Metalation of 2-Propenylphenol

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In order to generate 2-propenylphenolate, **PO**$^-$, as a potential ligand for oxomolybdenum compounds, the lithiation of the parent phenol derivative, **POH**, was investigated. Treatment of **POH** with BuLi in THF yielded a tetramer of the corresponding alkoxide "**POLi**" with a heterocubane structure in which the coordination spheres of the Li centres are completed by THF molecules, i.e. {Li(THF)[μ_3-OC_6H_4(CH=CH–CH_3)-2]}$_4$ (**1**). Compound **1** proved to be rather unreactive and unsuitable as a starting material for the introduction of the corresponding aryloxide ligands into the coordination sphere of molybdenum by salt metathesis. The latter did occur, however, when "**POLi**" was synthesised in the presence of 12-crown-4 and subsequently treated with molybdenyl chloride. This led to an unidentified aryloxide compound as well as to a hitherto unknown chlorooxomolybdate anion in the complexes [Li(12-crown-4)][MoO_2Cl_3(THF)] (**2**) and [{Li(12-crown-4)}$_2$Cl][MoO_2Cl_3(THF)] (**2′**) with an octahedral coordination sphere at the molybdenum centre in each case. An Mo(**PO**) complex was finally isolated for the first time when MoO_2(O*t*Bu)$_2$ was employed as a starting material and treated with "**POLi**" prepared in situ in the presence of the crown ether. This led to the isolation of [Li(12-crown-4)$_2$][MoO_2(**PO**)$_3$] (**3**), which represents a rare example of a five-coordinate dioxomolybdenum(VI) complex as well as being the first example among these complexes with a square-pyramidal ligand arrangement. Comparison of **2** with **3** suggests that the low coordination number of the 14-electron compound **3** originates from the bulkiness of the **PO**$^-$ ligands. The crystal structures of all three compounds **1**–**3** are discussed.

Introduction

In order to establish a potential model of the surface intermediates during the SOHIO process, in which propene is oxidised with O_2 on bismuth molybdate catalysts to give acrolein,[1] we have been interested in the synthesis of high-valent (π-allyl)Mo complexes. Since the tendency of (π-allyl)Mo units to release allyl radicals increases with increasing oxidation state of the molybdenum centre, we decided to tether the allyl ligand through a donor function to the molybdenum atom thereby increasing the stability of the Mo–allyl bonding. By using phosphane donor functions, we succeeded in isolating a stable (allyl)Mo^{IV} compound (Scheme 1) which was prepared from an (olefin/phosphane)Mo chelate complex.[2] In order to obtain (allyl)molybdenum compounds in even higher oxidation states, ideally containing oxo ligands at the same time, it would be advantageous to replace the phosphane donor function by a "harder" oxo donor function. We thus decided to exploit the behaviour of the potential **PO**$^-$ ligand in contact with high valent molybdenum compounds.

Results and Discussion

We envisioned that in-situ preparation of "**POLi**" as a source of **PO**$^-$ could be achieved simply by treatment of the parent phenol, **POH**, with BuLi in THF. Surprisingly, numerous attempted reactions between the corresponding reaction mixtures and high- or low-valent starting materials containing Mo–Cl units did not lead to LiCl salt metathesis. Since it has been shown in the past, that the structures and degree of aggregation of group 1 metal alkoxides can have a strong influence on their reactivity,[3] compound **1**, resulting from the lithiation reaction, was crystallised by cooling a concentrated solution in THF. A subsequent single-crystal X-ray diffraction study of **1** revealed the reason for its low reactivity; 4 equiv. of "**POLi**" assemble themselves in **1** to form an aggregate with an Li_4O_4 heterocubane core in the centre (see Figure 1 and Scheme 2). Each oxygen atom is thus connected to three Li cations as well as the aryl residue, while each Li ion is linked to three alkoxide oxygen atoms as well as to the O atom of a THF solvent molecule (selected bond lengths and angles are listed in Tables 1 and 2). While [Li(THF)(OPh)] forms a hexamer,[4] a heterocubane structure as shown in Scheme 2 was previously found for [Li(*N*-methylcaprolactam)(μ_3-OPh)]$_4$ [5] and, furthermore, it is reminiscent of the structure displayed by [Li(THF)O_3SCF_3]$_4$.[6] In this latter compound, the Li–O bonds are somewhat shorter than those observed for **1**

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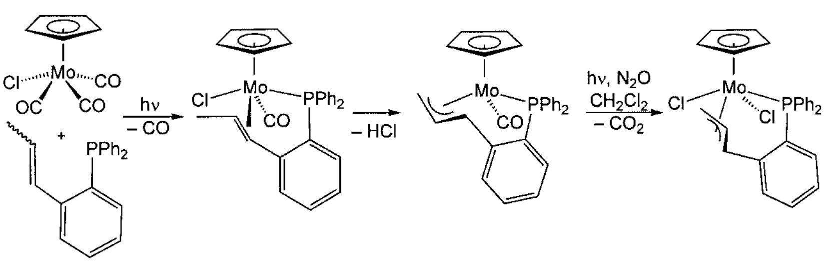


