

Heterometallic Complexes with Rhenium- and Iron-Bismuth Bonds

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

Reaction of equimolar amounts of $[\text{Bi}(\text{O}^t\text{Bu})_3]$ and $[\text{Cp}_2\text{ReH}]$ yields $[\text{Cp}_2\text{Re}-\text{Bi}(\text{O}^t\text{Bu})_2]$, **1**, when the reaction time is kept short. Treatment of $[\text{Bi}\{\text{OCH}(\text{CF}_3)_2\}_3(\text{thf})_2]$ with four equivalents of $[\text{Cp}_2\text{ReH}]$ leads to the heterotrinnuclear complex $[(\text{Cp}_2\text{Re})_2\text{Bi}\{\text{OCH}(\text{CF}_3)_2\}]$, **4**, with two Re–Bi bonds. A complex with a Bi–Fe bond was obtained in the reaction between $[\text{Cp}(\text{CO})_2\text{Fe}]_2$ and $[\text{Bi}(\text{OAc})_3]$: $[\text{Cp}(\text{CO})_2\text{Fe}-\text{Bi}(\text{OAc})_2]$, **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, Bi_2O_3 · MoO_3 and supported Re/Bi nanoparticles are interesting heterogenous catalysts [1–3], while a thin $[\text{BiFeO}_3]$ 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 $[\text{Bi}(\text{O}^t\text{Bu})_3]$ has led to a unique trinuclear compound $[\text{CpRe}(\mu-\eta^5, \eta^1-\text{C}_5\text{H}_4)\text{Bi}-\text{ReCp}_2]$, **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

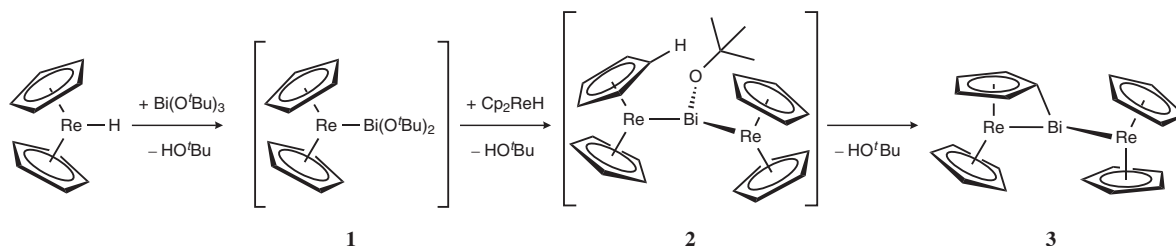
of two intermediates, which we assigned as $[\text{Cp}_2\text{Re}-\text{Bi}(\text{O}^t\text{Bu})_2]$, **1**, and $[(\text{Cp}_2\text{Re})_2\text{Bi}(\text{O}^t\text{Bu})]$, **2**, but these compounds eluded isolation due to fast subsequent reactions [13]. Analogs of **1**, $[\text{Cp}_2\text{Re}-\text{Bi}R_2]$, could be prepared for $R = \text{OCH}(\text{CF}_3)_2$, **I**, and $R = o\text{-tol}$, **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 BiFeO_3 (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.

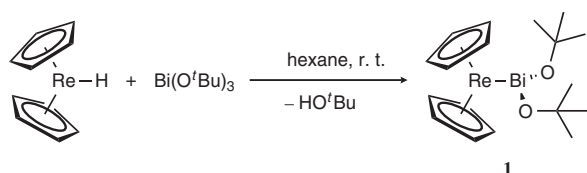
Results and Discussion

Complex synthesis and characterization

The synthesis of **3** from $[\text{Cp}_2\text{ReH}]$ and $[\text{Bi}(\text{O}^t\text{Bu})_3]$ had been carried out previously in *n*-hexane at room temperature. Under these conditions the intermediate **1** reacts with $[\text{Cp}_2\text{ReH}]$ first to give **2** and then to



Scheme 1. Synthesis of **3** by reaction of two equiv. of $[\text{Cp}_2\text{ReH}]$ with $[\text{Bi}(\text{O}^t\text{Bu})_3]$.



