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FULL PAPER

Synthesis and structures of dioxo-Mo(VI) and -W(VI) amides

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Treatment of $[MO_2Cl_2{\cdot}(DME)]$ (M = Mo, W; DME = 1,2-dimethoxyethane) with the lithium reagents LiL^n [$L^1 = {}^-N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$, $L^2 = {}^-N(SiBu^tMe_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$, $L^3 = {}^-N(SiBu^tPh_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$] afforded the corresponding *cis*-dioxo-Mo(VI) amido complexes $[MoO_2(L^n)_2]$ ($L^n = L^1$ **1**, $L^n = L^2$ **2**, $L^n = L^3$ **3**) and *cis*-dioxo-W(VI) amido complexes $[WO_2(L^n)_2]$ ($L^n = L^1$ **4**, $L^n = L^2$ **5**, $L^n = L^3$ **6**). X-Ray crystallography shows that compounds **1**, **2**, **4** and **5** are mononuclear with the amido ligands bound to the metal centres in a N,N-chelating fashion forming highly strained four-membered metallacyclic rings with biting angles N_{amido}–M–N_{py} around 60°. The Mo–N_{amido} and W–N_{amido} distances are comparable which fall in the range of 2.070–2.081 Å.

Introduction

The study of oxo-molybdenum and -tungsten complexes has attracted considerable interest in recent years because of their relevance to some biological and industrial oxidation processes.[1] A number of dioxo-molybdenum and -tungsten complexes with various supporting ligands have been reported as models for the active site of molybdenum- and tungsten-containing oxotransferases.[2] In addition, oxo-molybdenum and -tungsten complexes are also known to be intermediates in a number of metal oxide catalysed reactions.[3,4]

The chemistry of transition metal amides has received a great deal of attention because of the potential application of these complexes to facilitate carbon–nitrogen bond formation.[5,6] Although a wide range of early transition metal amido complexes of the types $[M(NR_2)_n]$ and $[ML_m(NR_2)_n]$ have been reported,[5] studies on amido complexes of late transition metals are rare. In fact, the number of structurally authenticated metal amides decreases on crossing to the right-hand side of the periodic table.[5] For molybdenum and tungsten amides,[7] a wide variety of stable oxidation states (*i.e.*, $Mo^{III–VI}$, $W^{III–VI}$) are known with the +3 state being the most common. Mo(III) and W(III) amides tend to associate to form binuclear compounds with the general formula $[M_2(NR_2)_6]$ (M = Mo, W; R = Me, Et).[8,9] Reports on Mo(VI) and W(VI) amides, on the other hand, are rare and amido complexes of their *cis*-dioxo derivatives are, to our knowledge, unprecedented. This may be attributed to the limited availability of suitable starting materials for the preparation of dioxo-Mo(VI) and -W(VI) amido complexes (*vide infra*).

The chemistry of metal complexes containing pyridine-functionalised amido ligands of the type **I**–**III** (Chart 1) has attracted much interest.[10–15] These ligands can ligate to metal centres in a number of binding modes, for example as monodentate amide, bidentate N,N-bridge or N,N-chelate. In addition, they are capable of forming metal complexes with unusual coordination geometry as well as different states of association. A number of novel main-group and transition metal complexes containing N-substituted pyridine-amido ligands, such as $[{}^-N(Ph)(2\text{-}C_5H_4N)]$,[10b,11,12] $[{}^-N(2\text{-}C_5H_4N)_2]$,[13,14d] $[{}^-N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]$,[14] and $[{}^-N(SiMe_3)(2\text{-}C_5H_3N\text{-}4\text{-}Me)]$[15] have been synthesised and structurally characterised. It is believed that the presence of the bulky substituents on these ligands exerts a stabilising effect to the corresponding metal complexes and prevents the formation of insoluble polymeric species. Currently, we have focused our attention on the use of sterically demanding amido ligands in the preparation of otherwise kinetically labile amido metal complexes. In this paper, we report the synthesis and structural characterisation of a series of high-valent *cis*-dioxo-Mo(VI) and -W(VI) complexes derived from the sterically encumbered amido ligands $[{}^-N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]$,[14] $[{}^-N(SiBu^tMe_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]$[16] and $[{}^-N(SiBu^tPh_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]$.[16]

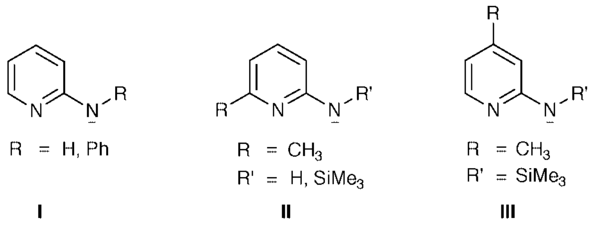

Chart 1

Results and discussion

Preparation of *cis*-dioxo-Mo(VI) and -W(VI) amido complexes

Treatment of a solution of $[MO_2Cl_2{\cdot}(DME)]$ (M = Mo, W; DME = 1,2-dimethoxyethane)[17] in THF with two equivalents of the lithium amides LiL^n [$L^1 = {}^-N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$,[14a] $L^2 = {}^-N(SiBu^tMe_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$,[16] $L^3 = {}^-N(SiBu^tPh_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$[16]] in the same solvent at ambient temperature afforded the corresponding mononuclear *cis*-dioxo-Mo(VI) (**1**–**3**) and -W(VI) (**4**–**6**) amido complexes in satisfactory yields (Scheme 1). Attempted reactions of $[Li(TMEDA)\{N(Ph)(2\text{-}C_5H_4N)\}]$ (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine), which was prepared by lithiation of 2-anilinopyridine with a hexane solution of $LiBu^n$–TMEDA, with $[MO_2Cl_2{\cdot}(DME)]$ were unsuccessful. Only a dark brown intractable oily residue was obtained.

