ORGANOMETALLICS

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Does an Axial Propeller Shape on a Dirhodium(III,III) Core Affect Equatorial Ligand Chirality?

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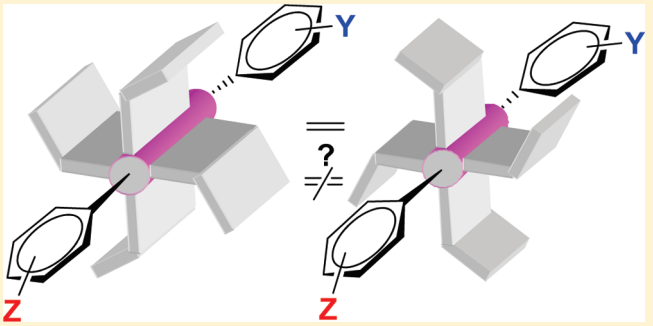
Supporting Information

ABSTRACT: The dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) framework, which exists solely in a propeller conformation, has been prepared with nonidentical apical aryl ligands. The presence of these nonidentical ligands on the propeller conformation was expected to define this structural unit as a chiral element and the resulting aryl(1)aryl(2)dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) as a chiral compound. Dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) compounds having phenyl and *p*-tolyl, 1-(3-phenylphenyl) and 2-methoxy-6-naphthyl, and *p*-(*N*-*p*-toluenesulfonylpyrolinamidophenyl) apical ligands were prepared and subjected to chromatographic, NMR, and X-ray crystallographic analysis to ascertain if the propeller core provided a chiral element that could define two enantiomers when dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) was bound to nonidentical apical aryl ligands. X-ray analysis suggests chirality in those compounds for which structures could be obtained, but chromatographic analyses were not able to separate enantiomers. Studies of dirhodium(III,III) tetrakis-(1-aza-2-cyclooctanoate) compounds possessing different apical ligands by NMR spectroscopy using binuclear chiral lanthanide−silver shift reagents were also performed, but conclusive evidence for chirality in these dirhodium complexes was not obtained.



INTRODUCTION

We have recently reported the preparation and structural characterization of thermally and chemically stable paddlewheel dirhodium(III,III) compounds with phenyl substituents in the axial positions and lactamates as the bridging ligands.[1] When the lactamate ligand is caprolactam, two noninterconvertable conformational isomers are formed, one having a biplanar orientation of the caprolactamate ligands and the other with a propeller orientation (Figure 1).[2] These conformational isomers differ in the orientation of the bridging caprolactamate ligands and possess unique spectral, chromatographic, and chemical properties.[2,3] Attempts to force the thermal interconversion of these configurational isomers in the solid state (up to 240 °C) or in solution (refluxing chlorobenzene at 130 °C, 24 h) have not been successful. Both remain intact when subjected to these conditions. The biplanar and propeller conformers are related to each other by "flipping" two oppositely placed seven-membered rings with atomic motion basically restricted to the three methylene groups most distant from the amide functional group, and the source for the restriction of this atomic motion is not revealed through either examination of molecular models or DFT calculations.[2] In both conformers, a severe bending of the Rh−Rh−Ph bond axis from 180°, a major opening of the Rh−O−C angle, and a less pronounced closing of the Rh−N−C angle from the ideal 120° are observed by single-crystal X-ray analysis.

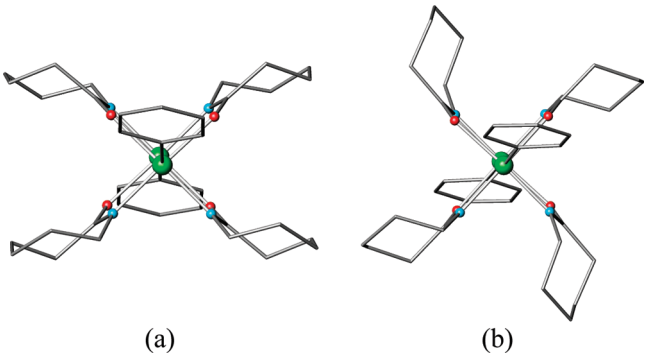


Figure 1. Bisphenyldirhodium(III,III) tetrakis(caprolactamate) core shown along the rhodium−rhodium bond axis in (a) biplanar and (b) propeller conformations. Red balls are O, blue are N, and green are Rh atoms.

Received: April 9, 2011
Published: June 13, 2011

   dx.doi.org/10.1021/om2003078 | *Organometallics* 2011, 30, 3619–3627

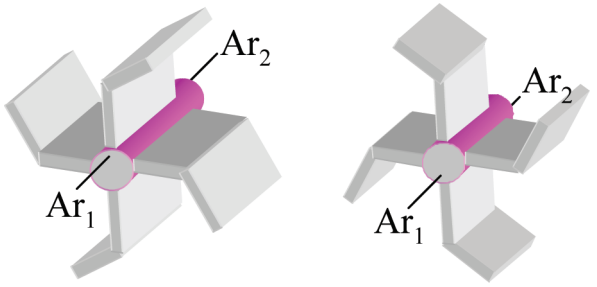


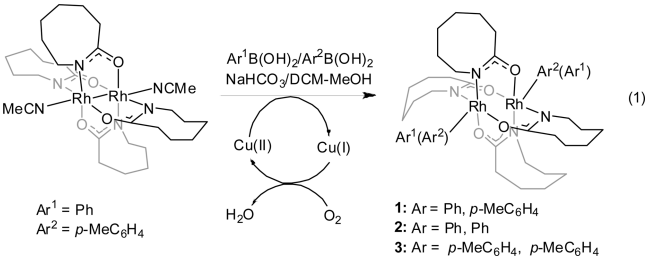
Figure 2. Propeller structures with nonidentical apical ligands differentiated by reflection or inversion.

With caprolactamate as the axial ligand, the biplanar conformer (Figure 1a) is the major isomer, and the propeller conformer (Figure 1b) is the minor stereoisomer. However, only bisphenyldirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) having the propeller conformation is formed with the higher homologue of caprolactam, 1-aza-2-cyclooctanone (ACOH), as the bridging ligand.[2] Molecular propellers have been recognized in organic chemistry as well-defined architectures that can exhibit restricted conformational equilibria,[4] and significant advances in stereochemical applications have resulted from these studies,[5] but there have been no previous reports of a propeller structure having a dimetallic core. However, although previously reported carbon-based molecular propellers often have a low energy barrier for interconversion between the two forms, the propeller conformation in bisphenyldirhodium(III,III) carboxamidates does not exhibit an energetically favorable interconversion between biplanar and propeller conformers even at high temperatures as a solid or in solution.[2] As a consequence, with the assumption that the two propeller conformational isomers of a bisaryldirhodium(III,III) carboxamidate (Figure 2, where the two aryl apical ligands are not identical) do not interconvert, we envisioned that placing two nonidentical structural units at the axial positions of dirhodium(III,III) 1-aza-2-cyclooctanoate would result in a pair of enantiomers and that having chiral units in those axial positions would produce diastereoisomers in numbers that corresponded to the number of chiral centers.

