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A $(H_2O)_4$/crown ether network spanned between organometallic complex metal fragments†

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$[Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy^*)Cl]$ undergoes trigonal twist rearrangements in solution, so that three isomers are coexisting. It was used as a starting material leading to a dinuclear complex containing a hydrogen-bonded network of H_2O and crown-ether molecules between two $Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy^*)$ moieties.

Organometal oxo moieties are sometimes suggested as intermediates in heterogeneously catalysed oxidations and one example entails the O_2-oxidation of propene by bismuth molybdates yielding acrolein.[1] 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 modelled on this situation. Correspondingly, we have a long-standing interest in the synthesis of molybdenum compounds containing at the same time "soft" π-allyl ligands and "hard" alkoxo, hydroxo and ultimately oxo ligands.[2] Recently, the first crystal structure of a complex was published by Pérez *et al.*, where a π-allyl Mo unit meets an aqua ligand,[3] and here we report the serendipitous finding of an H-bonded network of water/crown ether molecules being clamped between two π-allyl $Mo(CO)_2$ complex metal fragments.

We had experienced previously that the organometallic framework in $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy)(O{=}CMe_2)]^+$ cations (bipy = 2,2′-bipyridine) survives an aqueous environment, so that an acetone solution of such cations could be reacted with sodium molybdate dissolved in water, thus yielding the first known π-allyl molybdenum oxo compound.[2f] As the latter was insoluble in all common solvents, we considered 2,2′-bipyridine being substituted by *t*Bu residues in the 4/4′ positions (bipy*)[4] as a potential ligand in such investigations, since it was anticipated to promote solubility. Hence, the corresponding chloride complex $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy^*)Cl]$, **1**, (Scheme 1) was prepared‡ *via* reaction of $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2Cl]$[5] with bipy*, and Fig. 1 shows the result of an X-ray crystal structure analysis, which, however, can merely serve as a proof of configuration: all crystallisation attempts yielded only crystals of low quality that did not allow a sufficiently accurate analysis. Bond lengths and angles can thus not be discussed but the molecular structure and configuration as shown in Fig. 1 is beyond doubt. The molecules of **1** show a non-crystallographic plane of symmetry, and the conformation of the allyl ligand with respect to a plane through the two carbonyl C atoms and the terminal C atoms of the allyl ligand is *exo*—an arrangement that has been found in all structurally characterised $Mo(\eta^3\text{-}C_3H_5)(CO)_2$ compounds so far.[6a] While neutral representatives (for instance $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy)Cl]$)[5,6b,6c] are often poorly soluble in common organic solvents the *t*Bu substituted derivative **1** is easily dissolved so that it could be subjected to solution studies. Considering the symmetry of **1** in the crystalline state (Fig. 1) a singlet and two doublets were expected in the low field region of the ^1H NMR spectrum for the bipy* ligand. However, two sets of signals for both the bipy* and the allyl ligands are observed for **1** dissolved in CD_2Cl_2 in a ratio of *ca.* 1 : 2, which start coalescence at around 55 °C. In $CDCl_3$ solution‡ a 1 : 1 ratio is observed, showing that the solvent influences the position of the equilibrium—probably through its polarity.[2c] A second, faster dynamic process can be slowed down on the NMR timescale by lowering the temperature. The process involves only one of the two sets of signals, which on cooling continuously broadens and partly vanishes at −30 °C (coalescence) to finally split into two new sets of signals in a 1 : 1 ratio at −65 °C: the spectrum of an asymmetric complex. The most likely interpretation for these findings is the following: the asymmetric signal pattern corresponds to the enantiomeric structures **B** and **C**, respectively, formed from the more stable starting geometry **A** (which is found in the crystalline material) through a trigonal twist rearrangement (ttr),[7,2b,2e] which is slow enough in the entire temperature range investigated to allow the independent observation of both types of isomers, **A** and **B**/**C**.[8] On the other hand **B** is converted through a faster ttr into its enantiomer **C** (and *vice versa*), which naturally shows the same NMR spectrum, and on warming to temperatures above −30 °C the conversion between **B** and **C** reaches a rate that leads to an averaging of the corresponding signal sets, pretending a second symmetric structure at rt.

