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

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Abstract

Five novel homoleptic heterobimetallic bismuth(II)-rhodium(II) carboxylate complexes—

BiRh(TPA)$_4$ (**1**), *BiRh(but)$_4$* (**2**), *BiRh(piv)$_4$* (**3**), *BiRh(esp)$_2$* (**4**), and *BiRh(OAc)$_4$* (**5**) —

were synthesized in good yields by equatorial ligand substitution starting from

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.
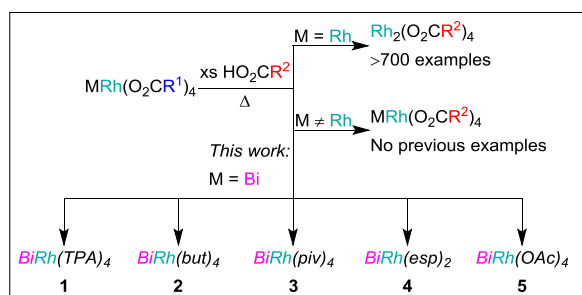
Introduction

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 $BiRh(O_2CCF_3)_4$.[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_2CCF_3 and $O_2CCF_2CF_3$).[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

$BiRh(O_2CCF_3)_4$ 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. $BiRh(TFA)_4$[13] and H_2esp[15] were prepared according to literature procedures. Dichloromethane (DCM), diethyl ether (Et_2O), ethyl acetate (EtOAc), hexane, methanol (MeOH), chloroform-*d* (CDCl3), butyric acid, pivalic acic, triphenylacetic acid, acetic acid, and potassium carbonate (K_2CO_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 $AgNO_3$ 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

(K_2CO_3 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**•CH_2Cl_2 were

obtained by layering a concentrated DCM solution of **1** with hexane. Anal. Calcd

BiRhC$_{80}$H$_{60}$O$_8$•(0.5 CH_2Cl_2): C 64.3, H 4.1. Found: C 64.0, H 4.8. ESI-MS (positive ion,

CH_3CN): *m/z* 1461 ([M+H]$^+$, 6%). ^{1}H NMR (CDCl$_3$, 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). ^{13}C{^{1}H} NMR

(CDCl$_3$, 125 MHz, ppm): δ 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.

*BiRh(but)$_4$•(H$_2$O) (**2**•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): δ 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): δ 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.

*BiRh(piv)$_4$•(H$_2$O) (**3**•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 $BiRhC_{20}H_{36}O_8 \cdot H_2O$: C 32.7, H 5.2. Found: C 32.7, H 5.1. ESI-MS (positive

ion, CH_3CN): *m/z* 717 ([M+H]$^+$, 100%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.93 (2H, s),

1.05 (36H, s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, ppm): δ 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.

BiRh(esp)$_2$ (4). Solid $BiRh(TFA)_4$ (63.6 mg, 0.0833 mmol) and H_2esp (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_2CO_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_2O 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): δ 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). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, ppm): δ 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.

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 H_2O, DCM, hexanes, MeOH and dried *in vacuo*. Yield: 35.4 mg, 98.4%. Anal. Calcd $BiRhC_8H_{12}O_8$: 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 F^2 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**•CH_2Cl_2 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. $[MoW]^{4+}$ compounds), it was not immediately obvious whether the $[BiRh]^{4+}$ core, having a lower metal-metal bond order, would be robust enough to survive these reaction conditions. Nevertheless, we tested reactions of $BiRh(O_2CCF_3)_4$ with excess carboxylic acids to see (by ^{19}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 $BiRh(TPA)_4$ (**1**), $BiRh(but)_4$ (**2**), $BiRh(piv)_4$ (**3**), $BiRh(esp)_2$ (**4**), and $BiRh(OAc)_4$ (**5**) in useful yields starting from $BiRh(TFA)_4$[13] (TPA = triphenylacetate, but = butyrate, piv = pivalate, esp = α,α,α',α'-tetramethyl-1,3-benzenedipropionate, OAc = acetete, and TFA = trifluoroacetate); (see Chart 1). Complete equatorial ligand exchange was observed for all compounds by either refluxing a toluene solution of $BiRh(TFA)_4$ and excess ligand through a soxhlet extractor containing K_2CO_3 (**1** and **4**) or by successive heating and distillation of excess acid (**2**, **3**, and **5**), as evidenced by silent ^{19}F{^{1}H} NMR spectra for **1-4**. The resulting yellow compounds **1-4** were all characterized by ^{1}H and ^{13}C{^{1}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 ^1H and $^{19}F\{^1H\}$ 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]
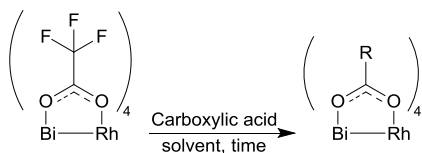
Chart 1. General reaction scheme and conditions for synthesis of complexes **1**-**5**.

