The $[Cl_2OMo(\mu\text{-}OC_2H_5)_2(\mu\text{-}HOC_2H_5)MoOCl_2]/PMe_3$ System: A Chameleon Yielding the X-ray Structures of $MoOCl_2(PMe_3)_3$, $MoOCl_3(PMe_3)_2$, $Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(PMe_3)_2(\mu_3\text{-}O)_2$, and $MoOCl_3(OPMe_3)(PMe_3)$†

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The reaction of $[Cl_2OMo(\mu\text{-}OC_2H_5)_2(\mu\text{-}HOC_2H_5)MoOCl_2]$ (**1**) with 5 equiv of PMe_3 provides a simple route to pure *mer*-$MoOCl_2(PMe_3)_3$ (**3**), so that its crystal structure could be determined [$C_9H_{27}Cl_2MoOP_3$, monoclinic, $P2_1/c$, $a = 17.138(3)$ Å, $b = 12.808(3)$ Å, $c = 19.226(4)$ Å, $\beta = 115.99(1)°$, $Z = 8$]. The mechanism of the conversion of **1** to **3** is complex, but one of the intermediates, $MoOCl_3(PMe_3)_2$ (**4**), can be isolated and crystallized, if **1** is reacted only with 3 instead of 5 equiv of PMe_3. **4** further reacts with an excess of PMe_3 to yield **3**, providing additional evidence for its intermediacy. The crystal structure of **4** could be determined [$C_6H_{18}Cl_3MoOP_2$, monoclinic, $P2_1/n$, $a = 6.468(1)$ Å, $b = 12.677(2)$ Å, $c = 17.791(2)$ Å, $\beta = 92.64(1)°$, $Z = 4$]. If **4** is not isolated directly after the reaction and its crystallization is attempted from the raw mixture, two different compounds are obtained and their crystal structures were determined: $MoOCl_3(OPMe_3)(PMe_3)$ (**5**) [$C_6H_{18}Cl_3MoO_2P_2$, monoclinic, $P2_1/n$, $a = 6.783(3)$ Å, $b = 12.623(4)$ Å, $c = 18.298(8)$ Å, $\beta = 98.58(3)°$, $Z = 4$] and $Mo_4O_4Cl_4(\mu_2\text{-}OC_2H_5)_4(PMe_3)_2(\mu_3\text{-}O)_2$ (**6**) [$C_{14}H_{38}Cl_4Mo_4O_{10}P_2$, monoclinic, $P2_1/c$, $a = 1117.6(2)$ Å, $b = 1161.6(2)$ Å, $c = 1277.1(3)$ Å, $\beta = 109.84(1)°$, $Z = 2$]. **4** reacts slowly with CH_2Cl_2 producing $[Me_3PH]^+[MoOCl_4(PMe_3)]^-$ (**7**), which can also be found among the products of attempts to crystallize **4** from CH_2Cl_2/petroleum ether mixtures, while its treatment with an excess of HCl produces $[Me_3PH]_2{}^+[MoOCl_5]^{2-}$ (**8**). The mechanism of the stepwise fragmentation of **1** yielding **3**−**7** is discussed.

Introduction

In 1970 Chatt et al. reported the syntheses of a series of oxomolybdenum complexes *mer*-$MoOX_2(PR_3)_3$ (X = Cl, Br, I, NCO, NCS; $PR_3 = PMe_2Ph$, P^nPr_2Ph, P^nBu_2Ph, $PMePh_2$, $PEtPh_2$, P^nPrPh_2) isolated either as green or as blue compounds depending on X and PR_3.[1] One of these complexes, *mer*-$MoOCl_2(PMe_2Ph)_3$, could even be generated in both colors, the blue species apparently being the more stable one. The initial assumption that the reason for this observation was the formation of two different geometrical isomers could be disproved by X-ray analyses of both forms.[1−3] However, these X-ray structures seemed to show that the two forms differed in the distortion of the polyhedra leading to different Mo═O bond lengths with the green isomer showing a longer bond [1.80(4) Å] compared to the blue one [1.676(7) Å]. These findings lead to the creation of the term “distortional isomers”,[3a] which was later on included within the description of the “bond-stretch isomerism”.[4] The trimethylphosphine analog *cis-mer*-$MoOCl_2(PMe_3)_3$ was synthesized for the first time by Carmona, Wilkinson, et al.[5] by the reaction of $MoCl_4(THF)_2$ with PMe_3 and H_2O in THF. Generally after this reaction a green isomer was obtained, even though sometimes formation of a blue isomer showing identical spectroscopical properties was observed as well.[5] The inability to generate the blue compound in a controlled fashion was explained by its lower stability. However, this conclusion is in clear contrast to Chatt’s results suggesting that the blue isomer with the shorter Mo═O bond length is more stable. The molecular structure of the green isomer of *cis-mer*-$MoOCl_2(PMe_3)_3$ was determined by X-ray methods in 1991.[7] The asymmetric unit contained two crystallographically independent molecules with different Mo═O bond lengths [1.698(8) and 1.866(7) Å]. Repetition of the X-ray analysis on a second crystal resulted in *two new* bond lengths [1.77(1) and 2.154(8) Å]. These findings could no longer be explained by the “bond-strech isomerism” since they would require the presence of four instead of just two minima on the potential energy hypersurface. After extended investigations it was found that the *real* reason for the many different bond lengths observed was a crystallographical disorder caused by co-crystallization of the isostructural yellow trichloride complex $MoCl_3(PMe_3)_3$ as an impurity.[8,9] This lead to the partial occupation of oxo sites by Cl ligands at a significantly longer distance. Varying degrees of impurity accordingly lead to different Mo═O bond lengths. After these discoveries the trichlorides[10] could also be detected as impurities in the “green isomers” of Chatt’s complexes so that there is no structural evidence for the bond-strech isomerism in those complexes that were originally proposed to exhibit the phenomenon.[7] A trichloride impurity could, however, not explain the differing

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† Dedicated to Prof. Dr. Walter Siebert on occasion of his 60th birthday.

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stretching frequencies $\nu(Mo{=}O)$ found for the blue and the green isomers [blue, 954 cm^{-1}; green 943 cm^{-1}].[3] In their original report Chatt et al. started their synthesis with the reaction of $MoCl_5$ with EtOH leading to a brown oil which was subsequently treated with PMe_2Ph.[1] This was reported to yield the "blue isomer" [$\nu(Mo{=}O) = 954$ cm^{-1}]. Trying to reproduce the experiment, Gibson and co-workers[11] isolated a green oil after treatment of $MoCl_5$ with EtOH, from which after addition of PMe_2Ph blue crystals corresponding to *mer*-$MoOCl_2(PMe_2Ph)_3$ were obtained, being identical, however, with those spectroscopically and structurally characterized by Enemark[12] and Parkin et al.[6] and showing a $\nu(Mo{=}O)$ frequency of 943 cm^{-1}. If traces of water were added to the green oil before reacting it with the phosphine it turned brown and led finally after reaction with the phosphine to *mer*-$MoOCl_2(PMe_2Ph)_3$ with $\nu(Mo{=}O) = 954$ cm^{-1}. Accordingly there are in fact two different crystalline forms of this compound with slightly different structural and IR-spectroscopical properties in the solid state. Since Gibson et al. also redetermined the two crystal structures already existing, for each of these forms now two sets of Mo=O bond lenghts are available, blue I (Chatt), with 1.663(2)[2] and 1.676(7) Å,[11] and blue II (Enemark/Parkin), with 1.675(3)[7] and 1.682(7) Å.[11] No reliable crystal structure could so far be determined for *mer*-$MoOCl_2(PMe_3)_3$ since contamination by the trichloride complex remained a problem in its synthesis. It should be noted though that Mayer et al. observed the formation of this compound (although it was not isolated) during the reaction of $Cl_2Mo(PMe_3)_4$ with O_2 or ethylene oxide in sealed NMR tubes.[13]

