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Synthesis, characterisation and reactivity of the molybdenum(VI) dimethyl complex $[Mo(NR)_2Me_2]$ ($R = 2,6\text{-}Pr^i{}_2C_6H_3$)

Vernon C. Gibson,*[a] Carl Redshaw,[a] Gary L. P. Walker,[a] Judith A. K. Howard,[b] Vanessa J. Hoy,[b] Jacqueline M. Cole,[b] Lyudmila G. Kuzmina[b] and Dinali S. De Silva[b]

[a] *Department of Chemistry, Imperial College, London, UK SW7 2AY*
[b] *Department of Chemistry, University Science Laboratories, South Road, Durham, UK DH1 3LE*

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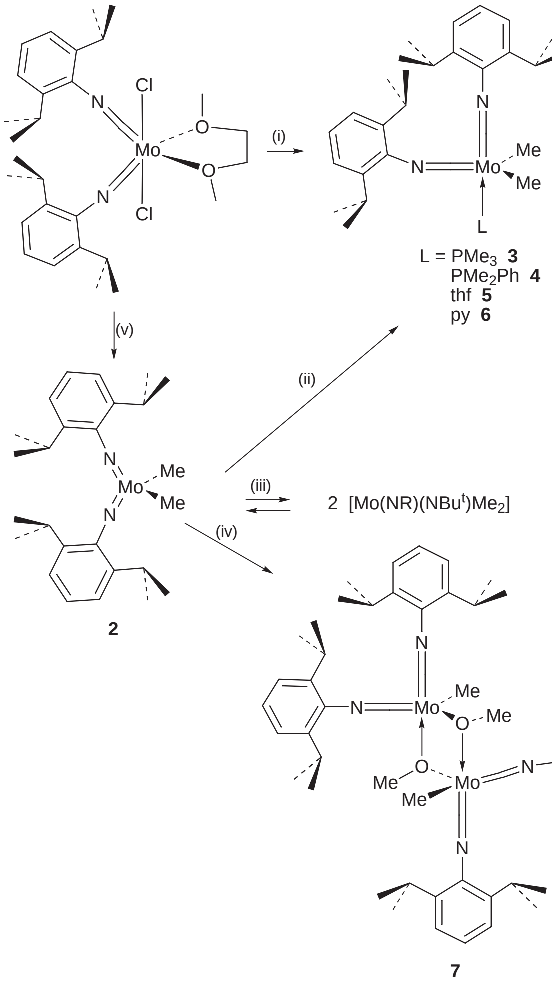
The reaction of $[Mo(NR)_2Cl_2(dme)]$ ($R = 2,6\text{-}Pr^i{}_2C_6H_3$, dme = 1,2-dimethoxyethane) with 2 equivalents of methylmagnesium bromide in diethyl ether afforded $[Mo(NR)_2Me_2]$ **2** as a red crystalline solid in good yield. Treatment of **2** with the donor molecules tetrahydrofuran (thf), pyridine, PMe_3, and PMe_2Ph gave the five-coordinate adducts $[Mo(NR)_2Me_2(L)]$ ($L = PMe_3$ **3**, PMe_2Ph **4**, thf **5** or pyridine **6**). Exposure of solutions of **2** to atmospheric dioxygen afforded the orange methoxide-bridged complex $[\{Mo(NR)_2Me(\mu\text{-}OMe)\}_2]$ **7**. $[\{Mo(NBu^t)_2Me(\mu\text{-}OMe)\}_n]$, **8** ($n$ = 1 or 2) was obtained from the reaction of $[\{Mo(NBu^t)_2Me_2\}_2]$ **1** with dioxygen. The crystal structures of **2**, **4** and **7** have been determined.

In 1980, Nugent and Harlow[1] described the first molybdenum imido alkyl complex, $[Mo(NBu^t)_2Me_2]$ **1**, which they showed exists as an imido-bridged dimer. They also noted that the violet solutions of **1** are readily discharged upon introduction of donor molecules such as phosphines or pyridine, or upon exposure to dioxygen. The precise nature of the products was not established.

We have been investigating the chemistry of the bis(2,6-diisopropylphenylimido)molybdenum system[2] and describe herein the synthesis and X-ray structural characterisation of $[Mo(NR)_2Me_2]$ **2** ($R = 2,6\text{-}Pr^i{}_2C_6H_3$), a mononuclear analogue of **1**. The reactivity of **2** towards a similar range of donor molecules and dioxygen has been examined with a view to gaining insight into the intriguing reactivity noted earlier by Nugent and Harlow.



Scheme 1 (i) PR_3, 2MgMeBr, Et_2O; (ii) thf or py, room temperature (r.t.); (iii) $\frac{1}{2}[Mo(NBu^t)_2Me_2]$, benzene, r.t.; (iv) O_2, toluene, r.t.; (v) 2MgMeBr, Et_2O.

Results and discussion

Synthesis and characterisation of $[Mo(NR)_2Me_2]$ 2

Treatment of $[Mo(NR)_2Cl_2(dme)]$[3] ($R = 2,6\text{-}Pr^i{}_2C_6H_3$, dme = 1,2-dimethoxyethane) with 2 equivalents of MgMeBr in diethyl ether, followed by work-up and recrystallisation from a concentrated pentane solution, gives $[Mo(NR)_2Me_2]$ **2** as deep red, highly air and moisture sensitive crystals in 75% isolated yield (Scheme 1). The ^1H NMR spectrum of **2** is consistent with a C_{2v} symmetric species, the Mo–CH_3 groups resonating at δ 1.39. This is to higher frequency than the corresponding methyl resonance of **1** (δ 1.13[1]) consistent with the greater electron-withdrawing effect of the arylimido ligand. Analogously, the ^{13}C NMR spectrum of **2** reveals a quartet resonance at δ 37.74 due to the metal-bonded carbons, *cf.* δ 28.30 for **1**.

