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Intermediates and products of the reaction of $MoCl_5$ with ethanol: crystal structures of $[MoOCl_3(EtOH)]$ and $H[MoOCl_4]\cdot 2EtOH$

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An intermediate in the ethanolysis reactions of $MoCl_5$, $[MoOCl_3(EtOH)]$ **2**, has been isolated after the reaction of $MoCl_5$ with 2 equivalents of EtOH and its crystal structure was determined. Treatment of $MoCl_5$ with 2.5 equivalents of EtOH and subsequent cooling as well as the reaction of $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$ **1** with HCl(g) yield a product which has been identified as $H[MoOCl_4]\cdot 2EtOH$ **3** by X-ray crystallography. The mechanisms leading to **1**–**3** are discussed. The reactions of **2** with donors have been investigated and $[Cl_2OMo(\mu\text{-}OPr)_2(\mu\text{-}HOPr)MoOCl_2]$ **4** was obtained as a first derivative of **1** after the reaction of $MoCl_5$ with PrOH.

The reaction of $MoCl_5$ with EtOH inspite of being seemingly trivial still causes confusion. In 1930 Wardlaw and Webb[1] reported that at room temperature it results in the formation of a green oil containing $MoOCl_3$ in one form or another as suggested by its reaction with $[C_5H_5NH]Cl$ to yield $[C_5H_5NH][MoOCl_4]$. On the other hand Butcher and Chatt[2] obtained a brown oil, the colour of which was rationalised later by Gibson and co-workers[3] as due to the presence of traces of moisture. However, on treatment with phosphines these two different oils yielded two different distortional isomers of $[MoOCl_2(PR_3)_3]$ with differing spectroscopic properties.[3] In 1958 Bradley *et al.*[4] described the synthesis of $[\{Mo(OEt)_2Cl_3\}_2]$ from the reaction of $MoCl_5$ with an excess of EtOH at −78 °C, and recently after treatment of $MoCl_5$ with 2.5 equivalents of EtOH in $CHCl_3$ at room temperature we isolated the dimeric complex $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$ **1** in almost quantitative yield.[5] The stoichiometry of the reaction has been verified by isolating the products EtCl and HCl, when the reaction was performed in a sealed vessel. These were the only products to be isolated having an appreciable volatility at 178 K. The failure to detect any diethyl ether enabled us to propose a reaction sequence (1) and

$$MoCl_5 + 2\,EtOH \xrightarrow{-2HCl} [Mo(OEt)_2Cl_3] \xrightarrow{-EtCl} [MoO(OEt)Cl_2] \xrightarrow{[MoO(OEt)Cl_2]EtOH} \mathbf{1} \quad (1)$$

to rule out a different possible mechanism for the decomposition of the postulated intermediate $[Mo(OEt)_2Cl_3]$ therein *via* the pathway (2), which had been suggested previously to be

$$[Mo(OR)_2Cl_3] \longrightarrow [MoOCl_3] + R_2O \quad (2)$$

the essential reaction step in the methanolysis (R = Me) of $MoCl_5$.[6]

Moreover the reaction generating complex **1** shows some peculiarities: after the addition of stoichiometric amounts of EtOH to $MoCl_5$ a green solution is obtained turning brown while the volatiles are removed and finally yielding the orange complex **1**. This redissolves giving an orange colour in CH_2Cl_2, switching to green again on treatment with gaseous, anhydrous HCl. This colour change can only be explained by the presence of highly reactive monomeric species stabilised by HCl (the variation between green and orange-brown is reminiscent of the different observations made by Wardlaw and Chatt already mentioned). In this contribution the isolation and crystal structures of two such reactive intermediates are described.

