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Synthesis of Heterometallic Bismuth/Molydenum Alkoxides and Their Behavior on Silica Surfaces[§]

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The reaction of $[(C_3H_5)Mo(CO)_2(CH_3CN)_2Cl]$, **2**, with $[Bi(OCH_2CH_2OCH_3)_3]_2$ on a large scale leads to the novel molybdenum/bismuth alkoxide $[(C_3H_5)Mo(CO)_2(\mu\text{-}\kappa O,2\kappa O'\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}\kappa O\text{-}OCH_2CH_2OCH_3)BiCl]$, **6**, as the main product as well as to $[(C_3H_5)Mo(CO)_2(\mu\text{-}\kappa O,2\kappa O'\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}Cl)BiCl]$, **4**, as a byproduct. Both compounds were characterized by elemental analysis, IR, and NMR spectroscopy as well as by X-ray diffraction. If **6** is brought into contact with a large excess of silica gel, aggregation and condensation reactions are initiated, which led to clusters of ca. 200 nm size spread over the silica surface. When the resulting material is calcinated at 350 °C in the presence of O_2, all organic ligands are eliminated and the metal oxo units rearrange: SEM/EDX measurements showed afterward Mo-free bismuth oxo clusters with sizes between 30 and 1000 nm, which are distributed together with molybdenum oxo particles of lower nuclearity over the silica surface. If such a material is employed as a potential catalyst for the propene oxidation under technical conditions, no activity is observed. If, however, the process is performed under very low pressures, a conversion of 5% is found. This result is discussed in the context of the mechanism proposed for the technical oxidation of propene to acrolein on bismuthmolybdate catalysts.

Introduction

The unique property of $n MoO_3/Bi_2O_3$ phases to act as catalysts for the allylic oxidation of propene[1] remains a subject of intense discussion.[2] The results of recent investigations concerning heterogeneous oxidations on Mo/Bi oxide surfaces suggest that the oxygen atoms found in the organic oxidation products have their origin in previously *bridging* positions,[3−5] so that Bi(μ-O)Mo moieties are currently thought to be the active oxo transfer sites also during the propene oxidation. This encourages research with the aim of preparing molecular species containing both Mo and Bi being linked by oxygen-containing, or ideally "pure", oxo ligands.[6] In this context we have recently reported the first heterometallic Mo/Bi alkoxide complexes.[7,8] Their syntheses was achieved starting from molybdenum organyls, where a part of the coordination sphere at Mo is shielded by tightly bound organic ligands: $[Cp_2MoCl_2]$ was chosen to be treated with in situ prepared $[Bi(OEt)_3]_x$, yielding $[Cp_2Mo(\mu\text{-}OEt)_2Bi(OEt)_2Cl]$, **1**, with a Mo and a Bi center being bridged by two ethanolate ligands.[7] Reaction of $[((CH_3)C_3H_4)Mo(CO)_2(CH_3CN)_2Cl]$, $\mathbf{2^{me}}$ (the suffix "me" denotes the methyl substitution at the allyl ligand), with $[Bi(OEt)_3]_x$ provided the heterotetranuclear complex $[((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}OEt)_3Bi(\mu\text{-}OEt)_2Bi(\mu\text{-}OEt)_3Mo(CO)_2((CH_3)C_3H_4)]$, $\mathbf{3^{me}}$, in good yields,[8] and treatment with $[Bi(OCH_2CH_2OCH_3)_3]_2$, a dinuclear chloro alkoxide $[((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}\kappa O,2\kappa O'\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}Cl)BiCl]$, $\mathbf{4^{me}}$. Pretreatment of $\mathbf{2^{me}}$ with

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[§] Dedicated to Prof. Dr. G. Huttner on the occasion of his 65th birthday.

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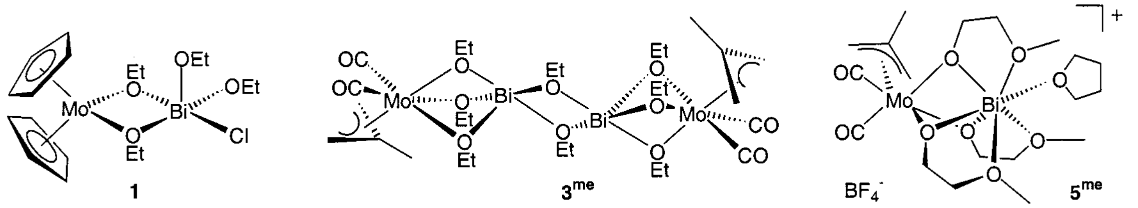
Scheme 1



$AgBF_4$ and subsequent reaction with $[Bi(OCH_2CH_2OCH_3)_3]_2$ further led[8] to the chloride-free complex $[((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}\kappa O,2\kappa O'\text{-}OCH_2CH_2OCH_3)_3Bi(thf)][BF_4]$, **5**^{me}.

