



Phenyl bismuth β -diketonate complexes: Synthesis and structural characterization

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ABSTRACT

The first examples of arylbismuth diketonate complexes are reported. Phenylbismuth(III) bis(hexafluoroacetylacetonate), $\text{BiPh}(\text{hfac})_2$ (**1**) and its adducts $[\text{BiPh}(\text{hfac})_2(\text{L})]$ (Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; L = H_2O (**1a**), Me_2CO (**1b**), THF (**1c**), DMA (*N,N*-dimethylacetamide) (**1d**), DMSO (**1e**), PhCN (**1f**), as well as a mixed hexafluoroacetylacetonate–trifluoroacetate complex, $[\text{BiPh}(\text{hfac})(\text{O}_2\text{CCF}_3)]_2$ (**2**), have been synthesized and characterized. Compound **1** is isolated from the reaction of BiPh_3 with 2 equiv. of Hhfac in dry hexanes. Compound **2** can be synthesized using two different routes: one utilizes the reaction between stoichiometric amounts of **1** and $\text{CF}_3\text{CO}_2\text{H}$, while the second method involves the interaction of the previously described $\text{BiPh}_2(\text{O}_2\text{CCF}_3)$ (**3**) with Hhfac. Crystallographic analysis of the $[\text{BiPh}(\text{hfac})_2(\text{L})]$ adducts reveals a pentagonal pyramidal geometry around the metal center; similarly, the dinuclear $[\text{BiPh}(\text{hfac})(\text{O}_2\text{CCF}_3)]_2$ complex is composed of two distorted pentagonal pyramids connected into dimers by the bridging carboxylate groups. The effect of replacing the Lewis base in the coordination sphere of Bi(III) on the coordination polyhedron and crystal packing is discussed. The ^1H and ^{19}F NMR spectra of the title complexes at room temperature indicate single environments for the hfac group and suggest that they are fluxional in solutions on the NMR time scale. Compounds **1** and **2** are promising starting materials in the chemistry of bismuth(III) and as building blocks for the construction of heterometallic species.

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1. Introduction

Despite of the fact that metal β -diketonates represent one of the oldest and most studied classes of coordination compounds, there is a continuous interest in exploring their synthesis and properties. These compounds are useful in a number of applications, mainly due to their high volatility and solubility in common organic solvents. β -Diketonates proved themselves as very versatile chelating ligands to form stable complexes with almost all metal ions, including such electropositive elements as the alkali-earth [1,2] or lanthanide metals [2,3]. High volatility of metal β -diketonates is associated with an efficient shielding of the positively charged metal ions from the intermolecular interactions by surrounding hydrocarbon or fluorocarbon shells [2]. It is known that in addition to their ability to chelate the metal ions, β -diketonates can also fulfill bridging functions. The degree of oligomerization depends on many factors, including the nature of the metal ion and the electronic and steric effects of the ligands. Large metal ions with pronounced electron deficiency tend to favor bridging linkages over terminal ones, however this tendency is substantially or fully reduced in the presence of Lewis bases.

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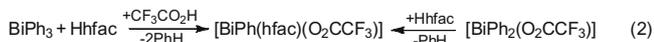
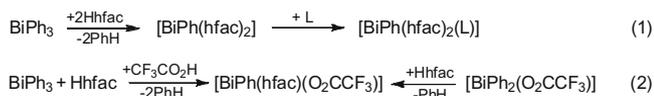
The interest in bismuth(III) β -diketonates has mainly arisen from their utility in different CVD processes. β -Diketonate complexes are usually synthesized by methods similar to those described for the alkoxides [4]. The metathesis reaction of bismuth halides with alkali metal salts of the corresponding diketones has been successfully employed to produce Bi(III) diketonates, however additional purification steps are usually required to remove possible halide contamination. An alternative approach is the acidolysis reaction of triphenylbismuth with β -diketonates. The latter reaction can be performed in an appropriate solvent or solventless. The crystal structures of bismuth(III) β -diketonates have been shown to exhibit considerable diversity. As a consequence of the pronounced Lewis acidity of the bismuth atom and the Lewis basic behavior of the diketonate ligands, there is a remarkable tendency to form oligomers or polymers with one or several bridging atoms. Thus, in two of the most studied bismuth(III) compounds from this class, $\text{Bi}(\text{hfac})_3$ [5] and $\text{Bi}(\text{thd})_3$ [6,7] (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione), the ligands display strong chelating and relatively weaker bridging functions; the latter function is responsible for the assembly of the two complexes into dimers through Bi...O interactions. Recently, new research directions have emerged for bismuth(III) β -diketonate complexes, such as their use in assembly of heterometallic complexes [5] and polynuclear oxo-clusters [8].

While the chemistry of tris-diketonate bismuth complexes is well developed, no data are available on the corresponding arylbismuth diketonate compounds. These compounds are likely formed

as intermediates during the reaction of BiPh_3 with the corresponding β -diketones. However, their isolation may present difficulties due to possible formation of polymeric species. This could be due in part to the large size of Bi(III) (ionic radius 1.03 Å), which allows for high coordination numbers without significant steric constraints, thus favoring the association of Bi(III) centers. In order to control the oligomerization process, one possibility is to use the idea of “solvent control”. In this approach a coordinating solvent forms a stable adduct with the corresponding metal ion, preventing bridging interactions. We attempted to perform the reaction of BiPh_3 with 2 equiv. Hhfac in hexane with subsequent addition of some coordinating molecules. In this paper, we report the synthesis and characterization of phenylbismuth(III) hexafluoroacetylacetonate, (**1**), and its adducts $[\text{BiPh}(\text{hfac})_2(\text{L})]$ (**1a–1f**), as well as a dimeric hexafluoroacetate–trifluoroacetate complex, $[\text{BiPh}(\text{hfac})(\text{O}_2\text{CCF}_3)]_2$ (**2**), obtained by two different synthetic procedures (Scheme 1).

2. Results and discussion

Triphenylbismuth reacts upon reflux with 2 equiv. of hexafluoroacetylacetonate in dry hexanes to produce a yellow solution. Partial removal of the solvent in vacuum and cooling down the concentrated solution to -20°C provides microcrystalline powder of $\text{BiPh}(\text{hfac})_2$ (**1**), as confirmed by spectroscopic and elemental analyses. Attempts to grow single crystals of **1** from non-coordinating solvents were unsuccessful. In the presence of coordinating solvents it turned out that **1** can easily form monoadducts. Thus, yellow crystalline solids of the corresponding adducts **1a–1f** can be isolated from hexanes solution of **1** in the presence of small amounts of H_2O (**1a**), Me_2CO (**1b**), THF (**1c**), DMA (**1d**), DMSO (**1e**), and PhCN (**1f**). Complex **2** was obtained by subsequent addition of 1 equiv. of Hhfac and 1 equiv. of trifluoroacetic acid to BiPh_3 in hexanes. The same compound can be obtained in a lower yield from the reaction of $\text{BiPh}_2(\text{O}_2\text{CCF}_3)$ (**3**) (synthesized as described in [9]) with 1 equiv. of Hhfac (Scheme 1). All isolated β -diketonate complexes appear as yellow–orange, air-sensitive, shiny crystalline solids. They are sparingly soluble in methanol, acetone, dichloromethane and chloroform, but less so in diethylether and hydrocarbons. The newly-synthesized compounds were characterized by IR and NMR spectroscopy as well as by single-crystal X-ray diffraction. The IR spectra exhibit, as expected, the corresponding $\text{C}=\text{O}$ hfac[−] stretches in the range of $1634\text{--}1640\text{ cm}^{-1}$. These bands are at significantly lower energies than those found for free Hhfac (1689 cm^{-1}) and are indicative of β -diketonate chelation to Bi(III). The ^1H and ^{19}F NMR spectra of the isolated complexes at room temperature revealed single environments for the hfac[−] group suggesting that the diketonate ligands are able to undergo ligand exchange processes at a rate that is fast on the NMR time scale. The ortho, meta, and para-protons of the phenyl group are centered at $\sim 8.2\text{--}8.3\text{ ppm}$ (d), $\sim 7.9\text{--}8.0\text{ ppm}$ (t), and $\sim 7.4\text{--}7.5\text{ ppm}$ (t), respectively. The ^1H NMR spectra contain no signals of the di- and triarilated species, which does not support the occurrence of aryl redistribution reactions. Such reactions are commonly encountered in the solution chemistry of arylantimony and arylbismuth complexes [10,11].