At this point it is useful to consider the symmetry of biplanar and propeller complexes. As can be seen from Figure 1a, the biplanar core of dirhodium(III,III) caprolactamate (excluding its apical phenyl ligands) has a vertical mirror plane, which, along with a horizontal 2-fold axis, yields an inversion center and, therefore, 2/*m* symmetry. In contrast, the propeller core (from Figure 1b) only has an inversion center. If both apical ligands are the same (e.g., phenyl), the symmetry of the structure can be as high as that of the core assuming that there are no packing or other distortion effects. On the other hand, the presence of nonidentical apical ligands on a dirhodium(III,III) carboxamidate core can yield asymmetric or chiral complexes (Figure 2). The formal exchange of nonidentical apical ligands on the propeller core yields a structure of different chirality due to the presence of the inversion center in the core (an operation that is equivalent to inversion or reflection).

RESULTS AND DISCUSSION

Using the protocol for formation of mixed bisaryldirhodium(III,III) caprolactamates,[6] phenyl(*p*-tolyl)dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) was constructed from dirhodium(II,II) 1-aza-2-cyclooctanoate (HACO), phenylboronic acid, and *p*-tolylboronic acid, catalyzed by copper(II) sulfate (eq 1). The products consisted of phenyl(*p*-tolyl)dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) (**1**) as well as bisphenyldirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) (**2**) and bis(*p*-tolyl)dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) (**3**) in a nearly statistical 48:22:26 ratio, which was expected. Attempts to chromatographically separate the enantiomers of compound **1** using comprehensive chiral SFC, HPLC, and RP-HPC screening were unsuccessful, and only one peak for **1** was detected. While this battery of chromatographic methods is generally successful in at least partially resolving the enantiomers of most chiral analytes, one should not draw a conclusion from these negative results that reflect on the chirality of the sample.



(1)

The crystal structure of **1** was solved in the chiral $P2_1$ space group, showing ordered distribution of phenyl and *p*-tolyl ligands in apical positions as shown in Figure 3. The mirror image configuration can be imagined as the inverse image of the complex depicted in Figure 3 or, which is identical, the configuration when phenyl and *p*-tolyl apical ligands are exchanged. However, the crystal of **1** does not consist of a single configuration of **1**, as it shows merohedral twinning refined to an approximate 1:1 ratio. In other words, each crystal domain or mosaic block consists of only one configuration, but different domains have different configurations of the complex. Additional evidence of such a distribution of configurations follows from less computationally suitable results when centrosymmetric space group $P2_1/c$ is used, in which both conformers are superimposed; this yields a 6.3% *R*-factor for the $P2_1/c$ space group versus a 4.5% *R*-factor in the chiral $P2_1$ group.

Recognizing that the subtle structural differences between phenyl and *p*-tolyl may not have provided adequate separation of enantiomers of **1** on the chiral columns that were employed, and relying on the observed merohedral twinning refined to an approximate 1:1 ratio with **1** as a suggestion of chirality, two bulky and more structurally different aryl groups were used to prepare [1-(3-phenylphenyl)](2-methoxy-6-naphthyl)dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) (**4**) from dirhodium(II,II) 1-aza-2-cyclooctanoate, *m*-biphenylboronic acid, and 2-methoxy-6-naphthylboronic acid, catalyzed by copper(II) sulfate (eq 2). The chromatographic ratio of the three products was 22 (**5**):41 (**4**):17 (**6**). Compound **4**, with its apical 3-phenylphenyl and 2-methoxy-6-naphthyl ligands, was separated from **5** and **6** by either column chromatography or preparative TLC, isolated in relatively low yield, and characterized spectroscopically. Even though the homobis-aryldirhodium(III,III) isomers (**5** and **6**) have retention volumes significantly different from that for **4** lying between them, there was no separation of **4** into enantiomers observed under a broad set of conditions. Again, attempts to chromatographically separate the enantiomers of compound **4**

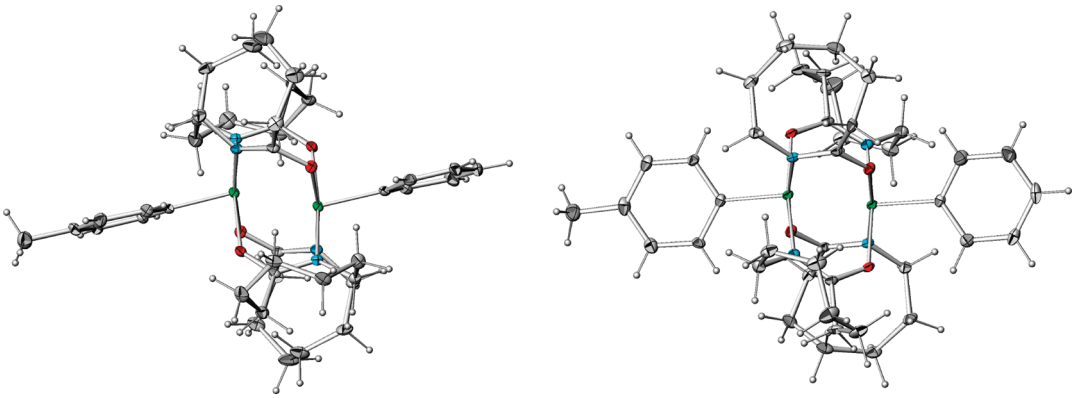


Figure 3. Phenyl(*p*-tolyl)dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) (**1**) in two views that are perpendicular to each other, showing the anisotropic atomic displacement ellipsoids for the non-hydrogen atoms at the 30% probability level. Hydrogen atoms are displayed with an arbitrarily small radius.

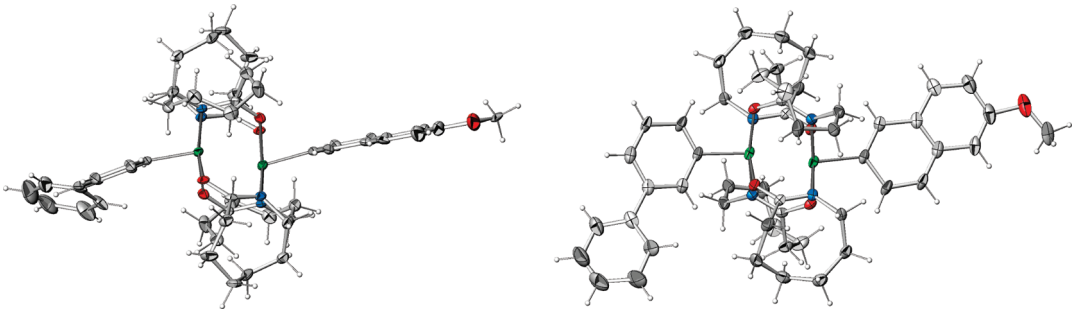
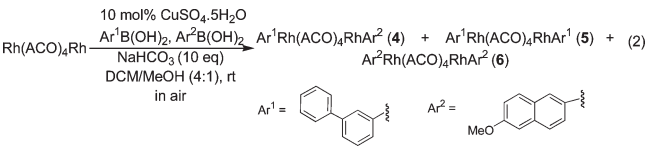


Figure 4. 1-(3-Phenylphenyl)(2-methoxy-6-naphthyl)dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) (**4**) in two views that are perpendicular to each other showing the anisotropic atomic displacement ellipsoids for the non-hydrogen atoms at the 30% probability level. Hydrogen atoms are displayed with an arbitrarily small radius.

using comprehensive chiral SFC, HPLC, and RP-HPC screening were unsuccessful.



Dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) **4** crystallizes in the monoclinic non-centrosymmetric space group *Pc*. A general view of **4** in two orientations that are perpendicular to each other is shown in Figure 4; both apical ligands are tilted from the Rh−Rh axis toward the O atoms of the 1-aza-2-cyclooctanoate ligands. As is reported for **1** with poor correlation, fitting the experimental data for structure **4** with centrosymmetric $P2_1/c$ symmetry is much worse than the fit with *Pc* symmetry. Also, although the structure of **4** in the chiral $P2_1$ group yields a better fit than with the centrosymmetric model, its agreement with experiment, including reflection absences, is worse than in the model with *Pc* symmetry. Thus the model with *Pc* symmetry was accepted as the most adequate description of the structure of **4**. Note that *Pc* is an acentric symmetry group, but due to the presence of a *c*-glide plane, it is not chiral. Thus, contrary to the chiral $P2_1$ group, in which all molecules within the crystal (or in the presence of merohedral twinning within the domain) are of the same chirality, in the *Pc* symmetry group the molecules of the same chirality (in this particular structure) form a layer between a pair of parallel *c*-planes. The neighboring layers are a reflection of each other, differing by the chirality of the molecules.

The crystal structure determination reveals the presence of merohedral twinning in a 3:2 ratio, which in this particular case can be described as follows: in the *Pc* group molecules are of different chirality, but their orientation (orientation of apical ligands in this case) is the same. The merohedral twinning introduces an inversion center that relates different domains so that the orientation of molecules in domains alternates.

In addition to merohedral twinning and the ordered alteration of chirality in the layers, the molecules of different conformations are disordered in such a way that their cores perfectly coincide, but their apical ligands, 3-phenylphenyl (PP) and 2-methoxy-6-naphthyl (MNP), are superimposed onto each other in a 3:1 ratio. The superimposed conformers shown in Figure 5 are of opposite chirality and can be transformed into each other by either inversion or reflection. Swapping apical ligands also changes chirality and is identical to the above transformations.

The crystal structure of **4** is further complicated by having every other 1-aza-2-cyclooctanoate ligand on the dirhodium core randomly accepting an alternate conformation (Figure 6a and b), which is observed as a superposition of two conformations in an approximate 7:2 ratio. Only the two ligands opposite each other alter their shape, while two other ligands show no disorder. Essentially the same disorder was found in bisphenyldirhodium(III,III) 1-aza-2-cyclooctanoate complex **2**.[2] The main conformation of complex **4** shown in Figure 5a is found in all known

dx.doi.org/10.1021/om2003078 |*Organometallics* 2011, 30, 3619–3627

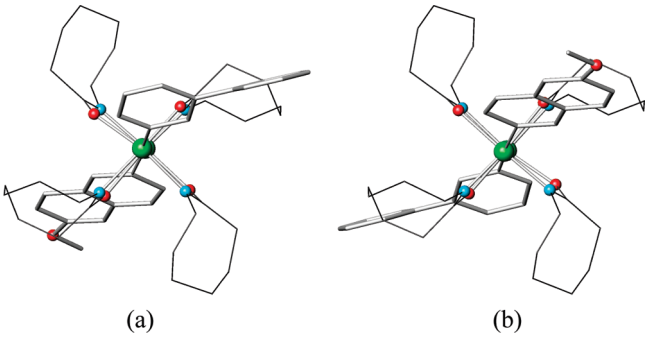


Figure 5. View of two conformations in **4**, major (a) and minor (b), that are superimposed onto each other in a 0.74 to 0.26 ratio. The conformations (a) and (b) are inverse images of each other.

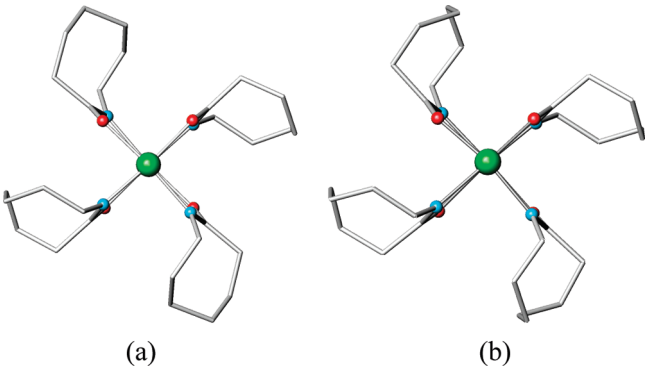


Figure 6. Views along the Rh−Rh bond axis showing two variants of the propeller configurations of dirhodium(III,III) with 1-aza-2-cyclooctanoate (ACO) ligands: (a) in **1** and essentially the same main conformation in **4**, and (b) alternate conformation in **4**.

propeller structures of dirhodium(III,III) 1-aza-2-cyclooctanoate including complex **1**, whose conformation is essentially the same as for the major conformer of compound **4**. As can be seen from Figure 6a there are two different shapes of the ligands. These two alternate conformations of ligands are schematically represented in Figure 7a and b, respectively, where the signs of corresponding torsion angles are shown. Thus the main conformation of the complex **4** and the only conformation in **1** could be denoted by the sequence a,b,−a,−b describing conformation of individual ligands, where the negative sign denotes inversion. Note that signs of torsion angles are opposite for ligands trans to each other due to inversion symmetry of the core.

The configuration of the 1-aza-2-cyclooctanoate ligands that are trans to each other on the dirhodium core changes from a to b and −a to −b, respectively, by flipping two carbon atoms that are opposite the N−C(O) bond (Figure 6). Thus when ligands that are trans to each other have the alternative configuration of that shown in Figure 6b, all ligands become identical (with respect to the inversion), as shown in Figure 7b, and the configuration of the core can be described as b,b,−b,−b.

To better probe the propeller conformation of dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) as a chiral unit, we prepared bis-aryldirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) with chiral *N*-*p*-toluenesulfonylprolinamide attachments that were at the para positions. Both D- and L-prolinamide derivatives were prepared, yielding single compounds that were characterized

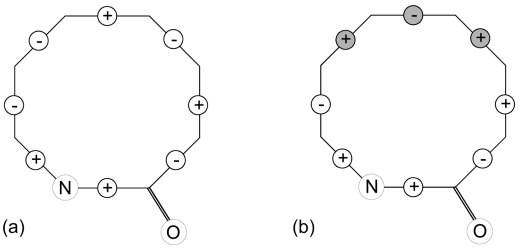
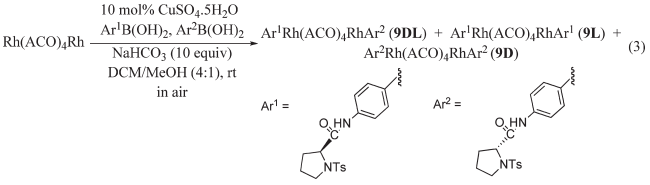