Scheme 1

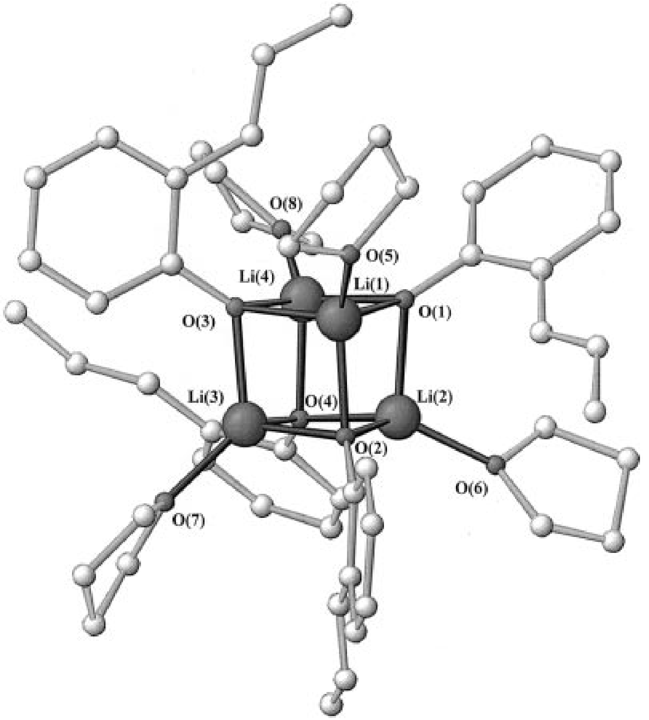
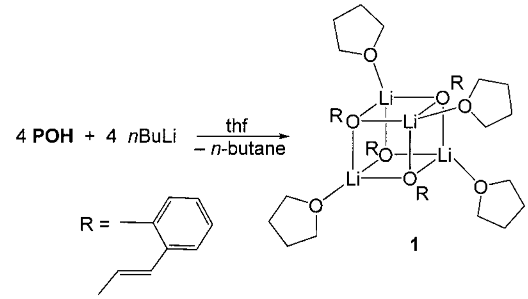


Figure 1. Molecular structure of **1** with partial atom labelling scheme; hydrogen atoms have been omitted for clarity

Table 2. Selected bond angles [°] for **1**

Li(1)−O(1)−Li(4)	85.3(3)	O(1)−Li(1)−O(2)	94.5(2)
Li(1)−O(1)−Li(2)	85.2(2)	O(1)−Li(1)−O(3)	95.1(2)
Li(4)−O(1)−Li(2)	83.5(3)	O(2)−Li(1)−O(3)	96.3(2)
Li(2)−O(2)−Li(1)	85.4(2)	O(2)−Li(2)−O(4)	95.3(2)
Li(2)−O(2)−Li(3)	84.4(3)	O(2)−Li(2)−O(1)	94.1(2)
Li(1)−O(2)−Li(3)	83.8(3)	O(4)−Li(2)−O(1)	97.6(2)
Li(3)−O(3)−Li(4)	85.6(3)	O(4)−Li(3)−O(3)	95.4(2)
Li(3)−O(3)−Li(1)	83.9(2)	O(4)−Li(3)−O(2)	94.2(2)
Li(4)−O(3)−Li(1)	84.1(3)	O(3)−Li(3)−O(2)	95.9(2)
Li(3)−O(4)−Li(2)	85.4(2)	O(3)−Li(4)−O(1)	94.9(3)
Li(3)−O(4)−Li(4)	85.0(3)	O(3)−Li(4)−O(4)	93.3(2)
Li(2)−O(4)−Li(4)	82.8(2)	O(1)−Li(4)−O(4)	96.1(3)



Scheme 2

Table 1. Selected bond lengths [Å] for **1**

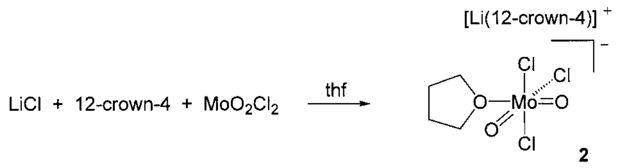
O(1)−Li(1)	1.928(5)	O(4)−Li(4)	1.996(5)
O(1)−Li(4)	1.953(4)	O(5)−Li(1)	1.917(5)
O(1)−Li(2)	1.960(5)	O(6)−Li(2)	1.913(5)
O(2)−Li(2)	1.931(5)	O(7)−Li(3)	1.925(5)
O(2)−Li(1)	1.949(5)	O(8)−Li(4)	1.906(4)
O(2)−Li(3)	1.980(5)	Li(1)−Li(3)	2.623(6)
O(3)−Li(3)	1.952(5)	Li(1)−Li(4)	2.629(6)
O(3)−Li(4)	1.952(5)	Li(1)−Li(2)	2.631(6)
O(3)−Li(1)	1.971(5)	Li(2)−Li(4)	2.604(6)
O(4)−Li(3)	1.930(5)	Li(2)−Li(3)	2.626(6)
O(4)−Li(2)	1.942(5)	Li(3)−Li(4)	2.652(6)