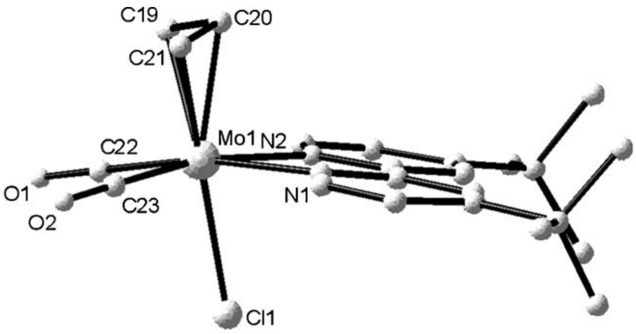
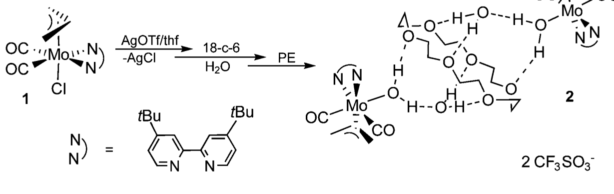


Fig. 1 The molecular structure of **1**.



Scheme 1

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† Electronic supplementary information (ESI) available: spectroscopic/analytical details concerning **1** and **2**, temperature dependent NMR spectra. See http://www.rsc.org/suppdata/cc/b4/b407475k/

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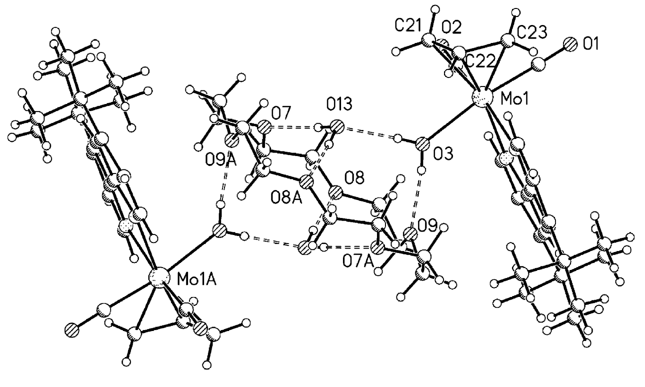
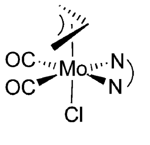
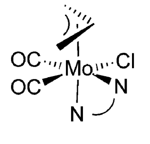


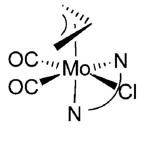
Fig. 2 The molecular structure of the dication $[\{Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy^*)H_2O\}_2\{(H_2O)_2/18\text{-crown-}6\}]^{2+}$ in **2**. Selected bond lengths [Å] and angles [°]: Mo1–O3 2.2196(13), Mo1–C21 2.3275(19), Mo1–C22 2.1900(19), Mo1–C23 2.3028(19), Mo1–CO(1) 1.9571(19), Mo1–CO(2) 1.971(2), O3–O13 2.612(17), O3–O9 2.704(16), O13–O7 2.852(17), O13–O8A 2.843(17), CO1–Mo1–CO2 79.92(9), C22–Mo1–O3 88.11(7).



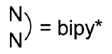
A



B



C



In order to make a coordination site accessible for molybdate anions, **1** was then treated in thf solution with AgO_3SCF_3. The potentially[2d] resulting $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy^*)(thf)]SO_3CF_3$ was reacted *in situ* at rt with a mixture of thf, K_2MoO_4 (1 eq.) and 18-crown-6 (1 eq.) to which, for solubility reasons, water was added subsequently. Overlaying with light petrol led to good yields of a red crystalline compound that was identified as $[\{Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy^*)H_2O\}_2\{(H_2O)_2/18\text{-crown-}6\}][CF_3SO_3]_2$, **2**, crystallising together with an additional 18-crown-6 molecule; the crystal structure§ of the dication in **2** is displayed in Fig. 2.

Obviously, the thf ligands of the starting material were replaced not by molybdate units (K_2MoO_4 can thus be omitted in the system) but by water molecules (Scheme 1) so that $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy^*)(H_2O)]^+$ cations result, whose bond lengths and angles compare well to those found in other $Mo(\eta^3\text{-}C_3H_5)(CO)_2$(bipy) complexes.[6] Two such cations arrange themselves within the crystal pairwise in a centrosymmetric fashion, which provides the aqua ligands with the possibility to form two hydrogen bridges each—one to a second water molecule (*d*(O3–O13) = 2.612(17) Å) and one to the O atom of a crown ether molecule (*d*(O3–O9) = 2.704(16) Å) being "clamped" between the two cations. The second water molecule in turn undergoes two further hydrogen bonds to oxygen atoms of the crown ether molecule (*d*(O13–O7) = 2.852(17) Å, *d*(O13–O8A) = 2.843(17) Å), so that in fact all crown ether oxygen atoms are involved in hydrogen bridges—three coming from each side (cationic units). Hence, **2** exhibits several combinations of features, that are often considered as contradictive: (i) organometallic moieties and H_2O molecules, (ii) soft organic ligands beside hard oxo containing ligands at a molybdenum centre,[2,3] and (iii) a protic, polar clustering of molecules spanned by two lipophilic complex metal fragments. Hence, under certain conditions an interesting structural chemistry rather than decomposition may well be discovered on deliberate addition of water also to other organometallic reactions. This will become the subject of a more detailed study in the future.

