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Organometallic Mo–O–Bi complexes

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Dedicated to Prof. Dr. Gottfried Huttner on the occasion of his 68th birthday.

Abstract

The reaction between Ph_3BiBr_2 and wet $[NBu_4]_2[MoO_4]$ leads to a white solid that according to Klemperer and Liu analyses as $[NBu_4]_2[BiPh_3(MoO_4)_2] \cdot 3H_2O$ ($\mathbf{1^{aq}}$). Working under strictly anhydrous conditions allowed us the isolation of the solvate-free complex $[NBu_4]_2[BiPh_3(MoO_4)_2]$ (**1**), which in contrast to $\mathbf{1^{aq}}$ could also be characterised by means of single crystal X-ray diffraction. The results reveal a structure with a Bi^V ion being surrounded by three phenyl substituents and two molybdate units. Remarkably the resulting two Mo^{VI}–O–Bi^V linkages are linear and according to a DFT investigation this is due to a predominantly ionic interaction between the O and Bi atoms. Moreover a novel Mo^{VI}–O–Bi^{III} complex, $NBu_4[\{Cp*Mo(O)_2\text{-}\mu\text{-O-}\}_2(Bi(o\text{-tolyl})_2)]$ (**2**), has been prepared via reaction of the coordination polymer $[(Cp*Mo(O)_2)\text{-}\mu\text{-O-}(Bi(o\text{-tolyl})_2)]_n$ with $[NBu_4][Cp*MoO_3]$ and the crystal structure of **2** has been investigated. According to DFT results the character of the bonds within the bent Mo–O–Bi unit is described most appropriately as covalent. The structure of **2** is discussed also with respect to corresponding Mo–O–Bi moieties occurring in bismuthmolybdate catalysts, for which it could represent a molecular structural model.
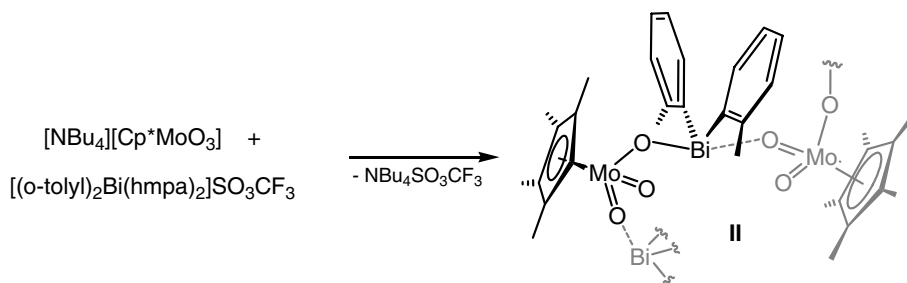© 2005 Elsevier B.V. All rights reserved.

1. Introduction

$nMoO_3/Bi_2O_3$ phases represent heterogeneous catalysts for the allylic oxidation of propene. The reasons why exactly this combination of metals is most efficient are still discussed controversially [1]. The favourable properties of bismuthmolybdates might be related inter alia to the presence of Mo–O–Bi linkages on the surface of these solids assuming that such assemblies possess favourable H abstraction or radical trapping properties. This hypothesis naturally stimulates attempts aimed at establishing Mo–O–Bi units also in molecular compounds, however, until recently, there was no structurally characterised molecular Mo–O–Bi complex exis-

tent in the literature [2]. Only recently, we achieved the synthesis and isolation of such complexes by combining experiences we made in Mo/Bi alkoxide chemistry [3] with results described in an early literature report.

In 1980, Klemperer and Liu reacted Ph_3BiBr_2 with $[NBu_4]_2[MoO_4]$ that contained significant amounts of water and obtained a white solid that analysed as $[NBu_4]_2[BiPh_3(MoO_4)_2] \cdot 3H_2O$ ($\mathbf{1^{aq}}$) [4]. A structure with a Bi^V ion being surrounded by three phenyl substituents and two molybdate units was envisioned, while the additional water molecules were proposed to act only as solvate molecules. Unfortunately, it was not possible to perform an X-ray crystal structure analysis which could have supported that idea. Having experienced that Mo/Bi alkoxides became accessible when *organo* molybdenum starting materials were employed [3] we performed the reaction reported by Klemperer replacing the molybdate by an *organo* molybdenum(VI)oxo anion, namely

