yellow extracts to −20 °C yielded yellow crystals of the previously reported $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})_2\mathrm{H_2}]$.[50] Yield 40 mg, 71%.

With hydrogen chloride. Compound **15** (0.20 g, 0.62 mmol) in thf (100 $\mathrm{cm^3}$) was treated with hydrogen chloride gas by purging for 2 min at −80 °C. The red-purple solution rapidly became pale yellow-green, and a dark green solid precipitated. The solution was filtered and the precipitate recrystallised from hot acetone, yielding dark green crystals of the previously reported $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})_2\mathrm{Cl_2}]$.[24,50] Yield *ca.* 0.10 g, 50%.

Structure Determination of $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})(\mathrm{PMe_3})_2(\mathrm{NBu^t})][\mathrm{C_5H_4Me}]$ **30**.—$\mathrm{C_{22}H_{43}MoNP_2}$, $M = 479.46$, crystal size = 0.20 × 0.30 × 0.30 mm, monoclinic, space group $P2_1/m$, $a = 8.328(1)$, $b = 17.971(2)$, $c = 9.176(2)$ Å, $\beta = 111.95(1)°$, $U = 1273.8$ Å^3, $Z = 2$ (cation lies across mirror plane, anion lies on inversion centre), $D_c = 1.24\ \mathrm{g\ cm^{-3}}$, $\mu = 6.32\ \mathrm{cm^{-1}}$, $F(000) = 504$, $\lambda(\mathrm{Mo\text{-}K\alpha}) = 0.710\,69$ Å, $2 < 2\theta < 48°$, scan mode $\omega\text{–}2\theta$, total unique data 2074, observations [$I > 3\sigma(I)$] 1580, variables 166, observations/variables 9.5, Chebyshev parameters 16.3, −25.2, 14.0, −6.89, $R_{\mathrm{merge}} = 0.027$, $R = 0.054$, $R' = 0.049$.

A red crystal of compound **30** was sealed in a Lindemann glass capillary under $\mathrm{N_2}$ 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 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[52] based on azimuthal scan data was applied. Equivalent reflections were merged and systematically absent reflections rejected. The molybdenum atom position was determined from a Patterson synthesis. Subsequent Fourier-difference syntheses revealed the positions of all other non-hydrogen atoms of the $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4Me})(\mathrm{PMe_3})_2(\mathrm{NBu^t})]^+$ cation. The Mo atom lies on a mirror plane at $y = \frac{1}{4}$. Two sites were found for the $\mathrm{NBu^t}$ group N and C atoms (*i.e.* none of these atoms lies at $y = \frac{1}{4}$) and were treated as being statistically disordered either side of the mirror plane (the atoms of the $\mathrm{NBu^t}$ group were each assigned 0.5 chemical occupancy factors). The η-$\mathrm{C_5H_4Me}$ methyl group carbon, C(7), did not lie on $y = \frac{1}{4}$ and so was assigned a chemical occupancy factor of 0.5 and was also treated as being disordered either side of the mirror plane. The η-$\mathrm{C_5H_4Me}$ ring (metal-bound) carbons showed no evidence of disorder with C(4) at $y = \frac{1}{4}$. Further Fourier-difference syntheses revealed electron density located about ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) which was successfully modelled as a planar $\mathrm{C_5H_4Me}$ anion disordered across the crystallographic inversion centre. Atoms C(102), C(103), C(104) and C(105) were assigned chemical occupancy factors of 0.5 and C(101) one of 1.0. The refinement was found to be considerably more stable and produced smaller estimated standard deviations (e.s.d.s) and more chemically reasonable bond lengths and angles in the centrosymmetric $P2_1/m$ as compared with the alternative choice of space group $P2_1$ in which the disorder persisted.

Non-hydrogen atoms were refined with anisotropic thermal parameters subject to slack restraints. 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 [53] was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter [54]) in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS suite [55] on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Neutral atom scattering factors were taken from the usual sources.[56]

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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