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# From Solid State to Solution: Advancing Chemistry of Bi–Bi and Bi–Rh Paddlewheel Carboxylates

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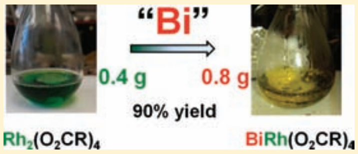
Ⓢ *Supporting Information*



**ABSTRACT:** The first successful high-yield solution synthesis of homobimetallic $Bi_2(O_2CCF_3)_4$ (**1**), as well as heterobimetallic $BiRh(O_2CCF_3)_4$ (**2**) and $BiRh(O_2CCF_2CF_3)_4$ (**3**), complexes is reported. It is based on one-pot reduction reactions starting from Bi(III) and Rh(II) carboxylates and using Bi metal as a reducing agent. The presence of small amounts of diphenyl ether was found to facilitate this reaction, most probably because of its good solubilizing and $\pi$-stabilizing abilities. The latter is illustrated by the isolation and structural characterization of a $\pi$-adduct of **1** with diphenyl ether, $[Bi_2(O_2CCF_3)_4 \cdot 1/2Ph_2O]$. Importantly, the new approach expands to solution the chemistry of Bi(II) that was previously limited to the solid state only. The solution procedure developed for the preparation of heterometallic $BiRh(O_2CCF_3)_4$ is now one step shorter and gives the product in excellent yield compared with the previously reported method based on sublimation-deposition technique. It is also performed on a greater scale (~10–20 times) and makes further scale-up feasible, if needed. Moreover, it eliminates the isolation of the hard-to-handle unsolvated Bi(II) trifluoroacetate used earlier as a starting material. A new polymorph of $BiRh(O_2CCF_3)_4$ (**2**) was crystallized from solution in this work. The solution approach was also applied to the synthesis of a new heterobimetallic carboxylate with perfluorinated propionate ligands, $BiRh(O_2CCF_2CF_3)_4$ (**3**). All products are fully characterized by spectroscopic and single crystal X-ray diffraction methods. Complexes **2** and **3** exhibit similar solid state structures based on heterobimetallic paddlewheel units forming infinite 1D chains through intermolecular Rh···O interactions.

## ■ INTRODUCTION

The study of dinuclear transition metal paddlewheel complexes[1] has been an active area of research because of broad applications in catalysis,[2] materials chemistry, and supramolecular assembling.[3] It was also found that several divalent main group elements such as Cd,[4] Ba,[5] Sr,[5c] Hg,[6] and Bi[7] exhibit the same paddlewheel type of structure with carboxylates bridges, although only when stabilized by axial $\sigma$- (Cd, Sr, and Ba) or $\pi$-donor (Hg and Bi) ligation. Dibismuth(II,II) tetra(trifluoroacetate) in its unligated form has initially been prepared using a gas-phase comproportionation reaction between Bi(III) trifluoroacetate and bismuth metal.[8] Interestingly, this first "inorganic" salt of Bi in oxidation state +2 has been found to act as a metalloligand in reactions with transition metal complexes to afford heterobimetallic homoleptic carboxylates $BiM(O_2CCF_3)_4$ (M = Ru, Rh).[9] These heterometallic molecules maintain paddlewheel structures with single bismuth–transition metal bonds. They were found to retain heterometallic structure in solution and to exhibit an avid one-end Lewis acidity at the transition metal site only, with the bismuth center showing neither Lewis acidic nor basic properties. Further development of the above synthetic approach led to the isolation of heterometallic (bismuth–rhodium) mixed-ligand compounds, $BiRh(O_2CCF_3)_x(O_2CR)_{4-x}$ ($x$ = 2, 3; R = $CH_3$, $C(CH_3)_3$), including those carrying homochiral carboxylates.[10] These unique heterobimetallic species were shown to exhibit interesting properties and reactivity. For example, a rare instance of a metal-site-controlled arene coordination ($\eta^6$-Bi/$\eta^2$-Rh) was found in the heterobimetallic Bi–Rh complex with pyrene.[11] Moreover, several well-characterized Bi–Rh paddlewheel carboxylates have been tested as catalysts in model reactions of cyclopropanation and C–H insertion with various diazo substrates.[12] Heterobimetallic Bi–Rh molecules were confirmed to exhibit catalytic activity in the transformation of diazo compounds similar to that of homometallic dirhodium counterparts, unambiguously illustrating that only one Rh-end of a paddlewheel unit is required for the above catalytic transformations. This finding has been utilized in the development of recyclable heterogeneous dirhodium catalysts embedded in nanoporous organosilica hosts through axial coordination.[13]

Preparation of heterobimetallic Bi–Rh carboxylates has initially been achieved using our original low-temperature solid state/gas phase technique[9] that is carried out on a microscale level in sealed evacuated ampules.[3b] Notably, this solvent-free method is limited to volatile reagents and products only. Further studies of these unique molecules and their practical applications in catalysis required a more conventional route and larger quantities of the heterobimetallic products. In this work, we successfully extended the solid state/gas phase

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synthetic approach to solution. We targeted the preparation procedure that could preferably be executed in one step, does not require a special handling or glassware construction, uses readily available starting materials, and also allows a sufficient product scale-up.