Legend Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione;
L = H_2O , Me_2CO , THF, DMA, DMSO, PhCN.

Scheme 1.

The thermal decomposition of the complexes was investigated by TGA and the residues were analyzed by X-ray powder diffraction (XRPD). In all cases, it was found that the compounds undergo thermal decomposition in two or three stages upon heating and do not exhibit any apparent mass loss of the diketonates due to sublimation. The thermogravimetric plots for **1**, **1c** and **1e** (Fig. 1) are qualitatively similar in stages of weight loss up to 550°C . The release of coordinated Lewis base molecules in the adducts is not observed as a separate step. Compound **1** displays a sharp melting point at $82\text{--}83^\circ\text{C}$. The decomposition of **1** proceeds in several steps and is punctuated by an abrupt mass loss ($\sim 62\%$) between 195 and 340°C . The XRPD study of the residue resulted upon thermal decomposition of **1** in Ar probed the formation of a complex mixture with BiOF being a major phase. The formation of BiOF upon thermal treatment of fluorine-containing bismuth(III) compounds has been previously reported in the literature [12,13]. The thermal decomposition of the adducts **1a–1f** somewhat mirrors what was observed for the thermolysis of **1**. In each case, the thermal decomposition of the complex proceeds in several steps with an abrupt mass loss that includes removal of the corresponding neutral ligand. Interestingly, the thermolysis of **1**, **1a–1f** and **2** in air at 550°C for 1 h resulted exclusively in monoclinic $\alpha\text{-Bi}_2\text{O}_3$ (Fig. 2).

The molecular structures of compounds **1a–1f** and **2** were established by single-crystal X-ray diffraction. X-ray quality crystals can be grown directly from the reaction mixtures. All compounds were found to crystallize in the monoclinic crystal system ($P2_1/c$, $P2_1/n$ or $C2/c$ space groups). The $\text{BiPh}(\text{hfac})_2\text{L}$ adducts adopt a pentagonal pyramidal geometry with the metal center coordinated by the phenyl group, two chelating β -diketonate

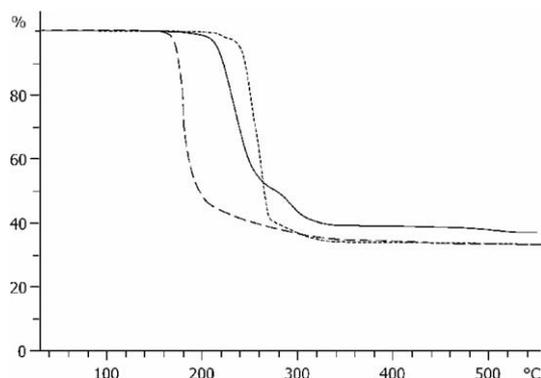


Fig. 1. TGA curves of **1** (—), **1c** (---) and **1e** (.....).

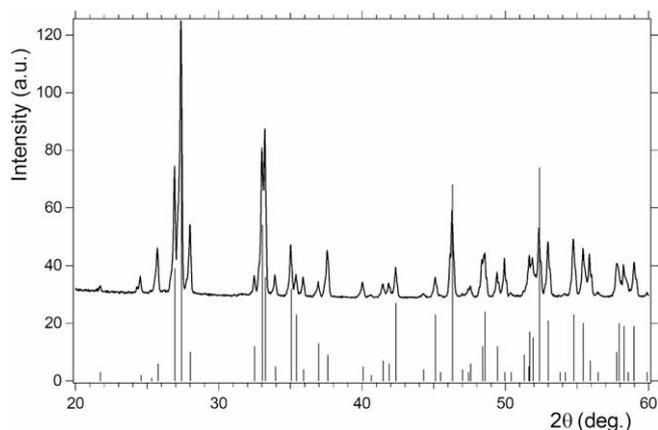
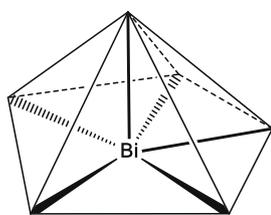


Fig. 2. X-ray powder diffraction pattern of the decomposition product of **1** in air and its comparison to $\alpha\text{-Bi}_2\text{O}_3$ phase, JCPDS No. 00-041-1449.

ligands, and a terminal monodentate O- or N- neutral donor. Complex **2** represents a dimer formed by bridging trifluoroacetate groups. The carboxylate ligand acts in an *aniso*-bidentate coordination mode [14,15] to one Bi atom and also performs a bridging function to the other Bi(III) center of the dimer. The coordination environment of the six-coordinate bismuth centers in **1a–1f** and **2** are best described as pentagonal pyramidal. A void, presumably occupied by a stereochemically active lone electron pair (SALEP), can be identified in the coordination polyhedron (Scheme 2). In other structurally characterized monoaryl-bismuth complexes, the SALEP is directed opposite to the *ipso* carbon of the phenyl group [10]. In terms of the terminology introduced by Shimoni-Livny et al. [16], the geometry of Bi(III) in **1a–1f** and **2** can be regarded as *hemidirected*, with a gap in the coordination sphere, as opposed to *holodirected* coordination, in which the bonds are directed throughout the globe of the coordination sphere.

The aryl ligand occupies the apical position of the bismuth coordination sphere, while the basal plane is completed by five oxygen donors for complexes **1a–1e** and **2**, or four oxygen and one nitrogen donor in complex **1f** (Figs. 3–9). The equatorial plane in **1a–1f** is formed by two chelating β -diketonate ligands and a coordinated Lewis base molecule. Complex **2** represents an example of the relatively rare Bi(III) complexes containing three different substituents. Each Bi atom in the dimeric unit of **2** is surrounded in the equatorial plane by two O atoms from one hfac ligand, two O atoms of a bridging carboxylate group, and one O atom from the carboxylate ligand attached to the second bismuth atom. The coordination environment of the Bi(III) centers in **2** represents two fused pentagonal pyramids, similar to those found in **1a–1e**, sharing one common edge and connecting O(22) and O(22A) atoms. Fig. 8 represents this type of coordination polyhedron in **1a** compared with the corresponding Bi(III) polyhedra in **2**. The open site



Scheme 2.