The dioxo-Mo(VI) complexes **1**–**3** and the dioxo-W(VI) analogues **4**–**6** are bright yellow crystals and pale yellow crystals, respectively. They are readily soluble in common organic solvents such as THF, toluene, and CH_2Cl_2. However, they are only sparingly soluble in saturated hydrocarbon solvents such as hexane. Complexes **1**–**6** are sensitive to moisture. They decompose to unidentified black substances upon attempted melting point measurement. Complexes **1** and **2** and **4**–**5** were purified by recrystallisation from dry toluene under an inert atmosphere, whereas complexes **3** and **6** were purified by

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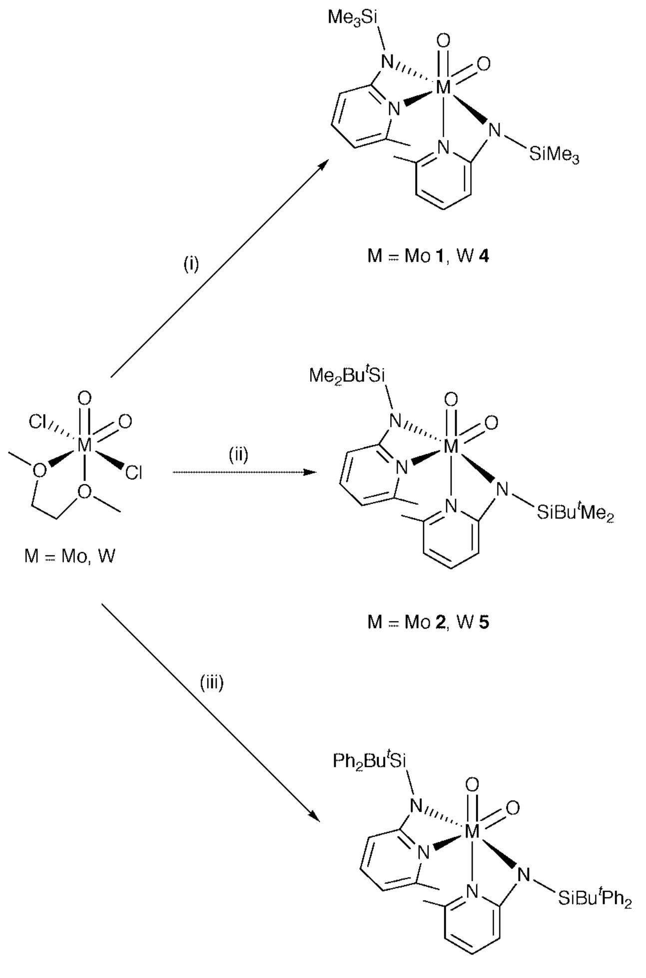

Scheme 1 (i) $[\{Li(OEt_2)(L^1)\}_2]$; (ii) $[Li(TMEDA)(L^2)]$; (iii) $[Li(TMEDA)(L^3)]$.

column chromatography using dry dichloromethane as the eluent.

The molecular structures of complexes **1**, **2**, **4** and **5** have been confirmed by single-crystal X-ray analysis. In principle, three pairs of diastereomers (**IV**–**VI**), and their enantiomers, would be expected for this type of *cis*-dioxo complex (Chart 2).

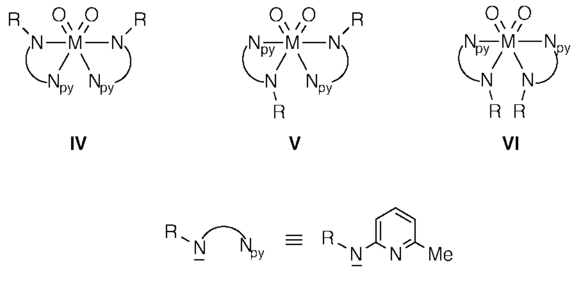

Chart 2 R = $SiMe_3$ or $SiBu^tMe_2$.

However, in the present work, only diastereomer **IV** and its enantiomer, with O being *trans* to the pyridine N atom, have been isolated for these complexes. This may be attributed to a strong *trans* influence of the oxo ligands which renders the formation of diastereomers **V** and **VI** unfavourable.

In the preparation of complexes **1**–**6**, $[MoO_2Cl_2{\cdot}(DME)]$ and $[WO_2Cl_2{\cdot}(DME)]$ were employed as the reagents. The DME-adducts can be readily prepared from $MOCl_4$ (M = Mo, W), $(Me_3Si)_2O$, and DME.[17] In contrast to the commonly used reagents such as $[MO_2Cl_2]$ and $[MO_2(acac)_2]$ (M = Mo, W), the DME-adducts possess better solubility in common organic solvents such as CH_2Cl_2, THF and MeCN. The DME and Cl ligands are also labile and can readily be substituted by other ligands. Thus, the DME-adducts serve as excellent starting materials for various molybdenum(VI) and tungsten(VI) complexes, especially for those which are sensitive to air and moisture. The versatility of $[WO_2Cl_2{\cdot}(DME)]$ as a precursor to a number of *cis*-dioxo-W(VI) complexes has recently been reported by Wong *et al.*[18]