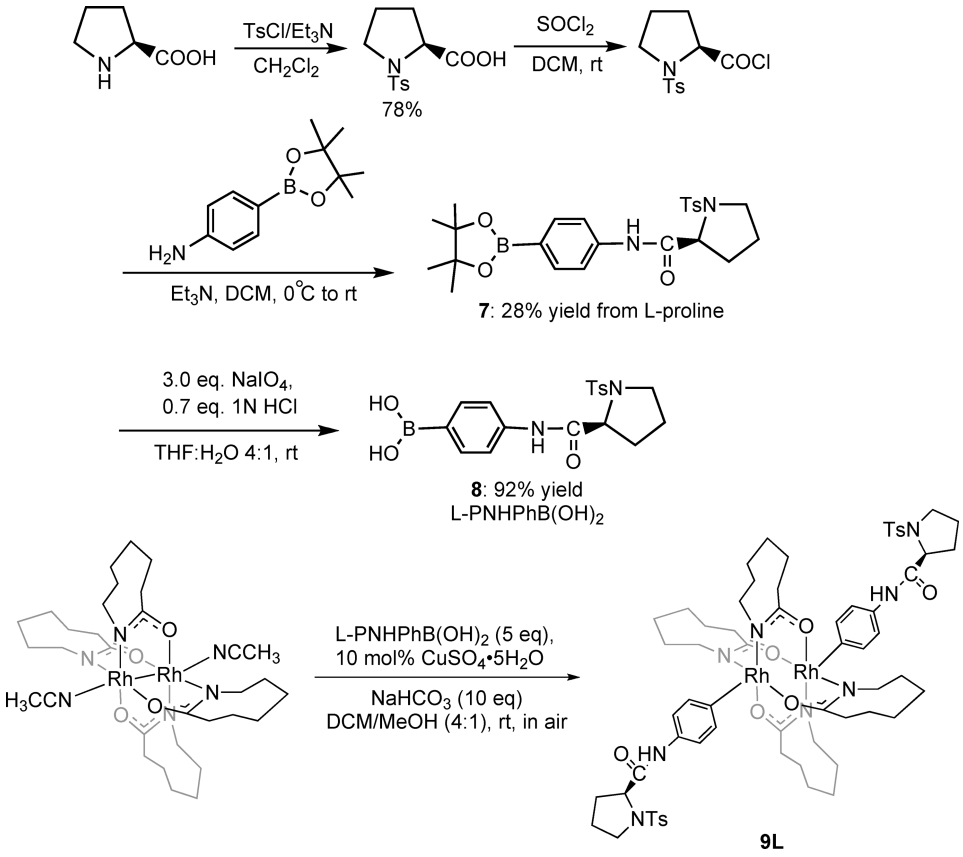
Figure 7. Alternate conformation of ligands: (a) signs of torsion angles in the conformation described by Figure 6a; (b) signs of torsion angles in the conformation described by Figure 6b. The gray circles in (b) show the changes in signs of (b) compared to (a); the main difference is in flipping the upper two carbon atoms that are opposite the N−C(O) bond.

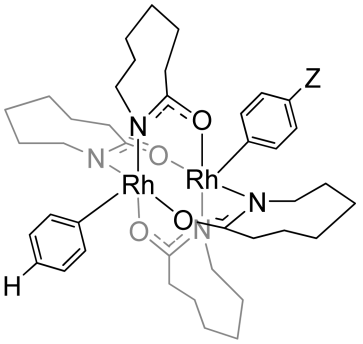
spectroscopically and chromatographically. The process employed with L-proline to form **9L** is shown in Scheme 1, and the same procedures were employed with D-proline to form **9D**. For each of **9L** and **9D** only one compound was chromatographically separable, and **9L** was cleanly distinguished from **9D**. In a separate experiment racemic D,L-proline was employed with the expectation of formation of **9L**, **9D**, and the bis-aryldirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) with both D- and L-prolinamide attachments (**9DL**), which was expected to be formed in a 1(**9L**):2(**9DL**):1(**9D**) ratio (eq 3). Chromatographic analysis, however, exhibited signals for only two distinguishable materials in a 1:1 ratio, presumably because differentiation was restricted only to the D- and L-prolinamide attachments. These analyses do indicate that association with the stationary phase of the column is localized on only one apical ligand without observable influence on the second apical ligand in the same molecule.



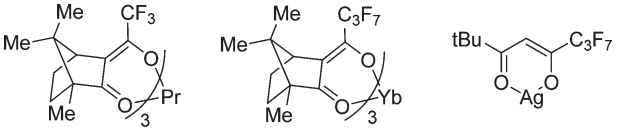
The absence of chromatographic separation of what we believed should be diastereoisomers prompted us to investigate the possible separation of enantiomers through the use of NMR chiral shift reagents.[7] Addition of lanthanide shift reagents to organic compounds generally results in shifts of resonances to higher (or lower) frequency with the shift determined primarily by the distance of the given type of proton (or other NMR active atom) from the donor group. Ideally, the six-coordinate lanthanide complex forms a weak addition complex that is in fast exchange with the unbound organic substrate on the NMR time scale. The induced shifts are caused by a large difference in the magnetic susceptibility tensors for the seven-coordinate complex. Analyses of chiral alkenes and arenes are particularly difficult.[8] However, a chiral lanthanide shift reagent in combination with silver ion has been shown to cause detectable shifts.[9] In these cases induced shifts are observed from a mixed complex that forms between the chiral hydrocarbon that is weakly associated with the silver ion in solution. The dirhodium(III,III) complexes **10**−**12** are substantially shielded from dipolar interactions, but weak association with silver ion should be feasible, and the chiral lanthanide reagent is expected to induce NMR shifts in selected ACO proton signals if the dirhodium complex is a racemic mixture.

Scheme 1. Synthesis of Arylboronic Acid 8 and Dirhodium Complex 9





10: Z = F
11: Z = Br
12: Z = H



13a **13b** **14**

Initial experiments were performed on **10** and **11** with chiral praseodymium or ytterbium camphorates (**13**) and the silver diketonate Ag(fod) (**14**). The dirhodium compound was dissolved in $CDCl_3$, and the chiral lanthanide reagent was added in portions, followed by the silver diketonate, also in portions (Figure 8). Only line broadening of the ^1H NMR signals of both aromatic and aliphatic hydrogens was observed with the additions of the chiral lanthanide salts, suggesting the absence of association between the chiral praseodymium (Figure 8) or ytterbium (Figure 9) camphorates and **10** or **11**. However, upon addition of Ag(fod), an immediate and continuing separation of signals at δ 3.2 (hydrogens of CH_2 adjacent to the amide N) and 2.3 (hydrogens of CH_2 adjacent to the carbonyl group) into two multiplets occurred. Changes in the chemical shift positions of these signals to lower field occurred from sequential additions of silver ion, along with the increasing separation of their multiplets, whose integration was 1:1. The separation of multiplets originally at δ 3.2 and 2.3 was approximately the same, but greater with dirhodium(III,III) compound **11** than with **10**. In addition, the chemical shift positions of the hydrogens on the aromatic rings moved to lower field upon addition of silver ion, with the change in chemical shift positions being much greater for the phenyl substituent than for the para-substituted ring substituent. This is consistent with the expected π-coordination of silver(I) with arenes, and the preference for the phenyl ring is expected from published reports.[10]