(1.928−1.996 Å) which in turn compare well with those found in [Li(*N*-methylcaprolactam)(μ_3-OPh)]$_4$ (1.88−2.00 Å). The Li−Li distances are all very similar (2.604−2.652 Å) and only somewhat longer than those in organolithium compounds with a heterocubane structure such as [Li(THF)*t*BuCH$_2$CH$_2$]$_4$ (2.479 Å in average).[7] The bond angles within the cubes amount to 90±8°, i.e. the cubic geometry is only slightly distorted. Even though a (*Z*)/(*E*) ligand mixture (1:5) was employed for the synthesis of **1**, only (*E*)- configured olefinic moieties were found in the molecular structure of **1** as shown by X-ray crystallography and there is no evidence for (*Z*)-configured groups in the crystalline bulk material on the basis of NMR spectroscopic investigations (signal assignments are supported by ^{1}H-^{1}H-COSY and ^{1}H-^{13}C-HSQC spectroscopic data and are thus unambiguous). Apparently, crystallisation proceeds only for the (all-*E*) arrangement and hence the yield of crystalline material is only 17%.

It is also clear from Figure 1 that the Li$_4$O$_4$ core is effectively shielded by the large organic residues as well as the THF residues which altogether form a lipophilic-like layer around the alkoxide O atoms. Hence, a reaction with Mo−Cl units or even with water is indeed problematic. Accordingly, **1** proved to be stable to air whereas [Li(*N*-methylcaprolactam)(μ_3-OPh)]$_4$ was reported[5] to be air-sensitive.

To avoid formation of the stable tetrameric form of "**PO-Li**" in solution, i.e. **1**, and to thus obtain it in a more reactive state, 12-crown-4 was employed in subsequent experiments to separate the Li^+ ions. These potential ligands must be added to **POH** previous to the addition of BuLi and the resultant mixture has to be employed in situ since subsequent treatment of **1** with 12-crown-4 in THF does not enhance the reactivity.

Among other starting materials, MoO_2Cl_2 was chosen for treatment with 1 equiv. of "**POLi**" prepared by the abovementioned route in the presence of 12-crown-4. Some of the MoO_2Cl_2 reacts to give a molybdenum aryloxide compound which, however, could neither be isolated in a pure state nor identified while the remainder apparently reacts with the Li(12-crown-4)Cl thus formed to give **2** with the hitherto unknown simple chlorooxo anion $[MoO_2Cl_3(THF)]^-$ (Scheme 3).



Scheme 3

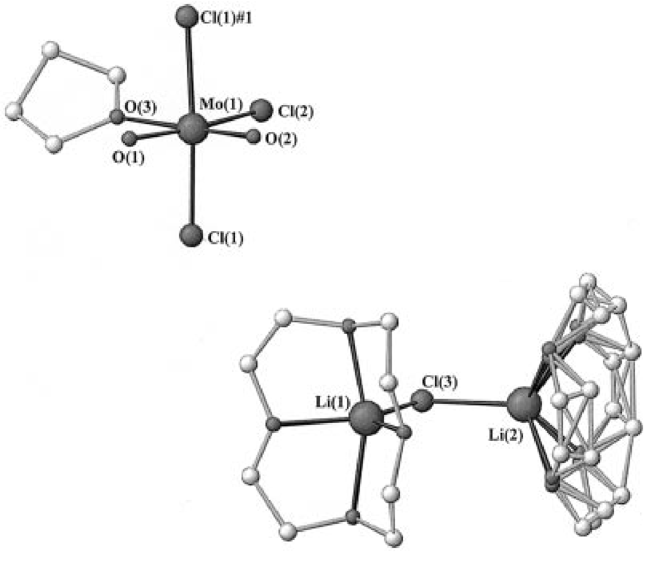


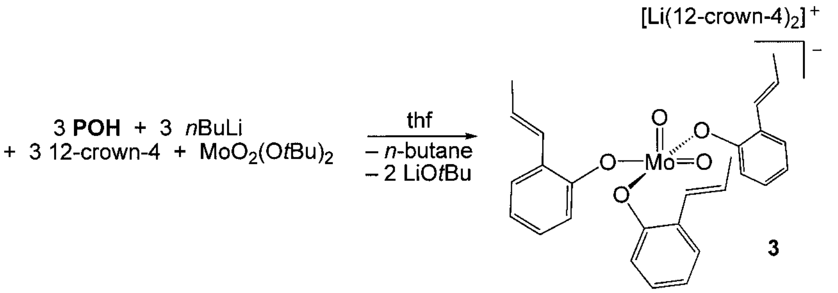
Figure 2. Molecular structure of **2′** with partial atom labelling scheme; hydrogen atoms have been omitted for clarity

