ELSEVIER

Journal of Organometallic Chemistry 580 (1999) 214–224

Journal of Organo metallic Chemistry

Syntheses and X-ray structures of complexes with (η^3-allyl)Mo-units in oxygen-rich coordination spheres

Cornelia Borgmann, Christian Limberg *, Elisabeth Kaifer, Hans Pritzkow, László Zsolnai

Institut für Anorganische Chemie der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received 16 October 1998

Abstract

The reaction of $Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl$ with $AgBF_4$ in THF yields the cationic complex $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2(THF)]^+[BF_4]^-$, **1**, whose X-ray structure has been determined. Oxo nucleophiles are capable of replacing the weakly bound THF molecule in **1** and under simultaneous loss of CH_3CN the resulting complexes aggregate to oligonuclear compounds. Accordingly, the reactions with NaOMe and KOH yield $[Na(THF)_4]^+[(\eta^3\text{-}C_3H_4(CH_3))(CO)_2Mo(\mu\text{-}OCH_3)_3Mo(CO)_2(\eta^3\text{-}C_3H_4(CH_3))]^-$, **2** and $[K(18\text{-crown-}6)]^+[[Mo(\eta^3\text{-}C_3H_4(CH_3))(CO)_2]_3(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)]^-$, **3**, which were characterized by means of single crystal X-ray diffraction. Due to fluoride abstraction from BF_4^- the reaction of **1** with KOH also yields fluorinated derivatives of **3** but incorporation of fluorine in **3** can be avoided if AgO_3SCF_3 rather than $AgBF_4$ is used to generate the cation of **1**. For purposes of comparison the dinuclear complex $[K(18\text{-crown-}6)]^+[[Mo(\eta^3\text{-}C_3H_4(CH_3))(CO)_2]_2(\mu_2\text{-}F)_3]^-$, **4**, has been prepared, too, showing fluoride bridges and K···F bonding. The chemical properties and the structures of these compounds in solution as well as their role as structural models for intermediates during molybdenum oxide catalysed propene oxidation are discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum complexes; Oxygen; Allyl

---

1. Introduction

The range of organic ligands found in organometallic oxo compounds is quite restricted, the majority being either η^5-C_5R_5 or alkyl or aryl groups having no β-hydrogen atom [1]. Organotransition–metal chalcogenide complexes of this type are noteworthy in representing a link between solid, more or less ionic, metal chalcogenides and low-valent molecular organometallic systems. Moreover, organometallic intermediates may participate in polar oxygen-transfer reactions [2] and in recent years it has been shown that the relatively nonpolar M–C bonds of oxo- and peroxometal complexes functionalized by organic groups can exist under catalytic conditions—such units are sometimes even essential to the activity and lifetime of the catalyst [3].

Despite the potential importance of organomolybdenum oxo systems containing molybdenum in the highest oxidation states +5 and +6 as catalytic intermediates in industrial processes [2], few model complexes of this sort are known as yet. One example of heterogeneous catalysis where such species might play a significant role entails the oxidation of propene to acroleine using MoO_3/Bi_2O_3 as the catalyst and this has gained considerable technical importance. Nonetheless, the reaction mechanism has remained for the most part speculative. The results of their experiments on isotopic enrichment lead Grasselli and Burrington to suggest the intermediate formation of symmetric π-allyl complexes (or the chemisorption of a delocalized allyl radicals) to Mo centers of the catalysts surface [4]. Furthermore recent investigations suggest that in heterogeneous oxidation catalyses where Mo-oxides are employed, the

---

* Corresponding author. Tel.: +49-6221-546450; fax: +49-6221-545707.

E-mail address: limberg@sun0.urz.uni-heidelberg.de (C. Limberg)

0022-328X/99/$ - see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S0022-328X(98)01149-8

oxygen atoms found in the organic oxidation products have their origin in previously *bridging* positions [5]. So far there are no compounds existent in the literature which could be regarded as functional models for the oxo molybdenum π-allyl surface intermediates under discussion and only few allyl molybdenum compounds containing ligands with oxygen donor functions of any kind have been synthesized and structurally characterized [6]. This justifies research with the aim of establishing procedures suited to give access to complexes where *hard* oxygen-containing ligands can be found adjacent to *soft* allyl ligands at molybdenum centers.

In this contribution it is shown that complexes with (η^3-allyl)Mo-units in oxygen-rich coordination spheres containing RO^- ligands can be obtained if cationic complexes with labile ligands are employed as starting materials.

2. Results and discussion

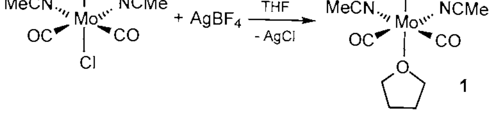
Common synthetic routes established for the preparation of organometaloxides are not suitable for the synthesis of compounds bearing the allylmolybdenum oxo fragment [7].

An alternative way to introduce an Mo–O link in organomolybdenum compounds—the substitution of leaving groups in stable organometallic compounds by oxygen containing ligands—can be equally problematic when the organic group corresponds to allyl: It is well known that various types of nucleophiles add to metal-coordinated allyl ligands [8] leading to structurally diverse η^2-olefin complexes and this fact is widely used in organic synthesis [9].

Our research focused on the introduction of RO^- ligands (R = H or organic group) into the coordination sphere of compounds bearing allyl molybdenum fragments, which are particularly stabilized by carbonyl co-ligands as in complexes with $(C_3H_5)Mo^{II}(CO)_2$ units. However, in neutral representatives of the latter the terminal carbons of the η^3-allyl moiety are very prone to attack by nucleophiles [8]. If a positive electric charge is introduced at the metal centers of such complexes, for instance by replacement of one carbonyl ligand by a nitrosyl group, the attraction of a negatively charged nucleophile by the metal center might be enhanced but the affinity of the allyl ligand towards nucleophiles is increased, too [10]. Consequently the aim was to prepare cationic allyl molybdenum complexes *possessing labile ligands* so that the metal centers can compete with the allyl group in directing the incoming nucleophile. The finding that the cations $[Mo(\eta^3\text{-}C_3H_5)bipy(CO)_2S]^+$ (where S is a solvent molecule) react with carboxylates to yield $Mo(\eta^3\text{-}C_3H_5)bipy(CO)_2(\eta^1\text{-}O_2CR)$ complexes [11] encouraged an investigation concerning the reactions of $Mo(\eta^3\text{-}C_3H_5)L_2(CO)_2Cl$ compounds with oxo nucleophiles after pretreatment with $AgBF_4$. If L_2 corresponds to bipy, of course, the introduction of only *one* oxo ligand at the Mo center is possible and for the reasons mentioned above we are interested in oxygen rich Mo coordination spheres. This lead us to choose the corresponding acetonitrile/methallyl analogue, $Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl$ [12], as the starting material, where the acetonitrile donor functions are potentially exchangeable by the free electron pairs of polyfunctional oxo ligands, too. Methallyl instead of allyl ligands were used in order to somewhat increase the steric bulk at the Mo centers and to thereby gain kinetic stability of the resulting products.

2.1. Synthesis of $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2(THF)]^+[BF_4]^-$, **1**

$Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl$ reacts in THF solution with $AgBF_4$ under formation of AgCl and an orange solution from which a yellow solid can be obtained after cooling. The formation of acetone complexes $[Mo(\eta^3\text{-}C_3H_5)bipy(CO)_2(acetone)]^+[BF_4]^-$ in the reaction of the corresponding bipy complex with $AgBF_4$ [13] suggested the yellow solid mentioned above to correspond to the cationic complex $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2(THF)]^+[BF_4]^-$, **1**, which was supported by the spectroscopic data. The overall appearance of the ^{1}H-NMR spectrum of **1** strongly depends on the solvent employed, since both the THF and the acetonitrile ligands are exchangeable. Consequently in CD_3CN the signals of one allyl species $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CD_3CN)_3(CO)_2]^+$ are observed while in d_6-acetone three sets are obtained (compare Table 1) which probably correspond to an equilibrium involving the cations: $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2(d_6\text{-acetone})]^+$, $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)(CO)_2(d_6\text{-acetone})_2]^+$, and $[Mo(\eta^3\text{-}C_3H_4(CH_3)(d_6\text{-acetone})_3(CO)_2]^+$. **1** shows a reversible oxidation wave at $E_{1/2} = 956$ mV (vs. SCE). A single-crystal diffraction analysis unequivocally proved the formation of $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2(THF)]^+[BF_4]^-$, **1**, as depicted in Eq. (1) and Fig. 1. Selected bond lengths and angles are given in Table 2.