Spectroscopic characterisation

Infra-red spectra for the molybdenum compounds $[MoO_2(L'')_2]$ (**1**–**3**) show the characteristic asymmetric and symmetric Mo=O stretches at 909–915 and 940–942 cm^{-1}, respectively,[18] whereas the tungsten analogues **4**–**6** show similar vibrational bands at 916–918 and 958–961 cm^{-1}. The latter bands occur at 7–21 cm^{-1} higher than those of the molybdenum congeners.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**–**6** show only one set of resonances, indicating that the two amido ligands in each complex molecule are equivalent. This is consistent with a C_2 molecular symmetry for complexes **1**–**6**. It is noteworthy that the two methyl substituents on the silyl group of the ligand $[^-N(SiBu^tMe_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]$ are prochiral. The solid state structures of **2** and **5** reveal that the two methyl substituents are non-equivalent (*vide infra*). In solution, the ^1H NMR spectra of **2** and **5** show two singlets (0.40 and 0.70 ppm for **2**, 0.39 and 0.75 ppm for **5**) for the $SiMe_2$ moiety. The non-equivalence of the two methyl substituents has also been observed in their $^{13}C\{^1H\}$ NMR spectra. The two prochiral methyl substituents on the Si atom are non-equivalent in the presence of a chiral metal centre. The same feature should also be expected for complexes **3** and **6** in relation to the two phenyl substituents of the ligand $[^-N(SiBu^tPh_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]$. However, the ^1H NMR signals due to the phenyl ring protons of these two complexes appear as overlapping signals at 7.3–8.1 ppm, making their assignment difficult to be carried out. Nevertheless, in their $^{13}C\{^1H\}$ NMR spectra, thirteen separate signals (five due to the pyridine ring and eight due to the phenyl rings) are observed. This is consistent with the presence of the two non-equivalent phenyl substituents on these complexes in solution state.

Compounds **1**, **2**, **4** and **5** have also been characterised by electron impact (EI) mass spectrometry. The $[M^+]$ species with correct isotopic distribution patterns have been identified for all complexes.

X-Ray structural studies

Complexes **1** and **4** are isomorphous and crystallise in the monoclinic system with space group $P2_1/c$, whilst the isomorphous pair **2** and **5** crystallise in the orthorhombic space group *Pbca*. Complexes **1**, **2**, **4** and **5** are mononuclear and exhibit a distorted octahedral geometry around each Mo(VI) and W(VI) centre. Each pair of the amido ligands binds in a *N*,*N*-chelating manner forming highly strained four-membered rings. Each oxo ligand is located *trans* to a pyridyl nitrogen of each amido ligand.

The molecular structures of complexes **1**, **2**, **4** and **5** along with the atom numbering schemes are depicted in Figs. 1–4, respectively. Selected bond distances (Å) and angles (°) for all four complexes are given in Table 1. Each of the molecules exhibits C_2 symmetry with a crystallographic 2-fold axis bisecting the O–M–O angle. The Mo=O distances (1.689–1.694 Å) and W=O distances (1.697–1.718 Å) are within the range typical for oxomolybdenum[19] and oxotungsten units,[20] with the W=O distances of **4** and **5** being only marginally longer (by 0.01–0.03 Å) than the Mo=O distances of **1** and **2**. The $M\text{–}N_{pyridyl}$ bond distances, *viz.* 2.334(2) and 2.350(2) Å in $[MoO_2(L^1)_2]$ (**1**), 2.318(3) and 2.331(3) Å in $[MoO_2(L^2)_2]$ (**2**), 2.315(4) and 2.333(4) Å in $[WO_2(L^1)_2]$ (**4**), and 2.315(2) and 2.327(2) Å in $[WO_2(L^2)_2]$ (**5**) are not significantly different from each other.

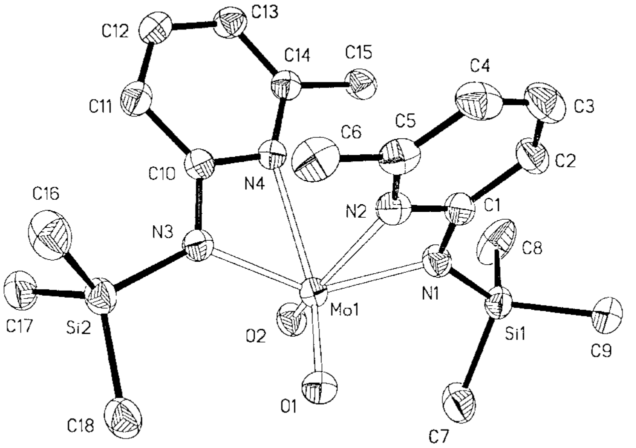

Fig. 1 ORTEP[26] diagram of $[MoO_2(L^1)_2]$ **1**, using 20% probability ellipsoids.

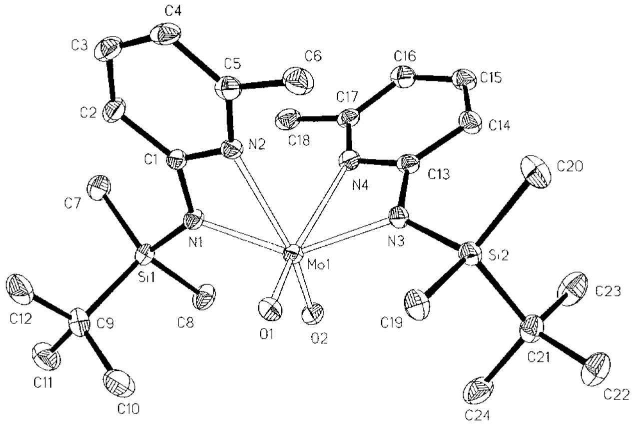

Fig. 2 ORTEP diagram of $[MoO_2(L^2)_2]$ **2**, using 20% probability ellipsoids.

