1044 *Organometallics* **2000,** *19,* 1044−1050

Syntheses of Heteronuclear Molybdenum/Bismuth Alkoxides Stabilized by Organic Ligands

Marc Hunger, Christian Limberg,* and Peter Kircher

Universität Heidelberg, Anorganisch-Chemisches Institut,
Im Neuenheimer Feld 270, D-69120 Heidelberg

Received October 18, 1999

Reaction of $[((CH_3)C_3H_4)Mo(CO)_2(CH_3CN)_2Cl]$, **2**, with $[Bi(OEt)_3]_x$ provides the heterotetranuclear complex $[((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}OEt)_3Bi(\mu\text{-}OEt)_2Bi(\mu\text{-}OEt)_3Mo(CO)_2((CH_3)C_3H_4)]$, **3**, in good yields. If **2** is reacted with $[Bi(OCH_2CH_2OCH_3)_3]_2$, a dinuclear chloro alkoxide $[((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}\kappa O,2\kappa O'\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}Cl)BiCl]$, **4**, is obtained, while pretreatment of **2** with $AgBF_4$ and subsequent reaction with $[Bi(OCH_2CH_2OCH_3)_3]_2$ leads to the chloride-free complex $[((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}\kappa O,2\kappa O'\text{-}OCH_2CH_2OCH_3)_3Bi(thf)][BF_4]$, **6**, with a Bi center surrounded by seven oxygen donors. All compounds have been characterized by NMR and IR spectroscopy as well as elemental analysis, and their crystal structures were determined by means of single-crystal X-ray diffraction. **3**, **4**, and **6** belong to the few compounds known (there is only one other precedent) where Mo and Bi centers are bridged by oxygen-containing ligands and can therefore be considered as cornerstones on the way to the synthesis of yet unknown molecular compounds with Mo−O−Bi functions resembling those occurring on the surface of $n MoO_3-Bi_2O_3$ catalysts.

Introduction

The unique property of $n MoO_3/Bi_2O_3$ to act as a heterogeneous catalyst for the technical propene oxidation[1a] to acrolein remains a subject of intense discussion.[1b] The results of their experiments on isotopic enrichment lead Grasselli and Burrington to suggest the intermediate formation of symmetric π-allyl complexes (or the chemisorption of delocalized allyl radicals)[1b,2] at Mo centers of the catalysts surface. Furthermore recent investigations concerning heterogeneous oxidation catalyses on Mo/Bi oxides suggest that the oxygen atoms found in the organic oxidation products have their origin in previously *bridging* positions,[1c] so that $Bi(\mu\text{-}O)Mo$ moieties are currently thought to be the active oxo transfer sites also in propene oxidation. If this hypothesis is correct, the formation of acrolein in this process may well be explained in terms of an allyl shift to (or trapping of allyl radicals by) $Bi(\mu\text{-}O)Mo$ functions, followed by a hydrogen atom abstraction from the resulting allyloxy unit. This encourages research with the aim of preparing molecular species containing both Mo and Bi in oxo environments being linked by oxygen-containing (or ideally "pure" oxo) ligands. In this context the corresponding heterometallic alkoxides are of particular interest, as studies concerning polynuclear metal alkoxides have clearly shown that they are capable of simulating the structures and some of the properties of metal oxides.[3] There is, however, a dearth of information about even the *homo*metallic alkoxides of bismuth.[4] While several groups have claimed the existence of a bismuth−transition metal precursor in their sol−gel processes[5] only two *hetero*metallic alkoxide complexes containing Bi and a transition metal (V[4a] and Ti[6a]) had been isolated and described structurally until recently. This is particularly surprising, as an increasing number of advanced oxide materials based on bismuth appear to display attractive properties,[6] and mixed-metal alkoxides could act as single-source precursors.

Recently we have reported the synthesis of the first mixed Bi/Mo alkoxide, representing at the same time the only structurally characterized example of a molecular compound with a discrete oxo linkage of any type between Bi and Mo.[7] All initial attempts to prepare the aforementioned type of species via methods established

---

* Corresponding author. E-mail: Limberg@sun0.urz.uni-heidelberg.de. Fax: 06221/545707.

[1] (a) Grasselli, R. K.; Burrington, J. D. *Ind. Engl. Chem. Prod. Res. Dev.* **1984**, *23*, 394. (b) Belgacem, J.; Kress, J.; Osborn, J. A. *J. Mol. Catal.* **1994**, *86*, 267. (c) Ono, T.; Numata, H.; Ogata, N. *J. Mol. Catal.* **1996**, *105*, 31. Kinne, M.; Heidenreich, A.; Rademann, K. *Angew. Chem.* **1998**, *110*, 2637; *Angew. Chem., Int. Ed.* **1998**, *37*, 2509.

[2] Anderson, A. B.; Ewing, D. W.; Kim, Y.; Grasselli, R. K.; Burrington, J. D.; Brazdil, J. F. *J. Catal.* **1985**, *96*, 222. Keulks, G. W.; Krenzke, L. D.; Notermann, T. M. *Adv. Catal.* **1978**, *27*, 183. Grasselli, R. K.; Burrington, J. D. *Adv. Catal.* **1981**, *30*, 133.

[3] Chisholm, M. H. In *Inorganic Chemistry Towards the 21st Century*; American Chemical Society: Washington, DC, 1983; Chapter 16, p 243. Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, *11*, 663, and cited references.

[4] a) Pell, J. W.; Davis, W. C.; zur Loye, H. C. *Inorg. Chem.* **1996**, *35*, 5754. (b) Hodge, P.; James, S. C.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1998**, 4049, and references cited. (c) James, S. C.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1999**, 2837. (d) Jones C. M.; Burkart M. D.; Whitmire K. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1638−1639.

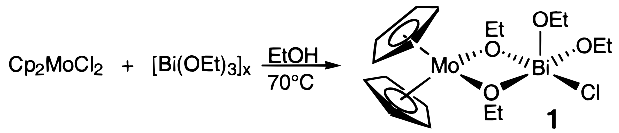
[5] (a) Toyoda, M.; Payne, D. A. *Mater. Lett.* **1993**, *18*, 84. (b) Yamaguchi, O.; Maruyama, N.; Hirota, K. *Ceram. Trans. J.* **1991**, *90*, 111. (c) Hirota, K.; Komatsu, G.; Takemura, H.; Yamaguchi, O. *Ceram. Int.* **1992**, 285. (d) Turova, N. Y.; Kessler, V. G.; Kucheiko, S. I.; *Polyhedron* **1991**, *10*, 2617.