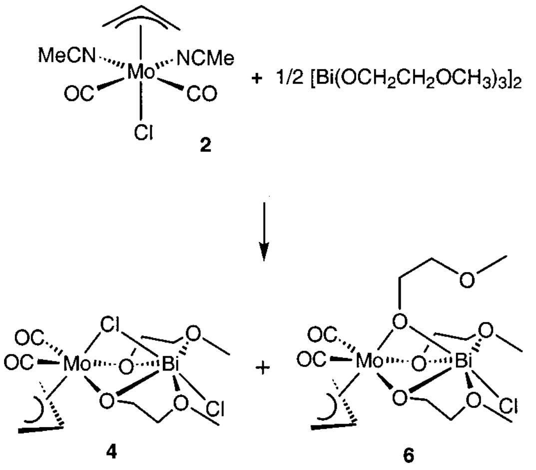
Hence, organomolybdenum/bismuth alkoxides (that bring together main group and transition metal chemistry as well as organometallic and coordination chemistry) are accessible now.

At this stage it seemed reasonable to contemplate the following: It is known that only the *combination* of Bi and Mo effect the heterogeneous propene oxidation[1−5] (neither neat MoO_3 nor neat Bi_2O_3 is capable of producing acrolein), and metal alkoxides have established themselves as useful starting materials for the deposition of the parent metal *oxides*. Considering that for the first time (and uniquely) we had molecular compounds at hand that are composed of Mo as well as Bi centers being linked by alkoxide ligands, naturally the question arose, whether such complexes can also serve as suitable single-source precursors for the deposition of novel molybdenumoxo/bismuthoxo structures on inert supports. This was to be investigated, however, not with the target of developing an improved catalyst for the propene oxidation: even if this were possible, such a catalyst would not be capable of competing with the easily accessible, cheap bismuthmolybdates employed so far. The goal was primarily to modify such catalysts in order to possibly obtain information concerning their function.

Results and Discussion

Synthesis of a Suitable Molybdenumbismuth Alkoxide. In the first step of this investigation it was necessary to scale-up the synthesis of a suitable MoBi alkoxide, so that it would be employable in a series of experiments in sufficient quantities. Compounds **3**^{me} and **1** were excluded due to their high sensitivities, and **5**^{me} was excluded because of its ionic character. This led us to perform the synthesis that had provided **4**^{me} on a larger scale but with an *allyl* instead of a *methallyl* ligand, as previous studies[9] had suggested that methyl substitution on the allyl ligand has no influence on the product formation. **2** was thus reacted with $[Bi(OCH_2CH_2OCH_3)_3]_2$ in a 2:1 ratio on a 0.18 molar scale (Scheme 2). An orange solution and a brown precipitate formed (in close analogy with the reaction that had led to **4**^{me}), which were separated via filtration. On cooling of the solution, large amounts of a yellow-orange microcrystalline material precipitated together with smaller quantities of orange-red crystals. Both compounds were separated from each other mechanically in a glovebox, recrystallized independently, and subsequently investigated by means of IR and NMR spectroscopy, single-crystal X-ray diffraction, and elemental analyses: the minor product was identified as the expected derivative of **4**^{me}, $[(C_3H_5)Mo(CO)_2(\mu\text{-}\kappa O,2\kappa O'\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}Cl)BiCl]$, **4**, while the major product proved to consist of $[(C_3H_5)Mo(CO)_2(\mu\text{-}\kappa O,2\kappa O'\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}\kappa O\text{-}OCH_2CH_2OCH_3)BiCl]$, **6**, which represents a new type of Mo/Bi-alkoxide complex. **6** actually is the more "reasonable product" of a 1:1 stoichiometry reaction of **2** and the monomeric $[Bi(OCH_2CH_2OCH_3)_3]$ unit (as employed), since it contains all their components (except for the acetonitrile ligands) in an exact 1:1 ratio (note that due to its two Cl ligands, **4** can only form in a 2:1 reaction). The solubility of **6** at −30 °C in thf is far lower than that of **4**, which much facilitates their separation. Why has a product corresponding to **6** (**6**^{me}) not been isolated after the experiments that had led to **4**^{me}? As reported,[8] in the former experiments three different allylmolybdenum species formed, whose ratio depended on the ratio of the starting materials employed and of which only **4**^{me} could be crystallized/identified. In light of the present findings one of the two other species might have been **6**^{me}, the methallyl derivative of **6**. A possible reason for the failure to isolate **6**^{me} in the former experiments might be a potentially higher solubility in thf, leading to a situation where **4**^{me} crystallizes first (as opposed to **4**, which is more soluble than **6**). In addition, a scale-up of the reaction seems to shift the product ratio significantly into the direction of the product of stoichiometrical conversion (see above).

Scheme 2



Naturally, the crystal structure of **4** (Figure 1) is not so much different from the one[8] adopted by **4**^{me}, where the arrangement of ligands around the Mo center is comparable