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 ^1H 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_2Cl_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.
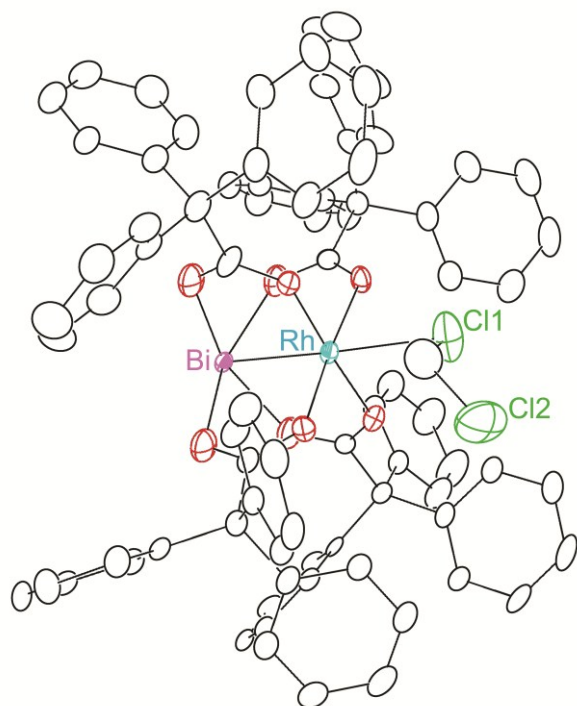
Figure 1. X-ray crystal structure of **1**•CH$_2$Cl$_2$, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and two disordered CH$_2$Cl$_2$ molecules have been omitted for clarity.

Table 1
Crystallographic data for **1**•CH$_2$Cl$_2$ at 100 K.

Identification code	**1**·CH$_2$Cl$_2$
Empirical formula	Bi Ru C$_{83}$ H$_{66}$ O$_8$ Cl$_6$
Formula weight	1715.94
Temperature	100(1) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P\,2_1/n$
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) Å^3
Z	4
Density (calculated)	1.450 g/cm^3
Crystal size	0.391 x 0.116 x 0.056 mm^3
Data / restraints / parameters	15663/ 0 / 820
Goodness-of-fit on F^2	1.169
Final $R^{a,b}$ indices [I>2$\sigma(I)$]	R$_1$ = 0.0422, wR$_2$ = 0.0952
R indices (all data)	R$_1$ = 0.0448, wR$_2$ = 0.0964

[a]R$_1$ = $\Sigma||F_0| - |F_c||/\Sigma|F_0|$

[b]$wR_2 = |[\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]]1/2$, $w = 1/\sigma^2(F_0^2) + (aP)^2 + bP$, where $P = [max(0 \text{ or } F_0^2) + 2(F_c^2)]/3$.

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 CH_2Cl_2 molecule is 2.741(2) Å. The bond
distances in the related $Rh_2(TPA)_4·2CH_2Cl_2$ complex[24] are 2.3708(5), 2.033[3], and
2.651[1] Å for Rh–Rh, Rh–O_{av}, and Rh···Cl_{av}, respectively (Table 2). Although the M–M
distance appears longer in **1**·CH_2Cl_2, the formal shortness ratio (FSR)[1,25] is calculated
to be 0.917 for **1**·CH_2Cl_2 compared to 0.948 for the $Rh_2(TPA)_4·2CH_2Cl_2$, 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**·CH_2Cl_2 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·CH_2Cl_2 and $Rh_2(TPA)_4·2CH_2Cl_2$[24]

Compound	**1**·CH_2Cl_2	$Rh_2(TPA)_4·2CH_2Cl_2$
M–Rh	2.5326(3)	2.3708(5)
Rh–O_{av}	2.028[4]	2.033[3]
Bi–O_{av}	2.358[5]	–
Rh···Cl	2.741(2)	2.651[1]

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.[6] 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_2Cl_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).[26] 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
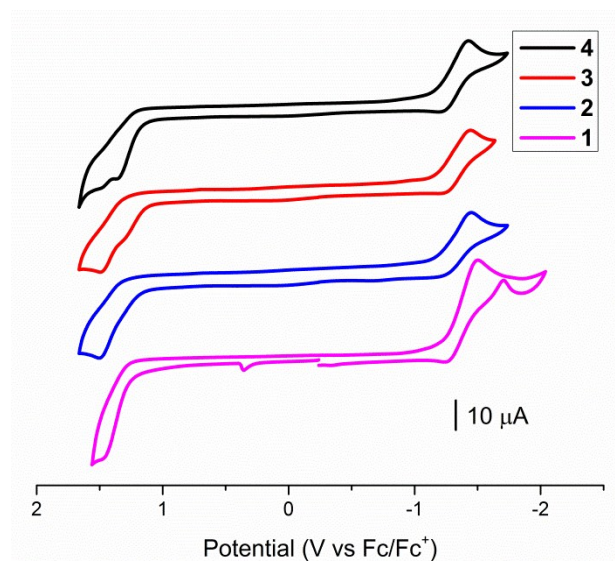
conditions.

Figure 2. Cyclic voltammograms of **1-4** in CH_2Cl_2 with scan rate = 100 mv/s (0.1 M TBAH).

Table 3. Comparison of Electrochemical Data for Compounds **1-4**[a], $Rh_2(OAc)_4$[27], and $Rh_2(esp)_2$[26].

Compound	$[MRh]^{3+/4+}$ E_{pc} (V)	$[MRh]^{4+/5+}$ E_{pa} (V)	Reference
1	−1.50	1.46	This work
2	−1.45	1.49	This work
3	−1.44	1.30	This work
4	−1.43	1.34	This work
$Rh_2(OAc)_4$	–	0.77	27
$Rh_2(esp)_2$	–	0.80	26

[a]All potentials are versus Fc/Fc$^+$ in CH_2Cl_2.

Conclusions

Carboxylate exchange is a viable synthetic method for Bi–Rh tetracarboxylate compounds. Five novel heterobimetallic Bi–Rh compounds, BiRh(TPA)$_4$, BiRh(but)$_4$,

$BiRh(piv)_4$, $BiRh(esp)_2$, 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.

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Notes

The authors declare no competing financial interest.

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