Table 1 Bond distances (Å) and angles (°) in complex **2**

Mo−O(2)	1.641(2)	Mo−H(10)	2.46(4)
Mo−O(1)	2.102(2)	Cl(1)···H(10)	2.70(4)
Mo−Cl(2)	2.3116(8)	O(1)−C(1)	1.472(3)
Mo−Cl(3)	2.3213(7)	C(1)−C(2)	1.500(4)
Mo−Cl(1)	2.3997(8)		
O(2)−Mo−O(1)	99.35(9)	Cl(3)−Mo−Cl(1)	88.63(3)
O(2)−Mo−Cl(2)	102.29(7)	O(2)−Mo−H(10)	103.9(9)
O(1)−Mo−Cl(2)	88.90(5)	O(1)−Mo−H(10)	15.1(9)
O(2)−Mo−Cl(3)	101.65(7)	Cl(2)−Mo−H(10)	101.8(9)
O(1)−Mo−Cl(3)	158.28(6)	Cl(3)−Mo−H(10)	147.5(9)
Cl(2)−Mo−Cl(3)	91.98(3)	Cl(1)−Mo−H(10)	67.5(9)
O(2)−Mo−Cl(1)	99.84(7)	Mo−Cl(1)−H(10)	57.3(8)
O(1)−Mo−Cl(1)	82.38(5)	C(1)−O(1)−Mo	130.0(2)
Cl(2)−Mo−Cl(1)	157.25(2)	O(1)−C(1)−C(2)	110.0(2)

Results and Discussion

The reaction of $MoCl_5$ with just 2 rather than 2.5 equivalents of EtOH should prevent the quantitative generation of complex **1** since not enough EtOH is available for the formation of the EtOH bridge present in it. In this case the stabilisation of a dimer once formed is impossible so that there should be a chance to isolate one or more of the monomeric intermediates. When a concentrated solution of $MoCl_5$ in CH_2Cl_2 is treated with 2 equivalents of EtOH an unstable green solution is obtained, from which a greyish solid is precipitating continuously. Cooling of a freshly filtered solution to −78 °C results in the separation of considerable amounts of green crystals, which proved to be highly reactive, immediately liquidising in contact with traces of water (for instance at glass walls) to a brown oil. Crystals suitable for a structure analysis could be obtained by recrystallisation and in agreement with spectroscopic and other data these were found to consist of $[MoOCl_3(EtOH)]$ **2**, the structure of which is shown in Fig. 1. Bond lengths and angles are presented in Table 1.

Compound **2** exists as a discrete molecule showing a tetragonal-pyramidal geometry with the Mo placed 0.429 Å above the plane defined by Cl(1)–Cl(3) and O(1). At 1.641(2) Å the Mo=O bond is remarkably short as compared to those of

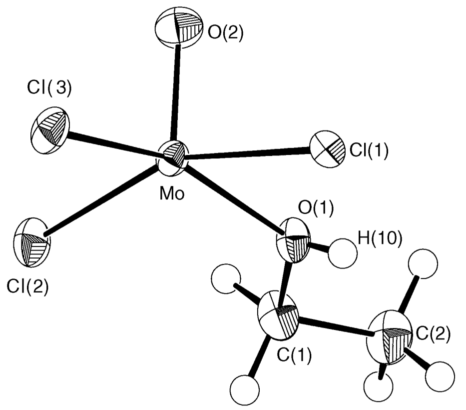


Fig. 1 Molecular structure of compound **2**

other molybdenum(V) compounds[7] bearing ligands in *trans* position to the Mo=O bond. Structural studies on a number of six-co-ordinate oxomolybdenum(V) complexes have shown that there is a significant lengthening of the molybdenum–ligand distance *trans* to the oxo-group (see ref. 1 in ref. 8). This lengthening is due to the *trans* influence of the oxo-group, which also facilitates the formation of five-co-ordinate species, especially in solutions of poorly co-ordinating solvents.[8] Kinetic studies of substitution reactions of complexes such as $[MoOCl_3X_2]^{n-}$ in dichloromethane[9] suggest such five-co-ordinate species as intermediates and one such example is compound **2**, although it is not formed in a substitution reaction. The absence of a ligand in *trans* position to the oxygen produces a definite electron deficiency at the Mo in **2** and enables participation of the lone pairs at the O atom in the bonding to Mo, formally producing a Mo≡O triple bond. This goes together with an increased bond order and force constant which is reflected by a comparatively high frequency for the ν(Mo=O) vibration being masked by the band for ν(C–O) at 1013 cm^{-1}. Since normally EtOH ligands do not show a considerable *trans* influence it is not surprising that the Mo–Cl bonds are all of comparable length. The Mo–O(1) distance of 2.102(2) Å lies within the region characteristic for such bonds.[10]

