Molybdenum(VI) Bisimidoaryl Phenoxide and Alkoxide Complexes: Molecular Structures of $[Mo(NAr)_2(OCMe_2\text{-}2\text{-}py)(CH_2SiMe_3)]$ and $[\{Mo(NAr)_2Me(OMe)\}_2]$

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The synthesis and characterisation is reported of new, five-coordinate molybdenum(VI) bisimidoaryl complexes $[Mo(NAr)_2(O\text{-}N)(R)]$ [Ar = $C_6H_3(iPr)_2$-2,6; *O-N* = 2-pyridyldiphenylmethoxide (**a**), 2-pyridyldimethylmethoxide (**b**), 8-quinolinolate (**c**); R = Cl, Me, CH_2SiMe_3] and the corresponding bisalkoxide (**a**, **b**) and bisphenolate [**c**, **d** = $(OC_6H_4CH_2NMe_2\text{-}2)^-$] Mo^{VI} bisimidoaryl complexes $[Mo(NAr)_2(O\text{-}N)_2]$. These complexes can be formed by simple alcoholysis reactions between $[Mo(NAr)_2Cl_2(DME)]$ and the appropriate alcohol in the presence of Et_3N. The remaining chloride can be replaced by a methyl or trimethylsilylmethyl group by transmetallation with MeMgCl or $LiCH_2SiMe_3$. The solid state structure of $[Mo(NAr)_2(OCMe_2\text{-}2\text{-}py)(CH_2SiMe_3)]$ (**5**) has been determined by single-crystal X-ray analysis. A similar synthetic procedure was used to synthesise and characterise $[\{Mo(NAr)_2Me(OMe)\}_2]$ (**7**). The two methoxide ligands bridge between the two molybdenum(VI) nuclei. Compounds in which the ligand can form six-membered chelate rings {like $[Mo(NAr)_2(OC_6H_4CH_2NMe_2\text{-}2)_2]$ (**9**) and analogues} are usually difficult to obtain in a pure form and yields are typically low.

Introduction

Alkoxide and phenoxide ligands play an important role in catalysts developed for classical olefin metathesis polymerisation. The stability, reactivity and selectivity of the catalysts is often determined by the nature of the ancillary alkoxide or phenoxide ligands, as reported by Schrock,[1] Grubbs,[2] Basset[3] and others for $[WCl_{6-x}(OAr)_x]$ (x = 0−4, 6) or $[WOCl_{4-n}(OAr)_n]$ (n = 0−4) catalysts.[4] Van der Schaaf et al. have shown that the use of intramolecularly coordinating alkoxide and phenoxide ligands in tungsten(VI) alkylidene complexes yields complexes with special properties.[5] Enhanced stability, high ring-opening metathesis polymerisation (ROMP) activity (turnover frequency < 1/h at 20°C; > 20000/h at 70°C) and selectivity, and unexpected so-called "latent" behaviour were found.[6] Analogous compounds based on molybdenum as the active metal centre are desirable because molybdenum catalysts appear to tolerate functionalities to a greater degree than the corresponding tungsten catalysts.[7] Therefore, we have prepared and characterised a series of molybdenum(VI) bisimidoaryl phenoxide and alkoxide complexes containing a potentially intramolecularly coordinating amine. The ligands we used, depicted in Figure 1, are all monoanionic, potentially *O,N*-chelating ligands, i.e. $[OCPh_2\text{-}2\text{-pyridyl}]^-$ (**a**),[6][8] $[OCMe_2\text{-}2\text{-pyridyl}]^-$ (**b**),[6] 8-oxyquinolinate (**c**)[6] and $[OC_6H_4CH_2NMe_2\text{-}2]^-$ (**d**).[5]

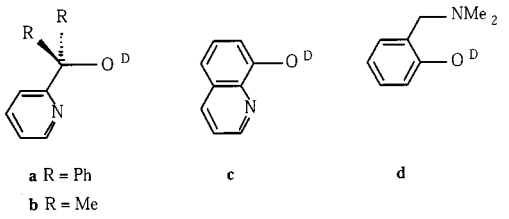

Figure 1. Selected alkoxide and phenoxide ligands with potentially *ortho*-chelating amine donors

At this point we have focused on the synthesis of Mo^{VI} compounds with the general formula $[Mo(NAr)_2(O\text{-}N)(R)]$ (*O-N* = **a**, **b**, **c** or **d**; R = Cl, Me, CH_2SiMe_3; Ar = 2,6-diisopropylphenyl) and the corresponding bisalkoxide (**a**, **b**) and bisphenolate (**c**, **d**) Mo^{VI} complexes $[Mo(NAr)_2(O\text{-}N)_2]$.

