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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

# Molybdenum complexes derived from the oxydianiline [(2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O]: Synthesis, characterization and ε-caprolactone ROP capability.

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Received (in XXX, XXX) XthXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

DOI: 10.1039/b000000x

**Abstract** The reaction of Na<sub>2</sub>MoO<sub>4</sub> with 2,2'-oxydianiline (2-aminophenylether), (2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O, LH<sub>4</sub>, in DME (DME=1,2-dimethoxyethane) in the presence of Et<sub>3</sub>N and Me<sub>3</sub>SiCl afforded either the bis(imido) molybdenum(VI) complex {Mo(L)Cl<sub>2</sub>(DME)} (**1**), where L = (2-NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O, or the molybdenum(V) salt [Mo(L')Cl<sub>4</sub>][Et<sub>3</sub>NH] (**2**), where L' = [(2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(2-NC<sub>6</sub>H<sub>4</sub>)O], depending on the work-up method employed. The same diamine reacted with *in-situ* [Mo(NtBu)<sub>2</sub>Cl<sub>2</sub>(DME)] afforded a tetra-nuclear complex [Mo<sub>4</sub>Cl<sub>3</sub>(NtBu)<sub>3</sub>(OSiMe<sub>3</sub>)(μ<sub>4</sub>-O)(L)<sub>2</sub>(L')<sub>2</sub>]·2MeCN (**3**·2MeCN). The crystal structures of **1**, **2** and **3**·2MeCN have been determined. The structure of the bis(imido) complex **1** contains two unique molecules paired up via weak π-stacking, whereas the structure of **2** contains a chelating amine/imido ligand, and is made up of discrete units of two cations and two anions which are interacting via H-bonding. The tetra-nuclear structure **3** contains four different types of distorted octahedral molybdenum centre, and a bent Me<sub>3</sub>SiO group thought to originate from the precursor synthesis. Complexes **1** - **3** have been screened for their ability to ring open polymerize (ROP) ε-caprolactone. For **1** and **3** (not **2**), conversion rates were good (> 90 %) at high temperatures (100 °C) over 6 - 24 h, and the polymerization proceeded in a living manner.

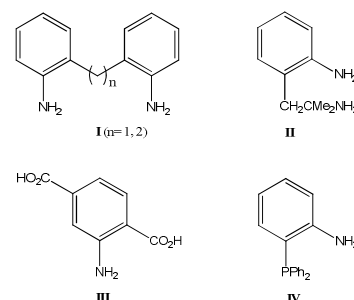
## Introduction

Entry into molybdenum(VI) organoimido [Mo=NR] chemistry, which has proved pivotal in designing new ring opening metathesis polymerization (ROMP) catalysts over the years, [1] is convenient via the one-pot 'sodium molybdate' route, [2] or when basicity permits, the '*tert*-butylimido exchange' route. [3] Such methods have allowed for the introduction of a range of organoimido groups with varying electronic and steric properties, which ultimately can be used to affect/control the polymerization processes. In the 'molybdate prep', a limited number of potentially chelating anilines/amines have been employed, namely types **I** or **II** (see scheme 1), which have resulted in bis(imido) type ligation forming 7, 8 or 9 membered chelate rings. [4] By contrast, the use of highly functionalized anilines, such as 2-aminoterephthalic acid **III**, instead have been shown to form triethylammonium salts, the anions of which bear an imido group together with a chelate ligand derived from the functionalized aniline. [5] An intriguing example is the use of 2-diphenylphosphinoaniline [1,2-(NH<sub>2</sub>)(PPh<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>] **IV** which, when employed in the 'sodium molybdate' route, results in a novel MoNC<sub>2</sub>PN six-membered ring derived from P-N coupling, whereas bridging imido/terminal phosphine ligation results from the use of **IV** in the 'imido exchange' route. [6]

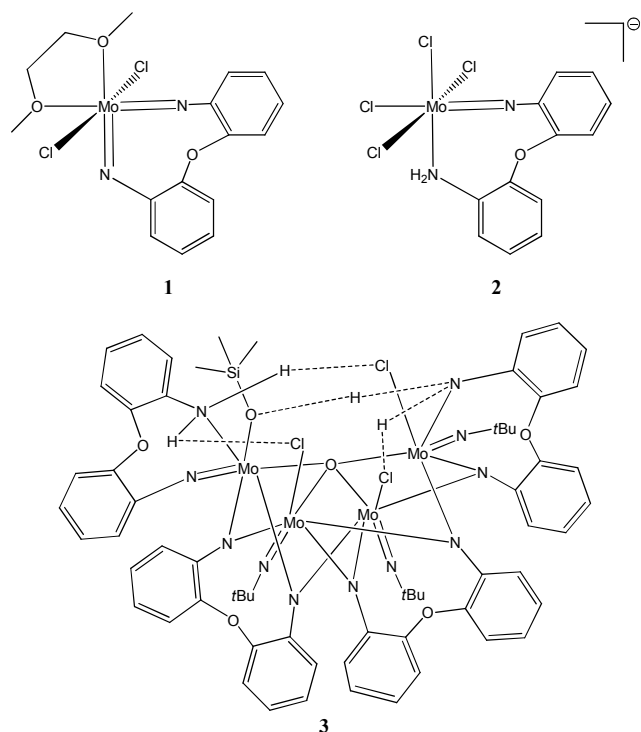
With this in mind, we have turned our attention to the use of the potentially chelating 2,2'-oxydianiline (2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O, and find that its use in the 'sodium molybdate' route affords either a mononuclear Mo(VI) bis(imido) complex **1** or a Mo(V) salt complex **2** bearing a chelating amine/imide ligand in the anion,

depending on the work-up employed. By contrast, the 'imido exchange' route affords a more complicated tetra-nuclear product **3** that contains four different molybdenum coordination environments (see scheme 2). The molecular structures of these complexes are reported herein. A search of the Cambridge Crystallographic database (CSD) revealed 62 hits for motifs derived from (2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O binding to any metal; the majority of these examples contained larger (mostly Schiff-like) ligands incorporating the backbone of the dianiline. Indeed, there was only one recent structural report of complexes (of palladium) incorporating (2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O type ligands or the deprotonated version thereof. [7]