Crystals of complex **2** were grown from a saturated pentane solution at −35 °C. The molecular structure is shown in Fig. 1; selected bond lengths and angles are collected in Table 1. The geometry about the metal centre is best described as distorted tetrahedral, with interligand angles in the range 107.5–113.6°. The aromatic rings of the imido ligands lie 'face to face'. The distances of 1.749(4) Å for the Mo–N bonds and 1.389(6) Å for the N–C(*ipso*) bonds, combined with angles of 159.6(3)° for the Mo–N–C connection, are consistent with a linear arylimido ligand.[4] The Mo–C bond distance, at 2.109(5) Å, is relatively short when compared to those of other terminal methyl ligands (2.254 Å mean, 2.189 Å lower quartile[5]). A subsequent neutron structure determination[6] on **2** has revealed possible multiple α-agostic interactions between the molybdenum centre and the hydrogens of the methyl ligands.

Attempts to prepare the mixed bis(imido)molybdenum

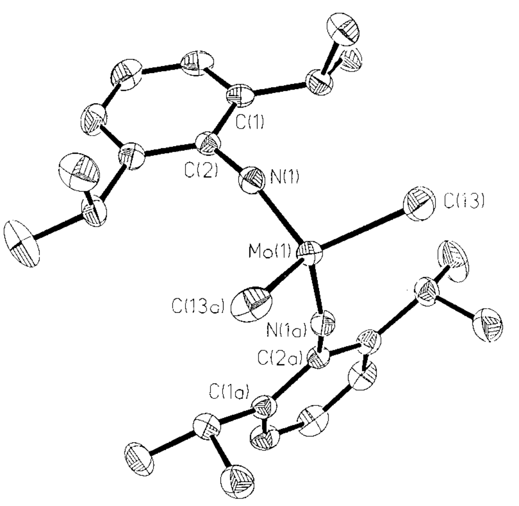


Fig. 1 Molecular structure of complex **2**, without H atoms and with key atoms labelled.

complex, $[\mathrm{Mo(NR)(NBu^t)Me_2}]$, a hybrid of **1** and **2**, were unsuccessful. Treatment of $[\mathrm{Mo(NR)(NBu^t)Cl_2(dme)}]$[7] with 2 equivalents of methylmagnesium bromide afforded $[\{\mathrm{Mo(NBu^t)_2Me_2}\}_2]$ **1** as the only isolable product in *ca.* 30% yield. It seemed likely that the mixed imido species was generated but that **1** was subsequently formed by exchange of imido ligands between molybdenum centres.[8] In order to establish whether or not imido ligand exchange was occurring, the reaction between **1** and **2** was investigated by NMR spectroscopy. The complex $[\{\mathrm{Mo(NBu^t)_2Me_2}\}_2]$ **1** was mixed with 2 equivalents of $[\mathrm{Mo(NR)_2Me_2}]$ **2** in an NMR tube, dissolved in d_8-toluene (400 µl), and the ^{1}H and ^{13}C NMR spectra recorded. The ^{1}H NMR spectrum revealed a new doublet signal at δ 1.26 (12 H) with an associated singlet resonance at δ 1.15 (9 H) due to the methyl hydrogens of the isopropyl and *tert*-butyl groups of $[\{\mathrm{Mo(NR)(NBu^t)Me_2}\}_n]$ ($n = 1$ or 2). The isopropyl-methine and metal-bound methyl groups appeared as a septet at δ 3.62 (4 H) and a singlet at δ 1.13 (6 H) respectively. The ^{13}C NMR spectrum gave a metal-bound methyl carbon resonance at δ 32.46, a value intermediate to those found for **1** (δ 28.30) and **2** (δ 37.74). An equilibrium in favour of $[\{\mathrm{Mo(NR)(NBu^t)Me_2}\}_n]$ [for $n = 1$, K_{eq} (298 K) = 24] was attained after 24 h at room temperature [eqn. (1)]. The difficulties in crystallising this product are most

$$[\mathrm{Mo(NR)_2Me_2}] + \tfrac{1}{2}[\{\mathrm{Mo(NBu^t)_2Me_2}\}_2] \rightleftharpoons 2\,[\mathrm{Mo(NR)(NBu^t)Me_2}] \quad (1)$$

likely due to the lower solubility of dimeric **1** which precipitates from solution thereby driving the equilibrium back towards **1** and **2**. These solubility characteristics provide an indication that $[\mathrm{Mo(NR)(NBu^t)Me_2}]$ is likely to be monomeric, since the less solubilising characteristics of the arylimido ligand would be expected to lead to preferential precipitation of the mixed-imido product if it were a dimer.

Base adducts of $[\mathrm{Mo(NR)_2Me_2}]$ 2

Treatment of $[\mathrm{Mo(NR)_2Cl_2(dme)}]$ with 2 equivalents of methylmagnesium bromide, in the presence of an excess of the phosphine $\mathrm{PMe_3}$ or $\mathrm{PMe_2Ph}$, afforded the monophosphine adducts $[\mathrm{Mo(NR)_2Me_2(PMe_3)}]$ **3** and $\mathrm{Mo(NR)_2Me_2(PMe_2Ph)}]$ **4** as orange crystalline materials in 70 and 76% yield respectively.

