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Expanding the Family of Heterobimetallic Bi–Rh Paddlewheel Carboxylate Complexes via Equatorial Carboxylate Exchange

Travis L. Sunderland and John F. Berry*

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706, United States

Email: berry@chem.wisc.edu
Abstract

Five novel homoleptic heterobimetallic bismuth(II)-rhodium(II) carboxylate complexes—$\text{BiRh(TPA)}_4$ (1), $\text{BiRh(but)}_4$ (2), $\text{BiRh(piv)}_4$ (3), $\text{BiRh(esp)}_2$ (4), and $\text{BiRh(OAc)}_4$ (5) — were synthesized in good yields by equatorial ligand substitution starting from $\text{BiRh(TFA)}_4$ (TPA = triphenylacetate, but = butyrate, piv = pivalate, esp = α,α,α',α'-tetramethyl-1,3-benzenedipropionate, OAc = acetate, and TFA = trifluoroacetate). We report here $^1$H and $^{13}$C{$_^1$H} NMR spectra and cyclic voltammograms for complexes 1-4, and IR spectra for all complexes. Irreversible redox waves appear between −1.4 to −1.5 V for [BiRh]$^{3+/4+}$ couples and 1.3 to 1.5 V vs Fc/Fc$^+$ for [BiRh]$^{4+/5+}$ couples for complexes 1-4 indicating a wide range of stability for the compounds. The X-ray crystal structure of 1 reveals a Bi–Rh distance of 2.53 Å.

Introduction

Dinuclear transition metal paddlewheel complexes$^{1,2}$ have been of considerable interest in a wide variety of applications including catalysis.$^{3-5}$ Dirhodium tetracarboxylate complexes have been intensely studied for their ability to promote reactions resulting in the functionalization of C–H bonds,$^6$ specifically metal nitrenoid$^7$ and carbenoid$^{8-10}$ transfer chemistry. Catalyst design has driven many of the major
advances in this field, and is a contributing factor why more than 1500 Rh$_2$ complexes have been synthesized.$^6$ Of these, tetracarboxylate compounds are well-represented and are readily accessible through a variety of synthetic routes.$^1$

In 2005, Dikarev and coworkers reported the first example of a heterobimetallic homoleptic Bi–Rh tetracarboxylate paddlewheel complex with the solid state synthesis of BiRh(O$_2$CCF$_3$)$_4$.$^{11}$ Further exploration of this solid state technique has afforded three other examples of heteroleptic heterobimetallic carboxylate complexes.$^{12}$ Recently, a synthetic route to heterobimetallic Bi–Rh complexes was adapted to solution phase chemistry using perfluorinated carboxylates (O$_2$CCF$_3$ and O$_2$CCF$_2$CF$_3$).$^{13}$ These Bi–Rh compounds are interesting because they are the first examples of a heterobimetallic M–M bonded core containing Rh and their design was driven by the need to replace expensive and rare precious metals with cheap and earth abundant alternatives while maintaining their functionality. Three of these Bi–Rh complexes have been tested for their ability to perform metal carbenoid transformations, a hallmark of the analogous Rh$_2$ complexes.$^{14}$ The heterobimetallic complexes were successfully able to perform both cyclopropanation and C–H insertion reactions with donor/acceptor diazo compounds with similar or better chemo- and diastereoselectivites to their Rh$_2$ analogues.

Access to novel heterobimetallic Bi–Rh complexes has been limited to the above mentioned solid state methods for volatile compounds or solution phase methods with perfluorinated ligands. Thus, in comparison to the extremely large and versatile family of Rh$_2$ complexes, Bi–Rh chemistry is severely limited and only five examples are known that contain highly electron-withdrawing carboxylate ligands. In this work, we report efficient carboxylate exchange reactions starting from the well characterized
BiRh(O$_2$CCF$_3$)$_4$ that can now be expanded to a wide variety of compounds; synthesis of five new Bi–Rh tetracarboxylate complexes reported here now doubles the number of existing Bi–Rh complexes. This is the first report of performing equatorial ligand exchange reactions on a heterobimetallic M–M bonded core containing Rh. Rapid expansion of the library of heterobimetallic Bi–Rh complexes is now possible and will facilitate further study of their potential uses in catalysis and other important applications.