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$$2\ [NBu_4][Cp*MoO_3]\ +\ Ph_3BiBr_2 \xrightarrow[-\ 2\ NBu_4Br]{}$$
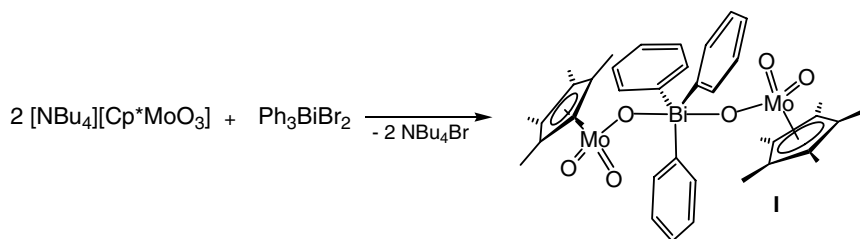
Scheme 1. The synthesis of **I**.

$$[NBu_4][Cp*MoO_3]\ +$$
$$[(o\text{-tolyl})_2Bi(hmpa)_2]SO_3CF_3 \xrightarrow[-\ NBu_4SO_3CF_3]{}$$

Scheme 2. The synthesis of **II**.

$[Cp*MoO_3]^-$: Treatment of Ph_3BiBr_2 [5] with two equivalents of $[NBu_4][Cp*MoO_3]$ [6] led to $[(Cp*Mo(O)_2\text{-}\mu\text{-}O)_2BiPh_3]$ (**I**), and a single crystal X-ray analysis revealed the first structurally authenticated Mo–O–Bi linkages in a molecular compound [7] (Scheme 1). Having accessed the area of Mo^{VI}–O–Bi^V compounds the next target was obvious: by the majority, it is believed that Bi^V ions [8] do not play significant roles under the conditions of the SOHIO process; Bi^{III} centres are thought to be more important within the catalytic cycle [1], so that in the next step the synthesis of the first Mo^{VI}–O–Bi^{III} complex was pursued. We succeeded finally with the isolation of $[(Cp*Mo(O)_2)\text{-}\mu\text{-}O\text{-}(Bi(o\text{-tolyl})_2)]_n$ (**II**), which represents a coordination polymer [7] (Scheme 2).

2. Results and discussion

Bearing in mind the above mentioned results two questions arose:

1) What is the nature of the compound $\mathbf{1^{aq}}$ Klemperer prepared in 1980? Did he have a molecular complex with Mo^{VI}–O–Bi^V linkages in his hands, and if yes: How does this compound compare structurally to **I** containing *organo* molybdate moieties?
2) Is it possible to break down coordination polymer **II** via treatment with additional $[NBu_4][Cp*MoO_3]$ in order to form a hypervalent anion of the type $[\{Cp*Mo(O)_2\text{-}\mu\text{-}O\text{-}\}_2(Bi(o\text{-tolyl})_2)]^-$?

The present paper addresses these two questions.

In order to obtain crystals of Klemperers product we decided to follow his synthetic route [4] but under strict anhydrous conditions, so that not $\mathbf{1^{aq}}$ but solvate free $[NBu_4]_2[BiPh_3(MoO_4)_2]$ (**1**), would be produced. Hence, the starting material $[NBu_4]_2[MoO_4]$, which after its synthesis from MoO_3 and $[NBu_4]OH$ contains significant amounts of water and had been employed in this form by Klemperer, was vigorously dried before it was reacted with Ph_3BiBr_2. After work up a white solid was obtained which could be recrystallised from acetonitrile/diethyl ether. Finally single crystals suitable for an X-ray diffraction analysis were obtained, and the result is shown in Fig. 1 (also compare Scheme 3).