Accordingly, for the formation of **2**, addition of **POH** is not necessary as shown by an analogous experiment performed without **POH** (1 equiv. of MoO_2Cl_2 then reacts to give LiCl and "MoO_2Bu_2" which decomposes while the other equiv. reacts with LiCl to give **2**). The chemistry of chlorooxomolybdenum compounds has been well explored and a large variety of such complexes (charged and uncharged) has been synthesised in the past.[8] The anion of **2** was unknown until now and while comparable anions of the type $[MoO_2Cl_3L]^-$ (with L = any donor) have been synthesised, for instance with L = H_2O,[9] their structures have so far eluded determination. Hence, attempts were made to crystallise **2** directly from the reaction mixture produced as described above. This led to crystals of **2′** where the $[Li(12\text{-crown-}4)]^+$ cation is replaced by the novel cation $[\{Li(12\text{-crown-}4)\}_2Cl]^+$. The molecular structure is shown in Figure 2 (selected bond lengths and angles are listed in Table 3). The cation is composed of two $[Li(12\text{-crown-}4)]^+$ moieties which both coordinate to a chloride anion at almost identical distances [Li(1)−Cl(3) 2.305(9) Å; Li(2)−Cl(3) 2.310(8) Å]. One of the 12-crown-4 ligands is disordered with respect to both C and O atoms. The crystal structure of the neutral complex [Li(12-crown-4)Cl] has been determined previously.[10] A comparison with the corresponding $[\{Li(12\text{-crown-}4)\}_2Cl]^+$ cation in **2′** revealed that, as expected in the absence of the second $[Li(12\text{-crown-}4)]^+$ cation, the remaining Li−Cl bond is somewhat shorter [2.290(4) Å]. The difference is, however, not as large as might have been expected. In contrast to [Li(12-crown-4)Cl], in which all Li−O distances are equal, the Li−O bonds within each of the [Li(12-crown-4)] moieties in **2′** are all different, spanning a range of 1.976−2.210 Å. The Mo centre of the anion is surrounded by its ligands in a distorted octahedral geometry. The bond lengths of the two Mo=O groups are significantly different since the comparatively weak THF donor is found in a *trans* position to O2 [→ strong bond to Mo; 1.670(5) Å] while a chloro ligand is bonded in a *trans* position to O1 [→ weaker bond to Mo; 1.704 Å]. The bond angle O2−Mo−O1 amounts to 102.9° and thus compares well with the angles found in other octahedral complexes containing the MoO_2^{2+} unit.

Table 3. Selected bond lengths [Å] and bond angles [°] for **2′**

Mo(1)−O(2)	1.670(5)	Mo(1)−Cl(1)	2.380(2)
Mo(1)−O(1)	1.704(4)	Mo(1)−Cl(2)	2.510(2)
Mo(1)−O(3)	2.293(3)	Li(1)−Cl(3)	2.305(9)
		Li(2)−Cl(3)	2.310(8)
O(2)−Mo(1)−O(1)	102.9(2)	O(3)−Mo(1)−Cl(1)	82.92(5)
O(2)−Mo(1)−O(3)	174.0(3)	O(2)−Mo(1)−Cl(2)	93.8(2)
O(1)−Mo(1)−O(3)	83.1(3)	O(1)−Mo(1)−Cl(2)	163.3(2)
O(2)−Mo(1)−Cl(1)	96.58(5)	O(3)−Mo(1)−Cl(2)	80.24(9)
O(1)−Mo(1)−Cl(1)	93.58(4)	Cl(1)−Mo(1)−Cl(2)	84.39(3)

Since the tendency of MoO_2^{2+} units to bind chloride is clearly very strong, $MoO_2(OtBu)_2$ was subsequently chosen as the starting material in order to finally obtain and isolate a $\mathbf{PO}^-$ complex by the synthetic route discussed above (direct treatment with **POH** leads to an air-sensitive brown oil which could not be purified sufficiently to allow its identification). After workup, a yellow, microcrystalline, very air-sensitive solid was obtained. IR spectroscopic measurements indicated the presence of an MoO_2 moiety whereas the ^1H NMR spectrum showed signals for (*E*)-configured **PO** residues [again there was no evidence for (*Z*) moieties] and 12-crown-4. Recrystallisation from 1,4-dioxane/hexane provided crystals suitable for a single-crystal X-ray diffraction study which indicated the composition [Li(12-crown-