**Experimental**

**Materials and Methods.**

All reactions were carried out using oven dried glassware under a dry N$_2$ atmosphere using Schlenk techniques and glovebox methods. Toluene was purified using a Vacuum Atmospheres solvent purification system. BiRh(TFA)$_4$ and H$_2$esp were prepared according to literature procedures. Dichloromethane (DCM), diethyl ether (Et$_2$O), ethyl acetate (EtOAc), hexane, methanol (MeOH), chloroform-d (CDCl$_3$), butyric acid, pivalic acid, triphenylacetic acid, acetic acid, and potassium carbonate (K$_2$CO$_3$) were purchased from Sigma-Aldrich and used without further purification. Flash column chromatography was performed on Silicycle Siliaflash silica gel (40-63 μm, 230-400 mesh). $^1$H NMR spectra were recorded on a Bruker Avance-500 MHz spectrometer. $^{13}$C NMR spectra were collected on a Bruker Avance-125 MHz spectrometer. $^1$H and $^{13}$C NMR shifts were referenced to residual solvent. $^1$H splitting patterns were designated as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), sextet (sex), and AB quartet (ABq). Cyclic voltammetry was performed in 10 mL DCM (dried over calcium hydride...
and freshly distilled prior to use) solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) with 1 mM analyte under an atmosphere of nitrogen. The electrodes consisted of a glassy carbon working electrode, a reference electrode made of a silver wire in a 10 mM AgNO₃ solution contained by a Vycor tip, and an auxiliary electrode of platinum wire. All cyclic voltammograms were referenced to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. Elemental analysis was carried out by Midwest Microlab, LLC, Indianapolis, IN. IR spectra were taken on a Bruker Tensor 27 FTIR spectrometer using an attenuated total reflectance (ATR) adapter. Mass spectra were obtained at the Paul Bender Chemical Instrumentation Center of the Chemistry Department of the University of Wisconsin–Madison using a Thermo Q Exactive™ Plus ESI-MS.

**BiRh(TPA)₄ (1).** Solid BiRh(TFA)₄ (45.7 mg, 0.0600 mmol) and triphenylacetic acid (138 mg, 0.477 mmol) were combined in a 25 mL Schlenk flask and suspended in 15 mL toluene. The yellow suspension was heated to reflux through a soxhlet extractor (K₂CO₃ in the thimble) at 145 °C using an oil bath for 40 h. After cooling to room temperature, the solvent was removed *in vacuo*. The solids were dissolved in a 20% hexane/DCM solution and passed through a silica plug. The yellow solution was collected and the solvent was removed *in vacuo*. The yellow product was recrystallized from DCM/hexane. Yield: 57.2 mg, 65.6%. X-ray quality crystals of 1·CH₂Cl₂ were obtained by layering a concentrated DCM solution of 1 with hexane. Anal. Calcd BiRhC₈₀H₆₀O₈•(0.5 CH₂Cl₂): C 64.3, H 4.1. Found: C 64.0, H 4.8. ESI-MS (positive ion, CH₃CN): *m/z* 1461 ([M+H]⁺, 6%). ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.10 (12H, t, *J* = 7.31 Hz), 6.91 (24H, dd, *J* = 7.91 Hz, 7.31 Hz), 6.73 (24H, d, *J* = 7.91 Hz). ¹³C{¹H} NMR
(CDCl$_3$, 125 MHz, ppm): $\delta$ 187.4, 143.6, 130.6, 127.5, 126.9, 69.0. IR (ATR, cm$^{-1}$): 1567 m, 1492 w, 1445 w, 1358 m, 1339 w, 1037 w, 906 br, 807 w, 759 m, 744 m, 735 m, 698 s, 674 m, 649 w, 622 w, 606 m.