Notes and references

‡ Spectroscopic data: **1**: δ_H ($CDCl_3$, rt): 9.00 (d, $^3J_{H\text{-}H}$ = 5.40 Hz, 2H, **B/C** $H^{6,6'}$), 8.78 (d, $^3J_{H\text{-}H}$ = 5.80 Hz, 2H, **A** $H^{6,6'}$), 8.07 (s, 2H, **B/C** $H^{3,3'}$), 8.02 (s, 2H, **A** $H^{3,3'}$), 7.59 (d, $^3J_{H\text{-}H}$ = 5.00 Hz, 2H, **B/C** $H^{5,5'}$), 7.47 (d, $^3J_{H\text{-}H}$ = 5.00 Hz, 2H, **A** $H^{5,5'}$), 3.83 (m, 1H, **B/C** H_m), 3.65 (d, $^3J_{H\text{-}H}$ = 6.49 Hz, 2H, **B/C** H_s), 3.03 (br, 3H, **A** H_m and **A** H_s), 1.46 (s, 18H, **B/C** $H_{t\text{-}Bu}$), 1.44 (s, 18H, **A** $H_{t\text{-}Bu}$); **2**: δ_H ($CDCl_3$, rt): 9.07 (d, $^3J_{H\text{-}H}$ = 5.12 Hz, 4H, $H^{6,6'}$), 8.05 (s, 4H, $H^{3,3'}$), 7.65 (d, $^3J_{H\text{-}H}$ = 5.12 Hz, 2H, $H^{5,5'}$), 4.04 (m, 2H, H_m), 3.69 (br, 52H, H_s + 18-crown-6), 1.57 (d, $^3J_{H\text{-}H}$ = 7.85 Hz, 4H, H_a), 1.46 (s, 36H, $H_{t\text{-}Bu}$); δ_C ($CDCl_3$, rt): 225.97 (s, 4C, *C*O), 164.79 (s, 4C, $C^{2,2'}$), 154.14 (s, 4C, $C^{4,4'}$), 152.16 (s, 4C, $C^{6,6'}$), 124.30 (s, 4C, $C^{5,5'}$), 119.18 (s, 4C, $C^{3,3'}$), 73.89 (s, 2C, C_m), 71.02 (s, 24C, 18-crown-6), 61.00 (s, 4C, C_t), 36.00 (s, 4C, $C_{iso\text{-}Bu}$), 30.71 (s, 12C, C_{Me})

§ Crystal data for **2** (18-c-6): $C_{72}H_{114}F_6Mo_2N_4O_{26}S_2$, M = 1821.69, triclinic, a = 10.3645(5), b = 13.1170(6), c = 17.6983(9) Å, ÿÿ̃ÿα = 104.817(1), β ÿ= 100.720(1), γ = 106.751(1)°, U = 2137.93(18) $Å^3$, T = 103(2) K, space group $P\bar{1}$ (no. 2), Z = 2, D_c = 1.415 g cm^3, μ(Mo-Kα) = 0.430 mm^{-1}, 47879 reflections measured, 14659 unique (R_{int} = 0.0298) which were used in all calculations. The final $wR(F^2)$ was 0.1018 (all data). CCDC 239590. See http://www.rsc.org/suppdata/cc/b4/b407475k/ for crystallographic data in .cif or other electronic format

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8 We cannot judge on the basis of the data obtained whether the ttr that **A** undergoes in solution, and which certainly leads to the second species with an asymmetric structure, is additionally accompanied by rotation of the allyl ligand. However, since no such processes have been observed for analogous compounds with bidentate phosphorus donor ligands[7a,b] (neutral bipy and phen complexes are often not soluble enough to be investigated in detail),[5,6] we consider it as unlikely. Allyl rotation has been discussed as the origin of a second set of signals at rt for cationic $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(bipy)L]^+$ species.[9,6a] However, our observations on gradual lowering of the temperature are not consistent with such a process without an additional ttr.

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