Interestingly enough the different isomers of *mer*-$MoOCl_2(PMe_2Ph)_3$ have been synthesized starting from $MoCl_5$ and EtOH, *i.e.* a mixture from which in the past the compound $[(EtO)_2MoCl_3]_2$[14] and—using stoichiometrical amounts of EtOH in $CHCl_3$ as a solvent—the dimeric complex $[Cl_2OMo(\mu\text{-}OC_2H_5)_2(\mu\text{-}HOC_2H_5)MoOCl_2]$ (**1**)[15] have been isolated. These findings suggests the investigation of the reaction of **1** with an excess of PMe_3, first to test the potential of **1** to act as a source for the synthesis of complexes of the type $MoOCl_2(PR_3)_3$ and second to produce crystals of pure $MoOCl_2(PMe_3)_3$ in order to determine the *real* Mo=O bond length of the compound. Both seemed to be attractive targets since in contrast to the hitherto known synthetic routes to these kind of complexes (reaction of $MoCl_4(THF)_2$ with H_2O/PMe_3[5] and reaction of $MoCl_5/EtOH$ with PMe_3[1]) no contamination by $MoCl_3(PMe_3)_3$ was to be expected. Additional stimulation for the investigation of this system came from the previous isolation of the tetrameric cluster $[Mo_4O_4Cl_4(\mu_2\text{-}OC_2H_5)_4(HOC_2H_5)_2(\mu_3\text{-}O)_2]$ (**2**)[16] after the reaction of **1** with 1 equiv of PMe_3. This reaction had been part of a series of experiments carried out in order to study the fragmentation and subsequent aggregation reactions of **1** in the presence of Lewis bases. Therefore employing an excess of PMe_3 in this reaction also serves this purpose.

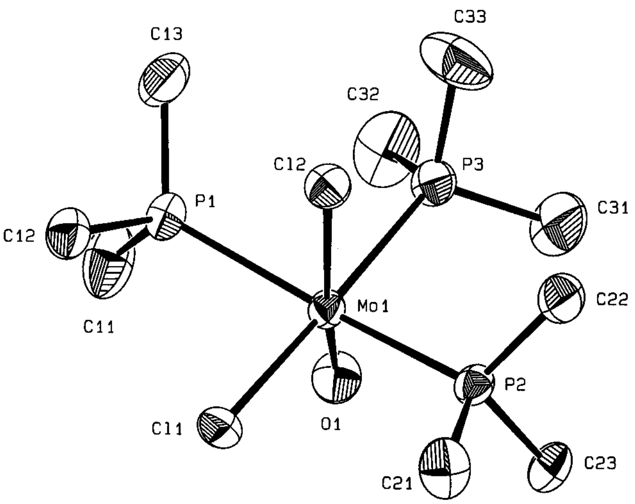

Figure 1. Molecular structure of $MoOCl_2(PMe_3)_3$ (**3**). In the interest of clarity, all hydrogen atoms have been omitted.

Table 1. Selected Bond Distances (Å) for $MoOCl_2(PMe_3)_3$ (**3**)

Mo(1)−O(1)	1.707(4)	Mo(2)−O(2)	1.691(4)
Mo(1)−Cl(1)	2.495(2)	Mo(2)−Cl(21)	2.485(2)
Mo(1)−P(3)	2.504(2)	Mo(2)−P(22)	2.511(2)
Mo(1)−P(2)	2.524(2)	Mo(2)−P(23)	2.529(2)
Mo(1)−P(1)	2.536(2)	Mo(2)−Cl(22)	2.531(2)
Mo(1)−Cl(2)	2.554(2)	Mo(2)−P(21)	2.543(2)

Table 2. Selected Bond Angles (deg) in $MoOCl_2(PMe_3)_3$ (**3**)

O(1)−Mo(1)−Cl(1)	169.5(2)	O(2)−Mo(2)−Cl(21)	169.5(2)
O(1)−Mo(1)−P(3)	96.3(2)	O(2)−Mo(2)−P(22)	96.3(2)
Cl(1)−Mo(1)−P(3)	85.5(1)	Cl(21)−Mo(2)−P(22)	85.5(1)
O(1)−Mo(1)−P(2)	94.3(2)	O(2)−Mo(2)−P(23)	94.3(2)
Cl(1)−Mo(1)−P(2)	82.8(1)	Cl(21)−Mo(2)−P(23)	82.8(1)
P(3)−Mo(1)−P(2)	167.26(6)	P(22)−Mo(2)−P(23)	167.26(6)
O(1)−Mo(1)−P(1)	102.9(2)	O(2)−Mo(2)−Cl(22)	102.9(2)
Cl(1)−Mo(1)−P(1)	87.4(1)	Cl(21)−Mo(2)−Cl(22)	87.4(1)
P(3)−Mo(1)−P(1)	90.75(7)	P(22)−Mo(2)−Cl(22)	90.75(7)
P(2)−Mo(1)−P(1)	93.77(7)	P(23)−Mo(2)−Cl(22)	93.77(7)
O(1)−Mo(1)−Cl(2)	90.0(2)	O(2)−Mo(2)−P(21)	90.0(2)
Cl(1)−Mo(1)−Cl(2)	79.7(1)	Cl(21)−Mo(2)−P(21)	79.7(1)
P(3)−Mo(1)−Cl(2)	88.25(6)	P(22)−Mo(2)−P(21)	88.25(6)
P(2)−Mo(1)−Cl(2)	84.69(6)	P(23)−Mo(2)−P(21)	84.69(6)
P(1)−Mo(1)−Cl(2)	167.11(6)	Cl(22)−Mo(2)−P(21)	167.11(6)

Results and Discussion

Slow treatment of a solution of **1** in toluene with 5 equiv of PMe_3 (1 M solution in toluene) initially yields a dark red solution which turns dark green within the next 12 h. After this solution was overlaid with petroleum ether 40/60, within 1 week blue crystals precipitate showing an elemental analysis and spectroscopic properties in agreement with the composition $MoOCl_2(PMe_3)_3$ (**3**). In order to determine the still unknown Mo=O bond length of this molecule [so far 1.698(8), 1.866(7), 1.77(1), and 2.154(8) Å had been found][9] an X-ray analysis was performed with a single crystal. The structure of one of the two independent molecules in the unit cell is shown in Figure 1 and bond distances and angles are given in Tables 1 and 2. The Mo=O bond lengths for the two different molecules amount to 1.707(4) and 1.691(4) Å which is just slightly longer than the distances found for the *pure* complexes *mer*-$MoOCl_2(PMe_2Ph)_3$ [vide supra]. The molecules posess a noncrystallographical C_s symmetry with very similar P−Mo bond lengths while the Cl ligands in *trans* position to the Mo=O bond are somewhat longer [2.554(2) and 2.543(2) Å] than those in the *cis* position [2.495(2) and 2.485(2) Å] due to the *trans* influence of the terminal oxygen. Furthermore the *trans* influence causes the O−Mo−P(1,2,3)/Cl(1) bond angles to become larger than 90°.