Scheme 4

4)$_2$][MoO$_2$(**PO**)$_3$] (**3**) (Scheme 4, Figure 3, selected bonds lengths and angles are listed in Table 4). The arrangement of the five oxygen atoms around the molybdenum centre represents a distorted square pyramid ($\tau^{[11]} = 0.1$) with O5 at the apical position. Five-coordinated dioxomolybdenum(VI) complexes such as the anion of **3** are rare. When formed, these 14-electron complexes are usually stabilised by additional donor molecules (e.g. solvent molecules such as here THF/dioxane) or aggregation. Accordingly, only five monomeric complexes displaying five-coordination in the solid state are known today[12–17] which uniformly exhibit trigonal-bipyramidal coordination geometries. The square-pyramidal arrangement of the ligands in **3** is thus unique. The successful isolation of the known compounds has been ascribed to the employment of bulky ligands and this hypothesis has very recently been confirmed in a systematic study.[16]

Table 4. Selected bond lengths [Å] and bond angles [°] for **3**

Mo(1)–O(5)	1.676(6)	Mo(1)–O(2)	1.977(4)
Mo(1)–O(4)	1.704(4)	O(1)–C(1)	1.357(6)
Mo(1)–O(1)	1.968(4)	O(2)–C(10)	1.332(7)
Mo(1)–O(3)	1.973(4)	O(3)–C(19)	1.342(7)
O(5)–Mo(1)–O(4)	105.8(2)	O(4)–Mo(1)–O(2)	144.0(2)
O(5)–Mo(1)–O(1)	104.1(2)	O(1)–Mo(1)–O(2)	80.5(2)
O(4)–Mo(1)–O(1)	90.3(2)	O(3)–Mo(1)–O(2)	80.1(2)
O(5)–Mo(1)–O(3)	103.8(2)	C(1)–O(1)–Mo(1)	128.5(3)
O(4)–Mo(1)–O(3)	92.3(2)	C(10)–O(2)–Mo(1)	136.1(4)
O(1)–Mo(1)–O(3)	150.2(2)	C(19)–O(3)–Mo(1)	126.4(3)
O(5)–Mo(1)–O(2)	110.2(2)		

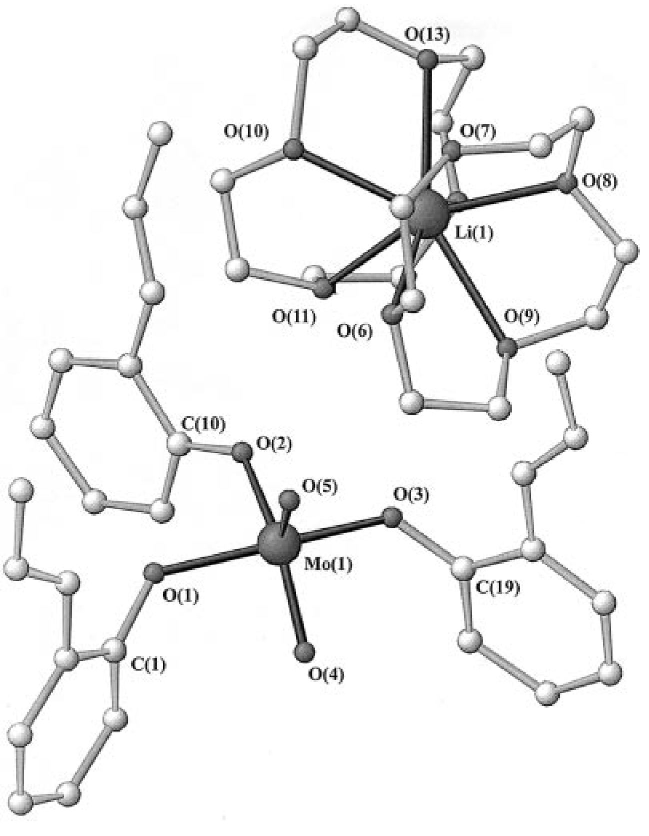


Figure 3. Molecular structure of **3** with partial atom labelling scheme; hydrogen atoms have been omitted for clarity

Along these lines, an explanation for the five-coordination of the molybdenum centre in **3** could also be based on the bulkiness of its aryl residues and the structural data support this assumption (see below).

Due to the square-pyramidal arrangement, the two terminal O atoms show quite different distances to Mo, i.e. the length of the bond between Mo and O5, lacking a *trans* ligand, amounts to 1.676(6) Å while the Mo–O4 bond is significantly longer [1.704(4) Å]. Atoms O1–O4 lie roughly in a plane (the deviations from the mean ideal plane amount to ±5.4 pm) and, as expected, the angles O5–Mo–O(1–4) are all somewhat larger than 90° (103.8–110.2°), the largest one occurring for O2 which is "clamped" by two bulky aryl residues so that C10 has to bend out of the basal plane. Furthermore, the small terminal oxo ligand O4 allows C1 and C19 to position themselves approximately within this plane. Accordingly, the O–Mo–O angles within the square base amount to 92.3–80.1°. In Figure 3 it can be seen that all aryl rings are arranged almost perpendicular to the basal plane to minimise steric crowding. All propenyl residues point in the same direction and an additional sixth ligand would have to approach from the other side where it would surely come into conflict with the aryl residues thus explaining the 5-coordination in the case of **3**. Due to the fact that three of these bulky aryloxide ligands were unexpectedly introduced at Mo in the course of the reaction shown in Scheme 4, an interaction between their olefinic functions and the Mo centre is clearly not possible either.