The co-ordination number of five stresses the intermediate character of compound **2**. Molybdenum complexes normally exhibit a marked tendency to obey the 18-electron rule and, moreover, the size of the Mo atom is such that six-fold co-ordination is commonly adopted.[11] Lower co-ordination numbers are most likely to arise as a response either to the requirements of the 18-electron rule or to the presence of bulky ligands.[11] Neither of these factors seems to apply to **2** so that its five-co-ordination should mainly be a result of the strong *trans* influence of the oxo-group and the absence of ligands with relatively strong σ-donor properties. Therefore its observed reactivity especially with regard to atmospheric water is only too understandable. Some five-co-ordinate complexes of the $OMoCl_3$ fragment are known.[8] A five-fold co-ordination of Mo in the solid state was demonstrated for the first time in 1975 for the complex $[MoOCl_3(S{=}PPh_3)]$[12] in which the $S{=}PPh_3$ shows a marked *trans* influence unlike the EtOH ligand in **2**. In contrast to **2** which forms an almost ideal square pyramid, $[MoOCl_3(S{=}PPh_3)]$ is strongly distorted in favour of a trigonal bipyramid. This compound is inert towards a twenty-fold excess of $S{=}PPh_3$ and from extended investigations concerning formation of and equilibria between five- and six-co-ordinate chlorooxomolybdenum(V) complexes in CH_2Cl_2 it was concluded that the presence of a sulfur donor may assist formation of a five-co-ordinate complex in solution.[8]

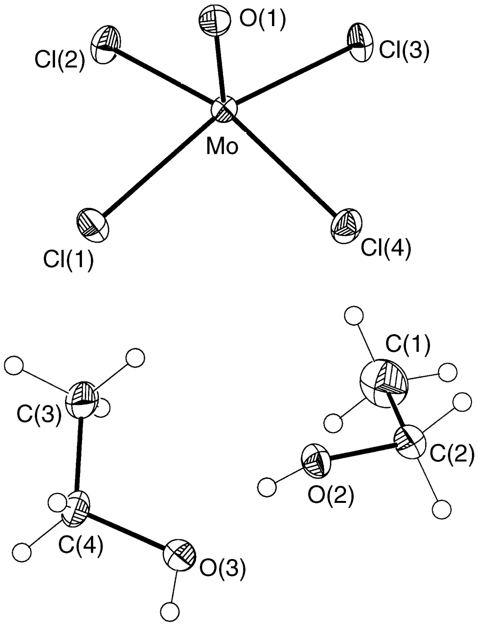


Fig. 2 Molecular structure of complex **3**; the proton representing the cation has been omitted

$$MoCl_5 + EtOH \xrightarrow{-HCl} [Mo(OEt)Cl_4] \xrightarrow{-EtCl} MoOCl_3 \xrightarrow{+EtOH} \underset{\mathbf{2}}{[MoOCl_3(EtOH)]} \qquad (3)$$

The isolation of complex **2** in addition to the results obtained previously[5] unequivocally shows that the first steps in the mechanism of the reaction of $MoCl_5$ with EtOH at room temperature should be as in equation (3). An intermediate $[Mo(OEt)_2Cl_3]$ is, at least at room temperature, not passed through. At low temperatures, however, the Mo=O bond formation *via* elimination of EtCl might be suppressed enabling the formation of $[Mo(OEt)_2Cl_3]$. This compound is highly electron deficient (11 valence electrons for Mo) and needs stabilisation by an additional ligand extending its co-ordination number to six. This requirement can be met by dimerisation yielding the stable compound $[\{Mo(OEt)_2Cl_3\}_2]$ which has been isolated.[4] A second possibility to trap $[Mo(OEt)_2Cl_3]$ proved to be the addition of an ammonium chloride to the solution after annealing to 0 °C producing the isolable anion $[Mo(OEt)_2Cl_4]^-$. Above 0 °C, however, complete decomposition occurs.[13] The reaction of **2** with 0.5 equivalent of EtOH yields, after removing of all volatiles, **1** in quantitative yield providing additional support for the intermediate character of **2** during the synthesis of **1**. This result encouraged attempts to isolate **2** directly from the green reaction mixture obtained after the addition of 2.5 equivalents of EtOH to a solution of $MoCl_5$. If such a solution is cooled to −78 °C during 2 d grass-green crystals precipitate which, however, do not correspond to **2**. After filtration at −78 °C they melt on annealing to temperatures above −10 °C forming an unstable green oil which upon evacuation of its crystallisation vessel slowly decomposes with evolution of HCl and EtOH (as detected by gas-phase IR spectroscopy) to yield the orange solid **1**. Since this green solid is not formed upon addition of only 2 equivalents of EtOH to $MoCl_5$ it should be richer in EtOH as compared to **2**. However, because of its high sensitivity with respect to air, low melting point, paramagnetism and decomposition *in vacuo* this compound is very difficult to analyse. Fortunately its crystals grown at −40 °C and picked at −78 °C were suitable for X-ray diffraction analysis establishing the composition $H[MoOCl_4]\cdot 2EtOH$ **3** for the molecules in the crystal (see Fig. 2, Table 2), which is also in complete agreement with the analytical data obtained.