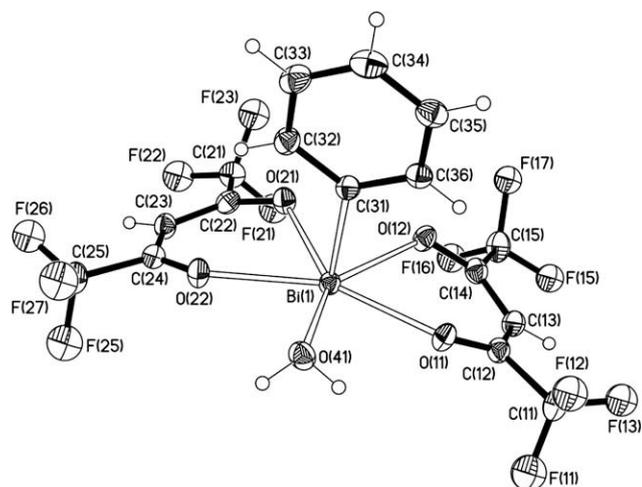


Fig. 3. Coordination environment of Bi(III) in **1a**; thermal ellipsoids are shown at 40% probability level. Only one orientation of the fluorine atoms is depicted.

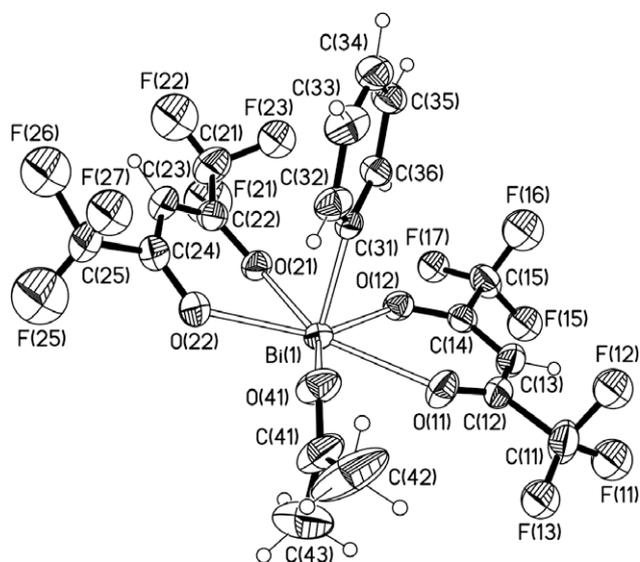


Fig. 4. Coordination environment of Bi(III) in **1b**.

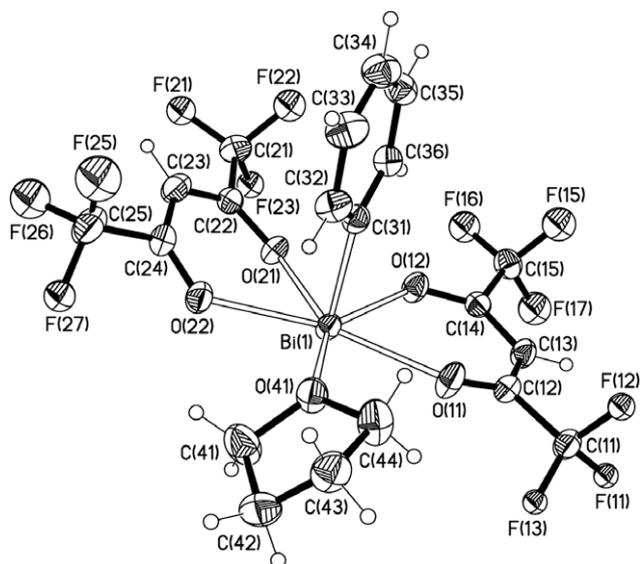
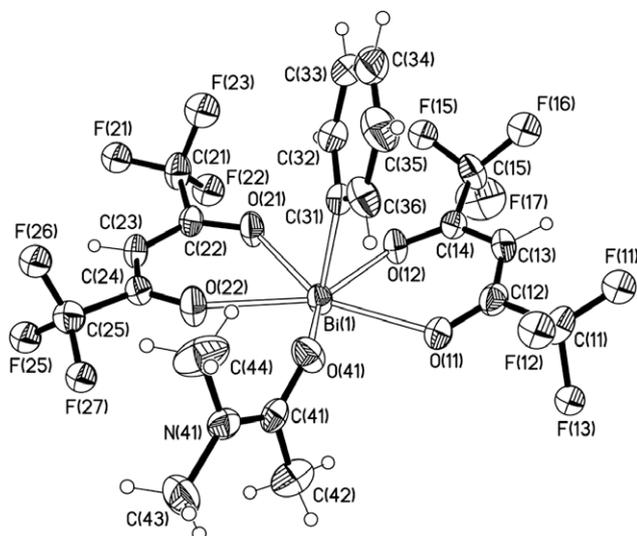
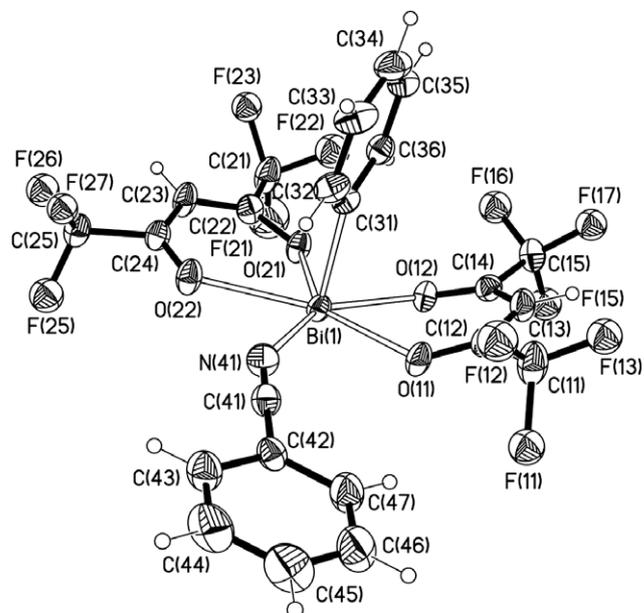
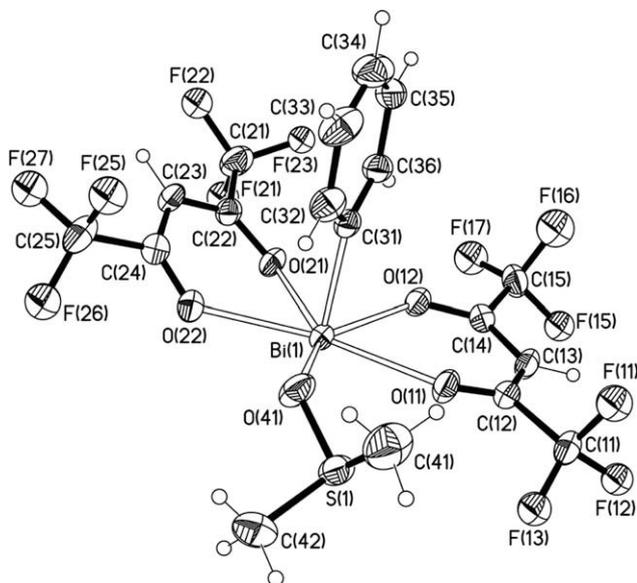
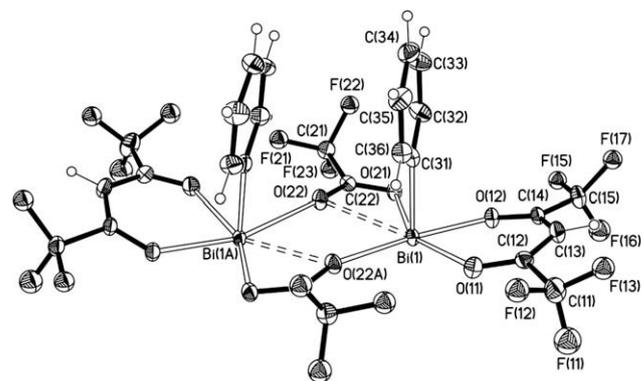


Fig. 5. Coordination environment of Bi(III) in **1c**.