(1)

Due to the disordering of both the THF ligand and the BF_4^- anion the molecules of **1** possess a crystallographic plane of symmetry containing C(1), C(3), Mo, and O(2). The conformation of the allyl ligand concerning a plane constructed from the two carbonyl carbons

Table 1
^{1}H-NMR data of compounds **1-5**, **3a**, **3b**, **3e**, **3f**

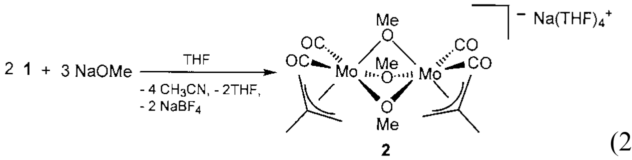
Number	Solvent	Methallyl			Other signals		
		H_{syn}	CH_3	H_{anti}			
					CD_3CN_{coord}	CH_3CN_{free}	THF_{free}
1	CD_3CN	3.42	2.23	1.40	2.37	2.01	3.68, 1.84
					CH_3CN_{coord}	CH_3CN_{free}	THF_{free}
1	d_6-acetone	3.47	2.27	1.39	2.56	2.09	3.66, 1.82
		3.46	2.23	1.39			
		3.44	2.17	1.37			
					CH_3O	$THF_{coord.}$	
2	d_8-THF	2.88 (4H)	1.99 (6H)	0.56 (4H)	5.19 (3H)	3.82	
					3.40 (6H)	1.95	
					μ_3-OH	μ_2-OH	18-crown-6
3	d_8-THF	2.50 (6H)	1.68 (9H)	0.33 (6H)	8.18 (1H)	−0.52 (3H)	3.67
3a	d_8-THF	2.79	1.73	0.62	9.53 (t, $^3J_{HF}$:4.4 Hz)	−0.52	3.67
3b		2.77	1.71	0.58	8.86 (d, $^3J_{HF}$:4.4 Hz)	0.48	
3e		2.59	1.67	0.36			
3f		2.54	1.60	0.31			
					μ_3-OH		18-crown-6
4	d_8-THF	2.87	1.78	0.48			3.69
3c		2.82	1.67	0.57	9.92(q, $^3J_{HF}$:4.4 Hz)		
							18-crown-6
5	d_8-THF	2.57 (4H)	1.89 (6H)	0.34 (4H)			3.70

and the terminal carbon atoms of the allyl ligand is *exo*—an arrangement which is often found to be more stable than the corresponding *endo* conformation [8a] and which is frequently accompanied by a decreased $M(CO)_2$ angle (< 90°), while the angle in *endo* structures is increased (> 90°) [14]. Accordingly the $Mo(CO)_2$ angle in **1** amounts to only 79.2(3)°. The cation of **1** as a whole shows a distorted octahedral geometry (under the condition that the allyl group is regarded as occupying just *one* coordination site). The Mo–O(2) distance of 2.190(5) Å lies within the range usually found for such bonds in Mo–THF complexes [15].

For subsequent reactions **1** was prepared in situ, the AgCl precipitated was filtered off the orange solution and the latter was directly employed without prior isolation of **1**.

2.2. The reaction of 1 with NaOMe

When a THF solution of **1** was reacted with two equivalents of NaOMe the solution turned bright yellow and $NaBF_4$ precipitated. Overlaying of the filtrate with light petroleum (40–60) resulted in the formation of yellow crystals in good yields which were shown to consist of $[Na(THF)_4]^+[(\eta^3\text{-}C_3H_4(CH_3))(CO)_2Mo(\mu\text{-}OCH_3)_3Mo(CO)_2(\eta^3\text{-}C_3H_4(CH_3))]^-$, **2** by means of IR and NMR spectroscopy as well as elemental analyses (Eq. (2)). Due to the strongly π-donating alkoxy ligands and the negative charge of the anion, the Mo centers are provided with sufficient electron density to enable efficient backbonding.



(2)

Therefore the carbonyl bands in the IR spectrum, which are usually located in the regions 1958–1919 and 1883–1818 cm^{-1} in $Mo(allyl)(CO)_2$ complexes [12,16], are found at 1889 and 1768 cm^{-1} for **2** and a reversible oxidation wave at 74 mV (vs. SCE) is also consistent with an enhanced electron density at the Mo centers in comparison to **1**. In addition an X-ray structure analysis was performed and the resulting structure for one anion in combination with one cation is shown in Fig. 2. Selected bond distances and angles are given in Table 3. The solid state structure of **2** consists of zigzag chains

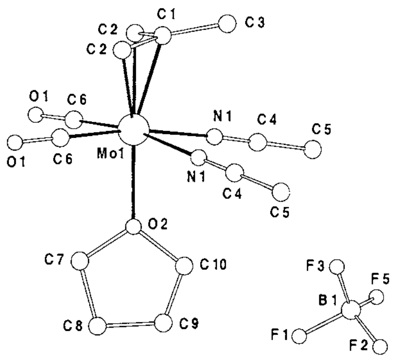


Fig. 1. Structural representation of **1**; hydrogen atoms have been omitted for clarity.

Table 2
Selected bond lengths (Å) and selected bond angles (deg) for **1**

Mo–C(1)	2.244(6)	OC–Mo–CO	79.2(3)
Mo–C(2)	2.322(5)	N–Mo–N	81.2(2)
Mo–C(6)	1.953(5)	OC–Mo–N_{trans}	170.2(2)
Mo–O(2)	2.190(5)	OC–Mo–N_{cis}	99.0(2)
Mo–N(1)	2.226(4)	O–Mo–C(1)	163.1(2)
C(6)–O(1)	1.162(6)	Mo–C–O	176.2(5)
N(1)–O(4)	1.131(6)		

with alternating cations $[Na(THF)_4]^+$ and anions $[(\eta^3\text{-}C_3H_4(CH_3))(CO)_2Mo(\mu\text{-}OCH_3)_3Mo(CO)_2(\eta^3\text{-}C_3H_4(CH_3))]^-$, each cation being linked to two anions via carbonyl oxygen atoms of the latter. Such an arrangement has already been observed in some other ionic carbonyl complexes [17]. Again, the geometry around the Mo centers is most conveniently described regarding the allyl groups as occupying just *one* coordination site. The coordination sphere is octahedral then with a facial arrangement of the methoxy ligands and this face is shared with a second identical octahedron in a way so that the complete binuclear anion apart from a C_2 axis possesses a plane of symmetry through both Mo atoms and O(5)/C(5). This is in contrast to the asymmetrical structure of the related anion $[(\eta^3\text{-}C_3H_5)(CO)_2Mo(\mu\text{-}Cl)_3Mo(CO)_2(\eta^3\text{-}C_3H_5)]^-$, which only possesses C_2 symmetry [18]. As found for **1** the averaged $Mo(CO)_2$ angles are smaller than 90° (78.0(2)°). In agreement with the stronger *trans* influence of CO versus allyl the Mo–O bonds *trans* to allyl (2.095(3) Å) are shorter than those *trans* to CO (2.182(3) Å).

Studies concerning metal alkoxides have clearly shown that they can model and simulate the properties and structures of metal oxides [19]. **2** should therefore already represent a useful structural model for allyl groups co-ordinated to the surface of molybdenum oxides although it does not contain *pure* oxo ligands, which—with respect to the aims mentioned in the Introduction—would be desirable. Brisdon et al. have shown that the anion of **2** can alternatively be generated by addition of Ph_4AsCl to basic methanolic solutions of $Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl$ [20]. However, our new synthetic route to such species has the advantage of being extendible to other oxo nucleophiles, which we intended to make use of in order to further approach allyl molybdenum oxide compounds. In the next step the methyl group of the nucleophile (MeO^-) was therefore replaced by hydrogen, i.e. KOH was employed instead of NaOMe as the reagent.

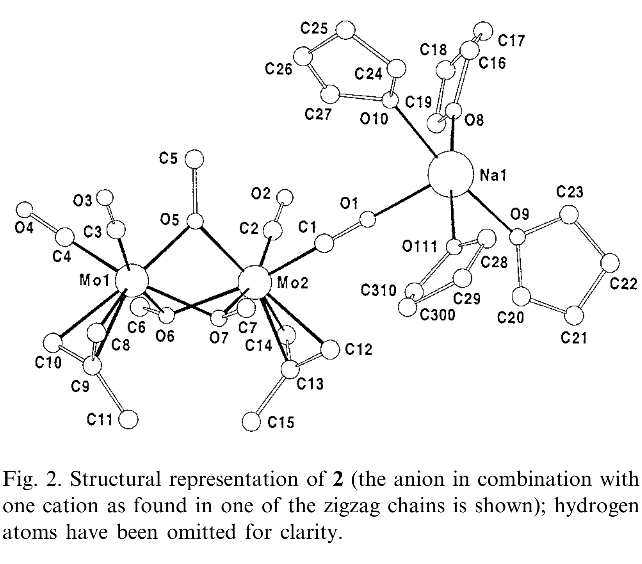


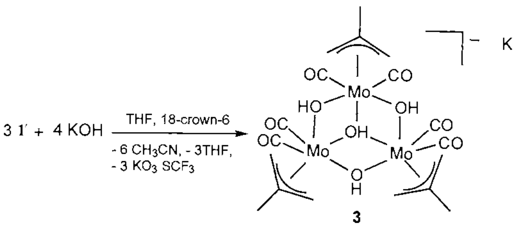
Fig. 2. Structural representation of **2** (the anion in combination with one cation as found in one of the zigzag chains is shown); hydrogen atoms have been omitted for clarity.