Despite the great success of molybdenum species in ROMP, the use of molybdenum in the ROP of cyclic esters, typically lactides or lactones, has received far less attention. [8] Given this, we have screened **1** - **3** for their ability to act as catalysts in the ROP of ε-caprolactone (in the presence of benzyl alcohol). Interest in poly(ε-caprolactone) stems from its use as a biodegradable polymer. [9]



**Scheme 1.** Ligands **I** to **III** previously employed in the 'sodium molybdate' route.

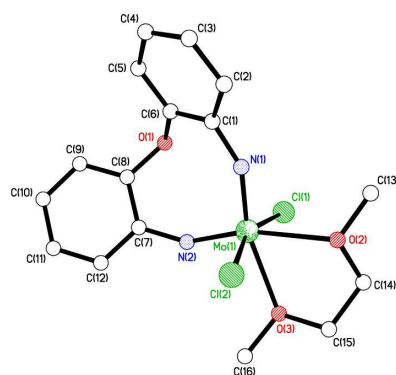


**Scheme 2.** Complexes **1** - **3** prepared herein.

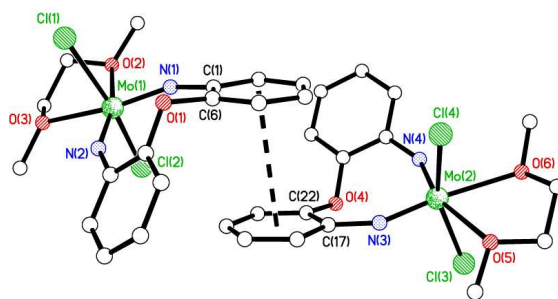
## 5 Results and discussion

### Synthesis

The reaction of  $\text{Na}_2\text{MoO}_4$  with  $(2\text{-NH}_2\text{C}_6\text{H}_4)_2\text{O}$  ( $\text{LH}_4$ ) in refluxing DME (DME=1,2-dimethoxyethane) in the presence of  $\text{Et}_3\text{N}$  and  $\text{Me}_3\text{SiCl}$  afforded, following filtration, cooling, and prolonged standing (1 -2 days) at ambient temperature, red crystals of the bis(imido) complex  $\{\text{Mo}(\text{L})\text{Cl}_2(\text{DME})\}$  (**1**), where  $\text{L} = (2\text{-NC}_6\text{H}_4)_2\text{O}$ , in good yield (ca. 60 %). A single crystal was subjected to X-ray diffraction and the molecular structure is shown in Figure 1, with selected bond lengths and angles given in the caption; crystallographic data are given in Table 2. There are two very similar molecules of  $\{\text{Mo}(\text{L})\text{Cl}_2(\text{DME})\}$  in the asymmetric unit. The molybdenum centre has a distorted octahedral geometry with *trans* chlorides and *cis*-chelating bis(imide) ligation. The Mo – N – C angles are about  $153^\circ$ , which is at the lower end of the range associated with linear imido groups. [10] The N(1) – Mo(1) – N(2) bite angle is  $101.21(11)^\circ$ , which is similar to the bite angle observed for the 8-membered ring formed in the chelating bis(imide) complex  $\{\text{Mo}[(2\text{-NC}_6\text{H}_4)_2\text{CH}_2]\text{Cl}_2(\text{DME})\}$  [ $100.8(5)^\circ$ ] derived from **I** ( $n = 1$ ). [4a] The two unique molecules pair up into weakly  $\pi$ -stacked units with a centroid-to-centroid distance of  $3.767 \text{ \AA}$  (see Figure 2). There are a number of intermolecular C–H...Cl interactions at ca.  $2.8 \text{ \AA}$ .



**Figure 1.** Molecular structure of  $\{\text{Mo}(\text{L})\text{Cl}_2(\text{DME})\}$  (**1**), showing the atom numbering scheme for one the two very similar molecules in the asymmetric unit. Hydrogen atoms have been omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Mo(1) – N(1) 1.738(2), Mo(1) – N(2) 1.745(2), Mo(1) – Cl(1) 2.4012(8), Mo(1) – Cl(2) 2.4024(8), Mo(1) – O(2) 2.381(2), Mo(1) – O(3) 2.369(2); N(1) – Mo(1) – N(2)  $101.21(11)$ , Cl(1) – Mo(1) – Cl(2)  $160.30(3)$ , Mo(1) – N(1) – C(1)  $152.9(2)$ , Mo(1) – N(2) – C(7)  $151.9(2)$ .

