Heterometallic Complexes with Rhenium- and Iron-Bismuth Bonds

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Received March 6, 2013
Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

Reaction of equimolar amounts of [Bi(OtBu)₃] and [Cp₂ReH] yields [Cp₂Re–Bi(OtBu)₂], 1, when the reaction time is kept short. Treatment of [Bi(OCH(CF₃)₂)₃(thf)]₂ with four equivalents of [Cp₂ReH] leads to the heterotrinuclear complex [(Cp₂Re)₂Bi(OCH(CF₃)₂)], 4, with two Re–Bi bonds. A complex with a Bi–Fe bond was obtained in the reaction between [Cp(CO)₂Fe]₂ and [Bi(OAc)₃]: [Cp(CO)₂Fe–Bi(OAc)₂], 5, was formed and found to crystallize as a dimer. The structures of 1 and 4 were also investigated.

Key words: Bismuth, Rhenium, Iron, Hydrides, Heterometallic Complexes

Introduction

Bismuth-containing bimetallic compounds have received considerable attention within the last years with respect to the development of advanced materials. Unlike the corresponding homometallic systems, the heterometallic materials offer specific applications due to the ability of two metals with differing characteristics to cooperate or to influence each other. Hence, for instance, Bi₂O₃, MoO₃, and supported Re/Bi nanoparticles are interesting heterogenous catalysts [1–3], while a thin [BiFeO₃] phase has multiferroic properties [4–6]. This motivates investigations also on soluble, molecular variants.

In previous work we could demonstrate that complexes containing Mo–Bi metal bonds with a defined Mo/Bi atom ratio can be constructed by reactions of molybdocene dihydrides with bismuth alkoxides [7–12]. We have also shown that this “hydride alkoxide” approach can be successfully extended to Re–Bi compounds [13].

The reaction of rhenocene hydride and [Bi(O’Bu)₃] has led to a unique trinuclear compound [CpRe(μ-η⁵, η¹-C₅H₄)Bi–ReCp₂], 3, with two Re–Bi metal bonds and a “bent bond” between the Bi atom and a C atom of one of the Cp rings (Scheme 1). Monitoring the reaction by NMR provided evidence for the occurrence of two intermediates, which we assigned as [Cp₂Re–Bi(O’Bu)₂], 1, and [(Cp₂Re)₂Bi(O’Bu)₂], 2, but these compounds eluded isolation due to fast subsequent reactions [13]. Analogs of 1, [Cp₂Re–BiR₂], could be prepared for R = OCH(CF₃)₂, I, and R=O-tol, II, as the electron-withdrawing alkoxide ligands slow down further reactions and as Bi–C bonds are relatively inert, respectively. Here we report how we got access to 1 itself by modifying the reaction conditions, and to an analog of 2 with a hexafluoro isopropyl residue.

Bearing in mind the unique interplay between iron and bismuth in multiferroic materials like BiFeO₃ (BFO) and a corresponding interest in Single Source Precursors (SSP), the synthesis of Fe/Bi systems has been pursued, too, and we provide first evidence here that Fe-Bi entities can be constructed by reactions of complexes with Fe–Fe bonds and bismuth acetate.

Results and Discussion

Complex synthesis and characterization

The synthesis of 3 from [Cp₂ReH] and [Bi(O’Bu)₃] had been carried out previously in n-hexane at room temperature. Under these conditions the intermediate 1 reacts with [Cp₂ReH] first to give 2 and then to
Scheme 1. Synthesis of 3 by reaction of two equiv. of [Cp₂ReH] with [Bi(OᵗBu)₃].