Results

Synthesis of Complexes 1−6

Direct alcoholysis of $[Mo(NAr)_2Cl_2(DME)]$ with $[HOCPh_2\text{-}2\text{-py}]$ in the presence of Et_3N afforded the mono(2-pyridyldiphenylmethoxide) molybdenum(VI) complex $[Mo(NAr)_2(OCPh_2\text{-}2\text{-py})Cl]$ (**1**) in almost quantitative yield. The analogous methylated compound $[Mo(NAr)_2(OCPh_2\text{-}2\text{-py})(Me)]$ (**2**) was obtained by reaction of **1** with MeMgCl. The corresponding bis(2-pyridyldiphenylmethoxide) molybdenum(VI) complex $[Mo(NAr)_2(OCPh_2\text{-}2\text{-py})_2]$ (**3**) was made by either treating **1** with one equivalent of

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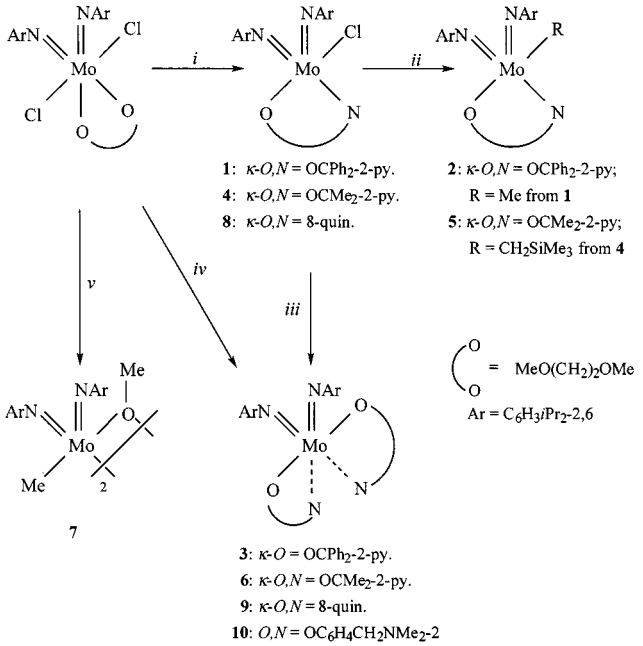
[LiOCPh$_2$-2-py] or by reaction of [Mo(NAr)$_2$Cl$_2$(DME)] with two equivalents of [LiOCPh$_2$-2-py] (see Scheme 1).



Scheme 1: *i*: The appropriate alcohol, Et_3N, $-Et_3NHCl$, −1,2 dimethoxyethane, Et_2O, > 95% yield; *ii*: **2**: MeMgCl, $-MgCl_2$, THF, 92% yield; **5**: $LiCH_2SiMe_3$, Et_2O, −LiCl, 80% yield; *iii* and *iv*: by reaction of lithium phenolates or alcoholysis, see experimental section; *v*: MeOH, Et_3N, $-Et_3NHCl$, MeMgCl, $-MgCl_2$, yield: 68% yield

All these compounds are intensely coloured, e.g. dark red (**1**), orange (**2**) and red/purple (**3**). The solid complexes **1** and **2** are moisture-sensitive but can be handled in air for short periods of time (less than 1 min.) without any noticeable decomposition. Compound **3** is stable in air even at high temperatures (> 200°C). The compounds containing the 2-pyridyldimethylmethoxide ligand [OCMe$_2$-2-py]$^-$ **(b)** (**4**: Cl, **5**: CH_2SiMe_3 and **6**: [OCMe$_2$-2-py]$^-$) can be made in a similar manner (see Scheme 1). NMR spectroscopy and elemental analysis confirmed their composition.

NMR-Spectroscopic Analysis

The ^{1}H NMR spectra of **1**−**6** (C_6D_6) show a septet and two doublet resonances for the *i*Pr *ortho* substituents of the NAr ligands. In the $^{13}C\{^1H\}$ NMR spectra these *i*Pr groups appear as three separate resonances indicating that all four *i*Pr groups are equivalent but that the CMe_2 moieties are diastereotopic. The R-substituents of the *O,N*-ligand (**a**: R = Ph; **b**: R = Me) of **1**, **2**, **4** and **5** show only one set of resonaces and are equivalent over the whole temperature range (220 K − 330 K) studied. These results indicate the presence of a molecular symmetry plane in the complexes, which renders both R-substituents in the *O,N*-ligands equivalent on the NMR time scale, but gives no further information about the actual coordination mode of the *O,N*-ligand. This can only be rationalised either by a structure in which the prochiral OC[1] and py-N centres are found in an apparent molecular symmetry plane in the case of Mo−N coordination, or when the *O,N*-ligand is monodentate O-bonding and the free pyridine substituent undergoes rapid rotation around the O−CR_2 bond.

The chemical shift difference ($\Delta\delta$)[9] between the hydrogen *ortho* to the pyridyl nitrogen in the complexes and that in the free parent ligand suggests that the pyridyl group coordinates intramolecularly in complexes **1** ($\Delta\delta$ = 1.35), **2** ($\Delta\delta$ = 0.59), **4** ($\Delta\delta$ = 1.19) and **5** ($\Delta\delta$ = 0.70). This implies that the apparent molecular symmetry plane in solution arises from fluxional processes involving alternating reversible N−Mo bond breaking and formation, and monodentate O-bonding. Finally, as compounds **1**, **2**, **4** and **5** have similar features in their NMR spectra it can be assumed that these compounds have the same structural characteristics.