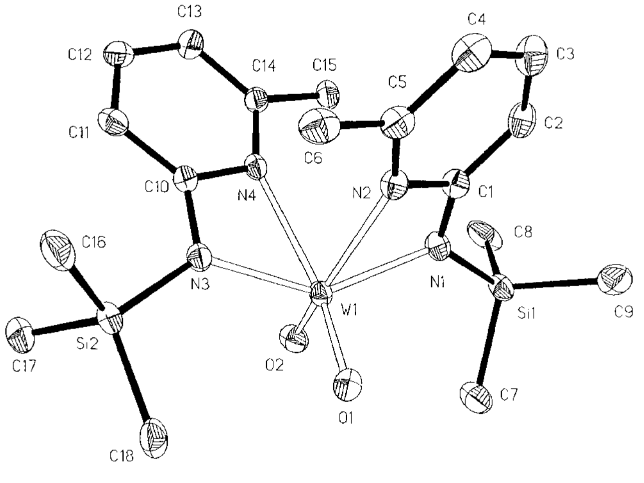

Fig. 3 ORTEP diagram of $[WO_2(L^1)_2]$ **4**, using 20% probability ellipsoids.

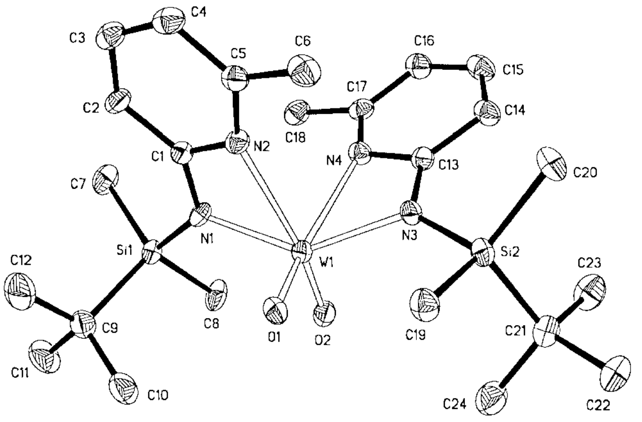

Fig. 4 ORTEP diagram of $[WO_2(L^2)_2]$ **5**, using 20% probability ellipsoids.

They are comparable to the Mo–$N_{pyridyl}$ distances of 2.363(4) Å in $[MoO_2(L\text{-}NO)_2]$ (**7**),[21] 2.336(9) and 2.359(8) in $[MoO_2(^tBuL\text{-}NO)_2]$ (**8**),[21] but slightly shorter than those of 2.411(5) Å in $[MoO_2(^tBuL\text{-}NS)_2]$[21] (**9**) and 2.417(4) Å in $[MoO_2(LNO_2)(Me_2SO)]$ (**10**).[22] The latter four complexes **7**–**10** contain either a pair of N,O- or N,S-bidentate ligands (as in **7**–**9**) or a N_2O-tridentate ligand (as in **10**) binding to the [*cis*-MoO_2] moiety with the pyridyl nitrogens being coordinating *trans* to the oxo ligands—a similar configuration as in complexes **1**–**6**. This reflects a strong *trans* influence of the oxo ligands. On the other hand, the M–$N_{pyridyl}$ distances in **1**–**6** are longer than that of 2.244(7) Å in $[MoO_2(LNS_2)]$ (**11**),[22] where the pyridyl nitrogen in the latter complex is not binding *trans* to the oxo ligand.

The amido nitrogen atoms [N(1) and N(3)] in **1**, **2**, **4** and **5** exhibit an approximately planar three-coordinate environment.† This is consistent with sp^2-hybridised nitrogen centres with the p-orbital being orthogonal to the trigonal plane which facilitates Si–N or M–N (d←p) π-bonding interactions. The Si–N distances of 1.728(2) and 1.755(2) Å in **1**, 1.741(3) and 1.754(3) Å in **2**, 1.754(4) and 1.753(4) Å in **4**, and 1.759(2) and 1.762(2) Å in **5** are within the range typical for aminosilanes.[5] This suggests that significant Si–N (d←p) π-interactions are present in these complexes. The observed Mo–N_{amido} and W–N_{amido} bond distances are somewhat similar, *viz.* 2.076(2)–2.077(2) Å in **1**, 2.074(2)–2.076(2) Å in **2**, 2.070(4)–2.076(5) Å in **4**, and 2.079(2)–2.081(2) Å in **5**. The W–N_{amido} bonds are only *ca.* 0.04 Å longer than those of 2.017(6) and 2.032(25) Å reported for the homoleptic W(VI) amido complex $[W(NMe_2)_6]$.[23] The M–N_{amido} bond lengths in **1**, **2**, **4** and **5** are marginally longer (by *ca.* 0.02–0.03 Å) than the calculated M–N single bond distance of 2.05 Å. This suggests that M–N (d←p) π-interactions in these complexes may be relatively less significant as compared to the Si–N π-interactions.

The bite angles N_{amido}–Mo–$N_{pyridyl}$ are 60.31(5) and 60.33(6)° in **1**, and 60.39(10)° and 60.82(10)° in **2**, whilst those of N_{amido}–W–$N_{pyridyl}$ are 60.49(14) and 60.62(13)° in **4**, and 60.30(7) and 60.38(7)° in **5**.

Conclusion

A series of *cis*-dioxo-Mo(VI) and -W(VI) amido complexes $[MO_2(L^n)_2]$ [M = Mo, W; $L^1 = {}^-N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$, $L^2 = {}^-N(SiBu^tMe_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$, $L^3 = {}^-N(SiBu^tPh_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$] have been prepared by the metathesis of chloride from $[MO_2Cl_2\cdot(DME)]$ with 2 equivalents of the appropriate sterically demanding N-functionalised amido ligands. $[MoO_2(L^1)_2]$ (**1**), $[MoO_2(L^2)_2]$ (**2**), $[WO_2(L^1)_2]$ (**4**), $[WO_2(L^2)_2]$ (**5**) have been structurally characterised by X-ray crystallographic studies. The amido ligands bind to the metal centres in a N,N-chelating fashion forming highly strained four-membered metallacyclic rings. To our knowledge, these novel complexes are the first examples of *cis*-dioxo-Mo(VI) and -W(VI) complexes containing N-functionalised amido ligands being synthesised and structurally characterised.