In accordance with the observations of Nugent and Harlow on the *tert*-butylimido system,[1] the ^{1}H and ^{13}C NMR spectra of complexes **3** and **4** reveal upfield shifts for the methyl resonances relative to the phosphine-free complex **2** [^{1}H NMR: δ 0.99 (**3**) and 1.05 (**4**) *cf.* 1.39 for **2**; ^{13}C NMR: δ 14.87 (**3**) and 16.06 (**4**), *cf.* 37.74 for **2**]. The larger shifts are observed for the more electron donating $\mathrm{PMe_3}$ derivative. An analogous shift to higher field is also seen for the phosphorus nucleus of **3** compared with **4** [δ −17.3 (**3**) and −4.0 (**4**)].

Table 1 Selected bond lengths (Å) and angles (°) for compound **2**

Mo(1)–N(1)	1.749(4)	N(1)–C(2)	1.389(6)
Mo(1)–C(13)	2.109(5)		
N(1)–Mo–N(1a)	112.6(2)	C(13)–Mo–C(13a)	113.6(3)
N(1)–Mo–C(13)	107.8(2)	C(2)–N(1)–Mo(1)	159.6(3)

Table 2 Selected bond lengths (Å) and angles (°) for compound **4**

Mo–N(1)	1.759(3)	Mo–P	2.6793(10)
Mo–N(2)	1.759(3)	N(1)–C(11)	1.394(4)
Mo–C(1)	2.299(3)	N(2)–C(21)	1.409(4)
Mo–C(2)	2.205(4)		
N(1)–Mo–N(2)	111.61(13)	Mo–N(1)–C(11)	175.9(3)
N(2)–Mo–C(2)	107.86(14)	Mo–N(2)–C(21)	151.9(2)
N(1)–Mo–C(2)	95.04(13)	N(1)–Mo–P	153.19(10)
N(2)–Mo–C(1)	107.90(12)	N(2)–Mo–P	95.20(9)
N(1)–Mo–C(1)	93.17(12)	C(1)–Mo–P	78.23(8)
C(1)–Mo–C(2)	137.10(13)	C(2)–Mo–P	75.69(10)

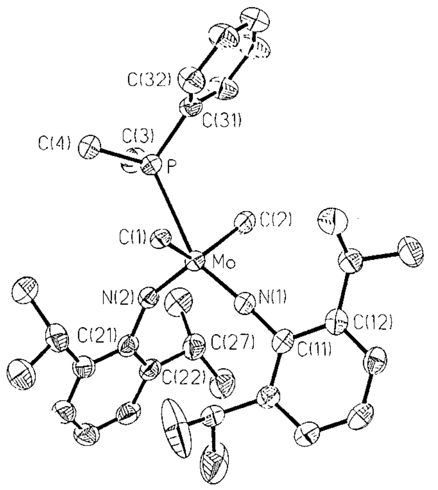


Fig. 2 Molecular structure of complex **4**, without H atoms and with key atoms labelled.

The thf complex $[\mathrm{Mo(NR)_2Me_2(thf)}]$ **5** is generated in high yield upon recrystallisation of **2** from thf solution, and its pyridine analogue, $[\mathrm{Mo(NR)_2Me_2(py)}]$ **6**, was accessed by treatment of a pentane solution of **2** with 1 equivalent of pyridine. The pyridine adduct has more pronounced upfield ^{1}H and ^{13}C NMR shifts [^{1}H NMR: δ 0.99, *cf.* 1.39 for **2**; ^{13}C NMR: δ 27.39, *cf.* 37.74 for **2**]. For **5**, the ^{1}H NMR shift of the methyl resonance is approximately the same as for base-free **2**, which is also true of the ^{13}C NMR shift [δ 36.70, *cf.* 37.74 for **2**] in line with thf being the weakest of these donor ligands.

In contrast to the stable adducts **3**–**6**, treatment of **2** with an excess of acetonitrile (4 equivalents) in d_6-benzene gave a product that was unstable to vacuum. The ^{1}H NMR spectrum indicated that an adduct had formed, evidenced by the upfield shift (δ 1.31) of the metal methyl resonance, but on removal of the volatile components and re-recording of the spectrum in fresh d_6-benzene **2** only was observed.

The molecular structure of complex **4** has been determined and is shown in Fig. 2; selected bond lengths and angles are collected in Table 2. The geometry about the metal centre in **4** is best described as distorted trigonal bipyramidal, with an imido ligand and phosphine molecule occupying the axial sites. There is a large disparity between the bend angles of the two imido ligands. The axial imido ligand is essentially linear (176.0°), whilst the equatorial imido ligand is borderline between 'bent'

Table 3 Selected bond lengths (Å) and angles (°) for complex **7**

Mo(1)–(1)	1.764(2)	Mo(1)–N(2)	1.754(2)
N(1)–C(1)	1.397(3)	N(2)–C(13)	1.401(3)
Mo(1)–C(25)	2.161(3)	Mo(1)–O(1)	2.048(2)
Mo(1)–O(1a)	2.207(2)	O(1)–C(26)	1.430(3)
Mo(1)–N(1)–C(1)	173.2(2)	Mo(1)–N(2)–C(13)	156.3(2)
O(1)–Mo(1)–O(1a)	68.42(7)	Mo(1)–O(1)–Mo(1a)	111.58(7)
Mo(1)–O(1)–C(26)	123.6(2)	Mo(1a)–O(1)–C(26)	123.2(2)
O(1)–Mo(1)–C(25)	131.34(9)	O(1)–Mo(1)–N(2)	117.65(9)
N(2)–Mo(1)–C(25)	103.5(1)	N(1)–Mo(1)–C(25)	93.6(1)
N(1)–Mo(1)–O(1)	97.27(8)	N(1)–Mo(1)–N(2)	107.82(9)
O(1a)–Mo(1)–C(25)	83.91(8)	O(1a)–Mo(1)–O(1)	68.42(7)
O(1a)–Mo(1)–N(2)	94.99(8)		