The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of compound **3** and **6** (C_6D_6) show two sets of resonances for the R-substituents in the OCR_2 (**3**: R = Ph; **6**: R = Me) moieties of the methoxide ligands. These R-substituents are diastereotopic because only one set of pyridyl carbons appears in the ^{13}C NMR spectrum. The very small chemical shift difference value of py-H^6 in **3** ($\Delta\delta$ = −0.11) suggests the absence of Mo−N bonding, making it a four-coordinate species. This is probably forced by the presence of sterically demanding phenyl substituents. In contrast, the corresponding chemical shift difference in **6** ($\Delta\delta$ = 0.79) does suggest an intramolecular coordination between Mo and N. In this particular case, coordination of the nitrogen atoms in both methoxide ligands would lead to a hexacoordinate molybdenum species in which the two imidoaryl ligands are likely to adopt a *cis* conformation to maximise d-orbital overlap between the π-electrons of the imido ligands and the empty d-orbitals.[10] For the same reason the pyridyl-N-donor ligands will be positioned *trans* with respect to each imidoaryl ligand. This would give hexacoordinate diimidoaryl molybdenum(VI) compounds, with a ligand array similar to that present in the solid-state structure of the analogous dioxo molybdenum(VI) compound found by Schultz et al.[8c]

Solid-State Structure of [Mo(NAr)$_2$(OCMe$_2$-2-py)(CH_2SiMe_3)] (5)

To get further insight into the molecular geometry of this series of molybdenum(VI) compounds, a single crystal X-ray structure determination of **5** was carried out and its molecular structure, with the adopted numbering scheme, is depicted in Figure 2. Selected bond lengths and angles are given in Table 1.

In compound **5** the ligands form a distorted trigonal bipyrimidal geometry around the Mo^{VI} centre (43.7% along the Berry pseudorotation coordinate from trigonal bipyramid to square pyramid) in which the N3-bonded imido ligand and N1 occupy the apical positions. The metal lies in the basal plane defined by O1, N2 and the C_{ipso} (C9) of the neosilyl (= CH_2SiMe_3) group. The *O,N*-ligand is didentate

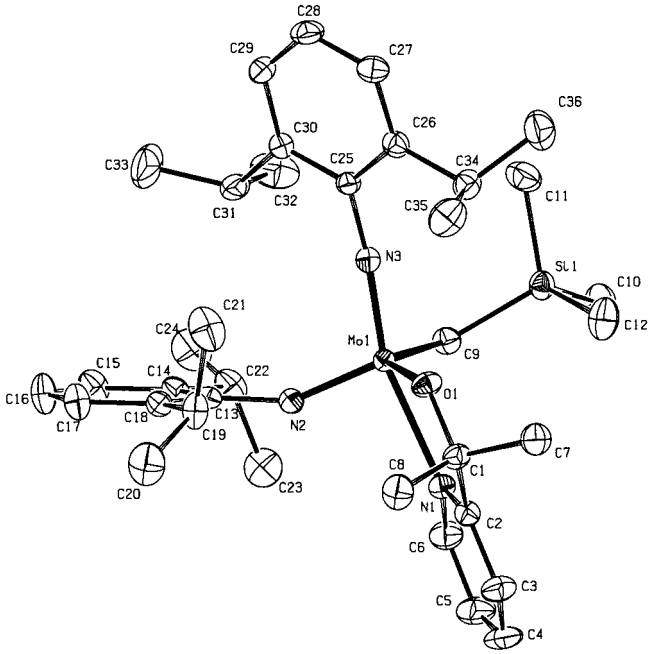


Figure 2. ORTEP drawing (50% probability atomic displacement ellipsoids) of **5**; hydrogen atoms have been omitted for clarity

chelating in the solid state with a Mo1−N1 bond length of 2.346(2) Å, typical for sp^2-nitrogen to molybdenum coordination[8c] and comparable to those found in corresponding tungsten complexes.[6][11] The metal-carbon bond length [Mo1−C9, 2.156(2) Å] observed for compound **5** is rather large (this bond in other molybdenum alkyl complexes lies in the range 2.08−2.20 Å).[12] The bond angle Mo1−C9−Si1 is larger than expected for a sp^3 carbon although similar bond angles have also been found in analogous *O,N*-ligand-containing tungsten neosilyl compounds.[6] No agostic interactions of the α-hydrogens were found (NMR, X-ray).

Table 1. Selected intramolecular distances [Å] and angles [°] of **5**[a]

Bond lengths [Å]		Bond angles [°]	
Mo1−O1	1.9504(19)	Mo1−O1−C1	128.96(13)
Mo1−N1	2.346(2)	Mo1−C9−Si1	116.82(11)
Mo1−N2	1.7686(18)	Mo1−N2−C13	152.52(15)
Mo1−N3	1.7529(19)	Mo1−N3−C25	172.95(18)
Mo1−C9	2.156(2)		
C9−Si1	1.864(2)		
O1−C1	1.406(3)		

[a] The estimated standard deviations of the last significant digits are shown in parentheses.