All atoms apart from the proton representing the cation for the corresponding tetrachlorooxomolybdate anion were found. The presence of this proton is nevertheless unambiguous because of two reasons. First, if there was no cation present the

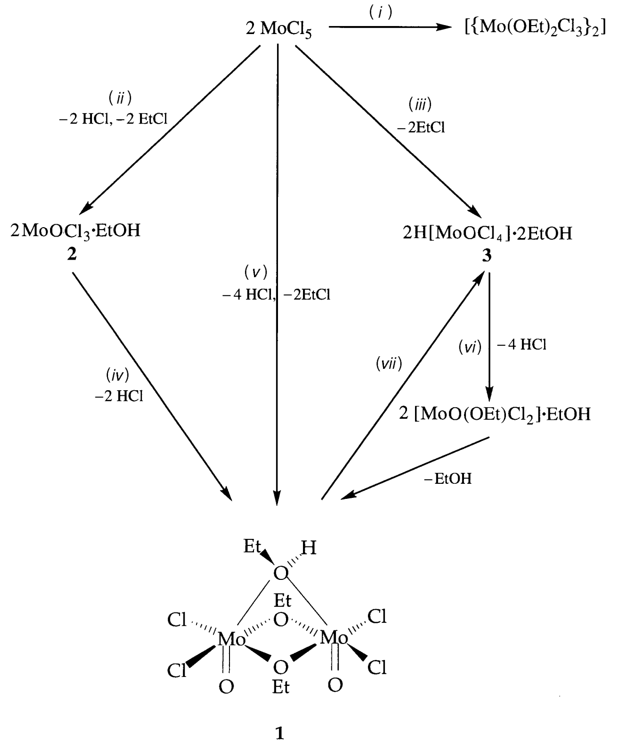
Table 2 Bond distances (Å) and angles (°) in complex **3**

Mo–O(1)	1.668(4)	C(1)–C(2)	1.46(2)
Mo–Cl(4)	2.343(2)	C(2)–O(2)	1.483(10)
Mo–Cl(2)	2.338(2)	C(3)–C(4)	1.543(13)
Mo–Cl(1)	2.355(2)	C(4)–O(3)	1.465(9)
Mo–Cl(3)	2.376(2)		
O(1)–Mo–Cl(4)	102.2(2)	O(1)–Mo–Cl(3)	103.1(3)
O(1)–Mo–Cl(2)	101.7(2)	Cl(4)–Mo–Cl(3)	87.43(8)
Cl(4)–Mo–Cl(2)	156.12(6)	Cl(2)–Mo–Cl(3)	87.82(6)
O(1)–Mo–Cl(1)	99.1(3)	Cl(1)–Mo–Cl(3)	157.82(6)
Cl(4)–Mo–Cl(1)	87.71(6)	C(1)–C(2)–O(2)	111.5(7)
Cl(2)–Mo–Cl(1)	87.92(8)		