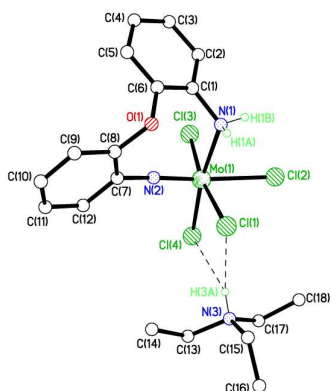


**Figure 2.** Paired-up molecules of **1**. Centroid-to-centroid distance is  $3.767 \text{ \AA}$ .

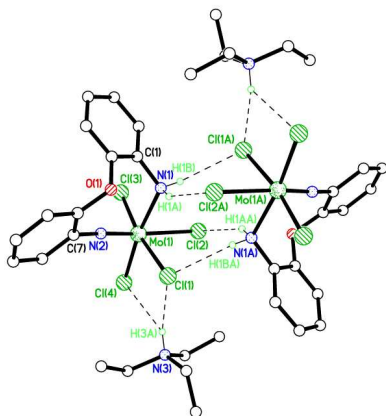
If the same reaction was worked up by removing the DME *in vacuo* and extracting the residue into warm acetonitrile, the yellow/brown molybdenum(V) amine/imide salt  $[\text{Mo}(\text{L}')\text{Cl}_4][\text{Et}_3\text{NH}]$  (**2**), where  $\text{L}' = [(2\text{-NH}_2\text{C}_6\text{H}_4)(2\text{-NC}_6\text{H}_4)\text{O}]$  (**2**) was isolated in ca. 30 % yield. The IR spectrum contained broad weak stretches in the  $\nu(\text{NH}/\text{NH}_2)$  region (ca.  $3068/3320 \text{ cm}^{-1}$ ), whilst signals in the  $^1\text{H}$  NMR spectrum were broad and uninformative, consistent with the presence of a Mo(V) centre. Reduction to Mo(V) during such syntheses has been noted previously, for example when using diphenylglycine. [5] The X-band EPR spectrum (see Fig. S1) of **2** was reminiscent of that recorded for  $[\text{MoOCl}_3]^-$ . [11]

Crystals of **2** suitable for an X-ray diffraction study were grown from acetonitrile on prolonged standing at ambient temperature. The molecular structure is shown in Figure 3 with selected bond lengths and angles given in the caption. Crystallographic data are presented in Table 2. The complex is a salt comprising an  $\text{Et}_3\text{NH}$  cation and an anion in which a chelating amine/imide ligand is bound to the molybdenum(V) centre (Figure 3). The  $\text{NH}_2$  groups are involved in H-bonding to two of the chlorides of a neighbouring anion giving a total of four H-bonds between anions. A third chloride and one of the others on each

molybdenum is involved in asymmetric, bifurcated, H-bonding with the cation. Given this, N(1), Cl(1), Cl(2) and Cl(4) are not subject to any disorder, whereas Cl(3) and the imido group at N(2), which are not involved in any H-bonding, are able to swap sites (major:minor disorder components = 0.805:0.195(4)). Overall, the structure is made up of discrete units of two cations and two anions, all H-bonded with the Cl(3) and with imido groups able to occupy either site (see Figure 4).



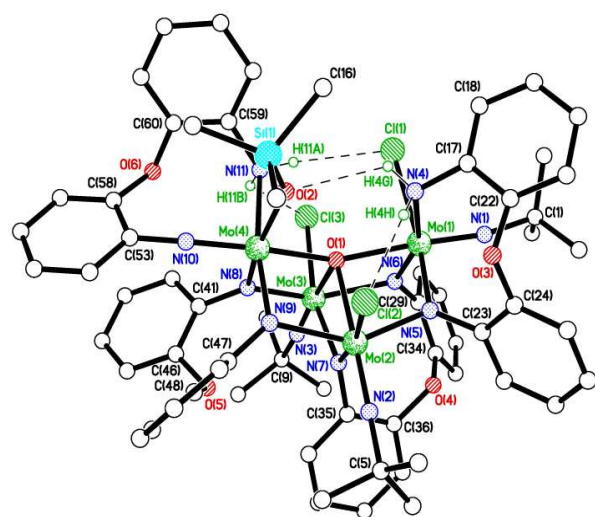
**Figure 3.** Molecular structure of  $[\text{Mo}(\text{L})\text{Cl}_4][\text{Et}_3\text{NH}]$  (**2**), showing the atom numbering scheme. Hydrogen atoms except those involved in H-bonds, and minor disorder components have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Mo(1) – N(1) 2.222(4), Mo(1) – N(2) 1.717(7), Mo(1) – Cl(1) 2.4631(12), Mo(1) – Cl(2) 2.4926(12), Mo(1) – Cl(3) 2.3454(18), Mo(1) – Cl(4) 2.3869(13); Mo(1) – N(1) – C(1) 118.6(3), Mo(1) – N(2) – C(7) 168.7(6).



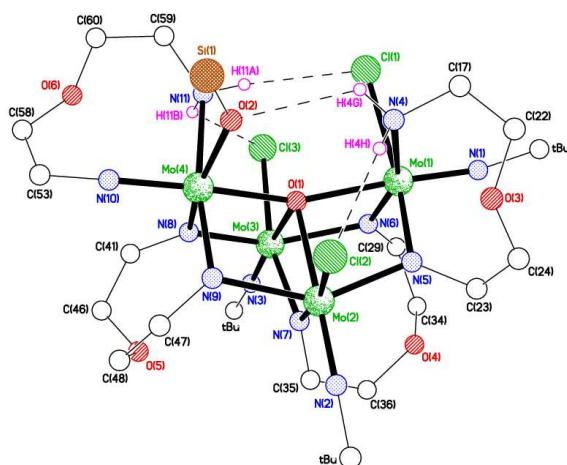
**Figure 4.** View of **2** showing the cation/anion H-bonding interactions. H-bond geometry (Å /  $^\circ$ ): Cl(1)⋯H(1BA) = 2.61(5), angle at H(1BA) = 142(5); Cl(2)⋯H(1AA) = 2.69(5), angle at H(1AA) = 152(5); Cl(1)⋯H(3A) = 2.31(6), angle at H(3A) = 165(5); Cl(4)⋯H(3A) = 3.00(6), angle at H(3A) = 114(4).