$\text{BiRh(but)}_4(\text{H}_2\text{O})$ (2$\cdot$H$_2$O). Solid BiRh(TFA)$_4$ (51.6 mg, 0.0676 mmol) and butyric acid (5 mL, 54.5 mmol) were combined in a 10 mL Schlenk flask, resulting in a clear yellow solution. This solution was heated to reflux at 155 °C using an oil bath for 1 h, after which the acid was distilled out under reduced pressure and this process was repeated one more time. The remaining yellow solid was dissolved in a 50% EtOAc/hexane solution and passed through a silica plug. The yellow solution was collected and the solvent was removed in vacuo. The yellow solid was then recrystallized with hot hexanes, filtered, washed with cold hexanes and dried in vacuo. Yield: 27.8 mg, 60.7%. Anal. Calcd BiRhC$_{16}$H$_{28}$O$_8$: C 29.1, H 4.3. Found: C 29.1, H 4.1. ESI-MS (positive ion, CH$_3$CN): $m/z$ 661 ([M+H]$^+$, 100%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 2.32 (8H, t, $J =$ 7.3 Hz), 1.64 (2H, s), 1.56 (8H, sex, $J =$ 7.3 Hz), 0.79 (12H, t, $J =$ 7.3 Hz). $^{13}$C($^1$H) NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 187.9, 37.9, 19.6, 13.6. IR (ATR, cm$^{-1}$): 2963 w, 2933 w, 2874 w, 1556 s, 1488 m, 1460 m, 1406 m, 1349 m, 1313 m, 1264 w, 1210 w, 1102 w, 897 w, 870 w, 803 w, 736 w, 668 m, 648 w, 634 w, 613 w, 608 w.

$\text{BiRh(piv)}_4(\text{H}_2\text{O})$ (3$\cdot$H$_2$O). Solid BiRh(TFA)$_4$ (50.9 mg, 0.0666 mmol) and pivalic acid (1.51 g, 14.8 mmol) were combined in a 10 mL Schlenk flask and sealed under static vacuum. The mixture was brought to 130 °C using an oil bath, resulting in a yellow solution. After heating for 1 h, the acid was distilled out under reduced pressure and this process was repeated one more time. The yellow solid was purified by flash column
chromatography on silica using DCM as the eluent ($R_f = 0.40$, DCM). The yellow solution was collected and the solvent was removed in vacuo. Yield: 40.0 mg, 81.7%.

Anal. Calcd BiRhC$_{20}$H$_{36}$O$_8$•H$_2$O: C 32.7, H 5.2. Found: C 32.7, H 5.1. ESI-MS (positive ion, CH$_3$CN): $m/z$ 717 ([M+H]$^+$, 100%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 1.93 (2H, s), 1.05 (36H, s). $^{13}$C($^1$H) NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 192.1, 40.3, 28.1. IR (ATR, cm$^{-1}$): 3491 br, 2962 w, 1556 s, 1483 m, 1411 s, 1224 m, 895 w, 800 w, 786 w, 747 w, 735 w, 709 w, 688 w, 680 w, 662 w, 649 w, 640 w, 634 s, 626 s, 613 m, 605 m.

$\text{BiRh(esp)}_2$ (4). Solid BiRh(TFA)$_4$ (63.6 mg, 0.0833 mmol) and H$_2$esp (278 mg, 0.237 mmol) were combined in a 25 mL Schlenk flask and dissolved in 15 mL toluene. The yellow solution was heated to reflux through a soxhlet extractor (K$_2$CO$_3$ in thimble) at 145 °C using an oil bath for 5 h during which some yellow precipitate formed. After cooling to room temperature, the solvent was removed in vacuo. The yellow solid was washed with Et$_2$O and dried in vacuo. Yield: 61.6 mg, 85.6%. Anal. Calcd BiRhC$_{32}$H$_{40}$O$_8$: C 44.5, H 4.7. Found: C 44.4, H 4.8. ESI-MS (positive ion, MeOH): $m/z$ 865 ([M+H]$^+$, 12%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.10 (2H, t, $J = 7.5$ Hz), 6.89 (4H, dd, $J = 7.5$ Hz, 1.6 Hz), 6.79 (2H, t, $J = 1.6$ Hz), 2.73, 2.68 (8H, ABq, $J_{AB} = 12.6$ Hz), 1.13 (12H, s), 1.08 (12H, s). $^{13}$C($^1$H) NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 189.9, 138.1, 130.7, 128.3, 127.1, 47.7, 45.9, 26.4, 26.0. IR (ATR, cm$^{-1}$): 2963 w, 2952 w, 2919 w, 1561 s, 1473 m, 1454 w, 1433 w, 1403 s, 1375 m, 1360 m, 1301 w, 1262 m, 1245 m, 1198 w, 1166 w, 1132 w, 965 w, 931 w, 904 w, 882 w, 826 m, 798 w, 783 m, 775 m, 747 m, 706 s, 632 s.

