ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 5681–5692 5681
DOI: 10.1021/om1005897

Impact of Ligand Modification on Structures and Catalytic Activities of Chelating Bis-Carbene Rhodium(I) Complexes†

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Received July 8, 2010

A series of novel chelating N-heterocyclic bis-carbene rhodium(I) complexes based on 1,2,4-triazoles, benzimidazoles, and imidazoles with varying bridge length and N substituents has been synthesized. In addition to their structural characterization, their catalytic activity in the hydrosilylation of 4-fluoroacetophenone with diphenylsilane has been examined. The results reveal that selectivities and turnover frequencies (TOFs) are influenced by bridge length, steric demand of the N substituents, and electronic properties of the heterocycle.

Introduction

The chemistry of N-heterocyclic carbenes (NHCs) and their application as strongly binding ligands of transition-metal complexes in homogeneous catalysis is a topic of high interest, apparent by the number of review articles and books published in this field during the course of the past several years.[1] In addition to the strong metal−carbon bond present in NHC metal complexes, bidentate bis-carbene ligands enhance stability as a result of the chelate effect and therefore offer important advantages over their monodentate analogues with regard to applications in catalysis. Cavell et al. predicted that reductive elimination, representing the most common decomposition mechanism of NHC-based catalysts in hydrogenation and hydroformylation, will be impeded by using chelating bis-NHC ligands.[2] In addition to bidentate Rh complexes with donor-functionalized mono-carbene ligands,[3] there are several examples of Rh complexes with imidazole (im),[4] benzimidazole (bim),[4p,5] and triazole (tri) based biscarbene ligands.[6] Some of them were successfully tested in different catalytic applications such as transfer hydrogenation,[4a,c,d] hydrosilylation,[4d,f,m,5b,c,e,h] hydrogenation,[5g] hydroformylation,[5g] oxidative kinetic resolution,[5h] and intramolecular hydroamination.[4b] It was shown that N-heterocyclic bis-carbene ligands allow a better control over the coordination sphere and the fine tuning of properties such as steric hindrance, bite angles, chirality, and fluxional behavior.[7] However, the influence of different types of

† Part of the Dietmar Seyferth Festschrift. Dedicated to Dietmar Seyferth.

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Published on Web 08/04/2010

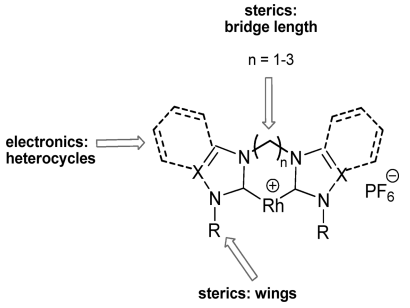

Figure 1. Catalyst design and tuning parameters: electronics: heterocycle (X = N, C); sterics, bridge length and wing substituents (R = alkyl or aryl substituent).

ligand modifications on the catalytic properties has not yet been systematically studied. Bidentate ligands of the type depicted in Figure 1 represent ideal candidates to examine the influence of ligand properties on structures and catalytic activities.

Some rhodium bis-carbene complexes of the motif depicted in Figure 1 have been reported in the literature. In contrast to imidazole-[4b,e,g,i−m] and benzimidazole-based[4p,5a,d,f,g] systems, triazole-based systems are less investigated, only two tetrakis-NHC rhodium complexes are known so far.[6a] Crabtree et al.[6b,c] recently prepared a novel bitriazole-2-ylidene ligand and its dinuclear Rh(I) complex, with the NHC ligand bridging two metal ions. However, to the best of our knowledge, none of the published Rh(I)-NHC complexes display the structural motif [Rh(COD)(bis-NHC)]X (NHC = 1,2,4-triazole, X = anion).