Table 3
Selected averaged bond lengths (Å) and bond angles (deg) for **2**

Mo–C_{meso}	2.229(5)	OC–Mo–CO	78.0(2)
Mo–$C_{term.}$	2.319(6)	Mo(1)–O(5)–Mo(2)	97.7(1)
Mo–CO	1.941(6)	Mo(1)–O(6/7)–Mo(2)	92.6(1)
Mo(1/2)–O(6/7)	2.182(3)	O(5)–Mo–O(6/7)	72.5(1)
Mo(1/2)–O(5)	2.095(3)	CO–Na–OC	175.7(2)
Na–OC	2.375(4)	Na–O–C	166.7(4)
C(1/2/3/4)–O(1/2/3/4)	1.167(6)		

2.3. The reaction of 1 with KOH

In order to enhance the solubility of KOH it was suspended in a THF solution of 18-crown-6, which was subsequently allowed to react with a solution of **1**. Work up of the filtrate and fractionated crystallization applying the overlaying technique yielded yellow crystals which, however, proved to contain fluorine. Although an IR spectrum clearly indicated the presence of the desired μ-OH ligands, on chemical grounds the coexistence of μ-F bridges was not unrealistic since BF_4^- is known to possess fluorinating properties [21]. In order to obtain F-free samples the $AgBF_4$ used to generate the requisite cation of **1** was replaced. $AgBPh_4$ failed to react due to its low solubility in THF and $AgClO_4$ completely decomposed the starting material but AgO_3SCF_3 reacted analogously to $AgBF_4$ yielding the cation of **1** with triflate as the counteranion **1′**. This salt was reacted as before with KOH in the presence of crown ether (Eq. (3)) and after the appropriate work up procedure crystalline material was obtained, which proved to consist of the compound $[K(18\text{-crown-6})]^+[[Mo(\eta^3\text{-}C_3H_4(CH_3))(CO)_2]_3(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)]^-$, **3**.



(3)

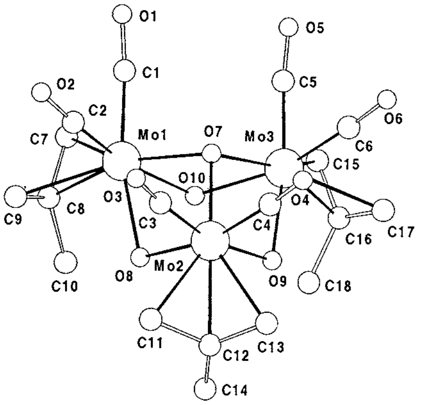


Fig. 3. Structural representation of the anion of **3**; hydrogen atoms have been omitted for clarity.

An X-ray diffraction analysis of a single crystal of **3** gave the structure shown in Fig. 3, where the cation $[K(18\text{-crown-}6)]^+$ and THF molecules included have been omitted (selected bond distances and angles are presented in Table 4). The anion consists of three $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CO)_2]$ units being linked via three μ_2-OH bridges and one μ_3-OH ligand. The arrangement of the Mo_3O_4 moiety can be regarded as a cubane type structure where one corner (one Mo center) is missing. Consequently, the average $HO_{\mu2}$–Mo–$OH_{\mu3}$ and Mo–$OH_{\mu3}$–Mo angles of 74.3(3) and 104.1(2) agree well with those commonly found in such arrangements [22]. The average Mo–$OH_{\mu2}$ distance (2.187(6) Å) lies within the expected range (1.917–2.216 Å) [23, 6d] and it is naturally smaller than the average Mo–$OH_{\mu3}$ distance (2.192(6) Å) lying just outside the usual range (2.203–2.261 Å) [24,22]. Each Mo center possesses a distorted octahedral environment where all allyl ligands are located in *trans* position to the μ_3-OH ligands. The structural situation of the $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CO)_2]$ fragments is very similar to those found in **1** and **2**. Only one other complex bearing (allyl)Mo(μ-OH) units had been previously structurally characterized: in attempts to substitute ligands in $Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl$ by dimethylbis(3,5-dimethyl-1-pyrazolyl)gallate adventitiously the compound $[Mo(\eta^3\text{-}C_3H_4(CH_3))(\mu\text{-}OH)_2(CO)_2(3,5\text{-diMepzH})]_2$ had been obtained, as evidenced by its X-ray structure [6d].

The IR spectrum of **3** contains three characteristic sharp bands at 3650, 3639 and 3509 cm^{-1} corresponding to ν(OH) vibrations of μ_2- and μ_3-OH groups, respectively, which are not involved in H bridging. Quite often such bands are not detected due to the low oscillator strengths of the OH bonds, but when observed they appear within a region of 3540–3750 cm^{-1} [22a,b, 24, 25].

Table 4
Selected averaged bond lengths (Å) and bond angles (deg) for **3**

Mo–OH(μ_2)	2.187(6)	Mo–O(7)–Mo	104.1(2)
Mo–OH(μ_3)	2.192(6)	O(7)–Mo–O(8/9/10)	74.3(3)
Mo–C_{meso}	2.208(9)	Mo–O(8/9/10)–Mo	104.4(2)
Mo–$C_{term.}$	2.334(9)	O(8/9/10)–Mo–O(8/9/10)	79.8(2)
Mo–CO	1.933(9)	Mo–C–O	173.0(8)
C–O	1.175(10)	OC–Mo–CO	76.0(4)

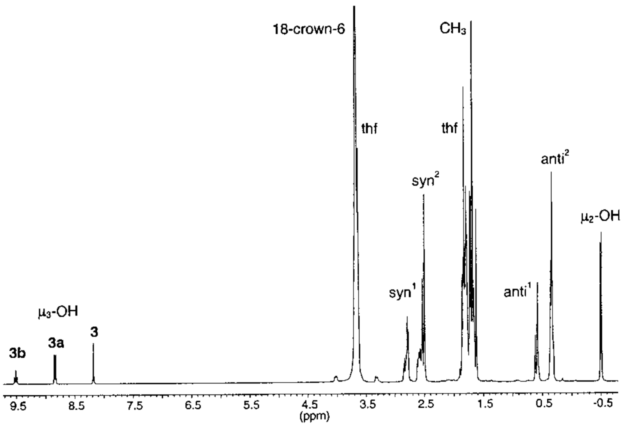


Fig. 4. ^{1}H-NMR spectrum of a mixture of **3**, **3a**, **3b**, **3e** and **3f** in d_8-THF solution.

d_8-THF solutions of crystalline **3** gave clean ^{1}H- and ^{13}C-NMR spectra showing signals for μ_3-OH, methallyl, and μ_2-OH protons with the correct integrals for a 1: 3: 3 ratio of these groups (compare Table 1). This is only possible if the solid state structure of **3** remains intact in solution. The chemical shift of the μ_2-OH protons (-0.52 ppm) corresponds well to the shift found for the μ_3-OH groups in $[NEt_4]_4[Mo(CO)_3(OH)]_4$ being different from the former ligands with respect to the bridging mode but having in common with those the CO groups in *trans* positions [24]. On the other hand the shift of the μ_3-OH group in **3** (8.20 ppm) is typical for acidic Mo–OH protons as in $[MoL(NO)(OH)_2]PF_6$ (L = Tris(i-Propyl)-1,4,7-Triazacyclononan) [25a].