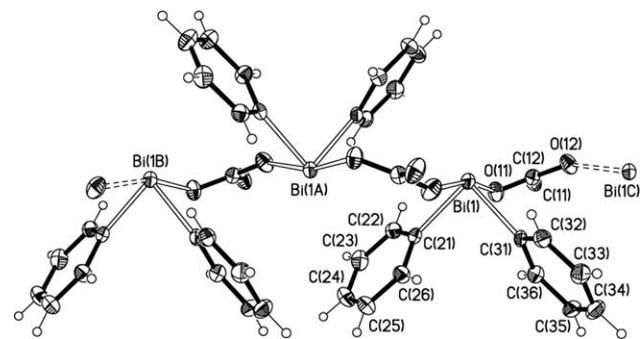
of the pyramid, opposed to the aryl group is believed to accommodate a SALEP, in which case the coordination polyhedron of Bi(III) in compounds **1a–1e** and **2** could be described as a ψ -pentagonal bipyramid [15] (Fig. 10).

The overall crystal structures of the phenylbismuth diketonate complexes **1a–1f** and **2** are shown in Figs. 3–9, with selected bond lengths and angles given in Table 2. The Bi–C_{aryl} bond distances in **1a–1f** and **2** are within 2.229(5)–2.242(5) Å range, comparable to those found in other arylbismuth carboxylates [10,17–20]. These distances are slightly shorter than the average Bi–C_{aryl} bond distance reported for BiPh₃, 2.268 Å [17]. The sum of valence angles in the equatorial plane of the bipyramid in **1a–1f** and **2** (358.9(1)–360.1(2)°) is close to 360°. The Bi(1) atoms in **1a–1e** form two chelate metalocycles Bi(1)O(11)C(12)C(13)C(14)O(12) and Bi(1)O(21)C(22)C(23)C(24)O(22) with the Bi–O bond distances between 2.380(4) and 2.518(4) Å. The oxygen atom of the coordinated water molecule in **1a** is at 2.456(4) Å, which is shorter than most of the Bi–O_{water} bond lengths in bismuth(III) complexes. The shortest Bi–O distance in **1a–1e** is found in the DMA adduct **1d**

Fig. 6. Coordination environment of Bi(III) in **1d**.Fig. 8. Coordination environment of Bi(III) in **1f**.Fig. 7. Coordination environment of Bi(III) in **1e**.Fig. 9. Coordination environment of Bi(III) in **2**.

(2.331(5) Å), while the longest belongs to the THF adduct **1c** (2.517(3) Å). The Bi–N bond in **1f** is 2.703(4) Å, which is slightly longer than the typical Bi–N coordination bonds. This weak Bi–N bond is situated in *trans* position relative to the O(12)–Bi(1)–O(21) angle.

The Bi–O chelating bonds with the hfac ligand in **2** are asymmetric (2.278(4) and 2.385(3) Å) and are shorter than the average value of such bonds found in **1a–1f** (2.436 Å). The trifluoroacetate anion acts in a tridentate-bridging fashion connecting the neighboring bismuth atoms into dimeric units. The Bi(1) atom in **2** is chelated by the oxygen atoms of the O(21)C(22)O(22) carboxylate group (Bi–O 2.399(4) and 2.761(4) Å), while the bridging bond Bi–O(22A) is 2.627(4) Å (Fig. 9). As a result, complex **2** shows the largest distribution in the length of the Bi–O bond distances among the complexes under investigation. It also exhibits the most variation in the equatorial angles of the bipyramid (50.5–85.3°), but despite this, the sum of the five angles (359.3°) is very close to the ideal planar value. The distortion of the pentagonal pyramidal coordination around the bismuth atom in **1a–1f** is clearly characterized by

Fig. 10. A fragment of the polymeric chain in the structure of **3**.

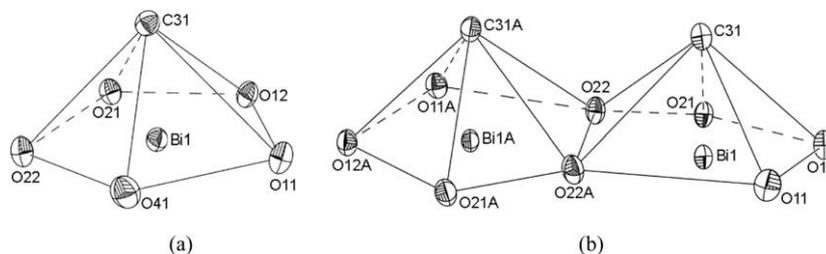
the variation in O–Bi–O angles, but to a lesser extent compared to **2**. The C–Bi–O angles in **1a–1f** and **2** generally deviate from 90° and are found in the range of 81.0° to 93.6°. In the crystal structure of BiPh₂(O₂CCF₃) (**3**), that we determined for the first time, the carboxylate ligand displays a different coordination mode compared to **2**. In **3** the trifluoroacetate group acts as a bidentate bridging (rather than chelating-bridging) ligand to generate polymeric chains (Fig. 10). The compound features a disphenoidal [21,22]

Table 1
Crystallographic data for **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **2**, and **3**.