Mo would be in the oxidation state +VI which would be surprising considering the conditions of formation and decomposition. Secondly its UV/VIS spectrum compares well with those of other $M^+[MoOCl_4]^-$ compounds.[14,15] Since all other H atoms could be located the reasons why the additional acidic proton could not be detected are unclear. Significant electron density could be found neither in the surroundings at the EtOH molecules nor at the oxide ligand [at 1.668(4) Å the Mo–O(1) bond represents a very strong Mo=O double bond]. Since the proton is not expected to be localised in complete isolation within the unit cell, the most likely explanation for its elusiveness would be its proximity to the Cl ligands resulting in a smeared electron density. The structure of the $[MoOCl_4]^-$ anion in **3** is similar to those determined previously.[16] The strong Mo=O bond exerts a powerful *trans* influence and the $[MoOCl_4]^-$ anion universally adopts a square-pyramidal geometry. Repulsion between the closely bound O atom and the chloride ligands increases the O–Mo–Cl angles [102.2(2), 101.7(2), 99.1(3), 103.1(3)°] which lie within the range defined as typical for oxo and nitrido complexes of the type $[MXCl_4]^-$ (X = N or O; M = Mo, Re, Ru or Os).[17] The $[MoOCl_4]^-$ anion in **3** shows a slight distortion from C_{4v} symmetry. A more pronounced distortion of this type had been observed in the compounds $[N(PPh_3)_2]^+[MoOCl_4]^-$[16] and $[N(PPh_3)_2]^+[TcOCl_4]^-$[18] and has been ascribed to the bulk of the $N(PPh_3)_2^+$ cations. In the unit cell of **3** besides the anions only H^+ and EtOH are present which makes it understandable that the distortion is only weak in **3**. Nevertheless the undistorted (though non-crystallographic) point symmetry of the anion in $[AsPh_4]$-$[MoOCl_4]$[19] appears to be unusual.

Complex **3** represents another example of a five-co-ordinate molybdenum centre (see discussion above). It should be noted, though, that consistent with what has been said above, tetrachlorooxomolybdate anions tend to extend their co-ordination number to six,[8] for instance by water, and are therefore unstable in the presence of moisture if they are not protected by bulky cations.[16]

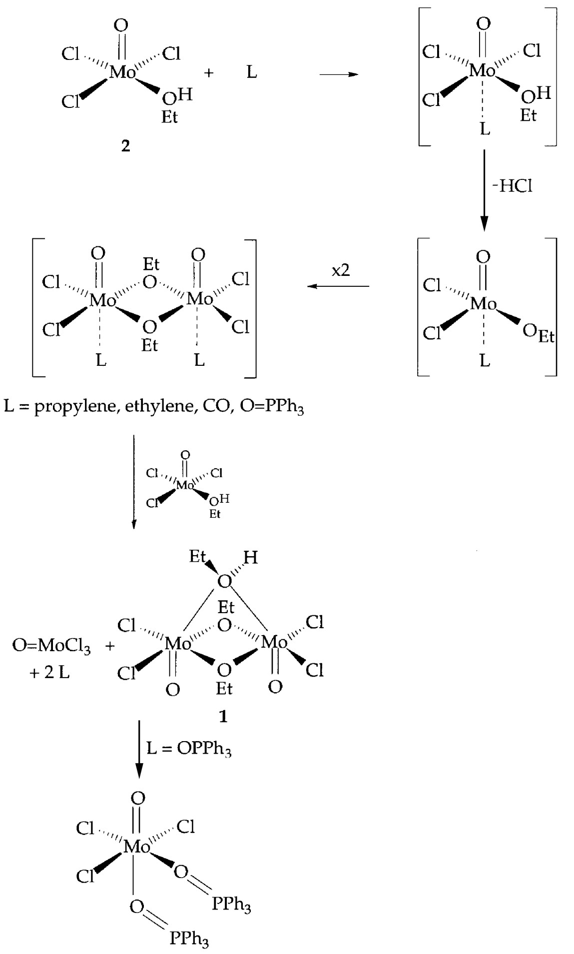
One additional argument for the location of the proton missing from the crystal structure of complex **3** near the Cl ligands is the experimental finding that pumping on crystals of **3** yields HCl and EtOH so that **1** is formed after dimerisation of the resulting fragments. As mentioned earlier, an orange solution of **1** changes to bright green after treatment with gaseous HCl, which means that its Mo–Mo bond is cleaved producing the monomers $H[MoOCl_4]$ again. Quite a number of salts with the tetrachlorooxomolybdate anion are known to date,[16] some of which have been mentioned in the above discussion. The parent acid of this series of salts in the free state has been mentioned only once before in the literature and was reported to be obtainable from the reaction of MoO_3 with HCl–HI–water.[15] Its characterisation was restricted to elemental analysis, magnetic susceptibility measurements, IR, electronic and X-ray powder spectra. From these data it was concluded that the solid-state structure of $H[MoOCl_4]$ should consist of a chloride-bridged dimer which is in clear contrast to the findings of this work. However, the UV/VIS spectrum compares well with that of **3**, while the IR spectra are not comparable since that of **3** is dominated by the bands corresponding to the EtOH molecules. Taking into account all the results described above Scheme 1 can be deduced.