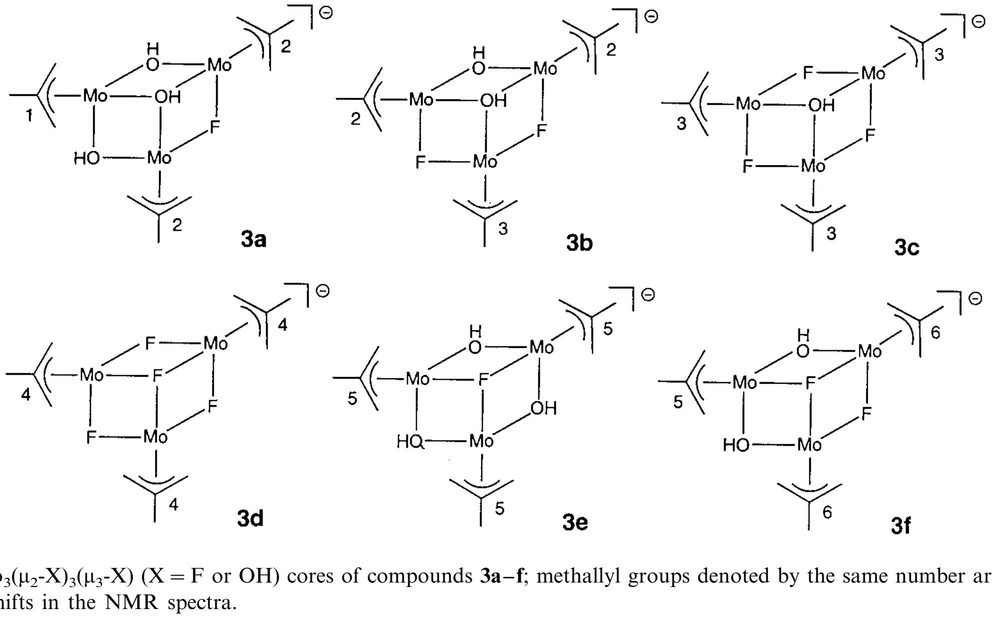
Having determined the structure of **3** and being familiar with its spectroscopic properties the fluoride containing crystals obtained after the reaction of **1** with KOH were reinvestigated. Their IR spectrum was identical to the one of **3**, but the ^{19}F-NMR spectrum detected two signals with chemical shifts expected for Mo–F moieties (-253.5 and -256.3 ppm). Complex ^{1}H-, ^{13}C-, and ^{1}H-^{13}C-HMQC-NMR spectra were obtained, showing the presence of at least four different Mo methallyl fragments, one set belonging to **3**. Careful analyses of these spectra showed that their complexity resulted from various species all possessing in principle structures as shown in Fig. 3 but differing in their degree of fluorination in the bridging positions: in the region of 8–10 ppm, where the μ_3-OH resonance of

3 appears, two further signals can be found (see Fig. 4), which are notable since they are coupled to F-nuclei ($J = 4.4$ Hz). The signal of **3** at 8.20 ppm is a singlet, the first additional resonance at 8.86 ppm a doublet while the second signal at 9.53 ppm is split to a triplet. All these features suggest their assignment to μ_3-OH hydrogens of **3a** (with one μ_2-OH group substituted by F) and **3b** (with two μ_2-OH groups substituted by F) as shown in Scheme 1. Their integral ratios differed from experiment to experiment and in one case it even turned out that the triplet was missing, i.e. **3b** had not been formed at all. However, this did not have a significant simplification of the spectra as a consequence, suggesting that there are even more species existent in solution than **3**, **3a** and **3b**. This interpretation is in agreement with the finding that the signals appearing in each of the regions for the *syn* and *anti* protons of the methallyl ligands can be divided into two groups (*syn*^{1}/*syn*^{2} and *anti*^{1}/*anti*^{2} in Fig. 4). As the *trans* ligands are expected to most significantly influence the chemical shifts of the methallyl protons, the observation of two groups of signals is most reasonably explained in terms of two general types of species possessing different ligands (HO and F) in *trans* positions to the allyl groups, which means that species fluorinated at the μ_3-positions (**3e** and **3f**) also have to be considered. The two signals found in the ^{19}F-NMR spectrum mentioned above would then correspond to bridging F ligands in the μ_2- and μ_3-modes, respectively. Apparently, the ^{1}H-NMR resonances belonging to the μ_2-OH groups of the individual species do not show a pronounced sensitivity to environmental changes, as they all appear between -0.48 and -0.51 ppm. Given that the species **3**, **3a**, **3b**, **3e** and **3f**, whose cores are shown in Scheme 1, are all present in solution, they should give rise to eight non-equivalent sets of allyl signals but, of course, due to overlap these are neither resolved in the ^{1}H-NMR or in the ^{13}C-NMR spectra. A significant variation in chemical shift would be expected for the allyl environments Mo(μ_3-OH)(μ_2-OH)$_2$, Mo(μ_3-OH)(μ_2-OH)(μ_2-F), Mo(μ_3-OH)(μ_2-F)$_2$, Mo(μ_3-F)(μ_2-OH)$_2$, and Mo(μ_3-F)(μ_2-OH)(μ_2-F) at most, so that all spectroscopic results are in agreement with the interpretations above. ^{19}F-NMR measurements in the presence of a standard showed that a maximum of 20% of all OH positions present in the bulk material are occupied by F centers in solution.

In order to obtain reliable data for the chemical shifts of allyl groups and μ_2-F ligands in fluorinated Mo compounds like **3a**, **3b**, **3e** and **3f**, suited to further support the assignments above, and also in order to elucidate whether the findings made so far could be used for the facile synthesis of organometal fluorides, attempts were made to generate the perfluorinated derivative **3d**.

*2.4. The reaction of **1** with KF*

The reaction of **1** with KF yielded a yellow solid and crystalline samples of the resulting product were produced in close analogy to the procedure as described before (Eq. (4)). As expected its IR spectrum looked very similar to the one of **3** but naturally the characteristic ν(OH) bands were missing (although very weak bands at 3709 and 3618 cm^{-1} could be observed). However, under the microscope two different types of crystals could be made out and an X-ray structure analysis of one of them showed that a dimeric species [K(18-crown-6)]$^+$[[Mo(η^3-C$_3$H$_4$(CH$_3$))(CO)$_2$]$_2$(μ_2-F)$_3$]$^-$, **4**, rather than [K(18-



Scheme 1. The Mo$_3$(μ_2-X)$_3$(μ_3-X) (X = F or OH) cores of compounds **3a–f**; methallyl groups denoted by the same number are expected to show similar chemical shifts in the NMR spectra.

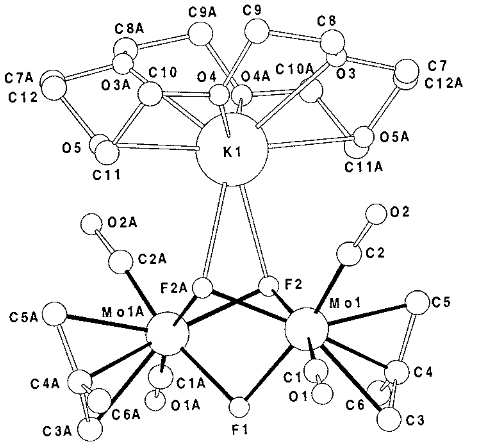
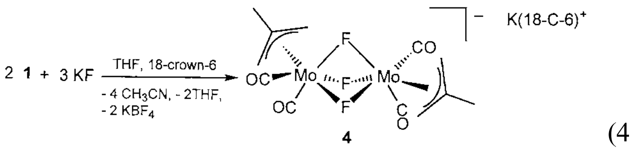


Fig. 5. Structural representation of **4**; hydrogen atoms have been omitted for clarity.

crown-6)]$^+$[[Mo(η^3-$C_3H_4(CH_3)$)$(CO)_2$]$_3$(μ_2-F)$_3$(μ_3-F)]$^-$, **3d**, had been obtained. As can be seen from Fig. 5 (selected bond lengths and angles are given in Table 5) the anion of **4** does not possess a plane of symmetry as the dimer **2** does but rather shows C_2 symmetry. It is therefore more related to the corresponding chloride [18] [(η^3-C_3H_5)$(CO)_2$Mo(μ-Cl)$_3$Mo$(CO)_2$(η^3-C_3H_5)]$^-$ but differs from it in that the cation is coordinated to two of the μ_2-F ligands at a distance of 2.879(1) Å, which is commonly accepted as a bonding interaction between K and F [26] and has a significant distortion of the crown ether ring as a consequence.



(4)

For comparison, the average distance of potassium to the oxygen atoms of the crown ether is by only 0.05 Å shorter. Remarkably, in spite of the contacts to the cation, the Mo–F bond lengths still all lie within a range typical for μ_2-F ligands (1.98–2.22 Å) [27,28]. However, the corresponding F atoms F(2) and F(2A) are asymmetrically placed between the two Mo atoms each showing one short (2.136(1) Å) and one long (2.215(1) Å) distance. The short one is comparable to the distances of the third F ligand symmetrically bonding to both Mo centers (2.130(1) Å), so that the long distance may well be the only consequence of the interaction with K$^+$. Such coordination of an alkaline metal to two F ligands has been observed before [28] in [Na(15-crown-5)]$_2$[$(NMoF_3)_2$(μ_2-F)$_2$] where the two sodium cations apart from being complexed by the crown ether oxygen atoms are additionally coordinated to two terminal F ligands on each of the two Mo centers. As above, the corresponding Mo–F bond lengths were observed to be hardly changed by complexation of Na$^+$. As a consequence of the small size of the bridging F ligands an approximation of the two Mo atoms to a distance of 3.162(1) Å can be noticed in **4**.