Use of the same dianiline, but using the ‘imido-exchange’ route via *in-situ* generated  $[\text{Mo}(\text{N}t\text{Bu})_2\text{Cl}_2(\text{DME})]$  led, following work-up, to the isolation of a purple crystall suitable for X-ray crystallography. We tried to grow single crystals suitable for X-ray diffraction from toluene, but were unsuccessful. However,

when the toluene was removed and these samples were taken up in acetonitrile, single crystal of X-ray diffraction quality were eventually obtained. The molecular structure revealed the structure  $[\text{Mo}_4\text{Cl}_3(\text{N}t\text{Bu})_3(\text{OSiMe}_3)(\mu_4\text{-O})(\text{L})_2(\text{L}')_2] \cdot 2\text{MeCN}$  (**3**·2MeCN) and this is shown in Figure 5, with selected bond lengths and angles given in the caption. All four molybdenum centres adopt different distorted octahedral geometries, but all are bound to the central  $\mu_4$ -oxo group. Given the complex nature of the structure, the core of **3** is also presented in Figure 6. The complexity of the structure is also reflected in the  $^1\text{H}$  NMR spectrum (for low field region, see Fig. S2), in which a number of the peaks are subject to ring currents which results in unusual high field chemical shifts for aromatic protons (as well as the *tert*-butyl/siloxide groups). [12] In the solid state structure, for Mo(1) and Mo(4), there is a chelating L' ligand present, but thereafter the coordination environments differ in that Mo(1) has a chloride and a near linear imido group [Mo(1) – N(1) – C(1) = 168.5(5)  $^\circ$ ], whereas Mo(4) has a bent siloxide group [Mo(4) – O(2) – Si(1) = 142.15(18)  $^\circ$ ] and two nitrogens of a chelating (2-NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O ligand which also acts as a bridge between Mo(2) and Mo(3). In the case of Mo(2) and Mo(3), the difference is essentially due to the nature of the bonding of the nitrogens derived from the precursor oxydianiline. For Mo(2), the ‘chelates’ are only bound in  $\eta^1$ -fashion, with that also bound to Mo(1) doing so via an NH<sub>2</sub> moiety, whereas for Mo(3) there is a bidentate chelating (2-NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O ligand present as well as an oxydianiline derived ligand binding in  $\eta^1$ -fashion. To complete the distorted octahedral environment, both Mo(2) and Mo(3) also bear a chloride as well as a linear *tert*-butylimido group [Mo(2/3) – N(2/3) – C(5/9) = 168.5(5) and 168.5(5)  $^\circ$ ]. In the structure, there are long bonds from the metals to the nitrogen atoms N(6) and N(9) at *ca.* 2.14 Å, however their near trigonal planar nature (as opposed to pyramidal) is consistent with a lack of protonation. There is some intramolecular H-bonding involving Cl(1) and Cl(3) with N(1)H<sub>2</sub>, Cl(2) with N(4)H<sub>2</sub> and O(2) with N(4)H<sub>2</sub>. The methyl groups of the OSiMe<sub>3</sub> group and the *t*Bu group at C(1) are disordered over two sets of positions: major:minor components 64(2):36(2) and 62.8:37.2(8)%, respectively. Whilst the origin of the central  $\mu_4$ -oxo is thought to be fortuitous oxygen, the siloxide group is thought to arise via excess Me<sub>3</sub>SiCl present in the system. We note that silyl ester group formation via Me<sub>3</sub>SiCl attack has previously been reported for the ‘sodium molybdate’ route when using anthranilic acid as the amine source. [5]



**Figure 5.** Molecular structure of  $[\text{Mo}_4\text{Cl}_3(\text{NtBu})_3(\text{OSiMe}_3)(\mu_4\text{-O})(\text{L})_2(\text{L}')_2]\cdot 2\text{MeCN}$  (**3**·2MeCN), showing the atom numbering scheme. Hydrogen atoms except those involved in H-bonds, and non-coordinated solvent molecules ( $2 \times \text{MeCN}$ ) have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Mo(1) – N(1) 1.713(4), Mo(1) – N(2) 1.718(4), Mo(1) – Cl(1) 2.4846(13), Mo(2) – Cl(2) 2.5224(10), Mo(3) – Cl(3) 2.4754(12), Mo(1) – N(1) – C(1) 168.5(5), Mo(2) – N(2) – C(5) 175.1(3), Mo(3) – N(3) – C(9) 175.4(4).



**Figure 6.** Core of complex **3**.

A search of the CSD revealed 1024 hits for  $\mu_4\text{-O}$  Mo species, the majority of which are hexamolybdate type species, whilst narrowing the search to those complexes also bearing an imido group gives 115 hits (again, many of these are imido functionalized hexamolybdates). [13]

#### Ring opening polymerization of $\epsilon$ -caprolactone

Complexes **1** – **3** have been screened for their ability to act as catalysts in the ring open polymerization of  $\epsilon$ -caprolactone and the results are depicted in Table 1. For **1** – **3**, runs were conducted in the presence of benzyl alcohol (BnOH), however, given the presence of the silyloxy group in the tetra-nuclear complex **3**,

this complex was also screened in the absence of BnOH. Results using **2** were not encouraging and so this complex is not discussed further. For catalytic systems utilizing **1** and **3**, at temperatures below  $80^\circ\text{C}$ , little or no activity was observed, however at higher temperatures, good conversions over 1 h were possible. All the polycaprolactone polymers (PCLs) obtained possessed a narrow distribution with unimodal characteristics [ $M_w/M_n = 1.10 - 1.82$ ]. There is a near linear relationship between monomer conversion and the  $M_n$  values for the polymers, which is indicative of a living polymerization process (see Figs. S3 and S4).