The complex anions of **3** and **2/2′** both contain an MoO_2^{2+} moiety and three anionic ligands. In the case of **2/2′** these are chloride ligands whereas in **3** they are bulky aryloxide ligands. The latter prevent binding of an additional neutral donor leading to five-coordination in **3** while the "compact" chloride ligands in **2/2′** permit coordination of an additional THF molecule.

Conclusion

In summary, we have clarified the unusual behaviour of lithiated **POH** by elucidating the molecular structure of the corresponding lithium aryloxide. It displays a heterocubane arrangement in which the organic ligands and residues insulate the inorganic core and, with this in mind, precautions could be taken to avoid formation of this structure. These enabled the synthesis and characterisation of the first Mo/**PO** complex **3**. Compound **3** is a rare example of a five-coordinate MoO_2^{2+} complex which, at the same time, represents the first example of an MoO_2^{2+} compound with a square-pyramidal arrangement of its ligands. Moreover, the first structural characterisation of a compound with an anion of the type $[MoO_2Cl_3L]^-$ has been achieved. Compound **2** contains such an anion where L is THF. Exchange of bulky **PO**$^-$ by Cl^- in the $[MoO_2X_3]^-$ moiety thus allows the additional coordination of a solvent molecule in **2** supporting the hypothesis that steric factors do indeed determine the coordination numbers observed in MoO_2^{2+} compounds.

Experimental Section

General Remarks: All manipulations were carried out with a vacuum line (at a background pressure $< 10^{-3}$ mbar), in a glovebox or by means of Schlenk-type techniques involving the use of dry argon. The $MoO_2(OtBu)_2$ complex was prepared as described in the literature.[18] All other starting materials were obtained commercially. Microanalyses were performed by the Analytische Laboratorien des Organisch-Chemischen Institutes der Universität Heidelberg using a Heraeus CHN-Analyser. All NMR spectra were recorded using a Bruker Avance-DPX 200 MHz spectrometer. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Digilab Excalibur™ FTS 3000 FTIR spectrometer. Low-resolution mass spectra were recorded with a Finnigan MAT 8400 instrument. High-resolution mass spectra were performed at the Zentrum für Massenspektrometrie des Organisch-Chemischen Instituts der Universität Heidelberg using a JEOL JMS-700 spectrometer. The ions were generated by EI (70 eV).

[Li(THF){μ$_3$-OC$_6$H$_4$(CH=CH−CH$_3$)-2}]$_4$ (1): A solution of 2-propenylphenol (1.00 g, 7.45 mmol) in THF (10 mL) was cooled to −20 °C and a BuLi solution (1.6 M in hexane, 4.66 mL) was added slowly. After warming to room temp., all volatiles were removed yielding analytically pure **1** (1.30 g 1.53 mmol, 82%). Crystals were obtained by cooling a THF solution to −30 °C for 12 h. $C_{52}H_{68}Li_4O_8$ (848.9): calcd. C 73.58, H 8.07; found C 73.40, H 8.14. MS (EI/LR): *m/z* (%) = 707 (25) [(5 **POLi**)$^+$ + Li], 560 (8) [(4 **POLi**)$^+$], 427 (100) [(3 **POLi**)$^+$ + Li], 287 (19) [(2 **POLi**) + Li], 280 (12) [(2 **POLi**)$^+$], 147 (100) [**POLi**$^+$ + Li], 134 (100) [**POH**$^+$]. MS (EI/HR): *m/z* found (calcd.) = 707.4242 (707.4227, Δm = 1.5 mmu) $[C_{45}H_{45}O_5{}^7Li_6]$, 706.4225 (706.4219, Δm = 0.6 mmu) $[C_{45}H_{45}O_5{}^6Li^7Li_5]$, 560.3282 (560.3254, Δm = 2.8 mmu) $[C_{36}H_{36}O_4{}^7Li_4]$, 427.2577 (427.2600, Δm = 2.3 mmu) $[C_{27}H_{27}O_3{}^7Li_4]$, 426.2599 (426.2591, Δm = 0.8 mmu) $[C_{27}H_{27}O_3{}^6Li^7Li_3]$, 287.1790 (287.1787, Δm = 0.3 mmu) $[C_{18}H_{18}O_2{}^7Li_3]$, 280.1633 (280.1627, Δm = 0.6 mmu) $[C_{18}H_{18}O_2{}^7Li_4]$. IR (KBr): $\tilde{\nu}$ = 3528 (w), 3054 (w), 3019 (w), 2976 (m), 2909 (w), 2876 (w), 2731 (w), 1589 (s), 1533 (m), 1476 (s),1447 (m), 1375 (w), 1304 (m), 1271 (m), 1184 (w), 1151 (m), 1105 (w), 1045 (m), 980 (m), 895 (w), 857 (m), 798 (m), 754 (s), 727 (m), 579 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.02 (m, 16 H, H$_{Ar}$), 6.87 (d, $^3J_{H,H}$ = 16.39 Hz, 4 H, CH$_3$CH=C*H*C$_6$H$_4$), 6.12 (m, 4 H, CH$_3$C*H*=CHC$_6$H$_4$), 3.53 (m, 16 H, THF), 1.70 (d, $^3J_{H,H}$ = 6.49 Hz, 12 H, C*H*$_3$CH=CHC$_6$H$_4$), 1.61 (m, 16 H, THF) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 164.15 (s, 4 C, C$_{Ar}$−O), 130−114 (m, 20 C, *C*$_{Ar}$), 128.57 (s, 4 C, CH$_3$CH=*C*HC$_6$H$_4$), 123.41 (s, 4 C, CH$_3$*C*H=CHC$_6$H$_4$), 68.46 (s, 8 C, THF), 25.64 (s, 8 C, THF), 18.84 (s, 4 C, *C*H$_3$CH=CHC$_6$H$_4$) ppm.