An interesting question is how the reduction of the Mo(V) centers in **1** to the Mo(IV) center in **3** proceeds. In principle of course trimethylphosphine can act as a reducing agent reacting with Mo=O groups to form $O{=}PMe_3$. However, both **1** and **3**

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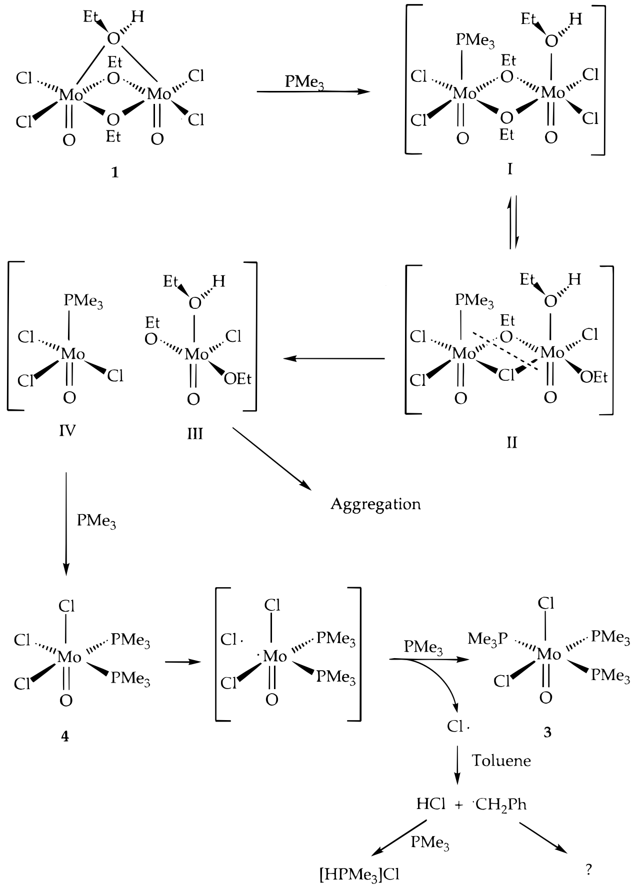
Scheme 1



posess a Mo═O group and both Cl atoms on the Mo centers of **1** are still present in **3** as well, so that the reduction of the metal centers must have occured *via* nonobvious pathways (a reduction of a Mo(IV) center to a Mo(III) center caused by the action of PMe_3 had been observed previously by Chatt and co-workers, too[1]). The previous isolation of the cluster compound **2** after treatment of **1** with 1 equiv of PMe_3 suggests that **1** is split into fragments of the type $MoO(OEt)_2Cl(HOEt)$ (**III**) and $MoOCl_3(PMe_3)$ (**IV**) initially as shown in Scheme 1. Formation of **2** then results from the formal condensation process of four units of **III** with elimination of EtOH and Et_2O {$4[OMo(OEt)_2Cl(HOEt)]$ (**III**) − $2OEt_2$ − 2HOEt → $[Mo_4O_4Cl_4(\mu_2\text{-}OC_2H_5)_4(HOC_2H_5)_2(\mu_3\text{-}O)_2]$ (**2**)}. Et_2O could be identified in the gas phase after the reaction which supports this suggestion.

The Mo atoms remain in the oxidation state +5 during that fragmentation and aggregation processes, respectively. On the other hand fragment **IV** could stabilize itself by picking up a further PMe_3 ligand yielding $MoOCl_3(PMe_3)_2$ (**4**) as shown in Scheme 1. One possibility for an intimate reduction mechanism involves reversible dissociation of a chlorine radical from $MoOCl_3(PMe_3)_2$ to afford $MoOCl_2(PMe_3)_2$ and Cl in a radical cage. The reduction process should then be triggered by excess of phosphine, this probably occuring with release of chlorine radicals, which chlorinate the solvent. Both the resulting HCl and the $MoOCl_2(PMe_3)_2$ would then eventually be trapped by the phosphine to give $[HPMe_3]Cl$ and **3**. To support this so far purely speculative mechanism, further experiments were performed. As can be seen in Scheme 1 the formation of **3** *via* the mechanism proposed takes at least 4 equiv of PMe_3 with respect to **1** and should therefore not occur on lowering the PMe_3 concentration in the system from 5:1 to 3:1. This assumption suggested the performance of the reaction using only a 3-fold excess of PMe_3 which indeed prevented the solution from turning green and caused the precipitation of appreciable amounts of a red solid. This can be isolated by filtration and purified by washing with toluene in which it is only sparingly soluble. Elemental and spectroscopic analysis showed this solid to be composed of $MoOCl_3(PMe_3)_2$ (**4**), which plays a major role in the mechanism depicted in Scheme 1 since it can be derived from fragment **IV** simply by addition of one PMe_3 ligand. To further prove the intermediacy of **4** during the synthesis of **3** it was reacted with excess PMe_3 in toluene yielding a blue solution of pure **3** and a white precipitate consisting of $[HPMe_3]Cl$ as evidenced by ^{31}P-NMR spectroscopy using D_2O as the solvent. Moreover, bibenzyl might well be a byproduct, although none of the organic products resulting from this reduction could be identified. As mentioned earlier, Chatt et al. observed the reduction of $Cl_4Mo(PR_3)_2$ to $Cl_3Mo(PR_3)_3$ by phosphine,[1] and Poli et al. found reduced products in addition to $[HPMe_3]Cl$ after the reaction of $MoCl_3$ with PMe_3,[17] so that the reactions shown at the bottom of Scheme 1 do not come as a complete surprise. However, these findings clearly support the mechanism proposed in Scheme 1 although the first steps have to remain speculative.

In order to grow crystals of **4** by the overlayering technique the suspension obtained directly after the reaction with PMe_3 was treated slowly with CH_2Cl_2 while stirring, thereby redissolving the solid **4** completely. After the solution was overlaid with petroleum ether 40/60 a microcrystalline bright green material together with large, bichroic green-brown, as well as bright red, well-formed crystals separated from the solution during 1 week. These three products precipitated in different regions on the glass walls of the Schlenk tube and could therefore easily be isolated by hand or alternatively by special washing procedures. Their identification will be discussed below.

The Green-Brown Crystals: None of these crystals examined on the diffractometer was suitable for an X-ray structure determination. By spectroscopic and elemental analysis the thin bichroic material was determined to be of the composition $OMoCl_3(OPMe_3)(PMe_3)$ (**5**). If it is redissolved in CH_2Cl_2 and overlayered with petroleum ether 40/60, dark green crystals separate from this mixture which were suitable for X-ray diffraction, and the result of the structure determination is shown in Figure 2. Bond lengths and angles are presented in Tables 3 and 4. **5** consists of an $O{=}MoCl_3$ fragment stabilized by one PMe_3 and one $OPMe_3$ ligand. The occurrance of the latter ligand can only be explained as follows: Simultanuous to the formation of **4** according to scheme 1 a molybdenum alkoxide based on fragment **III** is generated. This reacts during the long period of crystallization slowly with PMe_3 to produce $O{=}PMe_3$. The source of PMe_3 is either the excess of PMe_3 still present in solution or **4** itself, of which one PMe_3 ligand might be labile in solution and therefore capable of abstracting an oxygen atom from the alkoxide mentioned. After the dissolution of **4** by CH_2Cl_2 and subsequent overlayering of this mixture with petroleum ether 40/60, the $O{=}PMe_3$ thus formed then further reacts with **4** or its dissociation product generating the product **5**, which subsequently cystallizes. If pure **4** is dissolved in CH_2Cl_2 and overlayered with petroleum ether 40/60, neither are suitable crystals of **4** for X-ray diffraction obtained nor is formation of **5** observed, which supports the conclusion that the $OPMe_3$ oxygen has its origin in the alkoxide product of the reaction. **5** can be converted into **3** by treatment with excess of PMe_3, too.