Scheme 2. Synthesis of 1 by reaction of [Cp₂ReH] with [Bi(OᵗBu)₃].

yield 3 within 24 h. We have now accessed 1 by stirring the bright-orange solution of equimolar quantities of rhenocene hydride and [Bi(OᵗBu)₃] in n-hexane for three minutes at room temperature. It turned out that maintaining a short reaction time is crucial for a convenient synthesis of 1. With increasing reaction times increasingly decomposition to grey metallic bismuth was observed. However, concentration of the orange reaction mixture to half the volume after three minutes and slow evaporation of the remaining solvent at −30 °C resulted in the formation of thin, very heat- and air-sensitive light-yellow plates of 1 within 2 weeks in moderate yield (Scheme 2). 1 is readily soluble in all common solvents.

A proton nuclear resonance measurement of the yellow crystals dissolved in C₆D₆ confirmed the ¹H NMR data of 1 derived before from the spectrum of a reaction mixture [13]. A singlet resonance can be observed for all Cp protons at 4.24 ppm and a further one for the tert-butoxide moieties at 1.45 ppm.

A single-crystal X-ray diffraction analysis of 1 has revealed the expected molecular structure, which is depicted in Fig. 1. It is very similar to that of [Cp₂Re–Bi(OCH(CF₃)₂)]₂, 1 [13]. A phenocene fragment is connected to a bismuth alkoxide moiety through a Re–Bi single bond, the distance (2.7690(11) Å) of which is in between the corresponding distances in 1 (2.7032(3) Å) at the shorter end and [Cp₂Re–Bi(o-tol)]₂, 11 (2.8468(5) Å) at the longer end. Like in 1 and 11, the two Cp-Re–Bi angles differ significantly (Cp1–Re3–Bi1: 105.1(3)°; Cp2–Re3–Bi1: 100.7(3)°).

Surprisingly, the Cp1–Re3–Cp2 angle of 152.9(8)° (Cp-M-Cp is defined as the angle between the metal-Cp plane normals throughout this paper [14]) is comparable to that of the distorted phenocene unit in 3 (156.40(12)°), involving the (µ-η⁵,η¹-C₅H₄) ligand that bridges a Re–Bi metal bond.

Although various modifications with respect to the reaction conditions were tested, all attempts to isolate the intermediate 2 from a reaction mixture containing [Cp₂ReH]/[Bi(OᵗBu)₃] in the ratio
2 : 1 failed. Experiments to access an analog of 2 by replacing [Bi(O’Bu)3] with [Bi(OEt)3] did not proceed successfully, either. In previous work on [Cp2MoH2]/[Bi(OR)3] systems we were able to show that the progress of the alcohol elimination sensitively depends on the nature of the residues R of the alkoxides employed [7–13]. In case of hexafluoroiso-propyl residues, alcohol eliminations involving the Cp rings were suppressed [10]. Indeed, employing [Bi(OCH(CF3)2)3(thf)]2 in combination with [Cp2ReH] had allowed for the isolation of an I-analog [Cp2Re–Bi{OCH(CF3)2}]4, 4, which may also be part of an equilibrium within the system. Aiming at providing support for the occurrence of the intermediate 2 in the synthesis of 3 we now succeeded in preparing 4 by slowly adding a yellow solution of [Cp2ReH] in toluene to one fourth the equivalent of the dimer [Bi(OCH(CF3)2)3(thf)]2 in the same solvent at ambient temperature. A slow color change from yellow to orange and finally to dark green was observed (Scheme 3). Removing all volatiles at reduced pressure resulted in the isolation of 4 as a crude black powder. 4 is readily soluble in toluene, tetrahydrofuran, benzene, dichloromethane, acetonitrile, and diethyl ether, while its solubility in n-hexane is moderate.

The 1H NMR spectrum of 4 dissolved in C6D6 shows only one singlet for all Cp protons. This indicates that the two Cp2Re units are chemically equivalent, that the Cp ligands are able to rotate freely around their Cp–Re axis, and that in turn the Cp2Re fragments can rotate along the Re–Bi bonds with no significant barrier. The single proton at the hexafluoroiso-propoxide moiety gives rise to a septet at 4.44 ppm, which is shifted to higher field compared to that of the precursor 1 (C7D8: 5.04 ppm) [13].