[Li(12-crown-4)][MoCl$_3$O$_2$(THF)] (2): A solution of MoO_2Cl_2 (0.55 g, 2.79 mmol) in THF (40 mL) was cooled to −20 °C and 12-crown-4 was added (0.49 g, 2.79 mmol). To the resultant solution, butyllithium was slowly added (1.11 mL of a 2.5 M toluene solution) resulting in a change of the original yellow colour to a dark brown. After warming to room temp., the solution was stirred for 0.5 h and a fine black solid precipitated which was filtered. All volatiles were removed from the filtrate and the residue extracted with acetone (40 mL). Removal of the solvent yielded the pure product **2** (0.55 g, 1.13 mmol, 40.5%). $C_{12}H_{24}Cl_3LiMoO_7$ (489.6): calcd. C 29.44, H 4.94; found C 29.54, H 4.97. IR (KBr): $\tilde{\nu}$ = 2935 (m), 2877 (w), 1705 (m), 1452 (m), 1362 (m), 1286 (m), 1243 (m), 1136 (m), 1086 (s), 1021 (m), 985 (s), 927 (s), 860 (s), 741 (s), 529 (w), 423 (w) cm^{-1}. ^{1}H NMR ([D$_8$]THF): δ = 3.84 (s, 16 H, 12-crown-4), 3.63 (m, THF), 2.10 (s, acetone), 1.78 (m, THF) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 68.93 (s, 16 C, 12-crown-4), 68.49 (s, 2 C, THF). Crystals of **2′** could be obtained by extraction of the residue mentioned above with THF rather than acetone and cooling the resultant solution for several weeks to −28 °C.

[Li(12-crown-4)$_2$][MoO$_2${OC$_6$H$_4$(CH=CHCH$_3$)-2}$_3$] (3): A solution of 2-propenylphenol (1.04 g, 7.45 mmol) and 12-crown-4 (1.33 g, 7.56 mmol) in THF (10 mL) was cooled to −20 °C and BuLi was slowly added (3.1 mL 2.5 M solution in toluene). After stirring for 5 min, the resultant mixture was added slowly to $MoO_2(OtBu)_2$ (0.70 g, 2.57 mmol), dissolved in THF (10 mL) held at −20 °C. After stirring for 2 h, the resultant yellow-brown solution was reduced to a volume of 5 mL. After 24 h at −28 °C, microcrystalline **3** had precipitated and, due to the high sensitivity of **3** in the solid state (almost any manipulation caused the formation of a white solid at the surface) and the varying amounts of crown ether complexed to the lithium cations (NMR spectroscopy shows that the Li/crown ether ratios varies between 1:1 and 1:2), we failed to obtain a correct elemental analysis. Yield 0.993 g, 1.120 mmol, 43.6%. IR (KBr): $\tilde{\nu}$ = 2974 (w), 2913 (w), 2879 (w), 1590 (s), 1555 (w), 1477 (s), 1447 (s), 1371 (w), 1304 (m), 1246 (w), 1184 (w), 1146 (w), 1090 (m), 1045 (s), 980 (s), 926 (w), 856 (s), 799 (m), 755 (s), 727 (m), 579 (m), 418 (m) cm^{-1}. ^{1}H NMR ([D$_8$]THF, *T* = 30 °C): δ = 7.33 (br, 3 H, H$_{Ar}$), 7.03 (d, $^3J_{H,H}$ = 16.04 Hz, 3 H, CH$_3$CH=C*H*C$_6$H$_4$), 6.9−6.7 (br, 6 H, H$_{Ar}$), 6.42 (br, 3 H, H$_{Ar}$), 6.00 (m, 3 H, CH$_3$C*H*=CHC$_6$H$_4$), 3.65 (s, 12-crown-4), 1.67 (br, 9 H, C*H*$_3$CH=CHC$_6$H$_4$). ^{1}H NMR ([D$_8$]THF, *T* = −30 °C): δ = 7.33 (d, $^3J_{H,H}$ = 7.51 Hz, 3 H, H$_{Ar}$), 7.03 (d, $^3J_{H,H}$ = 16.04 Hz, 3 H, CH$_3$CH=C*H*C$_6$H$_4$), 6.9−6.7 (m, 6 H, H$_{Ar}$), 6.42 (t, 3 H, H$_{Ar}$), 6.00 (m, 3 H, CH$_3$C*H*=CHC$_6$H$_4$), 3.65 (s, 12-crown-4), 1.67 (d, $^3J_{H,H}$ = 6.49 Hz,