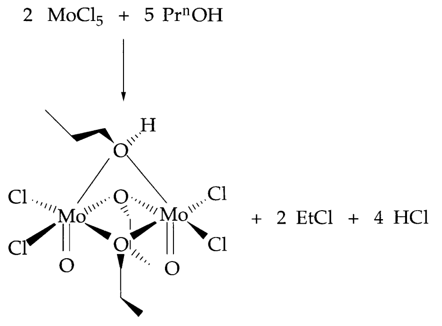
Scheme 1 (*i*) −78 °C, excess of EtOH; (*ii*) 4 EtOH, room temperature (r.t.) to −78 °C; (*iii*) 5 EtOH, r.t. to −78 °C; (*iv*) EtOH; (*v*) r.t., 5 EtOH; (*vi*) r.t., *in vacuo*; (*vii*) HCl (g)

As can be shown by NMR measurements on a CD_2Cl_2 solution of compound **2** in a flame-sealed NMR tube, quantitative decomposition occurs at room temperature with precipitation of oxomolybdenum chlorides within 3 d. The organic products remaining in solution thereafter could not be identified. As a solid **2** decomposes more slowly but should nevertheless be stored at −40 °C.

By isolation of compounds **2** and **3** most of the characteristics of the reaction of $MoCl_5$ with EtOH could be unravelled so that just by varying the reaction conditions appropriately one of four possible products can be obtained in good to quantitative yields. The five-fold co-ordination at the electron-deficient Mo in **2** invited investigations concerning reactions with π- and σ-donors. Starting from comparable compounds such reactions lead to the corresponding six-co-ordinate addition products.[8] On treatment of solutions of **2** in CH_2Cl_2 with gaseous CO, propylene or ethylene in each case the originally green solutions turned orange within 15 min and after removing the volatiles **1** could be isolated. This result can only be understood if it is assumed that these molecules initially co-ordinate at the free co-ordination site in **2** providing electron density to the Mo. This initiates elimination of HCl producing a 13-electron complex $[MoO(OEt)Cl_2L]$, which dimerises with elimination of L and co-ordination of an EtOH molecule from another molecule of **2**. Scheme 2 shows this possible reaction pathway explaining the experimental results. Unfortunately there is uncertainty concerning the fate of the $MoOCl_3$ which is expected to form simultaneously according to Scheme 2. However, employing the strong σ donor $OPPh_3$ as L which is capable of stabilising such fragments gave strong evidence for the formation of this side product, since a different reaction behaviour is observed in this case: the solution retains its green colour and after removing the volatiles a green oil is obtained. From the latter **1** can be extracted by diethyl ether in exactly the yield



Scheme 2



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Scheme 3

expected from Scheme 2, leaving behind a green solid which proved to consist of $[MoOCl_3(OPPh_3)_2]$.[20]

These reactions demonstrate that it is not possible to attach a ligand at the free co-ordination site of compound **2** since as soon as the molybdenum centre receives additional electron density decomposition reactions occur. Accordingly **2** can only exist in its free state which yet again underlines its intermediate character. There are, however, many syntheses in the literature starting from uncharacterised $MoCl_5$–EtOH mixtures[21] which must have contained, as the present work suggests, **1**, **2** and/or **3** which are all interconvertible. Therefore **2** can serve as a soluble, weighable equivalent of the otherwise polymeric $O{=}MoCl_3$ in reactions with this fragment.

These findings after studying the system $MoCl_5$–EtOH of course suggested investigations concerning reactions with different alcohols. Surprisingly, a derivative of complex **1** could only be obtained in one case: treating $MoCl_5$ with propanol produced $[Cl_2OMo(\mu\text{-}OPr)_2(\mu\text{-}HOPr)MoOCl_2]$ **4** (Scheme 3), while all other alcohols used, like methanol, allyl alcohol, phenol, pentafluorophenol and Bu^tOH, produced inhomogeneous brown oils or simply $MoOCl_3$ which precipitated.

Experimental

All manipulations were carried out with a vacuum line (at a background pressure $<10^{-4}$ mbar) or in a glove-box, or by means of Schlenk-type techniques involving the use of a dry argon atmosphere. Solvents were dried according to standard procedures; microanalyses were performed by the Analytische Laboratorien des Organisch-Chemischen Institutes der Universität Heidelberg. Infrared spectra were recorded with a Bruker IFS 66 FTIR spectrometer, ^1H NMR spectra of solutions using a Bruker AC 200 instrument operating at 200 MHz. The deuteriated solvents had been condensed into the NMR tubes previously before the tubes were flame-sealed. The UV/VIS spectra were measured on a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrophotometer. The X-ray diffraction measurements were made on single crystals on a Siemens P4 (Nicolet Syntex) R3m/V four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Fast atom bombardment mass spectra were recorded with a Finnigan MAT 8230 instrument.