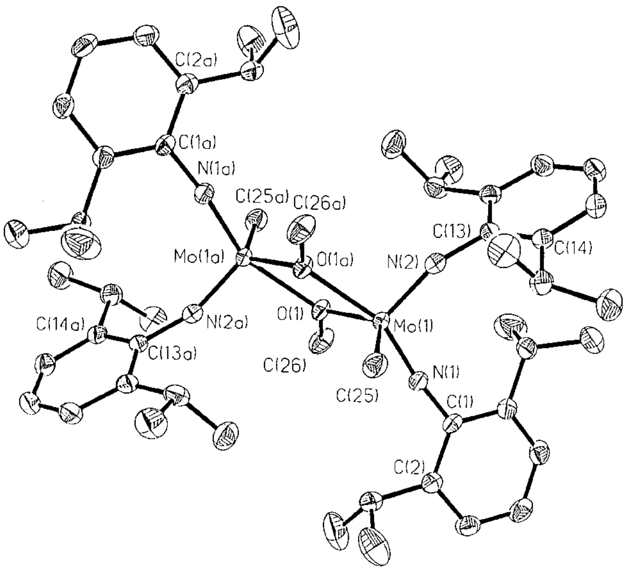


Fig. 3 Molecular structure of complex **7**, without H atoms and with key atoms labelled.

and 'linear' (152.0°). A similar significant bending at the nitrogen of the equatorial imido ligand in trigonal bipyramidal bis(imido)molybdenum compounds has been reported and good evidence has been presented for the five co-ordinate trigonal bipyramidal system that this is more likely to be due to an electronic effect rather than crystal packing.[9]

Reactivity towards dioxygen

Exposure of a pentane solution of [Mo(NR)$_2$Me$_2$] **2** to dry dioxygen gas, followed by recrystallisation, affords a bright orange crystalline product (**7**) in good yield (86%). The ^{1}H NMR spectrum of **7** reveals a singlet resonance at δ 1.45 due to the hydrogens of one metal-bound methyl group and a resonance, at δ 4.35, also integrating for three hydrogens of a methyl unit. The ^{13}C NMR spectrum gave corresponding resonances at δ 25.68 and 67.71 respectively for these methyl carbons. The identity of **7** could not be established with certainty from these NMR data, though the shifts of the new methyl group would be appropriate for a methoxide unit. A crystal structure determination on **7** was therefore undertaken.

Crystals suitable for an X-ray crystallographic study were obtained from within a sealed NMR sample tube that contained a saturated d$_6$-benzene solution of complex **7**, stored for several days at room temperature. The molecular structure is shown in Fig. 3; selected bond lengths and angles are presented in Table 3. Complex **7** is binuclear, the molybdenum centres being asymmetrically bridged by two methoxide ligands. The Mo–O distances are consistent with one 'normal' covalent bond [2.048(2) Å] and one dative covalent bond [2.207(2) Å] to each molybdenum atom. The five-co-ordinate geometry about each metal centre is best described as distorted trigonal bipyramidal, each molybdenum atom possessing a local geometry not dissimilar to that established for the phosphine adducts **3** and **4**. The axial sites are occupied by an arylimido ligand and a methoxide group bonded through a dative covalent interaction, the equatorial sites by a terminal methyl ligand, the second methoxide group, this time with the short Mo–O contact, and the second arylimido unit. The local geometry around the molybdenum centres is shown in Fig. 4.

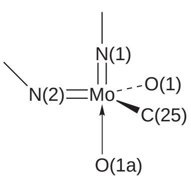


Fig. 4 The local geometry around the molybdenum centres of complex **7**.

The Mo–N–C angles for the axial [173.2(2)°] and equatorial [156.3(2)°] imido ligands are comparable in terms of size and orientation to those seen for **4** [175.9(3) and 151.9(2)°], wherein the equatorial imido unit is bent towards the adjacent axial linear imido group. A Mo–C distance of 2.161(3) Å for the terminal methyl ligands in **7** is intermediate between those of [Mo(NR)$_2$Me$_2$] [2.109(5) Å] and **4** [2.252(4) Å (average)].

Selective oxygen insertion into transition-metal methyl bonds has been seen in Group 4 chemistry by Lubben and Wolczanski,[10] the reaction of [Ti(tritox)Me$_3$] [tritox = (Me$_3$C)$_3$CO] with O$_2$ affording the methoxide-bridged product [{Ti(tritox)Me$_2$}$_2$(μ-OMe)$_2$]. This selective insertion into just one of the metal–carbon bonds bears close similarity to the reaction described here. Treatment of [M(tritox)$_2$Me$_2$] (M = Ti, Zr or Hf) with dioxygen does not stop at the first insertion product, instead proceeding to afford exclusively the bis(methoxide) product [M(tritox)$_2$(OMe)$_2$].[10] Contrastingly, **7** is unreactive towards further oxygen insertion to give [Mo(NR)$_2$(OMe)$_2$] even though the latter is accessible and stable.[11]

Finally, in order to provide clarification of Nugent and Harlow's observations[1] on the *tert*-butylimido system, we then treated a pentane solution of **1** with an atmosphere of dry dioxygen gas. This led to discharging of the violet solution to pale yellow in accordance with their report. Upon removal of the solvent, a sensitive free-flowing golden-yellow oil **8** was obtained. Its ^{1}H NMR spectrum (d$_8$-toluene) revealed resonances at δ 0.88 (3 H) and 4.00 (3 H) attributable to metal-bound methyl and methoxy groups respectively. The corresponding ^{13}C NMR resonances occur at δ 16.0 and 66.7, values comparable to those observed for the bis(arylimido)molybdenum methoxide species **7**.

