

# Reactivity Differences in the Syntheses of Chelating N-Heterocyclic Carbene Complexes of Rhodium Are Ascribed to Ligand Anisotropy

José A. Mata,<sup>†</sup> Anthony R. Chianese,<sup>†</sup> John R. Miecznikowski,<sup>†</sup> Macarena Poyatos,<sup>‡</sup> Eduardo Peris,<sup>‡</sup> Jack W. Faller,<sup>\*,†</sup> and Robert H. Crabtree<sup>\*,†</sup>

Chemistry Department, Yale University, 225 Prospect Street, New Haven, Connecticut 06520, and Departamento Química Inorgánica i Orgánica, Universitat Jaume I, Av. de Vicent Sos Baynat s/n, E-12071 Castellón, Spain

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Chelating bis(imidazolium) salts having  $(\text{CH}_2)_n$  chains of different lengths ( $n = 1-4$ ) linking the diazole rings show very large reactivity differences on metalation with  $[(\text{cod})\text{RhCl}]_2$ . Long linkers favor a square-planar Rh(I) product, while short linkers favor octahedral Rh(III). We ascribe the origin of the effect to the restricted rotation of the highly sterically anisotropic diazole rings and the different preferred orientations of these rings as  $n$  changes. Defining the  $x$  and  $y$  axes as the Rh–carbene bond directions, we find that with short linkers the diazole rings tend to be oriented close to the  $xy$  plane. This tends to favor Rh(III) because these complexes,  $[\text{Rh}(\text{bis-carbene})\text{I}_2(\text{OAc})]$ , have the lowest steric hindrance in the  $xy$  plane. With long linkers, the diazole rings tend to be aligned face to face along the  $\pm z$  axis. This tends to favor Rh(I) because these complexes,  $[(\text{cod})\text{Rh}(\text{bis-carbene})]\text{PF}_6$ , have the lowest steric hindrance along the  $\pm z$  axis. Crystallographic studies are reported. Electrospray MS data provide evidence for strong metal–carbene binding.

## Introduction

N-heterocyclic carbene (NHC) ligands derived from imidazolium salts are finding increasing use in organometallic chemistry and homogeneous catalysis.<sup>1</sup> We and others have been particularly interested in chelate and pincer carbenes as a way of extending the area to more complex ligands.<sup>2</sup> In such cases, the traditional metalation procedure involving deprotonation of the imidazolium precursor with strong bases is no longer useful,<sup>3</sup> because acidic groups very sensitive to strong bases are now present in many of the linkers. In such cases, milder procedures are needed that are compatible with more sensitive functionalities.

Two such mild procedures have been most widely adopted: transmetalation and direct metalation. Transmetalation typically involves treatment of the imidazo-

lium salt with  $\text{Ag}_2\text{O}$  to form the silver carbene complex, followed by transmetalation to a species such as  $(\text{MeCN})_2\text{PdCl}_2$  to give the metal carbene complex.<sup>4</sup> Even simpler is direct metalation, in which the reaction of the imidazolium salt takes place with a metal precursor, such as  $[(\text{cod})\text{RhCl}]_2$ , in the presence of a mild base such as  $\text{NaOAc}$  and other additives. In this case, the imidazolium salt is not deprotonated directly but only on interaction with the metal, most likely in the form of an acetate complex. If so, the reaction can then be considered as a type of  $\sigma$ -bond metathesis.

Prior work on chelating NHC complexes has tended to involve only the  $\text{CH}_2$  linker, although Green and co-workers observed a remarkable increase in the thermal stability of  $\text{NiMe}_2(\text{bis-NHC})$  using a  $(\text{CH}_2)_2$  linker as compared to a  $\text{CH}_2$  linker.<sup>5</sup> We now look at  $(\text{CH}_2)_n$ , where  $n = 1-4$ , and find a strong effect on the chemistry. We find that three product types are possible: chelates of Rh(I) and Rh(III) and 2:1 binuclear complexes of Rh(I) in which the ligand does not act as a chelate. For simplicity, we refer to these as Rh(I), Rh(III), and bis-Rh(I) species. One of the three tends to be formed preferentially, depending on the linker length. As discussed below, this effect depends on differences in the preferential conformation of the ligands depend-

\* To whom correspondence should be addressed. E-mail: john.faller@yale.edu (J.W.F.); robert.crabtree@yale.edu (R.H.C.). Fax: (203) 432-6144.

<sup>†</sup> Yale University.

<sup>‡</sup> Universitat Jaume I.

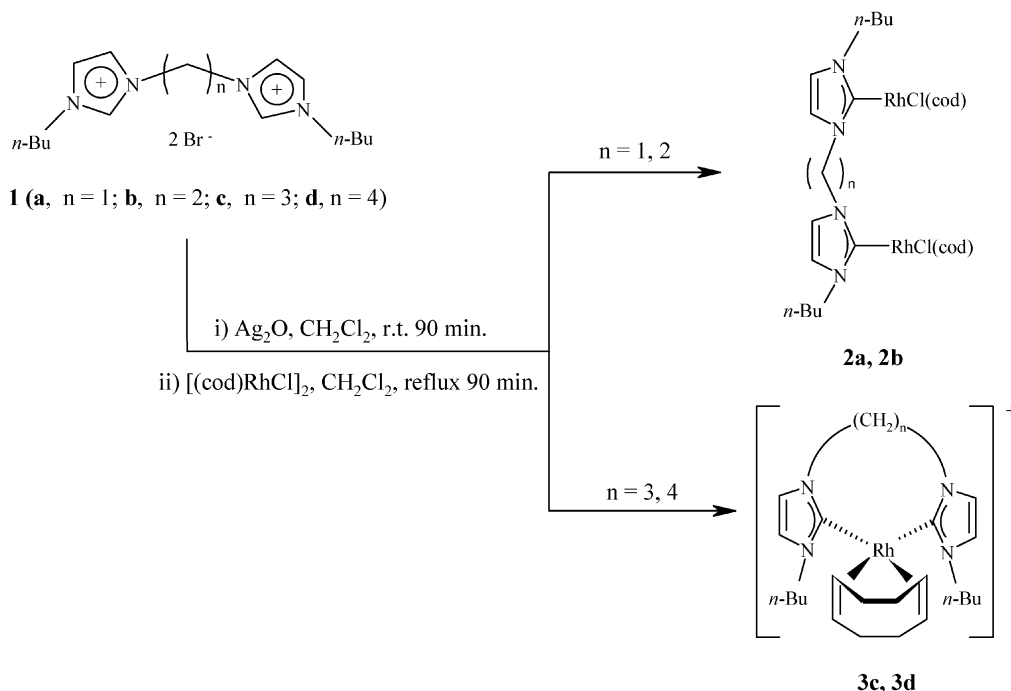
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**Scheme 1. Synthesis of Bis-Rh(I) and Rh(I) Complexes by Transmetalation with Reflux in a Two-Step Process**

ing on the linker length. When the two rings are linked by a short linker, they prefer a coplanar chelating arrangement that is sterically most compatible with octahedral Rh(III). Alternatively, they can still stabilize Rh(I), but only if they cease to chelate and instead form a bis-Rh(I) complex where the carbene rings are out of plane with respect to the square plane of each Rh(I). A long linker allows both rings to adopt an out-of-plane conformation even when chelating, and thus, such chelates can readily form Rh(I) species.

**Results****Syntheses of Imidazolium Ligand Precursors.**

The bis(imidazolium) salts were readily accessible by reaction of *n*-butylimidazole with the corresponding dibromides (e.g. dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane, and 1,4-dibromobutane). The products are colorless crystalline solids (except **1d**, which is an oil) and are very hygroscopic, with spectral properties analogous to those found for the many similar compounds that have been reported.<sup>6</sup>

**Transmetalation Reaction at Reflux.** Transmetalation has proved to be a promising procedure to obtain NHC complexes.<sup>7</sup> We report the synthesis of rhodium complexes of our NHCs by transmetalation from the corresponding silver carbene derivatives by a two-step

process. The first step involves deprotonation of the imidazolium salt with silver oxide to form the silver carbene species.<sup>8</sup> These can be isolated as a white powder, although we used them in situ after filtering through Celite to remove unreacted silver oxide and other solids. The addition of  $[(\text{cod})\text{RhCl}]_2$  immediately gave the desired product and a white suspension of silver chloride. The reaction was allowed to continue for 90 min at reflux to achieve completion. Depending on the linker length, two different kinds of compounds **2** and **3** were predominantly formed (Scheme 1).

When the linker is short ( $n = 1, 2$ ), compounds of type **2** are formed; we will refer to these as bis-Rh(I) complexes. In contrast, for the long linkers ( $n = 3, 4$ ), bis-chelating imidazolium complexes of type **3** are formed. Complex **2a** was obtained in a very low yield (5%) and was only characterized by NMR and mass spectrometry, although compounds similar to **2a** and **2b** have previously been reported with  $\text{R} = \text{Me}$ .<sup>9</sup> Purification was achieved by gradient column chromatography on silica gel. The large difference in retention times among **2**, **3**, and the starting materials makes this procedure very convenient. Elution with dichloromethane removes any unreacted  $[(\text{cod})\text{RhCl}]_2$ ; subsequent elution with a mixture at 50% (v/v) dichloromethane–acetone gives the bis-Rh(I) species **2**. Finally, elution with a solution of  $\text{KPF}_6$  in acetone gives the cationic bis-chelating complexes **3**. All these compounds are very stable to heat and air, even in solution. For the chelating complexes

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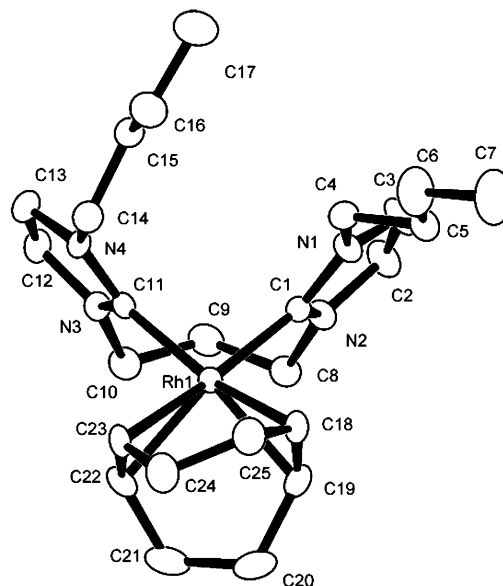
**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for **3c**, **3b**, and **6d**