	1a	1b	1c	1d	1e	1f	2	3
Formula	C ₁₆ H ₉ BiF ₁₂ O ₅			C ₁₉ H ₁₃ BiF ₁₂ O ₅	C ₂₀ H ₁₅ BiF ₁₂ O ₅			
C ₂₀ H ₁₆ BiF ₁₂ NO ₅								
C ₁₈ H ₁₃ BiF ₁₂ O ₅ S								
C ₂₃ H ₁₂ BiF ₁₂ NO ₄								
fw	718.21	758.27	772.30	787.32	778.32	803.32	1212.32	476.20
Cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P2 ₁ /c	C2/c	C2/c	P2 ₁ /n	C2/c	C2/c	C2/c	P2 ₁ 2 ₁ 2 ₁
a, (Å)	10.726(2)	20.517(4)	20.781(4)	12.092(2)	20.128(4)	26.892(5)	16.294(3)	8.800(2)
b, (Å)	10.602(2)	12.818(3)	12.905(3)	18.805(4)	12.996(3)	12.623(3)	16.185(3)	10.500(2)
c, (Å)	18.939(4)	18.685(4)	18.556(4)	12.363(3)	18.983(4)	16.518(3)	12.849(3)	15.556(3)
α (°)	90	90	90	90	90	90	90	90
β (°)	103.88(3)	93.36(3)	90.94(3)	114.31(3)	93.52(3)	111.61(3)	105.23(3)	90
γ (°)	90	90	90	90	90	90	90	90
V, (Å ³)	2090.9(7)	4906(2)	4976(2)	2562.0(9)	4957(2)	5213(2)	3270(1)	1437.5(5)
Z	4	8	8	4	8	8	8	4
D _{calc} , (g·cm ⁻³)	2.282	2.053	2.056	2.041	2.086	2.047	2.463	2.200
λ (Mo Kα), (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
2θ _{max} (°)	56.345	56.60	56.64	56.54	56.58	56.46	56.54	56.50
Absorption coefficient (mm ⁻¹)	8.565	7.307	7.205	7.001	7.316	6.881	10.900	12.296
Number of data collected	4902	5752	9928	9288	9892	9939	9926	6068
Unique reflections	4048	4887	5093	4381	4899	5145	3534	3093
Number of params refined	303	322	379	369	358	382	235	190
R ₁ [I > 2σ(I)]	0.0327	0.0391	0.0303	0.0487	0.0442	0.0309	0.0346	0.0287
wR ₂ [I > 2σ(I)]	0.0826	0.1117	0.0785	0.1330	0.1214	0.0833	0.0926	0.0654
Goodness-of-fit (GOF)	1.028	1.048	1.056	1.014	1.044	1.041	1.040	1.051
ρ _{fin} (max/min) (e Å ⁻³)	2.685/ -1.414	1.408/-0.773	1.361/ -0.668	2.206/-1.764	2.513/-1.179	1.876/-0.725	1.033/-1.899	2.61/-1.02

Table 2
Selected bond lengths (Å) and angles (°) for **1a–f** and **2**.

	1a	1b	1c	1d	1e	1f	2
Bi1–C31	2.238(5)	2.242(5)	2.238(4)	2.230(7)	2.241(5)	2.233(4)	2.229(5)
Bi1–O11	2.448(4)	2.470(4)	2.429(3)	2.402(5)	2.476(4)	2.485(3)	2.385(3)
Bi1–O12	2.432(3)	2.398(4)	2.413(3)	2.466(4)	2.475(4)	2.339(3)	2.278(4)
Bi1–O21	2.432(4)	2.380(4)	2.388(3)	2.518(4)	2.441(4)	2.332(3)	2.399(4)
Bi1–O22	2.466(3)	2.426(4)	2.457(3)	2.482(5)	2.426(4)	2.473(3)	2.761(4)
Bi1–EX [*]	2.456(4)	2.510(5)	2.517(3)	2.331(5)	2.360(4)	2.703(4)	2.627(4)
C31–Bi1–O11	87.5(2)	91.1(2)	90.3(1)	87.0(2)	88.7(2)	84.1(1)	86.2(1)
C31–Bi1–O12	87.8(2)	86.3(2)	86.0(1)	83.2(2)	84.5(2)	87.1(1)	89.2(1)
C31–Bi1–O21	87.6(2)	84.1(2)	85.3(1)	86.8(2)	83.8(2)	88.2(1)	86.7(1)
C31–Bi1–O22	88.6(2)	83.2(2)	82.1(1)	93.6(2)	83.6(2)	90.0(1)	81.0(1)
C31–Bi1–EX [*]	83.8(2)	85.0(2)	88.1(1)	84.8(2)	88.2(2)	89.2(1)	85.3(1)
O11–Bi1–O12	72.2(1)	73.2(1)	72.8(1)	72.5(2)	71.7(1)	73.0(1)	77.5(1)
O12–Bi1–O21	71.6(1)	71.6(2)	69.2(1)	71.3(1)	69.9(1)	71.5(1)	75.9(1)
O21–Bi1–O22	72.5(1)	73.3(2)	72.4(1)	70.9(2)	71.9(2)	74.4(1)	50.5(1)
O22–Bi1–EX [*]	72.8(1)	72.3(2)	73.4(1)	69.8(2)	72.8(2)	73.2(2)	70.1(1)
EX [*] –Bi1–O11	70.5(1)	68.7(2)	71.5(1)	75.6(2)	72.8(2)	67.7(1)	85.3(1)
O11–Bi1–O21	143.6(1)	144.7(2)	142.0(1)	143.8(2)	141.3(1)	144.0(1)	152.5(1)
O11–Bi1–O22	143.3(1)	140.9(2)	144.3(1)	145.1(2)	144.9(2)	140.5(1)	153.0(1)
O12–Bi1–O22	144.0(1)	144.2(2)	140.5(1)	142.2(2)	140.9(1)	145.8(1)	125.7(1)
O12–Bi1–EX [*]	142.1(1)	140.7(2)	143.8(1)	146.4(2)	143.8(2)	140.8(1)	162.2(1)
O21–Bi1–EX [*]	144.4(1)	144.9(2)	145.8(1)	139.0(2)	144.3(1)	147.5(1)	120.5(1)

* EX = O(41) for **1a–1e**, N(41) for **1f**, and O(22A) for **2**.**Fig. 11.** Coordination polyhedra of bismuth atoms in **1a** (a) and **2** (b).

Bi(III) center coordinated by two aryl groups and two oxygen atoms. The Bi–C distances in **3** are 2.232(5) and 2.243(6) Å, while the Bi–O distances are 2.358(4) and 2.464(4) Å. The separations observed between two Bi centers in **2** (4.392(4) Å) and **3** (4.431(3) Å) are less than the sum of van der Waals radii of two bismuth atoms (4.8 Å [17]). In both compounds the dimerization/polymerization brings the bismuth atoms into a close intermolecular contact.

Analysis of the data available from the Cambridge Structural Database indicates that the *hemidirected* pentagonal bipyramidal geometry found in complexes **1a–1f** and **2** (Fig. 11) is typical for aryl-bismuth complexes. Thus, the related arylbismuth(bis)salicylate adducts [BiPh(Hsal)₂(phen)] and [BiPh(Hsal)₂(bipy)] display a phenyl group in the apical position of the Bi(III) coordination polyhedron, with the base of the pentagonal pyramid being completed by three carboxylate oxygen atoms of a mono- and a bidentate salicylate ligand and two nitrogen atoms of the chelating diamine phen or bipy ligand [10]. Other structurally characterized BiPh(O₂CR)₂ complexes, including [BiPh(O₂CCH(CH₃)CH₂GePh₃)₂] [18], [BiPh(O₂CC₆H₂F₃-3,4,5)₂] [19], and [BiPh{(2-C₅H₄N)CO₂)}₂] [20] feature similar coordinations around the Bi(III) center. Interestingly enough, the geometries of the primary coordination spheres (up to ~2.5 Å) of Bi(III) in Bi(hfac)₃ [5] and Bi(thd)₃ [6,7] can also be represented as distorted pentagonal pyramids, if the secondary bonds are not being taken into account. This suggests the presence of a SALEP in both Bi(hfac)₃ [5] and Bi(thd)₃ [6,7]; subsequently, their coordination polyhedra can be viewed as distorted ψ -pentagonal bipyramids [21,22].