Formation of [{Mo(NAr)$_2$Me(OMe)}$_2$] (7)

In one attempt to synthesise the methylated derivative [Mo(NAr)$_2$(OCMe$_2$-2-py)(Me)] by reaction of compound **4** with a small excess of MeMgCl in THF, orange crystals of an unknown product (**7**) were obtained. NMR spectroscopy and elemental analysis pointed to the formation of a molybdenum compound containing one methyl, one methoxide and two imidoaryl ligands. However, compound **7** could not be synthesised again by the original synthetic route (**4** + MeMgCl in THF), not even in the presence of deliberately added air, water or methanol. Since the formation of a molybdenum compound such as **7** was unexpected and could not easily be rationalised, a single-crystal X-ray

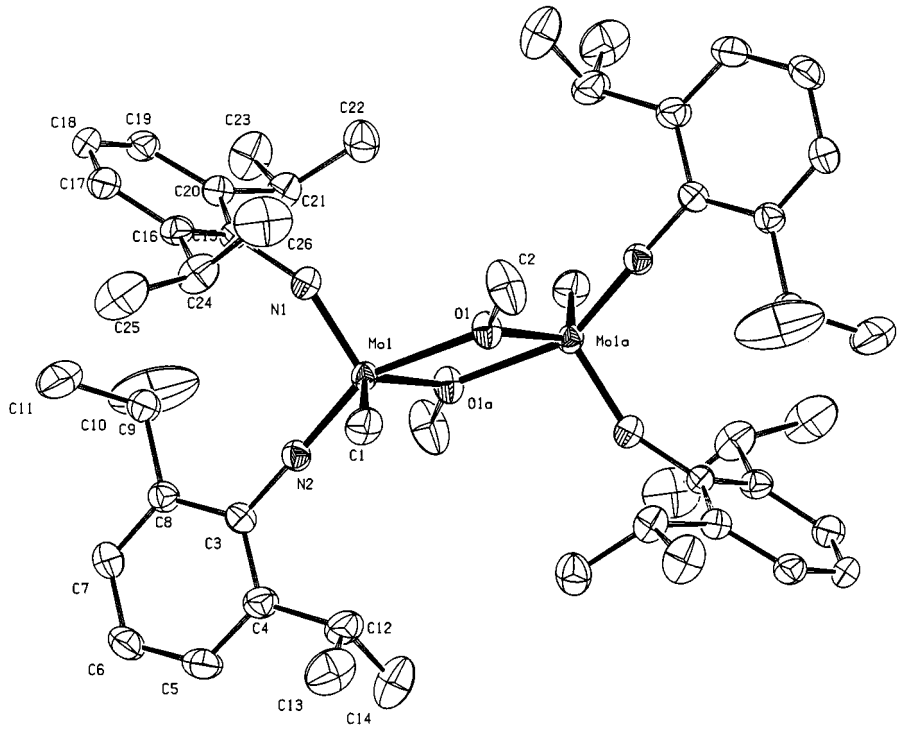


Figure 3. ORTEP drawing (50% probability atomic displacement ellipsoids) of **7**; hydrogen atoms have been omitted for clarity

analysis was carried out. The molecular structure of the orange compound, with the adopted numbering scheme, is depicted in Figure 3 and selected bond lengths and angles are given in Table 2.

Table 2. Selected geometrical details of **7**[a]

Bond lengths [Å]		Bond angles [°]	
Mo1−C1	2.161(4)	Mo1−O1−Mo1a	111.16(9)
Mo1−O1	2.157(2)	O1−Mo1−O1a	68.84(8)
Mo1−N1	1.757(3)	Mo1−N1−C15	153.7(2)
Mo1−N2	1.756(3)	Mo1−N2−C3	177.4(2)
N1−C15	1.388(4)		
N2−C3	1.383((4)		
O1−C2	1.421(5)		

[a] The estimated standard deviations of the last significant digits are shown in parentheses.

The solid state structure shows a dimeric compound in which each molybdenum nucleus indeed contains two imidoaryl ligands, one methyl group and one bridging methoxide ligand: [{Mo(NAr)$_2$Me(OMe)}$_2$] (**7**). Compound **7** has an inversion point positioned at the crossing of the virtual lines Mo1−Mo1a and O1−O1a. Each molybdenum centre has a distorted square-pyramidal coordination sphere (67.9% along the Berry-pseudorotation coordinate from trigonal bipyramid to square pyramid) in which the N1-bonded imido ligand occupies the apical position. The basal plane of the square pyramid is defined by N2, C1, O1 and O1a. Both molybdenum nuclei contain one bent [153.7(2)°] and one almost linear [177.4(2)°] imidoaryl ligand. The formation of bridging alkoxide or phenoxide ligands between two molybdenum (or tungsten) nuclei has previously been reported.[13]

Now that compound **7** had been fully analysed and characterised, a different synthetic route was developed using direct alcoholysis of [Mo(NAr)$_2$Cl$_2$(DME)] with MeOH (in presence of Et$_3$N) and subsequent reaction with MeMgCl. Compound **7** is thermally stable up to 185°C before decomposition takes place and decomposes in air within a few hours. It is soluble in most polar solvents (including CH_2Cl_2 and $CHCl_3$) but is only slightly soluble in benzene and toluene and does not dissolve in pentane or hexanes.