Table 5. Crystallographic data

	1	2′	3
Empirical formula	$C_{52}H_{68}Li_4O_8$	$C_4H_8Cl_3MoO_3$, $C_{16}H_{32}ClLi_2O_8$	$C_{27}H_{27}MoO_5$, $C_{16}H_{32}LiO_8$
Formula mass	848.82	708.14	886.78
Crystal size [mm]	0.38 × 0.30 × 0.23	0.20 × 0.16 × 0.10	0.25 × 0.25 × 0.20
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/m$	$P2_1/c$
Z	4	2	4
a [Å]	13.8574(10)	7.3426(12)	15.9953(9)
b [Å]	18.6508(13)	11.878(4)	12.0367(7)
c [Å]	19.2746(14)	17.197(5)	23.3104(13)
α [°]	86.674(2)	90	90
β [°]	87.4470(10)	94.813(14)	106.5460(10)
γ [°]	79.6330(10)	90	90
V [Å^3]	4889.0(6)	1494.5(7)	4302.1(4)
d(calcd.) [g cm^{-3}]	1.153	1.574	1.369
T [K]	103(2)	293(2)	103(2)
Max./min. Transmission	1.0000 and 0.9723	1.0000 and 0.7061	1.0000 and 0.9137
Diffractometer	Nonius Kappa CCD		
Radiation	Mo-$K_{a,}$ graphite-monochromated (λ = 0.71073 Å)		
Corrections	Lorentz polarisation factor		
Refinement	Full-matrix least-squares on F^2		
Absorption correction	Semi-empirical from equivalents		
Absorption coefficient [mm^{-1}]	0.074	0.847	0.368
F(000)	1824	728	1864
hkl range	h: −16 to 16	h: −10 to 9	h: −19 to 18
	k: −22 to 22	k: −17 to 17	k: 0 to 14
	l: 0 to 22	l: −25 to 25	l: 0 to 27
Θ range [°]	1.50 to 25.03	2.09 to 32.02	1.82 to 25.00
Measured reflections	53344	18492	25221
Independent reflections	17260	5346	7569
Observed reflections [$I > 2\sigma(I)$]	11563	4068	5591
Parameters	1506	270	531
R_1	0.0585	0.0662	0.0711
wR_2	0.1461	0.1304	0.1666
R (all)	0.0963	0.0919	0.0992
Residual electron density [eÅ^{-3}]	+0.942/−1.037	+2.932−2.868	+2.463−1.776

9 H, $CH_3CH{=}CHC_6H_4$) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]THF, T = 30 °C): δ = 164.77 (s, 3 C, C_{Ar}−O), 130−114 (m, 15 C, C_{Ar}), 128.77 (s, 3 C, $CH_3CH{=}CHC_6H_4$), 120.40 (s, 3 C, $CH_3CH{=}CHC_6H_4$), 71.25 (s, 12-crown-4), 18.23 (s, $CH_3CH{=}CHC_6H_4$) ppm. Recrystallisation of microcrystalline **3** from 1,4-dioxane/hexane at room temperature yielded crystals suitable for a single-crystal X-ray diffraction study.

X-ray Crystallographic Studies:[19] Crystals were obtained as described above. Diffraction data were recorded with a Bruker AXS Smart CCD diffractometer. Empirical absorption corrections were applied. The structures were solved using direct methods and refined anisotropically with the SHELXL-97[20] and SHELXS-97[21] programs. Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5 times those of the atoms to which they are attached. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma|F_o| - |F_o|/\Sigma|F_o|$, $R_w = [\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o)^2]^{0.5}$. Table 5 lists the crystallographic data.

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