Significant differences are observed in the way the monoaryl-bismuth hexafluoroacetylacetonate molecules are assembled in their crystal lattices. The six-coordinate complexes **1a–1f** and **2** are linked in their solid-state structures by hydrogen bonds as well as by secondary and/or van der Waals interactions. Intermolecular interactions between the bismuth atoms and the adjacent phenyl groups are present in **1a** as it is evident from Fig. 12. This type of weak π -bonding from the metal to the organic ligand is characteristic of a number of main group element-aryl complexes and is indicative of relatively electron-deficient metal centers [23]. The Bi–centroid contact in **1a** is 3.388(4) Å with a slight ring slippage of the Bi atom away from the line perpendicular to the ring plane. This distance is somewhat shorter than in [BiPhCl₂(THF)]_∞ (3.43 Å) [24], [BiPhBr₂(THF)]_∞ (3.47 Å) [25], and [BiPh₂(THF)]_∞ (3.54 Å) [25], similar to Bi(OSiPh₂^tBu)₃ (3.34 Å), but much longer than the shortest Bi–C_{arene} centroid contacts found in Bi(O{2,6-Me₂C₆H₃})₃ (2.98 Å) [26] and Bi(OC₆F₅)₃(C₆H₅CH₃)₂ (2.96 Å) [27]. It should be noted, however, that the oxygen atom of the ligand allows additional flexibility to adopt a favorable conformation for an optimized Bi–arene interaction. The coordination mode can be considered as roughly η^6 with Bi–C_{ph} distances between 3.513(4) and 3.792(4) Å. The bismuth–aromatic ring centroid distance in **1a** is thus closer to the upper range of reported values in the literature suggesting a rather weak contact. By means of these weak interactions the Bi(III) centers are capped by phenyl groups that connect them into a polymeric chain (Fig. 12). The Bi···Bi distance between the two neighboring atoms in the chain (5.317(5) Å) ex-

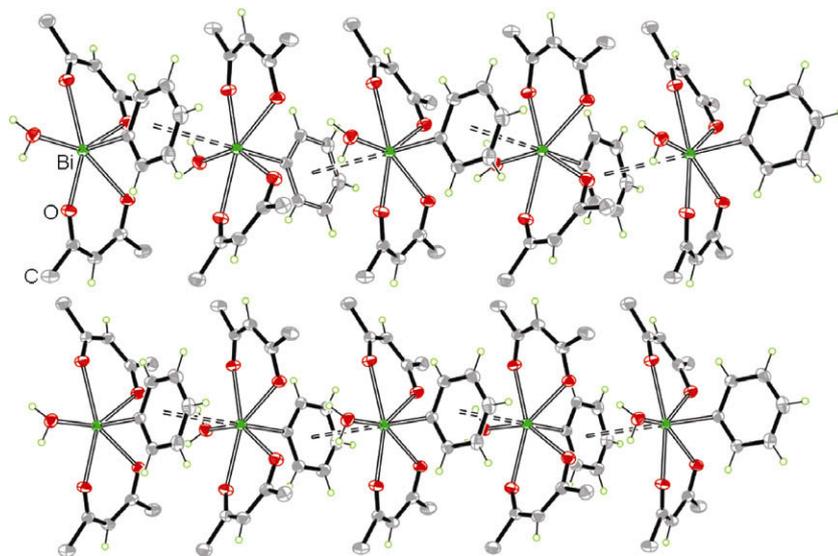


Fig. 12. Intermolecular interactions between bismuth atoms and the adjacent phenyl groups in **1a**. Fluorine atoms are omitted for clarity.

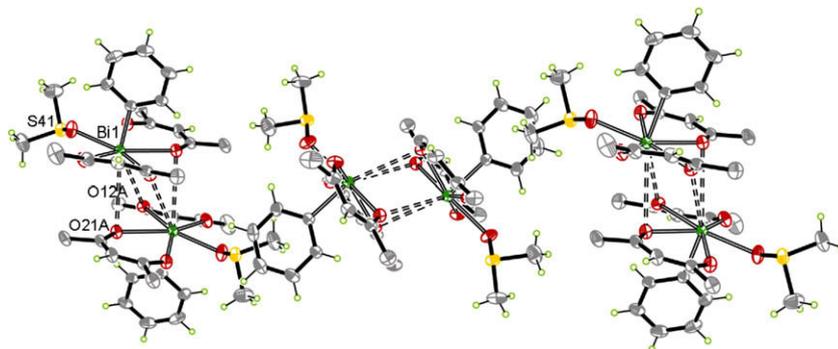


Fig. 13. Intermolecular interactions between the bismuth atoms and the adjacent diketonate O-atoms in **1e**. Fluorine atoms are omitted for clarity.

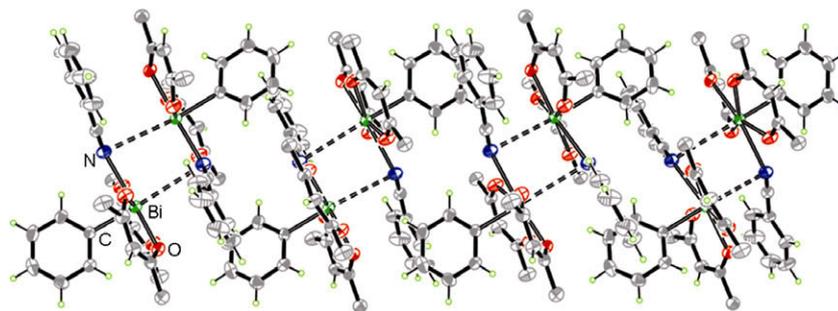


Fig. 14. Intermolecular interactions between the bismuth atoms and the neighboring N-atoms of PhCN ligands in **1f**. Fluorine atoms of the hfac groups are omitted for clarity.

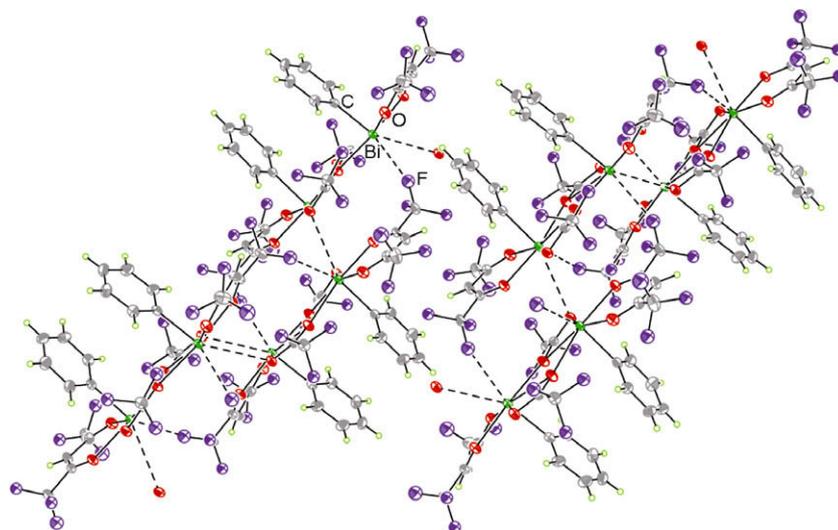


Fig. 15. Intermolecular interactions between the bismuth atoms and the neighboring O and F-atoms in **2**.

cludes any metal–metal interaction ($\sum r_{vdw}$ 4.8 Å) [17], while the corresponding distance between the chains is measured to 10.726(6) Å.