Synthesis and Characterisation of Complexes 8−10

The molybdenum bisimidoaryl phenoxide complexes containing the 8-quinolinolato ligand **c** (**8** and **9**) and the (dimethylamino)methyl phenoxide ligand **d** (**10**) were also synthesised by alcoholysis (see Scheme 1). The ^{1}H NMR spectra of **8** ($\Delta\delta$ = 1.20) and **9** ($\Delta\delta$ = 0.21)[14] suggest the presence of intramolecular coordination between Mo and the quinolinate nitrogen. The ^{1}H NMR spectroscopic data of **10** did not indicate the presence of such a Mo−N coordination since the H^6 proton is not shifted relative to that of the free parent 2-(dimethylamino)methyl phenol. Attempts to alkylate **8** by transmetallation reactions were unsuccessful as mixtures of the desired product and Li-**c** or ClMg-**c** that could not be separated were obtained. Apparently ligand exchange reactions do occur. Compounds in which the ligand can form six-membered chelate rings (like **10** and analogues) are usually difficult to obtain pure (also by transmetallation reactions using the sodium or lithium phenolates) and yields are typically low. Possibly, the formation of six-membered instead of five-membered chelate rings is thermodynamically less favoured.

Reactivity of the Complexes

Molybdenum(VI) complexes such as [Mo(NAr)$_2$(C$_6$H$_4$(CH$_2$NMe$_2$)-2)(Me)] react with *n*BuLi and, in the presence of dimethoxyethane (DME), the corresponding [Li(DME)$_2$Mo(NAr)$_2${C$_6$H$_4$(CH$_2$NMe$_2$)-2}(Me)(*n*Bu)] can be isolated.[15] This lithium molybdate(VI) compound can be thermally activated to give a mixture of paramagnetic Mo^V compounds, [Mo(NAr)$_2${C$_6$H$_4$(CH$_2$NMe$_2$)-2}(Me)] and [Mo(NAr)$_2${C$_6$H$_4$(CH$_2$NMe$_2$)-2}(*n*Bu)]. Small amounts of 1-butene were also detected as a result of β-H elimination reactions. This mixture becomes ROMP-active after dry air is bubbled through the solution. A tentative explanation for this is that dioxygen insertion into a Mo − C bond[16] may facilitate ligand-exchange reactions and alkylidene formation after α-H elimination.

According to their composition and structural features it is unlikely that complexes **1−10** as such can be active as ring-opening metathesis polymerisation (ROMP) catalysts. However, the reaction of compounds **2** and **5** with *n*BuLi gave products that show high ROMP activity with norbornene without activation with dry air. Analysis of these reaction products showed the presence of several Mo^V and Mo^{VI} complexes and [LiOCR$_2$-2-py] (R = Ph **2** and R = Me **5**) as a result of ligand exchange reactions. These unavoidable exchange reactions hamper the isolation of the active molybdenum alkylidene species although high molecular weight polynorbornene was found ($M_n = 1 \times 10^6$ g/mol, 90% *cis* double bonds, PDI = 2.5)

Experimental Section

General: Syntheses were carried out with standard Schlenk techniques under dry, oxygen-free nitrogen. Toluene, benzene, hexane, and pentane were carefully dried and distilled from sodium benzophenone-ketyl prior to use. CH_2Cl_2 was distilled from CaH_2. − NMR Spectra (^{1}H and ^{13}C{^{1}H}) were recorded on Bruker AC200 and Bruker AC300 spectrometers, with chemical shifts referenced to Me$_4$Si. − Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. − [Mo(NAr)$_2$Cl$_2$(DME)],[17] HOCPh$_2$-2-pyridyl,[6] [LiOCPh$_2$-2-pyridyl],[6] HOCMe$_2$-2-pyridyl,[6] [LiOCMe$_2$-2-pyridyl],[6] LiCH$_2$SiMe$_3$,[18] and 2-[(dimethylamino)methyl]phenol[5] were prepared according to literature procedures.

[Mo(NAr)$_2$(OCPh$_2$-2-py-*κ*-*O,N*)Cl] (1): To a solution of [Mo(NAr)$_2$Cl$_2$(DME)] (2.34 g, 3.85 mmol) in Et$_2$O/benzene (80 mL in a 1:1 ratio) was added Et$_3$N (0.6 mL, 4.3 mmol) and a solution of HOCPh$_2$-2-pyridyl (1.00 g, 3.85 mmol) in Et$_2$O (20 mL) at ambient temperature. After stirring for 2 h, an off-white precipitate was re-

moved by centrifugation. The solid was washed with Et_2O (2 × 40 mL) and the Et_2O washings were combined with the mother liquor. All volatiles were removed in vacuo leaving a red crystalline solid (2.85 g, 100%) which was pure according to NMR spectroscopy and elemental analysis. − M.p.: 168°C − ^{1}H NMR: δ = 9.53 (d, 1, py-H^6), 7.37 (dd, 4, Ph-H), 7.05 (m, 10, ArH), 6.95 (m, 3, ArH) 6.77 (m, 1, py-H) 6.54 (m, 1, py-H), 3.87 (sept, 4, C*H*Me$_2$), 1.24 (d, 12, CH*Me*$_2$), 1.09 (d, 12, CH*Me*$_2$). − ^{13}C NMR: δ = 167.7 (py-C^2), 155.0 (C*ipso* NAr), 149.5, 146.6 (Ar-C), 144.0 (C*para* NAr), 138.1, 128.8, 128.6, 128.3, 126.9, 124.8, 123.1, 122.8 (Ar-C), 95.9 (OC), 28.7 (*C*HMe$_2$), 24.1 (CH*Me*$_2$), 23.3 (CH*Me*$_2$). − $C_{42}H_{48}ClMoN_3O$ (742.26): C 67.96, H 6.52, N 5.66; found C 67.90, H 6.58, N 5.61.