Slow concentration of a diethyl ether solution of the dark-green solid at room temperature led within 2 weeks to black plates of 4, which were investigated by single-crystal X-ray diffraction (Fig. 2). The molecular structure features a bismuth center with an alkoxide group and two nearly identical Cp2Re moieties (Re–Bi: 2.8502(4) – 2.8590(4) Å and Cp-Re-Cp 151.08(30), 149.24(30)°), which are in good compliance with the rhenocene units in Re/Bi alkoxide complexes reported to date [13]. The H19 proton is the one in closest proximity to the O atom of the hexafluoroiso-propoxide ligand [d(C19–H19···O) = 2.99(1) Å with α(C19–H19···O) = 116°]. Since hydrogen bonds displaying donor-acceptor dis-
stances of 2.5–3.2 Å are usually categorized as “moderate, mostly electrostatic” [15], the contact H19⋯O indicates intramolecular H bonding. It has previously been suggested that such contacts initiate intramolecular alcohol elimination in Mo/Bi and Re/Bi systems [7–9, 13, 16]. The Cp3-Re2–Bi1 angle (107.22(11)°) compares well with the corresponding angle at Re1 (Cp1-Re1–Bi1: 105.68(11)°). Two weak hydrogen bonds involving H1 and H10 and F atoms of the CF3 groups (d(C1–H1⋯F4) = 3.32(1); d(C10–H10⋯F1) = 3.34(1) Å) are responsible for a symmetrical arrangement of the Cp2-Re1 unit towards the hexafluoro-iso-propoxide moiety.

Finally we sought to expand our studies to include Fe/Bi systems. Compared to Re-Bi compounds [2, 13, 17–19], more literature is available on complexes containing Fe–Bi bonds [20, 21]. The focus of our work was again on bismuthanes bearing a bismuth atom connected to organoiron fragments, such as η5-cyclopentadienyl dicarbonyl iron [Cp(CO)2Fe] (Fp). In this context, compounds like [[[η5-C5H5R](CO)2Fe]BiMe2] (R = H) , [[[η5-C5H5R](CO)2Fe]2BiX] (R = H, X = Cl, Br; R = Me, X = Cl) and [[[η5-C5H5R](CO)2Fe]2Bi] (R = H, Me) so far have mainly been prepared by salt metathesis reactions treating bismuth halides with alkali metal salts of the well-known Fp− anion [Cp(CO)2Fe]− [22–25]. A more facile route to FpBi complexes via cleavage of the Fe–Fe bond of the [Fp2] dimer in reactions with bismuth halides was first reported by Cullen and co-workers in 1971 for the synthesis of [FpBiCl2] [26], and recently successfully extended by Mehring and co-workers for the synthesis of [Fp5BiBr3] (Fp5 = Fp [Cp(CO)2Fe]; FpBi5 [[η5-C5H5−1,3,5-Br3](CO)2Fe]; Fp* [[η5−C5Me3](CO)2Fe]) setting out from [Fp5]2 and BiBr3 (Scheme 4) [27].

Obviously, the expansion of our hydride-alkoxide route to the synthesis of Fe–Bi compounds appeared attractive, but stable, readily accessible Fe–H precursor complexes are scarce. FpH can be synthesized setting out from NaFp, but its isolation is laborious and difficult. In the course of investigations of the reactions of mixtures containing FpH, dinuclear [Fp]2 was generated as a byproduct in the presence of bismuth alkoxides or bismuth acetate. In these experiments we noticed that [FpBi(OAc)2] (Ac = CH3CO), 5, can be conveniently prepared via the reaction of [Fp2] with bismuth acetate (Scheme 5). Stirring of an equimolar [Fp]2/[Bi(OAc)3] suspension in toluene at room temp.

temperature for a period of 72 h resulted in a bright-orange suspension, which was concentrated to one third of the volume. Subsequent filtration provided 5 in form of a crude yellow powder in an excellent yield of 89%.

