Dynamic Behaviour, Solution and Crystal Structure of an Allylmolybdenum/Oxo/Hydroxo Heterocubane

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Dedicated to Prof. Dr. Günter Helmchen on the occasion of his 60th birthday

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The synthesis of a highly unsymmetrical, chiral oxometallocubane anion $[\{(\pi\text{-}C_3H_5)Mo(CO)_2\}_4(\mu_3\text{-}OH)_3(\mu_3\text{-}O)]^-$ built up from organometallic moieties and oxo ligands is described. Its structure was investigated not only in the solid state (X-ray diffraction analysis) but also in solution applying modern sophisticated NMR techniques. It was thereby possible to identify a trigonal twist rearrangement as the process responsible for the fluxional behaviour of this compound in solution: the (π-allyl)Mo moieties are highly mobile, rotating on the "oxo surface" even at –65 °C. This complex can be regarded as a suitable model for (π-allyl)Mo units incorporated into molybdenum oxide surfaces.

Introduction

Organotransition metal oxide complexes are noteworthy in representing a link between solid, more or less ionic metal oxides and low-valent molecular organometallic systems. Despite their potential model character with respect to oxidation intermediates[1,2] — for instance in processes where organic substrates are converted catalytically on metal oxide surfaces — there are as yet surprisingly few known representatives with organic ligands other than Cp.[1−4] One example of heterogeneous catalysis, where organometallic oxo moieties might play a significant role, entails the oxidation of propene at bismuthmolybdates by O_2 to yield acrolein:[5,6] the rate determining step is proposed to lead to surface intermediates with π-allyl Mo units embedded in an oxidic environment, and this stimulates research with the aim of preparing molecular complexes being modelled on this situation.

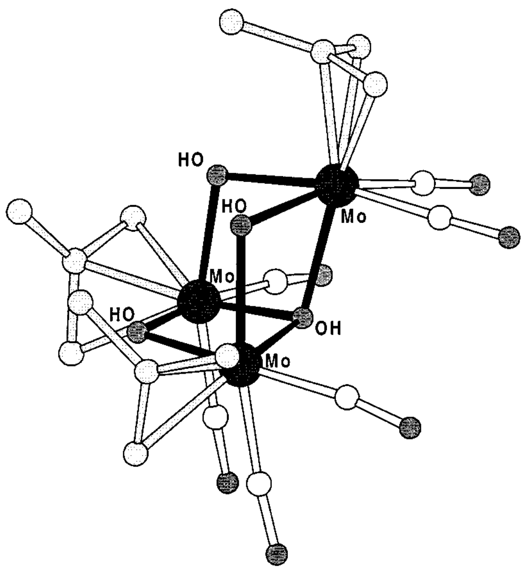
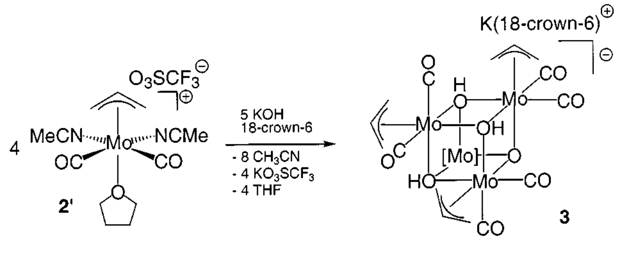


Figure 1. Molecular structure of **1**;[7] hydrogen atoms are omitted for clarity



Scheme 1

$[Mo] = (\pi\text{-}C_3H_5)(CO)_2Mo$

Results and Discussion

In a recent study[7] we were able to prepare a complex anion $[\{(C_4H_7)Mo(CO)_2\}_3(\mu\text{-}OH)_3(\mu_3\text{-}OH)]^-$ **(1)** with (π-methallyl)Mo units in a *hydroxide* ligand sphere by treatment of $[Mo(\pi\text{-methallyl})(CO)_2(NCCH_3)_2(THF)]O_3SCF_3$ **(2)** with KOH/18-crown-6. Methallyl ligands were chosen instead of allyl ligands as they often facilitate the interpretation of NMR spectra and, additionally, provide a kinetic stabilisation for labile compounds. However, looking at the crystal structure of **1** (Figure 1), it occurred to us that the methyl substituents at the allyl groups also have an influence on the product formation: the structure can be considered as being derived from a neutral cubane-like arrangement, where one corner, a $[(\pi\text{-}C_4H_7)Mo(CO)_2]^+$ unit, is missing because the methyl groups occupy the corresponding space. This suggested analogous experiments with the allyl-derivative of **2**, **2′**.[7] Reacting this compound with KOH/18-crown-6 (Scheme 1) provided, after appropriate