Experimental

General procedures

All manipulations were carried out under a purified nitrogen

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† Sum of bond angles (average) around the amido nitrogen centres is 358.3° for **1**, 359.6° for **2**, 358.3° for **4**, and 359.3° for **5**.

Table 1 Selected bond distances (Å) and angles (°) for complexes **1**, **2**, **4** and **5**

$[MoO_2(L^1)_2]$ **1**		$[WO_2(L^1)_2]$ **4**	
Mo(1)–O(1)	1.692(2)	W(1)–O(1)	1.712(4)
Mo(1)–O(2)	1.694(2)	W(1)–O(2)	1.718(4)
Mo(1)–N(1)	2.077(2)	W(1)–N(1)	2.076(5)
Mo(1)–N(3)	2.076(2)	W(1)–N(3)	2.070(4)
Mo(1)–N(2)	2.334(2)	W(1)–N(2)	2.333(4)
Mo(1)–N(4)	2.350(2)	W(1)–N(4)	2.315(4)
N(1)–C(1)	1.380(2)	N(1)–C(1)	1.349(6)
N(3)–C(10)	1.383(2)	N(3)–C(10)	1.393(6)
N(2)–C(1)	1.354(3)	N(2)–C(1)	1.368(6)
N(4)–C(10)	1.346(2)	N(4)–C(10)	1.352(5)
Si(1)–N(1)	1.748(2)	Si(1)–N(1)	1.754(4)
Si(2)–N(3)	1.755(2)	Si(2)–N(3)	1.753(4)
O(1)–Mo(1)–O(2)	105.13(7)	O(1)–W(1)–O(2)	104.13(18)
O(1)–Mo(1)–N(1)	104.63(7)	O(1)–W(1)–N(1)	104.23(16)
O(1)–Mo(1)–N(3)	98.26(7)	O(1)–W(1)–N(3)	98.77(17)
O(1)–Mo(1)–N(2)	95.24(7)	O(1)–W(1)–N(2)	95.39(16)
O(1)–Mo(1)–N(4)	156.38(6)	O(1)–W(1)–N(4)	157.22(16)
O(2)–Mo(1)–N(1)	95.70(6)	O(2)–W(1)–N(1)	96.72(15)
O(2)–Mo(1)–N(3)	105.36(7)	O(2)–W(1)–N(3)	104.96(16)
O(2)–Mo(1)–N(2)	152.17(6)	O(2)–W(1)–N(2)	153.37(15)
O(2)–Mo(1)–N(4)	91.13(7)	O(2)–W(1)–N(4)	91.44(16)
N(1)–Mo(1)–N(2)	60.33(6)	N(1)–W(1)–N(2)	60.49(14)
N(3)–Mo(1)–N(4)	60.31(5)	N(3)–W(1)–N(4)	60.62(13)
N(3)–Mo(1)–N(1)	143.52(6)	N(3)–W(1)–N(1)	143.32(14)
C(1)–N(1)–Si(1)	128.6(2)	C(1)–N(1)–Si(1)	129.3(4)
C(1)–N(1)–Mo(1)	100.41(2)	C(1)–N(1)–W(1)	100.3(3)
Si(1)–N(1)–Mo(1)	129.56(9)	Si(1)–N(1)–W(1)	129.1(2)
C(10)–N(3)–Si(2)	124.15(13)	C(10)–N(3)–Si(2)	123.8(3)
C(10)–N(3)–Mo(1)	100.34(11)	C(10)–N(3)–W(1)	100.4(3)
Si(2)–N(3)–Mo(1)	133.56(8)	Si(2)–N(3)–W(1)	133.6(2)
$[MoO_2(L^2)_2]$ **2**		$[WO_2(L^2)_2]$ **5**	
Mo(1)–O(1)	1.689(2)	W(1)–O(1)	1.699(2)
Mo(1)–O(2)	1.694(2)	W(1)–O(2)	1.697(2)
Mo(1)–N(1)	2.076(2)	W(1)–N(1)	2.079(2)
Mo(1)–N(3)	2.074(2)	W(1)–N(3)	2.081(2)
Mo(1)–N(2)	2.318(3)	W(1)–N(2)	2.315(2)
Mo(1)–N(4)	2.331(3)	W(1)–N(4)	2.327(2)
N(1)–C(1)	1.378(4)	N(1)–C(1)	1.375(3)
N(3)–C(13)	1.378(4)	N(3)–C(13)	1.387(3)
N(2)–C(1)	1.344(4)	N(2)–C(1)	1.344(3)
N(4)–C(13)	1.337(4)	N(4)–C(13)	1.336(3)
Si(1)–N(1)	1.741(3)	Si(1)–N(1)	1.759(2)
Si(2)–N(3)	1.754(3)	Si(2)–N(3)	1.762(2)
O(1)–Mo(1)–O(2)	105.04(12)	O(1)–W(1)–O(2)	104.67(9)
O(1)–Mo(1)–N(1)	105.03(10)	O(1)–W(1)–N(1)	105.22(8)
O(1)–Mo(1)–N(3)	97.49(11)	O(1)–W(1)–N(3)	97.93(8)
O(1)–Mo(1)–N(2)	90.00(10)	O(1)–W(1)–N(2)	90.82(8)
O(1)–Mo(1)–N(4)	154.65(11)	O(1)–W(1)–N(4)	154.92(8)
O(2)–Mo(1)–N(1)	97.33(11)	O(2)–W(1)–N(1)	97.76(8)
O(2)–Mo(1)–N(3)	104.10(11)	O(2)–W(1)–N(3)	103.85(8)
O(2)–Mo(1)–N(2)	156.51(10)	O(2)–W(1)–N(2)	156.33(8)
O(2)–Mo(1)–N(4)	93.16(11)	O(2)–W(1)–N(4)	93.38(8)
N(1)–Mo(1)–N(2)	60.82(10)	N(1)–W(1)–N(2)	60.38(7)
N(3)–Mo(1)–N(4)	60.39(10)	N(3)–W(1)–N(4)	60.30(7)
N(3)–Mo(1)–N(1)	143.56(11)	N(3)–W(1)–N(1)	143.01(8)
C(1)–N(1)–Si(1)	129.2(2)	C(1)–N(1)–Si(1)	129.1(2)
C(1)–N(1)–Mo(1)	99.26(19)	C(1)–N(1)–W(1)	99.88(14)
Si(1)–N(1)–Mo(1)	131.36(15)	Si(1)–N(1)–W(1)	130.60(10)
C(13)–N(3)–Si(2)	127.8(2)	C(13)–N(3)–Si(2)	128.0(2)
C(13)–N(3)–Mo(1)	99.8(2)	C(13)–N(3)–W(1)	99.70(14)
Si(2)–N(3)–Mo(1)	131.67(16)	Si(2)–N(3)–W(1)	131.35(11)