$\text{BiRh(OAc)}_4$ (5). Solid BiRh(TFA)$_4$ (50.1 mg, 0.0656 mmol) and acetic acid (5 mL, 87.4 mmol) were combined in a 10 mL Schlenk flask, resulting in a clear yellow solution.
This solution was heated to reflux at 125 °C using an oil bath for 1 h, after which the acid was distilled out under reduced pressure and this process was repeated one more time, during which a yellow solid precipitated from the reaction mixture. The remaining yellow solid (completely insoluble in all solvents) was washed with DI H₂O, DCM, hexanes, MeOH and dried in vacuo. Yield: 35.4 mg, 98.4%. Anal. Calcd BiRhC₈H₁₂O₈: C 17.5, H 2.2. Found: C 17.6, H 2.1. IR (ATR, cm⁻¹): 1556 s, 1485 w, 1412 s, 1345 m, 1043 w, 689 s, 625 m. Further spectral characterization was not possible due to the insolubility of the compound.

Crystallography

Crystallographic data were measured at the Molecular Structure Laboratory of the Chemistry Department of the University of Wisconsin–Madison. Crystals were selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. Each crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam using a video camera. The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEX-II diffractometer with Cu Kα (λ = 1.54178 Å) radiation. The data were collected using a routine to survey an entire sphere of reciprocal space and indexed by the SMART program.¹⁶ The structures were solved via direct methods and refined by iterative cycles of least-squares refinement on F² followed by difference Fourier synthesis.¹⁷,¹⁸ All H atoms were included in the final structure factor calculation at idealized positions and allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Single crystals of 1•CH₂Cl₂ suitable for structural determination were obtained by slow diffusion.
of hexane into a dichloromethane solution of 1. The unit cell contains an additional 8 molecules of dichloromethane which have been removed by SQUEEZE.