The IR spectrum of 5 in KBr exhibits three characteristic absorption bands in the carbonyl region at 2000 (vs), 1955 (vs) and 1921 (w) cm−1 and two absorption bands at 1559 (m), 1540 (m) cm−1 which account for the acetate residue. The solubility of 5 is moderate in polar solvents such as tetrahydrofuran and dichloromethane, and low in n-hexane, benzene and toluene. When 5 is dissolved in CDCl3 and investigated by 1H NMR spectroscopy, the proton resonance of the Cp ligand is observed at 4.98 ppm, whereas the signal of the two methyl groups is found at 2.06 ppm. Layering a concentrated dichloromethane solution of 5 with n-hexane at room temperature resulted within 3 d in the formation of large orange crystals, which were suitable for a single-crystal X-ray diffraction analysis (Fig. 3).

5 crystallizes as a dimer (with a crystallographic inversion center), in which two of the acetate ligands act as bridging units. Each bismuth atom is bound to one [Fp] moiety and additionally forms two primary (covalent) bonds to two acetate ligands (Bi–O1: 2.342(11) Å; Bi–O4: 2.353(10) Å). The angle between these O atoms (O1–Bi–O4 81.2(4)°) and also all Fe–Bi–O angles (92.9(3)–97.0(3)°) indicate that this bonding is mainly established through p orbitals at the Bi atom. The remaining two O atoms (O2, O6)
Experimental Section

General information

All manipulations were carried out in a glovebox, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The \(^1\)H, and \(^{13}\)C\(^{\text{\cite{1\text{H}}}}\) NMR spectra were recorded on Bruker AV 400 \(^{\text{\cite{1\text{H}}} 400.1\text{MHz}}\), \(^{13}\text{C}^{\text{\cite{1\text{H}}}}\), 100.6 MHz, \(^{19}\text{F}^{\text{\cite{1\text{H}}}},\text{ 376.4 MHz}\) or Bruker DPX 300 NMR spectrometers \(^{\text{\cite{1\text{H}}} 4, 300.1\text{MHz}}\), \(^{13}\text{C}^{\text{\cite{1\text{H}}}},\text{ 75.5 MHz, }^{19}\text{F},\text{ 282.4 MHz}\) in dry deoxygenated [D\(_2\)benzene, [D]chloroform or [D\(_2\)]dichloromethane as solvents. The spectra were calibrated against the internal residual proton and natural abundance \(^{13}\text{C}\) resonances of the deuterated solvent ([D\(_2\)]benzene \(\delta = 7.15\text{ ppm}\), \(\delta_{\text{C}} = 128.0\text{ ppm}\), [D]chloroform \(\delta = 7.26\text{ ppm}\), \(\delta_{\text{C}} = 77.0\text{ ppm}\), [D\(_2\)]dichloromethane \(\delta = 5.36\text{ ppm}\), \(\delta_{\text{C}} = 53.84\text{ ppm}\)). Microanalyses were performed on a HEK Atech Euro EA 3000 elemental analyzer. Infrared (IR) spectra were recorded in the region 4000 – 400 cm\(^{-1}\) using solid samples prepared as KBr pellets with a Shimadzu FTIR 8400S instrument.

Materials

Solvants were dried using a MBraun Solvent Purification System and degassed by vacuum-freezing cycles. [C\(_2\)p\(_2\)ReH] \([\text{\cite{28}}] \), [Bi(O\(_{\text{Ac}}\)]\(_3\) \([\text{\cite{29}}] \) and [Bi(O\(_{\text{Ac}}\))(CF\(_3\)]\(_2\)] (thf) \([\text{\cite{30, 31}}] \) were prepared according to the procedures described in the literature. [Bi(O\(_{\text{Ac}}\)]\(_3\) (99.99%, Sigma-Aldrich) and [F\(_2\)]\(_2\) (99% Acros Organics) were used as received.