## ■ RESULTS AND DISCUSSION

The initial gas-phase synthesis of unique heterobimetallic Bi−Rh carboxylate complexes[9] has immediately raised questions regarding their possible preparation using solution methods. Both $Bi_2^{4+}$ and $BiRh^{4+}$ core complexes were proven to retain their dinuclear paddlewheel structures in certain solvents, thus making their solution preparation feasible. Despite the fact that the solvent-free synthesis allowed us to access $BiRh(O_2CCF_3)_4$ and $BiRu(O_2CCF_3)_4$,[9] these reactions are rather capricious. They required very careful handling of the starting $Bi_2(O_2CCF_3)_4$ reagent, as well as the use of pure and totally unsolvated dirhodium(II,II) carboxylates. In addition, these reactions are not readily adaptable for a wide range of bridging carboxylate ligands and cannot be easily scaled up. All these obstacles motivated us to search for solution preparation methods of heterobimetallic carboxylate complexes.

Taking into account the high cost of Rh-containing compounds and the need to use Bi(II) starting materials, we first set to investigate the solution reaction of $Bi(O_2CCF_3)_3$ with metallic Bi as a reducing agent, as it affords the only known bismuth(II) carboxylate, $Bi_2(O_2CCF_3)_4$.[8]

$$4Bi(O_2CCF_3)_3 + 2Bi \rightarrow 3Bi_2(O_2CCF_3)_4 \qquad (1)$$

A color change of the reaction mixture can be used as a good initial indicator of the reaction progress, as a colorless Bi(III) species transforms into a vivid orange Bi(II) carboxylate. Our choice of solvents for developing the solution chemistry of Bi(II) has been limited to aromatic systems only. This is based on the fact that the interaction with $\pi$-donors having suitable orthogonal orbitals (for example, benzene or methylated benzenes) provides an additional stabilization of the $Bi_2^{4+}$ core, whereas any $\sigma$-donor destabilizes it.[11] Indeed, dibismuth(II,II) tetra(trifluoroacetate) quickly decomposes in solvents, such as diethyl ether, tetrahydrofuran, or water, but can be stored in sealed containers as a solution in toluene or xylenes for a long time.[8]

Our first attempts to prepare $Bi_2(O_2CCF_3)_4$ in solutions of toluene or xylenes by a prolonged reflux with an excess of elemental Bi have all failed. Some initial color change is observed when solvents are of the immaculate quality, but the product could not be readily isolated. The lack of experimental variables prevented further progress, until we found that diphenyl ether, despite having an O-atom (and thus being a potential $\sigma$-donor for the $Bi_2^{4+}$ core), could be an excellent solvent for this reaction. Notably, diphenyl ether was successfully used as a solvent medium for the redox reaction of $Mn(hfac)_3$ with Pb.[14]

DFT calculations for the $Bi_2(O_2CCF_3)_4$−$Ph_2O$ system showed that the $Bi_2^{4+}$ core is stabilized by the phenyl groups, while the O-site of diphenyl ether is not involved in coordination (Figure 1). The calculated coordination stabilization energy for aromatic rings of diphenyl ether falls between those of benzene and hexamethylbenzene ligands (7.7 vs 5.2 and 11.5 kcal/mol calculated at the PBE0//LANL2DZ(Bi)/6-311G(d,p) level of theory, respectively).

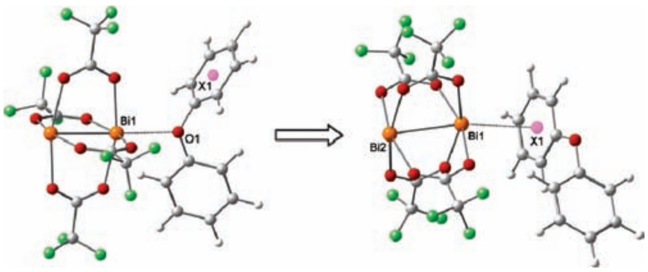

**Figure 1.** DFT (PBE0//LANL2DZ(Bi)/6-31G(d)) optimization: from the starting O-coordinated geometry to the optimized phenyl-site coordination.