Scheme 2. Synthesis of **1** by reaction of $[\text{Cp}_2\text{ReH}]$ with $[\text{Bi}(\text{O}^t\text{Bu})_3]$.

yield **3** within 24 h. We have now accessed **1** by stirring the bright-orange solution of equimolar quantities of rhenocene hydride and $[\text{Bi}(\text{O}^t\text{Bu})_3]$ 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 C_6D_6 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 $[\text{Cp}_2\text{Re}-\text{Bi}\{\text{OCH}(\text{CF}_3)_2\}_2]$, **I** [13]. A rhenocene 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 **I** (2.7032(3) Å) at the shorter end and $[\text{Cp}_2\text{Re}-\text{Bi}(o\text{-tol})_2]$, **II**, (2.8468(5) Å) and **3**

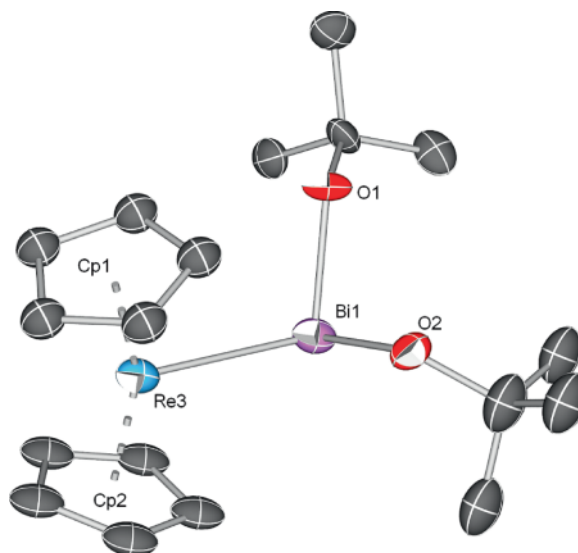
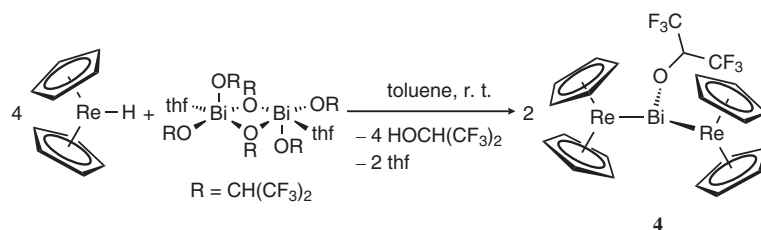


Fig. 1 (color online). Molecular structure of **1**. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Re3–Bi1 2.7690(11), Bi1–O1 2.123(12), Bi1–O2 2.139(12); Cp1–Re3–Cp2 152.9(8), Cp1–Re3–Bi1 105.1(3), Cp2–Re3–Bi1 100.7(3), O1–Bi1–O2 89.2(5), O1–Bi1–Re3 103.8(4), O2–Bi1–Re3 99.6(4).

(2.8652(6)–2.8934(6) Å) at the longer end. Like in **I** and **II**, 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 rhenocene unit in **3** (156.40(12)°), involving the $(\mu\text{-}\eta^5, \eta^1\text{-C}_5\text{H}_4)$ 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 $[\text{Cp}_2\text{ReH}]/[\text{Bi}(\text{O}^t\text{Bu})_3]$ in the ratio



Scheme 3. Synthesis of **4** by reaction of four equiv. of $[\text{Cp}_2\text{ReH}]$ with one equiv. of $[\text{Bi}\{\text{OCH}(\text{CF}_3)_2\}_3(\text{thf})]_2$.