<b>3c</b>		<b>3b</b>		<b>6d</b>	
		Rh–C(carbene)			
Rh(1)–C(1)	2.038(3)	Rh(1)–C(1)	2.034(4)	Rh(1)–C(1)	2.081(4)
Rh(1)–C(11)	2.029(3)	Rh(1)–C(10)	2.048(4)	Rh(1)–C(12)	2.082(4)
		Rh–C(cod)/Rh–CO			
Rh(1)–C(18)	2.185(3)	Rh(1)–C(17)	2.201(4)	Rh(1)–C(19)	1.896(5)
Rh(1)–C(19)	2.198(3)	Rh(1)–C(18)	2.184(4)	Rh(1)–C(20)	1.892(4)
Rh(1)–C(22)	2.175(3)	Rh(1)–C(21)	2.187(4)		
Rh(1)–C(23)	2.214(3)	Rh(1)–C(22)	2.198(5)		
		C–O			
				C(19)–O(1)	1.127(5)
				C(20)–O(2)	1.132(4)
		C(imid)–C(imid)			
C(2)–C(3)	1.342(4)	C(2)–C(3)	1.337(6)	C(2)–C(3)	1.335(5)
C(12)–C(13)	1.346(5)	C(11)–C(12)	1.334(6)	C(13)–C(14)	1.343(5)
		C(carbene)–N			
C(1)–N(1)	1.363(4)	C(1)–N(1)	1.367(5)	C(1)–N(1)	1.353(5)
C(1)–N(2)	1.360(4)	C(1)–N(2)	1.352(5)	C(1)–N(2)	1.350(5)
C(11)–N(3)	1.361(4)	C(10)–N(3)	1.362(5)	C(12)–N(3)	1.360(4)
C(11)–N(4)	1.355(4)	C(10)–N(4)	1.363(5)	C(12)–N(4)	1.348(5)
		Bite Angle (C–Rh–C)			
C(1)–Rh(1)–C(11)	87.60(12)	C(1)–Rh(1)–C(10)	84.0(2)	C(1)–Rh(1)–C(12)	91.0(1)
		N–C(carbene)–N			
N(1)–C(1)–N(2)	103.8(3)	N(1)–C(1)–N(2)	104.1(3)	N(1)–C(1)–N(2)	104.9(3)
N(3)–C(11)–N(4)	104.2(3)	N(3)–C(10)–N(4)	103.3(4)	N(3)–C(12)–N(4)	104.6(3)

**3** as chloride salts, some decomposition was observed over long periods (2 days). The compounds are more stable when the counterion is changed to the noncoordinating  $\text{PF}_6^-$ . The complete NMR assignments of **2** and **3** have been made by HETCOR and COSY experiments. The  $^1\text{H}$  NMR spectra of both types of complexes (**2** and **3**) show diastereotopic protons for the wingtip *n*-Bu groups. In both cases the origin of the diastereotopy resides in the restricted rotation around the metal–carbene bond. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra show the characteristic doublets assigned to C–Rh coupling for the carbene and cod vinyl moieties. The C(carbene) resonances appear at 181.1 ppm ( $^1J_{\text{C–Rh}} = 50.9$  Hz) for **2b**, 181.1 ppm ( $^1J_{\text{C–Rh}} = 53.7$  Hz) for **3c**, and 181.1 ppm ( $^1J_{\text{C–Rh}} = 52.9$  Hz) for **3d**; these values lie in the usual range. The complexes have two sets of signals for the vinylic carbons of the cod ligand for compound type **3** (syn and anti to linker) and four sets for the bis-Rh(I) compounds. In the latter, the vinylic carbons trans to Cl appear at lower frequencies and with higher coupling constants due to the lower trans influence of Cl. The NMR spectra of the two types of complexes, **2** and **3**, are therefore distinctive.

Positive ion ESMS analyses of the isolated products **2** in MeOH showed a low-intensity peak for  $[\text{M}^+ - \text{Cl}]$  ( $m/z$  718 for **2a** and  $m/z$  732 for **2b**) with the characteristic isotope distribution for an ion containing two rhodium atoms. The most intense peak appears for  $[\text{M}^+ - \text{Rh} - \text{cod} - 2\text{Cl}]$  ( $m/z$  472 for **2a** and  $m/z$  486 for **2b**). For compounds **3** the most intense peak is for  $[\text{M}^+]$  ( $m/z$  499 for **3c** and  $m/z$  514 for **3d**). In both cases (**2** and **3**), with increasing cone voltage, the last fragment observed corresponds to the bis-NHC ligand bound to Rh, consistent with strong metal–carbene bonding.

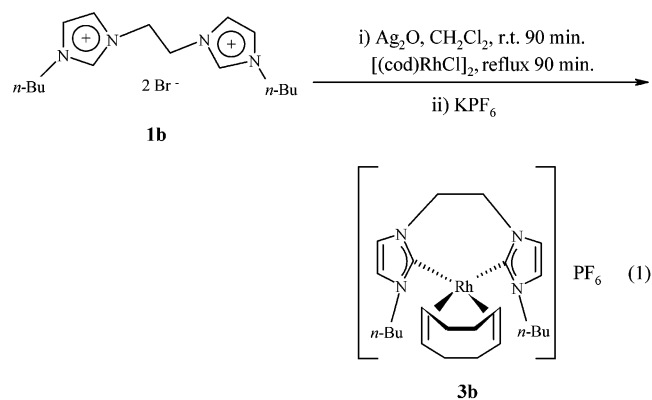
**Crystal Structure of 3c.** Crystals of **3c** suitable for X-ray diffraction were obtained by slow evaporation from a concentrated dichloromethane–hexanes solution, and the results confirmed the proposed structure. Selected bond lengths and angles are listed in Table 1.

**Figure 1.** ORTEP diagram of **3c**, showing 50% probability ellipsoids. Hydrogen atoms and the counterion ( $\text{Cl}^-$ ) are omitted for clarity.

The geometry at rhodium (Figure 1) is square planar, with the two imidazole rings of the chelating ligand (bite angle  $87.60(12)^\circ$ ) at a dihedral angle ( $\alpha$ ) of ca.  $78^\circ$ . The macrocyclic eight-membered ring adopts a boat-chair conformation, known for cyclooctane. The Rh–C(carbene) bond lengths of 2.038(3) and 2.029(3) Å are unexceptional. The C–C distances in the imidazole units are short (1.342(4) and 1.346(5) Å), as always observed for NHCs. The cod ligand adopts a slightly twisted conformation.

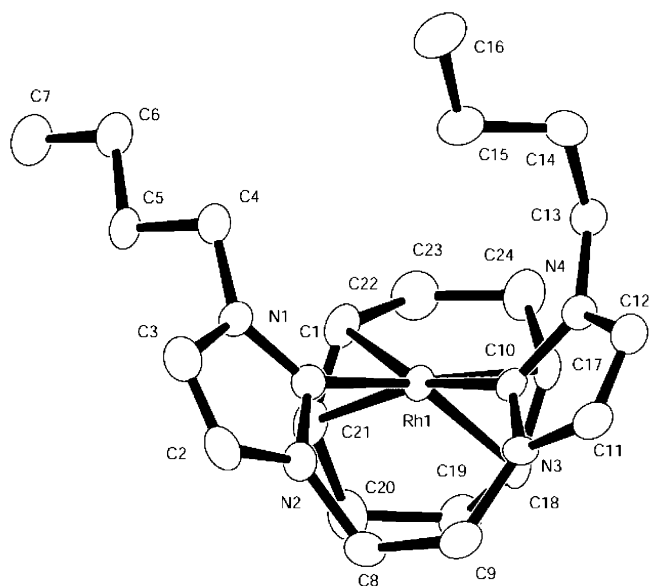
**Alternative Procedure for the Synthesis of 3b.** A surprising result was observed for the  $n = 2$  precursor ligand (**1b**). When the transmetalation reaction was carried out in one pot in the presence of the silver oxide throughout, without filtration, the chelate complex **3b**

was observed instead of the bis-Rh(I) species **2b** seen under the above conditions. This rearrangement happens only for this linker ( $n = 2$ ) (eq 1).

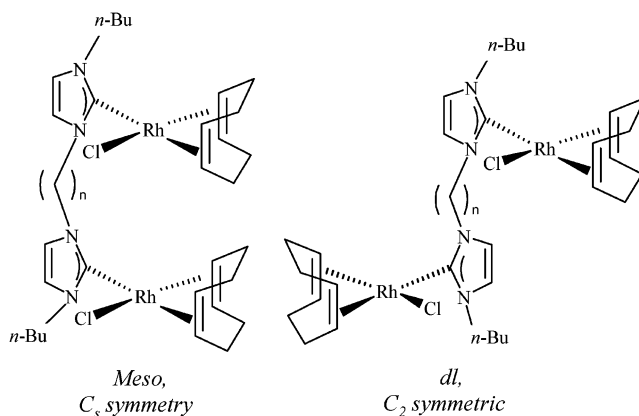


**Crystal Structure of 3b.** Crystals of compound **3b** suitable for X-ray diffraction were obtained by slow evaporation from a concentrated dichloromethane–hexanes solution. Selected bond lengths and angles are listed in Table 1. The geometry at rhodium (Figure 2) is square planar, with the two imidazole rings of the chelating ligand (bite angle  $84.0(2)^\circ$ ) at a dihedral angle ( $\alpha$ ) of ca.  $63.5^\circ$ . The seven-membered ring adopts a boat conformation, also known for cycloheptane. The Rh–C(carbene) bond lengths are 2.034(4) and 2.048(4) Å, as expected for NHCs. The C–C distances in the imidazole units are short (1.337(6) and 1.334(6) Å), and the cod ligand is a slightly twisted as before.

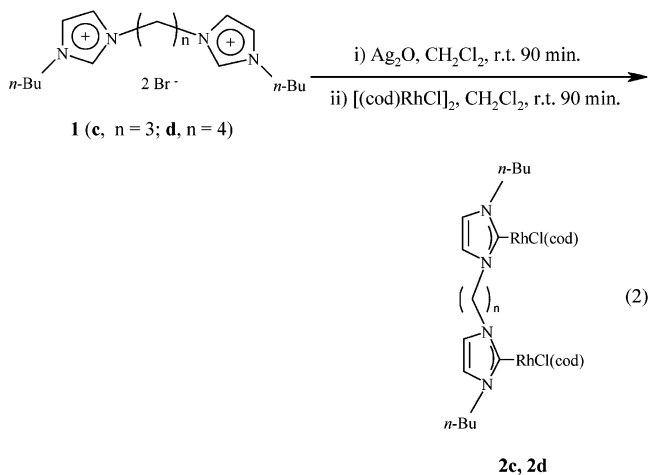
**Transmetalation at Room Temperature.** If we modify the conditions and avoid reflux in the transmetalation step, different reaction products are obtained for the long linkers. When the transmetalation is carried out at  $25^\circ\text{C}$ , the products are bis-Rh(I) species for all values of  $n$  (**2a–d**) (eq 2). Attempts to convert the isolated bis-Rh(I) complexes into the chelates (**3**) were unsuccessful, at least in refluxing dichloromethane with or without added silver oxide.



**Figure 2.** ORTEP diagram of **3b**, showing 50% probability ellipsoids. Hydrogen atoms and the counterion ( $\text{PF}_6^-$ ) are omitted for clarity.



**Figure 3.** *Meso* and *dl* diastereomers of bis-Rh(I) complexes **2a–d** resulting from the hindered rotation of the Rh–C(carbene) bond.