[6] (a) Parola, S.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Jagner, S.; Hakansson, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4631. (b) Jones, M. C.; Burkart, M. D.; Hutchison, J. C.; McKnight, A. L.; Whitmire, K. H. In *Materials Research Society Proceedings: Better Ceramics Through Chemistry V*; Hampden-Smith, M. J., Klemperer, W. G., Brinker, C. J., Eds.; 1992; Vol. 271, pp 149−154.

[7] Hunger, M.; Limberg, C.; Kircher, P. *Angew. Chem.* **1999**, *111*, 1171; *Angew. Chem., Int. Ed.* **1999**, *38*, 1105.

10.1021/om9908229 CCC: $19.00

Scheme 1



for the synthesis of other heterometallic alkoxides[8]—like for instance Lewis acid−base reactions of certain alkoxides of Mo and Bi, or by applying the principles of the non-hydrolytic gel formation process[9]—had yielded (in agreement with observations described in the literature[5]) insoluble, intractable solids. Since this is almost certainly a result of high aggregation levels, we decided to employ molybdenum organyls as starting materials, where a part of the coordination sphere at Mo is shielded by tightly bound organic ligands.[10] [Cp_2MoCl_2] was treated with in situ prepared $[Bi(OEt)_3]_x$ at 70 °C, yielding [$Cp_2Mo(\mu\text{-}OEt)_2Bi(OEt)_2Cl$], **1**, where a Mo and a Bi center are bridged by two ethanolate ligands.

The formation of **1** can be envisaged to proceed via contacts between [Cp_2MoCl_2] and coordinatively unsaturated $[Bi(OEt)_y]^{(3-y)+}$ centers mediated by Cl or EtO ligands. These initial contacts trigger ligand exchange reactions, which finally lead to a stable $Mo(\mu\text{-}OEt)_2Bi$ moiety. Only one of two original Cl ligands is found at the Bi center in **1**, the second one having been replaced by external EtO^-. After the concept of employing organomolybdenum compounds in reactions with Bi alkoxides had thus proved suitable for the synthesis of heteronuclear Mo/Bi alkoxides, experiments with *allyl molybdenum* compounds were considered, as allyl species play a significant role during the propene oxidation on the bismuthmolybdate surface (vide supra). Certainly alkoxide ligands cannot simulate special functions of oxo ligands, but once the next step (away from alkoxide toward oxo ligands, where current research focuses) is taken, allyl ligands will become very valuable: as the Mo−allyl linkage is easily cleaved homolytically if oxo ligands are present at the Mo center at the same time,[11] the Mo−allyl unit could serve as a source of allyl radicals in such compounds, thus enabling studies concerning their trapping by neighboring ligands.

Results and Discussion

Bearing the abovementioned arguments in mind and following Scheme 1, the employment of allyl molybdenum chloride compounds in reactions with $[Bi(OEt)_3]_x$ seemed reasonable. A well-known π-allyl−Mo compound with a Mo−Cl function and potential leaving groups (acetonitrile) is [$((CH_3)C_3H_4)Mo(CO)_2(CH_3CN)_2Cl$], **2**[12] (Scheme 2). Although the corresponding derivative of **2** with an unsubstituted allyl ligand can be readily made, too, **2** was chosen as the starting material, as methallyl ligands have the advantage of increasing the steric bulk at the Mo centers somewhat, so that the resulting products gain kinetic stability, and second they greatly facilitate NMR spectroscopic investigations. After treatment of **2** with 2/*x* equiv of $[Bi(OEt)_3]_x$ in thf a brown precipitate and a brownish-red solution were obtained. Layering of the filtrate with 40/60 petroleum ether lead to the precipitation of very air-sensitive red crystals of compound **3**, which was characterized by IR and NMR spectroscopy as well as by elemental analysis. A single-crystal X-ray structure determination finally revealed a constitution [$((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}OEt)_3Bi(\mu\text{-}OEt)_2Bi(\mu\text{-}OEt)_3Mo(CO)_2((CH_3)C_3H_4)$] for **3** (Scheme 2), and selected bond lengths and angles of its crystal structure (Figure 1) are listed in Table 1.

3 contains two $((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}OEt)_3Bi$ units bridged by two μ-OEt ligands in a fashion that creates a (crystallographical) inversion center. The Bi centers are thus pentacoordinated with a distorted square-based pyramidal arrangement of the ligands and the stereoactive lone pair occupying the ligand site missing for an octahedron. The two BiO_5 pentagons share one edge of their squares, so that these (and therefore O(40/40A), O(20/20A), and O(30/30A)) are situated roughly within a plane. The two axial ligands (O(10/10A)) are positioned on opposite sides of this plane, “pushing” the Bi centers out by 0.43 Å. There is precedent for this type of geometry in dinuclear Bi alkoxides of the general formula $[Bi_2(OR)_4(\mu\text{-}OR)_2L_2]$.[13,14] The arrangement of ligands around the Mo centers in **3** is comparable to the one found in the anion[15] $[((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}OMe)_3Mo(CO)_2((CH_3)C_3H_4)]^-$, leading to similar (slightly longer) Mo−O bond distances. Also in close analogy, the Mo−O bond found trans to allyl (2.080(5) Å) in **3** is somewhat shorter than the bonds trans to CO (2.248(5) and 2.250(5) Å), consistent with a stronger trans influence of CO. As a consequence, Bi−O(30) is significantly longer (2.405(5) Å) than Bi−O(20) (2.215(6) Å), which is in turn longer than Bi−O(10) (2.124(5) Å), having no ligand bound trans to it. The $Bi(\mu\text{-}OEt)_2Bi$ unit is therefore asymmetric, too, containing two significantly different Bi−O distances (Bi−O(40) = 2.224(5) Å and Bi−O(40A) = 2.407(5) Å). 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 to the corresponding endo conformation[16] and that is frequently accompanied by a decreased $M(CO)_2$ angle (<90°), while the angle in endo structures is increased (> 90°).[17] Accordingly the $Mo(CO)_2$ angle in **3** amounts to only 79.3(3)°.