We have also investigated the effect of the  $\epsilon\text{-CL}/\text{Mo}$  molar ratio on the catalytic behaviour (entries 7 - 9 for **1** and 13 and 18 - 20 for **3**). When the molar ratio  $\epsilon\text{-CL}:\text{Mo}$  was increased from 125 or 250 to 1000, the molecular weight for **1** initially decreased (from  $ca\ 21 \times 10^3\ \text{g mol}^{-1}$ ) and then remained relatively constant ( $ca\ 13 \times 10^3\ \text{g mol}^{-1}$ ), whereas for **3**, the molecular weight gradually increased from  $ca\ 5$  to  $53 \times 10^3\ \text{g mol}^{-1}$  with a gradual increase in the conversion rate, but with little change of molecular weight distribution (1.23 - 1.65).

In general, the resulting polymer molecular weight was lower than expected, which indicates that in most cases, there were significant *trans*-esterification reactions occurring as evidenced in the MALDI-TOF mass spectrum for run 10 (see Figure S5). However, in cases where there is better agreement between observed and calculated molecular weight, the MALDI-TOF mass spectrum reveals only a single population of peaks (see Figure S6 for run 18). In the  $^1\text{H}$  NMR spectra of the PCL (Figures S7 and S8), signals at around 7.34 and 5.15 ppm ( $\text{C}_6\text{H}_5\text{CH}_2^-$ ), and 3.62 ppm ( $\text{CH}_2\text{CH}_2\text{OH}$ ), with an integral ratio 5:2:2, indicated that the polymer chains are capped by a benzyl group and a hydroxy end group. This suggests that the polymerization occurs through insertion of a benzyl alkoxy group into CL.  $^{13}\text{C}$  NMR data (Figures S9 and S10) also revealed peaks at 128.2 ( $\text{C}_6\text{H}_5\text{CH}_2^-$ ), 66.2 ppm ( $\text{C}_6\text{H}_5\text{CH}_2^-$ ), 62.6 ppm ( $\text{CH}_2\text{CH}_2\text{OH}$ ) assigned to the respective end groups. The aforementioned MALDI-TOF spectra also revealed the presence of the benzyloxy initiating group and a series of peaks separated by 114.14 mass units.

The limited number of Mo systems reported thus far tend to only be active at elevated temperatures, for example ammonium decamolybdate can function as part of a melt at  $150^\circ\text{C}$  afforded good conversions over 2 h, [8c] whilst bis(salicylaldehydato)dioxomolybdenum can operate effectively at temperatures in excess of  $110^\circ\text{C}$  in mesitylene. [8f] In these molybdenum-based systems, *trans*-esterification has also been noted.

In terms of the end group for the PCL obtained when using **3**/no BnOH, we can only tentatively propose a siloxide as there is a peak at about 0 ppm that we can assign to the siloxide (run under grease-free conditions), however the polymer seems to form a coating which hampers attempts to obtain the MALDI-TOF mass spectrum and so we are only able to see low molecular weight (see ESI).

**Table 1.** ROP studies using complexes **1** – **3**.

Run	Pre- Cat	T (°C)	CL:Mo: BnOH	Time (h)	Conv <sup>a</sup> (%)	$M_{n, GPC}^b$	$M_{n, Cal}^c$	PDI
1	<b>1</b>	80	250:1:1	12	89	16.14	27.93	1.50
2	<b>1</b>	100	250:1:1	12	88	13.81	22.51	1.36
3	<b>1</b>	120	250:1:1	12	89	14.97	27.93	1.66
4	<b>1</b>	100	250:1:1	1	72	5.58	20.05	1.10
5	<b>1</b>	100	250:1:1	6	79	11.43	25.08	1.23
6	<b>1</b>	100	250:1:1	24	95	16.61	27.07	1.44
7	<b>1</b>	100	250:1:1	12	95	21.43	27.07	1.82
8	<b>1</b>	100	500:1:1	12	96	12.41	54.72	1.44
9	<b>1</b>	100	1000:1:1	12	92	13.51	104.8	1.33
10	<b>2</b>	120	250:1:1	24	61	1.83	17.58	1.21
11	<b>3</b>	50	250:1:1	24	3	--	0.853	--
12	<b>3</b>	80	250:1:1	24	85	4.77	24.22	1.10
13	<b>3</b>	100	250:1:1	24	95	20.33	27.07	1.65
14	<b>3</b>	120	250:1:1	24	94	16.26	26.79	1.10
15	<b>3</b>	100	250:1:1	1	91	5.77	22.51	1.50
16	<b>3</b>	100	250:1:1	6	92	10.11	26.22	1.29
17	<b>3</b>	100	250:1:1	12	93	14.52	26.50	1.56
18	<b>3</b>	100	125:1:1	24	80	5.42	11.40	1.65
19	<b>3</b>	100	500:1:1	24	95	22.99	118.7	1.65
20	<b>3</b>	100	1000:1:1	24	97	29.92	242.5	1.23
21	<b>3</b>	110	250:1:0	12	98	17.21	27.93	1.73

