Bismuth Complexes

Intramolecular C–H Activation in Complexes with Mo–Bi Metal Bonds**

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Dedicated to Professor Helmut Werner
on the occasion of his 70th birthday

The unique property of nMoO3/Bi2O3 phases to act as catalysts for the allylic oxidation of propene remains a subject of intense discussion,[1] that stimulates research with respect to the element combination Mo/Bi on the molecular level.[2–5] Among the known compounds containing these two metals one class exhibits direct Mo–Bi metal bonds, and, bearing in mind the oxygenating properties of bismuthmolybdate phases, it seems interesting to investigate the behavior of such linkages on exposure to oxidants. Such a study, however, is only possible, if the residual complex is not affected by the oxidizing-agent employed, and until recently all known compounds with Mo–Bi units (e.g. [ClBi{Mo(CO)3Cp}2][3] and [Mo2(CO)4(μ-η1:η1-Bi2)]4) (Cp = C5H5, MeCp = C5H4Me) as well as certain others[5]) contained ligands that are not inert under oxidizing conditions. We have recently found a synthetic route leading to compounds with both Mo and Bi centers in oxidatively robust coordination spheres and with the Mo centers in comparatively high oxidation states: For instance treatment of [Cp2MoH2] with [{Bi{OCH(CF3)2}3(thf)}2] provided [Cp2Mo{Bi{OCH(CF3)2}2}2] (1), which functions as an effective epoxidation precatalyst.[6] Herein we describe the investigation of the system [66CrCp2MoH3]/Bi(OtBu)3 that revealed a remarkable C–H activation process.

The reaction between [66CrCp2MoH3] and Bi(OtBu)3 in a 1:2 ratio (Scheme 1) yields [66CrCp2Mo(Bi(OtBu)3)2] (2), the replacement of the electron-poor hexafluoroisopropyl residues employed in the synthesis of 1 by the electron-rich tert-butyl residues does not alter the outcome of the reaction. The molecular structure[7] of 2 is depicted in Figure 1. While the Bi–Bi separation of 3.487 Å is too long to be interpreted in terms of a Bi–Bi bond, the Bi-Mo-Bi angle of 75.27° is even smaller than the H-Mo-H angle in [Cp2MoH3] (75.5°)[8] which means that there are no significant repulsive forces between the two Bi(OR)3 moieties bound to the Mo center. Unlike the

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reaction leading to 1, the synthesis of 2, as followed visually, as well as indicated by its yield proved to be very sensitive to the reaction conditions. This observation gave rise to the following thoughts: from its bond lengths and angles, 2 is an unstrained molecule and should undergo a condensation reaction with excessive molybdocenedihydride, under elimination of two further equivalents of tert-butyl alcohol to give 3 (Scheme 1); this should lead to Mo–Bi–Mo angles of approximately 105°, that is, angles that are common to unstrained bismuthanes. Hence, the synthesis of 3 was attempted by adjustment of the stoichiometry of the two reagents $^{[10]}$Cp$_2$MoH$_2$ and Bi(OtBu)$_3$ in Scheme 1 from 1:2 (required for the formation of 2) to 1:1. These experiments were successful but only when they were carried out in petroleum ether from which 3 precipitates directly as black crystals suitable for an X-ray crystal-structure analysis (Figure 2).

Recently, a dibismuthene complex was described containing a Me$_3$SiCH$_2$Bi=BiCH$_2$SiMe$_3$ ligand coordinated to two $\text{W(CO)}_5$ moieties in a $\mu_3$-$\eta^1$-$\eta^1$ fashion$^{[9]}$ but the Bi–Bi separation in 3 is too long (3.633 Å) for a corresponding bismuthene complex. The Mo–Bi bonds (2.960, 2.924 Å) are somewhat longer than those in 2 (2.855 Å) as are the Bi–O bonds. Bi-Mo-Bi and Mo-Bi-Mo angles of 76.3° and 103.7°, respectively, are indicative of an unstrained structure (see above). During the NMR spectroscopic characterization of 3 in C$_6$D$_6$, it became clear why all attempts to isolate 3 had failed when its synthesis was pursued in benzene or toluene, solvents in which it is soluble. Compound 3 decomposes in solution within a few hours to give two diamagnetic compounds 4 and 4’ (ratio 1:0.8) with rather complex 1H NMR spectra. Subsequent investigations showed that 4 and 4’ can be obtained on a preparative scale when an equimolar solution of $^{[10]}$Cp$_2$MoH$_2$ and Bi(OtBu)$_3$ in toluene is allowed to react at room temperature for 2 days. Cooling of such a toluene solution provides pure 4 in form of black crystals, and a single crystal X-ray diffraction study$^{[7]}$ finally revealed its constitution and deviation from 3: the $\eta^1$-$\mu_3$-CpMo[Bi(OtBu)$_2$] moiety in 3 undergoes two intramolecular tert-butyl alcohol eliminations leading to a—to our knowledge—hitherto unprecedented bonding situation, where a still almost planar $\mu_3$-$\eta^1$-$\eta^1$-Cp ligand bridges three metal centers, which are additionally linked by metal bonds (Scheme 1, Figure 3). This unusual arrangement features Bi–C bonds that are bent by about 40° out of the mean plane defined by the C$_5$ unit. This large bending angle combined with a nonetheless only slight distortion of the Cp ring, which consequently retains its