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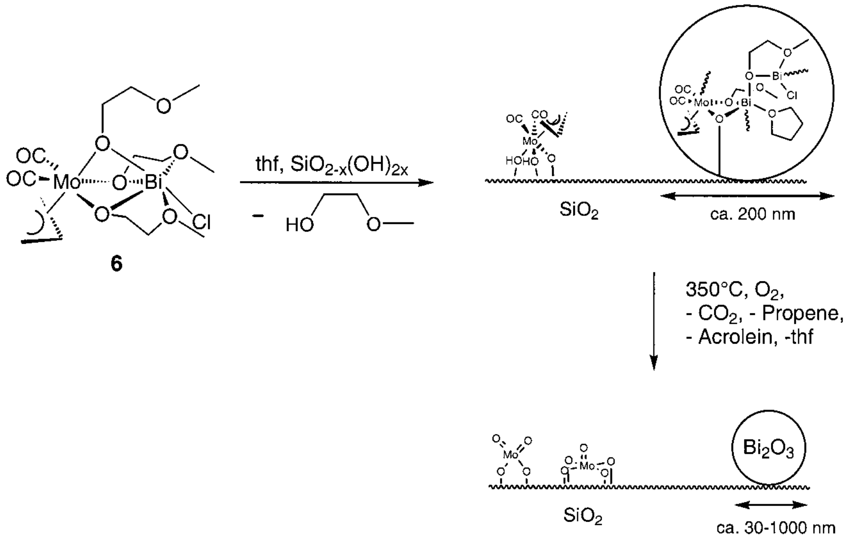
(9) (a) Compare: Borgmann, C.; Limberg, C.; Zsolnai, L.; Heinze, K. Z. *Naturforsch.* **1999**, *54b*, 473−481. (b) Hunger, M. Ph.D. Thesis, Heidelberg, 1999.

Scheme 3



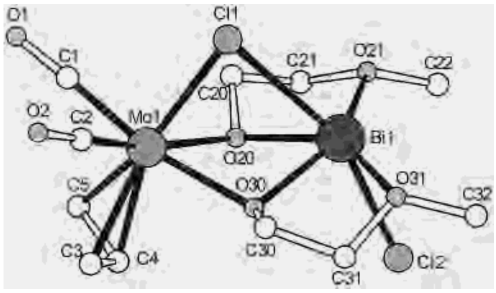


Figure 1. Molecular structure of **4**·0.8thf with partial atom-labeling scheme. The thf solvent molecule has been omitted for clarity.

to that found in the anion[9a] $[(C_3H_5)Mo(CO)_2(\mu\text{-}OMe)_3Mo(CO)_2(C_3H_5)]^-$, leading to similar (slightly longer) Mo−O bond distances. The conformation of the allyl ligand concerning a plane constructed from the two carbonyl carbons and the terminal carbon atoms of the allyl ligand is *exo*, an arrangement that is often found to be more stable in comparison with the corresponding *endo* conformation[10] and that is frequently accompanied by a decreased $M(CO)_2$ angle (<90°), while the angle in *endo* structures is increased (>90°).[11] Accordingly, the $Mo(CO)_2$ angle in **4** amounts to only 75.9(2)°. The bridging Cl ligand is found in *trans* positions to the allyl group at the Mo center and to the terminal Cl ligand at the Bi center [Cl−Bi−Cl = 159.2(1)°]. The Bi−Cl(2) bond length of 2.527(4) Å is quite similar to the average of 2.532 Å found in a $Cl_3Bi(\mu\text{-}O(R)-)_3$ moiety[12] and typical for terminal Bi−Cl bond distances, which are usually about 2.6 Å.[13] The Bi−Cl(1) bond, 2.876(4) Å, is comparatively long (even for a bridging Cl ligand), and it should therefore be regarded as weak.[14] The additional four donor functions provided by the alkoxide ligands force the Bi center into a coordination sphere that could be described as a distorted pentagonal bipyramid, if the lone pair of the Bi center is assumed to be stereoactive: O(20/21/30/31) are lying in a plane leaving enough space for the lone pair to be located within this plane, too, as O(31)−Bi−O(21) amounts to not less than 148.1(4)°. The axial ligands of such a bipyramid (or distorted octahedron, if the lone pair is disregarded) are represented by the two Cl atoms. A noncrystallographic plane of symmetry can be drawn through Mo/Bi/Cl(1) mirroring O(20) by O(30) and O(21) by O(31), and consequently it is not surprising that these pairs of atoms show similar bond distances to Bi.

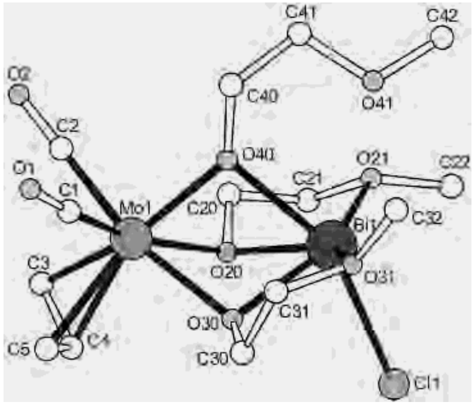


Figure 2. Molecular structure of **6** with partial atom-labeling scheme.