atmosphere using standard Schlenk techniques or in a glove box. Solvents were dried over and distilled from calcium hydride (dichloromethane and hexane) or sodium benzophenone (THF, diethyl ether, and toluene), and degassed twice before use. All other reagents were used as received. $[\{Li(OEt_2)(L^1)\}_2]$,[14a] $[Li(TMEDA)(L^2)]$,[16] $[Li(TMEDA)(L^3)]$,[16] and $[MO_2Cl_2\cdot(DME)]$ (M = Mo, W)[17] were prepared as described.

Physical measurements

All ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DPX 300 spectrometer. Chemical shifts were referenced to residual solvent protons of $\delta = 7.15$ for C_6D_6 or internal TMS standard. Infra-red spectra were taken on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. EI mass spectra were obtained on a Hewlett-Packard 5989B Mass Engine spectrometer. Elemental analyses were performed by MEDAC Ltd., Brunel University, UK.

X-Ray crystallography

The crystallographic data for compounds **1**, **2**, **4** and **5** are shown in Table 2. All crystals were grown from toluene solutions. Single crystals suitable for X-ray diffraction studies were sealed in capillaries under dinitrogen. X-Ray data were collected on a Rigaku RAXIS-IIC diffractometer at 294 K using graphite-monochromatised Mo-K_α radiation ($\lambda = 0.71073$ Å) by taking oscillation photos. Computations were performed using the SHELX-97 PC program package on a PC 486 computer. The structures were solved by direct phase determination and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms.[24] Hydrogen atoms were introduced in their idealised positions and included in structure factors calculations with assigned isotropic temperature factors.[25]

CCDC reference number 186/1779.

See http://www.rsc.org/suppdata/dt/a9/a907811h/ for crystallographic files in .cif format.

Preparations

$[MoO_2(L^1)_2]$ 1. To a colourless solution of $[MoO_2Cl_2\cdot(DME)]$ (0.58 g, 2.0 mmol) in THF (30 ml) at room temperature was added dropwise a solution of $[\{Li(OEt_2)(L^1)\}_2]$ (1.04 g, 2.0 mmol) in Et_2O (30 ml). The resulting solution changed from yellow to reddish brown with a grey precipitate. Stirring was continued for a further period of 5 h. All volatiles were removed under reduced pressure to give a dark brown residue, which was extracted with toluene (100 ml) and stirred for another 1 h. The precipitate was removed by filtration and the reddish brown filtrate was concentrated to *ca.* 50 ml for crystallisation. Upon standing at room temperature for one night, bright yellow crystals of **1** were obtained. They were washed with cold hexane and dried *in vacuo*. Yield: 0.75 g (77%). Mp: 146–148 °C (dec.). ^1H NMR (C_6D_6, 300 MHz): δ 0.47 (s, 18 H, $SiMe_3$), 2.04 (s, 6 H, Me), 5.81 (d, $J = 7.4$, 2 H, C_5H_3N), 6.07 (d, $J = 8.4$ Hz, 2 H, C_5H_3N), 6.79 (t, $J = 7.9$ Hz, 2 H, C_5H_3N). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz): δ 1.5 (Si*Me*$_3$), 21.8 (Py*Me*), 106.7, 112.7, 139.7, 154.4, 167.6 (C_5H_3N). IR (KBr, cm^{-1}): 2958m, 2896w, 1596s, 1459s, 1409m, 1378m, 1322s, 1248s, 1161m, 1080s, 1011w, 965m, 940s, 909s, 840s, 781s, 732m, 685m, 635w, 617w, 554w, 436m. EI-MS (70 eV): $m/z = 488$ (M^+, 100%). Anal. Found: C, 44.10; H, 6.15; N, 11.40. Calcd. for $C_{18}H_{30}MoN_4O_2Si_2$: C, 44.43; H, 6.21; N, 11.51%.