Synthesis of $[MoOCl_3(EtOH)]$ 2

Molybdenum pentachloride (11.3 g, 0.041 mol) was placed in a Schlenk tube and suspended in CH_2Cl_2 (30 cm^3). Ethanol (3.8 g, 0.082 mol) was added carefully within 1 h by means of a syringe, causing a considerable evolution of gas so that a second needle was needed as exhaust in the septum sealing the Schlenk tube. Shortly before the addition was complete a greyish solid formed which was filtered off after the last drop of EtOH had entered the tube. The filtrate was cooled to −78 °C causing 6.2 g (0.023 mol, 56%) of compound **2** to precipitate in the form of dark green crystals, which were freed from the solution *via* a cannula at −78 °C. They are extremely sensitive to air and show a good solubility in CH_2Cl_2, while they are only moderately soluble in $CHCl_3$. They decompose on heating to 49 °C. By concentrating the filtrate and further cooling the yield could be improved, although the second fraction was not as pure as the first. When **2** was redissolved in CH_2Cl_2 and treated with 0.5 equivalent of EtOH after 5 min of stirring and removal of the volatiles, **1** was isolated in quantitative yield.

Complex **2** (Found: C, 9.15; H, 2.35; Cl, 39.75. $C_2H_6Cl_3MoO_2$ requires C, 9.1; H, 2.3; Cl, 40.25%); $\tilde{\nu}/cm^{-1}$(KBr) 3413m (br), 2976w, 2933w, 1459w, 1381w, 1258w, 1082m, 1013s, 896m, 805m and 728m; ^1H NMR (200 MHz, CD_2Cl_2, 20 °C, $SiMe_4$): δ_H 3.7 (s, br) and 6.9 (s, br); electron-impact mass spectrum: m/z 200 (100, $M^+ - EtCl$), 165 (50, $M^+ - EtCl - Cl$), 149 (20, $M^+ - OEt - 2Cl$), 130 (15, MoO_2^+) and 114 (12%, MoO^+); ESR (CH_2Cl_2) $g = 1.956$.

Crystal structure of $[MoOCl_3(EtOH)]$ 2

Crystals of compound **2** were suspended in an oil in the glove-box, quickly selected under the microscope and frozen to 200 K.

Crystal data. $C_2H_6Cl_3MoO_2$, $M = 264.36$, monoclinic, space group $P2_1/n$, $a = 5.702(1)$, $b = 8.237(1)$, $c = 16.831(4)$ Å, $\beta = 99.18(2)°$, $U = 780.40$ Å^3, $2.45 < \theta < 27.99°$, $Z = 4$, green plates, crystal size 0.50 × 0.40 × 0.20 mm, $T = 200$ K, $\mu = 2.57$ mm^{-1}, $D_c = 2.250$ g cm^{-3}, $F(000) = 508$.

Data collection and processing. 2063 Reflections measured ($\theta_{max} = 27.99°$), 1884 unique ($R_{int} = 0.0180$), 1709 with $I > 2\sigma(I)$, which were used in all calculations.

Structure analysis and refinement. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on F^2, SHELXL 93,[22] with anisotropic thermal parameters for all non-hydrogen atoms. An experimental absorption correction using ψ scans, $\Delta\psi = 10°$, was applied. Atom H(10) was located from the Fourier-difference map and refined isotropically. All other hydrogen atoms were calculated by the use of a riding model. Final $R1 = 0.0227$ (based on F), and $wR2 = 0.0536$ (based on F^2) for 78 parameters [$w^{-1} = \sigma^2(F) + 0.003F_o{}^2$]. The final difference-synthesis maximum and minimum were 0.489 and -0.444 e Å^{-3}, respectively.