The crystal structure of **6** (Figure 2) can be derived from that of **4** by exchanging the bridging Cl ligand for a bridging 2-methoxyethoxide ligand with the methoxy donor function remaining dangling: the distance Bi−O(41), 2.912 Å, is much longer than the distances Bi−O(21)/O(31) [2.634(3) and 2.614(3) Å] and should thus *not* represent a reasonably strong bond. The Cl/OR exchange naturally has an impact on the terminal Bi−Cl bond distance, being located in *trans* position to that ligand: due to the electron-richness of the alkoxide ligand (in comparison to Cl in **4**), it is enlarged to 2.698(2) Å. All other distances are increased, too, but only slightly. The Mo−O bond in *trans* position to the allyl ligand

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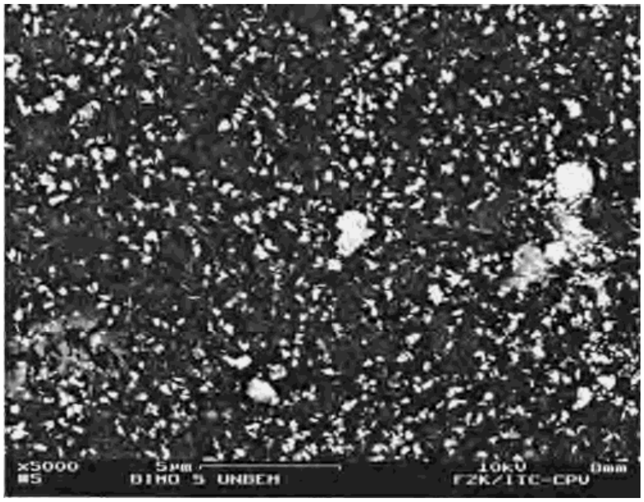

Figure 3. SEM micrograph (backscattered electrons (BSE), $m = 5.000\times$) for one of the silica grains after stirring **6**/thf over the silica gel; the white spots represent the Mo/Bi clusters.

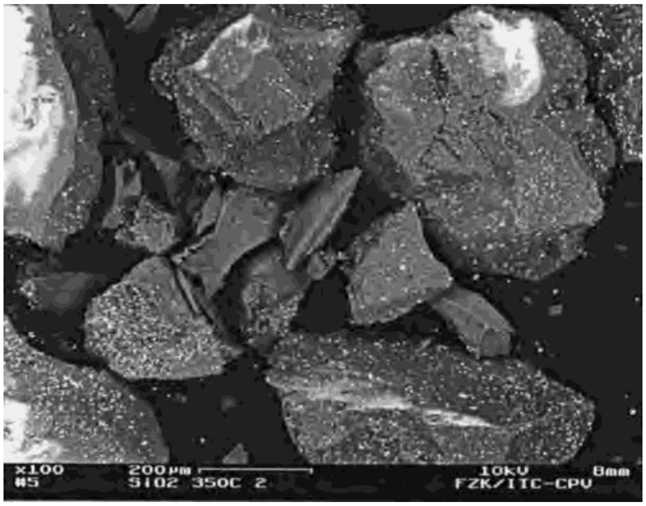

Figure 4. SEM micrograph (mixed secondary electrons (SE) and BSE, $m = 100\times$) for some of the silica grains after calcinations at 350 °C in the presence of oxygen; the white spots represent the bismuth oxo clusters.

[2.085(2) Å] in **6** is somewhat shorter than the bonds *trans* to CO [2.221(2) and 2.254(3) Å], consistent with a stronger *trans* influence of CO.

Of all molybdenum bismuth alkoxides known so far,[7,8] **6** is certainly the one that is most stable to moisture: it can even be handled in air for short periods of time and thus seemed to be the ideal starting material for experiments with the aim of compositing Mo/Bi/O structures on inert supports, as mentioned in the Introduction. Silica gel was chosen as the supporting material, and treatment with **6** (followed by heating in the presence of O_2) could be imagined to give rise to two interesting situations: (i) first of all there was the possibility that such a procedure would lead to dinuclear Mo−O−Bi moieties isolated in a silica matrix, in which case the chemistry of bare Mo−O−Bi linkages could have been studied for the first time; (ii) on the other hand, the acidic Si−OH functions of the silica could be envisaged to induce aggregation and condensation reactions, finally leading to nanoscopic systems on an inert support.

Reactions of 6 on a Silica Surface. A 250-fold excess of SiO_2 was treated with **6** dissolved in thf and the mixture stirred for 30 min. During this time the silica absorbs **6** under elimination of 2-methoxyethanol (as evidenced by means of GC/MS measurements), thereby decolorizing the formerly orange liquid phase; the silica itself changes color from white to yellow-orange. After removing all volatiles in vacuo SEM/EDX measurements performed for some representative silica grains showed clusters of around 200 nm size stochastically distributed over their surface (Figure 3); that is, the contact of **6** with the silica surface initiates aggregation and condensation reactions of the originally dinuclear units. The Mo:Bi ratio within these clusters amounts to ca. 1:2, so that the surface around them must be comparatively rich in molybdenum oxo species. Calcination of this material at 350 °C in the presence of oxygen leads to the oxidative termination and thus elimination of all organic ligands, while the metal oxo units rearrange: SEM/EDX investigations of the—now brightly white—grains subsequently show molybdenum-free bismuth oxo clusters with sizes between 30 and 1000 nm, which can be found spread over the silica surface together with molybdenum oxo particles of much smaller sizes (Figure 4). For the generation of such a surface situation dinuclear alkoxidic Mo/Bi moieties being prone to aggregate/condensate on contact with Si−OH functions as in **6** are, apparently, prerequisites: If **2** and [Bi(O^{t}Bu)$_3$] (which are known to *not* react with each other)[9b] are dissolved in thf, brought into contact with silica gel, and then treated as described above for **6**, no bismuth oxo clusters can be observed afterward on the silica suface: instead, both molybdenum and bismuth oxides are distributed homogeneously on the surfaces (there are only a few points with an accumulation of bismuthoxide units).