$[MoO_2(L^2)_2]$ 2. To a colourless solution of $[MoO_2Cl_2\cdot(DME)]$ (0.58 g, 2.0 mmol) in THF (30 ml) was added dropwise a solution of $[Li(TMEDA)(L^2)]$ (1.38 g, 4.0 mmol) in Et_2O (20 ml) at room temperature. The solution quickly afforded a reddish brown colour with a grey precipitate. After being stirred for 5 h, all volatiles were removed under reduced pressure to give a dark brown residue. It was extracted with toluene (100 ml) and the solution was filtered. The reddish brown filtrate was concentrated to *ca.* 20 ml under reduced pressure. Upon standing at room temperature for one night, bright yellow crystals of compound **2** were obtained. They were washed with cold hexane and dried *in vacuo*. Yield: 1.18 g (72%). Mp: 174–176 °C (dec.). ^1H NMR (C_6D_6, 300 MHz): δ 0.40 (s, 6 H, SiMe), 0.70 (s, 6 H, SiMe), 1.15 (s, 18 H, $SiBu^t$), 2.05 (s, 6 H, Me), 5.80 (d,

Table 2 Crystal data for complexes **1**, **2**, **4** and **5**

	1	**2**	**4**	**5**
Molecular formula	$C_{18}H_{30}N_4O_2Si_2Mo$	$C_{24}H_{42}N_4O_2Si_2Mo$	$C_{18}H_{30}N_4O_2Si_2W$	$C_{24}H_{42}N_4O_2Si_2W$
Molecular weight	486.58	570.74	574.49	658.65
Crystal size/mm	0.42 × 0.40 × 0.12	0.36 × 0.34 × 0.24	0.42 × 0.34 × 0.32	0.30 × 0.28 × 0.26
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pbca*	$P2_1/c$	*Pbca*
a/Å	13.931(3)	16.342(3)	13.965(3)	16.299(3)
b/Å	11.888(2)	16.007(3)	11.848(2)	16.059(3)
c/Å	14.295(3)	22.218(4)	14.239(3)	22.341(5)
β/°	97.38(3)	—	97.91(3)	—
Z	4	8	4	8
V/Å^3	2347.8(8)	5812(2)	2333.8(8)	5848(2)
Density/g cm^{-3}	1.377	1.305	1.635	1.496
μ/mm^{-1}	0.680	0.560	5.071	4.058
Reflections collected	7569	6879	4590	15760
Unique data measured	4261	3798	4590	4963
Observed data with $I \geq 2\sigma(I)$	4261	3746	4590	4963
No. of variables	245	349	245	322
$R1$	0.0372	0.0743	0.0392	0.0609
wR	0.1390	0.2048	0.1461	0.1812

$J = 7.4$ Hz, 2 H, C_5H_3N), 6.28 (d, $J = 8.5$ Hz, 2 H, C_5H_3N), 6.81 (t, $J = 8.0$ Hz, 2 H, C_5H_3N). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz): δ −1.6 (Si*Me*), −1.5 (Si*Me*), 21.8 (Py*Me*), 21.9 (Si*C*Me$_3$), 27.3 (SiC*Me*$_3$), 107.5, 112.9, 139.5, 154.0, 168.5 (C_5H_3N). IR (KBr, cm^{-1}): 2956m, 2925m, 2885w, 2858m, 1594s, 1457s, 1405w, 1324s, 1247m, 1163w, 1078m, 1007w, 942m, 909s, 822s, 726w, 677w, 446w. EI-MS (70 eV): $m/z = 572$ (M$^+$, 9%). Anal. Found: C, 50.03; H, 7.16; N, 9.97. Calcd. for $C_{24}H_{42}MoN_4O_2Si_2$: C, 50.51; H, 7.42; N, 9.81%.

[MoO$_2$(L^3)$_2$] 3. To a colourless solution of [MoO$_2$Cl$_2$·(DME)] (0.58 g, 2.0 mmol) in THF (30 ml) was added dropwise a yellow solution of [Li(TMEDA)(L^3)] (1.88 g, 4.0 mmol) in THF (15 ml) at room temperature. The resulting solution quickly turned yellowish-brown. It was stirred for 5 h. All volatiles were then removed under reduced pressure. The resulting dark brown residue was extracted with toluene (100 ml), filtered, and concentrated under reduced pressure. It was chromatographed on a silica gel column using CH_2Cl_2 as eluent. The first bright yellow band was collected and concentrated to afford a yellow solid of **3**. Yield: 1.28 g (78%). Mp: 139–141 °C (dec.). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.33 (s, 18 H, SiBu^t), 2.15 (s, 6 H, Me), 5.79 (d, $J = 8.4$ Hz, 2 H, C_5H_3N), 6.18 (d, $J = 7.5$ Hz, 2 H, C_5H_3N), 6.91 (t, $J = 8.0$ Hz, 2 H, C_5H_3N), 7.33–7.41 (m, 12 H, C_6H_5), 7.77–7.76 (m, 4 H, C_6H_5), 8.01–8.04 (m, 4 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz): δ 20.5 (Py*Me*), 22.3 (Si*C*Me$_3$), 28.1 (SiC*Me*$_3$), 109.7, 113.2 (C_5H_3N), 127.4, 127.6, 129.1, 129.2, 135.1, 135.6, 136.2, 136.7 (C_6H_5), 139.0, 153.5, 168.3 (C_5H_3N). IR (KBr, cm^{-1}): 3067w, 2962m, 2863w, 1607m, 1481s, 1450m, 1361w, 1277s, 1108w, 1027w, 940s, 915s, 862m, 761m, 637w, 567w.