The Red Crystals. The crystals can be freed from any impurities by washing them with CH_2Cl_2. Their spectroscopic and analytical data as well as a crystal structure determination

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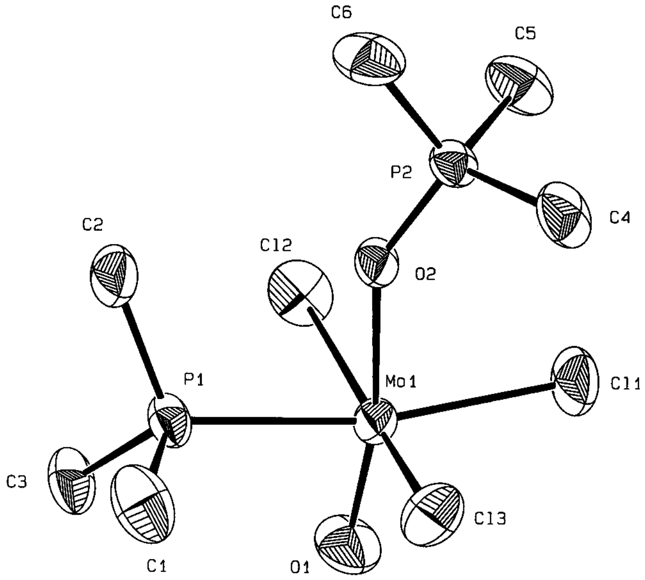

Figure 2. Molecular structure of $MoOCl_3(OPMe_3)(PMe_3)$ (**5**). In the interest of clarity, all hydrogen atoms have been omitted.

Table 3. Bond Distances (Å) for $MoOCl_3(OPMe_3)(PMe_3)$ (**5**)

Mo(1)−O(1)	1.684(4)	P(1)−C(3)	1.807(5)
Mo(1)−O(2)	2.146(3)	P(1)−C(2)	1.802(6)
Mo(1)−Cl(3)	2.363(2)	P(1)−C(1)	1.816(7)
Mo(1)−Cl(2)	2.409(2)	P(2)−C(4)	1.776(6)
Mo(1)−Cl(1)	2.413(2)	P(2)−C(6)	1.779(6)
O(2)−P(2)	2.543(2)	P(2)−C(5)	1.795(6)

Table 4. Bond Angles (deg) in $MoOCl_3(OPMe_3)(PMe_3)$ (**5**)

O(1)−Mo(1)−O(2)	169.5(2)	Cl(1)−Mo(1)−P(1)	167.11(6)
O(1)−Mo(1)−Cl(3)	96.3(2)	P(2)−O(2)−Mo(1)	143.5(2)
O(2)−Mo(1)−Cl(3)	85.5(1)	C(3)−P(1)−C(2)	104.8(3)
O(1)−Mo(1)−Cl(2)	94.3(2)	C(3)−P(1)−C(1)	104.8(3)
O(2)−Mo(1)−Cl(2)	82.8(1)	C(2)−P(1)−C(1)	105.2(4)
Cl(3)−Mo(1)−Cl(2)	167.26(6)	C(3)−P(1)−Mo(1)	110.8(2)
O(1)−Mo(1)−Cl(1)	102.9(2)	C(2)−P(1)−Mo(1)	113.5(2)
O(2)−Mo(1)−Cl(1)	87.4(1)	C(1)−P(1)−Mo(1)	116.7(2)
Cl(3)−Mo(1)−Cl(1)	90.75(7)	O(2)−P(2)−C(4)	111.6(3)
Cl(2)−Mo(1)−Cl(1)	93.77(7)	O(2)−P(2)−C(6)	109.6(3)
O(1)−Mo(1)−P(1)	90.0(2)	C(4)−P(2)−C(6)	106.9(3)
O(2)−Mo(1)−P(1)	79.7(1)	O(2)−P(2)−C(5)	112.2(3)
Cl(3)−Mo(1)−P(1)	88.25(6)	C(4)−P(2)−C(5)	109.1(3)
Cl(2)−Mo(1)−P(1)	84.69(6)	C(6)−P(2)−C(5)	107.2(3)

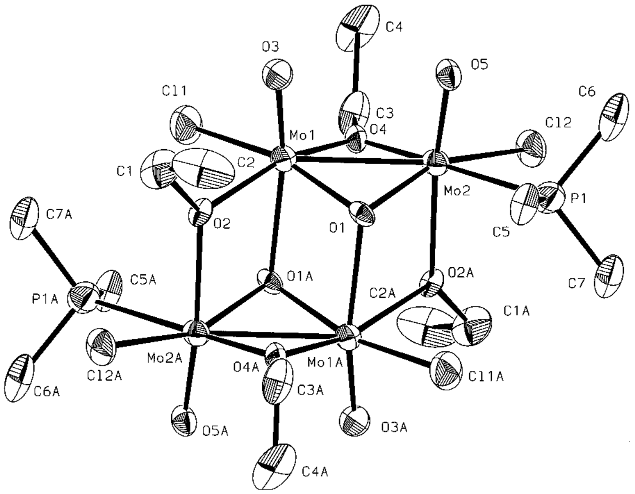

Figure 3. Molecular structure of $Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(PMe_3)_2(\mu_3\text{-}O)_2$ (**6**). In the interest of clarity, all hydrogen atoms have been omitted.

Table 5. Selected Bond Distances (Å) for $Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(PMe_3)_2(\mu_3\text{-}O)_2$ (**6**)

Mo(1)−O(3)	1.68(1)	Mo(1)−O(2)	2.08(1)
Mo(1)−O(1A)	2.25(1)	Mo(1)−O(4)	1.99(1)
Mo(1)−O(1)	2.01(1)	Mo(1)−Cl(1)	2.384(5)
Mo(1)−Mo(2A)	2.683(1)	Mo(2)−O(5)	1.69(1)
Mo(2)−O(1)	1.96(1)	Mo(2)−O(2A)	2.19(1)
Mo(2)−O(4)	2.03(1)	Mo(2)−Cl(2)	2.385(5)
Mo(2)−P(1)	2.612(6)	Mo(2)−Mo(1A)	2.675(2)

Table 6. Selected Bond Angles (deg) in $Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(PMe_3)_2(\mu_3\text{-}O)_2$ (**6**)

O(3)−Mo(1)−O(2)	93.3(5)	O(3)−Mo(1)−O(1A)	163.3(5)
O(2)−Mo(1)−O(1A)	70.1(4)	O(3)−Mo(1)−O(4)	93.2(3)
O(2)−Mo(1)−O(4)	160.1(5)	O(1A)−Mo(1)−O(4)	90.7(4)
O(3)−Mo(1)−O(1)	100.4(5)	O(2)−Mo(1)−O(1)	87.8(4)
O(1A)−Mo(1)−O(1)	77.2(4)	O(4)−Mo(1)−O(1)	93.0(4)
O(3)−Mo(1)−Cl(1)	94.1(5)	O(1A)−Mo(1)−Cl(1)	87.9(3)
O(2)−Mo(1)−Cl(1)	88.0(4)	O(4)−Mo(1)−Cl(1)	86.2(4)
O(1)−Mo(1)−Cl(1)	165.1(3)	Cl(1)−Mo(1)−Mo(2)	135.0(2)
O(3)−Mo(1)−Mo(2)	96.0(4)	O(2)−Mo(1)−Mo(2)	134.8(3)
O(1A)−Mo(1)−Mo(2)	94.2(3)	O(4)−Mo(1)−Mo(2)	48.9(3)
O(1)−Mo(1)−Mo(2)	47.0(3)	Cl(2)−Mo(2)−Mo(1)	136.2(1)
O(5)−Mo(2)−O(1)	103.8(5)	O(5)−Mo(2)−O(2A)	169.9(5)
O(1)−Mo(2)−O(2A)	73.6(4)	O(5)−Mo(2)−O(4)	101.8(5)
O(1)−Mo(2)−O(4)	93.2(5)	O(2A)−Mo(2)−O(4)	88.2(5)
O(5)−Mo(2)−Cl(2)	96.7(4)	O(1)−Mo(2)−Cl(2)	158.6(3)
O(2A)−Mo(2)−Cl(2)	85.2(2)	O(4)−Mo(2)−Cl(2)	88.6(3)
O(5)−Mo(2)−P(1)	81.5(4)	O(1)−Mo(2)−P(1)	91.8(3)
O(2A)−Mo(2)−P(1)	88.7(3)	O(4)−Mo(2)−P(1)	173.2(4)
Cl(2)−Mo(2)−P(1)	85.1(2)	O(5)−Mo(2)−Mo(1)	95.4(4)
O(1)−Mo(2)−Mo(1)	48.4(3)	O(2A)−Mo(2)−Mo(1)	90.0(3)
O(4)−Mo(2)−Mo(1)	47.7(3)		