<sup>a</sup> By <sup>1</sup>H NMR analysis; <sup>b</sup>  $\times 10^{-3}$ , Obtained from GPC analysis times 0.56. 5 mL of dry toluene were transferred into a Schlenk tube containing the desired amount of catalyst. The solution was stirred and maintained at the polymerization temperature with the aid of an oil bath. Benzyl alcohol was then added from a 0.6 M solution in toluene. After an additional five minutes, the polymerization was started by the addition of 1.0 mL of  $\epsilon$ -caprolactone; <sup>c</sup>  $\times 10^{-3}$ , (F.W.[M]/[BnOH])(conversion),

In conclusion, use of (2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O (LH<sub>4</sub>) in the ‘molybdate prep’ afforded different types of imido complex depending on the work-up, namely the bis(imido) molybdenum(VI) complex {Mo(L)Cl<sub>2</sub>(DME)} (**1**) or a molybdenum(V) amine/imide salt [Mo(L')Cl<sub>4</sub>][Et<sub>3</sub>NH] (**2**) (L' = [(2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(2-NC<sub>6</sub>H<sub>4</sub>O)]). An imido exchange reaction using *in-situ* [Mo(NtBu)<sub>2</sub>Cl<sub>2</sub>(DME)] led to the isolation of an usual tetranuclear complex, namely [Mo<sub>4</sub>Cl<sub>3</sub>(NtBu)<sub>3</sub>(OSiMe<sub>3</sub>)( $\mu_4$ -O)(L)<sub>2</sub>(L')<sub>2</sub>].2MeCN (**3**-2MeCN). The structure of **3** contains four different octahedral molybdenum environments. Complexes **1** and **3** were shown to be capable of the ROP of  $\epsilon$ -caprolactone at temperatures  $\geq 80$  °C with good conversions in the presence of benzyl alcohol, affording moderate molecular weight ( $M_n = ca 5 - 30 \times 10^3$  g mol<sup>-1</sup>) polymers. Silyloxy **3** is also capable of the ROP of  $\epsilon$ -caprolactone with good conversion in the absence of benzyl alcohol.

## Experimental

### General:

All manipulations were carried out under an atmosphere of dry nitrogen using conventional Schlenk and cannula techniques or in

a conventional nitrogen-filled glove box. DME was refluxed over sodium and benzophenone. Toluene was refluxed over sodium. Acetonitrile was refluxed over calcium hydride. All solvents were distilled and degassed prior to use. IR spectra (nujol mulls, KBr windows) were recorded on a Nicolet Avatar 360 FT IR spectrometer; <sup>1</sup>H NMR spectra were recorded at room temperature on a Varian VXR 400 S spectrometer at 400 MHz or a Gemini 300 NMR spectrometer or a Bruker Advance DPX-300 spectrometer at 300 MHz. The <sup>1</sup>H NMR spectra were calibrated against the residual protio impurity of the deuterated solvent. The EPR of **2** was recorded on a Bruker EMX -10/12 spectrometer. Elemental analyses were performed by the elemental analysis service at the London Metropolitan University or at Sichuan University. Matrix Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrometry was performed in a Bruker autoflex III smart beam in linear mode, and the spectra were acquired by averaging at least 100 laser shots. 2,5-Dihydroxybenzoic acid was used as the matrix and THF as solvent, except in the case of the sample form **3** with no benzyl alcohol for which 9-nitroanthracene was employed as matrix. Sodium chloride was dissolved in methanol and used as the ionizing agent. Samples were prepared by mixing 20  $\mu$ l of matrix solution in THF (2 mg/ml) with 20  $\mu$ l of matrix solution (10 mg/ml) and 1  $\mu$ l of a solution of ionizing agent (1 mg/ml). Then 1 ml of these mixtures was deposited on a target plate and allowed to dry in air at ambient temperature. The precursor [Mo(NtBu)<sub>2</sub>Cl<sub>2</sub>(DME)] was prepared by the literature method, [14] whilst the oxydianiline was prepared by the method of Randell *et al.* [15]

### Synthesis of {Mo[(2-NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O]Cl<sub>2</sub>(DME)} (**1**)

To Na<sub>2</sub>MoO<sub>4</sub> (3.00 g, 14.6 mmol) and (2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O (2.92 g, 14.6 mmol) in DME (200 ml) were added Et<sub>3</sub>N (7.73 ml, 58.3 mmol) and Me<sub>3</sub>SiCl (14.95 ml, 116.5 mmol), and the system was heated to 90 °C for 12 h. On cooling, filtration followed by concentration to about half volume afforded small red prisms of **1** on prolonged standing (1 - 2 days) at ambient temperature. Yield 3.96 g, 60 %. C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Cl<sub>2</sub>Mo requires C 42.40, H 4.00, N 6.18 %. Found: C 41.98, H 4.10, N 6.18 %. IR: 3090w, 3058w, 3012w, 2069w, 2932w, 2884w, 2829w, 1625w, 1576w, 1492w, 1462m, 1444m, 1366w, 1320w, 1300m, 1261m, 1243m, 1204m, 1187m, 1152w, 1106m, 1090m, 1052s, 1032m, 1020m, 1008m, 990w, 978m, 939w, 862s, 851m, 828w, 796m, 771m, 762m, 746m, 675w, 665w, 599w, 566w, 544w, 504m, 451m, 428w, 412w. Mass spec (EI): 493.0808 [M + K]<sup>+</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.59 (dd, *J* 8.4 Hz, *J'* 1.2 Hz, 2H, arylH), 7.18 (td, *J* 7.6 Hz, *J'* 1.6 Hz, 2H, arylH), 7.10 (td, *J* 8.0 Hz, *J'* 1.6 Hz, 2H, arylH), 6.68 (dd, *J* 8.0 Hz, *J'* 1.6 Hz, 2H, arylH), 3.97 (bs, 6H, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.55 (bs, 4H, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>).