In order to understand the intricate interplay of electronic and steric effects, a series of analogous Rh(I) complexes of the type [Rh(COD)(bis-NHC)]PF_6 was prepared, exhibiting a set of systematically varied bis-NHC ligands based on 1,2,4-triazole, benzimidazole, and imidazole. A comparative study of [$RhI(CO)_2$(NHC)] complexes revealed that the σ-donor ability increases in the order 1,2,4-triazole < benzimidazole < imidazole.[6a] The catalytic performance can be modified via the σ-donor ability of a ligand. It was shown, for example, that the donor capability of the NHC ligand in catalysts of the type [IrX(COD)(NHC)] (X = I, COD = cyclooctadiene) has a significant impact on the initiation time and the reaction rates of the transfer hydrogenation of acetophenone and acetonaphthone.[8]

In the present work the synthetic procedure for the preparation of such Rh(I) complexes with novel chelating bis-carbene NHC ligands is presented, along with their structural characterization. The new complexes were tested as catalysts for the hydrosilylation of 4-fluoroacetophenone with diphenylsilane as a model reaction. The influence of the different carbene moieties, particularly the bridge length (n = 1−3), the heterocycle composition, and the wingtip groups on the structure, stability, and catalytic activity of the resulting Rh complexes is discussed.

Results and Discussion

The preparation of the azolium salts **1** as ligand precursors is straightforward and high-yielding. N-substituted azoles readily react with dibromomethane, 1,2-dibromoethane, and 1,3-dibromopropane in THF to form the bromide salts (Scheme 1).[6a,9]

In order to isolate the bis-carbene complexes in high yields, it is necessary to exclude halides or other coordinating anions from the reaction mixture, which requires an anion exchange of Br^- to PF_6^- prior to the complex synthesis.[4b] Following an adapted literature procedure, the metal complexes have been prepared under mild conditions.[10] $[Rh(OEt)COD]_2$ is obtained from $[RhCl(COD)]_2$ with in situ generated NaOEt for the synthesis of triazole- and imidazole-based complexes. For the benzimidazole-based complexes, readily synthesized $[Rh(OEt)COD]_2$ is added as a THF solution to the reaction mixture of the benzimidazolium salt with NaOEt in MeOH. Subsequently, $[Rh(OEt)COD]_2$ reacts with the azolium salts **2** to give the corresponding complexes of type **3** (Scheme 2), which are obtained in high yields (80−98%).

In contrast to earlier reports,[4e,g,l] the formation of dinuclear Rh species is not observed. Our investigation indicates that the formation of dinuclear species does not primarily depend on the interplay between bridge length and wingtips,[4l] but rather on the synthetic method used to prepare the complexes.[4b]

The stability of the complex changes significantly with varying bridge length. Whereas all complexes with ethylene and propylene bridges are stable to prolonged exposure to air, water, and high temperatures (up to 200 °C; confirmed by TG/MS measurements), the complexes with a methylene bridge decompose in solution—depending on the heterocycles—after a few minutes (imidazole- and benzimidazole-based complexes) to several days (triazole-based complexes).

The isolated complexes were characterized by elemental analysis, FAB mass spectrometry, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and X-ray crystallography. Evidence for the coordination of the carbene carbon atom to the rhodium atom is obtained by $^{13}C\{^1H\}$ NMR spectroscopy. A doublet resonance in the typical range of δ 178−195 ppm ($^1J_{Rh-C(carbene)}$ = 50−55 Hz) is observed for all complexes.[4g,5a,6a] The ^1H NMR spectrum reflects the rigidity of the bis-carbene complexes. In the case of **tri-3$^{1\text{-Me}}$**, the ^1H NMR spectrum displays two methylene C−H resonances with a $^2J_{H-H}$ coupling constant of approximately 13 Hz. The magnetic inequivalence of the methylene protons indicates a nonfluxional behavior at room temperature. A boat-to-boat inversion of the six-membered metallacycle does not occur. The rigidity of the complexes with an ethylene bridge was also confirmed by ^1H NMR spectra, as two different multiplets of the linker protons are present in each case, as shown for **im-3$^{2\text{-Me}}$** in Figure 2 as a representative example.