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{scheme1.png}
\caption{Scheme 1. Reactions within the system $^{[10]}$Cp$_2$MoH$_2$/Bi(OtBu)$_3$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Molecular structure of 2; all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo–Bi 2.8551(9), Bi–O1 2.159(5), Bi–O2 2.117(4), Bi–Bi 3.487(2), Bi-Mo-Bi 75.27(3), O(1)-Bi-O2 89.5(2), Mo-Bi-O1 102.9(2), Mo-Bi-O2 94.0(2).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure2.png}
\caption{Molecular structure of 3; the butyl hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo–Bi 2.960(2), Mo–Bi 2.924(1), Bi–O1 3.6333(9), Bi–O 2.215(5), Bi-Mo-Bi 76.3(1), Mo–Bi–Mo 103.7(4), Mo–Bi–O 106.6(2), Mo–Bi–O 101.9(2).}
\end{figure}
of all the signals to the individual protons in 4. These methods additionally identified 4 as an isomer of 4 differing from it in that the methyl group of the bridging MeC,H ligand is not located at C3 (Figure 3) but at C2. The two isomers are not interconvertible under moderate conditions: warming to 60°C did not alter the spectra significantly.

The reaction between [64]Cp,MoH] and Bi(OBu), in the ratio 1:1 was monitored at room temperature by means of 1H NMR spectroscopy. This study revealed, that after mixing of the reactants all the Bi(OBu)2 is immediately consumed to give a mixture consisting of [64]Cp,MoH], 2, and the novel monohydride complex [64]Cp,Mo[Bi(OBu)]H] (5) in a ratio of 1:1.5. Complex 5 proved to be the most reactive species in the mixture decomposing with a half-life of approximately 15 min through two pathways (Scheme 2): in one, two molecules of 5 eliminate tert-butyl alcohol to give 3, while the other is a much slower process, in which two molecules of 5 form the metathesis products [64]Cp,MoH] and 2. After complete conversion of 5 the concentration of 3 rapidly decreases since its subsequent reaction to 4 and tert-butyl alcohol is much faster than its formation from [64]Cp,MoH] and 2. When the concentration of 3 is negligible the composition of the mixture changes only slowly and the conversion of [64]Cp,MoH] and 2 into 4 and 4 takes days to get near completion (it can be accelerated by warming).

Naturally the question arises, how the intramolecular alcohol eliminations within 3 which lead to 4 can proceed, bearing in mind that they require the cleavage of a non-activated C–H bond, which would not normally be considered as being acidic enough to be susceptible to an attack by an alkoxy function. However, the crystal structure of 3 reveals that for each alkoxy oxygen atom there is one cyclopentadienyl hydrogen atom (namely H1 for O for O) whose position is calculated to be only 2.161 Å away from it (the corresponding O···C separations amount to 3.014 Å). This finding indicates that in dissolved 3 the C–H bonds of its Cp rings might be activated by “complex-induced proximity effects” facilitating elimination of alcohol. For the formation of 4 this requires a sequential process. After the first Bi–C bond formation the resulting molecule has to rearrange by an inversion of the configuration of the second Bi atom, so that both Bi atoms are linked to the same C5 ring.

**Experimental Section**

All manipulations were carried out under an argon atmosphere using dried solvents.

2: A solution of [64]Cp,MoH] (0.200 g, 0.78 mmol) in petroleum ether (10 mL) was added to a stirred suspension of Bi(OBu)2 (0.669 g, 0.78 mmol).
1.56 mmol) in petroleum ether (10 mL). The resulting clear red solution was stirred for 1.5 h at room temperature, and eventually became cloudy. Concentrating the solution and cooling it to ~30°C yielded overnight 0.65 g (0.68 mmol; 86%) 2 in form of red-orange crystals. 3.98 (m, 4H, Cp), 3.64 (m, 4H, Cp), 1.74 (s, 12H, MeCp), 1.68 (s, 6H, MeCp), 1.62 ppm (s, 3H, H24); 1H NMR (300 MHz, C6D6): δ = 5.03 (m, 4H, Cp), 3.98 (m, 4H, Cp), 3.64 (m, 4H, Cp), 1.74 (s, 12H, MeCp), 1.37 ppm (s, 18H, OC(CH3)3).