### Synthesis of {Mo[(2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(2-NC<sub>6</sub>H<sub>4</sub>O)]Cl<sub>4</sub>}[Et<sub>3</sub>NH] (**2**)

To Na<sub>2</sub>MoO<sub>4</sub> (3.00 g, 14.6 mmol) and (2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O (2.92 g, 14.6 mmol) in DME (200 ml) were added Et<sub>3</sub>N (7.73 ml, 58.3 mmol) and Me<sub>3</sub>SiCl (14.95 ml, 116.5 mmol), and the system was heated to 90 °C for 12 h. On cooling, volatiles were removed *in-vacuo*, and the residue was extracted into warm (using a heat gun) acetonitrile (100 ml). Prolonged standing at ambient temperature

afforded small yellow/brown prisms of **2**. Yield 2.51 g, 32 %.  $C_{18}H_{26}N_3OCl_4Mo$  requires C 40.17, H 4.87, N 7.81 %. Found: C 40.34, H 4.90, N 8.05 %. IR: 3320bm, 3068m, 2981s, 2946s, 2767w, 2744w, 2680s, 2603s, 2537w, 2500s, 2361w, 1640w, 1477s, 1445m, 1399s, 1388m, 1368w, 1332w, 1264m, 1174m, 1097m, 1077bm, 1038s, 852w, 808s, 613bw, 426w. Mass spec (EI): 437.29  $[M-Et_3NH]^+$ , 401.26  $[M-Et_3NH-Cl]^+$ .  $^1H$  NMR ( $C_6D_6$ , 400 MHz): only features associated with the cation were observed at  $\delta$  11.72 (bs, 1H, NH), 3.04 (m, 6H,  $NCH_2CH_3$ ), 3.04 (m,  $J$  7.6 Hz, 9H,  $NCH_2CH_3$ ). EPR (X-band, solid, 110 K):  $g = 1.94$ .

**Synthesis of**  $[Mo_4Cl_3(NtBu)_3(OSiMe_3)(\mu_4-O)(L)_2(L')_2] \cdot 2MeCN$  (3·2MeCN)

To  $Na_2MoO_4$  (3.00 g, 14.6 mmol) and *tert*-butylamine (1.99 ml, 29.1 mmol) in DME (200 ml) were added  $Et_3N$  (7.73 ml, 58.3 mmol) and  $Me_3SiCl$  (14.95 ml, 116.5 mmol), and the system was heated to 90 °C for 12 h. On cooling, (2- $NH_2C_6H_4$ ) $_2O$  (2.91 g, 14.6 mmol) in toluene (50 ml) was added and the system was refluxed for 12 h. Volatiles were then removed and the resulting purple solid was washed with cold petroleum ether (10 ml) and then extracted in MeCN (30 ml) and on prolonged standing (1 – 2 days), small red/purple prisms of **3** formed. Yield 3.12 g, 51 %.  $C_{63}H_{72}N_{11}O_6Cl_3SiMo_4 \cdot 1/2$  toluene (sample dried *in-vacuo* for 2 h, -2MeCN) requires C 48.58, H 4.63, N 9.37 %. Found: C 48.30, H 4.79, N 9.01 %. IR: 3434bm, 3336w, 3194w, 3125w, 3059w, 2971w, 2949w, 2921w, 2894w, 2850w, 1623w, 1603w, 1582w, 1560w, 1498m, 1472s, 1444m, 1401w, 1359w, 1334w, 1269m, 1246s, 1206m, 1189m, 1156w, 1101m, 1071w, 1032w, 993w, 938w, 877m, 853w, 836w, 815w, 801w, 764m, 752m, 730w, 686w, 664m, 610w, 583w, 552w, 506w, 455w. Mass spec (EI): 1665.2712  $[M-Me]^+$ .  $^1H$  NMR ( $C_6D_6$ , 400 MHz): 9.37 (bs, 2H,  $NH_2$ ), 8.22 (dd,  $J$  8.0 Hz,  $J'$  1.6 Hz, 1H, *arylH*), 8.09 (dd,  $J$  8.0 Hz,  $J'$  1.6 Hz, 1H, *arylH*), 7.98 (dd,  $J$  7.6 Hz,  $J'$  1.6 Hz, 1H, *arylH*), 7.88 (dd,  $J$  8.0 Hz,  $J'$  1.6 Hz, 1H, *arylH*), 7.83 (dd,  $J$  8.0 Hz,  $J'$  1.2 Hz, 1H, *arylH*), 7.78 (dd,  $J$  7.6 Hz,  $J'$  1.6 Hz, 1H, *arylH*), 7.67 (m, 2H, *arylH*), 7.33 (dd,  $J$  8.4 Hz,  $J'$  1.6 Hz, 1H, *arylH*), 7.25 (dd,  $J$  8.0 Hz,  $J'$  1.2 Hz, 1H, *arylH*), 7.19 (dt,  $J$  8.0 Hz,  $J'$  1.2 Hz, 2H, *arylH*), 7.11 - 7.01 (overlapping m, 2H, *arylH*), 6.95 - 6.83 (overlapping m, 6 $^{1/2}$ H, *arylH* + toluene), 6.78 - 6.73 (m, 4H, *arylH*), 6.67 - 6.59 (overlapping m, 6H, *arylH*), 6.39 (dt,  $J$  7.6 Hz,  $J'$  1.6 Hz, 1H, *arylH*), 6.27 - 6.24 (overlapping m, 2H, *arylH*), 5.81 (bs, 2H,  $NH_2$ ), 5.29 (dd,  $J$  7.6 Hz,  $J'$  1.2 Hz, 1H, *o-arylH*), 2.07 (s, 1.5H, toluene), 0.69 (s, 9H,  $C(CH_3)_3$ ), 0.32 (s, 9H,  $C(CH_3)_3$ ), 0.29 (s, 9H,  $C(CH_3)_3$ ), 0.26 (s, 6H,  $CH_3CN$ ), -0.07 (s, 9H,  $OSiMe_3$ ).