Conclusion

This study has shown that the 2,6-diisopropylphenylimido ligand stabilises a mononuclear molybdenum(VI) dimethyl species in contrast to the *tert*-butylimido ligand which affords an imido-bridged dimer. A subsequent study of the reactions of [Mo(NR)$_2$Me$_2$] towards donor molecules and dioxygen, and the characterisation of the products by NMR spectroscopy and X-ray crystallography, have allowed the origin of the earlier observations of Nugent and Harlow on the *tert*-butylimido system to be rationalised. The selective insertion of oxygen into just one of the molybdenum-bonded methyl groups to give a methoxy-bridged dimer is particularly noteworthy.

Experimental

General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Durham, Medac Ltd and at Imperial College. The NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 (^{1}H), 100.6 (^{13}C) and 100.0 MHz (^{31}P) with chemical shifts referenced to the residual protio impurity of the deuteriated solvent, IR spectra (Nujol mulls, KBr or CsI windows) on Perkin-Elmer 577 and 457 grating spectrophotometers. The complex [Mo(NR)$_2$Cl$_2$(dme)] was prepared by the previously reported method.[2] Trimethylphosphine was prepared by the method of Wolfsberger and Schmidbaur.[12] All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparations

[Mo(NR)$_2$Me$_2$] 2. To a solution of [Mo(NR)$_2$Cl$_2$(dme)] (5.0 g, 8.23 mmol) in diethyl ether (100 cm^3) at −78 °C was slowly added (over about 20 min) MgMeBr (5.5 cm^3, 3.0 M solution, 16.46 mmol) in diethyl ether (10 cm^3). After slowly warming to ambient temperature and stirring for 12 h the orange suspension was filtered. The remaining solid was further extracted with diethyl ether (2 × 50 cm^3) and pentane (50 cm^3). The volatiles were removed from the combined extracts to afford a red solid. Extraction into pentane (60 cm^3) and cooling to −78 °C gave complex **2** as orange-red crystals. Yield 2.94 g, 75% (Found: C, 65.63; H, 8.39; N, 5.84. Calc. for $\mathrm{C_{26}H_{40}MoN_2}$: C, 65.53; H, 8.46; N, 5.88%). IR: 3057s, 1916w, 1570w, 1324vs, 1272vs, 1225m, 1177w, 1149m, 1114m, 1058m, 1046m, 985s, 933m, 896w, 794s, 752vs, 612w, 581w, 562w, 536w, 516s and 457m cm^{-1}. ^{1}H NMR (d$_6$-benzene, 298 K): δ 6.10–6.97 (m, 6 H, *m*- and *p*-H of $\mathrm{C_6H_3Pr^i_2}$-2,6), 3.64 (sept, 4 H, $^3J_{\mathrm{HH}}$ 6.8, C*H*Me$_2$), 1.39 (s, 6 H, CH$_3$) and 1.13 (d, 24 H, $^3J_{\mathrm{HH}}$ 6.8 Hz, CH*Me*$_2$). ^{13}C NMR (d$_6$-benzene, 298 K): δ 153.09 (s, *ipso*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 142.44 (s, *o*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 126.21 (d, $^1J_{\mathrm{CH}}$ 159.8, *p*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 122.75 (d, $^1J_{\mathrm{CH}}$ 158.7, *m*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 37.74 (q, $^1J_{\mathrm{CH}}$ 125.8, CH$_3$), 28.86 (d, $^1J_{\mathrm{CH}}$ 128.1, *C*HMe$_2$) and 23.27 (q, $^1J_{\mathrm{CH}}$ 125.9, CH*Me*$_2$).

[Mo(NR)$_2$Me$_2$(PMe$_3$)] 3. Onto a frozen mixture of [Mo(NR)$_2$Cl$_2$(dme)] (2.19 g, 3.6 mmol) and diethyl ether (100 cm^3) at −198 °C was vacuum transferred PMe$_3$ (0.76 g, 10 mmol). On slowly warming to −78 °C MgMeBr (2.4 cm^3, 3.0 M solution, 7.2 mmol) was added and the mixture stirred at ambient temperature for 12 h. The volatile components were then removed *in vacuo* and the residue was extracted into pentane to give, upon cooling to −40 °C, orange crystals of complex **3**. Yield 1.4 g, 70% (Found: C, 63.30; H, 9.14; N, 5.07. Calc. for $\mathrm{C_{29}H_{49}MoN_2P}$: C, 63.03; H, 8.04; N, 5.07%). IR: 1620w, 1583w, 1421m, 1359s, 1331m, 1273s, 1224w, 1175w, 1156w, 1112w, 1097w, 1056w, 1045w, 1024m, 978s, 957w, 934m, 849m, 829m, 801m, 793m, 762vs, 752vs, 674w, 543m, 532m and 508m cm^{-1}. ^{1}H NMR (d$_6$-benzene, 298 K): δ 7.09–6.99 (m, 6 H, *m*- and *p*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 3.91 (sept, 4 H, $^3J_{\mathrm{HH}}$ 6.8, C*H*Me$_2$), 1.20 (d, 24 H, $^3J_{\mathrm{HH}}$ 6.8, CH*Me*$_2$), 0.99 (s, 6 H, C*H*$_3$) and 0.88 (d, 9 H, $^2J_{\mathrm{PH}}$ 6.8 Hz, PMe$_3$). ^{13}C NMR (d$_6$-benzene, 298 K): δ 153.30 (s, *ipso*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 144.03 (s, *o*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 125.23 (d, $^1J_{\mathrm{CH}}$ 159.2, *p*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 122.60 (d, $^1J_{\mathrm{CH}}$ 156.9, *m*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 28.49 (d, $^1J_{\mathrm{CH}}$ 129.1 Hz, *C*HMe$_2$), 23.84 (qd, $^1J_{\mathrm{CH}}$ 125.8, $^2J_{\mathrm{CH}}$ 5.4, CH*Me*$_2$), 14.87 (q, $^1J_{\mathrm{CH}}$ 126.0, CH$_3$) and 13.35 [dq, $^1J_{\mathrm{CH}}$ 130.0, $^1J_{\mathrm{CP}}$ 15.2 Hz, P(CH$_3$)$_3$]. ^{31}P NMR (C$_6$D$_6$, 298 K): δ −17.27 (s, PMe$_3$).