If the material obtained starting from **6** is employed as a potential catalyst for the propene oxidation under technical conditions, no activity can be observed. This situation changes when the pressure is drastically decreased, i.e., when a propene/oxygen/argon mixture (4/8/88) is sucked at a very low pressure through a tube (30 cm) containing the supported oxides (ca. 400 mg of Bi/Mo distributed on 10 g of silica) under high vacuum: a propene conversion of 5% is observed then, which is remarkable considering that the technical process requires tubes with a length of 4 m size and 3 cm thickness being filled with the neat bismuthmolybdates in order to reach a 95% conversion.

The products of the present conversion were collected in a trap cooled by liquid nitrogen, and—as expected—they consisted of acrolein and acetaldehyde (the latter has been suggested[5] to represent a *decomposition product* of allyl radicals chemisorbed at Mo^{VI} oxo moieties, which are the same intermediates that lead to acrolein during the propene oxidation in the “constructive” reaction channel) in a ratio of 2:1, as detected NMR spectroscopically. The above-mentioned conversion of 5%, which was also determined by means of NMR, represents a lower limit, since some of the acrolein accumulated in the trap polymerized during the process of its annealing. A temperature of 350 °C proved to be ideal for reaching a maximum conversion: Lower temperatures decreased the conversion, while higher temperatures had little effect, apart from a change occurring with the silica/MoBiO material (at 450 °C it turns orange, indicating that the metal oxo components arrange themselves to form bismuthmolybdate phases).

During the oxidation procedure, the Bi/Mo-covered silica turns brown; it can, however, be bleached to the original bright white color again in a pure oxygen atmosphere at 350 °C. The process of reduction and oxidation can be repeated several times.

If **2** rather than **6** is employed as the starting material for the procedure described above, an analogous attempt to oxidize propene leads to an oxidative conversion of only 1% and the color of the molybdenumoxide-coated silica does not change, proving that the bismuthoxide units are essential for the oxidation of propene.

Conclusions

In summary, it is true: both molybdenum and bismuth are essential for a successful, allylic oxidation of propene, but our results cast doubt whether they necessarily have to be linked covalently as part of a bismuthmolybdate phase. Apparently, it is sufficient, when bismuth oxo clusters are present, which can initiate the allylic H atom abstraction,[4] as well as molybdenum oxo units in close proximity, which are able to trap and convert the allyl radicals formed. The most important advantage of the bismuthmolybdates with respect to the catalysis would then be their oxidic solid state structure allowing a rapid reoxidation of the surface via ion transport.[1−5]

Of course it is (on the basis of SEM/EDX) not possible to exclude the presence of a small number of Bi−O−Mo linkages on the silica surfaces in our experiments, whose activity would, however, have to be very high to solely explain the conversion observed. Nevertheless, we will test this hypothesis, not only in order to get clarity with regard to that question but also for another reason: If—against intuition—Mo−O−Bi moieties have an outstanding oxygenation capacity, this would open up completely new possibilities, and we are thus currently developing starting materials (Bi/Mo alkoxides) that will allow us such an investigation.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**·0.8thf

Bi(1)−O(30)	2.150(9)	Mo(1)−C(2)	1.93(2)
Bi(1)−O(20)	2.19(2)	Mo(1)−O(20)	2.204(9)
Bi(1)−Cl(2)	2.527(4)	Mo(1)−C(4)	2.21(2)
Bi(1)−O(31)	2.57(2)	Mo(1)−O(30)	2.21(2)
Bi(1)−O(21)	2.62(2)	Mo(1)−C(3)	2.28(3)
Bi(1)−Cl(1)	2.876(4)	Mo(1)−C(5)	2.34(2)
Bi(1)−Mo(1)	3.358(2)	Mo(1)−Cl(1)	2.511(5)
Mo(1)−C(1)	1.90(3)		

O(30)−Bi(1)−O(20)	72.0(4)	C(2)−Mo(1)−O(20)	167.9(7)
O(30)−Bi(1)−Cl(2)	90.7(3)	C(1)−Mo(1)−C(4)	106.1(8)
O(20)−Bi(1)−Cl(2)	94.6(3)	C(2)−Mo(1)−C(4)	104.3(7)
O(30)−Bi(1)−O(31)	69.9(4)	C(2)−Mo(1)−O(30)	106.1(6)
O(20)−Bi(1)−O(31)	141.8(3)	O(20)−Mo(1)−O(30)	70.5(3)
Cl(2)−Bi(1)−O(31)	84.2(2)	C(1)−Mo(1)−Cl(1)	92.8(5)
O(30)−Bi(1)−O(21)	140.2(4)	C(2)−Mo(1)−Cl(1)	88.2(6)
O(20)−Bi(1)−O(21)	69.0(4)	O(20)−Mo(1)−Cl(1)	79.8(4)
Cl(2)−Bi(1)−O(21)	85.0(3)	C(4)−Mo(1)−Cl(1)	159.0(5)
O(31)−Bi(1)−O(21)	148.1(4)	O(30)−Mo(1)−Cl(1)	76.8(3)
O(30)−Bi(1)−Cl(1)	70.1(2)	Mo(1)−Cl(1)−Bi(1)	76.8(2)
O(20)−Bi(1)−Cl(1)	72.1(3)	C(20)−O(20)−Bi(1)	115.1(9)
Cl(2)−Bi(1)−Cl(1)	159.1(2)	C(20)−O(20)−Mo(1)	119.8(8)
O(31)−Bi(1)−Cl(1)	96.2(2)	Bi(1)−O(20)−Mo(1)	99.7(4)
O(21)−Bi(1)−Cl(1)	104.3(2)	C(21)−O(21)−Bi(1)	108.0(8)
C(1)−Mo(1)−C(2)	78.5(7)	C(30)−O(30)−Bi(1)	118.3(10)
C(1)−Mo(1)−O(20)	102.7(5)	C(30)−O(30)−Mo(1)	120.8(8)
Bi(1)−O(30)−Mo(1)	100.5(3)	C(32)−O(31)−Bi(1)	119.8(8)
C(31)−O(31)−Bi(1)	106.0(10)	C(3)−C(4)−C(5)	115.9(16)