Rhenocenylbismuth-bis-1-butoxide, \(1\)

A yellow solution of [C\(_2\)p\(_2\)ReH] (50.0 mg, 0.157 mmol, 1 equiv.) in 7.5 mL of \(n\)-hexane was added dropwise to a stirred colorless solution of [Bi(O\(_{\text{Ac}}\)]\(_3\) (67.5 mg, 0.157 mmol, 1 equiv.) dissolved in the same solvent (5 mL) at ambient temperature. During the addition the color changed from colorless to bright orange. After completed addition the resulting orange solution was stirred for 3 min at ambient temperature and subsequently concentrated to half the volume. Slow evaporation of the remaining solvent at –30 °C resulted in the formation of thin, very temperature- and air-sensitive light-yellow plates of [C\(_2\)p\(_2\)Re-Bi(O\(_{\text{Ac}}\)]\(_3\), in white, to yellow. (yield: 54.0 mg, 0.080 mmol, 51%). – \(^1\)H NMR \((C_6D_6, 300\text{MHz})\): \(\delta = 4.24\) (s, 10 H, C\(_5\)CH), 1.45 (s, 18 H, C(CH\(_3\))\(_3\)). – \(^{13}\)C\(^{\text{\cite{1\text{H}}}}\) NMR \((C_6D_6, 75\text{MHz})\): \(\delta = 72.0\) (C(CH\(_3\))\(_3\)), 68.2 (C\(_5\)CH), 35.4 (C(CH\(_3\))\(_3\)). – IR (KBr): ν (cm\(^{-1}\)) = 3071 (w), 2063 (w), 1455 (w), 1430 (w), 1416 (w), 1384 (w), 1355 (w), 1175 (w), 1124 (w), 1075 (w), 921 (w), 874 (w), 760 (w), 697 (w), 595 (w), 556 (w). – Anal. (%) for C\(_{18}\)H\(_{30}\)BiO\(_2\)Re (671.60): calcd. C 32.19, H 4.20; found C 32.60, H 4.20.

Conclusions

We have isolated and fully characterized two heterometallic Re-Bi complexes, the identification of which supports a reaction sequence as proposed previously to rationalize the formation of 3. 1 corresponds to a suggested intermediate, and 4 is an analog of 2.

Furthermore we have found that bismuth acetates can add to Fe–Fe bonds: 5 could be obtained by cleavage of the Fe–Fe bond in [F\(_2\)]\(_2\) by [Bi(O\(_{\text{Ac}}\)]\(_3\), a reaction path that so far has only been observed for bismuth halides.
A yellow solution of [Cp₂ReH] (100.0 mg, 0.315 mmol, 4 equiv.) in 12 mL of toluene was added dropwise to a stirred colorless solution of [Bi(OH)(CF₃)$_3$]$_3$(thf)$_2$ (123.0 mg, 0.079 mmol, 1 equiv.) in the same solvent (12 mL) at ambient temperature. During the addition the color changed from colorless to yellow via orange and green to finally black green. After completed addition the resulting black-green solution was stirred for 1 h at ambient temperature. The solvent was evaporated under reduced pressure to yield 141.3 mg of a crude black powder. Slow concentration of a diethyl ether solution of the black residue at room temperature resulted in the precipitation of black crystals of pure [(Cp₂Re)₂Bi(OCH(CF₃)$_2$)$_2$], 4, within 7 d (yield: 40.5 mg, 0.040 mmol, 25%). – ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ = 4.44 (s, 1 H, $^{3}$J$_{HH}$ = 5.65 Hz, CH), 4.20 (s, 20 H, $^{13}$C(CH)$_3$), – $^{19}$F NMR (CDCl₃, 282 MHz): δ = −74.0 (d, 6 F, $^{3}$J$_{HF}$ = 6.79 Hz, CF$_2$), – IR (KBr): ν(cm$^{-1}$) = 3109 (w), 3093 (w), 3069 (w), 2962 (w), 2806 (w), 1412 (w), 1395 (m), 1359 (w), 1273 (m), 1261 (m), 1250 (m), 1200 (s), 1166 (vs), 1137 (m), 1102 (m), 1095 (m), 1087 (m), 1057 (m), 1009 (m), 982 (w), 906 (w), 877 (w), 847 (m), 828 (m), 738 (m), 684 (m). – Anal. (%) for C$_2$H$_2$BiReO$_4$Re: C 26.21, H 2.20; found C 26.10, H 2.42.

