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Tuning the Properties at Heterobimetallic Core: Mixed-Ligand Bismuth−Rhodium Paddlewheel Carboxylates

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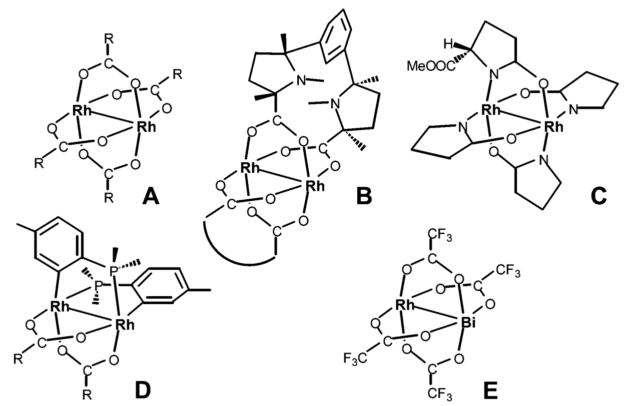
The use of tetrabridged dirhodium(II,II) carboxylates, $Rh_2(O_2CR)_4$ (Chart 1**A**), as catalysts for the reactions of diazo compounds has developed into a powerful tool in synthetic organic chemistry.[1] Dirhodium complexes are known[2] to catalyze a great variety of chemical processes ranging from C−H activation and X−H (X = N, O, Si, S) insertion to cyclopropanation, cyclopropenation, and ylide transformation.

The development of chiral tetrabridged dirhodium(II,II) catalysts has mainly been centered around two major directions. The first includes modification of the bridging carboxylate ligands by introducing various alkyl-, aryl-, and perfluorinated groups, as well as dicarboxylates. The most effective enantioselective versions were found to be chiral *N*-arylsulfonylprolinates (**B**)[3] and phthalimide-protected amino acid derivatives.[4] The second approach involves a partial[5] or full replacement of carboxylates by other bridging monoanionic ligands. High selectivity in the formation of chiral organic molecules has been achieved with carboximidates (**C**)[6] constructed from a broad selection of chiral ligands, such as pyrrolidinones, oxazolidinones, imidazolidinones, and azetidinones. This group also includes C_2 symmetric binaphthoyl phosphates[7] and orthometalated phosphines (**D**).[8]

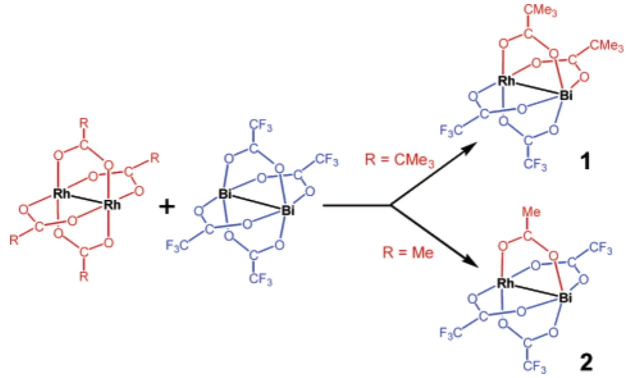
We have recently introduced an additional route for modification of the rigid core dirhodium paddlewheel catalysts: formation of a heterobimetallic unit by replacing one of the rhodium atoms with less expensive metal (**E**). This idea is based on computational[9] and inhibition kinetic studies[10] of the rhodium-catalyzed carbenoid reactions indicating that the active $[Rh_2]$ catalyst uses only one of its two coordination sites at a time for carbene binding. Additional support for our approach comes from the fact that dirhodium catalysts coordinated through one end to polymer-supported pyridine[11] display similar reactivity and selectivity to their homogeneous counterparts.

By utilizing the unique ability of bismuth(II) trifluoroacetate[12] to act as a metalloligand toward transition metal fragments, we suggested a preparative solid-state technique that affords heterobimetallic homoleptic carboxylate $BiRh(O_2CCF_3)_4$.[13] The heterometallic molecule maintains a paddlewheel structure with a single bismuth−rhodium bond and exhibits an avid one-end Lewis acidity at the transition metal site only. Further study of the reactivity of $[Bi_2(O_2CCF_3)_4]$ has led to the development of an effective synthetic route to make heterobimetallic mixed-carboxylate complexes (Scheme 1). Herein we describe the one-step synthesis and characterization of the first two bismuth−rhodium mixed-ligand carboxylates, [*cis*-$BiRh(O_2CCF_3)_2(O_2CBu^t)_2$] (**1**) and [$BiRh(O_2CCF_3)_3(O_2CMe)$] (**2**).

Chart 1



Scheme 1



Compounds **1** and **2** have been obtained from solid-state reactions by heating stoichiometric mixtures of $[Bi_2(O_2CCF_3)_4]$ and unsolvated dirhodium carboxylates $[Rh_2(O_2CR)_4]$ (R = Bu^t (**1**) and Me (**2**)) in sealed ampules at 110−125 °C. The products were deposited in the form of large yellow crystals in the cold zone of the tube where the temperature was set about 5 °C lower. The completion of the reaction takes from 3 to 7 days, and the products may be collected in pure form, free of any impurities. It is important that our synthetic approach allows isolation of a single phase that is the most volatile product condensing in the cold end of the reaction vessel. The characterization of bulk products by NMR and X-ray powder diffraction confirmed the absence of other compounds in each case as well as the absence of the trans-isomeric form of **1**. Only when the reaction temperature was increased above 140 °C did we observe the presence of small amounts of different crystals in the case of pivalate. NMR study indicated that the second product contains [$BiRh(O_2CCF_3)_3(O_2CBu^t)$] (**3**) complex, and X-ray analysis revealed it to be cocrystallized with **1** in the solid-state structure.