[Mo(NR)$_2$Me$_2$(PMe$_2$Ph)] 4. The same procedure was adopted as described for complex **3**, but using PMe$_2$Ph. Orange **5** was obtained in 76% yield (Found: C, 66.49; H, 8.46; N, 4.41. Calc. for $\mathrm{C_{34}H_{51}MoN_2P}$: C, 66.43; H, 8.36; N, 4.56%). IR: 3046w, 1421m, 1358w, 1336w, 1323w, 1271m, 1223w, 1176w, 1153w, 1112w, 1099w, 1059w, 1047w, 1027w, 998w, 977s, 944s, 935m, 914m, 904vs, 865w, 837w, 800m, 756vs, 743s, 694m, 675w, 613w and 491w cm^{-1}. Mass spectrum (CI, NH$_4^+$, *m*/*z*): 600, [M − CH$_3$]$^+$; 585, [M − 2CH$_3$]$^+$ and 478, [M − PMe$_2$Ph + H]$^+$. ^{1}H NMR (d$_6$-benzene, 298 K): δ 7.40 (td, 2 H, $^3J_{\mathrm{HH}}$ 8.5, $^3J_{\mathrm{PH}} = 1.8$, PPh), 6.40–7.10 (m, 9 H, aryl H), 3.91 (sept, 4 H, $^3J_{\mathrm{HH}}$ 6.8, C*H*Me$_2$), 1.28 (d, 6 H, $^2J_{\mathrm{PH}}$ 6.4, PMe$_2$Ph), 1.22 (d, 24 H, $^3J_{\mathrm{HH}}$ 6.8 Hz, CH*Me*$_2$) and 1.05 (s, 6 H, CH$_3$). ^{13}C NMR (d$_6$-benzene, 298 K): δ 153.31 (*ipso*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 144.19 (*o*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 135.70 (d, $^1J_{\mathrm{CP}}$ 26.2, *ipso*-C of PMe$_2$Ph), 130.98 (dm, $^2J_{\mathrm{CP}}$ 11.0, *o*-C of PMe$_2$Ph), 129.70 (d, $^4J_{\mathrm{CP}}$ 1.5, *p*-C of PMe$_2$Ph), 128.74 (dm, $^3J_{\mathrm{CP}}$ 8.7, *m*-C of PMe$_2$Ph), 125.36 (d, $^1J_{\mathrm{CH}}$ 158.2, *p*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 122.67 (ddd, $^1J_{\mathrm{CH}}$ 154.5, $^2J_{\mathrm{CH}}$ 7.2, $^3J_{\mathrm{CH}}$ 4.9, *m*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 28.49 (dq, $^1J_{\mathrm{CH}}$ 128.5, $^2J_{\mathrm{CH}}$ 3.7, *C*HMe$_2$), 23.88 (qm, $^1J_{\mathrm{CH}}$ 125.1, CH*Me*$_2$), 16.06 (q, $^1J_{\mathrm{CH}}$ 125.2, CH$_3$) and 12.44 (qd, $^1J_{\mathrm{CH}}$ 129.7, $^2J_{\mathrm{CP}}$ 15.5 Hz, P*Me*$_2$Ph). ^{31}P NMR (C$_6$D$_6$): δ −4.0 (s, PMe$_2$Ph).

[Mo(NR)$_2$Me$_2$(thf)] 5. To solid complex **2** (0.375 g, 0.79 mmol) was added thf (20 cm^3). After stirring for 5–10 min at room temperature the volatile components were removed under reduced pressure to afford **5** as an orange solid. Yield 0.4 g, 92% (Found: C, 65.5; H, 8.7; N, 5.5. Calc. for $\mathrm{C_{30}H_{48}MoN_2O}$: C, 65.7; H, 8.8; N, 5.1%). IR: 3058m, 1571w, 1378s, 1326s, 1278s, 1226w, 1197m, 1179m, 1148m, 1101w, 1059w, 985m, 935w, 894w, 795m, 775s and 752s cm^{-1}. Mass spectrum (EI, *m*/*z*): 478, [M − thf]$^+$. ^{1}H NMR (d$_6$-benzene, 298 K): δ 6.92–7.00 (m, 6 H, *m*- and *p*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 3.66 (sept, 4 H, $^3J_{\mathrm{HH}}$ 6.9, C*H*Me$_2$), 3.59 (br t, 4 H, thf), 1.39 (br t, 4 H, thf), 1.36 (s, 6 H, CH$_3$) and 1.14 (d, 24 H, $^3J_{\mathrm{HH}}$ 6.9 Hz, CH*Me*$_2$). ^{13}C NMR (d$_6$-benzene, 298 K): δ 153.13 (s, *ipso*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 142.54 (s, *o*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 126.12 (d, $^1J_{\mathrm{CH}}$ 159.7, *p*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 122.75 (dt†, $^1J_{\mathrm{CH}}$ 156.7, *m*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 68.13 (t, 37.74 $^1J_{\mathrm{CH}}$ 145.3, thf), 36.70 (q, $^1J_{\mathrm{CH}}$ 132.5, *C*HMe$_2$), 25.73 (t, $^1J_{\mathrm{CH}}$ 132.5 Hz, thf) and 23.24 (q, $^1J_{\mathrm{CH}} = 125.8$ Hz, CH*Me*$_2$).