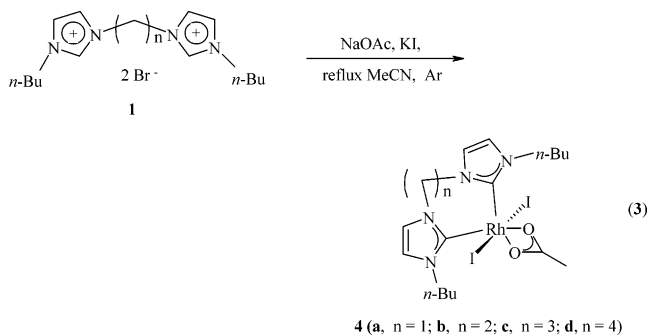


*Meso* ( $C_s$ ) and *dl* ( $C_2$ ) forms are seen for **2b–d**, resulting from the hindered rotation of the Rh–C(carbene) bond (Figure 3).<sup>10</sup> For **2a**, only one set of NMR resonances is observed for the protons of the imidazole ring, indicating that only one diastereomer is formed. In the *meso* diastereomer, the protons of the methylene linker would be inequivalent; therefore, an AB pattern would be expected. In the *dl* diastereomer, the methylene protons are equivalent and would resonate as a 2H singlet. In fact, a singlet is observed for **2a**, indicating exclusive formation of the *dl* isomer. This is consistent with the reported  $^1\text{H}$  NMR spectra and crystal structures of similar prior examples.<sup>9</sup> As the linker becomes longer, the communication between the two metal centers becomes weaker, which leads to an increasing proportion of the *meso* diastereomer. For  $n = 2$  (**2b**), one diastereomer is formed almost exclusively (95:5 ratio). Although NMR spectroscopy cannot distinguish between the *meso* and *dl* isomers for the  $n = 2$  case, a closely related compound was shown to be the *dl* isomer by X-ray diffraction.<sup>9a,c</sup> It is very likely that our major product is also the *dl* isomer. For  $n = 3$  (**2c**), a 60:40 (*dl*:*meso*) mixture of diastereomers is formed, and for  $n = 4$  the two isomers are in a 50:50 ratio, as expected when the metal centers are too far apart to influence the chirality of the other.

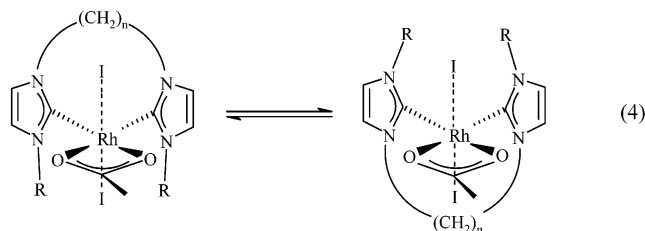
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**Direct Metalation.** We have previously found<sup>11</sup> that direct metalation is possible with NaOAc as external base in the presence of KI as coligand. Although the mechanism is not well understood, the metalation is very general and occurs for a variety of bases (NaOAc, NEt<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and KO-*t*-Bu) and reflux temperatures (refluxing MeCN, bp 82 °C; refluxing EtCN, bp 108 °C). For all linker lengths the Rh(III) species **4** are obtained (eq 3).



Purification is again possible by column chromatography, as for **2** and **3**. The retention time on silica gel is shorter than for **2** and **3**, and dichloromethane–acetone (3/1 v/v) was enough to elute the complexes. For the short linkers the yields are moderate to high (*n* = 1, yield 74%; *n* = 2, yield 42%), but for *n* = 3, 4, yields are low (ca. 10%). The complexes were fully characterized, and the NMR spectra were similar to those previously reported for this class of complexes. For short linkers (*n* = 1, 2), the protons of the methylene linker are equivalent and resonate as a 2H (**4a**) or 4H (**4b**) singlet, indicating a boat-to-boat interconversion at room temperature (eq 4). For the longer *n* = 3, 4 cases, no



interconversion between the different conformations of the macrocyclic eight- or nine-membered rings was observed. The linker (CH<sub>2</sub>)<sub>*n*</sub> protons become diastereotopic, as the process shown in eq 4 becomes slow. No significant changes for compounds **4c** and **4d** were observed on varying the temperature up to 120 °C.<sup>12</sup>

Positive ion ESMS analysis of the isolated products **4** in MeOH showed an intense peak for [M<sup>+</sup> + Na] (*m/z* 713 for **4b**, *m/z* 727 for **4c**, *m/z* 741 for **4d**). Increasing the cone voltage resulted in the loss of acetate and iodide; the last fragment observed is the [bis(NHC)-Rh]<sup>+</sup> fragment, as for **2** and **3** (*m/z* 391 [M<sup>+</sup> – CH<sub>3</sub>COO – 2I] for **4c**), consistent with strong metal–carbene bonding.

Very recently, Field et al. have reported the syntheses of chelating NHC complexes of Rh(I) with *n* = 1. The procedure used involves direct metalation using a basic metal and a completely halide-free medium.<sup>13</sup>

**Carbonyl Derivatives.** The cod ligand in complexes **2c,d** and **3c,d** was easily displaced by passing CO (1 atm) through a dichloromethane solution for 10 min (Scheme 2). IR spectroscopy shows two strong bands in the carbonyl region indicating a *cis* configuration. The <sup>1</sup>H NMR spectra of **5c,d** show one set of signals for the bis-chelating ligand, in contrast to the *meso/dl* pairs seen for **2c,d**. Substitution of the bulkier cod by the very small COs leads to decreased steric interactions and free rotation around the metal–NHC bond, as seen previously.<sup>7a</sup> One compound is now observed, as the *meso* and *dl* atropisomers now interconvert on the NMR time scale.

The <sup>13</sup>C NMR spectra of **6c,d** show two doublets corresponding to the two different carbons directly bonded to Rh (187.9 ppm (<sup>1</sup>*J*<sub>CO–Rh</sub> = 50.4 Hz) and 171.3 ppm (<sup>1</sup>*J*<sub>C(carbene)–Rh</sub> = 45.6 Hz) for **6c** and 186.6 ppm (<sup>1</sup>*J*<sub>CO–Rh</sub> = 56.2 Hz) and 169.7 ppm (<sup>1</sup>*J*<sub>C(carbene)–Rh</sub> = 45.5 Hz) for **6d**). On the other hand, in the <sup>13</sup>C NMR spectra of **5b–d**, three high-frequency doublets are observed; two arise from the inequivalent carbonyl carbons and the third from the rhodium-bound carbene. The resonances are assigned by analogy to similar compounds described by Field.<sup>13</sup> The carbonyl carbon *trans* to the NHC ligand shows a weaker coupling to <sup>103</sup>Rh (<sup>1</sup>*J*<sub>CO–Rh</sub> = 53.4 Hz, for **5d**), compared to that *trans* to chloride (<sup>1</sup>*J*<sub>CO–Rh</sub> = 74.3 Hz, for **5d**). This is indicative of the higher *trans* effect of the NHC ligand.

**Crystal Structure of 6d.** Crystals of compound **6d** suitable for X-ray diffraction were obtained by slow evaporation from a concentrated dichloromethane–hexanes solution. Selected bond lengths and angles are listed in Table 1. The geometry at Rh (Figure 4) is square planar, with the two imidazole rings of the chelating ligand (bite angle 91.0(1)°) at a dihedral angle (α) of ca. 85°. The macrocyclic nine-membered ring adopts a pseudo-twist-boat conformation similar to the previous cases. The Rh–CO distances of 1.896(5) and 1.892(4) Å lie in the expected range. This is the second crystal structure reported for a Rh–NHC group *trans* to a carbonyl group.<sup>13</sup> As a consequence, the Rh–C(carbene) bond lengths (2.081(4) and 2.082(4) Å) are elongated by 0.03 Å compared to the standard Rh–C(carbene) length found for analogous compounds.<sup>14</sup>

## Discussion

We report reactivity effects that we ascribe to the high anisotropy<sup>15</sup> of the diazole rings of the N-heterocyclic carbene. The widely used phosphine ligands are cone-shaped, in contrast to the fan-shaped NHCs, which have a sterically unhindered slim axis orthogonal to the bulky imidazole ring plane.<sup>16</sup> When free rotation around the metal–NHC bond is possible, the NHC is expected to

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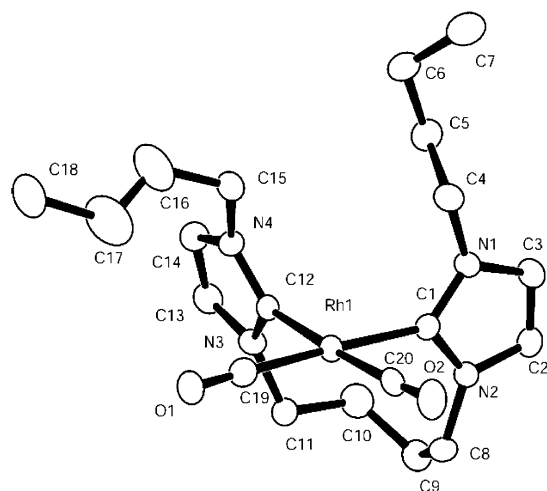
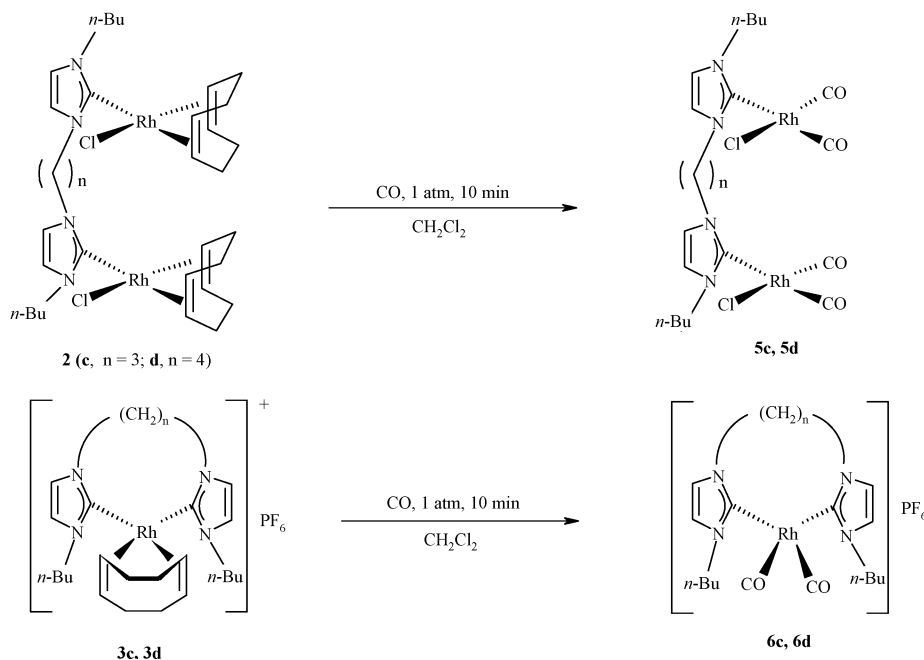
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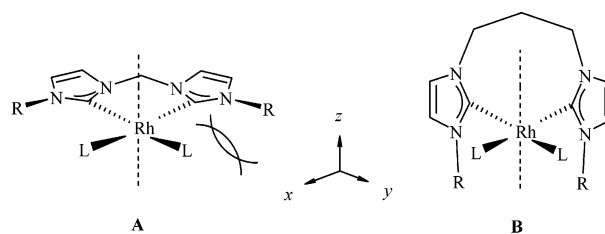
## Scheme 2. Synthesis of the Carbonyl Derivatives



**Figure 4.** ORTEP diagram of **6d**, showing 50% probability ellipsoids. Hydrogen atoms and the counterion ( $\text{PF}_6^-$ ) are omitted for clarity.

rotate to present its slim axis to the bulky plane of the complex to minimize steric interference between the NHC and the rest of the complex. The full steric effect of the NHC's bulky axis may therefore be muted. As an example, monodentate carbene complexes of  $d^8$  square-planar metals always have the plane of the NHC essentially perpendicular to the sterically crowded square plane of the complex.<sup>17</sup> The bulky NHC diazole ring plane is now directed toward the empty positions in the  $\pm z$  direction, the slim axis of the complex, and the slim NHC axis lies in the bulky  $xy$  plane of the complex. Previous NMR studies of monocarbene complexes indicate<sup>7a,18</sup> that the barriers for rotation around the metal–ligand bond can be rather high and that these barriers are predominantly decided by steric congestion in the transition state as the bulky plane of the ligand and complex become coincident during the rotation.