Both complexes **1** and **2** are highly volatile and can be quantitatively resublimed at about 90 °C. They show better thermal stability than homoleptic bismuth−rhodium trifluoroacetate, decomposing around 270 °C in a sealed ampule. The mixed-ligand carboxylates display a remarkable air and moisture stability, contrary to both homo- and heterometallic trifluoroacetates. Bismuth−rhodium carboxylates are soluble in most common coordinating and aromatic solvents, with **1** even showing limited solubility in hexanes.

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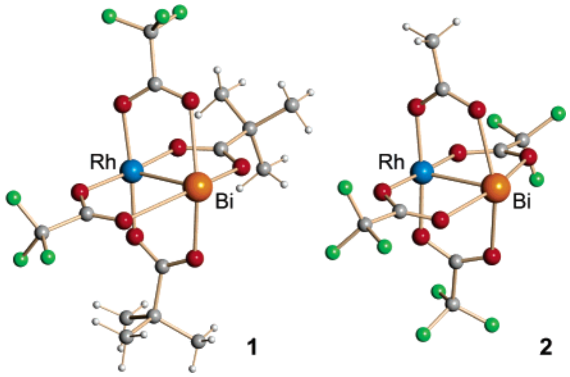

Figure 1. Mixed-ligand heterobimetallic paddlewheel carboxylates [*cis*-$BiRh(O_2CCF_3)_2(O_2CBu^t)_2$] (**1**) and [$BiRh(O_2CCF_3)_3(O_2CMe)$] (**2**).

The crystal structures of **1** and **2** are built of heterobimetallic paddlewheel units (Figure 1). The pivalate groups in **1** have been found to occupy cis-positions of the tetrabridged molecule. Each bismuth atom maintains a distorted square-pyramidal geometry composed of one Rh and four O atoms, while similar coordination around the rhodium atom is more regular. The Bi−Rh distances are 2.5317(2) and 2.5398(3) Å for **1** and **2**, respectively. These are essentially the same as the Bi−Rh distance in homoleptic [$BiRh(O_2CCF_3)_4$] (2.5493(3) Å) that has been shown[13] to correspond to a single metal−metal bond. In the solid state, the heterobimetallic molecules **1** and **2** form infinite chains due to axial coordination of the rhodium center to one of the bismuth-bound carboxylate oxygens from a neighboring unit. While in the structure of **2** this oxygen atom comes from the acetate group, in the structure of **1** it belongs to the electron-withdrawing trifluoroacetate ligand. After modeling an alternative arrangement for an axial coordination, we concluded that it happens for steric reasons.

The dimeric structure of the heterometallic molecules remains intact in solution. That was confirmed by mass spectroscopic studies as well as by comparison of IR spectra of solid and solution samples. In addition, the paddlewheel molecules can be crystallized from coordinating solvents in the form of adducts with Lewis bases. The crystal structure of one such adduct of [$BiRh(O_2CCF_3)_2(O_2CBu^t)_2$] with pivalic acid (**4**) has been determined to reveal that complex **1** indeed acts as a one-end Lewis acid with the donor oxygen atom coordinated to the Rh end of the heterobimetallic unit.

The synthetic method based on interaction of bismuth(II) trifluoroacetate with rhodium(II) carboxylates allows us to effectively modify the structures of dirhodium catalysts. First, it affords one-end Lewis acids in which the second atom of the heterobimetallic unit does not participate in the coordination of basic substrates but can still act as an electron pool and as an anchor for the bridging ligands. Second, it permits us to tune finely the properties of the heterobimetallic molecules, such as thermal stability, moisture and air sensitivity, solubility, and volatility as well as Lewis acidity and steric hindrance about the rhodium axial coordination site. Most importantly, it facilitates the introduction of carboxylate ligands that would bring excellent control of regioselectivity, diastereoselectivity, and enantioselectivity in catalytic reactions. To illustrate the latter, we attempted a designed synthesis of a homochiral heterobimetallic molecule by reaction of bismuth(II) trifluoroacetate with dirhodium(II,II) (*S*)-(+)-2-methylbutyrate. According to NMR data of a bulk sample, the final product of the above reaction was the pure mixed-ligand complex, [$BiRh(O_2CCF_3)_3(O_2CBu^i)$] (**5**), harvesting only one chiral carboxylate ligand (Figure 2).

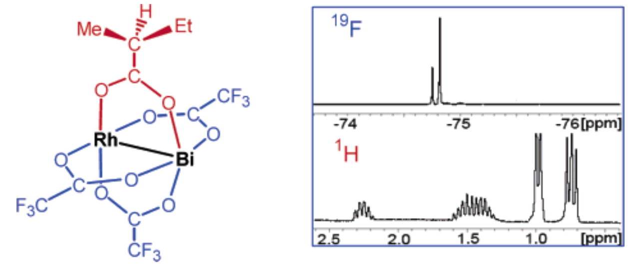

Figure 2. Homochiral heterobimetallic molecule [$BiRh(O_2CCF_3)_3((S)-(+)-O_2CBu^i)$] (**5**). The ^1H and ^{19}F NMR spectra are inset.

Herein we have described a general pathway leading to a new family of heterobimetallic (bismuth−rhodium) mixed-ligand carboxylates. All these molecules feature a paddlewheel structure that is retained in solution as well as upon coordination by donor groups. The molecules are avid one-end Lewis acids with only the transition metal end participating in the coordination of substrates bearing basic functionalities. Our preliminary results indicate that heterobimetallic molecules exhibit catalytic activity in the transformations of diazo compounds similar to that of homometallic dirhodium complexes. This investigation is underway and will be reported shortly.

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Supporting Information Available: Preparative details, analytical and spectroscopic data for **1**−**5**, and X-ray structural data for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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