In accord with theoretical predictions, the reaction of Bi(III) trifluoroacetate with Bi in diphenyl ether quickly produced a vivid orange color, which is characteristic for the formation of the $Bi_2^{4+}$-core carboxylates. The solution of $Bi_2(O_2CCF_3)_4$ in diphenyl ether is stable at ambient conditions, though it decomposes at highly elevated temperatures (~200 °C), which are still below the boiling point of $Ph_2O$ (bp = 258 °C at 1 atm). Thus, the use of diphenyl ether as a neat solvent can be synthetically challenging because of potential problems of the product thermal decomposition upon a prolonged evaporation of $Ph_2O$. Further experiments showed that diphenyl ether can be largely diluted with toluene up to ~1:200, and this would suffice for reaction to proceed, however the ratio of ~1:50 generally provides more consistent results. The replacement of oxygen in diphenyl ether by nitrogen or carbon leads to an initial color change of the reaction mixture; however, the reaction does not progress further, and the products could not be isolated. We have also attempted to replace Ph−O−Ph with Ph−O−$CF_3$ having a much lower boiling point (102 °C at 1 atm) with no success. Notably, the presence of $Ph_2O$, although not technically required for the reaction 1 to proceed, still plays a crucial facilitating role. Good solubilizing properties of $Ph_2O$ should be important as starting $Bi(O_2CCF_3)_3$ is soluble in $Ph_2O$ at ~80−90 °C, while it is not soluble in toluene or hexamethylbenzene/toluene solutions at these conditions. Diphenyl ether is also relatively viscous, thus allowing Bi metal particles to be more evenly distributed in solution, speeding up the overall reduction reaction. In contrast, Bi metal particles in toluene tend to stick to the flask walls leading to their partial deactivation. Finally, diphenyl ether also stabilizes the final product.

$Bi_2(O_2CCF_3)_4$ (**1**) was found to crystallize from the reaction mixture as a $\pi$-adduct with diphenyl ether, (**1**·1/2$Ph_2O$) (Figure 2), confirming the results of DFT prediction. The Bi−Bi bond length in the adduct is slightly elongated to 2.9606(3) from 2.9462(3) Å in its unsolvated form.[8] This elongation (~0.015 Å) is the same as in the complex of $Bi_2(O_2CCF_3)_4$ with *para*-xylene,[8] thus showing a similar strength of $\pi$-interactions. Relatively small changes of the Bi−Bi bond length imply that interactions of the bismuth(II) center with aromatic systems are relatively weak and do not disturb the dimetal unit. Nevertheless, it is known that adducts of $Bi_2(O_2CCF_3)_4$ with methylated benzenes are much less vulnerable to open atmosphere, with the hexamethylbenzene adduct being stable in air for days.[8]

Having the solution reduction procedure of Bi(III) to Bi(II) developed, we moved to investigate the formation of the heterobimetallic Bi−Rh trifluoroacetate according to the following steps:

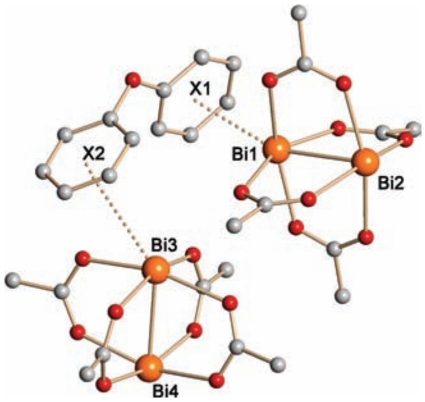

**Figure 2.** Fragment of the crystal structure of $[Bi_2(O_2CCF_3)_4 \cdot 1/2Ph_2O]$ (**1**·1/2Ph₂O). Fluorine and hydrogen atoms are omitted for clarity. Bi1−Bi2 = 2.9606(3) Å, Bi3−Bi4 = 2.9611(3) Å, Bi1−X1 = 3.311(5) Å, Bi3−X2 = 3.859(5) Å, Bi2−Bi1−X1 = 159.0(2)°, Bi4−Bi3−X2 = 146.9(2)°.

$$4Bi(O_2CCF_3)_3 + 2Bi \rightarrow 3Bi_2(O_2CCF_3)_4 \quad (2)$$

$$Bi_2(O_2CCF_3)_4 + Rh_2(O_2CCF_3)_4 \rightarrow 2BiRh(O_2CCF_3)_4 \quad (3)$$

A solution of $Bi_2(O_2CCF_3)_4$ in toluene/$Ph_2O$ prepared in situ by reduction of $Bi(O_2CCF_3)_3$ with metallic bismuth was filtered into solution of $Rh_2(O_2CCF_3)_4$ in toluene. Reflux for a week showed no signs of reaction. We have also attempted to use $Bi_2(O_2CCF_3)_4$ prepared by a previously published gas-phase method to react with $Rh_2(O_2CCF_3)_4$ in a variety of different solvent systems such as toluene, toluene/$Ph_2O$, $CCl_4$, or $CCl_4$/$Ph_2O$. No reaction occurred in all these cases. In contrast to the gas-phase, preformed $Bi_2(O_2CCF_3)_4$ does not react with $Rh_2(O_2CCF_3)_4$ in solution. Ultimately, after multiple attempts we have found and optimized conditions to perform this reaction in solution. It is important to carry out the reduction of Bi(III) to Bi(II) in the presence of a dirhodium carboxylate complex (one-pot synthesis). The final optimized procedure (eq 4) is thus one step shorter compared to the previously reported gas-phase method. Importantly, it avoids the isolation of the hard-to-handle Bi(II) carboxylate.