When the order of addition of silver(I) and chiral shift reagents was reversed, there was a surprising change in the outcome. Upon addition of Ag(fod), there was an immediate and continuing separation of signals at δ 3.2 and 2.3 into two multiplets with **11**, but much less so with **10**. In contrast to the opposite mode of addition where the multiplet separations at δ 3.2 and 2.3 were nearly identical, the separation of signals was

dx.doi.org/10.1021/om2003078 |*Organometallics* 2011, 30, 3619–3627

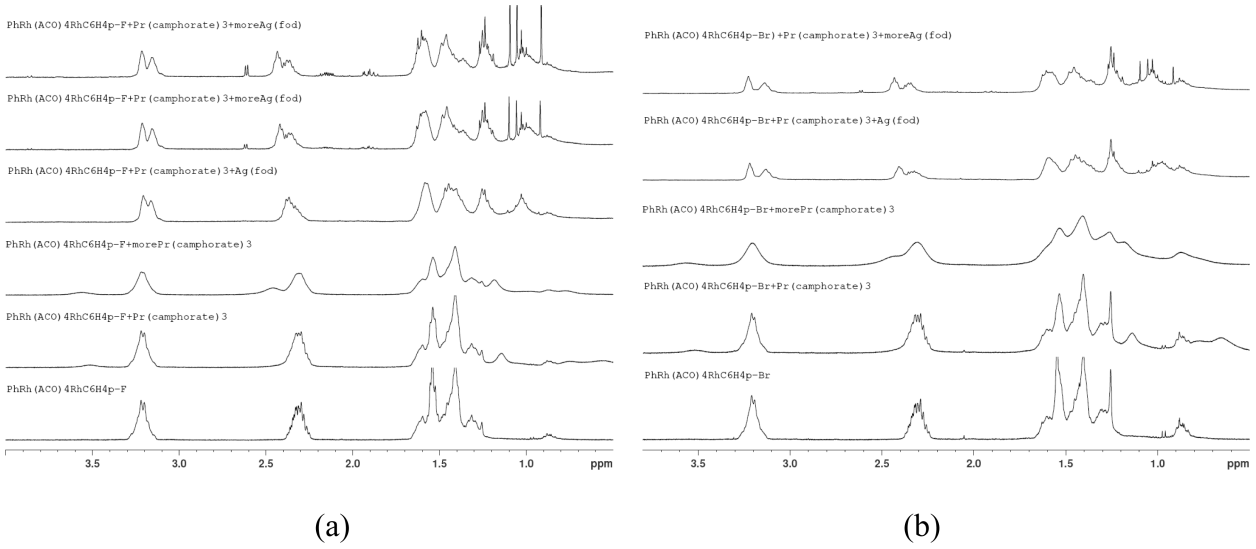


Figure 8. Proton NMR data of the aliphatic proton region for (a) **10** (5.7 mM in $CDCl_3$) and (b) **11** (5.3 mM in $CDCl_3$) with the Pr—Ag reagent (**13a** then **14**).

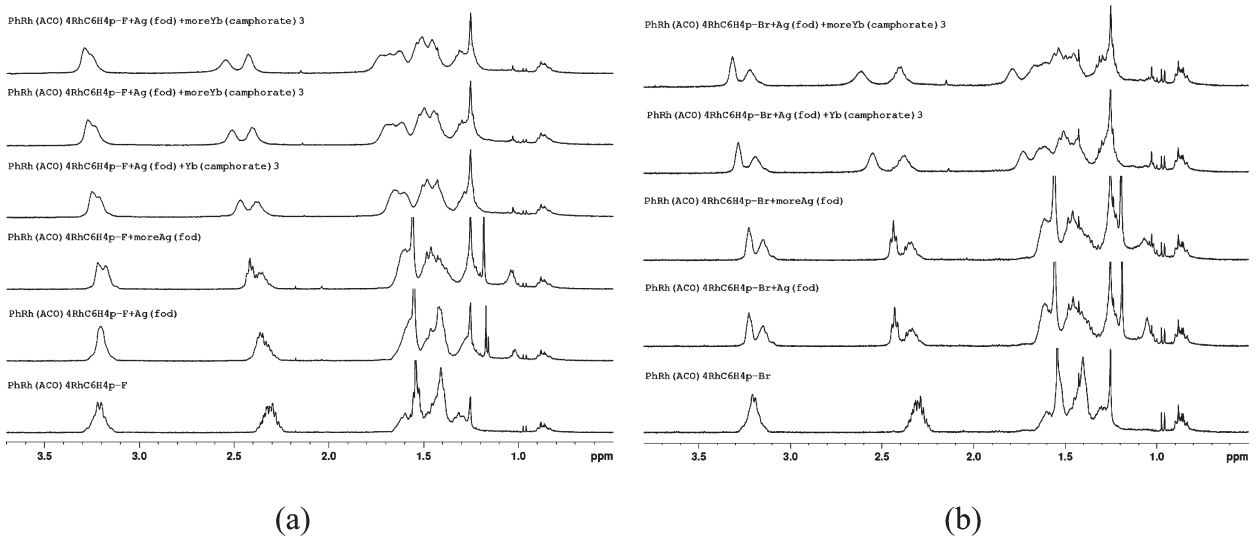
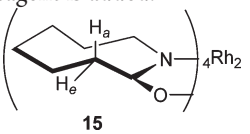


Figure 9. Proton NMR data for the aliphatic proton region of (a) **10** (3.7 mM in $CDCl_3$) and (b) **11** (3.5 mM in $CDCl_3$) with the Yb—Ag reagent (**14** then **13b**).

greater for the resonances at δ 2.3 than for those at δ 3.2 with the initial addition of silver(I). However, the integral ratios of the separated signals were again 1:1. Subsequent addition of the chiral lanthanide complex led to broadening and further separation of the signals (Figure 9). As in the previous mode of addition, the chemical shift positions of the hydrogens on the aromatic rings moved to lower field upon addition of silver ion, with the change in chemical shift positions being much greater for the phenyl substituent than for the para-substituted ring.

How does Ag(fod) induce a separation of signals at δ 3.2 and 2.3? One answer would be the preferential association onto one face of the aryl rings of either **10** or **11**. Preferential association should be on the more open face of the aryl ring, which would be anti to the two amide nitrogens on one face of the dirhodium(III, III) compound, and this association would be expected to influence the signals at δ 2.3 more than those at δ 3.2, which is what is observed. The appearance of what is seen as a triplet in the emerging separation (at 2.4—2.5 ppm in Figure 9) might suggest that the signals that are being separated in this case are the "axial" and "equatorial" hydrogens of the amide ligands (**15**). In other words, signal separation may be due to differentiation of proton signals on each amide, independent of the two aryl substituents. If this explanation is correct, however, Ag(fod) association with the symmetrical diphenyldirhodium(III,III) compound **12** should produce the same outcome, but, as seen from Figure 10, this is not the case. There is no separation of signals when Ag(fod) is added to **12**, and only line broadening occurs when chiral lanthanide reagent is added.



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dx.doi.org/10.1021/om2003078 |*Organometallics* 2011, 30, 3619–3627

An alternative explanation for this NMR signal splitting is that the on−off rate for silver ion association with each aryl group is rapid on the NMR time scale, but association with the phenyl ring moves the associated ligand signals more than association with the substituted aromatic ring. Complexation of Ag(fod) with the unsubstituted phenyl group on the dirhodium(III,III) core is preferred due to its higher electron density,[10] and this is supported by examination of aromatic regions in spectral data for dirhodium complexes **10** and **11** and comparing them with symmetrical diphenyldirhodium(III,III) compound **12** (Figure 11). Introduction of Ag(fod) to solutions of these dirhodium complexes induces proton NMR shifts of aryl group signals. Larger shifts are observed for the proton signals of the unsubstituted phenyl group, while the electron-poor aryl group possessing a fluorine atom has relatively small shifts of proton signals (Figure 11). Thus, the separation of signals at 3.2 and 2.3 ppm arises from the differences in association of the silver salt with aryl groups on opposite sides of dirhodium compounds.