Previous studies have demonstrated the mobility of the $((CH_3)C_3H_4)Mo(CO)_2$ complex fragment in alkoxide ligand spheres,[18] and the NMR spectroscopic investiga-

---

(8) Mehrotra, R. C.; Singh, A.; Sogani, S. *Chem. Soc. Rev.* **1994**, 215. Veith M.; Mathur, S.; Mathur C. *Polyhedron* **1998**, *17*, 1005−1034.

(9) Corriu, R.; Leclercq, D. *Angew. Chem.* **1996**, *108*, 1524; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1420.

(10) For organometallic alkoxides see: Veith, M.; Yu, E.-C.; Huch, V. *Chem. Eur. J.* **1995**, *1*, 26. Veith, M.; Mathur, S.; Huch, V. *J. Am. Chem. Soc.* **1996**, *118*, 903. Veith, M.; Mathur, S.; Huch, V. *Inorg. Chem.* **1996**, *35*, 7295. Veith, M.; Mathur, S.; Huch, V. *J. Chem. Soc., Dalton Trans.* **1996**, 2485. Veith, M.; Mathur, S.; Mathur, C.; Huch, V. *Organometallics* **1997**, *16*, 1292.

(11) Borgmann, C.; Limberg, C.; Zsolnai, L. *Chem. Commun.* **1998**, 2729.

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

(13) Massiani, M.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Daran, J. C. *Polyhedron* **1991**, *10*, 437.

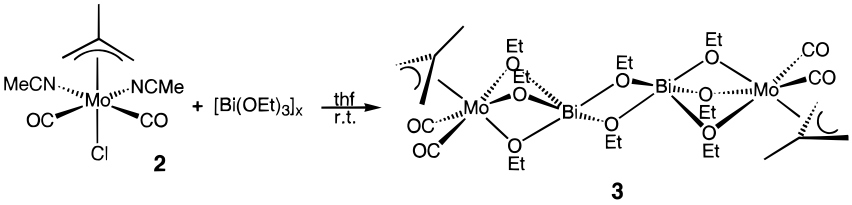
(14) a) Jones, M. C.; Burkart, M. D.; Bachmann, R. E.; Serra, D. L.; Hwu, S. J.; Whitmire, K. H. *Inorg. Chem.* **1993**, *32*, 5136. (b) Jones C. M.; Burkart M. D.; Whitmire K. H. *Angew. Chem.* **1992**, *104*, 466−467; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 451−452.

(15) Borgmann, C.; Limberg, C.; Kaifer, E.; Pritzkow, H.; Zsolnai, L. *J. Organomet. Chem.* **1999**, *580*, 214.

(16) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

(17) Frohnapfel, D. S.; White, P. S.; Templeton, J. L.; Rüegger, H.; Pregosin, P. S. *Organometallics* **1997**, *16*, 3737.

Scheme 2



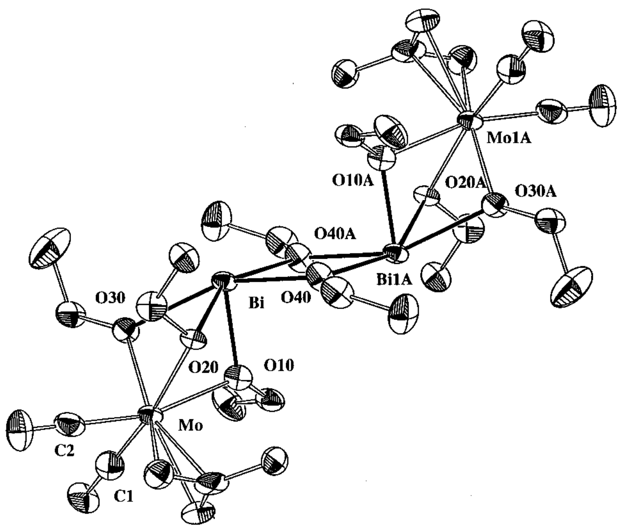


Figure 1. Molecular structure of **3** with partial atom-labeling scheme.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 3

Mo−O(10)	2.248(5)	Bi−O(10)	2.124(5)
Mo−O(20)	2.250(5)	Bi−O(20)	2.215(6)
Mo−O(30)	2.080(5)	Bi−O(30)	2.405(5)
O(10)−C(10)	1.446(9)	Bi−O(40)	2.224(5)
O(20)−C(20)	1.423(9)	Bi−O(40A)	2.407(5)
O(30)−C(30)	1.405(9)	O(40)−C(40)	1.435(9)
O(40)−Bi−O(40A)	69.6(2)	O(30)−Mo−O(20)	74.8(2)
O(10)−Bi−O(30)	69.98(19)	O(10)−Mo−O(20)	69.01(19)
O(20)−Bi−O(30)	69.34(18)	Bi−O(10)−Mo	97.2(2)
O(10)−Bi−O(20)	71.88(17)	Bi−O(20)−Mo	94.58(19)
O(30)−Mo−O(10)	74.0(2)	C(1)−Mo−C(2)	79.3(3)

tion of **1** provided evidence for a rapid exchange of the OEt ligands at room temperature.[7] Temperature-dependent ^{1}H NMR spectra of **3** in thf-d_8 revealed that it shows a dynamic behavior in solution, too: the broad singlet at 4.78 ppm (rt) corresponding to the average resonance for the methylene protons of all ethoxy groups shifts to 5.01 ppm on cooling to −10 °C, splitting at −30 °C to give *two* complex structured signals at −60 °C. Further cooling below −70 °C leads to changes in the fine structures and to the evolution of a third signal before the fine structure and resolution are lost due to viscosity effects; that is, at no stage is a constant signal pattern reached. Corresponding changes are also observed in the region for the signals of the methyl groups, while the allyl signals split at approximately −50 °C. Evidently the fluctionality of the system cannot be frozen out completely in the temperature range available, and the broadness of all signals combined with serious overlap did not allow for a determination of the nature of the process responsible. Although for these reasons the signals in the ethoxide region of the ^{1}H NMR spectrum could not be assigned, we can be sure about the observation of only one set of allyl signals at room temperature, suggesting that either the principal constitution of **3** persists or it splits into two equivalent halfs. Consequently **3** is isolated because it is either the thermodynamically favored or the least soluble species of a solution equilibrium, which lies almost completely on one side. Formally 2 equiv of [Bi(OEt)$_2$Cl] are generated per molecule of **3**, which—probably after dismutation reactions—form the precipitate obtained. In fact it turned out that the raw material isolated after removal of all volatiles from the filtrate directly after the reaction contains almost exclusively **3**, as judged by ^{1}H NMR spectroscopy. No additional signals could be detected, but the integrals for the ethoxide signals were somewhat too high (12%) and elemental analysis revealed a contamination by chloride (3%). These findings suggest the presence of a dismutation product, [EtOBiCl$_2$]$_x$, as the sole contamination (14 wt %) in the crude product, and from this information a near quantitative (84%) formation of **3** can be inferred.