$$4Bi(O_2CCF_3)_3 + 3Rh_2(O_2CCF_3)_4 + 2Bi \rightarrow 6BiRh_2(O_2CCF_3)_4 \quad (4)$$

The $BiRh(O_2CCF_3)_4$ product (**2**) was isolated in excellent yield (90%) on a 0.4 g scale. The reaction mixture changes from green (color of $Rh_2(O_2CCF_3)_4$) through cloudy brown to transparent yellow (color of $BiRh(O_2CCF_3)_4$) over the course of 48 h (Supporting Information, Figure S1). This process can be conveniently monitored by $^{19}F$ NMR spectroscopy, as the fluorine signal of $BiRh(O_2CCF_3)_4$ (∼−73 ppm) is well-separated from that of $Rh_2(O_2CCF_3)_4$ (∼−75 ppm) (Supporting Information Figure S2). For comparison, the yields in the solvent-free synthesis of $BiRh(O_2CCF_3)_4$ never exceeded 55% for the reaction performed on a much-smaller scale.[9]

Quite unexpectedly, $BiRh(O_2CCF_3)_4$ has crystallized in its unsolvated form from the solution reaction mixture. Neither toluene nor $Ph_2O$ were found to coordinate to open Rh or Bi ends of a bimetallic complex. Interestingly, while $Ph_2O$ shows high affinity toward $Bi_2(O_2CCF_3)_4$, the dirhodium complex $Rh_2(O_2CCF_3)_4$ avoids any axial ligation by diphenyl ether. It rather forms an adduct with toluene[15] from the toluene/$Ph_2O$ solvent system, even when the ratio of toluene to diphenyl ether is increased to 1:1. The X-ray diffraction analysis revealed the formation of a new polymorph of $BiRh(O_2CCF_3)_4$ isolated from solution. The latter crystallizes in the noncentrosymmetric $Pna2_1$ space group (Figure 3), while the previously reported polymorph[9] conforms to the centrosymmetric *Pbca* space group.

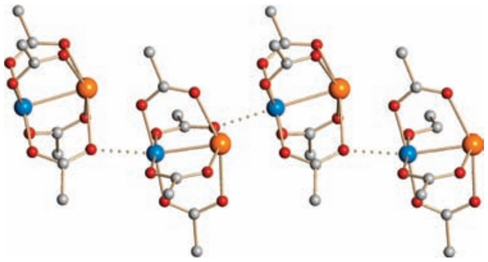

**Figure 3.** Fragment of a one-dimensional polymeric structure of $[BiRh(O_2CCF_3)_4]_\infty$. Fluorine atoms are omitted for clarity. Rh−Bi = 2.5571(6) Å, $Rh-O_{eq.av.}$ = 2.025(5) Å, $Bi-O_{eq.av.}$ = 2.412(5) Å, $Rh-O_{axial}$ = 2.534(5) Å, $O_{eq.}-Rh-O_{eq.(av.)}$ = 175.4(2)°, $O_{eq.}-Bi-O_{eq.(av.)}$ = 156.7(2)°, $Bi-Rh-O_{axial}$ = 168.2(2)°.

In the solid state, the heterobimetallic $BiRh(O_2CCF_3)_4$ molecules form an extended chain structure through axial coordination of the transition metal center to one of the Bi-bound carboxylate oxygen atoms from the neighboring unit (Figure 3). Similar 1D arrangement was also observed upon crystallization of $BiRh(O_2CCF_3)_4$ from the gas phase.[9] The difference between the two polymorphs shows up in packing of the extended 1D chains in the crystal (Supporting Information, Figure S3). It can be noted that packing of the heterobimetallic molecules into 1D polymeric chains seems more loose for the polymorph grown from solution at room temperature, as the Bi−Rh and $Rh-O_{axial}$ bond lengths are all longer than those in the polymorph crystallized from the gas phase at elevated temperature (2.5571(6) Å vs 2.5493(3) Å and 2.534(5) vs 2.413(3) Å, respectively).