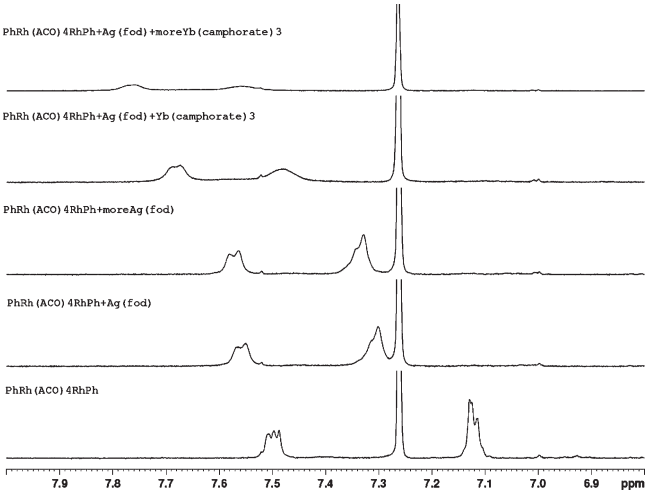

Figure 10. Proton NMR spectra of the aromatic proton region of **12** (3.8 mM in $CDCl_3$) with the Yb−Ag reagent (**14** then **13b**).

When the symmetrical complex **12** was examined by ^{13}C NMR spectroscopy, only one set of signals was detected for each carbon of the bridging lactam ligands. However, two sets of signals were observed for bridging lactam units of the unsymmetrical bisaryldirhodium(III,III) compounds. Those sets come from the 2,2-cis geometrical arrangement of bridging ligands, and attaching different apical ligands to the dirhodium core allows them to be differentiated. Consequent to this observation, we have examined the bisaryldirhodium(III,III) complex by ^{13}C NMR using a chiral silver reagent. The reagent of choice was a chiral silver camphorate derivative prepared according to a published procedure.[11] When this compound was added to **10**, collected ^{13}C NMR data showed no splitting due to coordination

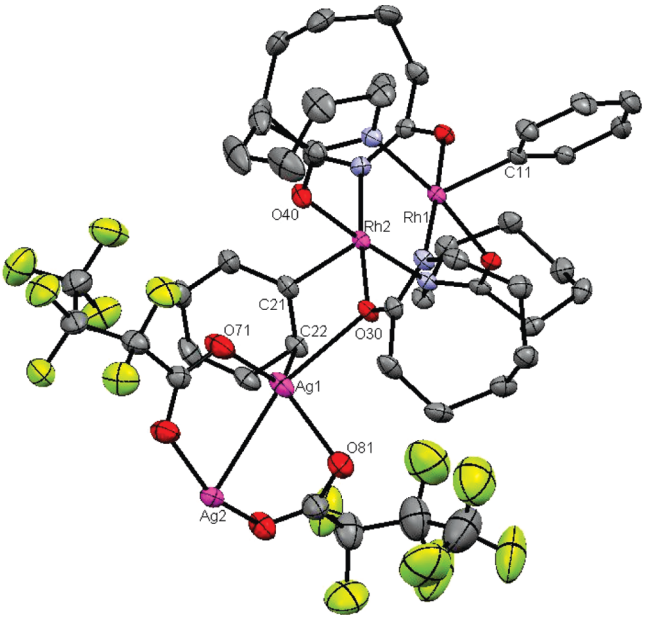

Figure 12. View of the bisphenydirhodium(III,III)−silver salt adduct (**12**). Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Rh−Rh 2.506; Rh−C 2.004 and 2.019; Ag−Ag 2.933; Ag−C 2.544; C−Rh−Rh 159.0 and 155.0; C−Ag−Ag 121.5.

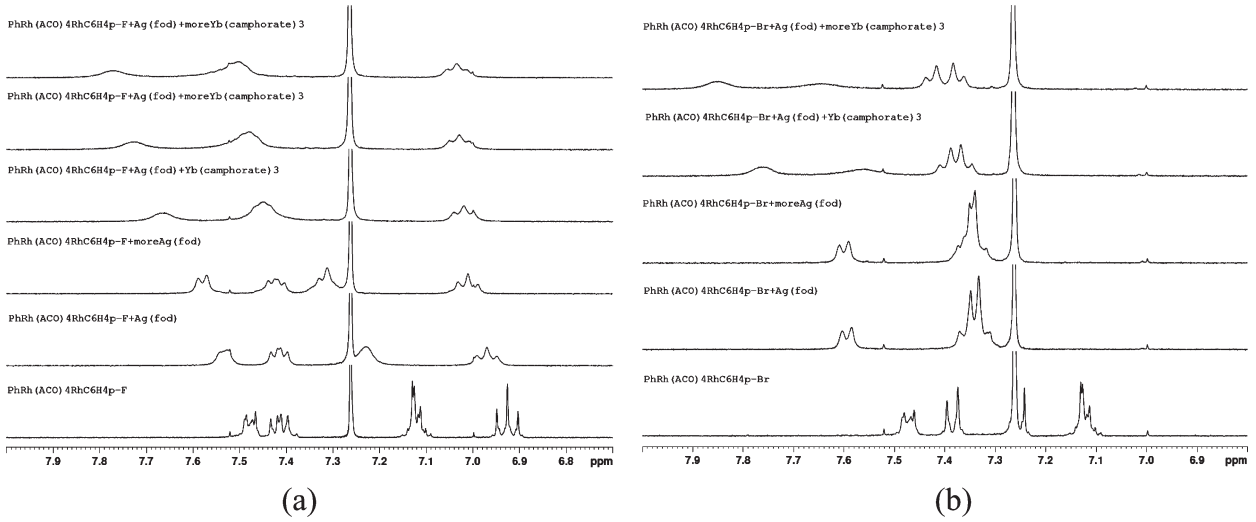

Figure 11. Proton NMR spectra of the aromatic proton regions for (a) **10** (3.7 mM in $CDCl_3$) and (b) **11** (3.5 mM in $CDCl_3$) with the Yb−Ag reagent (**14** then **13b**).

dx.doi.org/10.1021/om2003078 |*Organometallics* 2011, 30, 3619–3627

with the chiral silver reagent and did not provide evidence for dirhodium complex chirality. No splitting of signals from the bridging lactam or aryl groups was detected.