The situation is usefully altered in a chelate bis-NHC complex such as **A** or **B**, where the linker length can be



**Figure 5.** Influence of the chain length on the orientation of the diazole rings.

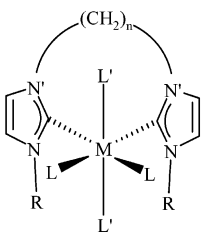
varied ( $n = 1\text{--}4$ ) (Figure 5). In any such chelate, rotation around the M–NHC bond would be expected to be very restricted, so that the bulky ligand axis might be forced into more or less close contact with the sterically crowded complex plane, depending on the linker length. The effective steric size of the ligand changes as a result of linker length, and this affects the reactivity of the complex.

Examination of models and crystal structures suggests that the preferred dihedral angle,  $\alpha$ , between the  $xy$  plane of the complex and the NHC ring plane is strongly dependent on the length of the linker (Table 2). For  $n = 1$ , the dihedral angle  $\alpha$  is ca.  $20^\circ$ , for  $n = 2$ ,  $\alpha$  is ca.  $60^\circ$ , for  $n = 3$ ,  $\alpha$  is ca.  $80^\circ$ , and for  $n = 4$ ,  $\alpha$  is ca.  $90^\circ$ . The dynamics of such systems may well be more complex than are revealed by static structures; correlated motion of the two NHC rings should be possible, for example.<sup>12</sup> For the shortest linker ( $n = 1$ ), the M(III) complexes show a small  $\alpha$  angle (entries 4–7) due to the bulky iodides in the  $\pm z$  direction. Substitution of one of these iodides by a bulkier group such as nortricyclyl leads to an even smaller  $\alpha$  angle (entry 8,  $\alpha =$

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Table 2. Comparative Data on Chelating Bis(carbenes)



entry	metal M	linker <i>n</i>	wingtips R	L	L'	bite angle C–M–C (deg)	$\alpha^a$ (deg)	ref
1 ( <b>3b</b> )	Rh(I)	2	<i>n</i> -Bu	cod		84.0	63.5	this work
2 ( <b>3c</b> )	Rh(I)	3	<i>n</i> -Bu	cod		87.6	78.0	this work
3 ( <b>6d</b> )	Rh(I)	4	<i>n</i> -Bu	CO, CO		91.0	84.3	this work
4	Rh(III)	1	<i>n</i> -Bu	CH <sub>3</sub> COO <sup>−</sup>	I, I	87.3	19.7	9c
5	Rh(III)	1	CH <sub>3</sub>	CH <sub>3</sub> CN, CH <sub>3</sub> CN	I, I	87.8	26.3	9c
6	Ir(III)	1	<i>i</i> -Pr	CH <sub>3</sub> COO <sup>−</sup>	I, I	86.4	19.5	11b
7	Ir(III)	1	neopentyl	CH <sub>3</sub> COO <sup>−</sup>	I, I	87.2	21.6	11b
8	Rh(III)	1	<i>n</i> -Bu	CH <sub>3</sub> COO <sup>−</sup>	I, ntc <sup>b</sup>	86.2	11.9	20
9	Rh(III)	<i>o</i> -phenylene	<i>n</i> -Bu	CH <sub>3</sub> COO <sup>−</sup>	I, I	92.2	33.4	11a
10	Rh(I)	<i>o</i> -xylylene	CH <sub>3</sub>	cod		90.6	86.6	19
11	Ni(II)	1	CH <sub>3</sub>	bis(carbene)		86.6	42.5	21
12	Pd(II)	1	CH <sub>3</sub>	I, I		83.2	47.3	22
13	Rh(I)	1	CH <sub>3</sub>	cod		83.2	45.7	13
14	Rh(I)	1	CH <sub>3</sub>	CO, CO		83.5	45.0	13

<sup>a</sup> Average angle between the two imidazolium ring planes and the *xy* plane of the metal complex or between dihedral angles. <sup>b</sup> ntc = nortricyclyl.

11.9°). In contrast, the M(I) square-planar complexes do not have any apical ligands; therefore,  $\alpha$  is larger (entries 11–14). These  $\alpha$  values and the different bite angles are a measure of flexibility of the bis-chelating NHC ligands. In the Rh(III) complexes, the acetate group (bite angle ca. 60°) in the *xy* plane is considered sterically less demanding than the iodides in the  $\pm z$  direction, so that the bulky ligand diazole planes can easily be aligned with the slim *xy* complex plane without excessive steric repulsions. In contrast, it is clear that the *n* = 4 linker favors the anisotropic square-planar Rh(I) species, where the orientation of the NHC ring naturally places the slim ligand axis in the bulky plane of the complex.<sup>19</sup> Each type of ligand evidently finds the best steric match within its preferred oxidation state. In the *n* = 1, 2 cases, steric factors should disfavor Rh(I) species, which would require the NHCs to lie closer to the bulky plane of the complex. The complex can avoid the problem by forming a Rh(III) or bis-Rh(I) species, but a Rh(I) complex can be formed under suitable synthetic conditions (entry 13 and complex **3b**).

An unsatisfactory aspect of the study is our failure to identify the oxidant responsible for conversion of the starting Rh(I) species to the Rh(III) product. Working under strict exclusion of air has no effect; therefore, this seems least unlikely is that when Rh(III) is formed, H<sub>2</sub> is lost after imidazolium C–H oxidative addition and  $\sigma$  bond metathesis involving the second CH bond. When Rh(I) is formed, the mild base present removes the CH protons of the imidazolium salt.

## Conclusion

Our results show that chelating NHC complexes tend to have preferred conformations that depend on the linker length. This preference in turn leads to kinetic

preferences in the reactions of the NHC precursors with metal salts to give Rh(III) or Rh(I) species, the latter either mononuclear or dinuclear, again depending on the linker length. These kinetic preferences appear in two different reaction types. Such principles may prove useful in the design of other multidentate NHC complexes. Other linker-dependent chemistry may also be possible in such systems.

## Experimental Section

**General Procedures.** The bis(imidazolium) ligand precursor **1a** and complex **4a** were prepared as previously described.<sup>11</sup> All other reagents and solvents (reagent grade) are commercially available and were used as received. NMR spectra were recorded on Bruker spectrometers operating at 300, 400, or 500 MHz (<sup>1</sup>H NMR) and 100 and 125 MHz (<sup>13</sup>C NMR), respectively, and referenced to SiMe<sub>4</sub> ( $\delta$  in ppm and *J* in hertz). NMR spectra were recorded at room temperature with CDCl<sub>3</sub> unless otherwise stated. Assignments are based on HETCOR, COSY, and DEPT experiments. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). Electro-spray mass spectra were recorded on a Micromass ZQ instrument using nitrogen as drying and nebulizing gas.

**Ethylenebis(*N*-*n*-butylimidazolium bromide) (1b).** 1-Butylimidazole (2.00 g, 16.1 mmol) and 1,2-dibromoethane (1.51 g, 8.01 mmol) were heated under reflux in toluene for 72 h. The oily precipitate was collected and was recrystallized by layering a dichloromethane solution with diethyl ether to give pure **1b** as clear, hygroscopic plates. Yield: 2.85 g, 82%. Anal. Calcd for C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>Br<sub>2</sub> (mol wt 436.24): C, 44.05; H, 6.47; N, 12.84. Found: C, 43.88; H, 6.39; N, 12.93. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  10.33 (t, <sup>4</sup>*J*<sub>H–H</sub> = 1.6 Hz, 2H, CH(imid)), 8.79 (t, <sup>3,4</sup>*J*<sub>H–H</sub> = 1.6 Hz, 2H, CH(imid)), 7.26 (t, <sup>3,4</sup>*J*<sub>H–H</sub> = 1.6 Hz, 2H, CH(imid)), 5.30 (s, 4H, CH<sub>2</sub>(linker)), 4.19 (t, <sup>3</sup>*J*<sub>H–H</sub> = 7.7 Hz, 4H, CH<sub>2</sub>(*n*-Bu)), 1.91 (m, 4H, CH<sub>2</sub>(*n*-Bu)), 1.39 (m, 4H, CH<sub>2</sub>(*n*-Bu)), 0.99 (t, <sup>3</sup>*J*<sub>H–H</sub> = 7.4 Hz, 6H, CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  136.7, 125.1, 121.3 (6C, C(imid)), 50.4 (2C, C(linker)), 48.0, 32.0, 19.7, 13.5 (8C, C(*n*-Bu)).

**Trimethylenebis(*N*-*n*-butylimidazolium bromide) (1c).** 1-Butylimidazole (1.85 g, 14.9 mmol) and 1,3-dibromoethane (500 mg, 2.48 mmol) were heated under reflux neat for 24 h

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at 100 °C. The product was crystallized and washed with diethyl ether to give pure **1c** as a white hygroscopic solid. Yield: 1.0 g, 90%. Anal. Calcd for  $C_{17}H_{30}N_4Br_2$  (mol wt 450.26): C, 45.35; H, 6.72; N, 12.44. Found: C, 45.88; H, 6.39; N, 12.31.  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta$  9.84 (s, 2H, CH(imid)), 7.97 (s, 2H, CH(imid)), 7.35 (s, 2H, CH(imid)), 4.56 (t,  $^3J_{H-H} = 7.0$  Hz, 4H,  $NCH_2$ (linker)), 4.08 (t,  $^3J_{H-H} = 7.5$  Hz, 4H,  $NCH_2$ (*n*-Bu)), 2.59 (q,  $^3J_{H-H} = 6.8$  Hz, 2H,  $CH_2$ (linker)), 1.67 (q,  $^3J_{H-H} = 7.5$  Hz, 4H,  $CH_2$ (*n*-Bu)), 1.14 (m, 4H,  $CH_2$ (*n*-Bu)), 0.70 (t,  $^3J_{H-H} = 7.3$  Hz, 6H,  $CH_3$ (*n*-Bu)).  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz):  $\delta$  136.6, 123.7, 122.5 (6C, C(imid)), 50.1, 31.3 (3C, C(linker)), 46.9, 32.1, 19.7, 13.7 (8C, C(*n*-Bu)).