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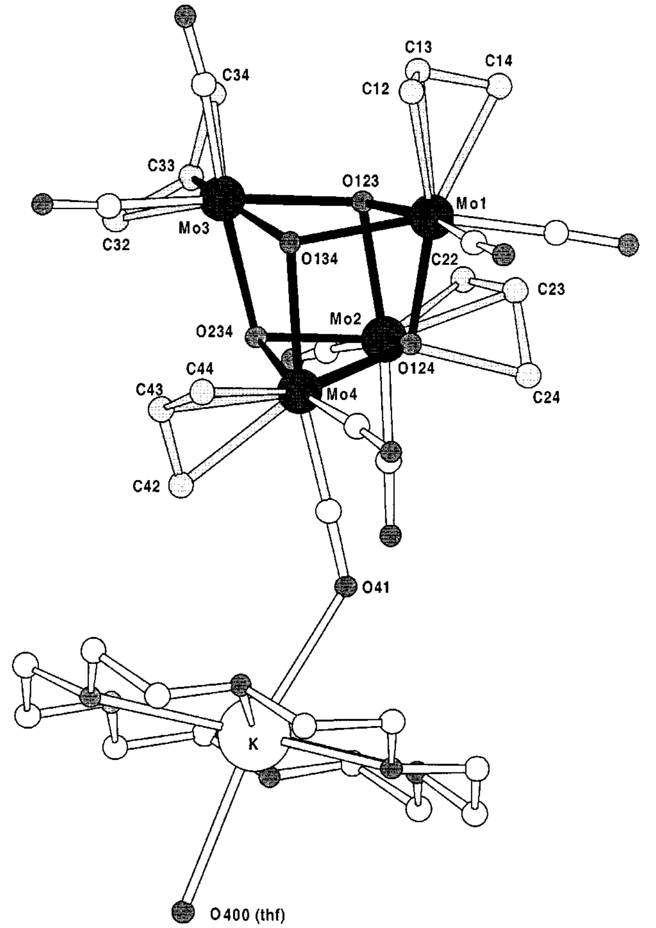


Figure 2. Molecular structure of one of the two independent, enantiomeric molecules of **3** found in the unit cell; all hydrogen atoms (and the additional 7.5 THF molecules within the cell) are omitted for clarity; selected bond lengths and angles (in Å and °): Mo(3)−O(234/123) 2.237(7)/2.261(7), Mo(1)−O(123/134) 2.327(6)/2.253(7), Mo(2)−O(123) 2.261(7), Mo(4)−O(134/234) 2.306(8)/2.259(7), Mo(3)−O(134) 2.143(8), Mo(2)−O(234) 2.195(7), Mo(2)−O(124) 2.118(7), Mo(1/4)−O(124) 2.050(7)/2.093(7), Mo(1)−C(12/13/14) 2.389(10)/2.237(11)/2.314(11), K(1)−O(41) 2.738(9), K(1)−O(400) 2.954(13); Mo(4)−O(124)−Mo(1) 108.9(3), Mo(4)−O(124)−Mo(2) 105.0(3), Mo(1)−O(124)−Mo(2) 108.8(3), Mo(3)−O(134)−Mo(4) 106.6(3), Mo(3)−O(134)−Mo(1) 106.9(3), Mo(1)−O(134)−Mo(4) 95.3(3)

work up, compound **3** as red crystals, one of which was analysed by X-ray diffraction (Figure 2).