[WO$_2$(L^1)$_2$] 4. A solution of [{Li(OEt$_2$)(L^1)}$_2$] (1.04 g, 2 mmol) in Et$_2$O (30 ml) was slowly added to a colourless solution of [WO$_2$Cl$_2$·(DME)] (0.75 g, 2 mmol) in THF (30 ml) at room temperature. The resulting solution turned from yellow to reddish brown. The reaction mixture was stirred for 5 h. All volatiles were then removed *in vacuo* and the residue was extracted with toluene (100 ml). The extract was filtered and the reddish brown filtrate was concentrated to *ca.* 50 ml for crystallisation. Upon standing at room temperature for one night, pale yellow crystals of compound **4** were obtained, which were washed with cold hexane and dried in *vacuo*. Yield: 0.75 g (65%). Mp: 146–148 °C (dec.). ^1H NMR (C_6D_6, 300 MHz): δ 0.49 (s, 18 H, SiMe$_3$), 2.00 (s, 6 H, Me), 5.85 (d, $J = 7.5$, 2 H, C_5H_3N), 6.05 (d, $J = 8.4$ Hz, 2 H, C_5H_3N), 6.79 (t, $J = 7.9$ Hz, 2 H, C_5H_3N). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz): δ 1.5 (Si*Me*$_3$), 21.7 (Py*Me*), 107.8, 113.0, 139.9, 153.8, 166.3 (C_5H_3N). IR (KBr, cm^{-1}): 2957m, 2901w, 1740m, 1595s, 1460s, 1405m, 1376m, 1331s, 1254s, 1161m, 1081s, 1013w, 958s, 917s, 843s, 782s, 733m, 688m, 637w, 553w, 438m. EI-MS (70 eV): $m/z = 574$ (M$^+$, 60%). Anal. Found: C, 37.07; H, 5.09; N, 9.68. Calcd. for $C_{18}H_{30}N_4O_2Si_2W$: C, 37.63; H, 5.26; N, 9.75%.

[WO$_2$(L^2)$_2$] 5. A solution of [Li(TMEDA)(L^2)] (1.38 g, 4 mmol) in Et$_2$O (20 ml) was slowly added to a colourless solution of [WO$_2$Cl$_2$·(DME)] (0.75 g, 2 mmol) in THF (30 ml) at ambient temperature. The solution quickly afforded a reddish brown colour. After being stirred for 5 h, all volatiles were removed under reduced pressure. The resultant dark brown residue was extracted with toluene (100 ml). It was filtered and the reddish brown filtrate was concentrated to *ca.* 20 ml. Pale yellow block-shaped crystals of **5** formed upon standing at room temperature for one night. They were washed with cold hexane and dried *in vacuo*. Yield: 0.93 g (71%). Mp: 196–198 °C (dec.). ^1H NMR (C_6D_6, 300 MHz): δ 0.39 (s, 6 H, SiMe). 0.75 (s, 6 H, SiMe), 1.17 (s, 18 H, SiBu^t), 2.01 (s, 6 H, Me), 5.84 (d, $J = 7.4$ Hz, 2 H, C_5H_3N), 6.28 (d, $J = 8.5$ Hz, 2 H, C_5H_3N), 6.81 (t, $J = 8.0$ Hz, 2 H, C_5H_3N). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz): δ −1.5 (Si*Me*), −1.4 (Si*Me*), 21.7 (Py*Me*), (Si*C*Me$_3$) obscured, 27.3 (SiC*Me*$_3$), 108.6, 113.2, 139.8, 153.4, 167.2 (C_5H_3N). IR (KBr, cm^{-1}): 2954m, 2926m, 2883w, 2859m, 1596s, 1568m, 1457s, 1407w, 1321s, 1250m, 1166w, 1080m, 1011w, 959m, 916s, 826s, 730w, 678w, 446w. EI-MS (70 eV): $m/z = 659$ (M$^+$, 4%). Anal. Found: C, 43.49; H, 6.22; N, 8.70. Calcd. for $C_{24}H_{42}N_4O_2Si_2W$: C, 43.77; H, 6.43; N, 8.50%.

[WO$_2$(L^3)$_2$] 6. To a colourless solution of [WO$_2$Cl$_2$·(DME)] (0.38 g, 1.0 mmol) in THF (30 ml) was added a pale yellow solution of [Li(TMEDA)(L^3)] (0.94 g, 2.0 mmol) in Et$_2$O (20 ml) dropwise at room temperature. The reaction mixture changed to yellowish-brown with a grey precipitate formed. Stirring was continued for 5 h and the volatiles were removed under reduced pressure. The dark brown residue was extracted with toluene (100 ml) for 1 h. After filtration, the reddish brown filtrate was concentrated and chromatographed on a silica gel column using CH_2Cl_2 as eluent. The first band was collected and evaporated to afford a pale yellow solid. Yield: 0.57 g (63%). Mp: 153–155 °C (dec.). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.37 (s, 18 H, SiBu^t), 2.12 (s, 6 H, Me), 5.83 (d, $J = 8.4$ Hz, 2 H, C_5H_3N), 6.27 (d, $J = 7.5$ Hz, 2 H, C_5H_3N), 6.96 (t, $J = 8.1$ Hz, 2 H, C_5H_3N), 7.34–7.41 (m, 12 H, C_6H_5), 7.77–7.80 (m, 4 H, C_6H_5), 8.05–8.08 (m, 4 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz): δ 20.4 (Py*Me*), 22.3 (Si*C*Me$_3$), 27.9 (SiC*Me*$_3$), 110.6, 113.7 (C_5H_3N), 127.5, 127.6, 129.2, 129.3, 134.7, 135.5, 136.3, 136.8 (C_6H_5), 139.3, 153.0, 166.8 (C_5H_3N). IR (KBr, cm^{-1}):

3067w, 2962m, 2871w, 1606m, 1485s, 1451m, 1364w, 1277s, 1158w, 1108w, 1053w, 1026w, 961s, 918s, 866m, 813w, 758m, 650m.

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