No bismuth–aromatic ring interactions are present in the crystal structures of the other adducts **1b–1f** or in **2**. In contrast to **1a**, the aryl groups in **1b–1e** are oriented away from each other. A closer look on the crystal packing in the adducts reveals some interesting aspects. It is known that the coordination sphere of Bi(III) can comprise both *primary* bonds as well as *secondary* bonds or *interactions*, with interatomic distances shorter than the sum of van der Waals radii. Thus, in **1b–1e** two diketonate oxygen atoms from the neighboring molecule are involved in weak interactions with an adjacent Bi(III) atom. Sawyer and Gillespie showed [21] that in some complexes such weak contacts may form around the direction of the lone pair, but not directly over it. Fig. 13 shows the formation of such weak contacts in the structure of **1e**. The Bi(1)···O(12A) and Bi(1)···O(21A) contacts in **1b**, **1c**, **1d** and **1e** are 3.525, 3.670, 3.518, 3.474 and, respectively, 3.411, 3.319, 3.750, 3.349 Å. The bismuth(III) lone pair of electrons, if it is considered stereochemically active, should occupy an axial position *trans* to the C(31) atom and being oriented between the O(12A) and O(21A) atoms. A drastic difference in the secondary bonding is observed in **1f**. Only a very weak interaction can be distinguished, involving Bi(III) and a nitrogen atom of the PhCN ligand (Bi(1)···N(41A) 3.489 Å) from an adjacent molecule (Fig. 14). A more complex picture is observed in **2**, which contains dimers of [BiPh(hfac)(O₂CCF₃)]. The dimers are connected in chains by means of very weak interactions between Bi(III) and one of hfac oxygen atoms (Bi(1)···O(21B) 3.308(4) Å) and of one F atoms (Bi(1)···F(16H)

3.356(5) Å) from two different [BiPh(hfac)(O₂CCF₃)] moieties as shown in Fig. 15. Similar secondary bonds are observed in Bi(hfac)₃ [5], though the contacts in the structure of the latter compound are considerably shorter (Bi···O 2.890(3) Å and Bi···F 3.174(4) Å). It has to be noted that the aryl groups from each Bi atom of the dimer **2** lie stacked with relatively long inter-ring separations in the range of 3.8–4.1 Å.

Comparing the packing arrangements of the complexes under investigation, it is found that when water is coordinated to Bi(III), the assembly through Bi–arene π complexation is favored, while when bulkier O-donor Lewis bases are present, secondary bonding with additional donor atoms from the neighboring complexes becomes more favorable. The dominant motif of assembly in **1b–1f** and **2** through the additional weak bonding appears to prevent Bi–aryl π -interactions observed in **1a**. It can be argued that the realization of one or the other weak bonding pattern is dependent upon the nature and availability of the donor atoms and specific steric constraints around each bismuth center. Crystal-packing forces may play an important role as well [10,28]. These results illustrate that the interactions between Bi atoms in phenylbismuth β -diketonate compounds are diverse and can involve hydrogen bonding, Bi–arene π complexation, as well as a weak secondary bonding of bismuth(III) centers with a range of donor atoms (N, O, F).

3. Conclusions

Monoarylbismuth diketonates have been reported for the first time, extending the (relatively small) list of metal complexes of

this type. The crystal structures of compounds **1a–1f** and **2** show that the coordination geometry of the bismuth(III) center takes the form of a distorted pentagonal pyramid. Depending upon the nature of the ligands the bismuth atoms are associated through weak secondary bonding in chains or layers by coordination of Bi(III) to (i) a phenyl group through weak π -bonding from the metal to the organic ligand as in **1a**; (ii) two diketonate oxygen atoms from the neighboring molecule as in **1b–1e**; (iii) a nitrogen atom from the adjacent molecule as in **1f**; or (iv) an oxygen and a fluorine atoms from two different [BiPh(hfac)(O₂CCF₃)] fragments as in **2**. Thermal decomposition of the complexes in air resulted in Bi₂O₃, while under argon BiOF was identified as the major decomposition product. The complexes are sufficiently soluble to be of interest as promising building blocks for the construction of heterometallic complexes. The presence of aryl functionality offers a wide variety of possibilities for further functionalization of these complexes, for instance, through the use of appropriate metalloligands.

4. Experimental section

4.1. General procedures

All chemicals, unless otherwise stated, were of reagent grade and used as received. Acetone was dried over Drierite and distilled over freshly activated molecular sieves. THF and hexanes were distilled from sodium-benzophenone ketyl before use. [BiPh₂(O₂CCF₃)] (**3**) was synthesized following a previously described procedure [9]. The reported IR data were obtained on a Perkin–Elmer FT-IR spectrometer using attenuated total reflection (ATR). NMR spectra were recorded at room temperature in CDCl₃ on a Bruker Avance 400 spectrometer, and the ¹H and ¹⁹F chemical shifts are reported relative to tetramethylsilane (TMS) and CFCl₃, respectively. Thermogravimetric measurements were carried out under argon or air at a heating rate of 10°/min using a Mettler Toledo TGA instrument. Elemental analysis was performed by Galbraith Laboratories Inc.

4.2. Synthesis of [BiPh(hfac)₂] (**1**)

440 mg (1 mmol) commercial BiPh₃ was loaded into a Schlenk flask and 10 mL dry hexanes was added. The mixture was stirred and heated to reflux to result in a complete dissolution of the solid. 280 μ L (2 mmol) Hhfac was added upon vigorous stirring within 10 min to produce a yellow solution, which was refluxed for additional 30 min. The solution was filtered under Ar and the filtrate was concentrated in vacuum and stored at –20 °C overnight. A yellow powder was produced in 65% yield. Anal. Calc. for C₁₆H₇F₁₂O₄Bi: C, 27.45; H, 1.01. Found: C, 27.41; H, 1.10%. FT-IR (ATR, cm⁻¹): 3180, 3060, 1640, 1609, 1556, 1530, 1445, 1339, 1254, 1195, 1141, 1085, 1052, 997, 917, 803, 733, 722, 689, 663, 581. ¹H NMR (CDCl₃): 8.26 (d, Ph, 2H), 8.07 (t, Ph, 2H), 7.41 (t, Ph, 1H), 5.95 (s, hfac, 2H). ¹⁹F NMR (CDCl₃): –76.79 (s, hfac, 12F).

4.3. Synthesis of [BiPh(hfac)₂(H₂O)] (**1a**)

When reagent-grade hexanes were used for the reaction described above, yellow crystals of **1a** were obtained in 52% yield. The water in the composition of complex **1a** almost certainly arises from traces of water in the solvent. Anal. Calc. for C₁₆H₉F₁₂O₅Bi: C, 26.76; H, 1.26. Found: C, 26.83; H, 1.38%. FT-IR (ATR, cm⁻¹): 3340, 3190, 3070, 2970, 1636, 1606, 1557, 1531, 1453, 1435, 1340, 1249, 1199, 1141, 1086, 1055, 1015, 997, 914, 803, 733, 722, 690, 663, 581. ¹H NMR (CDCl₃): 8.25 (d, Ph, 2H), 8.06 (t, Ph, 2H), 7.40 (t, Ph, 1H), 5.95 (s, hfac+H₂O, 4H). ¹⁹F NMR (CDCl₃): –76.79 (s, hfac, 12F).