Complex formation between the silver salt, Ag(fod), and phenyl group in bisphenyldirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) (**2**) was confirmed by single-crystal X-ray diffraction (Figure 12). The original diketonate ligand on silver salt **14** was transformed during crystallization into perfluorobutyrate, what most likely resulted through hydrolysis of the initial ligand by residual moisture. The structure depicted in Figure 12 is one of the first intermetallic silver−aryl complexes characterized by X-ray diffraction and is the only one with rhodium. Intermetallic platinum and gold silver−alkyne complexes have been reported.[12] Coordination of the silver ion with a phenyl group of **2** occurs in η^1 fashion and places silver atop the ortho carbon on the phenyl ligand. The Ag−C−C angles are 87.6° and 95.9°, respectively. The silver atom is also coordinated with one of the carboxamidate ligand carbonyl oxygens. The Rh−Rh−C angles of 159.0° and 155.0° did not change significantly compared to the structure without the silver complex.[2] Interestingly, apical phenyl ligands are not coplanar in this complex, and one of the phenyl groups has been rotated about 90° around the rhodium phenyl axis. The Rh−Rh distance has not been affected by complex formation with silver and is shorter only by 0.02 Å.

CONCLUSION

In summary, the chirality of paddlewheel dirhodium(III,III) complexes having different apical aryl substituents that is suggested from X-ray diffraction studies could not be confirmed by chromatographic or NMR spectroscopic analyses. Application of a broad variety of chromatographic and NMR methods did not distinguish between two enantiomers of a presumed racemic mixture. Although unlikely by analogy with the absence of conformational interconversion between biplanar and propeller conformations of bisphenyldirhodium(III,III) tetrakis(caprolactamate),[2] the possibility exists that the two propeller enantiomers are in rapid equilibrium. The absence of evidence for two enantiomers for nonsymmetrical apical aryl-substituted dirhodium(III,III) tetrakis(1-aza-2-cyclooctanoate) using well-established methodologies does suggest the limits of these methods or the existence of an as yet unknown characteristic of these unique organometallic compounds.

EXPERIMENTAL SECTION

General Procedures. Reactions were performed in oven-dried (140 °C) or flame-dried glassware under an atmosphere of dry N_2. Dichloromethane (DCM) was passed through a solvent column prior to use and was not distilled. Methanol was not distilled. Thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F_{254} plates, and the products on the developed chromatograms were visualized by UV lamp (254 nm). Column chromatography was performed using flash chromatography of the indicated system on silica gel (230−400 mesh). Arylboronic acids were purchased from Aldrich and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 on either Bruker Avance 400 or 600 MHz spectrometers. Chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (J) are given in hertz. IR spectra were recorded on a Jasco FTIR 4100 spectrometer. Mass spectra were obtained with a JEOL AccuTOF-CS spectrometer.

Procedure for the Synthesis of Phenyl(*p*-tolyl)dirhodium-(III,III) Tetrakis(1-aza-2-cyclooctanoate) (1). Bisacetonitriledirhodium tetrakis(1-aza-2-cyclooctanoate) $[Rh_2(ACO)_4(CH_3CN)_2]^2$ (48.0 mg, 0.060 mmol), phenylboronic acid (18.3 mg, 2.50 equiv), *p*-tolylboronic acid (20.4 mg, 2.50 equiv), and $NaHCO_3$ (50.4 mg, 10.0 equiv) were dissolved in 6.00 mL of CH_2Cl_2. Copper(II) sulfate (10.0 mol %) in 1.50 mL of MeOH was added to the above solution. The resulting purple mixture was stirred under air at room temperature for 12 h, during which the solution turned greenish-brown. After filtration of $NaHCO_3$ and evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to give the mixture of **1**, **2**, and **3** as a greenish-brown solid in 38% isolated yield (20.0 mg). Column chromatography could not separate these complexes. HPLC analysis on a C-18 column (CH_3CN/iPrOH, 87:13, 1.0 mL/min, 254 nm UV−vis) shows three peaks, which include two homoaryl compounds (**2** and **3**) and one heteroaryl (**1**) compound. Calculation based on HPLC and ^{1}H NMR analyses show the molar ratio of three compounds to be PhPh:PhTol:TolTol = 22:48:26. For HPLC analyses of the mixture, retention times of **2**, **1**, and **3** are 12.0, 14.6, and 17.8 min, respectively. A single crystal suitable for X-ray analysis was obtained from the mixture of **1**, **2**, and **3** in CH_2Cl_2. **1**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.47−7.50 (comp, 2H), 7.33 (d, 2H, J = 8.0 Hz), 7.09−7.11 (comp, 3H), 6.94 (d, 2H, J = 8.0 Hz), 3.15−3.26 (comp, 8H), 2.41 (s, 3H), 2.24−2.31 (comp, 8H), 1.22−1.58 (comp, 32H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 181.9, 136.5, 136.0, 132.8, 126.9, 125.8, 123.6, 53.3, 50.1, 33.4, 32.6, 28.0, 26.1, 25.1; HRMS (ESI) for $C_{41}H_{61}N_4O_4Rh_2$ $[M + H]^+$ calcd 879.2803, found 879.1859; for **2**: HRMS (ESI) for $C_{40}H_{59}N_4O_4Rh_2$ $[M + H]^+$ calcd 865.2646, found 865.1860; for **3**: HRMS (ESI) for $C_{42}H_{63}N_4O_4Rh_2$ $[M + H]^+$ calcd 893.2959, found 893.2034; IR (neat) 2923, 2854, 1658, 1633, 1579, 1454 cm^{-1}.

Procedure for the Synthesis of 1-(3-Phenylphenyl)(2-methoxy-6-naphthyl)dirhodium(III,III) Tetrakis(1-aza-2-cyclooctanoate) (4). $Rh_2(ACO)_4(CH_3CN)_2$ (48.0 mg, 0.060 mmol), 3-biphenylboronic acid (24.0 mg, 2.00 equiv), 6-methoxy-2-naphthaleneboronic acid (24.0 mg, 2.00 equiv), and $NaHCO_3$ (50.4 mg, 10.0 equiv) were dissolved in 6.00 mL of CH_2Cl_2. Copper(II) sulfate (10.0 mol %) in 1.50 mL of MeOH was added to the above solution. The resulting purple mixture was stirred under air at room temperature for 12 h, during which the solution turned yellowish-brown. After filtration and evaporation of the solvent under reduced pressure, the crude product was purified by preparative TLC on silica gel using CH_2Cl_2 as eluent to give the compound mixture of **4**, **5**, and **6** as a yellowish-brown solid in 10% yield. HPLC analysis of the reaction mixture on a C-18 column (CH_3CN/iPrOH, 87:13, 1.0 mL/min, 254 nm UV−vis) shows three peaks, which include two homoaryl compounds (**5** and **6**) and one heteroaryl compound (**4**) having retention times of 10.4 (**6**), 11.9 (**4**), and 13.3 min (**5**). The molar ratio of the three peaks is 22:41:17. A single crystal of **4** suitable for X-ray analysis was obtained by crystallization of **4** in CH_2Cl_2. **4**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.90 (s, 1H), 7.72−7.76 (comp, 4H), 7.63−7.66 (m, 1H), 7.54−7.57 (comp, 2H), 7.46−7.50 (comp, 2H), 7.37−7.42 (comp, 2H), 7.21−7.26 (comp, 2H), 7.11−7.14 (m, 1H), 3.98 (s, 3H), 3.25−3.38 (comp, 8H), 2.35−2.41 (comp, 8H), 1.27−1.66 (comp, 32H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 182.1, 157.7, 156.6, 146.7, 141.9, 140.4, 138.7, 135.6, 135.0, 133.5, 132.5, 129.5, 128.4, 128.2, 127.0, 126.6, 125.8, 125.3, 123.2, 122.8, 118.9, 117.1, 105.3, 55.1, 50.2, 33.3, 32.7, 28.0, 26.0, 25.1; HRMS (ESI) for $C_{51}H_{67}N_4O_5Rh_2$ $[M + H]^+$ calcd 1021.3222, found 1021.3059; IR (neat) 2923, 2854, 1648, 1572, 1541, 1454 cm^{-1}.