The crystals of **1** contain discrete molecular dianions which exhibit a crystallographical C_2-axis passing through the atoms C10, C7 and Bi. The Bi centre is situated in a slightly distorted trigonal bipyramidal ligand sphere (O1–Bi–O1′ 179.7(2), C1–Bi–O1 89.2(2), C1–Bi–O1′ 90.6(2), C7–Bi–O1 90.2(2), C1–Bi–C7 122.4(2), C1–Bi–C1′ 115.2(2)) with the oxygen atoms at the apical sites and the phenyl rings in the equatorial positions. Such a geometrical arrangement is typical for Ph_3BiX_2 structures [9]. The Mo–O–Bi moieties are nearly linear (Mo–O1–Bi 173.6(2)°) which is somewhat surprising and could be explained by an sp-hybridization of the O-atoms like in the polymorphs of $[Cp*Mo(O)_2]_2O$ [10] where the Mo–O–Mo angles amount to 172.7(3)°, 179.2(4)° and 180.0°. On the other hand these linear bridges could hint to a more ionic binding mode characterised by an electrostatic interaction between the molybdate units and the Ph_3Bi^{2+} entity. In order to get clarity about the bonding situation in **1** DFT calculations were carried out on the B3LYP/Lanl2dz level of theory. The crystal structure of the dianion of **1** was
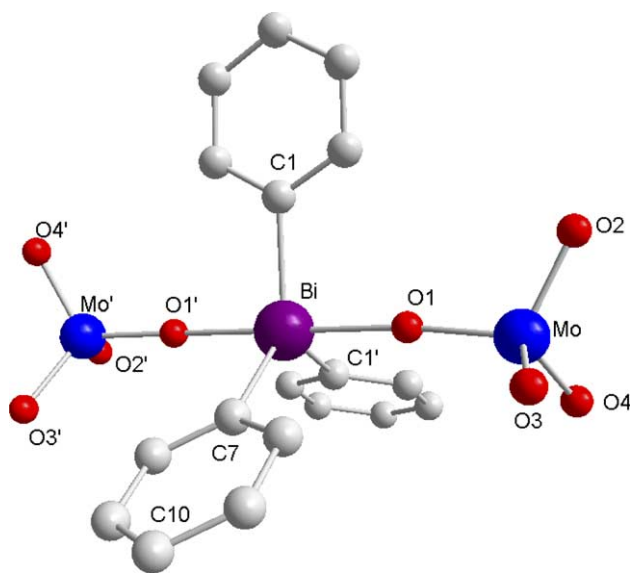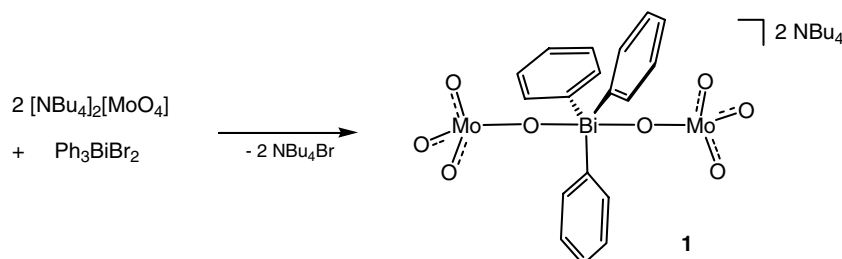
Fig. 1. Molecular structure of the dianion of **1**. The *n*-tetrabutylammonium cations and all hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): Bi–O1 2.169(3), Bi–C1 2.222(4), Bi–C7 2.219(6), Mo–O1 1.839(3), Mo–O2 1.734(2), Mo–O3 1.739(4), Mo–O4 1.730(3), O1–Bi–O1′ 179.7(2), Mo–O1–Bi 173.6(2), O1–Mo–O2 110.2(2), O1–Mo–O3 109.7(2), O1–Mo–O4 109.7(2), O2–Mo–O3 108.7(3), O2–Mo–O4 108.9(2), O3–Mo–O4 109.7(2), C1–Bi–C1′ 115.2(2), C1–Bi–C7 122.4(2), C1–Bi–O1 89.2(2), C1–Bi–O1′ 90.6(2), C7–Bi–O1 90.16(8).

employed as the starting geometry which was subsequently optimised. In the optimised structure all bond lengths and angles compare well to the experimental data (the average deviation of the bond lengths amounts to only 2.1%); the only marked difference between the experimental and the theoretical structure is the fact that the latter exhibits a perfect D_{3h} symmetry – as a result of a torsion around a Mo–O bond, probably due to the lack of crystal packing forces. The most interesting result of these calculations is the distribution of the charges: both the bridging O atoms and the Bi centre carry unusually high charges (O: −1.142 and Bi: 2.497, respectively), which hint to ionic subunits, and indeed an NBO analysis failed to detect a hybrid orbital between Bi and O. The interaction is thus of an electrostatic nature, and this is the explanation for the linear Mo–O–Bi arrangement. Nevertheless, the Bi–O dis

tances (2.169(3) Å) are somewhat shorter than those found in **I** (2.198(6) and 2.204(6) Å). This might be the effect of the diminished steric hindrance in **1** in comparison to **I** where a closer approach of the $Cp^*MoO_3^-$ moiety to the Bi^V centre might be prevented by Ph ↔ Cp* repulsive interactions. However, the Bi–O bonds are longer than those reported for the known μ-oxo bridged dinuclear organobismuth(V) compounds [Ar₃BiOBiAr₃(Y)₂] (Y = ClO₄⁻, CF₃SO₃⁻, Ar = Ph; Y = Cl⁻, Ar = 4-(Me₂N)C₆H₄), covering a range from 2.02–2.12 Å [11], which will be due to the ionic nature of the bonding in **1**. The Mo–O single bond distances of 1.839(3) Å appear quite short as compared to those in the polymorphs of [Cp*Mo(O)₂]₂O (1.855(6)–1.894(4) Å) [10] and this might as well be a result of the ionic character of the Bi–O interaction. The remaining Mo–O bonds have similar lengths (Mo–O2 1.734(2), Mo–O3 1.739(4), Mo–O4 1.730(3)) indicating a delocalization of the negative charge across the three MoO groups. Accordingly, they are longer than the "real" Mo=O double bonds in **I** (1.706(6)–1.728(6) Å) and those reported for the polymorphs of [Cp*Mo(O)₂]₂O (1.667(8)–1.721(5) Å) [10].