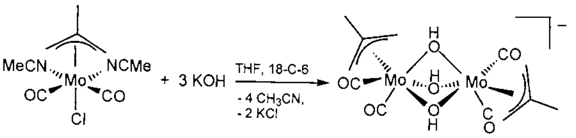
Table 5
Selected averaged bond lengths (Å) and bond angles (deg) for **4**

Mo(1)–C(3)	2.313(2)	OC–Mo–CO	76.6(1)
Mo(1)–C(4)	2.204(2)	F(1)–Mo–F(2/2A)	73.7(1)
Mo(1)–C(5)	2.295(2)	F(2)–Mo–F(2A)	69.2(1)
Mo(1)–F(1)	2.130(1)	Mo(1)–F(2)–Mo(1A)	93.2(1)
Mo(1)–F(2/2A)	2.175(1)	K(1)–F(2)–Mo(1)	95.1(1)
Mo–CO	1.937(2)		
C–O	1.163(2)		
K–F(2/2A)	2.879(1)		
K–O	2.827(2)		
Mo(1)···Mo(1A)	3.162(1)		

The material which had co-crystallized with **4** proved to be unsuitable for single crystal X-ray analysis. Brought into solution, a crystalline mixture containing **4** and the unknown complex showed only one signal in the ^{19}F-NMR spectrum (−255.2 ppm), indicating that the fluoride ligands in the unknown substance show the same bridging mode as those in **4**, as only then the μ_2-F resonances of both compounds can become accidentally isochronic [29] according to the data obtained for the fluorinated derivatives of **3**. Therefore—as anticipated—^{19}F-NMR spectroscopy is not capable of distinguishing between the two species present in solution but this situation changes if ^{1}H- and ^{13}C-NMR spectra are recorded where two sets of allyl/CO signals in a ratio of ca. 1:3 (compare Table 1) can be observed. Due to F-coupling, all signals belonging to the methallyl units appeared to be comparatively broad in the ^{1}H-NMR spectrum and in some cases this coupling could even be resolved. In addition a quartet at 9.92 ppm could be found, which—according to the arguments in Section 2.3—should be indicative of a μ_3-OH ligand with three μ_2-F bridges in close proximity and consequently suggests an assignment to **3c** having been formed due to adventitious water introduced by the starting material KF (which is very hard to rigorously dry). The more intense set of methallyl signals has the right integral for such a structure, however, as there is no further evidence the assignment to **3c** has to remain speculative. This notwithstanding the spectroscopic data found for **4** provide strong support for an interpretation of the spectra belonging to **3a**, **3b**, **3e** and **3f** as performed in Section 2.3.

2.5. *The reaction of Mo(η^3-$C_3H_4(CH_3)$)$(CH_3CN)_2(CO)_2$Cl with KOH*

After the successful syntheses of compounds bearing allyl-Mo fragments in oxygen-rich coordination spheres, we were interested in how much our choice of starting from cationic species like **1** did in fact influence the product formation. In one attempt $Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl$ was therefore directly reacted with KOH. After stirring a suspension of $Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl$, KOH and 18-crown-6 for 3 days, filtering, and overlaying with light petroleum, crystals were produced whose ^{1}H-NMR and ^{13}C-NMR spectra showed that a mayor and a minor product (10: 1) had been formed, the latter corresponding to **3**, which apparently had co-crystallized as an impurity. The IR spectrum provided evidence for a bridging OH ligand (3630 cm^{-1}) not belonging to **3**. While crystals of **3** are reasonably stable, the main product of aboves reaction is very sensitive, turning black on exposure to air and in perfect agreement with the elemental analysis we assign it to the dimer $[K(18\text{-crown-6})]^+[[Mo(\eta^3\text{-}C_3H_4(CH_3))(CO)_2]_2(\mu_2\text{-}OH)_3]^-$, **5**, which is expected to show the same type of structure as **4** (see Eq. (5)).



5

(5)

Unfortunately, the crystals obtained were not suitable for a single crystal X-ray analysis.

Bearing the findings of this experiment in mind, the employment of cationic species in syntheses as described above has certain advantages: the reactions are cleaner and complexes of higher nuclearity as **3** are not accessible in sufficient yields if neutral complexes are directly employed. However, especially **3** is of great value since it already contains a molybdenum oxo core in the form of a $Mo_3(\mu\text{-}OH)_4$ unit with coordinated allyl groups at the surface so that the initial aim of synthesising complexes with an improved model character with regard to oxo molybdenum allyl compounds has been approached. Further research will concern the investigation of the chemical properties of **3** and the reactions of **1** with reagents capable of transferring O^{2-} anions or O atoms in order to obtain compounds with pure O ligands.

3. Experimental

All manipulations were carried out with a vacuum line (at a background pressure = 10^{-4} mbar) or else in a glove-box, or by means of Schlenk-type techniques involving the use of a dry argon atmosphere. $Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl$ [12] has been prepared by a published procedure. 18-Crown-6 was used as obtained from commercial sources. Solvents were dried according to standard procedures; microanalyses were performed by the Analytische Laboratorien des Organisch-Chemischen Institutes der Universität Heidelberg. Cyclovoltammetry was performed with a EG&G PAR equipment (potentiostat/galvanostat 273) on 0.1 M NBu_4PF_6–THF solutions (potentials in mV on glassy carbon electrode, referenced to the SCE at ambient temperatures). The deuterated solvents had been condensed into the NMR tubes before the tubes were flame-sealed. Samples which had to contain known quantities of the standard $CFCl_3$ were prepared on a standardized vacuum line into which gaseous $CFCl_3$ was allowed to expand until a certain pressure had been reached (Hg manometer). The gas was then condensed into an NMR tube containing the substance of interest, which had been weighed into the tube in a glove box, as well as the solvent and the tube flame-sealed subsequently. The X-ray diffraction measurements were made on single crystals on a Siemens P4 (Nicolet Syntex) R3m/V four-circle diffractometer (**1** and **2**) with graphite-monochromated Mo–K_α radiation (λ = 0.71069 Å) or else (**3** and **4**) on a Nonius–Kappa CCD.

*3.1. $[(CH_3CN)_2Mo(\eta^3\text{-}C_3H_4(CH_3))(CO)_2(THF)]^+BF_4^-$ (**1**)*

A solution of 0.292 g (1.5 mmol) $AgBF_4$ in 5 ml THF was added to a solution of 0.487 g (1.5 mmol) of $Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl$ via cannula. Immediately AgCl precipitated as a greyish solid. After 5 min of stirring the suspension was filtered and the orange filtrate stored for 14 h at −20°C. The resulting yellow crystals were separated by filtering in the cold and dried in high vacuum (0.41 g, 0.9 mmol). Single crystals could be obtained by slowly cooling a saturated solution to 4°C. Yield = 61%: IR (KBr) 2982m, 2971m, 2918m, 2313w (ν_{CN}), 2285m (ν_{CN}), 1946vs (ν_{CO}), 1854 (ν_{C-O}), 1448w, 1420w, 1367w, 1343vw, 1283w, 1258w, 1098sh, 1058s, br ($\nu_{BF} + \nu_{CO}$), 1037sh, 946w, 811w, 629w, 608w, 562w, 548w, 530w, 519w, 506w, 485w, 467w cm^{-1}; ^{1}H-NMR (200 MHz, CD_3CN): compare Table 1, note that the signals observed belong to $[Mo(\eta^3\text{-}C_3H_4(CH_3))(CD_3CN)_3]^+$; $^{13}C\{^1H\}$ 135°-DEPT NMR (200 MHz, CD_3CN): δ 67.6 (s, OCH_2 (free THF)), 59.2 (s, $H_2CC(CH_3)CH_2$), 25.7 (s, OCH_2CH_2 (free THF)), 19.6 (s, $H_2CC(CH_3)CH_2$), 1.1 (s, free CH_3CN); $^{13}C\{^1H\}$-NMR (200 MHz, CD_3CN): δ 221.6 (s, CO), 117.7 (s, CH_3CN), 86.8 (s, $CH_2C(CH_3)CH_2$). Anal. Calc. for $C_{14}H_{21}BF_4MoN_2O_3$: C, 37.53; H, 4.72; N, 6.25. Found: C, 37.09; H, 4.58; N, 6.62. M.p.: 127°C dec.