**Tetramethylenebis(*N*-*n*-butylimidazolium bromide) (1d).** 1-Butylimidazole (2.35 g, 18.9 mmol) and 1,4-dibromobutane (500 mg, 2.32 mmol) were heated under reflux neat for 24 h at 80 °C. The product was washed with diethyl ether to give pure **1d** as a pale yellow oil. The compound was very hygroscopic, and satisfactory analysis could not be obtained. Yield: 0.90 g, 85%.  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta$  10.33 (s, 2H, CH(imid)), 8.05 (s, 2H, CH(imid)), 7.22 (s, 2H, CH(imid)), 4.56 (brs, 4H,  $NCH_2$ (linker)), 4.22 (t,  $^3J_{H-H} = 7.5$  Hz, 4H,  $NCH_2$ (*n*-Bu)), 2.15 (brs, 4H,  $CH_2$ (linker)), 1.85 (q,  $^3J_{H-H} = 7.5$  Hz, 4H,  $CH_2$ (*n*-Bu)), 1.33 (m, 4H,  $CH_2$ (*n*-Bu)), 0.91 (t,  $^3J_{H-H} = 7.0$  Hz, 6H,  $CH_3$ (*n*-Bu)).  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz):  $\delta$  136.8, 123.9, 122.3 (6C, C(imid)), 50.3, 27.0 (4C, C(linker)), 48.2, 32.4, 19.9, 13.9 (8C, C(*n*-Bu)).

**Transmetalation Reactions. General Procedure.** A suspension of the appropriate bis(imidazolium) dibromide (**1**; 1 equiv) and silver oxide (2.0 equiv) was stirred at room temperature for 1.5 h. Then, the mixture was filtered through Celite to remove unreacted silver oxide and insoluble residues. [(cod)RhCl] $_2$  (0.5 equiv) was added to the pale yellow solution. Immediately, the formation of a white precipitate was observed, and to complete the reaction, the mixture was stirred or heated under reflux for 1.5 h. The suspension was filtered through Celite to remove the silver salts, and the solution was concentrated under reduced pressure. The precipitate was dissolved in dichloromethane and purified by gradient column chromatography using silica gel.

**Methylenebis{(*N*-*n*-butylimidazol-2-ylidene)chloro(cyclooctadiene)rhodium} (2a).** Transmetalation was carried out at reflux in dichloromethane with methylenebis(*N*-*n*-butylimidazolium) dibromide (**1a**; 491 mg, 1.16 mmol), Ag $_2$ O (538 mg, 2.32 mmol), and [(cod)RhCl] $_2$  (286 mg, 0.58 mmol). Column chromatography involved washing with 1:4 ethyl acetate/hexanes to remove excess [Rh(cod)Cl] $_2$ , followed by elution of the product with 1:1 ethyl acetate/hexanes. Yield: 40 mg, 5%, based on rhodium. Electrospray MS (MeOH, 20 V, *m/z*): 717 ( $M^+ - Cl$ ), 471 ( $M^+ - Rh - cod - 2Cl$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.82 (d,  $^3J_{H-H} = 2.0$  Hz, 2H, CH(imid)); 7.48 (s, 2H,  $NCH_2N$ (linker)); 6.78 (d,  $^3J_{H-H} = 2.0$  Hz, 2H, CH(imid)); 5.15 (m, 2H, CH(cod)); 5.01 (m, 2H, CH(cod)); 4.51 (m, 4H,  $CH_2$ (*n*-Bu)); 3.38 (m, 2H, CH(cod)), 3.30 (m, 2H, CH(cod)); 2.59–2.27 (m, 8H,  $CH_2$ (cod)); 2.18–1.75 (m, 12H,  $CH_2$ (cod) and  $NCH_2CH_2$ (*n*-Bu)); 1.48 (sex,  $^3J_{H-H} = 7.4$  Hz, 4H,  $NCH_2CH_2CH_2$ (*n*-Bu)); 1.04 (t,  $^3J_{H-H} = 7.4$  Hz, 6H,  $NCH_2CH_2CH_2CH_3$ (*n*-Bu)).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  182.7 (d,  $^1J_{Rh-C} = 51.3$  Hz, C(carbene)); 121.7, 121.4 (CH(imid)); 99.8 (d,  $^1J_{Rh-C} = 6.8$  Hz, CH(cod)); 99.1 (d,  $^1J_{Rh-C} = 6.8$  Hz, CH(cod)); 69.8 (d,  $^1J_{Rh-C} = 14.7$  Hz, CH(cod)); 68.0 (d,  $^1J_{Rh-C} = 14.7$  Hz, CH(cod)); 63.5 ( $NCH_2N$ (linker)); 50.9 ( $NCH_2$ (*n*-Bu)); 34.0, 32.9 ( $CH_2$ (cod)); 32.3 ( $NCH_2CH_2$ (*n*-Bu)); 29.6, 28.5 ( $CH_2$ (cod)); 20.2 ( $NCH_2CH_2CH_2$ (*n*-Bu)); 13.9 ( $NCH_2CH_2CH_2CH_3$ (*n*-Bu)).

**Ethylenebis{(*N*-*n*-butylimidazol-2-ylidene)chloro(cyclooctadiene)rhodium} (2b).** Transmetalation was carried out at reflux in dichloromethane with ethylenebis(*N*-*n*-butylimidazolium) dibromide (**1b**; 342 mg, 0.78 mmol), Ag $_2$ O (362 mg, 1.56 mmol), and [(cod)RhCl] $_2$  (193 mg, 0.391 mmol). Column chromatography involved elution with  $CH_2Cl_2$  to remove unreacted [(cod)RhCl] $_2$  and then elution with acetone

to give compound **2b**, which was then recrystallized by layering a  $CH_2Cl_2$  solution with supernatant pentane. Yield: 198 mg, 66%, based on rhodium. Anal. Calcd for  $C_{32}H_{50}N_4Rh_2Cl_2$  (mol wt 767.51): C, 50.08; H, 6.57; N, 7.30. Found: C, 50.21; H, 6.55; N, 7.37. Electrospray MS (MeOH, 20 V, *m/z*): 732 ( $M^+ - Cl$ ), 486 ( $M^+ - Rh - cod - 2Cl$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  6.93 (d,  $^3J_{H-H} = 2.0$  Hz, 2H, CH(imid)); 6.51 (d,  $^3J_{H-H} = 2.0$  Hz, 2H, CH(imid)); 5.26 (d,  $^3J_{H-H} = 9.3$  Hz, 2H,  $NCH_2$ (linker)); 5.07 (m, 4H, CH(cod)); 5.03 (d,  $^3J_{H-H} = 9.3$  Hz, 2H,  $NCH_2$ (linker)); 4.56 (m, 2H,  $CH_2$ (*n*-Bu)); 4.43 (m, 2H,  $CH_2$ (*n*-Bu)); 3.29 (m, 4H, CH(cod)); 2.45 (m, 8H,  $CH_2$ (cod)); 1.98 (m, 8H,  $CH_2$ (cod)); 1.95 (m, 2H, *n*-Bu); 1.79 (m, 2H,  $CH_2$ (*n*-Bu)); 1.46 (m, 4H,  $CH_2$ (*n*-Bu)); 1.04 (t,  $^3J = 7.4$  Hz, 6H,  $CH_3$ (*n*-Bu)).  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  181.1 (d,  $^1J_{C-Rh} = 50.9$  Hz, 2C, C(carbene)); 123.9, 118.4 (4C, CH(imid)); 98.7 (d,  $^1J_{C-Rh} = 6.3$  Hz, 4C, CH(cod)); 69.0 (d,  $^1J_{C-Rh} = 14.6$  Hz, 2C, CH(cod)); 68.4 (d,  $^1J_{C-Rh} = 14.9$  Hz, 2C, CH(cod)), 50.9, 50.8 (4C,  $CH_2$ (linker) and  $CH_2$ (*n*-Bu)); 33.2, 33.1, 33.0 (6C,  $CH_2$ (cod) and  $CH_2$ (*n*-Bu)); 29.3, 28.9 (4C,  $CH_2$ (cod)); 20.2 (2C,  $CH_2$ (*n*-Bu)); 14.0 (2C,  $CH_3$ (*n*-Bu)). A pair of overlapping doublets representing CH(cod) carbons at 98.7 ppm was resolved in acetone- $d_6$ .

**Trimethylenebis{(*N*-*n*-butylimidazol-2-ylidene)chloro(cyclooctadiene)rhodium} (2c).** Transmetalation was carried out at room temperature in dichloromethane with trimethylenebis(*N*-*n*-butylimidazolium) dibromide (**1c**; 150 mg, 0.33 mmol), Ag $_2$ O (153 mg, 0.66 mmol), and [(cod)RhCl] $_2$  (84 mg, 0.17 mmol). Column chromatography involved elution with  $CH_2Cl_2$  to remove unreacted [(cod)RhCl] $_2$  and then elution with 50% (v/v) dichloromethane/acetone to give compound **2c**, which was then slowly recrystallized from  $CH_2Cl_2$ /hexanes. Yield: 65 mg, 49%, based on rhodium. Anal. Calcd for  $C_{33}H_{52}N_4Rh_2Cl_2$  (mol wt 781.53): C, 50.72; H, 6.71; N, 7.17. Found: C, 50.68; H, 6.55; N, 7.07. Electrospray MS (MeOH, 20 V, *m/z*): 746 ( $M^+ - Cl$ ), 500 ( $M^+ - Rh - cod - 2Cl$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ ; a mixture of diastereomers *dl:meso* (60:40) was present):  $\delta$  7.30 (d,  $^3J_{H-H} = 1.6$  Hz, 2H, CH(imid)); 7.10 (d,  $^3J_{H-H} = 1.6$  Hz, 1.2H, CH(imid)); 6.86 (d,  $^3J_{H-H} = 1.6$  Hz, 2H, CH(imid)); 6.65 (d,  $^3J_{H-H} = 1.6$  Hz, 1.2H, CH(imid)); 5.01–4.04 (m, (12 + 7.2)H,  $NCH_2$ (linker), CH(cod),  $CH_2$ (*n*-Bu)); 3.26–3.22 (m, (4 + 2.4)H, CH(cod)); 2.85–1.71 (m, (22 + 13.2)H,  $-CH_2$ (linker),  $CH_2$ (*n*-Bu),  $CH_2$ (cod)); 1.50–1.43 (m, (4 + 2.4)H,  $CH_2$ (*n*-Bu)); 1.02 (m, (6 + 3.6)H,  $CH_3$ (*n*-Bu)).  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  181.9 (d,  $^1J_{C-Rh} = 51.9$  Hz, C(carbene)); 181.4 (d,  $^1J_{C-Rh} = 50.4$  Hz, C(carbene)); 121.9, 121.8, 120.6, 120.4 (CH(imid)); 98.7 (d,  $^1J_{C-Rh} = 6.7$  Hz, CH(cod)); 98.6 (d,  $^1J_{C-Rh} = 6.8$  Hz, CH(cod)); 98.4 (d,  $^1J_{C-Rh} = 7.8$  Hz, CH(cod)); 98.1 (d,  $^1J_{C-Rh} = 6.5$  Hz, CH(cod)); 79.1 (d,  $^1J_{C-Rh} = 14.0$  Hz, CH(cod)); 69.3 (d,  $^1J_{C-Rh} = 14.6$  Hz, CH(cod)); 68.7 (d,  $^1J_{C-Rh} = 13.7$  Hz, CH(cod)); 68.3 (d,  $^1J_{C-Rh} = 14.8$  Hz, CH(cod)); 51.1, 51.0, 49.3, 48.6, 33.7, 33.5, 33.4, 32.9, 32.1, 31.6, 31.4, 31.3, 29.7, 29.4, 29.4, 29.0, 20.7, 20.6 ( $CH_2$ (linker),  $CH_2$ (*n*-Bu),  $CH_2$ (cod)); 14.3, 14.2 ( $CH_3$ (*n*-Bu)).