4.4. Synthesis of [BiPh(hfac)₂(Me₂CO)] (**1b**)

To the hexanes solution of **1** obtained as described above, 200 μ L dry Me₂CO was added via a Hamilton syringe. Yellow crystals formed in 58% yield. Anal. Calc. for C₂₀H₁₅F₁₂O₅Bi: C, 30.10; H, 1.73. Found: C, 30.60; H, 1.80%. FT-IR (ATR, cm⁻¹): 3180, 3070, 1638, 1553, 1526, 1456, 1433, 1380, 1251, 1192, 1137, 1118, 1090, 1055, 1016, 996, 843, 792, 735, 693, 678, 662, 579. ¹H NMR (CDCl₃): 8.24 (d, Ph, 2H), 8.07 (t, Ph, 2H), 7.42 (t, Ph, 1H), 5.97 (s, hfac), 2.19 (s, Me₂CO, 6H). ¹⁹F NMR (CDCl₃): –76.83 (s, hfac, 12F).

4.5. Synthesis of [BiPh(hfac)₂(THF)] (**1c**)

The yellow solution obtained by reaction of BiPh₃ and Hhfac in hexanes was treated with 200 μ L dry THF. Yellow crystals formed in 71% yield. Anal. Calc. for C₂₀H₁₅F₁₂O₅Bi: C, 31.10; H, 1.96. Found: C, 30.95; H, 2.03%. FT-IR (ATR, cm⁻¹): 3190, 3060, 2980, 1640, 1602, 1554, 1525, 1455, 1358, 1251, 1196, 1137, 1093, 1054, 1023, 997, 917, 862, 809, 795, 768, 733, 694, 661, 581. ¹H NMR (CDCl₃): 8.31 (d, Ph, 2H), 8.03 (t, Ph, 2H), 7.42 (t, Ph, 1H), 5.95 (s, hfac, 2H), 3.98 (m, THF, 4H), 1.96 (m, THF, 4H). ¹⁹F NMR (CDCl₃): –76.92 (s, hfac, 12F).

4.6. Synthesis of [BiPh(hfac)₂(DMA)] (**1d**)

The hexanes solution of **1** resulting from the reaction of BiPh₃ and Hhfac was treated with 200 μ L DMA via a Hamilton syringe. Yellow crystals formed in 67% yield. Anal. Calc. for C₂₀H₁₆F₁₂NO₅Bi: C, 31.51; H, 2.05. Found: C, 30.62; H, 1.98%. FT-IR (ATR, cm⁻¹): 3140, 3055, 2995, 1637, 1594, 1554, 1527, 1469, 1433, 1422, 1406, 1336, 1252, 1196, 1134, 1090, 1054, 1028, 996, 969, 795, 770, 751, 734, 693, 662, 614, 580. ¹H NMR (CDCl₃): 8.45 (d, Ph, 2H), 7.97 (t, Ph, 2H), 7.52 (t, Ph, 1H), 5.87 (s, hfac, 2H), 3.09 (s, DMA, 6H), 2.22 (s, DMA, 3H). ¹⁹F NMR (CDCl₃): –76.96 (s, hfac, 12F).

4.7. Synthesis of [BiPh(hfac)₂(DMSO)] (**1e**)

To the hexanes solution obtained by reaction of BiPh₃ and Hhfac as described above, 200 μ L DMSO was added via a Hamilton syringe. Yellow crystals formed in 85% yield. Anal. Calc. for C₁₈H₁₃F₁₂SO₅Bi: C, 27.78; H, 1.68. Found: C, 28.33; H, 1.76%. FT-IR (ATR, cm⁻¹): 3190, 3070, 1637, 1554, 1528, 1447, 1337, 1253, 1198, 1135, 1086, 1056, 1022, 997, 926, 799, 764, 741, 726, 689, 662, 579. ¹H NMR (CDCl₃): 8.25 (d, Ph, 2H), 8.05 (t, Ph, 2H), 7.42 (t, Ph, 1H), 5.91 (s, hfac, 2H), 2.71 (s, DMSO, 6H). ¹⁹F NMR (CDCl₃): –76.85 (s, hfac, 12F).

4.8. [BiPh(hfac)₂(PhCN)] (**1f**)

The hexanes solution resulting from the reaction of BiPh₃ and Hhfac was reacted with 0.103 g PhCN suspended in hexanes that was added upon vigorous stirring. Orange crystals formed in 73% yield from the filtrate. Anal. Calc. for C₂₃H₁₂F₁₂NO₄Bi: C, 34.39; H, 1.51. Found: C, 34.07; H, 1.62%. FT-IR (ATR, cm⁻¹): 3185, 3060, 2234, 1636, 1603, 1554, 1528, 1448, 1338, 1253, 1196, 1138, 1088, 1053, 997, 943, 801, 758, 741, 735, 693, 685, 662, 580, 555. ¹H NMR (CDCl₃): 8.31 (d, Ph, 2H), 8.05 (t, Ph, 2H), 7.49 (t, Ph, 2H), 7.36–7.74 (m, PhCN, 5H), 5.96 (s, hfac, 2H). ¹⁹F NMR (CDCl₃): –76.83 (s, hfac, 12F).

4.9. Synthesis of [BiPh(hfac)(O₂CCF₃)₂] (**2**)

440 mg (1 mmol) BiPh₃ were dissolved in 10 mL hexanes upon heating. 280 μ L (2 mmol) Hhfac was added within 10 min and the

mixture was refluxed for 30 min to form a yellow solution. The solution was filtered and 200 μL HO_2CCF_3 was added via a Hamilton syringe. Yellow crystals formed in 80% yield. The same compound was isolated in 45% yield from the reaction of $[\text{BiPh}_2(\text{O}_2\text{CCF}_3)]$ (synthesized by a previously described procedure [9]) with 1 equiv. Hhfac. Anal. Calc. for $\text{C}_{13}\text{H}_6\text{F}_3\text{O}_4\text{Bi}$: C, 25.76; H, 1.00. Found: C, 26.05; H, 1.12%. FT-IR (ATR, cm^{-1}): 3140, 1634, 1602, 1562, 1541, 1433, 1257, 1191, 1156, 1143, 1100, 1075, 942, 853, 816, 794, 743, 726, 664, 609, 584, 562. ^1H NMR (CDCl_3): 8.29 (d, Ph, 2H), 8.01 (t, Ph, 2H), 7.41 (t, Ph, 1H), 5.95 (s, hfac, 1H). ^{19}F NMR (CDCl_3): -76.78 (s, hfac, 6F), -77.59 (s, tfa, 3F).

4.10. X-ray structural determinations

Single-crystals of **1a–1f**, **2**, and **3** suitable for X-ray crystallography were taken as small plates or blocks directly from the reaction mixtures. The data for all complexes were collected at 173 K on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a Mo-target X-ray tube with 20 s exposure times. Analysis of the data showed negligible decay during data collection experiments. The frames were integrated with the Bruker SAINT software package and corrected for absorption effects using empirical method (SADABS). The structures were solved using direct methods and refined by full-matrix least-squares on F^2 using the Bruker SHELXL software package. The coordinates of bismuth atoms (and sulfur atom in **1e**) were found in direct method *E* maps. The remaining atoms were located after an alternative series of least-squares difference-Fourier cycles. Hydrogen atoms were included in idealized positions for structure factor calculations. Anisotropic displacement parameters were assigned to all atoms, except the hydrogens and disordered fluorines. The fluorine atoms of the CF_3 groups were found to be disordered over two or three rotational orientations. Relevant X-ray crystallographic data for all compounds are given in Table 1. Selected bond distances and angles are presented in Table 2.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.04.036.

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