showed them to consist of the tetrameric cluster $Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(PMe_3)_2(\mu_3\text{-}O)_2$ (**6**) (see Figure 3). **6** is only formed in low yield, being insoluble in solvents like toluene or CH_2Cl_2, which must mean that it is generated during the long period of crystallization *via* a decomposition process of the alkoxide present in the CH_2Cl_2 solution. The structure of **6** can be derived from the one of **2** by exchanging the terminal EtOH ligands by PMe_3 ligands. This apparently has as a consequence the complete insolubility of **6** in all common solvents (which do not decompose this compound) while **2** is slightly soluble in toluene and CH_2Cl_2. Since in the case of **2** it could be proved that the μ_3-O ligand present in the molecule is formed *via* C−O bond cleavage, it is very likely that such a process is responsible for the occurrence of the same ligand in **6** as well. **2** can be converted into **6** by treatment with a 2-fold excess of PMe_3 in low yield. Tables 5 and 6 list the principal bond lengths and angles. The structure consists of a tetrameric arrangement of four O=Mo−Cl units. Each O=Mo−Cl unit is linked by a Mo−Mo bond [2.675(2) Å] and a μ_2-OEt bridge to a second unit to form two dimers in the first place. Additionally, each Mo−Mo bond is spanned by a μ_3-O ligand; this links one dimer by its vacant coordination site to one Mo atom of the second dimer, whose other Mo atom is in turn linked *via* a μ_2-OEt bridge to one of the Mo atoms of the first dimer. Hence the average oxidation state of molybdenum in the cluster is +5, and the four Mo atoms yield a total of four electrons for metal-metal bonding. These are evidently used to form two localized metal−metal single bonds (i) between Mo(1) and Mo(2A) and (ii) between Mo(1A) and Mo(2), so that **6** is diamagnetic.

The bridging μ_2-OEt units are, as in **2**, almost planar in the immediate environment of the O atom. The geometry around the triply bridging oxygen atoms is distorted with three different O(1)−Mo(1,2,1A) bond lengths [*viz.* 2.01(1), 1.99(1), and 2.25(1) Å] and three different Mo-O-Mo angles [*viz.* 102.8(8), 109.1(5), and 84.6(4)° about O(1)]. The $Mo_3(\mu_3\text{-}O)$ interactions therefore afford a nonplanar OMo_3 moiety. The smallest angles and shortest bridges are associated with singly bonded Mo−Mo interactions, while the longest bridging bonds [O(1)−Mo(1) and O(1A)−Mo(1A)] are formed *trans* to terminal Mo=O bonds, in a manner consistent with the *trans* influence of such bonds. The unit formed by the atoms Mo(1), Mo(2A), O(2) and O(1A) is a folded bridge, respectively. Each Mo atom is bonded to a terminal O atom [O(3) and O(5)] at 1.68(1) and 1.69(1) Å. These oxygen atoms are in eclipsed positions, and the fold in the bridge decreases the contact between them. The Mo−O distances of the bridge are 1.99(1), 2.03(1), 2.01(1), and 1.99(1) Å, the Mo−O−Mo angles are 84.6(4) and 83.4(5)°, and the O−Mo−O angles are 93.0(4) and 93.2(5)°. It appears, then, that the bridge is remarkably symmetrical, despite the fact that O(2) belongs to an ethoxy ligand, whereas O(1) is an oxide ligand. Overall, the complex possesses an inversion center. The building blocks are most aptly described as distorted octahedra since the Mo−Mo bonds have little effect on the geometries of the individual coordination polyhedra. The four octahedra are linked together through edges in a manner similar to that found in $Ti_4(OEt)_{16}$,[18] the structure of which, determined in 1963, afforded the first experimental evidence in support of Bradley's theory regarding metal alkoxides (based on the desire of metal atoms to achieve their preferred coordination environments by the minimum degree of oligomerization).[19]

Apart from **2** the compounds $[Mo_4O_4Cl_4(\mu_3\text{-}O)_2(\mu_2\text{-}O^nPr)_4(HO^nPr)_2]$,[20,21] $[Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_2(O^iPr)_2(py)_4]$,[18] $\{Mo_4O_4Cl_4(\mu_2\text{-}OEt)_2(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(HOEt)_2]^{2-}\}$,[21,22] and $\{Mo_4O_4Cl_4(\mu_2\text{-}OH)_2(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(Hpz^{Me}2)_6]I_2\}$[23] also adopt structures comparable to **6**.

The Green Crystals. To unravel the identity of the green crystals co-crystallizing in the lower part of the Schlenk tube, they were purified by washing with CH_2Cl_2 (in which they are only marginally soluble) and analyzed subsequently. The data gave strong evidence that the compound has the constitution $[Me_3PH]^+[MoOCl_4PMe_3]^-$ (**7**). Formallly **7** can be derived from **4** by addition of 1 equiv of HCl. Since **7** is formed in low yields only on addition of CH_2Cl_2 to the reaction mixture, this solvent might be the source of HCl in a slow decomposition process. A control experiment to prove this statement inculded careful treatment of a CH_2Cl_2 solution of **4** with gaseous HCl. Although it did not lead to the synthesis of **7** rather than the immediate precipitation of pure $[Me_3PH]_2^+[MoOCl_5]^{2-}$ (**8**) (representing the product of addition of *2* equiv of HCl to **4**), this experiment still supports the formation of **7** *via* a contact of **4** with HCl. Only the very low HCl concentration under the conditions mentioned above and the insolubility of **7** in organic solvents allow its isolation and crystallization as described in the experimental part. Consequently, **7** can be converted into **8** *via* its dissolution in pure HCl_l at −30 °C in a high pressure tube. After evaporation of the HCl the residue consists of pure **8**.

After we found that no suitable crystals of **4** can be obtained using the overlayering technique, its crystallization was successfully attempted by cooling a CH_2Cl_2 solution of **4**. Its crystal structure is shown in Figure 4 and its bond lengths and angles are presented in Tables 7 and 8. In contrast to **5** in **4** the three Cl atoms are coordinated in a *fa*c fashion with one Cl ligand in a trans position to the O=Mo unit, a result suggesting the following sequence of ligand strength: $PMe_3 > Cl >$ $OPMe_3$. This is provided that the structures found for **4** and **5** represent the thermodynamically most stable stereoisomers. Moreover exchanging PMe_3 in **4** by $OPMe_3$ to yield **5** seems not only to cause significant structural changes but also to influence the electronic properties. Although both compounds are d^1-systems **5** is a bright green compound while **4** has a purple color. This observation is of course also reflected in their solution UV/vis spectra. In principle in both spectra CT-bands can be found at the same positions (ca. 300, 335, and 400 nm) but with quite different intensity ratios. **4** additionally gives rise to a band at 512 nm, which is responsible for its intense color. Complexes of $O{=}Mo^{3+}$ usually show two low-intensity low-energy bands: The first one around 750 nm is agreed to belong to a b_2^* ($4d_{xy}$, Mo−Cl π^*) → e^* ($4d_{xz,yz}$, Mo−O π^*) transition; the second one around 450−550 nm, however, was initially assigned to a b_2^* ($4d_{xy}$, Mo−Cl π^*) → b_1^* ($4d_{x^2-y^2}$, Mo−Cl σ^*) until Garner et al. provided strong evidence that an e(O $2p_{xy}$, Mo−O π) → b_2^*($4d_{xy}$, Mo−L(*cis*) π^*) CT transition should be responsible.[24] Its extinction coefficient varies for $OMoCl_3L_2$ complexes from 20 to 80 M^{-1} cm^{-1} depending on the nature of L causing the compounds to be of either green or red-brown appearance [L_2 = β-diketonates,[25] diphos,[26] phen[27] (brown), L = PPh_3,[28] $OP(NMe_2)_3$,[24] Cl,[29]