The Solid-State Structure of 3

Indeed, the sterically less demanding allyl ligands allow a fourth $[(\pi\text{-}C_3H_5)Mo(CO)_2]^+$ unit to complete the cubane-like geometry. This, however, further polarises the OH ligands thereby enhancing their acidity. Accordingly, after the formation of the neutral product $[\{(\pi\text{-}C_3H_5)Mo(CO)_2\}_4(\mu_3\text{-}OH)_4]$ one proton is abstracted by excess [(18-crown-6)K]OH leading to **3** which possesses a highly unsymmetrical (chiral) anion $[\{(\pi\text{-}C_3H_5)Mo(CO)_2\}_4(\mu_3\text{-}OH)_3(\mu_3\text{-}O)]^-$. Two of these anions can be found within the unit cell, each of them being connected through a carbonyl oxygen atom [(O(41) in Figure 2] to a K^+ cation coordinated by a crown ether and a THF molecule [O(400)]. The two resulting ion pairs **3** in the cell are enantiomers. None of the hydroxylic protons could be located in the structure analysis, so it is not immediately obvious which of the O atoms corresponds to the oxo ligand. However, this can be inferred from a comparison of the Mo−O bond lengths within **3**. Most of them can be assigned to one of two relatively narrow distance ranges i.e. **I:** Mo(3)−O(234/123) 2.237(7)/2.261(7), Mo(1)−O(123/134) 2.327(6)/2.253(7), Mo(2)−O(123) 2.261(7), Mo(4)−O(134/234) 2.306(8)/2.259(7) Å; **II:** Mo(3)−O(134) 2.143(8), Mo(2)−O(234) 2.195(7) Å. The group **I** bonds all have CO ligands bound *trans* to them, while group **II** bonds are located *trans* to allyl ligands and are somewhat shorter as the *trans* influence of the allyl group is weaker than that of CO. Only the bonds of O(124) do not fit into these groups: Mo(2)−O(124) [2.118(7) Å] with a CO ligand in the *trans* position clearly lies out of the region defined by the group **I** bonds, which are considerably longer. Furthermore, Mo(4)−O(124) and Mo(1)−O(124) (*trans* to allyl) are, at 2.050(7) and 2.093(7) Å, significantly shorter than the group **II** bonds. It is therefore reasonable to assign O(124) to the O^{2-} ligand within the complex.[8]

Compound **3** can thus be considered as a suitable, *soluble* model for (π-allyl)Mo units incorporated in molybdenum oxide surfaces, and a detailed NMR spectroscopic analysis of its dynamics promised to provide valuable information. The determination of the solution structure of **3** formed the basis for such an investigation.

The Solution Structure of 3

When dissolved in $[D_8]$THF, compound **3** shows, at room temp. (apart from the signals due to the crown ether), only three broad signals corresponding to averaged resonances of all H_{syn}, H_{anti}, and H_{meso} protons, i.e. **3** is highly fluxional in solution. No OH signals can be seen. On cooling of the sample, the spectrum dramatically changes in a continuous fashion until a stationary situation is reached at −65 °C. At this point a geometry of the anionic framework corresponding to the one in the crystal structure is frozen out on the ^{1}H NMR time scale, as shown by HSQC, HMBC,

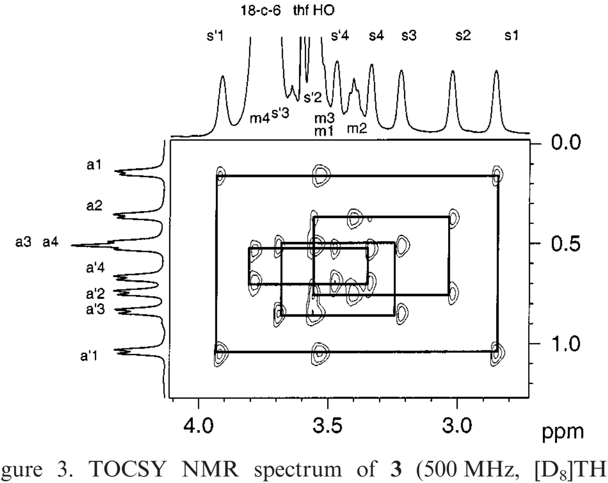
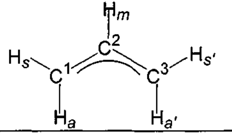


Figure 3. TOCSY NMR spectrum of **3** (500 MHz, $[D_8]$THF, −65 °C)

Table 1. ^1H and ^{13}C NMR shifts of the nuclei belonging to the four different allyl groups in **3** (500 MHz, [D_8]THF, −65 °C)