Procedure for the Synthesis of *p*-(*N*-*p*-Toluenesulfonylpyrolinamido)phenyl Boronic Acid Pinacol Ester (7a). L-Proline (1.00 g, 8.70 mmol) and *p*-toluenesulfonyl chloride (1.70 g, 8.90 mmol, 1.02 equiv) were dissolved in 30.0 mL of dry DCM. Triethylamine (3.00 mL, 2.50 equiv) was then added dropwise. The resulting mixture was stirred at room temperature for 16 h. Dilute hydrochloric

acid (0.50 M) was added to the mixture until the aqueous layer was at pH = 3. The mixture was washed with brine and extracted with DCM. The organic layer was dried over anhydrous magnesium sulfate and decanted. After evaporation of DCM, 1.83 g of *N*-*p*-toluenesulfonyl-L-proline was obtained as white solid in 78% yield and, without further purification, was dissolved in 10.0 mL of dry DCM. Thionyl chloride (1.00 mL, 2.00 equiv) was added, and the resulting mixture was stirred under nitrogen at room temperature for 16 h. The solvent was then evaporated under reduced pressure to give a yellow, viscous liquid that was dissolved in 30.0 mL of dry DCM. 4-Aminophenylboronic acid pinacol ester (0.60 g) was added to the DCM solution, followed by triethylamine (3.00 mL). The resulting mixture was stirred at 0 °C for 1 h. After evaporation of the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel using 2:1 (v/v) hexanes/ethyl acetate as eluent to give 1.13 g (2.40 mmol) of **7a** as a pale yellow solid in 69% overall yield from L-proline. The D-proline and racemic DL-proline derivatives were prepared using the same procedure and in the same overall yields. **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.71−7.76 (dd, 4H, J = 12.0, 8.0 Hz), 7.56−7.58 (d, 2H, J = 8.0 Hz), 7.32−7.34 (d, 2H, J = 8.0 Hz), 4.13−4.16 (m, 1H), 3.55−3.60 (m, 1H), 3.18−3.24 (m, 1H), 2.40 (s, 3H), 2.27−2.32 (m, 1H), 1.48−1.82 (comp, 3H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 144.7, 140.1, 135.7, 132.5, 130.1, 127.9, 118.7, 83.7, 63.0, 50.1, 29.5, 24.8, 24.4, 21.6; HRMS (ESI) for $C_{24}H_{32}BN_2O_5S$ $[M + H]^+$ calcd 471.2125, found 471.2039; IR (neat) 3265, 2989, 2972, 1681, 1598, 1538, 1396, 1342 cm^{-1}.

Procedure for the Synthesis of *p*-(*N*-*p*-Toluenesulfonylpyrolinamido)phenyl Boronic Acid (8a). Compound **7** (470 mg, 1.00 mmol) and sodium periodate (642 mg, 3.00 equiv) were stirred in 8.00 mL of a 4:1 mixture of THF and water for 1 h. Then aqueous hydrochloric acid (1.00 M, 0.70 mL) was added to the suspension. The resulting yellow mixture was stirred at ambient temperature for 6 h, then diluted with water and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over anhydrous sodium sulfate, and decanted. After evaporation of the solvent, 360 mg of a light yellow solid of **8** was obtained in 93% yield (0.93 mmol). D-Proline and racemic DL-proline derivatives were prepared using the same procedure and in the same overall yields. **8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.17 (d, 2H, J = 8.0 Hz), 7.70−7.76 (dd, 4H, J = 16.0, 8.0 Hz), 7.36 (d, 2H, J = 8.0 Hz), 4.19−4.22 (m, 1H), 3.57−3.65 (m, 1H), 3.22−3.28 (m, 1H), 2.42 (s, 3H), 2.25−2.35 (m, 1H), 1.81−1.84 (m, 1H), 1.67−1.80 (comp, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 144.7, 141.3, 136.7, 134.9, 132.5, 130.1, 127.9, 119.0, 63.0, 60.4, 24.5, 21.6, 21.0; HRMS (ESI) for $C_{18}H_{22}BN_2O_5S$ $[M + 1]^+$ calcd 389.1342, found 389.1316; IR (neat) 3378, 3338, 2974, 2954, 1686, 1595, 1532, 1327 cm^{-1}.

Procedure for the Synthesis of Bis[*p*-(*N*-*p*-toluenesulfonylpyrolinamidophenyl)]dirhodium(III) Tetrakis(1-aza-2-cyclooctanoate) (9). $Rh_2(ACO)_4(CH_3CN)_2$ (48.0 mg, 0.060 mmol), compound **8a** (116 mg, 5.00 equiv), and $NaHCO_3$ (50.4 mg, 10.0 equiv) were dissolved in 6.00 mL of CH_2Cl_2, and copper(II) sulfate (10.0 mol %) in 1.50 mL of MeOH was added. The resulting purple mixture was stirred under air at room temperature for 12 h, during which the solution turned yellowish-brown. After filtration and evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using 1:2 hexanes/ethyl acetate as eluent to give compound **9** as yellowish-brown solid in 40% yield (34.0 mg, 0.024 mmol). D-Proline and racemic DL-proline derivatives were prepared using the same procedure. **9**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 2H), 7.73−7.78 (comp, 4H), 7.34−7.48 (comp, 8H), 6.85−6.87 (comp, 4H), 4.14−4.22 (comp, 2H), 3.78 (s, 4H), 3.58−3.63 (comp, 2H), 3.19−3.25 (comp, 4H), 2.44 (s, 6H), 2.26−2.34 (comp, 4H), 1.34−1.81(comp, 14H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.0, 168.5, 156.5, 144.4, 136.3, 132.6, 130.5, 129.9, 128.8, 127.8, 121.6, 119.9, 117.7, 114.0, 62.8, 55.4, 50.0, 33.4, 32.6, 29.6, 28.0, 26.0, 25.0, 24.3, 21.5; HRMS (ESI) for $C_{64}H_{86}N_8NaO_{10}Rh_2S_2$ $[M + Na]^+$ calcd 1419.3916, found 1419.3378; IR (neat) 3342, 2927, 1677, 1597, 1581, 1510, 1342, 1158 cm^{-1}.

General Procedure for NMR Analyses with Chiral Shift Reagents. The bisaryldirhodium(III,III) (1-aza-2-cyclooctanoate) was dissolved in $CDCl_3$, and proton NMR data were obtained. Next, addition of lanthanide shift reagent or silver(I) salt followed portionwise. Proton NMR spectra were collected after addition of each shift reagent portion.

■ ASSOCIATED CONTENT

Supporting Information. NMR spectra of all new compounds. Crystallographic data for compounds **1**, **4**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We are grateful to the National Science Foundation (CHE-0456911) for their generous support. We also wish to thank J.-H. Xie for his early efforts to develop a detailed understanding of bisaryl dirhodium(III,III) carboxamidates.

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