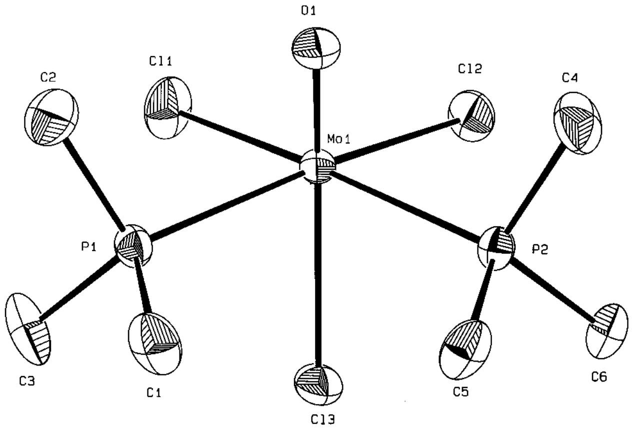

Figure 4. Molecular structure of $MoOCl_3(PMe_3)_2$ (**4**). In the interest of clarity, all hydrogen atoms have been omitted.

Table 7. Bond Distances (Å) for $MoOCl_3(PMe_3)_2$ (**4**)

Mo(1)−O(1)	1.676(4)	P(1)−C(3)	1.807(5)
Mo(1)−P(2)	2.5606(6)	Mo(1)−P(1)	2.5651(7)
P(1)−C(3)	1.800(3)	P(1)−C(2)	1.804(3)
Mo(1)−Cl(2)	2.3739(6)	P(1)−C(1)	1.808(3)
Mo(1)−Cl(1)	2.3877(7)	P(2)−C(4)	1.807(3)
Mo(1)−Cl(3)	2.5016(6)	P(2)−C(6)	1.809(2)
O(2)−P(2)	2.543(2)	P(2)−C(5)	1.809(3)

Table 8. Selected Bond Angles (deg) in $MoOCl_3(PMe_3)_2$ (**4**)

O(1)−Mo(1)−P(2)	86.48(6)	Cl(3)−Mo(1)−P(2)	79.21(2)
O(1)−Mo(1)−Cl(3)	156.95(6)	P(2)−Mo(1)−P(1)	104.04(2)
P(1)−Mo(1)−Cl(3)	79.19(2)	C(3)−P(1)−C(2)	105.6(2)
O(1)−Mo(1)−Cl(2)	104.01(6)	C(3)−P(1)−C(1)	103.6(1)
P(1)−Mo(1)−Cl(2)	167.72(2)	C(2)−P(1)−C(1)	104.1(2)
Cl(1)−Mo(1)−Cl(3)	93.83(2)	C(3)−P(1)−Mo(1)	115.07(9)
O(1)−Mo(1)−Cl(1)	102.42(6)	C(2)−P(1)−Mo(1)	108.0(1)
P(1)−Mo(1)−Cl(1)	81.81(2)	C(1)−P(1)−Mo(1)	119.09(9)
Cl(2)−Mo(1)−Cl(3)	91.99(2)	Cl(1)−Mo(1)−P(2)	169.72(2)
Cl(2)−Mo(1)−Cl(1)	90.35(2)	C(4)−P(2)−C(5)	104.4(1)
O(1)−Mo(1)−P(1)	86.98(6)	C(4)−P(2)−C(6)	104.8(1)
Cl(2)−Mo(1)−P(2)	82.42(2)		

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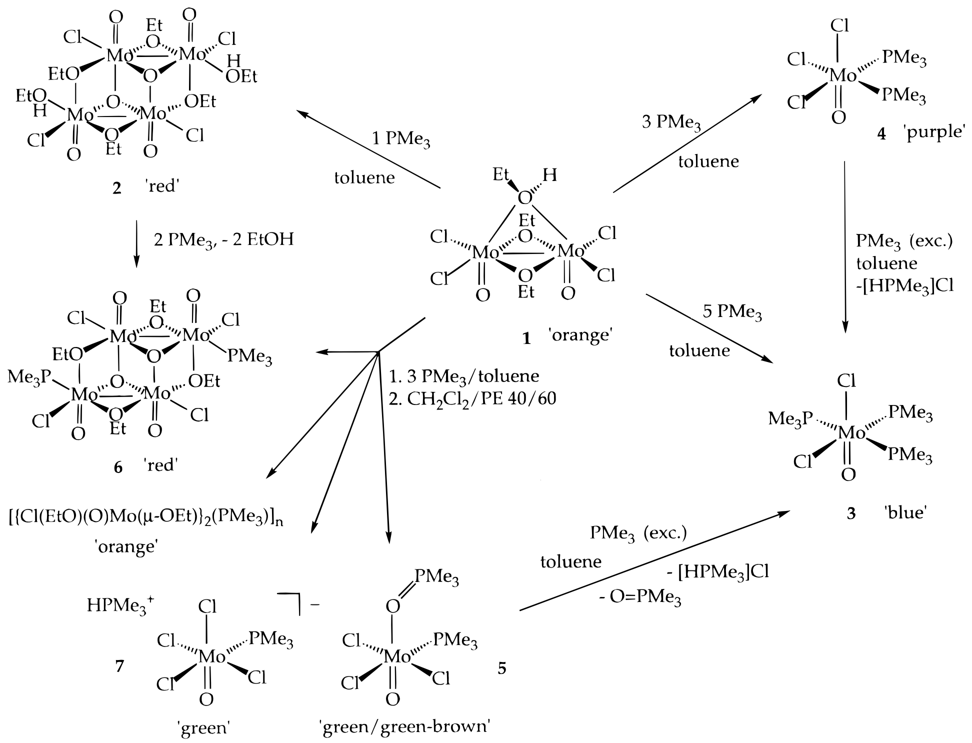
Scheme 2



$OPMe_3$,[30] $PMe_3/OPMe_3$ (green)]. However, in purple **4** this transition is extraordinarily high [ϵ = 1074 M^{-1} cm^{-1}], supporting Garners theory. In order to determine which structural arrangments (e.g. *fac*- or *mer*-coordination of the three Cl ligands) or ligand properties do take influence on ϵ more detailed structural information about such complexes especially for L = PRR′R″ would be necessary. It is interesting for instance that $OMoCl_3(PR_3)_2$ compounds are green for R = Ph[28] and purple for R = Me (**4**), although for $OMOCl_3(PPh_3)_2$ a *fac*-coordination of the Cl-ligands was suggested as well. Unfortunately, although quite a number of $OMoCl_3L_2$ complexes are known, to our knowledge **4** is the only one for which an X-ray structure determination was performed, so that a comparison with other structures is impossible. After the identification of compounds **3**−**7** there is one question remaining:

What happens to fragment III during the reactions of **1** with 3 equiv of PMe_3? Of course one hint is given by the isolation of **6**, although this compound, as mentioned earlier, is only a secondary product, formed in low yield by decomposition of an alkoxide. After crystallization of compounds **5**−**7**, the remaining brown solution was further overlayered with petroleum ether 40/60, which led to the precipitation of orange needles within 1 week. Their ^1H NMR spectrum is complicated but suggests that the compound contains three alkoxide groups in different environments and one PMe_3 ligand per two Mo atoms. Taking into account the elemental analysis, it is possible to suggest the compound to be an oligomer of the fragment [Cl(EtO)(O)Mo(μ-OEt)$_2$Mo(O)(OEt)(PMe_3)Cl], which could pretty well have its origin in fragment **III** of Scheme 1. IR and MS spectra did not give any further clues concerning the overall constitution and unfortunately the crystals were not suitable for X-ray diffraction so that their structure must remain unclear. They are formed in high yield though and can therefore account for the missing compound resulting from aggregation of fragment **III**. This alkoxide is probably supplying the oxygen for the generation of O═PMe_3 being found as a ligand in **5** as well as representing the parent compound of **6** which must be a product of its decomposition reaction.