*3.2. $[Na(THF)_4]^+[(\eta^3\text{-}C_3H_4(CH_3))(CO)_2Mo(\mu\text{-}OCH_3)_3\text{-}Mo(CO)_2(\eta^3\text{-}C_3H_4(CH_3))]^-$ (**2**)*

Anhydrous, reactive NaOMe has been prepared via reaction of 0.072 g (3.0 mmol) NaH with 0.096 g (3.0 mmol) MeOH in 15 ml THF. The suspension was stirred for 7 h at r.t. A solution of **1** in situ prepared as described above (0.487 g (1.5 mmol) $\mathrm{Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl}$; 0.292 g (1.5 mmol) $\mathrm{AgBF_4}$ in 5 ml THF) was added to aboves suspension via cannula. A finely divided white precipitate formed while the color of the solution brightened up. After 2 h of stirring the filtrate was overlayed with 100 ml of light petroleum and stored at −20°C for 14 h. The yellow crystals thereby produced were filtered off in the cold and dried in high vacuum (yield: 0.52 g (0.6 mmol) = 85%), the latter leading to a loss of some of the THF coordinated to the cation. Before drying the crystals were suitable for X-ray diffraction. IR (KBr) 3045w ($\nu_{\mathrm{HC=}}$), 2993m, 2945m, 2907s, 2881s, 2802s, 2787s, 1889vs (ν_{CO}), 1768vs (ν_{CO}), 1445m, 1092m, 1053s ($\nu_{\mathrm{C-O}}$), 1023s, 805w, 619w, 538m, 414m $\mathrm{cm^{-1}}$; ^{1}H-NMR (200 MHz, d_8-THF): compare Table 1; ^{13}C{^{1}H}-135°-DEPT-NMR (200 MHz, d_8-THF): δ 68.8 (s, $\mathrm{OCH_3}$, trans to methallyl), 65.8 (s, O*C*$\mathrm{H_2}$ (THF)), 59.5 (s, $\mathrm{OCH_3}$), 51.6 (s, $\mathrm{H_2\mathit{C}C(CH_3)\text{-}CH_2}$), 23.9 (s, $\mathrm{OCH_2\mathit{C}H_2}$ (THF)), 21.3 (s, $\mathrm{H_2CC(\mathit{C}H_3)\text{-}CH_2}$); ^{13}C{^{1}H}-NMR (200 MHz, d_8-THF): δ 233.3 (s, CO), 82.0 (s, $\mathrm{H_2C\mathit{C}(CH_3)CH_2}$). Anal. Calc. for $\mathrm{C_{19}H_{31}Mo_2NaO_8}$ (**2**, **3** THF lost on drying): C, 37.90; H, 5.19. Found: C, 37.57; H, 5.20. M.p.: 58–72°C dec.

3.3. *[K(18-crown-6)]$^+$[[Mo(η^3-$C_3H_4(CH_3)$)(CO)$_2$]$_3$(μ_2-OH)$_3$(μ_3-OH)]$^-$* (**3**) *and fluorinated derivatives* ***3a***, ***b***, ***e***, ***f***

A solution of **1** in situ prepared as described above (0.649 g (2.0 mmol) $\mathrm{Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2\text{-}(CO)_2Cl}$; 0.389 g (2.0 mmol) $\mathrm{AgBF_4}$ in 23 ml THF) was added to a suspension of 0.168 g (3.0 mmol) KOH and 0.793 g (3.0 mmol) 18-crown-6 in 10 ml THF. After 1 min the color of the solution turned red subsequently changing to yellow. After 3 h of stirring the white K(18-crown-6)$\mathrm{BF_4}$ precipitated was filtered off the solution and the bright yellow filtrate overlayed by 100 ml of light petroleum. Storing at −20°C for 14 h yields 0.28 g (0.3 mmol) of crystalline **3** and its fluorinated derivatives corresponding to a yield of 43%. ^{1}H-NMR (200 MHz, d_8-THF): compare Table 1; ^{13}C{^{1}H}-NMR (200 MHz, d_8-THF, **3**, **3a**, **3b**, **3e** and **3f**; all signals found are listed; the ones of **3** are underlined, the residual ones are envelopes of several resonances produced by **3a**, **3b**, **3e** and **3f**): δ $\underline{231.0}$, 230.8, 230.0 (s, CO), $\underline{78.3}$, 78.2, 81.3 (s, $\mathrm{H_2C\mathit{C}(CH_3)CH_2}$), $\underline{71.1}$ (s, 18-crown-6), $\underline{55.2}$, 59.4, 55.0 (s, $\mathrm{H_2\mathit{C}C(CH_3)CH_2}$), 19.6, 19.5, 19.3 (s, $\mathrm{H_2CC(\mathit{C}H_3)CH_2}$). **Selective synthesis of 3**: The fluorine free sample was prepared *via* the same procedure with the only alterations being the replacement of $\mathrm{AgBF_4}$ by $\mathrm{AgO_3SCF_3}$ and a longer stirring time of 14 h, the time it took the solution to turn completely yellow. Crystals suitable for X-ray diffraction were obtained by redissolution of a part of this material in THF and overlaying of this solution with light petroleum (−20°C). IR (KBr) 3650m (ν_{OH}), 3639m (ν_{OH}), 3509w (ν_{OH}), 3037w ($\nu_{\mathrm{HC=}}$), 2975m, 2950m, 2906s, 2875sh, 2827w, 1929vs (ν_{CO}), 1819vs (ν_{CO}), 1473m, 1455m, 1434m, 1353s, 1286w, 1251m, 1107vs, 1057sh, 1030m, 963s, 889w, 837m, 801m, 523m, 506m, 463m $\mathrm{cm^{-1}}$; Anal. Calc. for $\mathrm{C_{30}H_{49}KMo_3O_{16}}$: C, 36.30; H, 4.98. Found: C, 37.06; H, 5.31 (deviations are due to incorporation of THF in the crystal as evidenced by X-ray crystallography). M.p.: 142–188°C dec.

3.4. *[K(18-crown-6)]$^+$[[Mo(η^3-$C_3H_4(CH_3)$)(CO)$_2$]$_2$(μ_2-F)$_3$]$^-$* (**4**)

A solution of **1** in situ prepared as described above (0.649 g (2.0 mmol) $\mathrm{Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2\text{-}(CO)_2Cl}$; 0.389 g (2.0 mmol) $\mathrm{AgBF_4}$ in 23 ml THF) was added to a suspension of 0.168 g (3.0 mmol) KF and 0.793 g (3.0 mmol) 18-crown-6 in 10 ml THF. After 1 min the color of the solution turned red subsequently changing to yellow/orange. After 3 h of stirring the white K(18-crown-6)$\mathrm{BF_4}$ precipitated was filtered off the solution and the bright yellow filtrate overlayered by 100 ml of light petroleum. Storing at −20°C for 14 h yields 0.34 g (0.4 mmol) of crystalline **4** corresponding to a yield of 57%.

IR (KBr): 3045w ($\nu_{\mathrm{HC=}}$), 2985m, 2947sh, 2908m, 1933s (ν_{CO}), 1820s (ν_{CO}), 1473m, 1455m, 1434m, 1350m, 1297w, 1283w, 1247m, 1109s, 1029m, 959m, 837m, 643w, 569vw, 510w, 457m $\mathrm{cm^{-1}}$; ^{1}H-NMR (200 MHz, d_8-THF): compare Table 1; ^{13}C{^{1}H}-NMR (200 MHz, d_8-THF, the underlined signal belongs to **4**): δ 230.5, $\underline{229.3}$ (s, CO), $\underline{81.5}$, 80.6 (s, $\mathrm{H_2C\mathit{C}(CH_3)CH_2}$), 68.7 (s, 18-crown-6), 56.0, 52.4 (s, $\mathrm{H_2\mathit{C}C(CH_3)CH_2}$), 17.3 (q, $^3J_{\mathrm{CF}} = 4.6$ Hz, $\mathrm{H_2\mathit{C}C(CH_3)CH_2}$),16.8 (m, $\mathrm{H_2CC(\mathit{C}H_3)CH_2}$); ^{19}F-NMR ($d_8$-THF): δ −255.2 (s). Anal. Calc. for $\mathrm{C_{24}H_{38}F_3\text{-}KMo_2O_{10}}$: C, 39.83; H, 5.01. Found: C, 37.61; H, 5.33 (the deviations are due to the presence of the second compound).