It is important to describe the Bi(III) starting material used in the above reaction in more details. In general, $Bi(O_2CCF_3)_3$ is conveniently obtained by reacting $Bi_2O_3$ with a mixture of $CF_3CO_2H$ and $(CF_3CO)_2O$.[16] To make a greater variety of Bi(III) carboxylates the acidolysis of commercially available $BiPh_3$ is more synthetically viable.[17] Surprisingly, when $Bi(O_2CCF_3)_3$ obtained by the latter reaction was used as a starting material, no reaction (eq 4) was observed. Puzzled by this behavior, we then noted that the previously reported crystal structure of $Bi(O_2CCF_3)_3$ obtained from bismuth(III) oxide is an adduct with trifluoroacetic acid.[15] Single crystal X-ray diffraction analysis of $Bi(O_2CCF_3)_3$ obtained from $BiPh_3$ confirmed that the product crystallizes in the unsolvated form (Supporting Information Figures S4−S5 and Table S1). We then repeated the reduction reaction starting from $Bi(O_2CCF_3)_3$ obtained from $BiPh_3$ but in the presence of ∼1 equiv of trifluoroacetic acid, and the reaction proceeded in good yield, as previously observed. Therefore, the equations for both reduction processes should be rewritten in the modified forms (eq 5 and 6):

$$\mathrm{Bi(O_2CCF_3)_3 + Bi + HO_2CCF_3 \rightarrow Bi_2(O_2CCF_3)_4 + 1/2H_2} \quad (5)$$

$$\mathrm{Bi(O_2CCF_3)_3 + Rh_2(O_2CCF_3)_4 + Bi + HO_2CCF_3 \rightarrow 2BiRh(O_2CCF_3)_4 + 1/2H_2} \quad (6)$$

Trifluoroacetic acid in the above reaction is not a catalyst as it is being consumed over the course of reduction, as seen by the decrease of its $^{19}$F NMR peak intensity. An excess of acid is not favorable as it destroys the heterobimetallic complex, thus reducing the product yield.

Aiming at even more general and convenient preparation procedure to access heterobimetallic Bi−Rh carboxylates, we looked into the possibility to use only commercially available reagents. We found that $\mathrm{Bi(O_2CCF_3)_3}$ can be fully eliminated from the reaction (eq 7).

$$\mathrm{Rh_2(O_2CCF_3)_4 + 2Bi + 4HO_2CCF_3 \rightarrow 2BiRh(O_2CCF_3)_4 + 2H_2} \quad (7)$$

The use of $\mathrm{Ph_2O}$ in the above reaction is advantageous though not imperative. $^{19}$F NMR studies indicate that the reaction rate in $\mathrm{Ph_2O}$/toluene (1:40) is approximately two times faster than that in neat toluene (Supporting Information Figure S6). Unfortunately, the product yields are noticeably lower (~50%) and generally less consistent from run to run. Also, the reaction takes longer time (up to 4 days) to complete and is very sensitive to the amount of acid added. Larger quantities of trifluoroacetic acid and longer reflux time required for this reaction might be the reasons that cause low product yields. As the importance of an acid for the reduction reaction (eq 6) is now well established, we can suggest that diphenyl ether may also work as a proton transfer facilitator. In neat toluene, this might be a more constrained process. Also, $\mathrm{Ph_2O}$ stabilizes the product and, to some extent, may shield it from the destructive attack of the acid. Speculating about the role of $\mathrm{H^+}$ in the above process, one can note that the formation of heterobimetallic Bi−Rh core requires to cleave the carboxylate bridges from $\mathrm{Rh_2(O_2CCF_3)_4}$ as to yield some reactive monomeric rhodium species. The latter process can be facilitated by protonation of carboxylate ligands. It is worth mentioning here that the formation of $\mathrm{Bi_2(O_2CCF_3)_4}$ is completed in ~2 h. This is noticeably faster than the formation of a mixed Bi−Rh core. Thus, it can be speculated that the cleavage of the tetrabridged dirhodium core might be a rate-limiting step for the formation of $\mathrm{BiRh(O_2CCF_3)_4}$.

For the next step, we have expanded the experimental conditions developed for the high-yield synthesis of $\mathrm{BiRh(O_2CCF_3)_4}$ to another carboxylate. We have prepared a new Bi−Rh complex having a longer perfluorinated alkyl chain, $\mathrm{BiRh(O_2CCF_2CF_3)_4}$ (**3**). The gas-phase reaction tested in this work for comparison affords this complex in abysmal yield (~5%) over a long reaction time (3 weeks). In contrast, the solution method results in significantly better yields at much shorter reaction times (67%, 2 days). The formation of the target product **3** was proved by the similarity of its UV−vis and IR spectra with those of analogous $\mathrm{BiRh(O_2CCF_3)_4}$. The purity of the bulk product **3** was confirmed by elemental analysis and X-ray powder diffraction. Notably, the observed X-ray powder diffraction spectrum for the microcrystalline sample of **3** is well correlated with the simulated X-ray powder pattern based on the single crystal diffraction data (Supporting Information Figure S7).

The single crystal X-ray diffraction analysis of **3** revealed the formation of the Bi−Rh core with the metal−metal distance of 2.5651(5) Å (Figure 4a). This Bi−Rh bond length is significantly longer compared to those in both $\mathrm{BiRh(O_2CCF_3)_4}$ polymorphs. In the solid state, the formation of 1D polymeric chains is observed (Figure 4b), similarly to $\mathrm{[BiRh(O_2CCF_3)_4]_\infty}$. The $\mathrm{Rh{-}O_{axial}}$ bonding contact in **3** is shorter (2.458(3) Å) than that in **2** (2.534(5) Å), while being longer than in the polymorph crystallized from the gas-phase (2.413(3) Å).