In conclusion, this work sheds light into the very complex and sensitive system **1**/PMe_3 which is summarized in Scheme 2, and generates reproducibly simple oxomolybdenum chloride−phosphine complexes in addition to complex alkoxides *via* fragmentation of a metal alkoxide by a Lewis base.

Experimental Details

All manipulations were carried out with a vacuum line (at a background pressure of $<10^{-4}$ mbar) or else, in a glovebox, or by means of Schlenk-type techniques involving the use of a dry nitrogen atmosphere. Solvents were dried according to standard procedures; microanalyses were performed by the Analytische Laboratorien des Organisch-Chemischen Institutes der Universität Heidelberg. IR spectra were recorded with a Bruker IFS 66 FTIR spectrometer. ^1H and ^{31}P NMR spectra of solutions were recorded using a Bruker AC 200 instrument operating at 200 MHz. The deuteriated solvents had been condensed into the NMR tubes previously before they tubes were flame-sealed. UV/vis-spectra were measured on a Perkin Elmer Lamda 19 UV/vis/near-IR spectrophotometer (reflection spectra were obtained from carefully powderized samples in LiF, while solution spectra were taken in 10^{-3} M solutions in CH_2Cl_2). The DSC measurements were performed on a Mettler TG 50 thermobalance. 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. X-ray powder diagrams were obtained on a Siemens D500 powder diffractometer. FAB MS spectra were recorded with a Finnigan MAT 8230.

Synthesis of Dichloro(oxo)tris(trimethylphosphine)molybdenum(IV), 3. A 2.20 g (4.25 mmol) sample of **1**$\cdot 0.225CH_2Cl_2$[15] was loaded, together with a stir bar, into a flamed-out Schlenk-tube under an inert atmosphere. Then 20 cm^{-3} of toluene were added *via* cannula, the solid dissolved, and while the resulting solution was being stirred, it was reacted with 21 cm^{-3} of a 1 M PMe_3 solution in toluene. This caused the mixture to turn dark red initially, changing color to dark green after 12 h at room temperature. At the same time small amounts of dark red crystals precipitated. The filtrate was overlayered with

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Table 9. Selected Crystallographic Data for **3**−**6**

	3	**4**	**5**	**6**
empirical formula	$C_9H_{27}Cl_2MoOP_2$	$C_6H_{18}Cl_3MoOP_2$	$C_6H_{18}Cl_3MoO_2P_2$	$C_{14}H_{38}Cl_4Mo_4O_{10}P_2$
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	17.138(3)	6.468(1)	6.783(3)	11.176(2)
b/Å	12.808(3)	12.677(2)	12.623(4)	11.616(2)
c/Å	19.226(4)	17.791(2)	18.298(8)	12.771(3)
β/deg	115.99(1)	92.64(1)	98.58(3)	109.81(1)
V/Å^3	3793.40	1457.2(4)	1549.20	1559.50
Z	8	4	4	2
fw	411.055	370.43	386.430	953.940
T/K	210	200	200	200
λ/Å	0.71073	0.71073	0.71073	0.71073
R_1[a]	0.0372	0.0236	0.0369	0.080
wR_2[b]	0.0985	0.0588	0.1043	0.211
ρ_{calc}/g·cm^{-3}	1.440	1.688	1.657	1.982
μ/cm^{-1}	12.10	16.38	15.49	20.08

[a] $R_1 = \sum\{|F_o| - |F_c||/\sum|F_o|\}$ based on $I > 2\sigma(I)$. [b] $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{0.5}$, where w = weighting factor.

200 cm^{-3} of petrol ether 40/60 and within 6 d 0.82 g (2.20 mmol) of blue crystals of **3** formed. These decompose on heating between 60 and 90 °C, turning dark. More easily **3** can be isolated by simply cooling the filtrate to −80 °C which causes **3** to precipitate almost quantitatively from the solution.

IR (KBr)/cm^{-1}: $\tilde{\nu}$ = 2975 (w), 2908 (m), 1421 (m), 1300 (w), 1284 (s), 953 (vs), 854 (m), 733 (m), 671 (m). δ ^{31}P{^{1}H}(CDCl$_3$): −2.70 (t, ^2J(PP) = 21.61 Hz, 2P), −10.56 (d, ^2J(PP) = 21.61 Hz, 1P). δ^{1}H (C_6D_6): 1.40 (pt, N(PH) = 3.87 Hz, 18H), 1.30 (d, ^2J(PH) = 8.24 Hz, 9H). MS (FAB in Nibeol), m/z (%): 413 (19) [M$^+$ + H], 377 (69) [M$^+$ − Cl], 337 (98) [M$^+$ + H − Cl], 301 (100) [M$^+$ − PMe$_3$ − Cl], 260 (32) [M$^+$ + H −2PMe$_3$], 224 (12) [M$^+$ − 2PMe$_3$ − Cl]. Anal. Calcd for $C_9H_{27}Cl_2MoOP_3$ (M_r = 411.055): C, 26.30; H, 6.62; Cl, 17.25; P, 22.60. Found: C, 26.15; H, 6.56; Cl, 17.70; P, 22.12.

X-ray Crystallography of 3. Crystals obtained by the overlayering technique as described above were sealed in a matrix of an inert oil, and one of them was loaded on top of a fiber. Crystal data collection and refinement parameters are collected in Table 9. 2θ range = 4.0−42.0°; independent reflections, 4080; reflections with $I > 2\sigma$, 3598; R_1 = 0.0372, R_w = 0.0985, GOOF = 1.056; largest difference peak, 0.58 × 10^{-6} e/pm^3. Two independent molecules were found in the unit cell; in the second molecule the PMe$_3$ groups P(22) are rotationally disordered. Therefore C(221), C(222), and C(223) were refined anisotropically, but the residual C atoms participating in the disorder, however, were refined isotropically.

Trichloro(oxo)bis(trimethylphosphine)molybdenum(V), 4, and Bis(trimethylphosphonium) Pentachloro(oxo)molybdate(V). The synthesis was performed in close analogy to the one of **3** with the only difference that this time 4.00 g (7.4 mmol) of **1**·2.25 CH$_2$Cl$_2$, 20 cm^{-3} of toluene, and 22 cm^{-3} of the PMe$_3$ solution were employed. In this case the solution was still red after 12 h and a purple solid had precipitated. This was washed twice with toluene and dried under vacuum, yielding 3 g (6.0 mmol, 81%) of pure **4**.