2 : 1 failed. Experiments to access an analog of **2** by replacing $[\text{Bi}(\text{O}^i\text{Bu})_3]$ with $[\text{Bi}(\text{OEt})_3]_n$ did not proceed successfully, either. In previous work on $[\text{Cp}_2\text{MoH}_2]/[\text{Bi}(\text{OR})_3]$ 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 hexafluoro-*iso*-propyl residues, alcohol eliminations involving the Cp rings were suppressed [10]. Indeed, employing $[\text{Bi}\{\text{OCH}(\text{CF}_3)_2\}_3(\text{thf})]_2$ in combination with $[\text{Cp}_2\text{ReH}]$ had allowed for the isolation of an **1**-analog $[\text{Cp}_2\text{Re}-\text{Bi}\{\text{OCH}(\text{CF}_3)_2\}_2]$, **1**, and color changes observed in the presence of excessive $[\text{Cp}_2\text{ReH}]$ that vanished upon addition of further $[\text{Cp}_2\text{ReH}]$ had indicated that $[(\text{Cp}_2\text{Re})_2\text{Bi}\{\text{OCH}(\text{CF}_3)_2\}]$, **4**, 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 $[\text{Cp}_2\text{ReH}]$ in toluene to one fourth the equivalent of the dimer $[\text{Bi}\{\text{OCH}(\text{CF}_3)_2\}_3(\text{thf})]_2$ 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 C_6D_6 shows only one singlet for all Cp protons. This indicates that the two Cp_2Re units are chemically equivalent, that the Cp ligands are able to rotate freely around their Cp–Re axis, and that in turn the Cp_2Re fragments can rotate along the Re–Bi bonds with no significant barrier. The single proton at the hexafluoro-*iso*-propoxide moiety gives rise to a septet at 4.44 ppm, which is shifted to higher field compared to that of the precursor **1** (C_7D_8 : 5.04 ppm) [13].

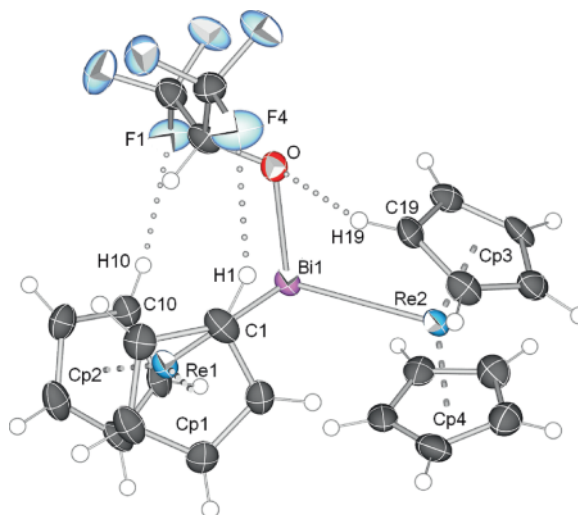


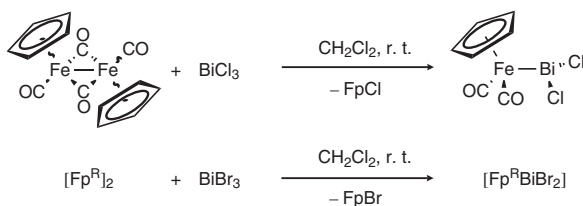
Fig. 2 (color online). Molecular structure of **4**. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Re1–Bi1 2.8502(4), Re2–Bi1 2.8590(4), Bi1–O 2.265(5); Re1–Bi1–Re2 116.63(1), Cp1–Re1–Cp2 151.08(30), Cp1–Re1–Bi1 105.68(11), Cp2–Re1–Bi1 101.11(11), Cp3–Re2–Cp4 149.24(30), Cp3–Re2–Bi1 107.22(11), Cp4–Re2–Bi1 99.41(12), O–Bi1–Re1 102.14(13), O–Bi1–Re2 101.53(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 Cp_2Re 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 hexafluoro-*iso*-propoxide ligand [$d(\text{C19}-\text{H19}\cdots\text{O}) = 2.99(1)$ Å with $\alpha(\text{C19}-\text{H19}\cdots\text{O}) = 116^\circ$]. Since hydrogen bonds displaying donor-acceptor dis-

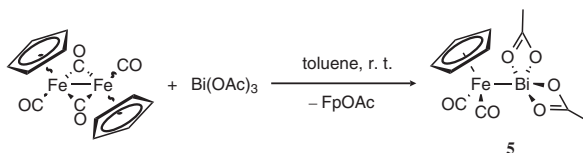
tances of 2.5–3.2 Å are usually categorized as “moderate, mostly electrostatic” [15], the contact H19...O indicates intramolecular H bonding. It has previously been suggested that such contacts initiate intramolecular alcohol elimination in Mo/Bi and Re/Bi systems [7–9, 13, 16]. The Cp3-Re2–Bi1 angle (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 ($d(\text{C1}–\text{H1} \cdots \text{F4}) = 3.32(1)$; $d(\text{C10}–\text{H10} \cdots \text{F1}) = 3.34(1)$ Å) are responsible for a symmetrical arrangement of the Cp₂Re1 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 η^5 -cyclopentadienyl dicarbonyl iron [Cp(CO)₂Fe] (Fp). In this context, compounds like $[\{(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})_2\text{Fe}\}\text{BiMe}_2]$ ($\text{R} = \text{H}$), $[\{(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})_2\text{Fe}\}_2\text{BiX}]$ ($\text{R} = \text{H}$, $\text{X} = \text{Cl}$, Br ; $\text{R} = \text{Me}$, $\text{X} = \text{Cl}$) and $[\{(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})_2\text{Fe}\}_3\text{Bi}]$ ($\text{R} = \text{H}$, 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 [Fp]₂ 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 [Fp^RBiBr₂] (Fp^R = Fp [Cp(CO)₂Fe]; Fp^{tBu} [($\eta^5\text{-C}_5\text{H}_3\text{-1,3-}^t\text{Bu}_2$)(CO)₂Fe]; Fp^{*} [($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂Fe]) setting out from [Fp^R]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 [Fp]₂ with bismuth acetate (Scheme 5). Stirring of an equimolar [Fp]₂/[Bi(OAc)₃] suspension in toluene at room tem-



Scheme 4. Synthesis of [FpBiCl₂] and [Fp^RBiBr₂] according to Cullen *et al.* and Mehring *et al.*, respectively (Fp^R = Fp [Cp(CO)₂Fe]; Fp^{tBu} [($\eta^5\text{-C}_5\text{H}_3\text{-1,3-}^t\text{Bu}_2$)(CO)₂Fe]; Fp^{*} [($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂Fe]) [26, 27].



Scheme 5. Synthesis of **5** by reaction of [Fp]₂ with [Bi(OAc)₃].

perature 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)

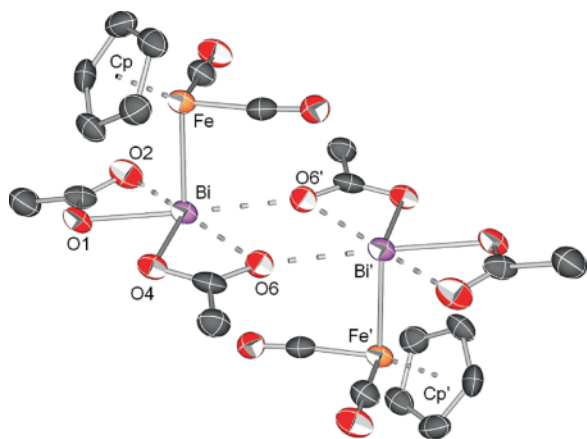


Fig. 3 (color online). Molecular structure of **5**. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–Bi 2.585(2), Bi–O1 2.342(11), Bi–O4 2.353(10), Bi–O2 2.604(12), Bi–O6 2.632(10), Bi–O6' 2.711(4), Bi–Bi' 4.3485(6); Cp–Fe–Bi 121.01(10), O1–Bi–O4 81.2(4), O1–Bi–Fe 97.0(3), O4–Bi–Fe 94.0(3), O1–Bi...O6' 153.14(15).

belonging to the carbonyl groups of the acetate ligands interact with the Bi center at significantly longer distances (Bi–O2 2.604(12) Å, Bi–O6 2.632(10) Å). Dimerization proceeds through a weak bonding between the acetate carbonyl group of a second molecule (O6', Bi–O6': 2.711(4) Å) and the Bi atom (O1–Bi...O6' 153.14(15)°). The geometry at the bismuth atoms is therefore best described as pentagonal pyramidal. Within the Bi₂O₂ core, the Bi–Bi' distance amounts to 4.3485(6) Å which is considered as non-bonding. The Bi–Fe distance is 2.585(2) Å and compares well with Bi–Fe distances in compounds like [Fp^RBiX₂] [21–26].

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 [Fp]₂ by [Bi(OAc)₃], a reaction path that so far has only been observed for bismuth halides.

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 ¹H, and ¹³C{¹H} NMR spectra were recorded on Bruker AV 400 (¹H, 400.1 MHz; ¹³C{¹H}, 100.6 MHz, ¹⁹F, 376.4 MHz) or Bruker DPX 300 NMR spectrometers (¹H, 300.1 MHz; ¹³C{¹H}, 75.5 MHz, ¹⁹F, 282.4 MHz) in dry deoxygenated [D₆]benzene, [D]chloroform or [D₂]dichloromethane as solvents. The spectra were calibrated against the internal residual proton and natural abundance ¹³C resonances of the deuterated solvent ([D₆]benzene δ_H = 7.15 ppm, δ_C = 128.0 ppm, [D]chloroform δ_H = 7.26 ppm, δ_C = 77.0 ppm, [D₂]dichloromethane δ_H = 5.36 ppm, δ_C = 53.84 ppm). Microanalyses were performed on a HEKAtech 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

Solvents were dried using a MBraun Solvent Purification System and degassed by vacuum-freezing cycles. [Cp₂ReH] [28], [Bi(O^tBu)₃] [29] and [Bi{OCH(CF₃)₂]₃(thf)₂] [30, 31] were prepared according to the procedures described in the literature. [Bi(OAc)₃] (99.99%, Sigma-Aldrich) and [Fp]₂ (99% Acros Organics) were used as received.

Rhenocenylobismuth-bis-^tbutoxide, **1**

A yellow solution of [Cp₂ReH] (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^tBu)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 [Cp₂Re–Bi(O^tBu)₂], **1**, within 2 weeks. (yield: 54.0 mg, 0.080 mmol, 51%). – ¹H NMR (C₆D₆, 300 MHz, 25 °C): δ = 4.24 (s, 10 H, CpCH), 1.45 (s, 18 H, C(CH₃)₃). – ¹³C{¹H} NMR (C₆D₆, 75 MHz): δ = 72.0 (C(CH₃)₃), 68.2 (CpCH), 35.4 (C(CH₃)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 C₁₈H₂₈BiO₂Re (671.60): calcd. C 32.19, H 4.20; found C 32.60, H 4.20.