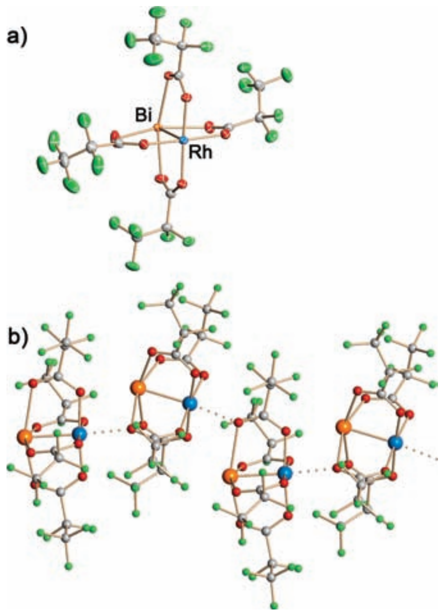

**Figure 4.** (a) ORTEP drawing of **3** with displacement ellipsoids shown at the 50% probability level. (b) A fragment of a one-dimensional polymeric structure of $\mathrm{[BiRh(O_2CCF_2CF_3)_4]_\infty}$. Rh−Bi = 2.5651(5) Å, $\mathrm{Rh{-}O_{eq.av.}}$ = 2.032(3) Å, $\mathrm{Bi{-}O_{eq.av.}}$ = 2.4293(5) Å, $\mathrm{Rh{-}O_{axial}}$ = 2.458(3) Å, $\mathrm{O_{eq.}{-}Rh{-}O_{eq.(av.)}}$ = 174.5(1)°, $\mathrm{O_{eq.}{-}Bi{-}O_{eq.(av.)}}$ = 158.7(1)°, $\mathrm{Bi{-}Rh{-}O_{axial}}$ = 174.9(1)°.

In conclusion, we have developed the first high-yield solution preparation method to access the homometallic dibismuth(II,II) and heterobimetallic Bi−Rh carboxylates starting from readily available Bi(III) and Rh(II) carboxylates and using metallic bismuth as a reducing agent. This should significantly expand the Bi(II) chemistry previously limited to the solid state only. Notably, the solution approach for the heterobimetallic Bi−Rh carboxylates is one step shorter than the previously reported method based on sublimation-deposition procedure, eliminating the isolation of the hard-to-handle Bi(II) trifluoroacetate. This reaction can now be performed on a gram scale and further scale-up is feasible. Importantly, the developed synthetic scheme can be applied to carboxylates that are nonvolatile and thus cannot be used in the gas-phase approach. These findings should facilitate the expansion of chemistry and practical applications of rare bismuth(II)-transition metal systems.

Table 1. Crystallographic Data for $[Bi_2(O_2CCF_3)_4{\cdot}1/2Ph_2O]$ ($1{\cdot}1/2Ph_2O$), $[BiRh(O_2CCF_3)_4]_\infty$ (2), and $[BiRh(O_2CCF_2CF_3)_4]_\infty$ (3)

| | $1{\cdot}1/2Ph_2O$ | 2 | 3 |
|---|---|---|---|
| empirical formula | $C_{28}H_{10}Bi_4F_{24}O_{17}$ | $BiRhC_8F_{12}O_8$ | $BiRhC_{12}F_{20}O_8$ |
| formula weight | 1910.28 | 763.97 | 964.01 |
| $T$ (K) | 173(2) | 173(2) | 100(2) |
| crystal system | monoclinic | orthorhombic | monoclinic |
| space group | $Cc$ | $Pna2_1$ | $P2_1/c$ |
| $a$ (Å) | 11.5233(4) | 9.7707(5) | 20.118(3) |
| $b$ (Å) | 22.6418(9) | 12.3992(7) | 11.5453(17) |
| $c$ (Å) | 17.2846(7) | 13.0323(7) | 9.8458(14) |
| $\alpha$ (deg) | 90 | 90 | 90 |
| $\beta$ (deg) | 91.8650(10) | 90 | 96.576(2) |
| $\gamma$ (deg) | 90 | 90 | 90 |
| $V$ (Å$^3$) | 4507.3(3) | 1578.85(15) | 2271.8(6) |
| $Z$ | 4 | 4 | 4 |
| R1[a], wR2[b] [$I > 2\sigma(I)$] | 0.0243, 0.0489 | 0.0264, 0.0561 | 0.0292, 0.0703 |
| R1[a], wR2[b] (all data) | 0.0276, 0.0502 | 0.0309, 0.0567 | 0.0355, 0.0743 |
| quality-of-fit[c] | 1.014 | 1.022 | 1.023 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] Quality-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