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **6**

Bi(1)−O(30)	2.207(2)	Mo(1)−C(2)	1.946(4)
Bi(1)−O(20)	2.220(2)	Mo(1)−O(40)	2.085(2)
Bi(1)−O(40)	2.307(3)	Mo(1)−C(4)	2.200(4)
Bi(1)−O(31)	2.614(3)	Mo(1)−O(30)	2.221(2)
Bi(1)−O(21)	2.634(3)	Mo(1)−O(20)	2.254(3)
Bi(1)−Cl(1)	2.698(2)	Mo(1)−C(3)	2.313(4)
Bi(1)−Mo(1)	3.284(2)	Mo(1)−C(5)	2.338(4)
Mo(1)−C(1)	1.942(5)		

O(30)−Bi(1)−O(20)	69.85(9)	O(40)−Mo(1)−O(30)	75.15(9)
O(30)−Bi(1)−O(40)	71.16(9)	C(4)−Mo(1)−O(30)	87.58(12)
O(20)−Bi(1)−O(40)	68.89(9)	C(1)−Mo(1)−O(20)	166.19(12)
O(30)−Bi(1)−O(31)	68.76(8)	C(2)−Mo(1)−O(20)	105.98(14)
O(20)−Bi(1)−O(31)	135.7(2)	O(40)−Mo(1)−O(20)	72.27(10)
O(40)−Bi(1)−O(31)	83.44(9)	C(4)−Mo(1)−O(20)	87.76(14)
O(30)−Bi(1)−O(21)	139.12(8)	O(30)−Mo(1)−O(20)	69.00(9)
O(20)−Bi(1)−O(21)	69.80(9)	C(20)−O(20)−Bi(1)	115.0(2)
O(40)−Bi(1)−O(21)	99.95(9)	C(20)−O(20)−Mo(1)	119.1(2)
O(31)−Bi(1)−O(21)	151.65(8)	Bi(1)−O(20)−Mo(1)	94.47(10)
O(30)−Bi(1)−Cl(1)	88.15(7)	C(22)−O(21)−Bi(1)	122.0(2)
O(20)−Bi(1)−Cl(1)	89.99(7)	C(21)−O(21)−Bi(1)	106.6(2)
O(40)−Bi(1)−Cl(1)	154.24(6)	C(30)−O(30)−Bi(1)	119.4(2)
O(31)−Bi(1)−Cl(1)	103.65(7)	C(30)−O(30)−Mo(1)	126.5(2)
O(21)−Bi(1)−Cl(1)	85.55(6)	Bi(1)−O(30)−Mo(1)	95.78(9)
C(1)−Mo(1)−C(2)	75.91(17)	C(32)−O(31)−Bi(1)	124.7(3)
C(1)−Mo(1)−O(40)	94.08(14)	C(31)−O(31)−Bi(1)	108.4(2)
C(2)−Mo(1)−O(40)	92.00(13)	C(40)−O(40)−Mo(1)	133.1(2)
C(1)−Mo(1)−C(4)	105.17(17)	C(40)−O(40)−Bi(1)	129.5(2)
C(2)−Mo(1)−C(4)	104.38(15)	Mo(1)−O(40)−Bi(1)	96.68(10)
O(40)−Mo(1)−C(4)	157.16(14)	C(1)−Mo(1)−O(30)	106.08(13)
C(2)−Mo(1)−O(30)	167.05(12)		

Experimental Section

General Procedures. All manipulations were carried out with a vacuum line (at a background pressure < 10^{-3} mbar) or in a glovebox (Ar atmosphere), or by means of Schlenk-type techniques involving the use of a dry argon atmosphere. Microanalyses were performed by the Analytische Laboratorien des Organisch-Chemischen Institutes der Universität Heidelberg using a CHN-Analyser Vario EL (Elementar). During the procedure necessary to be able to handle the substances there, **4**·0.8thf lost 0.3 equiv of the thf included in the crystals (according to the X-ray diffraction study), as evidenced by elemental analyses. The deuterated solvents were condensed into the NMR tubes before the tubes were flame-sealed. All NMR spectra were recorded using a Bruker Advance-DPX 200 (^{1}H, 200.132 MHZ; ^{13}C, 50.323 MHZ) spectrometer. Infrared (IR) spectra were recorded for samples embedded in KBr pellets using a Bio-Rad Excalibur FTS 3000. The pyrolyses were performed in a tube heater oven (Hereaus) with a heating zone of 30 cm and the GC/MS measurements on an Agilent (6890 (GC)/5973 (MS)) machine. The SEM/EDX investigation was carried out on a Leo DSM 982 Gemini field emission scanning electron microscope in connection with an Oxford Instruments LINK ISIS 300 energy dispersive X-ray analysis unit.