**Results and Discussion**

**Synthesis and Characterization**

Carboxylate exchange reactions are well-known synthetic methods in the chemistry of metal-metal bonded compounds.\(^1\) While this method has been used successfully on heterobimetallic compounds with strong quadruple bonds\(^{19}\) (e.g. $[\text{MoW}]^{4+}$ compounds), it was not immediately obvious whether the $[\text{BiRh}]^{4+}$ core, having a lower metal-metal bond order, would be robust enough to survive these reaction conditions. Nevertheless, we tested reactions of $\text{BiRh(O}_2\text{CCF}_3)_4$ with excess carboxylic acids to see (by $^{19}\text{F}$ NMR spectroscopy) whether carboxylate exchange takes place. Gratifyingly, these carboxylate exchange reactions were found to be quite clean and straightforward. Using carboxylate exchange, we have obtained $\text{BiRh(TPA)}_4$ (1), $\text{BiRh(but)}_4$ (2), $\text{BiRh(piv)}_4$ (3), $\text{BiRh(esp)}_2$ (4), and $\text{BiRh(OAc)}_4$ (5) in useful yields starting from $\text{BiRh(TFA)}_4$\(^{13}\) (TPA = triphenylacetate, but = butyrate, piv = pivalate, esp = $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,3-benzenedipropionate, OAc = acetate, and TFA = trifluoroacetate); (see Chart 1). Complete equatorial ligand exchange was observed for all compounds by either refluxing a toluene solution of $\text{BiRh(TFA)}_4$ and excess ligand through a soxhlet extractor containing $\text{K}_2\text{CO}_3$ (1 and 4) or by successive heating and distillation of excess acid (2, 3, and 5), as evidenced by silent $^{19}\text{F}{\{^{1}\text{H}}}$ NMR spectra for 1-4. The resulting yellow compounds 1-4 were all characterized by $^{1}\text{H}$ and $^{13}\text{C}{\{^{1}\text{H}}$ NMR and IR spectroscopy along with cyclic voltammetry, ESI-MS, and elemental analysis.
Compound 5 was characterized by elemental analysis and IR spectroscopy. A one-pot synthetic route to 1 was attempted by reacting elemental Bi with Bi(TFA)$_3$ and Rh$_2$(TFA)$_4$ in a suspension of toluene/diphenyl ether/HTFA (conditions typically used to form BiRh(TFA)$_4$)$^{13}$ with excess HTPA ligand present. This reaction resulted in a complex mixture of substituted homo- and heterobimetallic complexes that were not easily separable; therefore equatorial ligand exchange from pre-formed BiRh(TFA)$_4$ is the preferred route to the novel compounds discussed in this work. Attempts to synthesize 1 without the use of the soxhlet method described above resulted in incomplete substitution of all four TFA ligands; instead a trisubstitued complex, BiRh(TPA)$_3$(TFA), was observed and characterized by $^1$H and $^{19}$F/$^1$H NMR spectroscopies.$^{20}$ The observation of a partially substituted complex suggests that the equatorial ligands are exchanged in a stepwise fashion, similar to the ligand substitution mechanism for Rh$_2$-complexes.$^{21,22}$
The $^1$H NMR spectrum of 1 in CDCl$_3$ shows well resolved resonances in the aryl region with the para-hydrogen atoms at 7.10 ppm (t), meta-hydrogen atoms at 6.91 ppm (dd), and ortho-hydrogen atoms at 6.73 ppm (d) showing downfield shifts ($\Delta \delta = 0.02, 0.05,$ and $0.11$ ppm, respectively) compared to the spectrum of the analogous homobimetallic Rh$_2$(TPA)$_4$. The $^1$H NMR spectrum of 2 in CDCl$_3$ shows resonances at 2.32 ppm (t), 1.64 ppm (s) for an axially bound water molecule, 1.56 ppm (sex), and 0.79 ppm (t). The $^1$H NMR spectrum of 3 in CDCl$_3$ shows resonances at 1.93 ppm (s) for an axially bound water molecule and at 1.05 ppm (s) corresponding to the pivalate ligands. The $^1$H NMR spectrum of 4 in CDCl$_3$ shows aryl resonances at 7.10 ppm (t), 6.89 ppm (dd), and 6.79 ppm (t) along with alkyl resonances at 2.73 and 2.68 ppm (ABq), 1.13 ppm (s), and 1.08 ppm (s). There are two interesting distinctions in the $^1$H
NMR spectrum of 4 compared to that of the analogous homobimetallic Rh$_2$(esp)$_2$. First, both the methyl and methylene protons are diastereotopic in the heterobimetallic complex where they both appear as singlets in the homobimetallic complex. The heterobimetallic core causes these particular protons to be magnetically inequivalent due to the loss of symmetry along the M–M axis. Second, all of the $^1$H resonances in the Bi–Rh complex are shifted downfield compared to several Rh$_2$(esp)$_2$ complexes with various axially ligated molecules$^{23}$ with the exception of the aryl hydrogen at the 2-position of the ring ($\Delta\delta \sim 0.18$ ppm upfield), which points towards the metal-metal core.