Turning the attention now back onto Bi^{III} chemistry the above mentioned question (2) was tackled via treatment of **II** with [NBu₄][Cp*MoO₃]. On addition of one equivalent of [NBu₄][Cp*MoO₃] to a suspension of **II** in dichloromethane all solid is extracted into the solution. Removal of the solvent leads to a bright yellow solid which could be crystallised by slow evaporation of diethyl ether from a corresponding solution. Fig. 2 shows the result of an X-ray crystal structure analysis (also compare Scheme 4).

In the anion of **2** two $Cp^*MoO_3^-$ moieties are bound via an oxygen atom to a (*o*-tolyl)₂Bi⁺-fragment (*o*-tolyl = 2-(CH₃)C₆H₄) forming a 10 electron four-coordinated bismuth centre. There are two independent monomeric units present in the unit cell. The ligands surrounding the Bi centres in the anions of **2** show an overall equatorial vacant ψ-trigonal bipyramidal coordination geometry – often described as "seesaw" structure – which has been observed in the related halo anions [Ph₂BiX₂]⁻ (X = Br, I) [12] and [Ph₂Bi(O₂CCF₃)₂]⁻ [13], too. This kind of ligand arrangement can be

2 [NBu₄]₂[MoO₄]

+ Ph₃BiBr₂ $\xrightarrow{\text{- 2 NBu}_4\text{Br}}$
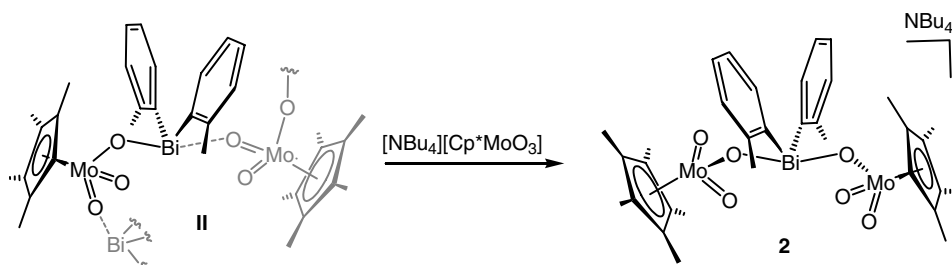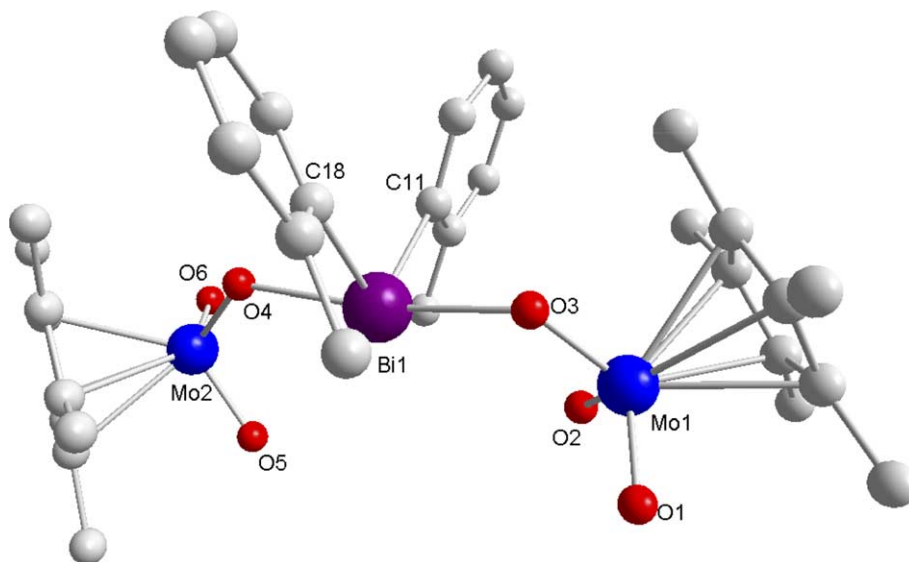
Scheme 3. The synthesis of **1**.

Scheme 4. The synthesis of **2**.