3.5. *[K(18-crown-6)]$^+$[[Mo(η^3-$C_3H_4(CH_3)$)(CO)$_2$]$_2$(μ_2-OH)$_3$]$^-$* (**5**)

A solution of 0.649 g (2.0 mmol) $\mathrm{Mo(\eta^3\text{-}C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl}$ in 40 ml of THF was stirred in the presence of 0.168 g (3.0 mmol) KOH and 0.793 g (3.0 mmol) 18-crown-6 for 3 d. The KCl precipitated was filtered off the solution and the yellow filtrate overlayed by 100 ml of light petroleum. Storing at −20°C for 14 h yields 0.44 g (0.6 mmol) of crystalline **5** corresponding to a yield of 58%.

IR (KBr): 3630m (ν_{OH}), 3027w ($\nu_{\mathrm{HC=}}$), 2976m, 2947m, 2906s, 2875sh, 2827w, 1922vs (ν_{CO}), 1825vs (ν_{CO}), 1474m, 1455m, 1434m, 1352s, 1283m, 1247m, 1108vs, 1029m, 963s, 892w, 865w, 837m, 805m, 784w, 636w, 619w, 527w, 506w, 467m $\mathrm{cm^{-1}}$; ^{1}H-NMR (200 MHz, d_8-THF: compare Table 1; ^{13}C{^{1}H}-NMR (200 MHz, d_8-THF): δ 235.1 (s, CO), 80.3 (s, $\mathrm{H_2C\mathit{C}(CH_3)CH_2}$),

Table 6
Crystal data and experimental parameters for the crystal structure analyses of **1**–**4**

	1 · THF	**2**	**3** · 3.5 THF	**4**
Empirical formula	$C_{14}H_{21}BF_4MoN_2O_3$	$C_{31}H_{55}Mo_2NaO_{11}$	$C_{44}H_{77}KMo_3O_{19.5}$	$C_{24}H_{38}F_3KMo_2O_{10}$
fw (g mol^{-1})	520.18	818.62	1245.00	774.53
Temp (K)	203(2)	200	200	200
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*C* 2/m	*P* 2_1/c	$P\bar{1}$	*C* 2/*c*
Lattice parameters				
a (Å)	14.336(7)	17.357(3)	16.904(3)	19.670(4)
b (Å)	9.923(5)	9.534(2)	17.201(3)	10.224(2)
c (Å)	16.646(8)	23.535(3)	21.470(4)	16.687(3)
α (°)	90	90	78.18(3)	90
β (°)	90.93(3)	103.500(10)	74.75(3)	117.30(3)
γ (°)	90	90	67.22(3)	90
V (Å^3)	2368(2)	3787(1)	5516(2)	2982(1)
Z value	4	4	2	8
D_{calc} (g cm^{-3})	1.459	1.436	1.415	1.725
μ (mm^{-1})	0.609	0.725	0.812	1.050
F_{000}	1064	1696	2290	1568
Crystal dimensions (mm)	0.53 × 0.45 × 0.17	0.30 × 0.30 × 0.30	0.15 × 0.15 × 0.25	0.10 × 0.10 × 0.20
2θ range (°)	4.9–59.9	2.4–50.1	3.0–52.2	4.6–52.5
Index ranges				
h	−20 to 20	0 to 20	−20 to 20	−24 to 24
k	0 to 13	0 to 11	−21 to 21	−12 to 12
l	0 to 23	−28 to 27	−26 to 26	−20 to 20
No. of reflections collected	3640	6958	64290	22766
No. of independent reflections	3640	6720	21126	2969
No. of reflections with $I \geq 2\sigma(I)$	2382	4855	6614	2648
Parameters	198	495	817	258
Goodness-of-fit on F^2	1.021	1.132	0.793	1.322
Largest diff. peak/hole (e Å^{-3})	0.618/−0.467	0.389/−0.390	0.835/−1.170	0.448/−0.409
R indices, $F^2 > 2\sigma(F^2)$	0.0601	0.0438	0.0624	0.0197
R_w	0.1401	0.0923	0.1503	0.0496
R indices (all data, F^2)	0.1119	0.0755	0.1548	0.0247
R_w	0.1614	0.1130	0.1592	0.0505

70.7 (s, 18-crown-6), 52.4 (s, $H_2C\mathit{C}(CH_3)CH_2$), 21.4 (s, $H_2CC(\mathit{C}H_3)CH_2$). Anal. Calc. for $C_{24}H_{41}KMo_2O_{13}$: C, 37.51; H, 5.38. Found: C, 37.59; H, 5.49. Dec. at 93°C.

3.6. X-ray diffraction data collection for **1**, **2**, **3** and **4**

Single crystals of the compounds were preselected in a glove box and immersed in fluorocarbon oil there. Individuals were then mounted on top of a fibre and quickly frozen to −70°C. Centered reflections were refined by least-squares calculations to indicate the unit cells. Unit cell and collection parameters for the complexes are listed in Table 6. Diffraction data were collected in the appropriate hemispheres and under the conditions specified also in Table 6.

3.7. Solution and refinement of the structures of **1**, **2**, **3** and **4**

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2, SHELXL-97 [30] with anisotropic thermal parameters for all non hydrogen atoms. Hydrogen atoms were calculated making use of a riding model. The final residuals are indicated in Table 6.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (C.L.) and the state of Baden-Württemberg (Landesgraduiertenförderung, C.B.) for scholarships as well as the Fonds der chemischen Industrie for financial. We also gratefully acknowledge the permanent, generous support from Professor G. Huttner.

References

[1] F. Bottomley, L. Sutin, Adv. Organomet. Chem. 28 (1988) 339.

[2] J. Sundermeyer, Angew. Chem. 105 (1993) 1195; Angew. Chem. Int. Ed. Engl. 32 (1993) 1144.

[3] W.A. Herrmann, R.W. Fischer, D.W. Marz, Angew. Chem. 103 (1991) 1706; Angew. Chem. Int. Ed. Engl. 30 (1991) 1638; W.A. Herrmann, R.W. Fischer, W. Scherer, M.U. Rauch, ibid. 105 (1993) 1209; 32 (1993) 1157.

[4] R.K. Grasselli, J.D. Burrington, Adv. Catal. 30 (1981) 133; G.W. Keulks, L.D. Krenzke, T.M. Notermann, Adv. Catal. 27 (1978) 183. R.K. Grasselli, J.D. Burrington, Ind. Engl. Chem. Prod. Res. Dev. 23 (1984) 394.

[5] T. Ono, N. Ogata, Y. Mijaryo, J. Catal. 161 (1996) 78. T. Ono, H. Numata, N. Ogata, J. Mol. Catal. 105 (1996) 31.

[6] (a) M.G.B. Drew, G.F. Griffin, Acta Cryst. Sect. B 35 (1979) 3036. (b) M.S. Kralik, J.P. Hutchinson, R.D. Ernst, J. Am. Chem. Soc. 107 (1985) 8296. (c) F. Dawans, J. Dewailly, J. Meunier-Piret, P. Piret, J. Organomet. Chem. 76 (1974) 53. (d) S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 66 (1988) 97. (e) V.S. Joshi, V.K. Kale, K.M. Sathe, A. Sarkar, S.S. Tavale, C.G. Suresh, Organometallics 10 (1991) 2898. (f) J.W. Faller, J.T. Nguyen, W. Ellis, M.R. Mazzieri, Organometallics 12 (1993) 1434. (g) N.J. Christensen, P. Legzdins, J. Trotter, V.C. Yee, Organometallics 10 (1991) 4021. (h) K.R. Breakell, S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 57 (1979) 139. (i) D. Mohr, H. Wienand, M.L. Ziegler, J. Organomet. Chem. 134 (1977) 281. (j) S.K. Chowdhury, V.S. Joshi, A.G. Samuel, V.G. Puranik, S.S. Tavale, A. Sarker, Organometallics, 13 (1994) 4092. (k) W. Kläui, A. Müller, W. Eberspach, R. Boese, I. Goldberg, J. Am. Chem. Soc. 109 (1987) 165; these references include ligands R_2O, RO^-, OH^-, $[P]–O^-$, $[S]–O^-$ but not RCO_2^-.

[7] C. Borgmann, C. Limberg, A. Driess, J. Organomet. Chem. 541 (1997) 367.

[8] (a) M.D. Curtis, O. Eisenstein, Organometallics 3 (1984) 887. (b) B.J. Brisdon, D.W. Brown, C.R. Willis, Polyhedron 5 (1986) 439. (c) B.M. Trost, M. Lautens, J. Am. Chem. Soc. 104 (1982) 5543. (d) R.H. Yu, J.S. McCallum, L.S. Liebeskind, Organometallics 13 (1994) 1476.

[9] Y.D. Ward, L.A. Villanueva, G.D. Allred, S.C. Payne, M.A. Semones, L.S. Liebeskind,Organometallics 14 (1995) 4132 and references therein.