Crystallography

The asymmetric unit of the monoclinic $P2_1/n$ crystal of 1 contains one Bi–Rh complex with one molecule of DCM axially bound to the Rh atom along with additional disordered solvent in the lattice. The molecular structure of 1•CH$_2$Cl$_2$, determined by single-crystal X-ray crystallography, and the summary of crystallographic data are shown in Figure 1 and Table 1, respectively. The structure has a typical paddlewheel geometry with the Bi atom in a distorted square pyramidal geometry coordinated by four O atoms and capped by the Rh atom. The Rh atom lies at the center of octahedron with four O atoms occupying the equatorial sites, a Bi atom and Cl atom from a DCM molecule occupy the axial sites.
Figure 1. X-ray crystal structure of 1•CH₂Cl₂, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and two disordered CH₂Cl₂ molecules have been omitted for clarity.

Table 1
Crystallographic data for 1•CH₂Cl₂ at 100 K.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>1•CH₂Cl₂</th>
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<tr>
<td>Empirical formula</td>
<td>Bi Ru C₉₃ H₆₆ O₈ Cl₆</td>
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<tr>
<td>Formula weight</td>
<td>1715.94</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(1) K</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>Space group</td>
<td>P 2₁/n</td>
</tr>
</tbody>
</table>
| Unit cell dimensions| a = 15.5675(3) Å  
b = 14.3374(3) Å  
c = 35.8081(8) Å  
α = 90°  
β = 100.401(1)°  
γ = 90° |
| Volume              | 7860.9(3) Å³ |
| Z                   | 4 |
| Density (calculated)| 1.450 g/cm³ |
| Crystal size        | 0.391 x 0.116 x 0.056 mm³ |
| Data / restraints / parameters | 15663/ 0 / 820 |
| Goodness-of-fit on F² | 1.169 |
| Final Rₐ,b indices [I>2σ(I)] | R₁ = 0.0422, wR₂ = 0.0952 |
| R indices (all data) | R₁ = 0.0448, wR₂ = 0.0964 |

*R₁ = Σ||F₀| - |Fₑ||/Σ|F₀|
\[ w = \{ \text{max}(0 \text{ or } F_0^2) + 2(F_c^2) \}/3. \]

The Bi–Rh bond distance is 2.5326(3) Å. The average M–O bond distances of 2.357[5] and 2.027[4] Å for Bi and Rh, respectively, are expectedly longer for the larger metal. The Rh–Cl distance to the axial CH₂Cl₂ molecule is 2.741(2) Å. The bond distances in the related Rh₂(TPA)₄•2CH₂Cl₂ complex⁴ are 2.3708(5), 2.033[3], and 2.651[1] Å for Rh–Rh, Rh–Oav, and Rh⋯Clav, respectively (Table 2). Although the M–M distance appears longer in 1•CH₂Cl₂, the formal shortness ratio (FSR)¹,²⁵ is calculated to be 0.917 for 1•CH₂Cl₂ compared to 0.948 for the Rh₂(TPA)₄•2CH₂Cl₂, suggesting a stronger M–M bond in the heterobimetallic complex. This added bond strength is likely attributed to increased polarization and ionic character of the M–M bond not present in the homobimetallic complex. The Bi–Rh, Bi–O, and Rh–O bond lengths for 1•CH₂Cl₂ lie in the expected regions of 2.53–2.57, 2.32–2.60, and 2.02–2.04 Å, respectively, for tetrabridged Bi–Rh carboxylate complexes.¹¹–¹³

**Table 2. Experimental Bond Distances (Å) for 1•CH₂Cl₂ and Rh₂(TPA)₄•2CH₂Cl₂⁴**

<table>
<thead>
<tr>
<th>Compound</th>
<th>1•CH₂Cl₂</th>
<th>Rh₂(TPA)₄•2CH₂Cl₂</th>
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<tr>
<td>M–Rh</td>
<td>2.5326(3)</td>
<td>2.3708(5)</td>
</tr>
<tr>
<td>Rh⋯Cl</td>
<td>2.741(2)</td>
<td>2.651[1]</td>
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Electrochemical Properties