Fig. 2. Molecular structure of one of the two independent molecular anions present in the unit cell identified for crystals of **2**. The corresponding *n*-tetrabutylammonium cation and all hydrogen atoms were omitted for clarity. The second anion contained in the asymmetric unit is an conformer of the former one with only slightly differing bond lengths and angles. Each unit cell additionally contains a disordered, non-localisable solvent molecule. Selected bond distances (Å) and angles (°): Bi1–O3 2.331(9), Bi1–O4 2.367(9), Bi1–C11 2.25(2), Bi1–C18 2.27(2), Mo1–O1 1.71(2), Mo1–O2 1.71(2), Mo1–O3 1.80(1), Mo2–O4 1.765(9), Mo2–O5 1.73(2), Mo2–O6 1.73(2), O3–Bi1–O4 170.9(3), Mo1–O3–Bi1 123.6(5), Mo2–O4–Bi1 129.2(5), C11–Bi1–C18 98.9(5), C11–Bi1–O3 88.2(4), C11–Bi1–O4 89.5(4), C18–Bi1–O3 87.9(4), C18–Bi1–O4 83.7(4), O2–Mo1–O1 104.8(6), O2–Mo1–O3 104.0(5), O1–Mo1–O3 108.0(6), O6–Mo2–O5 107.7(6), O6–Mo2–O4 105.6(5), O5–Mo2–O4 104.8(5).

rationalised following the discussion given by N.C. Norman, G.A. Orpen et al. [12]. Accordingly, the occupied orbitals of $[R_2BiX_2]^-$ complexes altogether are stabilised most when a structure with a C_{2v} symmetry is adopted; therefore structures with T_d or D_{4h} symmetry are energetically disfavoured [14]. Contemplating the construction of the anion of **2** starting from a hypothetical situation where the components $(o\text{-tolyl})_2Bi(O\text{-}Mo(O)_2Cp^*$ and $Cp^*MoO_3^-$ are separated and approach each other to form a bonding MO the relevant acceptor orbital would be the Bi–O σ^*-orbital thus leading to a nearly linear arrangement of the electronegative oxygen atoms [12]. The angle between the oxygen atoms (O3–Bi1–O4 170.9(3)°) is close to the ideal value of 180° and compares well with the corresponding one found in **II** (170.46(9)°). As observed in $[Ph_2BiI_2]^-$ [12b] or $[Ph_2Bi(O_2CCF_3)_2]^-$ [13], already, and predicted by a bonding model for AB_4 non-transition-element com-

plexes given by Gimarc [14], the apical ligands are slightly bent towards the phenyl groups. The angle between the *ipso* carbon atoms (C11–Bi1–C18 98.9(5)°) is significantly less than the ideal value for a trigonal bipyramid of 120°. Such acute angles are not uncommon in the stereochemistry of heavy main group elements. If the coordination is described as ψ-trigonal bipyramidal, a strong stereochemical effect of the bismuth lone pair on the C–Bi–C angle is implied. However, alternative bonding models based on unhybridised 6p orbitals with the lone pair of electrons at the bismuth centre in a 6s orbital appear equally appropriate [9], and indeed the results of the theoretical investigation described below show that this model is more appropriate for **2**.

Focussing on the closer surroundings of the Bi atom the structures of **II** and **2** are similar. However, while in case of **II** it is achieved via polymerisation of a hypothetical $[Cp^*MoO_3Bi(o\text{-tolyl})_2]$ molecule with $Cp^*MoO_3^-$

"ligands" acting as bridging units between two Bi centres, in **2** it results from the coordination of an additional Cp*MoO$_3^-$ anion to the above mentioned molecule. Hence, even though there is a close relationship between **II** and **2** being reflected in comparable bond lengths and angles, differences result from the fact that **2** exhibits a Mo–O–Bi–O–Mo unit, while **II** has to be regarded as containing Mo–O–Bi ··· O=Mo moieties. Consequently, the Bi–O bond lengths in **2** are quite similar (Bi1–O3 2.331(9), Bi1–O4 2.367(9) Å), while they are somewhat different in **II** (2.310(2), 2.385(2) Å). The Bi–O bonds in **2** are comparable to those displayed by the [Ph$_2$Bi(O$_2$CCF$_3$)$_2$]$^-$ anion (2.39(2) Å) [13] and the recently communicated bismuth-oxo cluster cation [Bi$_{22}$O$_{26}$]$^{14+}$ incorporating μ$_3$-O bridges with Bi–O bond lengths between 2.037 and 2.665 Å [15]. It is instructive to compare them also with those within the bismuth molybdate catalysts. In β-bismuthmolybdate, Bi$_2$Mo$_2$O$_9$ [16], for instance, the Bi–O bond distances lie in a range of 2.34(3)–2.79(3) Å, and those in **2** are positioned at the shorter edge of this range.