[Mo(NAr)$_2$(OCPh$_2$-2-py-κ-O,N)(Me)] (2): To a solution of **1** (0.44 g, 0.59 mmol) in THF (40 mL) was added 200 μl of a 3 M THF solution of MeMgCl (0.6 mmol). The reaction mixture was allowed to stir overnight. After 18 h all volatiles were removed in vacuo (3 h, 60°C). The remaining red solid was extracted with pentane (2 × 40 mL). The precipitate was removed by centrifugation, the pentane layers were collected, concentrated (30 mL), and stored at −30°C. After one week orange crystals (0.39 g, 0.54 mmol, 92% yield) were isolated that were pure according to NMR spectroscopy and elemental analysis. M.p.: 152°C − ^{1}H NMR: δ = 8.77 (d, 1, py-H^6), 7.47 (m, 4, Ph-H), 7.05 (m, 13, Ar-H), 6.75 (m, 1, py-H) 6.39 (m, 1, py-H), 3.84 (sept, 4, C*H*Me$_2$), 1.67 (s, 3, Mo−Me), 1.21 (d, 12, CH*Me*$_2$), 1.09 (d, 12, CH*Me*$_2$). − ^{13}C NMR: δ = 169.2 (py-C^2), 154.2 (C*ipso* NAr), 149.2, 148.0, 142.9, 137.7, 128.3, 128.1, 127.6, 125.3, 124.7, 123.0, 122.6 (Ar-C), 95.4 (OC), 28.6 (*C*HMe$_2$), 25.3 (Mo−Me), 24.5 (CH*Me*$_2$), 23.5 (CH*Me*$_2$). − $C_{43}H_{51}MoN_3O$ (721.84): C 71.55, H 7.12, N 5.82; found C 71.64, H 7.08, N 5.76.

[Mo(NAr)$_2$(OCPh$_2$-2-py-κ-O)$_2$] (3): To a solution of **1** (0.99 g, 1.34 mmol) in THF (60 mL) was added [Li−OCPh$_2$-2-pyridyl] (0.36 g, 1.34 mmol) as a solid. The reaction mixture was warmed to 50°C. After stirring two hours all volatiles were removed in vacuo (3 h, 60°C). The remaining red solid was extracted with CH_2Cl_2 (3 × 30 mL). The precipitate was removed by centrifugation, the CH_2Cl_2 layers were collected and concentrated to a volume of 10 mL. The remaining suspension was washed with pentane (3 × 20 mL), and the remaining solid dried in vacuo leaving a purple/red, air-stable product (1.23 g, 1.27 mmol, 95% yield). M.p.: > 200°C − ^{1}H NMR: δ = 8.07 (d, 2, py-H^6), 7.86 (d, 4, Ph-H), 7.47 (dd, 2, py-H), 7.26 (m, 4, Ph-H) 7.14−6.83 (m, 18, ArH), 6.58 (m, 2, py-H), 5.86 (m, 2, py-H), 4.31 (sept, 4, C*H*Me$_2$), 1.32 (d, 12, CH*Me*$_2$), 0.96 (d, 12, CH*Me*$_2$). − ^{13}C NMR: d = 164.9 (py-C^2), 155.0 (C*ipso* NAr), 151.3, 149.6, 149.2 (2 x), 141.6, 135.9, 129.6, 128.7, 127.9, 127.6, 127.1, 123.0, 122.9, 122.8, 121.5 (Ar-C), 94.1 (OC), 27.8 (*C*HMe$_2$), 24.9 (CH*Me*$_2$). − $C_{60}H_{62}MoN_4O_2$ (967.12): C 74.52, H 6.46, N 5.79; found C 74.38, H 6.43, N 5.72.

[Mo(NAr)$_2$(OCMe$_2$-2-py-κ-O,N)Cl] (4): An analogous method to that described for the synthesis of **1** was used. The synthesis was typically done on a 4 mmol scale using HOCMe$_2$-2-pyridyl. Yields are quantitative. M.p.: 177°C. − ^{1}H NMR: δ = 9.44 (d, 1, py-H^6), 7.06−6.92 (m, 7, Ar-H), 6.55 (m, 2, py-H), 4.08 (sept, 4, C*H*Me$_2$), 1.47 (s, 6, CMe$_2$), 1.28 (d, 12, CH*Me*$_2$), 1.20 (d, 12, CH*Me*$_2$). − ^{13}C NMR: δ = 171.4 (py-C^2), 154.8 (C*ipso* NAr), 149.2, 143.8, 139.1, 126.7, 122.8 (2 x), 120.1 (Ar-C), 86.4 (O*C*Me$_2$), 30.6 (OC*Me*$_2$), 28.6 (*C*HMe$_2$), 25.1 (CH*Me*$_2$), 23.4 (CH*Me*$_2$). − $C_{31}H_{44}ClMoN_3O$ (606.11): C 61.43, H 7.32, N 6.93; found C 61.49, H 7.29, N 6.82.