Why does the reaction of [Cp$_2$MoCl$_2$] with [Bi(OEt)$_3$]$_x$ provide a dinuclear heterometallic alkoxide, while an alkoxide-bridged dimer of such is formed in the reaction of **2**? An answer could be sought in the charge conditions: **1** contains a Cp$_2$Mo^{2+} unit, while **3** contains an (allyl)Mo(CO)$_2^+$ entity. To form neutral complexes with a Bi(OEt)$_3$ moiety, Cp$_2$Mo^{2+} needs two additional negatively charged ligands (EtO$^-$ and Cl$^-$), while (allyl)Mo(CO)$_2^+$ requires only one (EtO$^-$). When these ligands become part of the coordination sphere of Bi, this leads to a commonly found[4] five-coordinated center in the first case yielding **1**, while the Bi remains unsaturated (four-coordinated) in the latter. The resulting [(allyl)Mo(CO)$_2$(μ-OEt)$_3$Bi(OEt)] species has two options: it can coordinate a neutral ligand (thf) or dimerize. Apparently it prefers dimerization yielding **3**.

To obtain dinuclear compounds we decided to use alkoxide ligands, which intrinsically provide the desired neutral donors mentioned above. Hence [Bi(OCH$_2$CH$_2$OCH$_3$)$_3$]$_2$[13] was employed instead of [Bi(OEt)$_3$]$_x$. Its equimolar reaction with **2** in thf yields a brown precipitate as well as an orange solution. Layering of the filtrate with hexane yields an orange, crystalline material, which consists of [((CH$_3$)C$_3$H$_4$)Mo(CO)$_2$(μ-κO,2κO′-OCH$_2$CH$_2$OCH$_3$)$_2$(μ-Cl)BiCl], **4**, (Scheme 3), as evidenced by elemental analysis and IR and NMR spectroscopy, as well as a single-crystal X-ray structure determination (Figure 2, Table 2).

The geometry of the ((CH$_3$)C$_3$H$_4$)Mo(CO)$_2$ unit is very similar to that of **3**, with Mo−O distances comparable with the ones found there. 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

---

(18) Borgmann, C.; Limberg, C.; Zsolnai, L.; Heinze, K. *Z. Naturforsch.* **1999**, *54b*, 473.

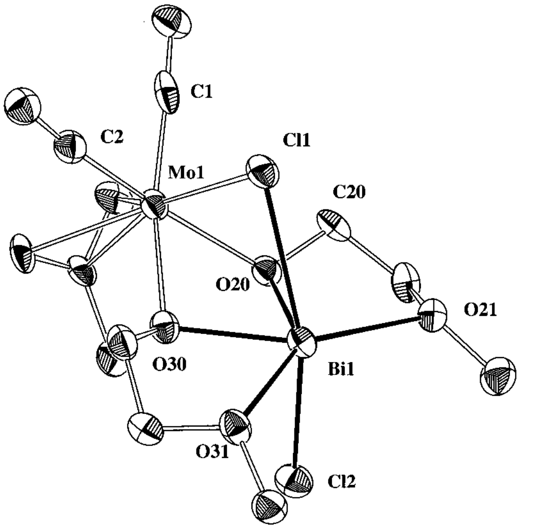
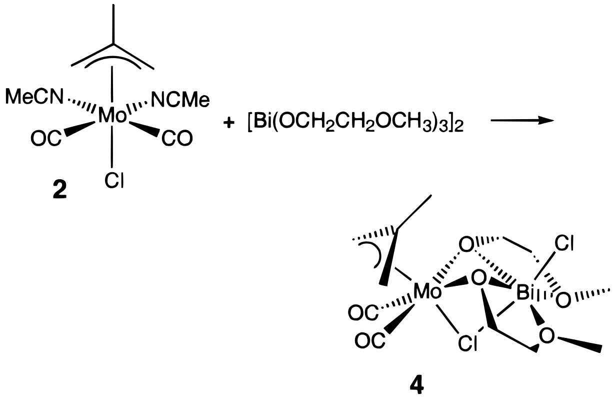


Figure 2. Molecular structure of one of the two independent molecules found in the unit cell of **4** with partial atom-labeling scheme. The thf molecule was omitted for clarity.

Scheme 3



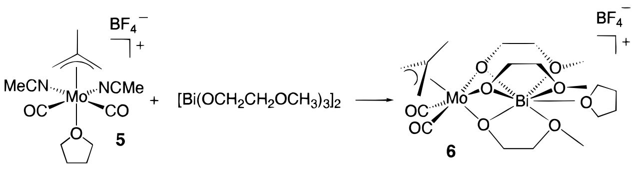
2 **4**

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 4

Bi(1)−O(30)	2.195(6)	Mo(1)−O(30)	2.227(6)
Bi(1)−O(20)	2.206(6)	Mo(1)−O(20)	2.213(6)
Bi(1)−Cl(2)	2.544(3)	Mo(1)−Cl(1)	2.549(3)
Bi(1)−O(21)	2.595(6)	O(20)−C(20)	1.442(11)
Bi(1)−O(31)	2.597(6)	Bi(1)−Cl(1)	2.906(3)
O(30)−Mo(1)−Cl(1)	78.71(17)	Cl(2)−Bi(1)−O(31)	84.14(16)
O(20)−Mo(1)−Cl(1)	78.61(17)	O(30)−Bi(1)−Cl(2)	92.67(17)
O(20)−Mo(1)−O(30)	71.6(2)	O(20)−Bi(1)−Cl(2)	91.88(17)
O(30)−Bi(1)−O(20)	72.3(2)	Cl(2)−Bi(1)−O(21)	84.27(15)
O(30)−Bi(1)−Cl(1)	71.58(17)	Mo(1)−Cl(1)−Bi(1)	76.11(7)
O(20)−Bi(1)−Cl(1)	71.13(17)	Bi(1)−O(20)−Mo(1)	99.6(2)
O(20)−Bi(1)−O(21)	69.6(2)	Bi(1)−O(30)−Mo(1)	99.5(2)
O(30)−Bi(1)−O(31)	69.3(2)	Cl(2)−Bi(1)−Cl(1)	159.47(8)
O(21)−Bi(1)−O(31)	147.5(2)		