	^{13}C			^1H				
Allyl group	C^1	C^2	C^3	H_a	$H_{a'}$	H_m	H_s	$H_{s'}$
1	49.8	64.7	77.7	0.14	1.04	3.54	2.85	3.91
2	53.3	60.5	81.0	0.36	0.74	3.39	3.02	3.55
3	55.0	59.3	79.1	0.50	0.84	3.55	3.22	3.64
4	53.5	58.3	79.4	0.52	0.67	3.78	3.34	3.47

TOCSY and NOESY NMR experiments: Each proton belonging to the anion of **3** now shows an individual signal (see Figure 3, where the absorptions of all the allylic protons and their correlations in the TOCSY spectrum are shown), and applying the above-mentioned methods it was possible to assign[9] all of them to a certain position in one of four allyl groups, as indicated in Table 1. The structure frozen out at that temperature thus has to belong to the C_1 point group. Furthermore, the signals of the OH protons can now be observed: A resonance at $\delta = -1.1$ with an integral of one proton should be assigned[10] to the HO(123) ligand, and a second one appearing at $\delta = 4.4$ must belong to HO(134).[12] Moreover, the NOESY spectrum reveals that the signal of HO(234) is hidden by the overlapping resonances of $H_{s'}$ belonging to allyl group 2, H_m of allyl group 3 and H_m of allyl group 1. All other features can also be interpreted in terms of the structure shown in Figure 2, but assignments other than the ones mentioned would be less unambiguous.

Dynamics of 3

Considering **3** as a model, and having identified the solution structure of its anion as being equivalent to the one in the solid state structure, the most important remaining question concerns the type of dynamic process responsible for the changes of the spectrum observed on annealing of the sample. Recently, we have been able to show[13] that in [(π-allyl)$(CO)_2Mo(OR)_3$] complex metal fragments the allyl ligands themselves are comparatively rigid (i.e. they are not involved in π-σ-π rearrangements or other processes involving Mo−C bond breaking), but that the (allyl)$Mo(CO)_2$ moiety is capable of "rotating" on the trigonal sphere formed by the three alkoxide ligands by a trigonal twist rearrangement[14−16] (see Figure 4). This process, which has been proved only for a few examples in the literature,[13−17] is also important in the case of **3**: in the NOESY spectrum, where the time scale is different from that of a "normal" ^1H NMR spectrum due to the long mixing times, exchange cross peaks with characteristic phases can be found between the signals within each of the proton groups (*syn*, *anti*, *meso*, OH), indicating that even at −65 °C there is a motion by which, for instance, not only the *anti* protons belonging to *one* allyl group but also those belonging to *different* allyl ligands become equivalent. This finding can only be understood if trigonal twist arrangements are operative. If, for instance, the (allyl)Mo(2)$(CO)_2$ unit of **3** as shown in Figure 2 is rotated (viewing this unit as shown in Figure 4) anticlockwise by 120° on the O(123/124/234) surface, the enantiomer of the structure shown in Figure 2 is obtained, which of course has identical NMR properties, but the ligands on Mo(4) now correspond to those of Mo(1) (and vice versa), while $H_2C(22)$ has turned into $H_2C(24)$. This causes typical exchange peaks in the NOESY spectrum, for instance, between the two H_a signals, the two H_s signals, the two $H_{a'}$ signals etc. belonging to C(22) and C(24). On further annealing this process becomes faster until the protons of the allyl groups on Mo(4) and Mo(1) [as well as those of C(22) and C(24)] become indistinguishable also on the time scale of the ^1H NMR spectrum showing coalescence. Similar effects occur when two or even three (allyl)Mo units rotate simultaneously, so that the dramatic changes of the spectra with temperature are understandable (the case becomes even more complicated if allowance for shifts of the hydroxylic protons is made at higher temperatures, which is not unreasonable).

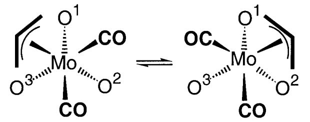


Figure 4. Trigonal twist rearrangement of a (π-allyl)Mo moiety on an oxo surface

In conclusion a novel organometallic oxomolydocubane **3** has been synthesised in a controlled fashion and analysed structurally. There is only one other compound known with a soft π-allyl and a hard oxo ligand being connected to one and the same Mo centre: [{$(C_4H_7)Mo(CO)_2$(bipy)}$_2$(μ-MoO_4-κ*O*,κ*O′*)], which is insoluble in all common solvents.[18] For **3**, however, it could be unequivocally proved that on dissolution not only does its constitution remain intact but the chiral structure it adopts in the crystal is thermodynamically favoured also in solution. Even at −65 °C the (π-allyl)Mo moieties are mobile, rotating an the "oxo surface". From the latter finding, conclusions can also be drawn concerning the dynamics of molybdenum oxide-supported (π-allyl)Mo fragments, as, for instance, those potentially formed as intermediates during the oxidation of propene with bismuthmolybdates.