Synthesis of $H[MoOCl_4]\cdot 2EtOH$ **3**

After the addition of 2.5 equivalents of EtOH to $MoCl_5$ as described elsewhere[5] the reaction mixture was cooled to -78 °C, causing complex **3** to precipitate in the form of grass-green crystals in 10% yield. These were freed from the solution *via* cannula at -78 °C. A better synthesis for **3** is the reaction of **1** with HCl. The compound **1**$\cdot 0.225CH_2Cl_2$ (1.3 g, 2.51 mmol) was dissolved in CH_2Cl_2 (30 cm^3) in a Schlenk tube and the solution frozen to 77 K. The reaction vessel was evacuated and an excess of HCl gas (7.5 mmol) cocondensed. The Schlenk tube was closed and the frozen reaction mixture warmed slowly to room temperature, turning green in the process. When annealing was complete the tube was cooled to -40 °C causing crystals of **3** (0.4 g, 1.15 mmol, 46%) to precipitate. They melt at approximately -10 °C and are very sensitive to air. $\tilde{\nu}$/cm^{-1}(film) 3437vs (br), 2984s, 1597s, 1446m, 1392s, 1265s, 1081s, 1001vs, 868s and 805s. $\lambda_{max}(CH_2Cl_2)$ 710, 440 and 300 nm. ^{1}H NMR (CD_2Cl_2): δ_H 2.36 (br, CH_3) and 4.60 (br, CH_2).

Crystal structure of $H[MoOCl_4]\cdot 2EtOH$ **3**

Crystals of complex **3** were transferred while cooling in a stream of argon from a Schlenk tube in which they had been generated to a glass apparatus allowing cooling and selection of a suitable crystal at the same time. The crystal chosen was surrounded with an inert oil and frozen on the diffractometer to 123 K.

Crystal data. $C_4H_{13}Cl_4MoO_3$, $M = 346.88$, orthorhombic, space group $Pna2_1$, $a = 8.447(2)$, $b = 10.831(3)$, $c = 13.359(2)$ Å, $U = 1222.2(4)$ Å^3, $2.42 < \theta < 32.32°$, $Z = 4$, green blocks, crystal size $0.37 \times 0.32 \times 0.24$ mm, $T = 123(2)$ K, $\mu = 2.57$ mm^{-1}, $D_c = 1.885$ g cm^{-3}, $F(000) = 684$.

Data collection and processing. 2830 Reflections measured ($\theta_{max} = 32.32°$), 2048 unique ($R_{int} = 0.0608$), 1944 with $I > 2\sigma(I)$, which were used in all calculations.

Structure analysis and refinement. The structure was solved and refined and an absorption correction applied as for compound **2**. All H atoms at the EtOH molecules could be located from the Fourier-difference map and were refined isotropically. Subsequently, the methyl and methylene hydrogens were treated as rigid groups and refined isotropically with 1.2 U_{eq} and 1.5 U_{eq} of the corresponding C atoms. Final $R1 = 0.0430$ (based on F), and $wR2 = 0.1200$ (based on F^2) for 113 parameters [$w^{-1} = \sigma^2(F) + 0.003F_o{}^2$]. The final difference-synthesis maximum and minimum were 0.4043 and -0.2187 e Å^{-3}, respectively.

Atomic coordinates, thermal parameters, and bond lengths and angles for both structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/432.

Synthesis of $[Cl_2OMo(\mu\text{-}OPr)_2(\mu\text{-}HOPr)MoOCl_2]$ **4**

The synthesis was closely analogous to that one described for complex **1**[4] using PrOH instead of EtOH (Found: C, 19.9; H, 4.1; Cl, 26.1. $C_9H_{22}Cl_4Mo_2O_5$ requires C, 19.9; H, 4.05; Cl, 25.8%. $\tilde{\nu}$/cm^{-1}(KBr) 3248m, 2968m, 2973w, 1461m, 1454m, 1395m, 1381m, 1266w, 1226w, 1100w, 1040m, 1010vs, 980vs, 942vs, 886s, 858m and 752m. ^{1}H NMR (200 MHz, CD_2Cl_2, 20 °C, $SiMe_4$): δ_H 0.96 [3 H, br, $HO(CH_2)_2CH_3$], 1.08 [6 H, t, J(HH) 7.0 Hz, $O(CH_2)_2CH_3$], 1.80 (2 H, br, $HOCH_2CH_2CH_3$), 2.10 (4 H, m, $OCH_2CH_2CH_3$), 3.60 (2 H, br, $HOCH_2CH_2CH_3$) and 5.98 (4 H, br, $OCH_2CH_2CH_3$).

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