(Cl−Bi−Cl = 159.47(8)°). The Bi−Cl(2) bond length of 2.544(3) Å is quite similar to the average of 2.532 Å found in a $Cl_3Bi(\mu\text{-}O(R)-)_3$ moiety[4a] and typical for terminal Bi−Cl bond distances, which are usually about 2.6 Å.[19] The Bi−Cl(1) bond (2.906(3) Å) is quite long (even for a bridging Cl ligand), and it should therefore be regarded as weak.[4b] The additional four donor functions provided by the alkoxide ligands force the Bi center into a coordination sphere, which can be described as a distorted pentagonal bipyramid where one of the equatorial ligands is represented by the stereoactive lone pair of Bi: 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 147.5(2)°. The axial ligands of the bipyramid are represented by the two Cl atoms. A noncrystallographic plane of symmetry can be drawn through Mo/Bi/Cl(1) mirroring O(20) into O(30) and O(21) into O(31), so that it is not surprising that these pairs of atoms show similar bond distances to Bi. Those of O(20) and O(30) (being bonded to Mo trans to CO) are in turn similar to Bi−O(10/20) in **3**.

Scheme 4



5 **6**

As mentioned above, the reaction in Scheme 3 yields a solution as well as a precipitate. **4**, which was isolated from the solution, contains two Cl ligands, although only one is present in the starting material. Therefore an alkoxide-rich species lacking Cl ligands must be formed simultaneously, and accordingly the yield of **4** amounts to only 48%. Indeed, ^1H NMR investigations of the filtrates obtained from concentration-dependent experiments revealed that in the reaction of **2** with 0.5 equiv of $[Bi(OCH_2CH_2OCH_3)_3]_2$ (i.e., Mo:Bi = 1:1) three allyl-containing products are generated, one of them representing the main product **3** (no precipitate is formed!). However, in the equimolar reaction (Mo:Bi = 1:2) of **2** and $[Bi(OCH_2CH_2OCH_3)_3]_2$ (from which **4** can be isolated) **4** is surprisingly formed as the sole soluble product, and consequently the alkoxide-rich species must undergo further aggregation reactions with excessive $[Bi(OCH_2CH_2OCH_3)_3]$ units, finally becoming part of the precipitate. Hardly any precipitate is obtained if **2** is employed in a 4-fold excess (Mo:Bi = 2:1) with respect to $[Bi(OCH_2CH_2OCH_3)_3]_2$. **4** forms as the mayor product, which is, however, contaminated again, probably by a homonuclear Mo alkoxide. Consequently the equimolar reaction provides the purest **4**, with the disadvantage that a part of $[Bi(OCH_2CH_2OCH_3)_3]_2$ is sacrificed then.

As mentioned above, it is very likely that the reaction of Scheme 3 additionally provides an alkoxide-rich Mo/Bi compound, but the simultaneous formation of the chloro compound **3** together with at least one other allyl molybdenum species as well as subsequent aggregation reactions prevented its isolation. To generate a chloride-free Bi/Mo/$-OCH_2CH_2OCH_3$ compound as the main product and to thereby facilitate its isolation, the Cl ligand of **2** was removed by $AgBF_4$ (producing complex **5** as shown in Scheme 4)[15] prior to its treatment with the bismuth alkoxide. The equimolar reaction of **5** with $[Bi(OCH_2CH_2OCH_3)_3]_2$ again yields a brown precipitate and an orange solution. Layering of the filtrate with 40/60 petroleum ether leads to $[((CH_3)C_3H_4)Mo(CO)_2(\mu\text{-}\kappa O,2\kappa O'\text{-}OCH_2CH_2OCH_3)_3Bi(thf)][BF_4]$, **6**, in 20% crystalline yield (before this purification step the yield is probably far higher), as shown in Scheme 4. **6** was

---

[19] Norman, N. C. Phosphorus *Sulfur Silicon Relat. Elem.* **1994**, *87*, 167. Carmalt, C. J.; Norman, N. C. In *Chemistry of Arsenic, Antimony and Bismuth*; Norman, N. C., Ed.; Blackie Academic & Professional: London, 1988; Chapter 1.

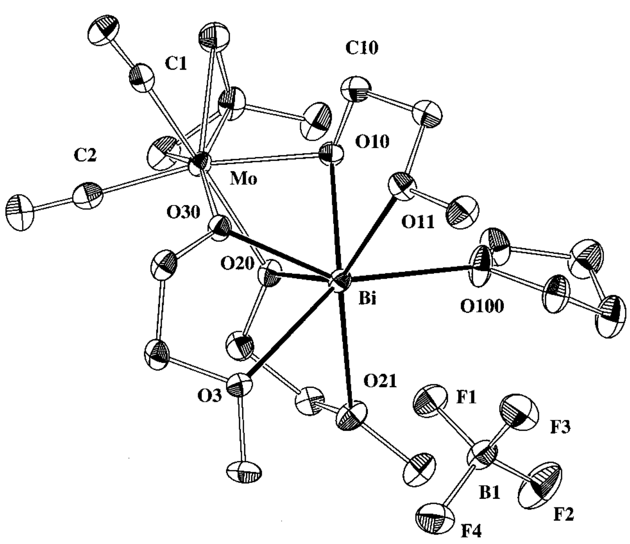


Figure 3. Molecular structure of **6** with partial atom-labeling scheme.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 6