The Mo–O single bond distances in **2** amount to 1.80(1) (Mo1–O3) and 1.765(9) Å (Mo2–O4) and are thus similar to the corresponding bonds in **II** (1.786(2) Å). They are at the upper end of the range the Mo–O bond lengths define in the Bi$_2$Mo$_2$O$_9$ solid (1.71(3)–1.78(3) Å) [16], and at the same time they are significantly shorter than the ones found in the polymorphs of [Cp*Mo(O)$_2$]$_2$O (1.855(6)–1.894(4) Å) [10]. In contrast to **1** the Mo–O–Bi moieties in **2** are bent, and the bending is stronger (Mo1–O3–Bi1 123.6(5)°, Mo2–O4–Bi1 129.2(5)°) than the one observed in **II** (160.6(2)°, 138.0(2)°). The Mo=O double bond lengths are with 1.71(2) (Mo1–O1, Mo1–O2) and 1.73(2) Å (Mo2–O5, Mo2–O6) comparable to the Mo=O bonds in the other known Cp*MoO$_2$–O–Bi complexes (1.720(2) Å in **II**, 1.706(6)–1.728(6) Å in **I**), but they are at the upper end of the range the Mo=O bond lengths define in the [Cp*Mo(O)$_2$]$_2$O system (1.667(8)–1.721(5) Å). In this context, it is noteworthy that the distances between Bi1 and O2/O5 amount to 3.55 and 3.71 Å, respectively, which is smaller than the sum of the Bi/O van der Waals radii ($\sum_{r,vdW.}$ (Bi, O) = 3.9 Å). This might be indicative of additional intramolecular secondary interactions [17] as they have been observed already for compounds like Ph$_3$Bi[(O$_3$SC$_6$H$_5$)]$_2$ [18] (besides the two strong Bi–O bonds there are additional secondary Bi ··· O=S interactions with distances of 3.129 and 3.431 Å). Even shorter secondary bonds are found in the carboxylato derivatives R$_3$Bi[OC(O)CR']$_2$ (see [9] for further examples). Following the theoretical results obtained for **1** with the linear Mo–O–Bi bridges, naturally interest arose in the bonding situation of **2** exhibiting the bent Mo–O–Bi moieties. Again the crystal structure results served to start a geometry optimisation (B3LYP/Lanl2dz). The experimental structure was ni-

cely reproduced at this level with an average deviation of 2.0% for the bond lengths. The match with respect to the bond angles is excellent, too; only the Mo–O–Bi angles are overestimated by the calculation, which might be explained by a comparatively shallow potential for this unit as expected (minimal forces, like for instance crystal packing, would then lead to a large effect, as the rise in energy is small; note that gas phase conditions are considered in the calculation!). The only marked difference between the experimental and the theoretical structure again results from a symmetrisation that has occurred for the theoretical structure (C_2 symmetry after a torsion around one of the Mo–O bonds) probably also due to a lack of crystal packing forces. An NBO analysis reveals a charge distribution (O: −0.892, Bi: 1.67) that supports a covalent bonding within the Mo–O–Bi units (also compare Fig. 3); i.e. **1** and **2** are quite different compounds. Having treated **2** on the theoretical level another obvious point of interest was the character of the Bi lone pair; the hybridisation of such lone pairs is often a matter of intense discussion (vide supra). According to the results of the calculation it has 6s-character in **2**.

Finally it has to be noted that both compounds **1** and **2** are astonishingly stable. Their inertness with respect to molecular oxygen will be due to the high oxidation states of the metal centres, their resistance to moisture has to be explained presumably by the low polarity of the organometallic moieties; a steric shielding by the organic ligands might provide some kinetic stabilisation.

Mo–O–Bi complexes represent a long-sought class of compounds and the successful isolation of **1** and **2** as reported in addition to **I** and **II** shows that there is finally an access. While with **1** an older literature compound has been identified **2** represents a novel type of complex containing two Mo^{VI}–O–Bi^{III} units in a hypervalent bismuthate anion. The results entail further investigations with respect to the chemical properties of such Mo–O–Bi compounds, i.e. their behaviour in the pres-
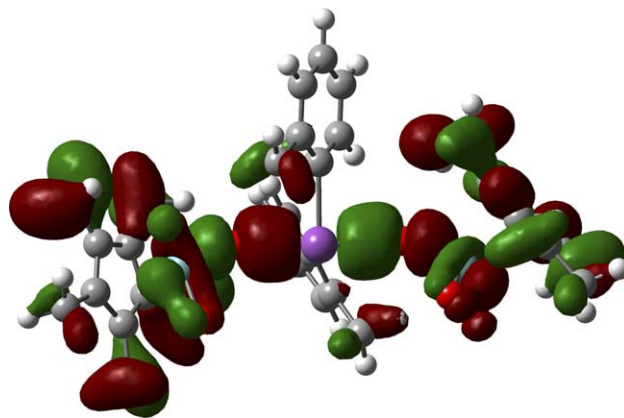

Fig. 3. Occupied MO 118 being obviously constructed by positive overlaps between Bi and O atom orbitals.

ence of hydrocarbons like olefines, substrates with weak C–H bonds as well as organic radicals, to fathom their potential as functional models for Mo–O–Bi units on bismuthmolybdate surfaces.