This splitting can be explained as an AA′XX′ spin system being caused by a fixed C_1-symmetric arrangement of the ligands. This is realized in a boat conformation of the seven-membered metallacycle,[4g] as illustrated in Figure 3, in which axial (H^A and $H^{A'}$) and equatorial (H^X and $H^{X'}$) protons are chemically but not magnetically equivalent. This interpretation is supported by a WinDNMR simulation of multiplet **A**, which matches the experimental spectrum, as can be seen in Figure 2 (right).

Crystals suitable for X-ray analysis were obtained for a number of complexes. The molecular structure of the cationic complex **tri-3$^{2\text{-Me}}$** in the solid state is depicted as an

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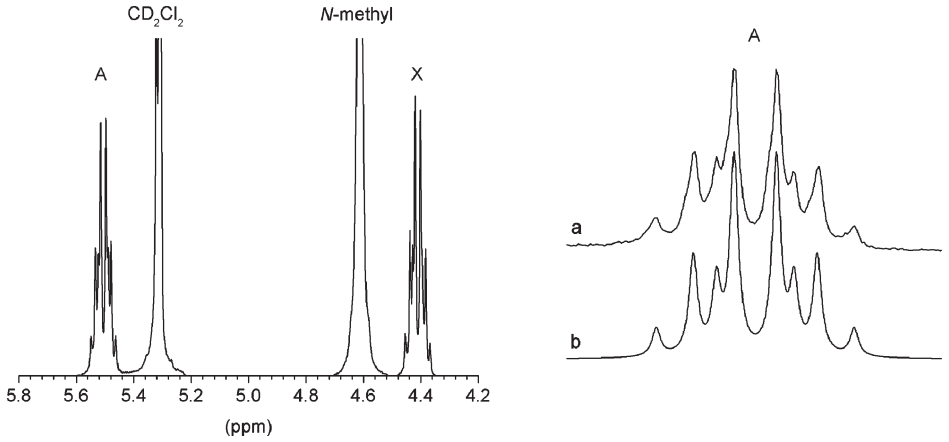
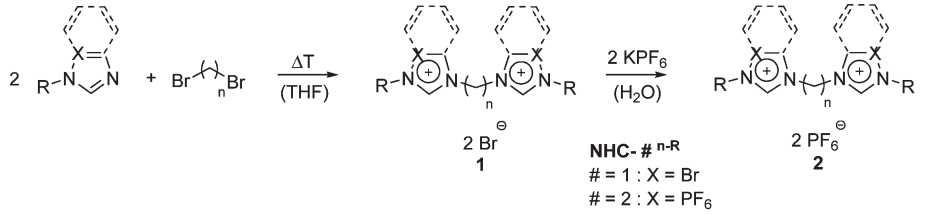


Figure 2. Section of the ^{1}H NMR spectrum of **im-3$^{2\text{-Me}}$** showing the bridging ethylene protons (left) and the experimental (a) and simulated (b) multiplet structure of **A** (right). WinDNMR simulation parameters: $J_{AA'} = 5.24$ Hz, $J_{XX'} = 5.26$ Hz, $J_{AX} = 14.5$ Hz, $J_{AX'} = -7.10$ Hz, $W_a = 1.78$ Hz.

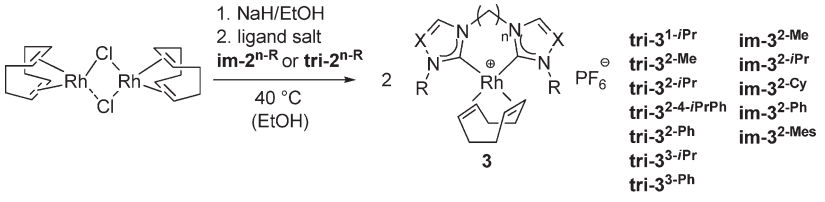
Scheme 1. