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Multimetallic systems composed of $CpFe(CO)_2$-, Cp_2Re- and $(RCO_2)_2Bi$- moieties

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Dedicated to Professor Heinrich Lang on occasion of his 60th birthday

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ABSTRACT

The reaction of $[Fp]_2$ (Fp = $(\eta^5\text{-}C_5H_5)(CO)_2Fe$) with bismuth formate was shown to proceed via Fe-Bi bond formation yielding $[Fp{-}Bi(O_2CH)_2]_n$, **1**, that could be crystallized in form of two polymorphs. These differ in the way the $[Fp{-}Bi(O_2CH)_2]$ units are connected via bridging formate ligands to yield the respective coordination polymers. The acetate derivative $[Fp{-}Bi(O_2CCH_3)_2]$ was used as a precursor compound targeting at the construction of an additional transition metal-bismuth bond: the reaction of $[Fp{-}Bi(O_2CCH_3)_2]$ with $[Cp_2ReH]$ likely yields in the envisaged complex $[Fp{-}Bi(O_2CCH_3)ReCp_2]$ first but then undergoes further transformation due to the presence of chloride and acetic acid in solution, which lead to the formation of $[Fp{-}Bi(Cl)ReCp_2]$, **3**, and $[Cp_2Re{-}Bi(O_2CCH_3)_2]$, **4**, respectively. The identity of the heterotrimetallic compound **3** was established by a single-crystal X-ray diffraction analysis, while an independent synthetic route (reaction of $[Cp_2ReH]$ with $[Bi(O_2CCH_3)_3]$) was developed for **4** in order to unambiguously identify **4** also as the product of the reaction between $[Fp{-}Bi(O_2CCH_3)_2]$ and $[Cp_2ReH]$.

1. Introduction

The element bismuth is characterized by several special features. It is the heaviest of the stable elements, and hence it has a large ion radius and its electron shell is easily polarisable. Moreover, despite the free electron pair, bismuth(III) units can even show a pronounced Lewis acidic character [1]. The combination of these characteristics translates also into interesting properties of bismuth-containing materials, in particular of multimetallic systems. Hence, for instance, the mixed oxide $Bi_2O_3 \cdot MoO_3$ and supported Re/Bi nanoparticles represent effcient heterogenous catalysts [2–4], and in $BiFeO_3$ (BFO) the unique interplay between iron and bismuth leads to multiferroic properties [5–7]. This motivates the construction and investigation of molecular transition metal–bismuth compounds that feature structural units of the materials but are soluble or that may be utilized as *single source precursors* (SSP).

In recent years we have found ways to access molecular Mo–O–Bi compounds and demonstrated 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 [8–13]. We have shown, too, that this "hydride-alkoxide approach" can also be utilized to create Re–Bi compounds via reactions of rhenocene hydride with bismuth alkoxides [14]. An extension of this protocol also to the synthesis of complexes with Fe–Bi entities, of which only a few representatives are known [15–26], was the obvious to test next, i.e. reactions of bismuth alkoxides with iron hydrides. However, recently we reported a precedent case proving that in principle Fe–Bi units can be constructed, avoiding iron hydrides as precursors, by reactions of complexes with Fe–Fe bonds and bismuth carboxylates: The reaction between $[Fp]_2$ (Fp = $(\eta^5\text{-}C_5H_5)(CO)_2Fe$) and $[Bi(O_2CCH_3)_3]$ yielded $[Fp{-}Bi(O_2CCH_3)_2]$, **I** (see Scheme 1), [27].

In the next step we were interested in three questions:

(i) Is it possible to also employ the simplest bismuth carboxylate, bismuth formate, as precursor?
(ii) Will a bismuth carboxylate, like bismuth alkoxides, also react with a transition metal hydride, and if yes,
(iii) is it possible to utilize this for the development of heterotrimetallic systems?

Here we report first results on these topics.

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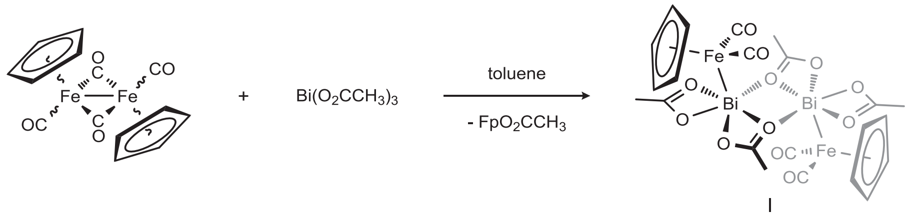

Scheme 1. Synthesis of [Fp–Bi(O_2CCH_3)$_2$], **I** [27].

2. Results and discussion

To continue our investigations on reactions of the dimer $[Fp]_2$ with bismuth carboxylates we used bismuth formate $[Bi(O_2CH)_3]$ as the bismuth carboxylate, since it does not contain organic residues and thus heterobimetallic compounds potentially generated could represent valuable starting materials for BFO oxides due to the facile elimination of CO_2 at elevated temperatures. The reaction between $[Fp]_2$ and the formate was carried out in formic acid due to the insolubility of bismuth formate in all common organic solvents. Stirring an equimolar reaction mixture of $[Fp]_2$ and $[Bi(O_2CH)_3]$ in concentrated formic acid for 6 h at 50 °C led to a bright red solution, which was filtered off from unreacted $[Bi(O_2CH)_3]$ (extension of the reaction time or applying higher temperatures led to green colored solutions and metallic bismuth mirrors deposited). Subsequent concentration of the filtrate and layering with diethyl ether resulted in the crystallization of $[Fp–Bi(O_2CH)_2]$, **1** (in form of two polymorphs, **1a** and **1b**) in high yields of *ca.* 80% (Scheme 2), and its purity was confirmed by an elemental analysis. **1** exhibited low solubility in all common organic solvents but was readily soluble in concentrated formic acid.

A proton nuclear resonance measurement of **1** dissolved in $CDCl_3$ showed one singlet for the formate protons at 9.33 ppm, that is, at lower field, than the corresponding signal of neat formic acid ($CDCl_3$: 8.06 ppm). The resonance of the Cp protons appeared at 5.05 ppm, similar to the one of the Cp protons of the acetate compound **I** ($CDCl_3$: 4.98 ppm).

To selectively crystallize $[Fp–Bi(\eta^1–O_2CH)(\eta^2\text{-}O_2CH)]_n$, **1a**, the red reaction solution (formic acid) was concentrated to 2 mL, cooled to −40 °C, layered with cold diethyl ether (−80 °C) and stored at −30 °C. After a few days this procedure resulted in red crystals of **1a** which were isolated by filtration. The molecular structure of **1a** as derived from a single-crystal X-ray investigation is shown in Fig. 1, and it confirmed the chemical formula derived from the ^{1}H NMR data and elemental analysis. The structure of **1a** showed extended disorder for the Cp rings and CO groups.

The iron center of the Fp unit is directly bound to a bismuth formate moiety via a Fe–Bi metal–metal bond (Fe–Bi 2.5904(7) Å, Cp–Fe–Bi 119.80(4)°), and the structural parameters correspond to those of known Fe–Bi complexes [15–26]. However, in comparison to the structure of the acetate **I** there are major differences regarding the coordination of the carboxylate ligands and their coordination modes. In the molecular structure of **I** both acetate residues at the bismuth atom coordinate in a η^2 fashion, as often observed for carboxylate moieties, and one of them acts as a bridging $\mu\text{-}\eta^2\text{-}O_2CCH_3$ ligand to a second Fe–Bi unit (see Scheme 1). However the determined structural data of **1a** clearly show that only one of the two O_2CH ligands at the bismuth atom binds in a η^2 mode (Bi–O4 2.406(4) Å, Bi···O3′ 2.659(5) Å, Bi···O3 2.780(4) Å), while the other one favours a η^1 coordination mode (Bi–O5 2.292(4) Å). Since the formate ligands require less space than acetate, these η^1 bonded representatives can form bridges to a second $[Fp–Bi(O_2CH)_2]_2$ unit and in turn this unit can bind back via another $\eta^1\text{-}HCO_2^-$ ligand (Bi···O6‴ 2.696(5) Å). Hence, a two dimensional (layered) coordination polymer is constructed, in contrast to the dimeric structure of **I**. Like in **I** the bismuth atoms are surrounded by six donor atoms. Five oxygen atoms (O3, O3′, O4, O5, O6‴) define the base of a distorted pentagonal pyramid (O4–Bi···O6‴ 157.48(18)°, O5–Bi···O3 159.86(15)°, O3′···Bi···O6‴ 141.06(15)°), whose top is occupied by the iron atom of the Fp fragment (O4–Bi–Fe 97.47(13)°, O5–Bi–Fe 88.64(10)°). Additionally, there is a weak secondary interaction of the O6 oxygen atom with the bismuth atom (Bi···O6 3.251(6) Å). Similar to the one of **I** the structure of **1a** exhibits a crystallographic inversion center within the center of a $[Bi_2O_2]$ diamond motif.

Surprisingly, recrystallizing **1a** from formic acid at room temperature as well as slow crystallization directly from the reaction mixture by layering of the filtrate with diethyl ether (without prior cooling to −40 °C) and storing it at room temperature (instead of −30 °C) led to red crystals of $[Fp–Bi(\eta^1\text{-}O_2CH)_2]_n$, **1b**. A single-crystal X-ray diffraction analysis of **1b** revealed (in contrast to the layered structure of **1a**) a chain-like molecular structure, which is depicted in Fig. 2.

Again, the connection of the organometallic Fp unit with the bismuth atom takes place by means of a covalent σ bond (Fe–Bi 2.5889(9) Å, Cp–Fe–Bi 120.81(2)°). Two primary bonds at the bismuth atom (Bi–O2 2.366(5) Å, Bi–O4 2.303(5) Å) are formed to two formate ligands. The angle between the O atoms (O2–Bi–O4 82.85(19)°) and all Fe–Bi–O angles (O2–Bi–Fe 88.58(13)°, O4–Bi–Fe 88.73(18)°) indicate that this bonding is mainly established through *p* orbitals. Two secondary contacts with formate ligands (O6′ und O5″) are observed which originate from two distinct neighbouring $[Fp–Bi(O_2CH)_2]$ units within the chain. Since the associated distances (Bi···O5″ 2.603(5) Å, Bi···O6′ 2.65(5) Å) are shorter than the corresponding distances to the oxygen atoms O5 and O6 (Bi···O5 2.810(5) Å, Bi···O6 3.207(5) Å) within the same unit, it seems appropriate to assign a η^1 coordination mode to the formate ligands forming the primary bonds. The atoms [O4|O2|O6′|O5″] and the Fe atom form a square pyramidal coordination sphere for the Bi atom (O2–Bi···O5″ 166.67(17)°, O4–Bi···O6′ 162.95(18)°).

The acquired X-ray data allowed for a rational approach to optimize the synthesis and increase the yields of **1a** and **1b**, respectively, as on this basis their powder diffraction patterns could be predicted. The simulations could then be used to monitor the outcome of subsequent variations of the crystallization conditions by P-XRD. This way the procedures outlined above were established leading to **1a** and **1b** in form of pure phases, as evidenced by their P-XRD patterns shown in Fig. 3 (**1a**: *a*, **1b**: *c*); their simulated data are depicted in Fig. 3, too (**1a**: *b*, **1b**: *d*), for comparison. The pattern of **1a** shows peaks with high intensities at $2\Theta = 9, 13, 14, 15$ and 16° (9.9, 6.8, 6.3, 6.0, 5.5 Å). For **1b** the distribution of peaks is more lucid, only three intense signals in a range from 5 to 20° are detected at $2\Theta = 11$, 13 and 16° (7.8, 6.6, 5.7 Å).

With the successful isolation of crystalline **1a** and **1b** in pure form we were now interested whether **1a** and **1b** show distinct IR

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