3: A solution of [90CP-MeOH] (0.200 g, 0.78 mmol) in petroleum ether (10 mL) was added to a stirred solution of Bi(OBu), (0.334 g, 0.78 mmol) in petroleum ether (10 mL). A red solution was formed, which turned black after a few minutes. The reaction mixture was filtered and the filtrate stored at room temperature without further stirring. After 1 h black needles of 3 precipitated, and after 12 h the solution is removed by filtration. The crystals are washed with petroleum ether repeatedly to yield 184 mg (0.17 mmol; 43%) of pure 3. 1H NMR (300 MHz, C6D6): δ = 5.03 (m, 4H, Cp), 3.98 (m, 4H, Cp), 3.64 (m, 4H, Cp), 1.74 (s, 12H, MeCp), 1.37 ppm (s, 18H, OC(CH3)3).

4: Toluene (4 mL) was added to a solid mixture of [90CP-MeOH] (0.100 g, 0.39 mmol) and Bi(OBu), (0.167 g, 0.39 mmol). Shaking the mixture resulted in a red solution, that turned black within 5 min. The reaction mixture was allowed to stand at room temperature for 2 days, then petroleum ether (2 mL) was added. After cooling the mixture to ~30°C for 3 days 0.059 g (0.064 mmol; 33%) of 4 were isolated in form of black crystals. 3H NMR (300 MHz, C6D6): δ = 6.21 (s, 2H, H2), 4.89 (m, 2H, H9,15), 4.84 (m, 2H, H9,10), 4.32 (m, 2H, H8,11), 4.25 (m, 2H, H13,16), 3.76 (m, 2H, H20,21), 3.24 (m, 2H, H19,22), 2.00 (s, 3H, H6), 1.68 (s, 6H, H12,18), 1.62 ppm (s, 18H, OC(CH3)3).

Correct elemental analyses (C,H) were obtained for all three complexes. NMR data for 5: 1H NMR (300 MHz, C6D6): δ = 4.56 (m, 6H of Cp signals arising from 2 and 5), 4.53 (m, 2H, Cp), 4.43 (m, mixture of Cp signals arising from 5 and [90CP-MeOH]1/2), 4.17 (m, 2H, Cp), 1.73 (s, 6H, MeCp), 1.48 (s, 18H, OC(CH3)3), -11.17 ppm (s, 1H, MoH).

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[7] Data for the X-ray structure analyses: 2: C9H48Bi3Mo6O39, M = 964.58, monoclinic, space group C2/c, a = 13.038(4), b = 16.264(6), c = 16.435(5) Å, β = 112.67(3)°, V = 3235.1(18) Å3, Z = 4, T = 180(2) K, F(000) = 1242, μ = 11.261 mm−1, θ = 2.10–22.3°, reflections collected 7318, independent reflections 2013 [RF = 0.0528], GoF = 1.018, R = 0.0265, wR = 0.0580, largest diffraction peak and hole 0.653/−1.316 e Å−3; 3: C9H48Bi3Mo6O39, M = 1072.53, monoclinic, space group P21/n, a = 11.7096(16), b = 9.3532(16), c = 14.8522(17) Å, β = 90.023(17)°, V = 1623.1(4) Å3, Z = 2, T = 180(2) K, F(000) = 1008, μ = 11.590 mm−1, θ = 2.21–25.25°, reflections collected 9139, independent reflections 2791 [RF = 0.0855], GoF = 0.969, R = 0.0355, wRF2 = 0.0716, largest diffraction peak and hole 1.711/−1.440 e Å−3; 4: C9H48Bi3Mo6O39, M = 924.29, monoclinic, space group P21/n, a = 7.4941(12), b = 21.093(5), c = 14.192(2) Å, β = 91.62(2)°, V = 2242.6(7) Å3, Z = 4, T = 180(2) K, F(000) = 1680, μ = 16.747 mm−1, θ = 2.41–25.25°, reflections collected 14593, independent reflections 3990 [RF = 0.0910], GoF = 1.056, R = 0.0514; wRF2 = 0.1333, largest diffraction peak and hole 4.311/−2.580 e Å−3. All data were collected on a Stoe IPDSI using MoKα radiation, λ = 0.71073 Å, and the structures were solved by direct methods (program: SHELXL-97), refined versus F2 (program: SHELXL-97) with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. CCDC 225730 (2), CCDC 225731 (3), CCDC 225732 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (44)1223-336-033; or deposit@ccdc.cam.ac.uk).
[11] The B3LYP/Lanl2dz; pseudo = Lanl2 for C/H (Stuttgart RSC 1997, ECP (Mo) cc-pVDZ-P (Bi)) level of theory (G98) proved to reproduce the crystal structure of 4 reasonably well, and this result was used as a basis for a calculation with the AIMP 2000 program. The most recent investigations concerning the stem complex of 4 (lacking the methyl groups) show that the use of ECPs does not lead to significant alterations in comparison to an all-electron treatment; a detailed theoretical investigation will be reported elsewhere.
[12] Indeed the above mentioned NMR experiment revealed the occurrence of intermediates on the way from 3 to 4/4′.