Experimental Section

Synthesis of 3: A solution of AgO$_3$SCF$_3$ (0.51 g, 2.0 mmol) in 8 mL THF was added to a solution of **2′**[7] (0.62 g, 2.0 mmol) with a cannula. Immediately, AgCl precipitated as a greyish solid. The filtrate was added to a suspension of KOH (0.18 g, 3.0 mmol) and 18-crown-6 (0.79 g. 3.0 mmol) in 10 mL THF. After stirring for 3 h the precipitated white K(18-crown-6)O$_3$SCF$_3$ was filtered off from the red-orange solution, which was subsequently layered with 100 mL of light petroleum. Storing at −20 °C for 6 days yielded 0.41 g (0.3 mmol) of analytically pure, crystalline **3·3.75THF** corresponding to a yield of 55%. ^{1}H and ^{13}C NMR (500 MHz, [D$_8$]THF): see Table 1. − IR (KBr): $\tilde{\nu}$ = 1915 (br, s)/1821 (br, s) [ν(CO)], 3606 (m)/3563 (m) [ν(OH)] cm^{-1}. − C$_{39}$H$_{61}$KMo$_4$O$_{19.75}$ (1267.78) [**3·1.75 THF**; 2 molecules of THF per molecule of **3** are lost on drying]: calcd. C 36.95, H 4.85; found C 36.59, H 5.11.

X-ray Crystallography

3·3.75THF: C$_{32}$H$_{47}$KMo$_4$O$_{18}$·C$_{15}$H$_{30}$O$_{3.75}$, M_r = 14.12, monoclinic, space group *Cc*, Z = 4, a = 13.756(3), b = 28.077(6), c = 33.650(7) Å, β = 101.72(3), V = 12725.00 Å^3, 3.4 < 2θ < 52.0°, ω-scan, T = 200 K, δ_{cald} = 1.547 g cm^{-3}, measured 31925, independent 24490, and observed reflections 20526 with $I > 2\sigma(I)$, Lp correction, 1472 refined parameters with R = 0.070, residual electron density (max./min.): 1.244/−0.911 eÅ^{-3}; Mo-K_α radiation, λ = 0.71073 Å, was used and the structures were solved by direct methods (program: SHELXS-97) and refined versus F^2 (program: SHELXL-97) with anisotropic temperature factors for all non-hydrogen atoms, apart from C(22) and some of the atoms belonging to the THF molecules, which could only be refined isotropically.
Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146570. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[8] Repeated crystallisations of **3** applying various techniques and solvent mixtures yielded crystals differing in their space groups and the numbers of THF molecules within the unit cells; the structure of the anion, however, always remained identical to the one depicted in Figure 2 (within the frames given by the errors). In one case the protons at the O(134) and O(234) atoms could even be located.

[9] The signals of the *syn* and *anti* protons connected to a certain terminal C atom were identified by means of HSQC and HMBC NMR spectra, while the two terminal CH$_2$ groups belonging to one and the same allyl group (i.e. C^{1}H$_a$H$_s$ and C^{3}H$_{a'}$H$_{s'}$ connected through C^{2}H$_m$, compare the designations in Table 1) were correlated by TOCSY NMR spectra (Figure 3).

[10] NMR studies concerning the anion **1**[7] and other carbonyl(hydroxo)molybdenum complexes[11] showed that μ$_x$-OH resonances are increasingly shifted to higher field, the more CO ligands can be found *trans* to the *x* Mo−OH bonds, and HO(123) bears the maximum of three CO ligands in *trans* position to it.

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[12] In a NOESY NMR spectrum this signal shows intense cross peaks to only two of the eight *anti* protons (H$_{a'}$ of the allyl groups designated as 2 and 4 in Table 1), and it is therefore reasonable to assign it to HO(134) as, unlike HO(234), it is exactly in such a situation where it is close only to the *anti* protons at C(44) and C(12).

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