Dirhodium tetracarboxylate complexes show characteristic redox waves for the [Rh$_2$]$^{4+/5+}$ couple; however electrochemical properties of Bi–Rh compounds have not previously been investigated. A high band gap is indicated for the complexes due to their pale yellow color, and thus redox events are not predicted to be very accessible. The cyclic voltammograms (CVs) of 1-4 are shown in Figure 2. The CVs were measured in 0.1 M tetrabutylammonium hexafluorophosphate (TBAH)/CH$_2$Cl$_2$. All complexes display an irreversible [BiRh]$^{3+/4+}$ couple at highly negative potentials, $E_{pc} = -1.50$ V, $-1.45$ V, $-1.44$ V, and $-1.43$ V vs ferrocene/ferrocenium (Fc/Fc$^+$) for 1-4, respectively. This reduction becomes more reversible upon faster scan rates, suggesting a fast chemical change following electron transfer for all complexes (see SI Figure S5). The complexes also display an irreversible [BiRh]$^{4+/5+}$ couple at positive potentials, $E_{pa} = 1.31$ V, 1.30 V, and 1.34 V vs Fc/Fc$^+$ for 2-4, respectively. The [BiRh]$^{4+/5+}$ couple of 4 is shifted by 0.54 V to higher potential vs the analogous Rh$_2$(esp)$_2$ complex, which shows a reversible redox couple at $E_{1/2} = 0.80$ V vs Fc/Fc$^+$ (Table 3). All of the complexes are stable across a wide range of potentials. This redox stability could be advantageous in catalysis requiring harsh oxidative or reductive conditions.
Figure 2. Cyclic voltammograms of 1-4 in CH₂Cl₂ with scan rate = 100 mv/s (0.1 M TBAH).

Table 3. Comparison of Electrochemical Data for Compounds 1-4<sup>a</sup>, Rh<sub>2</sub>(OAc)<sub>4</sub>\textsuperscript{27}, and Rh<sub>2</sub>(esp)<sub>2</sub>\textsuperscript{26}.

<table>
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<th>Compound</th>
<th>[MRh]&lt;sup&gt;3+/4+&lt;/sup&gt; ( E_{pc} ) (V)</th>
<th>[MRh]&lt;sup&gt;4+/5+&lt;/sup&gt; ( E_{pa} ) (V)</th>
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<td>4</td>
<td>-1.43</td>
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</tr>
<tr>
<td>Rh&lt;sub&gt;2&lt;/sub&gt;(OAc)&lt;sub&gt;4&lt;/sub&gt;</td>
<td>–</td>
<td>0.77</td>
<td>27</td>
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<sup>a</sup>All potentials are versus Fc/Fc\(^+\) in CH₂Cl₂.

Conclusions

Carboxylate exchange is a viable synthetic method for Bi–Rh tetracarboxylate compounds. Five novel heterobimetallic Bi–Rh compounds, BiRh(TPA)<sub>4</sub>, BiRh(but)<sub>4</sub>,
BiRh(piv)$_4$, BiRh(esp)$_2$, and BiRh(OAc)$_4$ have now been prepared from the equatorial ligand exchange reaction of BiRh(TFA)$_4$. These complexes have doubled the library of known heterobimetallic Bi–Rh carboxylate complexes and are the first examples that contain no perfluorinated ligands. This is also the first example of solution phase equatorial ligand exchange from BiRh(TFA)$_4$ leading to the synthesis of novel homoleptic Bi–Rh carboxylate complexes. This synthetic advance should enable the rapid derivatization of the Bi–Rh core to include numerous ligands of interest (not just carboxylates) used in applications such as catalysis. Routes to these complexes along with exploration of their catalytic activity are currently underway in our laboratory.

Author Information

Corresponding Author

*E-mail: berry@chem.wisc.edu

Notes

The authors declare no competing financial interest.

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(20) $^1$H NMR (CDCl$_3$, 400 MHz, ppm) δ 7.20 (2H, t, J = 7.2 Hz), 7.15 (1H, t, J = 7.2 Hz), 7.11 (4H, t, J = 7.2 Hz), 7.00 (2H, t, J = 7.2 Hz), 6.84 (6H, d, J = 7.2 Hz), $^{19}$F($^1$H) NMR (CDCl$_3$, 376.5 MHz, ppm) 72.5 (s).