[Mo(NR)$_2$Me$_2$(py)] 6. To complex **2** (0.524 g, 1.1 mmol) in pentane (20 cm^3) was added pyridine (0.087 g, 1.1 mmol) in pentane (10 cm^3). After stirring for 30 min the yellow solution was filtered from the suspension. The remaining residue was washed with pentane (20 cm^3), and the combined extracts were reduced to half-volume and cooled to 0 °C for 12 h to afford **6** as orange cubes. Yield 0.52 g, 82% (Found: C, 67.08; H, 8.44; N, 7.56. Calc. for $\mathrm{C_{31}H_{45}MoN_3}$: C, 67.01; H, 8.16; N, 7.56%). IR: 1620w, 1601w, 1584w, 1418w, 1377m, 1357w, 1289w, 1215w, 1176w, 1147w, 1096w, 1039w, 1011w, 972m, 933w, 844s, 799s, 755s, 709s, 627w and 408w cm^{-1}. ^{1}H NMR (d$_8$-toluene, 298 K): δ 8.53 (dd, 2 H, $^3J_{\mathrm{HH}}$ 6.3, $^4J_{\mathrm{HH}}$ 1.6, py), 6.90–7.04 (m, 6 H, *m*- and *p*-C of $\mathrm{C_6H_3Pr^i_2}$-2,6), 6.75 (tt, 1 H, $^3J_{\mathrm{HH}}$ 7.6, $^4J_{\mathrm{HH}}$ 1.6, py), 6.46 (m, 2 H, py), 3.93 (sept, 4 H, $^3J_{\mathrm{HH}}$ 6.9, C*H*Me$_2$), 1.19 (d, 24 H, $^3J_{\mathrm{HH}}$ 6.8 Hz, CH*Me*$_2$) and 0.99 (s, 6 H, C*H*$_3$). ^{13}C NMR (d$_8$-toluene, 298 K): δ 153.42 (s, *ipso*-C of C$_6$H$_3$), 150.16 (d, $^1J_{\mathrm{CH}}$ 181.6, py C$_o$), 143.81 (s, *o*-C of C$_6$H$_3$), 129.54 (d, py C$_p$), 128.61 (d, py C$_m$), 125.14 (dt, $^1J_{\mathrm{CH}}$ 165.9, $^2J_{\mathrm{CH}}$ 6.8, *p*-C of C$_6$H$_3$), 124.63 (ddd, $^1J_{\mathrm{CH}}$ 155.6, *m*-C of C$_6$H$_3$), 28.53 (dq, $^1J_{\mathrm{CH}}$ 129.2, $^2J_{\mathrm{CH}}$ 3.8, *C*HMe$_2$), 27.39 (q, $^1J_{\mathrm{CH}}$ 125.1, CH$_3$) and 23.97 (qm, $^1J_{\mathrm{CH}}$ 125.5 Hz, CH*Me*$_2$).

[{Mo(NR)$_2$Me(μ-OMe)}$_2$] 7. Dry oxygen gas was passed through a solution of complex **1** (1.0 g, 1.65 mmol) in toluene (40 cm^3). After 5 min, the volatile components were removed *in vacuo*, and the residue was extracted with diethyl ether (3 × 40 cm^3). Cooling to −78 °C afforded orange **7**. Yield 1.4 g, 86% (Found: C, 63.43; H, 7.87; N, 6.04. Calc. for $\mathrm{C_{52}H_{80}Mo_2N_4O_2}$: C, 63.40; H, 8.19; N, 5.69%). IR: 2721w, 1584w, 1410w, 1350m, 1320m, 1269s, 1223w, 1160w, 1094w, 1054w, 1021m, 975m, 933m, 895w, 795m, 755s, 687w, 573w, 546w and 496w cm^{-1}. Mass spectrum (EI, *m*/*z*): 939 [M − CH$_3$ − OCH$_3$]$^+$; 492, [$\tfrac{1}{2}$M]$^+$; and 477, [$\tfrac{1}{2}$M − CH$_3$]$^+$. ^{1}H NMR (d$_6$-benzene, 298 K):

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† Resolution insufficient to determine $^3J_{\mathrm{HH}}$.