**Tetramethylenebis{(*N*-*n*-butylimidazol-2-ylidene)chloro(cyclooctadiene)rhodium} (2d).** Transmetalation was carried out at room temperature in dichloromethane with tetramethylenebis(*N*-*n*-butylimidazolium) dibromide (**1d**; 150 mg, 0.32 mmol), Ag $_2$ O (148 mg, 0.64 mmol), and [(cod)RhCl] $_2$  (79 mg, 0.16 mmol). Column chromatography involved elution with  $CH_2Cl_2$  to remove unreacted [(cod)RhCl] $_2$  and then elution with 50% (v/v) dichloromethane/acetone to give **2d**, which was then slowly recrystallized by layering a  $CH_2Cl_2$  solution with pentane. Yield: 102 mg, 80%, based on rhodium. Anal. Calcd for  $C_{34}H_{54}N_4Rh_2Cl_2$  (mol wt 795.56): C, 51.33; H, 6.84; N, 7.04. Found: C, 51.37; H, 6.75; N, 7.06. Electrospray MS (MeOH, 20 V, *m/z*): 760 ( $M^+ - Cl$ ), 513 ( $M^+ - Rh - cod - 2Cl$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ ; a mixture of diastereomers *dl:meso* (50:50) was present):  $\delta$  7.00 (d,  $^3J_{H-H} = 1.8$  Hz, 2H, CH(imid)); 6.92 (d,  $^3J_{H-H} = 2.1$  Hz, 2H, CH(imid)); 6.83 (d,  $^3J_{H-H} = 1.8$  Hz, 2H, CH(imid)); 6.76 (d,  $^3J_{H-H} = 2.1$  Hz, 2H, CH(imid)); 5.03–4.11 (m, (12 + 12)H,  $NCH_2$ (linker), CH(cod),  $CH_2$ (*n*-Bu));



3.28–3.20 (m, (4 + 4)H, CH(cod)); 2.39–1.73 (m, (24 + 24)H, –CH<sub>2</sub>(linker), CH<sub>2</sub>(*n*-Bu), CH<sub>2</sub>(cod)); 1.49–1.44 (m, (4 + 4)H, CH<sub>2</sub>(*n*-Bu)); 1.16 (m, (6 + 6)H, CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 182.1 (d, <sup>1</sup>J<sub>C–Rh</sub> = 51.5 Hz, C(carbene)); δ 181.8 (d, <sup>1</sup>J<sub>C–Rh</sub> = 51.2 Hz, C(carbene)); 121.7, 121.5, 120.7, 120.5 (CH(imid)); 98.7, 68.7, 68.5, 51.3, 50.8 (CH(cod)); 33.6, 33.5, 32.1, 29.6, 29.5, 29.4, 28.5 (CH<sub>2</sub>(linker), CH<sub>2</sub>(*n*-Bu), CH<sub>2</sub>(cod)); 14.4, 14.3 (CH<sub>3</sub>(*n*-Bu)).

**Ethylenebis(*N*-*n*-butylimidazol-2-ylidene)(cyclooctadiene)rhodium Hexafluorophosphate (3b).** Transmetalation was carried out in refluxing dichloromethane with ethylenebis(*N*-*n*-butylimidazolium) dibromide (**1b**; 158 mg, 0.36 mmol), Ag<sub>2</sub>O (126 mg, 0.54 mmol), and [(cod)RhCl]<sub>2</sub> (89 mg, 0.18 mmol). In contrast with the general procedure, excess silver oxide was not removed by filtration before addition of [(cod)RhCl]<sub>2</sub>. Flash column chromatography involved washing with 1:1 CH<sub>2</sub>Cl<sub>2</sub>/acetone followed by elution with acetone containing KPF<sub>6</sub> (150 mg) to give compound **3b** as a PF<sub>6</sub><sup>–</sup> salt. Analytically pure material was obtained by crystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane. Yield: 170 mg, 74%. Anal. Calcd for C<sub>24</sub>H<sub>38</sub>N<sub>4</sub>RhPF<sub>6</sub> (mol wt 630.47): C, 45.72; H, 6.08; N, 8.89. Found: C, 45.58; H, 6.10; N, 8.92. Electrospray MS (MeOH, 40 V, *m/z*): 485 (M<sup>+</sup>), 377 (M<sup>+</sup> – cod). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.02 (d, <sup>3</sup>J<sub>H–H</sub> = 1.9 Hz, 2H, CH(imid)); 6.87 (d, <sup>3</sup>J<sub>H–H</sub> = 1.9 Hz, 2H, CH(imid)); 5.55 (m, 2H, NCH<sub>2</sub>(linker)); 4.61 (m, 2H, CH(cod)); 4.49 (m, 2H, CH(cod)); 4.44 (m, 2H, NCH<sub>2</sub>(linker)); 4.11 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 2.43 (m, 2H, CH<sub>2</sub>(cod)); 2.36 (m, 2H, CH<sub>2</sub>(cod)); 2.25 (m, 2H, CH<sub>2</sub>(cod)); 2.15 (m, 2H, CH<sub>2</sub>(cod)); 1.81 (m, 2H, CH<sub>2</sub>(*n*-Bu)); 1.68 (m, 2H, CH<sub>2</sub>(*n*-Bu)); 1.36 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 0.97 (t, <sup>3</sup>J<sub>H–H</sub> = 7.5 Hz, 2H, CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 179.4 (d, <sup>1</sup>J<sub>C–Rh</sub> = 52.0 Hz, 2C, C(carbene)); 123.3, 121.2 (4C, CH(imid)); 90.7 (d, <sup>1</sup>J<sub>C–Rh</sub> = 8.2 Hz, 2C, CH(cod)); 87.3 (d, <sup>1</sup>J<sub>C–Rh</sub> = 7.9 Hz, 2C, CH(cod)); 51.6 (2C, NCH<sub>2</sub>(*n*-Bu)); 48.4 (2C, NCH<sub>2</sub>(linker)); 34.0 (2C, CH<sub>2</sub>(*n*-Bu)); 33.6 (2C, CH<sub>2</sub>(linker)); 31.2, 31.1 (4C, CH<sub>2</sub>(cod)); 20.5 (2C, CH<sub>2</sub>(*n*-Bu)); 14.0 (2C, CH<sub>3</sub>(*n*-Bu)).

**Trimethylenebis(*N*-*n*-butylimidazol-2-ylidene)(cyclooctadiene)rhodium Hexafluorophosphate (3c).** Transmetalation was carried out in refluxing dichloromethane with trimethylenebis(*N*-*n*-butylimidazolium) dibromide (320 mg, 0.71 mmol), Ag<sub>2</sub>O (411.3 mg, 1.78 mmol), and [(cod)RhCl]<sub>2</sub> (175.1 mg, 0.36 mmol). Column chromatography involved elution with CH<sub>2</sub>Cl<sub>2</sub> and then elution with CH<sub>2</sub>Cl<sub>2</sub>/acetone (50%) containing KPF<sub>6</sub> (150 mg) to give compound **3c** as a PF<sub>6</sub><sup>–</sup> salt. Analytically pure material was obtained by crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexanes. Yield: 320 mg, 70%. Anal. Calcd for C<sub>25</sub>H<sub>40</sub>N<sub>4</sub>RhPF<sub>6</sub> (mol wt 644.50): C, 46.59; H, 6.26; N, 8.69. Found: C, 46.63; H, 6.29; N, 8.70. Electrospray MS (MeOH, 40 V, *m/z*): 499 (M<sup>+</sup>), 391 (M<sup>+</sup> – cod). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.24 (d, <sup>3</sup>J<sub>H–H</sub> = 2.0 Hz, 2H, CH(imid)); 6.88 (d, <sup>3</sup>J<sub>H–H</sub> = 2.0 Hz, 2H, CH(imid)); 4.86 (dd, <sup>3</sup>J<sub>H–H</sub> = 14.3 Hz, <sup>3</sup>J<sub>H–H</sub> = 11.3 Hz, 2H, NCH<sub>2</sub>(linker)); 4.56–4.47 (m, 6H, 2H NCH<sub>2</sub>(linker), 2H CH(cod), 2H CH<sub>2</sub>(*n*-Bu)); 3.96 (brs, 2H, CH(cod)); 3.98–3.92 (m, 2H, CH<sub>2</sub>(*n*-Bu)); 2.57–2.54 (m, 1H, CH<sub>2</sub>(linker)); 2.46–2.37 (m, 4H, CH<sub>2</sub>(cod)); 2.27–2.19 (m, 4H, CH<sub>2</sub>(cod)); 2.05–2.02 (m, 1H, CH<sub>2</sub>(linker)); 1.80–1.75 (m, 2H, CH<sub>2</sub>(*n*-Bu)); 1.69–1.64 (m, 2H, CH<sub>2</sub>(*n*-Bu)); 1.51–1.43 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.02 (t, 6H, <sup>3</sup>J<sub>H–H</sub> = 7.5 Hz, CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 181.1 (d, <sup>1</sup>J<sub>C–Rh</sub> = 53.7 Hz, 2C, C(carbene)); 124.4, 120.6 (4C, CH(imid)); 90.1 (d, <sup>1</sup>J<sub>C–Rh</sub> = 7.9 Hz, 2C, CH(cod)); 88.3 (d, <sup>1</sup>J<sub>C–Rh</sub> = 8.3 Hz, 2C, CH(cod)); 53.1 (2C, NCH<sub>2</sub>(linker)); 51.2 (2C, NCH<sub>2</sub>(*n*-Bu)); 33.8 (2C, CH<sub>2</sub>(*n*-Bu)); 33.6 (1C, CH<sub>2</sub>(linker)); 31.3, 31.2 (4C, CH<sub>2</sub>(cod)); 20.8 (2C, CH<sub>2</sub>(*n*-Bu)); 14.3 (2C, CH<sub>3</sub>(*n*-Bu)).