[10] J.W. Faller, C. Lambert, Tetrahedron 41 (1985) 5755; J.W. Faller, K.H. Chao, J. Am. Chem. Soc. 105 (1983) 3893.

[11] B.J. Brisdon, A. Day, J. Organomet. Chem. 221 (1981) 279.

[12] H. tom Dieck, H. Friedel, J. Organomet. Chem. 14 (1968) 375; R.G. Hayter, J. Organomet. Chem. 13 (1968) P1.

[13] P. Powell, J. Organomet. Chem. 129 (1977) 175.

[14] D.S. Frohnapfel, P.S. White, J.L. Templeton, H. Rüegger, P.S. Pregosin, Organometallics 16 (1997) 3737.

[15] (a) J.-C. Tsai, M. Kahn, K.M. Nicholas, Organometallics 8 (1989) 2967. (b) A. Gourdon, K. Prout, Acta Crystallogr. B38 (1982) 1596. (c) F.A. Cotton, R. Poli, Inorg. Chem. 26 (1987) 1514. (d) A. Hills, G.J. Leigh, J. Hutchinson, J.A. Zubieta, J. Chem. Soc. Dalton Trans. (1985) 1069. (e) P. Hofacker, A. Werth, A. Neuhaus, B. Neumüller, F. Weller, K. Dehnicke, D. Fenske, Chem. -Ztg. 115 (1991) 321. (f) M. Rhiel, S. Wocadlo, W. Massa, K. Dehnicke, Z. Anorg. Allg. Chem. 622 (1996) 1195. (g) D.M. Baird, A.L. Rheingold, S.D. Croll, A.T. DiCenso, Inorg. Chem. 1986 (25) 3458.

[16] P.K. Baker, A.E. Jenkins, J. Organomet. Chem. 545 (1997) 125; C.G. Hull, M.H.B. Stiddard, J. Organomet. Chem. 9 (1967) 519.

[17] N. Hu, G. Nie, Z. Jin, W. Chen, J. Organomet. Chem. 377 (1989) 137; M.K. Cooper, P.A. Duckworth, K. Henrick, M. McPartlin, J. Chem. Soc. Dalton Trans. (1981) 2357; M.K. Cooper, P.A. Duckworth, K. Henrick, M. McPartlin, J. Organomet. Chem. 212 (1981) C10; L.M. Clarkson, W. Clegg, N.C. Norman, A.J. Tucker, P.M. Webster, Inorg. Chem. 27 (1988) 2653; A.S.C. Chan, H.-S. Shieh, J.R. Hill, J. Organomet. Chem. 279 (1985) 171.

[18] M.G.B. Drew, B.J. Brisdon, M. Cartwright, Inorg. Chim. Acta 36 (1979) 127.

[19] M.H. Chisholm, Inorganic chemistry towards the 21st century, Chapter 16, Am. Chem. Soc., Washington, DC, 1983, pp. 243–272.

[20] B.J. Brisdon, M. Cartwright, A.G. Hodson, J. Organomet. Chem. 277 (1984) 85; the first synthetic route to this anion started from $Et_4N^+[(\eta^3\text{-}C_3H_4(CH_3])(CO)_2Mo(\mu\text{-}Cl)_3Mo(CO)_2(\eta^3\text{-}C_3H_4(CH_3))]^-$ which was reacted with NaOMe (compare H.D. Murdoch, R. Henzi, J. Organomet. Chem. 5 (1966) 552.

[21] A. Ford, E. Sinn, S. Woodward, Polyhedron 13 (1994) 635; F.A. Cotton, J.L. Eglin, K.J. Wiesinger, Inorg. Chim. Acta 195 (1992) 11; P. Rosendorfer, C. Robl, W. Beck, Gazzetta Chim. Ital. 123 (1993) 145; M.R. Churchill, F.J. Rotella, Inorg. Chem. 17 (1978) 668; J.A. Carroll, R.E. Cobbledick, F.W.B. Einstein, N. Farrel, D. Sutton, P. Vogel, Inorg. Chem. 16 (1976) 2462; M. Haidi, T. Kodama, M. Sato, M. Harakawa, Y. Uchida, Inorg. Chem. 15 (1976) 2964; J.H. Matonic, S.J. Chen, L.E. Pence, K.R. Dunbar, Polyhedron 11 (1992) 541; R.H. Crabtree, G.G. Hlatky, E.M. Holt, J. Am. Chem. Soc. 105 (1983) 7302.

[22] A. Beyerholm, M. Brorson, M. Minelli, L.K. Skov, Inorg. Chem. 31 (1992) 3672; U. Sartorelli, L. Garlaschelli, G. Ciani, G. Bonora, Inorg. Chim. Acta 5 (1971) 191; A.S. Faust, L.F. Dahl J. Am. Chem. Soc. 92 (1970) 7337; T.J. McNeese, T.E. Mueller, D.A. Wierda, D.J. Darensbourg, Inorg. Chem. 24 (1985) 3465; V.G. Albano, G. Ciani, M. Manassero, M. Sansoni, J. Organomet. Chem. 34 (1972) 353; B. Nuber, F. Oberdorfer, M.L. Ziegler, Acta Cryst. B37 (1981) 2062; D. Bright, J. Chem. Soc. Chem. Commun. (1970) 1169; J.M. Basset, A. Choplin, J. Mol. Catal. 21 (1983) 95; Y.J. Yermakov, J. Mol. Catal. 21 (1983) 35; R. Barth, B.C. Gates, Y. Zhao, H. Knözinger, J. Hulse, J. Catal. 82 (1983) 147; A. Brenner, D.A. Hucul, J. Am. Chem. Soc. 102 (1980) 2484; T.G. Spiro, D.H. Templeton, A. Zalkin, Inorg. Chem. 7 (1968) 2165; M. Herberhold, G. Süß, J. Ellermann, H. Gäbelein, Chem. Ber. 111 (1978) 2931.

[23] (a) R. Alvarez, J.L. Atwood, E. Carmona, P.J. Pérez, M.L. Poveda, R.D. Rogers, Inorg. Chem. 30 (1991) 1493; (b) J.-G. Ren, H. Tomita, M. Minato, T. Ito, K. Osakada, M. Yamasaki, Organometallics 15 (1996) 852; (c) K. Wieghardt, M. Hahn, W. Swiridoff, J.Weiss, Inorg. Chem. 23 (1984) 94; (d) M.C. Couldwell, B. Meunier, K. Prout, Acta Crystallogr. B35 (1979) 603; K. Prout, M.C. Couldwell, Acta Crystallogr. B33 (1977) 2146.

[24] J.T. Lin, S.K. Yeh, G.H. Lee, Y. Wang, J. Organomet. Chem. 361 (1989) 89.

[25] (a) J. Böhmer, G. Haselhorst, K. Wieghardt, B.Nuber, Angew. Chem. 106 (1994) 1556; Angew. Chem. Int. Ed. Engl. 33 (1994) 1473; (b) K. Wieghardt, U. Bossek, A. Neves, B. Nuber, J. Weiss, Inorg. Chem. 28 (1989) 432; (c) F.W.S. Benfield, M.L.H. Green, J. Chem. Soc. Dalton Trans. (1974) 1244; (d) V.W. Day, M.F. Fredrich, W.G. Klemperer, R.-S. Liu, J. Am. Chem. Soc. 101 (1979) 491.

[26] H. Plenio, Chem. Rev. 97 (1997) 3363.

[27] A. Ford, E. Sinn, S. Woodward, Polyhedron 13 (1994) 635; M. Leimkühler, N. Buchholz, R. Mattes, Z. Naturforsch. 44b (1989) 389; A.J. Edwards, R.D. Peacock, R.W.H. Small, J. Chem. Soc. (1962) 4486; M.H. Chisholm, D.L. Clark, J.C. Huffman, Polyhedron 4 (1985) 1203; M.H. Chisholm, D.L. Clark, R.J. Errington, K. Folting, J.C. Huffman, Inorg. Chem. 27 (1988) 2071; A.J. Edwards, D.R. Slim, J.E. Guerchais, R. Kergoat, J. Chem. Soc. Dalton Trans. (1980) 289.

[28] K. Völp, K. Dehnicke, D. Fenske, Z. Anorg. Allg. Chem. 572 (1989) 26.

[29] Apparently, the chemical shifts in the ^{19}F-NMR spectra are not very sensitive to minor variations of the chemical environments in such compounds, and this becomes most obvious if the μ_2-F shifts belonging to **3a** and **3b** are compared to the ^{19}F-NMR resonance of **4**: although **4** is quite a different complex $\Delta\delta$ amounts to only 1.1 ppm.

[30] G.M. Sheldrick, Program for Crystal Structure Refinement, University of Göttingen, 1997.