δ 7.10–6.90 (m, 12 H, *m*- and *p*-C of $C_6H_3Pr^i_2$-2,6), 4.35 (s, 6 H, OCH_3), 3.83 (sept, 8 H, $^3J_{HH}$ 6.9, $CHMe_2$), 1.45 (s, 6 H, CH_3), 1.25 (d, 24 H, $^3J_{HH}$ 6.9 Hz, $CH\mathit{Me}_2$) and 1.18 (d, 24 H, $^3J_{HH}$ 6.9, $CH\mathit{Me}_2$). ^{13}C NMR (d_6-benzene, 298 K): δ 152.59 (s, *ipso*-C of $C_6H_3Pr^i_2$-2,6), 144.23 (s, *o*-C of $C_6H_3Pr^i_2$-2,6), 126.70 (d, $^1J_{CH}$ 159.5, *p*-C of $C_6H_3Pr^i_2$-2,6), 122.68 (d, $^1J_{CH}$ 156.5, *m*-C of $C_6H_3Pr^i_2$-2,6), 67.71 (q, $^1J_{CH}$ 143.0 ,OCH_3), 28.76 (dq, $^1J_{CH}$ 128.5, $^2J_{CH}$ 3.5, $\mathit{C}HMe_2$), 25.68 (q, $^1J_{CH}$ 128.0, CH_3), 24.21 (qm, $^1J_{CH}$ 126.0, $CH\mathit{Me}_2$) and 23.64 (qm, $^1J_{CH}$ 125.8Hz, $CH\mathit{Me}_2$).

[{Mo(NBu^t)$_2$Me(μ-OMe)}$_n$] 8 (*n* = 1 or 2). As for complex **7**, but using [Mo(NBu^t)$_2$Me$_2$]. Yield 82% (Found: C, 39.1; H, 7.6; N, 9.0. Calc. for $C_{20}H_{48}Mo_2N_4O_2$: C, 42.2; H, 8.5; N, 9.9%). Satisfactory microanalytical data could not be obtained due to the air sensitivity of this oil. IR: 2969s, 2922s, 2894s, 2861m, 2820m, 1471w, 1452m, 1383w, 1355s, 1256s, 1219s, 1152w, 1121m, 1064m, 1034s, 804m, 686m, 593m, 568m, 525m, 495m, 467w and 442w cm^{-1}. Mass spectrum (CI, *m*/*z*): and 271, $[\frac{1}{2}M - CH_3]^+$. ^1H NMR (d_8-toluene, 298 K): δ 4.0 (s, 6 H, OCH_3), 1.30 [s, 36 H, $(CH_3)_3C$] and 0.88 (s, 6 H, CH_3). ^{13}C NMR (d_8-toluene, 298 K): δ 137.80 (s, $N\mathit{C}Me_3$), 66.69 (q, $^1J_{CH}$ 141.5, OCH_3), 31.89 (q, $^1J_{CH}$ 126.1, $NC\mathit{Me}_3$) and 16.00 (q, $^1J_{CH}$ 126.6 Hz, CH_3).

Crystallography

The air sensitive samples were mounted on glass fibres using a perfluoropolyether oil.[13] Crystal data were collected at 150 K, using a Siemens SMART CCD (**4** and **7**) or a Siemens P4 diffractometer (**2**). Graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. In the case of data collections performed with the Siemens SMART, cell parameters were refined using 512 reflections from all regions of reciprocal space and data were reduced using the SAINT program.[14] In the case of data collections performed with the Siemens P4, cell parameters were determined from 20 reflections located using a hemispherical search and data were reduced using XSCANS.[15] The structures were solved by direct methods (**2**, **4** and **7**) using the SHELXS 86 program[16] and refined by full matrix least squares methods on F^2 using SHELXL 93.[17] Atomic scattering factors were taken from ref. 18.

Positional and anisotropic atomic dispacement parameters were refined for all non-hydrogen atoms, except those of the disordered pentane solvent in complex **4** (see below). Hydrogen atoms were placed geometrically and positional parameters were refined using a riding model (including free rotation about C–C bonds for methyl groups). Isotropic atomic displacement parameters were constrained to be 1.2 (1.5 for methyl groups) times the equivalent isotropic atomic displacement parameter of the adjacent heavy atom.

Complex **4** contains a pentane solvent molecule disordered over two symmetry related sites, each with occupancy 0.5. Positional and isotropic atomic displacement parameters were refined for the pentane carbon atoms. The pentane hydrogen atoms were not included in the final model.

Crystal data. For **2**: $C_{26}H_{40}MoN_2$, $M = 476.54$, monoclinic, space group *C*2/*c*, $a = 20.240(4)$, $b = 6.5500(10)$, $c = 19.910(4)$ Å, $\beta = 103.99(3)°$, $U = 2561.2(8)$ Å^3, $Z = 4$, μ(Mo-Kα) = 0.53 mm^{-1}, 2936 reflections measured, 2253 unique ($R_{int} = 0.0356$) which were used in all calculations. The final $wR(F^2)$ was 0.1191, $R1 = 0.0466$. For **4**: $C_{34}H_{51}MoN_2P{\cdot}C_5H_{12}$, $M = 686.82$, monoclinic, space group $P2_1/c$, $a = 9.8278(7)$, $b = 14.6163(10)$, $c = 25.183(2)$ Å, $\beta = 94.6660(10)°$, $U = 3605.4(4)$ Å^3, $Z = 4$, μ(Mo-Kα) = 0.44 mm^{-1}, 15240 reflections measured, 6306 unique ($R_{int} = 0.0459$). The final $wR(F^2)$ was 0.1124, $R1 = 0.0475$. For **7**: $C_{52}H_{80}Mo_2N_4O_2{\cdot}2C_6D_6$, $M = 1147.30$, triclinic, space group $P\bar{1}$, $a = 10.0757(6)$, $b = 11.3939(7)$, $c = 14.3761(9)$ Å, $\alpha = 93.136(1)$, $\beta = 99.548(1)$, $\gamma = 111.915(1)°$, $U = 1497.6(3)$ Å^3, $Z = 1$, μ(Mo-Kα) = 0.46 mm^{-1}, 6468 reflections measured, 4795 unique ($R_{int} = 0.0206$). The final $wR(F^2)$ was 0.0806, $R1 = 0.0288$.

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