Mo–O(10)	2.237(3)	Bi–O(10)	2.204(3)
Mo–O(20)	2.213(3)	Bi–O(20)	2.180(3)
Mo–O(30)	2.135(3)	Bi–O(30)	2.226(3)
Bi–O(11)	2.595(3)	Bi–O(31)	2.649(3)
Bi–O(21)	2.708(3)	Bi–O(100)	2.572(3)
O(10)–C(10)	1.430(5)		
O(30)–Mo–O(20)	75.31(11)	Bi–O(10)–Mo	93.88(11)
O(30)–Mo–O(10)	70.75(11)	Bi–O(20)–Mo	95.22(11)
O(20)–Mo–O(10)	68.71(11)	Mo–O(30)–Bi	96.11(12)
O(20)–Bi–O(10)	69.90(11)	O(20)–Bi–O(30)	74.15(11)
O(10)–Bi–O(30)	69.75(11)		
O(11)–Bi–O(31)	109.47(9)	O(100)–Bi–O(11)	83.33(10)
O(100)–Bi–O(21)	76.52(11)	O(31)–Bi–O(21)	76.52(9)
O(31)–Bi–Mo	96.75(7)	O(21)–Bi–Mo	108.32(7)
O(11)–Bi–Mo	101.06(7)	O(100)–Bi–Mo	114.00(7)
O(21)–Bi–O(11)	149.19(9)	O(31)–Bi–O(100)	144.10(10)

characterized by elemental analysis as well as IR and NMR spectroscopy, and a single-crystal X-ray diffraction study gave the molecular structure shown in Figure 3 (compare Table 3).

As in **3**, the Mo and Bi centers in **6** are bridged by three alkoxide functions again. Aided by the chelating effect, all three ether donor functions are coordinated to the Bi center, too, so that the $[((CH_3)C_3H_4)Mo(CO)_2(OCH_2CH_2OCH_3)_3]^{2-}$ entity can be formally regarded as a cryptant type “ligand” (being, however, open at one end), burying the Bi^{3+} center in its inside. However, the thirst of Bi for oxygen donors seems not to be quenched completely by that, as it coordinates an additional thf molecule, which can be removed under vacuum. The ligands at the Bi center reach a geometry that can be described as distorted dodecahedral if the stereoactive lone pair is considered, too: one face of the dodecahedron is represented by O(10), O(20), and O(30). The Bi center is sandwiched between this face and a plane roughly defined by O(11), O(21), O(31), and O(100), and it is located 0.64 Å above the best plane in a direction toward the Mo center. On the other side of this plane there remains a void, where probably the lone pair of Bi occupies the site missing for a complete dodecahedral coordination sphere. As one would expect, the bond distances Bi–O(10/20/30) (2.204(3), 2.180(3), and 2.226(3) Å) are similar to those found in **3** and **4**. As in **3**, the binding of O(30) to Bi is weakened by its strong binding to Mo [due to the weaker trans influence of allyl (Mo–O(30): 2.135(3) Å) as compared to CO (Mo–O(10/20): 2.237(3)/2.213(3) Å)]. Also, not surprisingly, these Bi–O(10/20/30) distances are shorter than those found for the ethereal functions (Bi–O(11/21/31) = 2.595(3), 2.708(3), and 2.649(3) Å), and the thf molecule coordinates at a distance of 2.572(3) Å, which is close to the usual range found[4b] for Bi–O bonds where O belongs to thf (2.6–2.8 Å). This remarkable compound contains a (π-allyl)Mo unit in an oxygen-rich coordination sphere with a Bi center in the second coordination sphere being complexed itself by not less than seven O donors. It therefore meets some of the requirements for a structural model complex with respect to potential surface intermediates during bismuthmolybdate-catalyzed propene oxidation.

Furthermore the compounds **3**, **4,** and **6** with five, six, and seven-coordinate Bi centers nicely highlight why difficulties have been encountered in attempts to prepare heterodinuclear Mo/Bi alkoxides simply by reacting their alkoxides with each other: if Mo in addition to Bi is provided with a maximum freedom for coordination of O-donors, i.e., if it is *not* partly shielded by organic ligands, high-nuclear, insoluble alkoxides are formed, which elude characterization (a principal alternative might be the employment of bulky organic groups at the alkoxide ligands; however, in our hands only intractable solids were obtained, for instance, in reactions of $Bi(O^tBu)_3$).

Making use of the principles described, current research focuses on the preparation of the first compounds with oxo-bridges between Mo and Bi. Bearing this goal in mind, additional reactions with **3** and **4** will be carried out, aiming at substituting the chloride ligands for instance by $Mo–O^-$ functions.

Experimental Section

General Procedures. All manipulations were carried out with a vacuum line (at a background pressure < 10^{-3} mbar), or in a glovebox, 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 Heraeus. Samples were prepared in a glovebox. During the procedure necessary to be able to handle the substances in the glovebox, **4·thf** lost hardly any thf; **6**, however, lost almost all thf. Residual and missing thf, respectively, explain why the deviations of the carbon analyses are slightly outside the usual range. The deviation of the value for **3** probably results from the extreme sensitivity of the substance. The deuterated solvents were condensed into the NMR tubes before the tubes were flame-sealed. All NMR spectra were recorded using a Bruker Avance-DPX 200 (^1H 200,132 MHZ; ^{13}C 50.323 MHZ) spectrometer. Infrared (IR) spectra were recorded using samples prepared as KBr pellets using a Bruker FT-IR spectrometer IFS-66.

The melting/decomposition points were recorded in a sealed glass tube using a Gallenkamp type melting point apparatus MFB 595010.

Materials. Tetrahydrofuran (thf) was distilled from potassium metal under Ar. Petroleum ether (40/60) was distilled from P_4O_{10} under Ar. $[Mo(\eta^3-C_3H_4(CH_3))(CH_3CN)_2(CO)_2Cl]$,[12] $[Bi(OEt)_3]_x$,[13] and $[Bi(OCH_2CH_2OCH_3)_3]_2$[14a] were prepared by published procedures.