**Tetramethylenebis(*N*-*n*-butylimidazol-2-ylidene)(cyclooctadiene)rhodium Hexafluorophosphate (3d).** Transmetalation was carried out in refluxing dichloromethane with tetramethylenebis(*N*-*n*-butylimidazolium) dibromide (**1d**; 300 mg, 0.65 mmol), Ag<sub>2</sub>O (374 mg, 1.62 mmol), and [(cod)RhCl]<sub>2</sub> (163 mg, 0.33 mmol). Column chromatography involved elution with CH<sub>2</sub>Cl<sub>2</sub> and then elution with CH<sub>2</sub>Cl<sub>2</sub>/acetone (50%)

containing KPF<sub>6</sub> (150 mg) to give compound **3d** as a PF<sub>6</sub><sup>–</sup> salt. Analytically pure material was obtained by crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexanes. Yield: 125 mg, 30%. Anal. Calcd for C<sub>26</sub>H<sub>42</sub>N<sub>4</sub>RhPF<sub>6</sub> (mol wt 658.52): C, 47.42; H, 6.43; N, 8.51. Found: C, 47.53; H, 6.49; N, 8.53. Electrospray MS (MeOH, 40 V, *m/z*): 514 (M<sup>+</sup>), 405 (M<sup>+</sup> – cod). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.98 (d, <sup>3</sup>J<sub>H–H</sub> = 2.0 Hz, 2H, CH(imid)); 6.95 (d, <sup>3</sup>J<sub>H–H</sub> = 2.0 Hz, 2H, CH(imid)); 5.19–5.14 (m, 2H, NCH<sub>2</sub>(linker)); 4.55–4.50 (m, 2H, NCH<sub>2</sub>(*n*-Bu)); 4.27–4.12 (m, 6H, 2H NCH<sub>2</sub>(linker), 4H CH(cod)); 4.10–4.07 (m, 2H, NCH<sub>2</sub>(*n*-Bu)); 2.48–2.41 (m, 2H, CH<sub>2</sub>(*n*-Bu)); 2.38–2.30 (m, 6H, 2H CH<sub>2</sub>(*n*-Bu), 4H CH<sub>2</sub>(cod)); 2.25–2.19 (m, 4H, CH<sub>2</sub>(cod)); 2.05–2.02 (m, 2H, CH<sub>2</sub>(linker)); 1.73–1.69 (m, 2H, CH<sub>2</sub>(linker)); 1.50–1.43 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.03 (t, 6H, <sup>3</sup>J<sub>H–H</sub> = 7.6 Hz, CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 181.1 (d, <sup>1</sup>J<sub>C–Rh</sub> = 52.9 Hz, 2C, C(carbene)); 123.9, 121.2 (4C, CH(imid)); 91.0 (d, <sup>1</sup>J<sub>C–Rh</sub> = 8.0 Hz, 2C, CH(cod)); 88.5 (d, <sup>1</sup>J<sub>C–Rh</sub> = 7.5 Hz, 2C, CH(cod)); 53.4 (2C, NCH<sub>2</sub>(linker)); 51.2 (2C, NCH<sub>2</sub>(*n*-Bu)); 33.8 (2C, CH<sub>2</sub>(*n*-Bu)); 32.4, 31.3 (4C, CH<sub>2</sub>(cod)); 27.6 (2C, CH<sub>2</sub>(linker)); 20.7 (2C, CH<sub>2</sub>(*n*-Bu)); 14.1 (2C, CH<sub>3</sub>(*n*-Bu)).

**Direct Metalation Reactions. General Procedure.** A suspension of the appropriate bis(imidazolium) dibromide (**1**; 1 equiv), KI (2.5 equiv), NaOAc (2.5 equiv), and [(cod)RhCl]<sub>2</sub> (0.5 equiv) was heated at reflux in MeCN (30 mL) for 15 h. The suspension was filtered through Celite to remove insoluble salts, and the solution was concentrated under reduced pressure. The precipitate was dissolved in dichloromethane and purified by gradient column chromatography using silica gel. Elution with dichloromethane gave a [(cod)RhCl]<sub>2</sub> fraction, and subsequent elution with 50% (v/v) dichloromethane/acetone gave **4** as orange solids.

**[Ethylenebis(*N*-*n*-Butylimidazol-2-ylidene)]diiodo(acetato)rhodium (4b).** Metalation was carried out with ethylenebis(*N*-*n*-butylimidazolium) dibromide (**1b**; 263 mg, 0.60 mmol), KI (418 mg, 2.52 mmol), NaOAc (209 mg, 2.55 mmol), and [(cod)RhCl]<sub>2</sub> (152.5 mg, 0.31 mmol). Yield: 174 mg, 42%. Anal. Calcd for C<sub>18</sub>H<sub>29</sub>N<sub>4</sub>RhI<sub>2</sub>O<sub>2</sub> (mol wt 690.17): C, 31.33; H, 4.24; N, 8.12. Found: C, 34.93; H, 4.64; N, 7.31. Despite several attempts, no better elemental analysis could be obtained. Similar analysis problems with carbene complexes have been reported.<sup>23</sup> Electrospray MS (MeOH, 40 V, *m/z*): 713 (M<sup>+</sup> + Na), 631 (M<sup>+</sup> – CH<sub>3</sub>COO), 563 (M<sup>+</sup> – I), 436 (M<sup>+</sup> – 2I), 377 (M<sup>+</sup> – 2I – CH<sub>3</sub>COO). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.03 (d, <sup>3</sup>J<sub>H–H</sub> = 1.90 Hz, 2H, CH(imid)); 6.85 (d, <sup>3</sup>J<sub>H–H</sub> = 1.8 Hz, 2H, CH(imid)); 4.53–4.50 (m, 4H, NCH<sub>2</sub>(*n*-Bu)); 4.39 (s, 4H, CH<sub>2</sub>(linker)); 2.05 (s, 3H, CH<sub>3</sub>COO<sup>–</sup>); 1.98–1.94 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.58–1.52 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 0.99 (t, 6H, <sup>3</sup>J<sub>H–H</sub> = 7.5 Hz CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 188.3 (1C, COO<sup>–</sup>); 147.5 (d, <sup>1</sup>J<sub>C–Rh</sub> = 45.1 Hz, 2C, C(carbene)); 123.4, 123.3 (4C, CH(imid)); 52.0, 51.6, 33.6, 20.1 (8C, CH<sub>2</sub>(linker), CH<sub>2</sub>(*n*-Bu)); 24.9, 14.0 (3C, CH<sub>3</sub>COO<sup>–</sup>, CH<sub>3</sub>(*n*-Bu)).

**[Trimethylenebis(*N*-*n*-Butylimidazol-2-ylidene)]diiodo(acetato)rhodium (4c).** Metalation was carried out with trimethylenebis(*N*-*n*-butylimidazolium) dibromide (**1c**; 300 mg, 0.67 mmol), KI (279 mg, 1.68 mmol), NaOAc (138 mg, 1.68 mmol), and [(cod)RhCl]<sub>2</sub> (162.7 mg, 0.33 mmol). Yield: 47 mg, 10%. Anal. Calcd for C<sub>19</sub>H<sub>31</sub>N<sub>4</sub>RhI<sub>2</sub>O<sub>2</sub> (mol wt 704.19): C, 32.41; H, 4.43; N, 7.96. Found: C, 32.53; H, 4.39; N, 7.94. Electrospray MS (MeOH, 40 V, *m/z*): 727 (M<sup>+</sup> + Na), 645 (M<sup>+</sup> – CH<sub>3</sub>COO), 577 (M<sup>+</sup> – I), 450 (M<sup>+</sup> – 2I), 391 (M<sup>+</sup> – 2I – CH<sub>3</sub>COO). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.14 (d, <sup>3</sup>J<sub>H–H</sub> = 2.0 Hz, 2H, CH(imid)); 6.90 (d, <sup>3</sup>J<sub>H–H</sub> = 1.6 Hz, 2H, CH(imid));

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4.75–4.68 (m, 2H, NCH<sub>2</sub>(linker)); 4.42–4.34 (m, 2H, NCH<sub>2</sub>(linker)); 4.05–3.99 (m, 2H, NCH<sub>2</sub>(*n*-Bu)); 3.76–3.72 (m, 2H, NCH<sub>2</sub>(*n*-Bu)); 1.97 (s, 3H, CH<sub>3</sub>COO<sup>−</sup>); 1.94–1.88 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.85–1.80 (m, 2H, NCH<sub>2</sub>(linker)); 1.55–1.48 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 0.99 (t, 6H, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 188.9 (1C, COO<sup>−</sup>); 152.2 (d, <sup>1</sup>J<sub>C-Rh</sub> = 46.5 Hz, 2C, C(carbene)); 124.2, 122.4 (4C, CH(imid)); 52.6, 47.5, 34.3, 32.3, 20.3 (9C, CH<sub>2</sub>(linker), CH<sub>2</sub>(*n*-Bu)); 25.2, 14.3 (3C, CH<sub>3</sub>COO<sup>−</sup>, CH<sub>3</sub>(*n*-Bu)).

**[Tetramethylenebis(*N*-*n*-butylimidazol-2-ylidene)]diiodo(acetato)rhodium (4d).** Metalation was carried out with tetramethylenebis(*N*-*n*-butylimidazolium) dibromide (**1d**; 200 mg, 0.43 mmol), KI (375 mg, 2.25 mmol), NaOAc (185 mg, 2.25 mmol), and [(cod)RhCl]<sub>2</sub> (162.7 mg, 0.33 mmol). Yield: 18 mg, 6%. Anal. Calcd for C<sub>20</sub>H<sub>33</sub>N<sub>4</sub>RhI<sub>2</sub>O<sub>2</sub> (mol wt 718.22): C, 33.45; H, 4.63; N, 7.80. Found: C, 33.43; H, 4.60; N, 7.75. Electrospray MS (MeOH, 40 V, *m/z*): 741 (M<sup>+</sup> + Na), 659 (M<sup>+</sup> − CH<sub>3</sub>COO), 591 (M<sup>+</sup> − I), 464 (M<sup>+</sup> − 2I), 405 (M<sup>+</sup> − 2I − CH<sub>3</sub>COO). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.09 (d, <sup>3</sup>J<sub>H-H</sub> = 1.6 Hz, 2H, CH(imid)); 6.86 (d, <sup>3</sup>J<sub>H-H</sub> = 1.6 Hz, 2H, CH(imid)); 4.46–4.09 (m, 6H, NCH<sub>2</sub>(linker), NCH<sub>2</sub>(*n*-Bu)); 2.33–2.24 (m, 2H, NCH<sub>2</sub>(*n*-Bu)); 1.99 (s, 3H, CH<sub>3</sub>COO<sup>−</sup>); 1.95–1.90 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.78–1.71 (m, 4H, CH<sub>2</sub>(linker)); 1.46–1.41 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 0.98 (t, 6H, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz CH<sub>3</sub>(*n*-Bu)).

**Carbonyl Derivatives. General Procedure.** CO gas (1 atm, 10 mL/min) was passed through a solution of **2** or **3** (100 mg) in dichloromethane (15 mL) for 10 min. The solution was concentrated (ca. 5 mL) under reduced pressure, and hexanes were added to get dicarbonyl compounds **5** and **6**, in high yields (85–95%). Analytically pure samples were obtained by slow recrystallization of dichloromethane/hexanes mixtures.