3. Experimental

3.1. General procedures

All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 NMR spectrometer (^1H, 400.13 MHz; ^{13}C, 100.61 MHz) with CD_2Cl_2 as solvent at 22 °C. The ^1H and $^{13}C\{^1H\}$ NMR spectra were calibrated against the residual proton and natural abundance ^{13}C resonances of the deuterated solvent (dichloromethane-d_2, δ_H 5.32 ppm and δ_C 53.5 ppm). Microanalyses were performed on a Leco CHNS-932 elemental analyser. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Digilab Excalibur FTS 4000 FTIR-spectrometer.

3.2. Materials

Solvents were purified, dried and degassed prior to use. Ph_3BiBr_2 was prepared according to a literature procedure [5] and was recrystallised by slow addition of ethanol to a saturated toluene solution. $[(n-C_4H_9)_4N]_2[MoO_4]$ was prepared following the method of Klemperer [4] and then thoroughly dried by heating to 100 °C in vacuo overnight. $[(n-C_4H_9)_4N][Cp*MoO_3]$ [6] and **II** [7] were prepared according to the literature procedure.

3.3. $[NBu_4]_2[(MoO_4)_2BiPh_3]$ (1)

1 was prepared following a procedure described by Klemperer [4] with some modifications. To a stirred, cloudy solution of $[(n-C_4H_9)_4N]_2[MoO_4]$ prepared from 1.056 g (7.33 mmol) MoO_3 and 14.7 ml $[(n-C_4H_9)_4NOH]$ (1 M solution in methanol; 14.70 mmol) in 20 ml CH_2Cl_2 was added a solution of 2.20 g (3.67 mmol) Ph_3BiBr_2 in 20 ml CH_2Cl_2. The reaction mixture was stirred overnight at r.t., filtered and concentrated to approx. 15 ml. By excessive addition of diethyl ether pure **1** was precipitated. After filtration the white residue was washed with ether and dried in vacuo to yield 3.65 g (2.93 mmol; 80%) of **1**, which can be recrystallised from a mixture of acetonitrile and ether. ^1H NMR (CD_2Cl_2): $\delta = 8.44$ (d, 6H, *o*-phenyl), 7.62 (m, 6H, *m*-phenyl), 7.42 (m, 3H, *p*-phenyl), 3.24 (m, 16H, N–CH_2–), 1.60 (m, 16H, N–CH$_2$CH_2–), 1.35 (m, 16H, –CH_2CH$_3$), 0.94 ppm (m, 24H, –CH_3). ^{13}C NMR (CD_2Cl_2): $\delta = $ 157.1/135.23/130.8 (phenyl-C), 58.8/24.0/19.8/13.5 ppm (n –(C_4H_9)); signals for the *ipso* carbon atoms were

not detected. IR (KBr): v [cm^{-1}] 3073 w, 3051 m, 2961 s, 2931 s, 2872 s, 1561 m, 1493 s, 1468 vs, 1435 s, 1384 m, 1261 w, 1172 w, 1154 w, 1107 w, 1066 w, 1028 w, 1012 m, 991 s, 929 w, 909 m, 871 vs, 804 w, 734 vs, 685 w, 448 w. Anal. Calc. for $C_{50}H_{87}N_2BiMo_2O_8$: C, 48.23; H, 7.04; N, 2.25. Found: C, 48.46; H, 7.03; N, 2.29%.

3.4. $[NBu_4][(Cp*MoO_3)_2Bi(o\text{-}tolyl)_2]$ (2)

To a stirred yellow suspension of 40 mg (0.06 mmol) $[(o\text{-}tolyl)_2BiOMo(O)_2Cp*]_n$ in 2.5 ml CH_2Cl_2 a solution of 31.1 mg (0.06 mmol) $[(n-C_4H_9)_4N][Cp*MoO_3]$ in 2.5 ml CH_2Cl_2 was added. A clear yellow solution formed which was stirred at r.t. for 15 min. The solvent was evaporated to yield 68.0 mg (95 %) of pure **2**, which can be recrystallised by cooling a saturated solution in diethyl ether. ^1H NMR (CD_2Cl_2): $\delta = $ 8.29 (dd, 2H, $^3J = 7.39$ Hz, $^4J = 1.07$ Hz, HC-CBi), 7.49 (d, 2H, $^3J = 7.47$ Hz, HC–CCH$_3$), 7.43 (m, 2H), 7.28 (m, 2H), 3.21 (m, 8H, NC$_4$H$_9$), 2.54 (s, 6H, Ar–CH_3), 1.68 (s, 30H, Cp*–CH_3), 1.64 (m, 8H, NC$_4$H$_9$), 1.42 (m, 8H, NC$_4$H$_9$), 1.02 (t, 12H, $^3J = 7.25$ Hz, NC$_4$H$_9$). ^{13}C NMR (CD_2Cl_2): $\delta = $ 145.1/138.6/131.7/129.1/127.8 (Ar–C), 115.9 (Cp*), 58.8/23.9/19.9/13.6 (NC$_4$H$_9$), 24.4 (Ar–CH$_3$), 10.1 (Cp*-CH$_3$). IR (KBr): v [cm^{-1}] 3049 w, 2963 s, 2933 m, 2916 m, 2875 m, 1630 br, 1489 w, 1448 m, 1380 m, 1262 w, 1202 m, 1173 w, 1157 w, 1115 m, 1103 m, 1087 w, 1068 w, 1058 w, 1029 w, 878 vs, 849 vs, 819 m, 802 m, 779 m, 742 vs, 727 vs, 705 m, 624 w, 411 w. Anal. Calc. for $C_{50}H_{80}NBiMo_2O_6$: C, 50.38; H, 6.76; N, 1.18. Found: C, 50.35; H, 7.02; N, 1.09%.