$[((CH_3)C_3H_4)(CO)_2Mo(\mu-OEt)_3Bi(\mu-OEt)_2Bi(\mu-OEt)_3Mo((CH_3)C_3H_4)(CO)_2]$ (3). A solution of 0.25 g (0.77 mmol) of

Table 4. Crystal Data and Structure Refinement Details for Compounds 3, 4, and 6

	3	**4**·thf	**6**
empirical formula	$C_{28}H_{54}O_{12}Mo_2Bi_2$	$C_{32}H_{58}Cl_4O_{14}Mo_2Bi_2$	$C_{19}H_{36}BO_9F_4MoBi$
fw	1192.57	1418.4	800.21
cryst color, habit	red/orange, blades	orange, blades	yellow, needles
cryst dimens, mm	0.30 × 0.40 × 0.10	0.050 × 0.15 × 0.10	0.20 × 0.20 × 0.25
cryst syst	monoclinic	triclinic	triclinic
lattice type	primitive	primitive	primitive
lattice params			
a, Å	9.867(2)	7.338(2)	8.761(2)
b, Å	14.489(3)	12.245(2)	9.396(2)
c, Å	13.813(3)	26.194(5)	17.674(4)
α, deg		85.91(3)	103.35(3)
β, deg	107.13(3)	82.66(3)	93.88(3)
γ, deg		79.02(3)	108.50(3)
V, Å^3	1887.2(7)	2288.90	1326.70
space group[20]	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
Z	2	2	2
D_{calcd}, g/cm^3	2.099	2.046	2.003
F_{000}	1136	1344	776
temp, °C	−73	−55	−73
μ (Mo Kα), cm^{-1}	99.99	84.90	71.68
diffractometer	Nonius Kappa CCD		
radiation	Mo Kα, graphite monochromated ($\lambda = 0.71073$ Å)		
detector position, mm	34		
exposure time, s/frame	2	5	3
scan type	ω(1 deg/frame)		
$2\theta_{\max}$, deg	52.0	49.0	52.0
no. of rflns measd.			
total	9798	22826	20998
unique	3702	7063	5203
R_{int}	0.0425	0.0384	0.0559
corrns	Lorentz−polarization factor		
structure soln	direct-method (SHELXS-97; SHELXL-97)[21]		
refinement	full-matrix least-squares		
anomalous dispersion	all non-hydrogen atoms		
no. of observns ($I > 2.\sigma(I)$)	3135	5695	4766
no. of variables	206	495	335
rfln/param ratio	15.21	11.50	14.22
residuals:			
R	0.0465	0.0483	0.0278
R_{w}	0.1168	0.1203	0.0629
R(all)	0.1222	0.1300	0.0649
goodness of fit	1.057	1.038	1.051
max peak, e/Å^3	2.519	2.924	2.007
min peak, e/Å^3	−3.157	−2.478	−1.070
abs corr			SORTAN[22]

$[Mo((CH_3)C_3H_4)(CO)_2(CH_3CN)_2Cl]$ in 20 mL of thf was added dropwise to a suspension of 0.53 g (1.54 mmol) of $[Bi(OEt)_3]$ (prepared by ethanolysis of $[Bi(O^tBu)_3]$) in 40 mL of thf, yielding (initially) a clear red-orange solution. After the addition of all $[Mo((CH_3)C_3H_4)(CO)_2(CH_3CN)_2Cl]$ a dark brown precipitate and a brownish-red solution were obtained. The filtrate was reduced to dryness, leading to 0.45 g of a crude product consisting of 0.32 mmol (84% yield) of **3** contaminated by 0.19 mmol of $[EtOBiCl_2]$ (as indicated by a Cl analysis of 3% and the integrals of the ethoxy signals in the ^{1}H NMR spectrum). For further purification the solid was dissolved in 20−30 mL of thf, layered with hexane, and stored at 0 °C for 2 weeks, yielding red-orange crystals of **3** (decomposition at 130 °C).^{1}H NMR (thf-d_8): $\delta_H = 4.85$ (br, 16H, μ-$\mathrm{OC}H_2\mathrm{CH_3}$); 2.85 (s, 4H, $H_s\mathrm{H_aCC(CH_3)CH_a}H_s$); 2.05 (s, 6H, $\mathrm{H_sH_aCC(C}H_3\mathrm{)CH_aH_s}$); 1.25 (br, 24H, μ-$\mathrm{OCH_2C}H_3$); 0.76 (s, 4H, $\mathrm{H_s}H_a\mathrm{CC(CH_3)C}H_a\mathrm{H_s}$). ^{13}C{^{1}H} NMR (thf-d_8): $\delta = 234.3$ (s, *C*O), 86.4 (s, $\mathrm{H_2C}C\mathrm{(CH_3)CH_2}$), 64.9 (br, $\mathrm{O}C\mathrm{H_2CH_3}$), 55.5 (s, $\mathrm{H_2CC(CH_3)}C\mathrm{H_2}$), 21.6 (s, $\mathrm{OCH_2}C\mathrm{H_3}$), 20.8 (s, $\mathrm{H_2CC(}C\mathrm{H_3)CH_2}$). IR/KBr [cm^{-1}]: 2958 (vs); 2919 (sh); 2860 (s); 1925 (vs); 1826 (vs); 1444 (m); 1377 (m); 1088 (vs); 1037 (vs); 881 (s); 514 (br). Anal. Calcd for $C_{28}H_{54}Bi_2Mo_2O_{12}$: C, 28.20; H, 4.56. Found: C, 27.72; H, 4.47.