#### Ring opening polymerization

Typical polymerization procedures in the presence of one equivalent of benzyl alcohol (Table 1, run 1) are as follows. A toluene solution of **1** (0.030 mmol, 1.0 mL toluene) and BnOH (0.030 mmol) were added into a Schlenk tube in the glove-box at room temperature. The solution was stirred for 2 min, and then  $\epsilon$ -caprolactone (2.5 mmol) along with 1.5 mL toluene was added to the solution. The reaction mixture was then placed into an oil

bath pre-heated at 80 °C, and the solution was stirred for the prescribed time (12 h). The polymerization mixture was then quenched by addition of an excess of glacial acetic acid (0.2 mL) into the solution, and the resultant solution was then poured into methanol (200 mL). The resultant polymer was then collected on filter paper and was dried *in vacuo*.

#### Crystallography

Diffraction data for **1** were collected on an Agilent Xcalibur Eos CCD diffractometer at 148(2)K [16]. Diffraction data for **2** and **3**·2MeCN were measured on a Bruker SMART 1000 CCD diffractometer at 150(2)K. [17] Corrections were made for absorption and for Lorentz and  $L_p$  effects. [16, 17] The structures were solved by superflip (**1**) or direct methods (**2** and **3**·2MeCN) and refined on  $F^2$  by full-matrix-least squares. [17 - 20] H atoms on nitrogen were freely refined with similarity restraints on N–H bond lengths, those on C atoms were modelled using a riding model. In **2** atoms Cl(3) and N(2)/O(1)/C(7)>C(12) were modelled as two-fold positionally disordered with major component 80.5(4)%. In 3·2MeCN the whole *t*Bu group at C(1) was modelled with two fold disorder with major component 62.8(8)% and the methyl groups at Si(1) were similarly disordered with major component 64(2)%. One MeCN of crystallisation was modelled at full occupancy, while those at N(13) and N(14) were both modelled as two-fold disordered with the two components adding up to half an MeCN molecule.

CCDC 1013319, 1013320, and 1061146 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### Acknowledgements

Sichuan Normal University and the National Natural Science Foundation of China (grants 51443004 and 51273133) are thanked for financial support. CR thanks the EPSRC for the award of a travel grant and Dr Kevin Welham (University of Hull) for Mass Spectrometry data.

**Supporting Information Available:** X-ray crystallographic files CIF format for the structure determinations of compound **1**, **2** and **3**·2MeCN.

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**Table 2:** Crystallographic data for complexes **1**, **2** and **3**·2MeCN

Compound	<b>1</b>	<b>2</b>	<b>3</b> ·2MeCN
Formula	C <sub>16</sub> H <sub>18</sub> Cl <sub>2</sub> MoN <sub>2</sub> O <sub>3</sub>	C <sub>18</sub> H <sub>26</sub> Cl <sub>4</sub> MoN <sub>3</sub> O	C <sub>63</sub> H <sub>72</sub> Cl <sub>3</sub> Mo <sub>4</sub> N <sub>11</sub> O <sub>6</sub> Si·2(C <sub>2</sub> H <sub>3</sub> N)
Formula weight	453.16	538.16	1679.62
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>
Unit cell dimensions			
<i>a</i> (Å)	14.6075(3)	12.2120(7)	12.7371(4)
<i>b</i> (Å)	15.3236(3)	11.9077(7)	25.9749(8)



$c$ (Å)	32.3586(5)	17.0761(9)	24.2388(8)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90	102.0140(9)	100.0667(5)
$\gamma$ (°)	90	90	90
$V$ (Å <sup>3</sup> )	7243.1(2)	2428.8(2)	7895.8(4)
$Z$	16	4	4
Temperature (K)	148(2)	150(2)K	150(2)K
Wavelength (Å)	0.71073	0.71073	0.71073
Calculated density (g.cm <sup>-3</sup> )	1.662	1.472	1.413
Absorption coefficient (mm <sup>-1</sup> )	1.04	0.99	0.79
Transmission factors (min./max.)	0.816, 1.000	0.857, 0.961	0.574, 0.653
Crystal size (mm <sup>3</sup> )	0.30 × 0.20 × 0.20	0.16 × 0.08 × 0.04	0.79 × 0.61 × 0.59
$\vartheta$ (max) (°)	29.1	26.0	29.0
Reflections measured	47115	18535	68759
Unique reflections	8867	4758	18926
$R_{\text{int}}$	0.053	0.037	0.031
Reflections with $F^2 > 2\sigma(F^2)$	6660	3548	14618
Number of parameters	437	338	1017
$R_1 [F^2 > 2\sigma(F^2)]$	0.037	0.045	0.045
$wR_2$ (all data)	0.079	0.137	0.127
GOOF, $S$	1.05	1.07	1.15

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Largest difference			
peak and hole ( $e \text{ \AA}^{-3}$ )	0.68 and -0.52	0.95 and -0.53	1.51 and -1.35

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