[Mo(NAr)$_2$(OCMe$_2$-2-py-κ-O,N)(CH$_2$SiMe$_3$)] (5): To a solution of **3** (0.75 g, 1.24 mmol) in Et_2O (60 mL) was added a solution of LiCH$_2$SiMe$_3$ (0.12 g, 1.24 mmol) in Et_2O (20 mL) at −78°C. The reaction mixture was warmed to room temperature (0.5 h). After two hours the white precipitate was removed by centrifugation and the Et_2O layer was collected and concentrated (10 mL). The orange crystals were collected and dried in vacuo (0.65 g, 0.99 mmol, 80% yield). The crystalline material was pure according to NMR spectroscopy and elemental analysis. M.p.: 154°C. − ^{1}H NMR: δ = 8.95 (dd, 1, py-H^6), 7.07 (m, 7, Ar-H), 7.66 (m, 1, py-H), 6.56 (m, 1, py-H), 4.08 (sept, 4, C*H*Me$_2$), 1.71 (s, 2, Mo−CH$_2$Si), 1.57 (s, 6, OCMe$_2$), 1.32 (d, 12, CH*Me*$_2$), 1.21 (d, 12, CH*Me*$_2$). − ^{13}C NMR: δ = 172.1 (py-C^2), 154.6 (C*ipso* NAr, broad), 148.0, 142.9 (broad), 138.2, 124.8, 122.7, 122.5, 120.4 (Ar-C), 85.0 (O*C*Me$_2$), 32.4 (MoCH$_2$Si), 31.7 (OCMe$_2$), 28.3 (*C*HMe$_2$), 25.3 (CH*Me*$_2$), 23.2 (CH*Me*$_2$), 2.1 (SiMe$_3$). − $C_{36}H_{55}MoN_3OSi$ (669.88): C 64.55, H 8.28, N 6.27; found C 64.68, H 8.35, N 6.27.

[Mo(NAr)$_2$(OCMe$_2$-2-py-κ-O,N)$_2$] (6): An analogous method to that described for the synthesis of **3** was used but **4** was the starting material. The synthesis was typically done on a 2 mmol scale with HOCMe$_2$-2-pyridyl. Yield 91%. M.p.: >200°C. − ^{1}H NMR: δ = 9.04 (m, 2, py-H^6), 7.04 (m, 4, Ar-H), 6.88 (m, 4, Ar-H), 6.55 (m, 4, py-H), 4.35 (sept, 4, C*H*Me$_2$), 1.81 (s, 6, OCMe$_2$), 1.57 (s, 6, OCMe$_2$), 1.42 (d, 12, CH*Me*$_2$), 1.12 (d, 12, CH*Me*$_2$). − ^{13}C NMR: δ = 170.5 (py-C^2), 155.3 (C*ipso* NAr), 146.8, 142.3, 137.6, 123.2, 123.0, 121.5, 119.6 (Ar C), 83.0 (O*C*Me$_2$), 31.7 (OC*Me*$_2$), 27.5 (CH*Me*$_2$), 25.4 (OC*Me*$_2$), 24.3 (CH*Me*$_2$), 24.3 (*C*HMe$_2$). − $C_{38}H_{54}MoN_4O_2$ (694.82): C 65.69, H 7.83, N 8.06; found C 65.58, H 7.86, N 7.95.

[{Mo(NAr)$_2$Me(OMe)}$_2$] (7): To a solution of [Mo(NAr)$_2$Cl$_2$(DME)] (1.45 g, 2.38 mmol) in Et_2O (50 mL) was added Et_3N (0.5 mL, 3.6 mmol) and MeOH (96 μL, 2.38 mmol). After 1 h the precipitate that had formed was removed by centrifugation and the upper layer was collected. All volatiles were removed in vacuo from this upper layer and the remaining solid was dissolved in THF (40 mL). To the solution 0.79 mL of a 3 M THF solution of MeMgCl (2.38 mmol) was added at ambient temperature. After 2 h stirring all volatiles were removed *in vacuo* (3 h, 60°C) and the remaining solids were washed with pentane (2 × 20 mL). The remaining solid was isolated and recrystallised from Et_2O (60 mL). At −30°C red crystals could be isolated after 5 days (0.80 g, 68% yield, 1.62 mmol). M.p. with decomposition.: 185°C. − ^{1}H NMR: δ = 7.07−6.94 (m, 6, Ar-H), 4.36 (s, 3, Mo−CH$_3$), 3.84 (sept, 4, C*H*Me$_2$), 1.44 (s, 3, Mo−CH$_3$), 1.25 (d, 12, CH*Me*$_2$), 1.19 (d, 12, CH*Me*$_2$). − ^{13}C NMR: δ = 152.6 (C*ipso* NAr), 144.3, 126.7, 122.8 (Ar C), 67.7 (Mo−Me) 28.8 (*C*HMe$_2$), 25.5 (Mo−Me), 24.2 (CH*Me*$_2$), 23.7 (CH*Me*$_2$). − [(C$_{26}$H$_{40}$MoN$_2$O)$_2$] (985.12): C 63.40, H 8.19, N 5.69; found C 63.25, H 8.13, N 5.63.