UV/vis (1 × 10^{-3} M in CH$_2$Cl$_2$)/nm (M^{-1} cm^{-1}): 334 (3074), 407 (566), 512 (1074). IR (KBr)/cm^{-1}: $\tilde{\nu}$ = 2972 (w), 2904 (w), 1428 (m), 1413 (m), 1284 (s), 1110 (w), 963 (vs), 850(w), 748 (s). MS(EI), m/z (%): 370 (7) [M$^+$ − H], 352 (25) [M$^+$ − OH], 336 (50) [M$^+$ − HCl], 260 (56) [M$^+$ − HPMe$_3$Cl], 111 (81) [PMe$_3$Cl$^+$], 76 (100) [PMe$_3$]. Anal. Calcd for $C_6H_{18}Cl_3MoOP_2$ (M_r = 370.430): C, 19.44; H, 4.90. Found: C, 19.60; H 5.07. Slow diffusion of HCl gas into a red CH$_2$Cl$_2$ (20 cm^3) solution of 0.050 g (0.135 mmol) of **4** on a standard vacuum line under exclusion of air resulted in the precipitation of quantitative amounts of $[Me_3PH]_2{}^+[MoOCl_5]^{2-}$ (**8**) (0.055 g, 92%), accompanied by complete decolorization of the solution. IR (KBr)/cm^{-1}: $\tilde{\nu}$ = 2992 (s), 2911 (m), 1428 (w), 1413 (m), 1290 (m), 1110 (m), 1009 (s), 975 (vs), 953 (vs), 799 (w). MS(FAB in Nibeol), m/z (%): 408 (30) [M$^+$ − Cl], 368 (100) [M$^+$ − PMe$_3$ + H], 333 (16) [M$^+$ − OPMe$_3$]. Anal. Calcd for $C_6H_{20}Cl_5MoOP_2$ (M_r = 443.424): C, 16.25; H, 4.54. Found: C, 15.95; H 4.50.

X-ray Crystallography of 4. Crystals obtained by cooling a CH$_2$Cl$_2$ solution were sealed in a matrix of an inert oil, and one of them was loaded on top of a fiber. Crystal data collection and refinement parameters are collected in Table 9. 2θ range = 3.9−54.00°; independent reflections, 3184; reflections with $I > 2\sigma$, 2881; R_1 = 0.0236, R_w = 0.0588, GOOF = 1.062; largest difference peak, 0.556 × 10^{-6} e/pm^3.

Trichloro(oxo)(trimethylphosphine)(trimethylphosphine oxide)-molybdenum(V), 5, $Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(PMe_3)_2(\mu_3\text{-}O)_2$, 6, and Trimethylphosphonium Tetrachloro(oxo)(trimethylphosphine)molybdate-(V), 7. After the reaction described above for the synthesis of **4** the solid obtained was dissolved only just by slow addition of CH$_2$Cl$_2$. The red solution was filtered and overlayered with 200 cm^{-3} of petroleum ether 40/60, which caused the precipitation of 1.5 g (3.9 mmol, 52 %) of **5** in the form of brown-green crystals, an additional 150 mg of **7**, and 90 mg of **6**, within 6 d. Since the crystals of these three compounds separated in different regions of the Schlenk tube, they could easily be isolated by hand. **6** and **7** could further be purified by washing with CH$_2$Cl$_2$. A different working up procedure would include the extraction of **4** by CH$_2$Cl$_2$ and subsequent extraction of **7** with EtOH leaving behind pure **6**. **7** cannot be reisolated from the ethanolic solution.

5: Mp 184.2 °C. UV/vis (in LiF)/nm: 318, 437, 675 nm. UV/vis (1 × 10^{-3} M in CH$_2$Cl$_2$)/nm (M^{-1} cm^{-1}) 292 (3600), 335 (1400), 403 (2125). IR (KBr): $\tilde{\nu}$ = 2986 (w), 2908 (w), 1460 (m), 1311 (m), 1293 (s), 1287 (s), 1106 (vs), 969 (vs), 860 (m), 874 (w), 755 (s), 671 (w). MS(EI), m/z (%): 311 (11) [M$^+$ − PMe$_3$], 276 (40) [M$^+$ − PMe$_3$ − Cl], 241 (2) [M$^+$ − PMe$_3$ − 2Cl], 200 (10) [M$^+$ − 2PMe$_3$], 76 (100) [PMe$_3$]. Anal. Calcd for $C_6H_{18}Cl_3MoO_2P_2$ (M_r = 386.43): C, 18.65; H, 4.66; Cl, 27.56; P, 16.06. Found: C, 18.69; H, 4.76; Cl, 27.33; P 15.89.

Green crystals of **5** can be generated by dissolving the brown crystals in CH$_2$Cl$_2$ and overlayering the solution with petroleum ether 40/60. Mp: 193.9 °C. UV/vis (in LiF)/nm: 299, 416, 652. Although differing from the brown-green crystals in their melting point (in order to determine the melting point more precisely DSC measurements have been performed) and solid state UV/vis spectrum, they otherwise show identical properties (including their UV/vis spectra in solution, elemental analyses, and powder diffraction patterns). Further experiments showed that the green form of **5** is formed with an increasing concentration of CH$_2$Cl$_2$ in the crystallization vessel. Since the brown crystals have the same analytical data as the green ones, it has to be assumed that they represent some kind of geometrical isomers the brown crystals being kinetically favored under the conditions of crystallization while the green form is the thermodynamically more stable isomer. Such an isomerism could lead to different melting points and solid-state UV/vis spectra, while possibly the crystals are isotypical yielding similar powder diffraction patterns. Brought into solution again, the brown form rearranges so that the solution UV/vis spectra of both forms are identical.

X-ray Crystallography of 5. Crystals obtained by the overlayering technique as described above were sealed in a matrix of an inert oil, and one of them was loaded on top of a fiber. Crystal data collection and refinement parameters are collected in Table 9. 2θ range = 3.9−

46.0°; independent reflections, 2154; reflections with $I > 2\sigma$, 1739; $R_1 = 0.037$, $R_w = 0.143$, GOOF = 0.847; largest difference peak, 0.42×10^{-6} e/pm^3.

6: IR (KBr)/cm^{-1}: $\tilde{\nu} = 2974$ (w), 1441 (m), 1378 (w), 1279 (w), 1082 (m), 1031 (s), 979 (vs), 952 (vs), 952 (vs), 903 (m), 882 (m), 650 (s), 519 (m). Anal. Calcd for $C_{14}H_{38}Cl_4Mo_4O_{10}P_2$ (M_r = 943.56): C, 17.62; H, 3.98; Cl, 14.87. Found: C, 17.44; H, 4.09; Cl, 14.58. **6** is insoluble in common organic solvents.

X-ray Crystallography of 6. Crystals obtained by the overlayering technique as described above were sealed in a matrix of an inert oil, and one of them was loaded on top of a fiber. Crystal data collection and refinement parameters are collected in Table 9. 2θ range = 3.9−50.0°; independent reflections, 2750; reflections with $I > 2\sigma$, 1379; $R_1 = 0.080$, $R_w = 0.211$, GOOF = 0.952; largest difference peak, 1.13×10^{-6} e/pm^3. The comparatively high values for R are due to the very small dimensions of the crystal investigated.

7: mp 221.6 °C (dec. UV/vis (LiF)/nm: 318, 437, 675. IR (KBr)/cm^{-1}: $\tilde{\nu} = 2992$ (m), 2908 (m), 1450 (m), 1309 (m), 1290 (m), 1091 (m), 973 (m), 957 (s). MS(FAB in Nibeol), *m/z* (%): 408 (30) [$M^+ + H$]. Anal. Calcd for $C_6H_{19}Cl_4MoOP_2$ (M_r = 406.96): C, 17.71; H, 4.70; Cl, 34.84; P, 15.23. Found: C, 17.86; H, 4.86; Cl, 34.55; P, 15.21. **7** is insoluble in common organic solvents. In D_2O the phosphonium cation exanges H against D, yielding a ^{31}P-NMR resonance at −2.63 (t, $^1J(P-D) = 77.8$ Hz, *P*D).

X-ray Structure Determination of 3, 4, 5, and 6. In some cases before the actual data collection crystals proved to show only very weak reflections at higher values of θ and accordingly relatively low θ ranges were employed for the measurement. In all cases an experimental absorption correction using ψ-scan, $\Delta\psi = 10°$ was applied. All calculations were performed using SHELXT PLUS software package. Final refinement used the SHELXL-93[32] and SHELXS-86[31] programs.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **3**−**6** are available on the Internet only. Access information is given on any current masthead page.

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