## EXPERIMENTAL SECTION

**General Procedures.** All of the manipulations were carried out in a dry, oxygen-free, dinitrogen atmosphere by employing standard glovebox and Schlenk techniques. All chemicals, unless otherwise described, were purchased from Aldrich and used as received. Bi metal was purchased from Strem Chemicals. Diphenyl ether and toluene were freshly distilled prior to use. Rh(II) carboxylates were synthesized using the published procedure for dirhodium(II) tetra-(trifluoroacetate).[18] Bi(III) trifluoroacetate was prepared by either a reaction of $Bi_2O_3$ and trifluoroacetic acid[16] or an acidolysis of triphenyl bismuth.[17a] The attenuated total reflection infrared (ATR-IR) spectra of bulk solids or crushed crystals were recorded on a Perkin-Elmer Spectrum 100 spectrometer. $^{19}F$ NMR spectra were obtained using a Bruker Avance 400 spectrometer at 376.47 MHz. Chemical shifts ($\delta$) are reported in ppm relative to $CFCl_3$ for $^{19}F$. Elemental analyses were performed by Complete Analysis Laboratories, Inc., New Jersey, U.S.A..

**Synthesis of $Bi_2(O_2CCF_3)_4{\cdot}1/2Ph_2O$ ($1{\cdot}1/2Ph_2O$).** $Bi(O_2CCF_3)_3$ (0.4 g, 0.73 mmol) and Bi metal (0.8 g, 3.84 mmol) were loaded into a 50 mL Schlenk flask in a drybox. A mixture of 20 mL of toluene, 0.5 mL of diphenyl ether, and 0.05 mL of trifluoroacetic acid was added to the flask. The suspension was refluxed for 2 h with vigorous stirring affording a yellow solution. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was evaporated to a minimal volume of ~0.5 mL. The crystals of $Bi_2(O_2CCF_3)_4{\cdot}1/2Ph_2O$ were formed upon standing at room temperature for several hours. Yield: 0.60 g, 86%. $^{19}F$ NMR ($C_6D_6$): $\delta = -75.4$ (s). IR (cm$^{-1}$): $\nu$ = 1624s, 1489 m, 1444 m, 1218s, 1147s, 862 m, 846 m, 791s, 760w, 723s, 696 m, 605w. UV–vis (toluene/$Ph_2O$ 70:1): $\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$·cm$^{-1}$): 424 (782). All spectroscopic characteristics of **1** match the previously reported data.[8]

**Synthesis of $BiRh(O_2CCF_3)_4$ (2).** $Bi(O_2CCF_3)_3$ (0.4 g, 0.73 mmol), $Rh_2(O_2CCF_3)_4$ (0.4 g, 0.61 mmol), and Bi metal (0.8 g, 3.84 mmol) were loaded into a 50 mL Schlenk flask in a drybox. A mixture of 20 mL of toluene, 0.5 mL of diphenyl ether, and 0.05 mL of trifluoroacetic acid was added to the flask, and the suspension was refluxed for 2 days with vigorous stirring. The reaction is accompanied by a color change from green to yellow. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was evaporated to ~3–4 mL of its initial volume. The crystals of $BiRh(O_2CCF_3)_4$ were formed upon standing at room temperature for 2 h. Yield: 0.84 g, 90.3%. $^{19}F$ NMR ($C_6D_6$): $\delta = -73.4$ (s). IR (cm$^{-1}$): $\nu$ = 1631s, 1489s, 1445 m, 1180sh, 1145s, 858 m, 789 m, 748w, 725s, 693 m, 604w. UV–vis ($CHCl_3$) $\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$·cm$^{-1}$): 298 (2427), 360br (750). Anal. Calcd for $BiRhC_8F_{12}O_8$: C, 12.57%; H, 0.00%. Found: C, 12.29%; H, 0.21%. All spectroscopic characteristics of **2** match the previously reported data.[9]

**Synthesis of $Bi(O_2CCF_2CF_3)_3$.** $C_2F_5CO_2H$ (0.559 g, 3.41 mmol) in 1.0 mL of toluene was added slowly to a solution of $BiPh_3$ (0.500 g, 1.14 mmol) in 5.0 mL of toluene over 5 min. This leads to the exothermic reaction and the formation of a white precipitate. The reaction mixture was then refluxed for 20 min, and the resulting clear solution was evaporated to a 1/2 volume. The solution was kept at −5 °C leading to crystallization of the product. The white powder was filtered off, washed with 1.0 mL of cold toluene, and dried in vacuo overnight. Yield: 0.68 g, 86%. $^{19}F$ NMR ($C_6D_6$): −83.3 (s, $-CF_3$), −121.0 (s, $-CF_2$). IR (cm$^{-1}$): 1673 m, 1628 m, 1422w, 1324 m, 1212 m, 1190 m, 1151s, 1030s, 840 m, 755 m, 730s, 694w.