[Mo(NAr)$_2$(8-quin-κ-O,N)Cl] (8): An analogous method to that described for the synthesis of **1** was used. The synthesis was typically done on a 2 mmol scale with 8-quinolinol. Yield: 96%. M.p.: 194°C. − ^{1}H NMR: δ = 9.52 (d, 1, H^1-quin), 7.40 (dd, 1, H-quin), 7.22 (m, 8, Ar-H), 6.82 (dd, 1, H-quin) 6.60 (m, 1, quin-H), 4.03 (sept, 4, C*H*Me$_2$), 1.24 (d, 12, CH*Me*$_2$), 1.10 (d, 12, CH*Me*$_2$). − ^{13}C NMR: δ = 163.2 (C*ipso* quin), 154.4 (C*ipso* NAr), 149.4, 144.9 142.1, 139.1, 129.8, 127.9, 122.7, 122.0, 115.9, 114.6 (Ar C), 28.9 (*C*HMe$_2$), 24.2 (CH*Me*$_2$), 23.8 (CH*Me*$_2$). − $C_{33}H_{40}ClMoN_3O$ (626.10): C 63.31, H 6.44, N 6.71; found C 63.59, H 6.35, N 6.78.

[Mo(NAr)$_2$(8-quin-κ-O,N)$_2$] (9): To a solution of [Mo(NAr)$_2$Cl$_2$(DME)] (1.87 g, 3.08 mmol) in benzene (80 mL) was added Et_3N (1 mL, 7.2 mmol) and a solution of 8-quinolinol (0.89 g, 6.16 mmol) in Et_2O (20 mL) at ambient temperature. After stirring for 18 h, all volatiles were removed in vacuo and the remaining solid was extracted with pentane (5 × 40 mL). The precipitate was removed by centrifugation and the pentane layers were collected

and concentrated leaving a red crystalline solid (2.85 g, 100%) which was pure according to NMR spectroscopy and elemental analysis. NMR spectroscopy and elemental analysis showed the presence of one pentane solvent molecule per molybdenum atom in the crystals. M.p.: 182°C. – ^{1}H NMR: δ = 8.60 (d, 2, quin H[7]), 7.40–6.76 (m, 14, Ar-H), 6.23 (m, 2, quin H), 4.02 (sept, 4, C*H*Me$_2$), 1.35 (d, 12, CH*Me*$_2$), 0.97 (d, 12, CH*Me*$_2$). – ^{13}C NMR: δ = 164.3 (C*ipso* quin), 154.8 (C*ipso* NAr), 145.0, 141.7, 140.9, 137.4, 130.2, 129.9, 124.1, 122.5, 121.7, 114.8, 114.2 (Ar C), 28.5 (*C*HMe$_2$), 24.3 (CH*Me*$_2$), 24.0(CH*Me*$_2$). – $C_{47}H_{58}MoN_4O_2$ (806.95): C 69.96, H 7.25, N 6.94; found C 69.85, H 7.12, N 6.79.

[Mo(NAr)$_2$(OC$_6$H$_4$CH$_2$NMe$_2$-2)$_2$] (10): An analogous method to that described for the synthesis of **8** was used. The synthesis was typically done on a 4 mmol scale with two equivalents of 2-(dimethylamino)methyl phenol and an excess of Et$_3$N. The product was collected as a dark-red crystalline material from a concentrated pentane solution. Yield 28%. M.p.: 108°C. – ^{1}H NMR: δ = 7.17 (m, 4, Ar-H), 6.92 (m, 6, Ar-H), 6.84 (m, 4, ArH), 3.92 (sept, 4, C*H*Me$_2$), 3.74 (CH$_2$), 2.36 (N(CH$_3$)$_2$, 1.11 (d, 24, CH*Me*$_2$). – ^{13}C NMR: δ = 164.0 (C *ipso* OAr), 154.0 (C*ipso* NAr), 143.5, 130.1, 128.8, 126.2, 125.2, 123.0, 120.1, 119.8 (Ar C), 63.8 (CH$_2$), 47.5 (N(CH$_3$)$_2$, 28.0 (*C*HMe$_2$), 24.5 (CH*Me*$_2$). – $C_{42}H_{58}MoN_4O_2$ (746.89): C 67.54, H 7.83, N 7.50; found C 67.68, H 7.79, N 7.42.

Structure Determination and Refinement of 5 and 7: X-ray data were collected on an Enraf–Nonius CAD4T rotating anode diffractometer for a transparent, red/orange (**5**) or red (**7**) crystal glued on top of a glass fibre with inert fluorinated oil. The unit-cell parameters were checked for the presence of higher lattice symmetry. Data were corrected for Lorentz polarisation effects. An empirical absorption correction was applied (PLATON/DELABS).[19] The structures were solved by direct methods and subsequent difference Fourier techniques (SHELXS86).[20] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL93)[21] using no observance criterion. Hydrogen atoms were included on calculated positions, riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All hydrogen atoms were refined with a fixed isotropic atomic displacement parameter related to the value of the equivalent isotropic atomic displacement parameter of their carrier atom. Weights were optimised in the final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[22] Geometrical calculations and illustrations were performed with PLATON.[19] All calculations were performed on a DECstation 5000 cluster. Crystal data and numerical details of the structure determinations and refinements are collected in Table 3. Selected geometrical details of the structures of **5** and **7** are listed in Tables 1 and 2, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-106132 (structure **5**) and CCDC-106134 (structure **7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat). + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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