**Trimethylenebis{(*N*-*n*-butylimidazol-2-ylidene)chlorodicarbonylrhodium} (5c).** Anal. Calcd for C<sub>21</sub>H<sub>28</sub>N<sub>4</sub>Rh<sub>2</sub>Cl<sub>2</sub>O<sub>4</sub> (mol wt 677.21): C, 37.24; H, 4.17; N, 8.27. Found: C, 37.20; H, 4.15; N, 8.30. Electrospray MS (MeOH, 40 V, *m/z*): 665 (M<sup>+</sup> − Cl + Na), 447 (M<sup>+</sup> − Rh − 2Cl − 2CO), 419 (M<sup>+</sup> − Rh − 2Cl − 3CO), 391 (M<sup>+</sup> − Rh − 2Cl − 4CO). IR (cm<sup>−1</sup>): 2075.6, 1995.7. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.05 (s, 2H, CH(imid)); 6.90 (s, 2H, CH(imid)); 4.32–4.07 (m, 8H, CH<sub>2</sub>(linker), NCH<sub>2</sub>(*n*-Bu)); 2.42–2.37 (m, 2H, CH<sub>2</sub>(linker)); 1.87–1.82 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.39–1.34 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 0.97 (t, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, 6H, CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 185.9 (d, <sup>1</sup>J<sub>C-Rh</sub> = 53.8 Hz, 2C, CO(cis Cl)); 182.9 (d, <sup>1</sup>J<sub>C-Rh</sub> = 74.6 Hz, 2C, CO(trans Cl)); 172.5 (d, <sup>1</sup>J<sub>C-Rh</sub> = 43.4 Hz, 2C, C(carbene)); 123.0, 121.9 (4C, CH(imid)); 51.6, 49.5, 32.9, 28.7, 20.7 (9C, CH<sub>2</sub>(linker), CH<sub>2</sub>(*n*-Bu)); 14.2 (2C, CH<sub>3</sub>(*n*-Bu)).

**Tetramethylenebis{(*N*-*n*-butylimidazol-2-ylidene)chlorodicarbonylrhodium} (5d).** Anal. Calcd for C<sub>22</sub>H<sub>30</sub>N<sub>4</sub>Rh<sub>2</sub>Cl<sub>2</sub>O<sub>4</sub> (mol wt 691.23): C, 38.23; H, 4.37; N, 8.11. Found: C, 38.25; H, 4.26; N, 8.14. Electrospray MS (MeOH, 40 V, *m/z*): 678 (M<sup>+</sup> − Cl + Na), 461 (M<sup>+</sup> − Rh − 2Cl − 2CO), 432 (M<sup>+</sup> − Rh − 2Cl − 3CO), 405 (M<sup>+</sup> − Rh − 2Cl − 4CO). IR (cm<sup>−1</sup>): 2074.8, 1993.4. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.06 (brs, 2H, CH(imid)); 6.95 (brs, 2H, CH(imid)); 4.42–4.37 (m, 4H, CH<sub>2</sub>(linker)); 4.15–4.11 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 2.02–1.98 (m, 4H, CH<sub>2</sub>(linker)); 1.89–1.81 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.42–1.36 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 0.98 (t, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz, 6H, CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 186.0 (d, <sup>1</sup>J<sub>C-Rh</sub> = 53.4 Hz, 2C, CO(cis Cl)); 183.2 (d, <sup>1</sup>J<sub>C-Rh</sub> = 74.3 Hz, 2C, CO(trans Cl)); 173.7 (d, <sup>1</sup>J<sub>C-Rh</sub> = 43.0 Hz, 2C, C(carbene)); 122.2, 122.0 (4C, CH(imid)); 51.7, 51.1, 33.1, 27.7, 20.1 (10C, CH<sub>2</sub>(linker), CH<sub>2</sub>(*n*-Bu)); 14.0 (2C, CH<sub>3</sub>(*n*-Bu)).

**[Trimethylenebis(*N*-*n*-butylimidazol-2-ylidene)]dicarbonylrhodium Hexafluorophosphate (6c).** Anal. Calcd for C<sub>19</sub>H<sub>28</sub>N<sub>4</sub>RhO<sub>2</sub>PF<sub>6</sub> (mol wt 592.33): C, 38.53; H, 4.76; N, 9.46. Found: C, 38.57; H, 4.73; N, 9.45. Electrospray MS (MeOH, 20 V, *m/z*): 447 (M<sup>+</sup>), 419 (M<sup>+</sup> − CO), 391 (M<sup>+</sup> − 2CO). IR (cm<sup>−1</sup>): 2073.6, 2007.1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.10 (d, <sup>3</sup>J<sub>H-H</sub> = 1.8 Hz, 2H, CH(imid)); 6.98 (d, <sup>3</sup>J<sub>H-H</sub> = 2.1 Hz, 2H, CH(imid)); 4.64–4.56 (m, 2H, CH<sub>2</sub>(linker)); 4.38–4.21 (m, 4H, CH<sub>2</sub>(*n*-Bu), CH<sub>2</sub>(linker)); 3.99–3.91 (m, 2H, CH<sub>2</sub>(*n*-Bu));

**Table 3. Crystallographic Data for 3c, 3b, and 6d**

	3c	3b	6d
empirical formula	C <sub>25</sub> H <sub>40</sub> ClN <sub>4</sub> Rh	C <sub>24</sub> H <sub>38</sub> F <sub>6</sub> N <sub>4</sub> PRh	C <sub>20</sub> H <sub>30</sub> F <sub>6</sub> N <sub>4</sub> PO <sub>2</sub> Rh
mol wt	534.98	630.46	606.35
radiation; λ (Å)		Mo Kα (monochr); 0.710 69	
T (°C)	−90	−90	−90
cryst syst	monoclinic	monoclinic	monoclinic
space group	P2 <sub>1</sub> /c (No. 14)	P2 <sub>1</sub> /c (No. 14)	P2 <sub>1</sub> /c (No. 14)
a (Å)	12.0135(2)	12.3626(3)	8.0673(2)
b (Å)	10.9050(2)	15.8246(4)	17.9244(5)
c (Å)	19.7784(4)	13.6358(4)	17.2088(5)
β (deg)	103.3715(10)	96.4499(10)	92.3168(11)
V (Å <sup>3</sup> )	2520.87(8)	2650.73(11)	2486.38(10)
Z	4	4	4
D <sub>calcd</sub> (g cm <sup>−3</sup> )	1.409	1.580	1.620
μ(Mo Kα) (cm <sup>−1</sup> )	8.01	7.66	8.19
cryst size (mm)	0.14 × 0.14 × 0.22	0.10 × 0.12 × 0.17	0.10 × 0.12 × 0.14
total, unique no. of rflns	9930, 6055	9929, 6280	9930, 5785
R <sub>int</sub>	0.034	0.045	0.036
no. of params, restrictions	280, 0	325, 0	307, 0
R <sub>w</sub> <sup>a</sup> R <sub>w</sub> <sup>b</sup>	0.031, 0.031	0.038, 0.038	0.037, 0.040
GOF	1.13	1.19	1.31
min, max resid dens (e Å <sup>−3</sup> )	−0.39, 0.43	−0.58, 0.66	−0.69, 1.34

<sup>a</sup>  $R = \sum |F_o| - |F_c| / \sum |F_o|$ , for all  $I > 3\sigma(I)$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ .

2.41–2.32 (m, 1H, CH<sub>2</sub>(linker)); 2.19–2.13 (m, 1H, CH<sub>2</sub>(linker)); 1.79–1.70 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.45–1.34 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 0.98 (t, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 187.9 (d, <sup>1</sup>J<sub>C-Rh</sub> = 50.4 Hz, 2C, CO); 171.3 (d, <sup>1</sup>J<sub>C-Rh</sub> = 45.6 Hz, 2C, C(carbene)); 124.7, 122.6 (4C, CH(imid)); 53.6 (2C, NCH<sub>2</sub>(linker)); 51.9 (2C, NCH<sub>2</sub>(*n*-Bu)); 33.2 (2C, CH<sub>2</sub>(*n*-Bu)); 28.8 (1C, CH<sub>2</sub>(linker)); 20.3 (2C, CH<sub>2</sub>(*n*-Bu)); 14.0 (2C, CH<sub>3</sub>(*n*-Bu)).

**[Tetramethylenebis(*N*-*n*-butylimidazol-2-ylidene)]dicarbonylrhodium Hexafluorophosphate (6d).** Anal. Calcd for C<sub>20</sub>H<sub>30</sub>N<sub>4</sub>RhO<sub>2</sub>PF<sub>6</sub> (mol wt 606.36): C, 39.62; H, 4.99; N, 9.24. Found: C, 39.56; H, 4.86; N, 9.24. Electrospray MS (MeOH, 20 V, *m/z*): 461 (M<sup>+</sup>), 433 (M<sup>+</sup> − CO), 405 (M<sup>+</sup> − 2CO). IR (cm<sup>−1</sup>): 2074.6, 2005.7. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.13 (d, <sup>3</sup>J<sub>H-H</sub> = 2.0 Hz, 2H, CH(imid)); 7.10 (d, <sup>3</sup>J<sub>H-H</sub> = 1.6 Hz, 2H, CH(imid)); 4.63–4.54 (m, 2H, CH<sub>2</sub>(linker)); 4.19–4.14 (m, 4H, CH<sub>2</sub>(*n*-Bu), CH<sub>2</sub>(linker)); 4.12–4.09 (m, 2H, CH<sub>2</sub>(*n*-Bu)); 2.02 (brs, 2H, CH<sub>2</sub>(linker)); 1.82–1.75 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.47–1.35 (m, 4H, CH<sub>2</sub>(*n*-Bu)); 1.18 (brs, 2H, CH<sub>2</sub>(linker)); 0.98 (t, 6H, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz, CH<sub>3</sub>(*n*-Bu)). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 186.6 (d, <sup>1</sup>J<sub>C-Rh</sub> = 56.2 Hz, 2C, CO); 169.7 (d, <sup>1</sup>J<sub>C-Rh</sub> = 45.5 Hz, 2C, C(carbene)); 123.3, 123.0 (4C, CH(imid)); 51.6 (2C, NCH<sub>2</sub>(linker)); 47.1 (2C, NCH<sub>2</sub>(*n*-Bu)); 33.0 (2C, CH<sub>2</sub>(*n*-Bu)); 25.7 (2C, CH<sub>2</sub>(linker)); 20.1 (2C, CH<sub>2</sub>(*n*-Bu)); 14.0 (2C, CH<sub>3</sub>(*n*-Bu)).

**Structure Determination and Refinement of 3c, 3b, and 6d.** Crystals suitable for study were obtained by slow diffusion of hexanes into concentrated dichloromethane solutions of the complexes. Data were collected on a Nonius KappaCCD diffractometer (Mo Kα radiation) and processed using TEXAN for Windows.<sup>24</sup> The structures were solved by direct methods and expanded using Fourier techniques.<sup>25</sup> Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 3.

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**Supporting Information Available:** Details of the X-ray crystal structures, including tables giving atomic positions, bond distances, bond angles, and torsional angles; the crystallographic data are also available as CIF files. This

material is available free of charge via the Internet at <http://pubs.acs.org>.

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