Materials. Tetrahydrofuran (thf) was distilled from potassium metal under Ar. Petroleum ether (40/60) was distilled from P_4O_{10} under Ar. Mo(η^3-C_3H_5)(CH_3CN)$_2$(CO)$_2$Cl,[15] [Bi{OC(CH_3)$_3$}$_3$],[16]

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

Table 3. Crystal Data and Structure Refinement Details for Compounds **4**·0.8thf and **6**

	4·0.8thf	**6**
empirical formula	$C_{14.2}H_{27.4}BiCl_2MoO_{6.8}$	$C_{14}H_{26}BiClMoO_8$
fw	682.79	662.73
cryst color	orange-red blocks	yellow-orange blocks
cryst dimens, mm	0.20 × 0.20 × 0.13	0.20 × 0.15 × 0.10
cryst syst	monoclinic	monoclinic
lattice type	primitive	primitive
lattice params		
a, Å	12.980(3)	15.045(3)
b, Å	7.870(2)	9.190(2)
c, Å	21.787(4)	16.757(3)
α, deg	90	90
β, deg	99.48(3)	112.50(3)
γ, deg	90	90
V, Å^3	2195.2(8)	2140.5(7)
space group	$P2_1/n$	$P2_1/c$
Z	4	4
$D_{calcd,}$ g/cm^3	2.045	2.057
F_{000}	1276	1264
temp, K	200	200
μ(Mo Kα), mm^{-1}	0.10422	
diffractometer	Nonius Kappa CCD	
radiation	Mo Ka, graphite monochromated ($\lambda = 0.71073$ Å)	
detector position, mm	34	34
scan type	ω(1°/frame)	
$2\theta_{max}$, deg	55.2	60.0
limiting indices	$-16 \leq h \leq 14$ $-9 \leq k \leq 9$ $-28 \leq l \leq 28$	$-21 \leq h \leq 21$ $-10 \leq k \leq 12$ $-23 \leq l \leq 23$
no. of reflns measd		
total	4967	11 000
unique	3618	6194
R_{int}	0.0433	0.0290
corrns	Lorentz-polarization factor	
structure soln	direct method (SHELXS-97; SHELXL-97)	
refinement	full-matrix least-squares	
no. of observns ($I > 2\sigma(I)$)	2463	5296
no. of variables	227	246
reflns/param ratio	10.85	21.53
residuals		
R^a	0.066	0.0308
$R_w{}^a$	0.179^b	0.0686
R(all)^a	0.1045	0.0399
goodness of fit	1.061	1.064
final diff map		
max. peak, e/Å^3	1.458	1.563
min. peak, e/Å^3	−2.476	−1.993

[a] $R = \sum\{||F_o| - |F_c||/\sum|F_o|\}$ based on $I > 2\sigma(I)$; $R_w = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/\sum w(F_o{}^2)^2\}^{0.5}$. w = weighting factor. [b] Due to a lack of crystal quality, this value is quite (though not unduly) high.

and $[Bi(OCH_2CH_2OCH_3)_3]_2$[16] were prepared by published procedures. The silica gel (particle size 0.2−0.5 mm; BET-surface 300−400 m^2/g, pore volume 0.9−1.2 mL/g) was purchased from Merck and dried at 200 °C in high vacuum for 24 h.

$[(C_3H_5)(CO)_2Mo(\mu\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}Cl)BiCl\cdot0.8thf]$ (4·0.8thf) and $[(C_3H_5)Mo(CO)_2(\mu\text{-}\kappa O, 2\kappa O'\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}\kappa O\text{-}OCH_2CH_2OCH_3)BiCl]$ (6). A solution of 5.36 g (0.0172 mol) of $Mo(C_3H_5)(CO)_2(CH_3CN)_2Cl$ in 200 mL of thf was added dropwise to a solution of 7.98 g (0.0092 mol) of $[Bi(OCH_2CH_2OCH_3)_3]_2$ in 100 mL of thf. The resulting orange solution was isolated from the precipitate, which had formed simultaneously, via filtration and reduced to 150 mL. After storing at −30 °C for 1 week yellow-orange crystals of **6** as well as orange-red crystals of **4**·0.8thf were obtained, which were filtered off and separated from each other in a glovebox. After concentrating of the mother liquor, further cooling led to additional quantities of **4**·0.8thf and **6**, which were combined with those obtained before. Independent recrystallization from thf led to 0.92 g of **4**·0.8thf (1.35 mmol, 8%) and 5.23 g of **6** (7.89 mmol 46%).