**Synthesis of $BiRh(O_2CCF_2CF_3)_4$ (3).** $Bi(O_2CCF_2CF_3)_3$ (0.1 g, 0.14 mmol), $Rh_2(O_2CCF_2CF_3)_4$ (0.1 g, 0.12 mmol), and Bi metal (0.8 g, 3.84 mmol) were loaded into a 50 mL Schlenk flask in a drybox. A mixture of 20 mL of toluene, 0.5 mL of diphenyl ether, and 0.02 mL of pentafluoropropionic acid was added to the flask. The suspension was refluxed for 2 days with vigorous stirring accompanied by a color change from green to yellow. After cooling to room temperature, the reaction mixture was filtered to afford a yellow solution. Diphenyl ether was then distilled off in vacuo by directly connecting the receiving container to the reaction flask via a short V-shaped connector. The flask with the yellow solution was immersed into a sand or oil bath and kept at 70 °C. The obtained yellow solid was then further dried in vacuo for 3 days at 50 °C. Complex **3** is thermally unstable and overheating should be avoided. Yield: 155 mg, 67%. $^{19}F$ NMR ($C_6D_6$): −83.2 (s, $-CF_3$), −121.3 (s, $-CF_2$). IR (cm$^{-1}$): 1689s, 1642s, 1408 m, 1324 m, 1209 m, 1155s, 1095w, 1027s, 817 m, 786w, 730 m. UV–vis ($CHCl_3$) $\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$·cm$^{-1}$): 301 (2557), 359br (834). Anal. Calcd for $BiRhC_{12}F_{20}O_8$: C, 14.95%; H, 0.00%. Found: C, 15.06%; H, 0.18%. The X-ray powder diffraction spectrum of the bulk solid is consistent with the calculated pattern based on the single crystal data for $BiRh(O_2CCF_2CF_3)_4$ (**3**) (Supporting Information, Figure S8).

To obtain single crystalline material, 20 mg of the bulk solid were sealed in a small glass ampule and placed in an electric furnace having a small temperature gradient (~5 °C) along the length of the tube. After keeping this tube at 100 °C for 2 days, the yield of crystals is 16 mg, 80%. Needle-like yellow crystals suitable for X-ray characterization have been slowly grown by the same procedure at 90 °C within one week.

**Computational Details.** Full geometry optimizations were performed at the density functional theory level using the hybrid Perdew–Burke–Ernzerhof parameter-free exchange-correlation functional (PBE0).[19] Hay and Wadt effective core potential (ECP) and the LANL2DZ basis set were placed on Bi atoms,[20] while the 6-31G(d) basis sets were used for all other atoms. The true minima on potential energy surfaces were controlled by calculating the Hessian matrix and, as a consequence, harmonic frequencies. The lack of imaginary frequencies has indicated that the true minimum was achieved. See the Supporting Information for the calculated coordinates and the lowest frequencies for all computed complexes (Supporting Information Tables S2–S4). When optimizations were completed, single-point calculations were performed with the same basis sets on Bi and extended 6-311G(d,p) basis sets for all other atoms. All calculations were carried out in the frame of the Firefly program suite.[21] In this work, we were interested in qualitative evaluation of the possible Bi-arene complex formation, and thus the basis set of double-$\zeta$ quality and large pseudopotential were applied for the Bi atoms description. Even this approach still provides a relatively large total number of basis functions (651) for the geometry optimization of $Bi_2(O_2CCF_3)_4$–$Ph_2O$ system. For the quantitative description of the bonding between bismuth and arenes other methods and extended basis sets may be considered due to the importance of dispersion-type interactions. See, for example, Auer et al.[22]

**X-ray Crystallographic Procedures.** The X-ray data sets were collected on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda$ = 0.71073 Å). Data were corrected for absorption effects using the empirical method SADABS.[23] The structures were solved by direct methods and refined using the SHELXL software package.[24] All non-hydrogen atoms were refined anisotropically except the fluorine atoms of $CF_3$ groups in **1** that appeared to be disordered over three rotational orientations. Hydrogen atoms in $Ph_2O$ were included at idealized positions for structure factor calculations. **1**·1/2$Ph_2O$ is solved in the noncentrosymmetric space group *Cc*. The Flack parameter was found to be 0.371 and the final refinement cycles were carried out with TWIN and BASF 0.371 commands leading to improved R values, residual electron density, and standard deviations. Relevant crystallographic data for **1**·1/2$Ph_2O$, **2**, and **3** are summarized in Table 1.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

CIF files providing crystallographic data for compounds **1**·1/2$Ph_2O$, **2**, **3**, and $[Bi(O_2CCF_3)_3]$; X-ray powder pattern for **3**; computed coordinates for $[Bi_2(O_2CCF_3)_4\cdot Ph_2O]$; and all spectroscopic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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