Solid [Bi(OAc)$_3$] (54.55 mg, 0.141 mmol, 1 equiv.) was added to a vigorously stirred suspension of [Pf$_2$] (50 mg, 0.141 mmol, 1 equiv.) in toluene (10 mL) to give an orange suspension within 72 h at ambient temperature. The yellow solid was filtered off and washed with 3 portions of 2 mL diethyl ether to leave a yellow powder of 5 (yield: 63.6 mg, 0.126 mmol, 89 %). – ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ = 4.98 (s, 5 H, $^{3}$J$_{CH}$), 2.06 (s, 6 H, CH$_3$), – $^{13}$C NMR (CDCl₃, 300 MHz, 25 °C): δ = 5.02 (s, 5 H, $^{3}$J$_{CH}$), 2.00 (s, 6 H, CH$_3$), – $^{19}$F NMR (CDCl₃, 75 MHz): δ = 116.5 (2 C, CO$_2$), 114.0 (br, 2 C, O(O)CH), 84.5 (5 C, $^{3}$C(CH)), 33.6 (br, 2 C, CH$_3$), – IR (KBr): ν(cm$^{-1}$) = 3111 (w), 2963 (w), 2900 (vs), 1955 (vs), 1920 (w), 1559 (m), 1540 (w), 1429 (m), 1405 (m), 1386 (m), 1335 (w), 1241 (w), 1054 (w), 1014 (w), 875 (w), 851 (w), 663 (m), 630 (w), 582 (m), 577 (m), 513 (w). – Anal. (%) for C$_7$H$_{11}$BiFeO$_6$: C 54.03; found C 54.29, H 2.20; found C 54.26, H 2.20. – Anal. (%) for C$_{23}$H$_2$BiFeO$_4$Re: C 50.04; found C 50.04, H 2.20.

Crystal structure determinations

Suitable crystals of 1 were obtained by slow evaporation of the solvent from a saturated $n$-hexane solution at −30 °C. Single crystals of 4 were obtained by slow evaporation of the solvent from a saturated diethyl ether solution at room temperature. Layering 2 mL of a concentrated dichloromethane solution of the yellow powder of 5

\[\eta^2\text{-Cyclopentadienylidicarbonyliron-bismuth-di-} \eta^2\text{-acetate}, 5\]

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with 18 mL n-hexane at room temperature led to the formation of large orange crystals within 3 d. Crystal data and parameters are listed in Table 1. All data collections were performed at 100 K on a Stoe IPDS 2T diffractometer (MoKα radiation, λ = 0.71073 Å, graphite monochromator) equipped with an area detector. The structures were solved by Direct Methods (SHELXS-97) [32] and refined by full-matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97) [33]. Multi-scan correction (PLATON) [34] was applied for complex 5. Numerical absorption correction was applied for 1 and 4 based on a Gaussian algorithm, which is implemented in the X-RED program [35]. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were introduced at their idealized positions and were refined using a riding model. The program ORTEP-3 for Windows was used for generating the displacement ellipsoid drawings for this publication [36, 37].

CCDC 927834 (1), CCDC 927835 (4), and CCDC 927836 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the BMBF, and the Humboldt-Universität zu Berlin for financial support.