3.5. Crystal structure determinations

Suitable single crystals of **1** were obtained by preparing a saturated solution of **1** in a mixture of 31 ml acetonitrile and 51 ml of diethyl ether followed by cooling to 0 °C. Suitable single crystals of **2** were obtained by slow solvent evaporation from a saturated solution of **2** in diethyl ether. The crystal of **2** investigated revealed an intergrown from two domains which affected the quality of the crystal structure determination. The crystals were mounted on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS I for **1**, Stoe IPDS2T for **2**) using Mo Kα radiation, $\lambda = 0.71073$ Å, and the structures were solved by direct methods (SHELXS-97) [19], refined versus F^2 (SHELXL-97) [20] with anisotropic temperature factors for all non-hydrogen atoms (see Table 1). All hydrogen atoms were added geometrically and refined by using a riding model.

The crystallographic data (apart from structure factors) of **1** and **2** were deposited at the Cambridge Crystallographic Data Centre as supplementary publication

Table 1
Crystal data and experimental parameters for the crystal structure analysis of **1** and **2**

	1	**2**
Empirical formula	$C_{50}H_{87}BiMo_2N_2O_8$	$C_{50}H_{80}BiMo_2NO_6$
Formula mass (g mol^{-1})	1245.08	1192.04
Crystal size (mm)	$0.48 \times 0.44 \times 0.40$	$0.60 \times 0.40 \times 0.36$
Crystal system	Monoclinic	Triclinic
Space group (no.)	$C2/c$ (15)	$P\bar{1}$ (2)
Z	4	4
a (Å)	25.948(4)	13.678(2)
b (Å)	13.697(2)	16.120(3)
c (Å)	16.127(2)	26.457(3)
α (°)	90	81.57(2)
β (°)	92.60(2)	77.45(2)
γ (°)	90	79.20(2)
V (Å^3)	5726(2)	5559(2)
ρ_{calc} (g cm^{-3})	1.444	1.479
T (K)	180(2)	180(2)
Absorption correction	Semi-empirical from equivalents	Numerical
μ (mm^{-1})	3.544	3.648
T_{min}/T_{max}	0.3314/0.2811	0.3534/0.2182
$F(000)$	2528	2512
Index ranges	$-31 \leqslant h \leqslant 31, -16 \leqslant k \leqslant 16, -19 \leqslant l \leqslant 19$	$-15 \leqslant h \leqslant 15, -18 \leqslant k \leqslant 18, -30 \leqslant l \leqslant 30$
θ range (°)	2.79–25.25	2.13–24.10
Number of collected reflections	18,149	48,806
Number of independent reflections	5185 [$R_{int} = 0.053$]	16,547 [$R_{int} = 0.092$]
Number of reflections [$I > 2\sigma(I)$]	4604	12,114
Number of parameters	290	1107
R_1 [$I > 2\sigma(I)$]	0.0292	0.0750
wR_2 (all)	0.0731	0.2004
Maximum/minimum residual electron density (e Å^{-3})	+0.836/−1.024	+1.614/−2.353

nos. CCDC 262535 and 262536. Copies of the data can be ordered free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

3.6. Calculations

The calculations were performed using the GAUSSIAN-03 program package [21]. The optimisation and NBO analysis were carried out with the density functional theory (DFT) using the B3LYP functional in conjunction with a Lanl2dz basis set. Harmonic vibrational frequencies were predicted by numerical second derivatives using numerical calculated first derivatives. No negative frequencies were obtained, which proves that the calculated structures are in fact minima on the potential energy surface. Graphical representations of the molecular orbitals were obtained using Gaussview.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.04.059.

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