$[((CH_3)C_3H_4)(CO)_2Mo(\mu\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}Cl)BiCl\cdot thf]$ (4). A solution of 0.48 g (1.47 mmol) of $[Mo((CH_3)C_3H_4)(CO)_2(CH_3CN)_2Cl]$ in 30 mL of thf was added dropwise to a solution of 1.27 g (1.47 mmol) of $[Bi(OCH_2CH_2OCH_3)_3]_2$ in 50 mL of thf. The resulting orange solution was filtered off the precipitate, which had formed simultaneously, and reduced to 30 mL. After layering with 40/60 petroleum ether and storing at −20 °C for 2 weeks orange crystals of **4** (0.50 g (0.7 mmol), 48%; decomposition at 140 °C) were obtained. ^{1}H NMR (thf-d_8): $\delta_H = 4.84$ (m, br, 4H, μ-$\mathrm{OC}H_2\mathrm{CH_2OCH_3}$); 3.65 (m, 4H, μ-$\mathrm{OCH_2C}H_2\mathrm{OCH_3}$), 3.46 (s, 6H, μ-$\mathrm{OCH_2CH_2OC}H_3$); 2.82 (s, 2H, $H_s\mathrm{H_aCC(CH_3)CH_a}H_s$); 2.13 (s, 3H, $\mathrm{H_sH_aCC(C}H_3\mathrm{)CH_aH_s}$); 0.89 (s, 2H, $\mathrm{H_s}H_a\mathrm{CC(CH_3)C}H_a\mathrm{H_s}$). ^{13}C{^{1}H} NMR (thf-d_8): $\delta = 231.7$ (s, *C*O), 86.4 (s, $\mathrm{H_2C}C\mathrm{(CH_3)CH_2}$), 76.5 (s, $\mathrm{O}C\mathrm{H_2CH_2OCH_3}$), 68.2 (s, $\mathrm{OCH_2}C\mathrm{H_2OCH_3}$), 58.8 (s, $\mathrm{OCH_2CH_2O}C\mathrm{H_3}$), 54.0 (s, $\mathrm{H_2CC(CH_3)}C\mathrm{H_2}$), 21.2 (s, $\mathrm{H_2CC(}C\mathrm{H_3)CH_2}$). IR/KBr [cm^{-1}]: 2912 (vs); 2850 (s); 1942 (vs); 1835 (vs); 1452 (m); 1375 (w); 1350 (m); 1262 (w); 1234 (m); 1195 (m); 1064 (s); 1012 (s); 900 (s); 836 (s); (805 (w); 615 (w); 587 (m); 555 (w); 513 (w); 462 (m). Anal. Calcd for $C_{16}H_{29}BiCl_2MoO_7$ (709.22): C, 27.10; H, 4.12; Cl, 10.0. Found: C, 26.60; H, 4.11; Cl, 10.48.

$[((CH_3)C_3H_4)(CO)_2Mo(\mu\text{-}OCH_2CH_2OCH_3)_3Bi(thf)][BF_4]$ (6). A solution of 0.24 g of $AgBF_4$ (1.23 mmol) in 10 mL of thf was added dropwise to a solution of 0.40 g (1.23 mmol) of $[Mo(\eta^3\text{-}C_4H_7)(CO)_2(CH_3CN)_2Cl]$ in 20 mL of thf, leading to the precipitation of AgCl. After stirring overnight, the orange solution was filtered directly into a solution of 1.06 g (1.23 mmol) of $[Bi(OCH_2CH_2OCH_3)_3]_2$ in 40 mL of thf. The resulting beige precipitate was filtered off, and the clear solution was reduced to dryness. The residue was dissolved in 20−30 mL of thf, layered with 40/60 petroleum ether, and stored at −20

°C for 2 weeks. Yellow crystals of **6** (0.19 g (0.24 mmol), 20% yield, decomposition at 130 °C) were obtained. ^{1}H NMR (thf-d_8): $\delta_H = 4.86$ (m, br, 6H, μ-$OC\mathit{H}_2CH_2OCH_3$); 3.64 (m, 6H, μ-$OCH_2C\mathit{H}_2OCH_3$), 3.55 (s, 9H, μ-$OCH_2CH_2OC\mathit{H}_3$); 2.88 (s, 2H, $\mathit{H}_sH_aCC(CH_3)CH_a\mathit{H}_s$); 2.01 (s, 3H, $H_sH_aCC(C\mathit{H}_3)CH_aH_s$); 0,83 (s, 2H, $H_s\mathit{H}_aCC(CH_3)C\mathit{H}_aH_s$). ^{13}C{^{1}H} NMR (thf-d_8): $\delta = 233.5$ (s, *C*O), 87.7 (s, $H_2C\mathit{C}(CH_3)CH_2$), 76.76 (s, $O\mathit{C}H_2CH_2OCH_3$), 65.5 (s, $OCH_2\mathit{C}H_2OCH_3$), 59.5 (s, $OCH_2CH_2O\mathit{C}H_3$), 55.0 (s, $H_2\mathit{C}C(CH_3)\mathit{C}H_2$), 21.3 (s, $H_2CC(\mathit{C}H_3)CH_2$). IR/KBr [cm^{-1}]: 2921 (s); 2856 (sh); 1938 (vs); 1838 (vs); 1457 (m); 1350 (w); 1262 (w); 1234(w); 1195 (w); 1077 (br, vs); 900 (m); 837 (w); 801 (w); 590 (w); 559 (vw); 506 (vw); 473 (m). Anal. Calcd for $C_{15}H_{28}BBiF_4MoO_8$ (**6**−thf): C, 24.74; H, 3.88. Found: C, 25.28; H, 4.03.

Crystal Structure Determinations. Single crystals were grown by diffusion of petroleum ether (**4** and **6**) or hexane (**3**) into thf solutions of the compounds at 0 °C (**3**) or −20 °C (**4**, **6**) within 1−2 weeks. These crystals were preselected in a glovebox and immersed in fluorocarbon oil there. Individual crystals were then mounted on top of a fiber and quickly frozen to −70 °C. Centered reflections were refined by least-squares calculations to indicate the unit cells. Unit cell and collection parameters for the complexes are listed in Table 4. Diffraction data were collected in the appropriate hemispheres and under the conditions specified also in Table 4. The structures were solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the calculated idealized positions and refined isotropically. For complex **3** the hydrogen atoms at C(3) and C(5) were refined isotropically and then fixed. In the crystal of complex **4** there are two symmetry-independent molecules (plus one noncoordinated thf molecule each) per unit cell (one of these two molecules is shown in Figure 2). For complex **6** an absorption correction using SORTAV (a program included in the MAXUS[22] package of Nonius) was applied. For the graphical representation the programs XPMA and ZORTEP were used.[23]

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft for scholarships (C. L., Habilitandenstipendium; M. H., Graduiertenkolleg Heidelberg), the Fonds der Chemischen Industrie for funding, and Professor G. Huttner for his generous support.

Supporting Information Available: Listings of X-ray structural data for all complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9908229

---

(20) *International Tables for X-ray Crystallography*, Vol. 4; Kynoch-Press: Birmingham, 1974.

(21) Sheldrick, G. M. *SHELXS-97* and *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen, 1997.

(22) *SORTAN*, Data Collection Software; Nonius 1998; collect@nonius.com.

(23) Zsolnai, L.; Huttner, G. *XPMA*; Universität Heidelberg, 1998; http://www.rzuser.uni-heidelberg.de/~v54/xpm.html.