	1	4	5
Formula	C ₁₈ H ₂₈ BiO ₂ Re	C ₂₃ H ₂₁ BiF ₆ ORe ₂	C ₂₂ H ₂₂ Bi ₂ Fe ₂ O ₁₂
<i>M_r</i>	671.58	1008.78	1008.06
Crystal size, mm ³	0.30 × 0.22 × 0.06	0.32 × 0.23 × 0.04	0.40 × 0.36 × 0.08
Crystal system	monoclinic	orthorhombic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	16.2219(12)	17.4154(6)	7.1396(8)
<i>b</i> , Å	14.5231(7)	13.8193(3)	7.5161(8)
<i>c</i> , Å	17.2111(11)	19.2471(4)	12.4835(13)
α , deg	90	90	96.371(9)
β , deg	110.797(5)	90	90.086(9)
γ , deg	90	90	91.378(9)
<i>V</i> , Å ³	3790.6(4)	4632.2(2)	665.55(12)
<i>Z</i>	8	8	1
<i>D</i> _{calcd.} , g cm ^{−3}	2.35	2.89	2.52
<i>F</i> (000), e	2480	3632	468
μ (Mo <i>K</i> α), mm ^{−1}	15.7	18.1	14.3
θ range, deg	2.53–25.25	2.42–26.00	2.73–25.50
Refl. measd. / unique / <i>R</i> _{int}	13360 / 6824 / 0.1602	45067 / 4546 / 0.1460	8892 / 2478 / 0.1020
Refl. with <i>I</i> ₀ > 2 σ (<i>I</i> ₀)	5302	4322	2398
<i>R</i> 1 / <i>wR</i> 2 [<i>I</i> ₀ > 2 σ (<i>I</i> ₀)]	0.0848 / 0.2157	0.0371 / 0.1017	0.0556 / 0.1393
<i>R</i> 1 / <i>wR</i> 2 (all data)	0.1044 / 0.2337	0.0396 / 0.1039	0.0565 / 0.1397
GoF (<i>F</i> ²)	1.029	1.054	1.227
$\Delta\rho_{\text{fin}}$ (max / min), e Å ^{−3}	4.90 / −3.86	3.27 / −2.75	2.64 / −2.12
CCDC	927834	927835	927836

Table 1. Crystal data and numbers pertinent to data collection and structure refinement of **1**, **4** and **5**.

Di(rhenocenyl)bismuth-1,1,1,3,3,3-hexafluoro-2-propoxide, 4

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{OCH(CF₃)₂}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}], **4**, within 7 d (yield: 40.5 mg, 0.040 mmol, 25 %). – ¹H NMR (C₆D₆ 400 MHz, 25 °C): δ = 4.44 (sept, 1 H, ³*J*_{FH} = 6.56 Hz, CH), 4.20 (s, 20 H, CpCH). – ¹³C{¹H} NMR (C₆D₆ 75 MHz): δ = 124.9₃ (q, ¹*J*_{FC} = 287.32 Hz, CF₃), 124.8₉ (q, ¹*J*_{FC} = 287.98 Hz, CF₃), 78.0 (sept, ³*J*_{FC} = 30.28 Hz, CH), 68.9 (CpCH). – ¹⁹F NMR (C₆D₆, 282 MHz): δ = −74.0 (d, 6 F, ³*J*_{HF} = 6.79 Hz, CF₃). – IR (KBr): ν (cm^{−1}) = 3109 (w), 3093 (w), 3069 (w), 2962 (w), 2806 (w), 1412 (w), 1395 (w), 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 C₂₃H₂₁BiF₆ORe₂ (1008.80): calcd. C 27.38, H 2.10; found C 27.48, H 2.21.

η⁵-Cyclopentadienyldicarbonyliron-bismuth-di-η²-acetate, 5

Solid [Bi(OAc)₃] (54.55 mg, 0.141 mmol, 1 equiv.) was added to a vigorously stirred suspension of [Fp]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, CpCH), 2.06 (s, 6 H, CH₃). – ¹H NMR (CD₂Cl₂, 300 MHz, 25 °C): δ = 5.02 (s, 5 H, CpCH), 2.00 (s, 6 H, CH₃). – ¹³C{¹H} NMR (CD₂Cl₂, 75 MHz): δ 196.5 (2 C, CO), 180.6 (br, 2 C, O(O)CCH₃), 84.5 (5 C, CpCH), 23.6 (br, 2 C, CH₃). – IR (KBr): ν (cm^{−1}) = 3111 (w), 2963 (w), 2000 (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 C₁₁H₁₁BiFeO₆ (504.03): calcd. C 26.21, H 2.20; found C 26.10, H 2.42.

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**

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 (MoK α radiation, $\lambda = 0.71073$ 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.

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