4·0.8thf. ^{1}H NMR (thf-d_8): δ_H 4.88 (m, br, 4H, μ-OCH_2CH$_2$OCH$_3$); 3.65 (m, 4H, μ-OCH$_2$CH_2OCH$_3$), 3.64 (m, 1H, H$_s$H$_a$CCHCH$_a$H$_s$); 3.47 (s, 6H, μ-OCH$_2$CH$_2$OCH_3); 3.26 (d, 2H, H_sH$_a$CCHCH$_a$$H_{s,}$ $^3J_{HH}$ = 6.8 Hz); 0.96 (s, 2H, H$_s$$H_a$CCHC$H_aH_{s,}$ $^3J_{HH}$ = 9.8 Hz). IR/KBr [cm^{-1}]: 2916(m), 2855(m), 1935(vs), 1837(vs), 1461(w), 1351(w), 1265(w), 1233(w), 1200(w), 1117(m), 1106(m), 1078(s), 1059(s), 1016(m), 921(w), 899(m), 838(m), 796(w), 642(w), 592(w), 559(w), 505(w), 470(m), 436(w). Anal. Calcd for $C_{13}H_{23}BiCl_2MoO_{6.5}$ [**4**·0.5thf] (659.14): C, 23.69; H, 3.52. Found: C, 23.74; H, 3.65.

6. ^{1}H NMR (thf-d_8): δ_H 4.88 (m, br, 6H, μ-OCH_2CH$_2$OCH$_3$); 3.64 (m, 1H, H$_s$H$_a$CCHCH$_a$H$_s$); 3.63 (m, 6H, μ-OCH$_2$CH_2OCH$_3$), 3.44 (s, 9H, μ-OCH$_2$CH$_2$OCH_3); 3.20 (d, 2H, H_sH$_a$CCHCH$_a$$H_{s,}$ $^3J_{HH}$ = 7.0 Hz); 0.85 (s, 2H, H$_s$$H_a$CCHC$H_aH_{s,}$ $^3J_{HH}$ = 10.2 Hz). IR/KBr [cm^{-1}]: 2932(m), 2864(m), 1931(vs), 1847(vs), 1456(w), 1351(w), 1268(w), 1231(w), 1196(w), 1094(m), 1055(s), 1015(m), 899(m), 837(m), 602(w), 580(w), 502(w), 479(m). Anal. Calcd for $C_{14}H_{26}BiClMoO_8$ (662.73): C, 25.37; H, 3.95. Found: C, 25.40; H, 3.93.

Reaction of 6 with Silica Gel. In the inert atmosphere of a glovebox 0.45 g (0.68 mmol) of **6** was placed together with 10 g (0.17 mol) of SiO_2 into a Schlenk tube. Then 10 mL of thf was added via cannula, and the mixture was shaken vigorously until all of **6** had dissolved. It was then stirred for 30 min, during which time the liquid phase decolorized to pale yellow, while the silica grains turned orange. All volatiles were removed then (and investigated via GC/MS), and the material was dried under vacuum for 10 h. After SEM/EDX analysis the solid material was filled into a tube (50 cm size, 1.5 cm diameter), so that it was fixed between two tufts of glass wool (at a distance of ca. 30 cm) in the middle of the tube. The tube was closed at one end and evacuated through the other opening. It was subsequently placed into a tube heater oven so that the whole material was located in the heating zone, which was afterward allowed to rise in temperature to 350 °C. This led the material to adopt a homogeneously deep violet-black color. The volatiles thus generated were collected in a trap cooled with liquid nitrogen and found to consist mainly of thf, some propene, CO, CO_2, allyl alcohol, and a little acrolein. Subsequently, a stream of pure oxygen was blown under ambient pressure through the heated tube for 6 h, thereby completely bleaching the Mo/Bi silica to a bright white appearance.

To obtain information concerning the fate of the allyl ligands during this process, in one experiment pure oxygen was sucked through the tube filled with the orange material (which is obtained directly after the reaction of SiO_2 with **6**) at low pressure, and again all products generated were collected under dynamic vaccuum in a trap cooled by liquid nitrogen, while the temperature was constantly and slowly increased from room temperature until it had reached 350 °C. At that stage the material was white and the products in the trap were condensed in an NMR tube containing a known amount of a standard. After measuring an ^{1}H NMR spectrum and integration 50% of all allyl ligands initially employed could be accounted for. The latter had been converted into acrolein, acetaldehyde, and allyl alcohol in the ratio 1:2:6 (some of the acrolein that had initially formed could not be detected due to polymerization and is therefore missing in the mass balance).

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The subsequent oxidation of propene was performed as follows: a mixture of propene/oxygen/argon (1:2:22) was prepared in a 2 L flask equipped with a greaseless tap. The flask was connected to the pyrolysis tube containing the material, whose preparation is described above. The other end of the tube was connected to a U-trap and the entire apparatus evacuated. Subsequently the trap was cooled by liquid nitrogen and the tube heated to 350 °C. Finally the tap of the flask was slightly opened so that the gaseous mixture was sucked through the pyrolysis tube within 8 h (all products, as well as unconverted propene, being held in the trap). After finishing the experiment the content of the trap was analyzed by means of NMR spectroscopy.

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Supporting Information Available: Listings of X-ray structural data (ORTEP plots, crystallographic information files; CIF) for all complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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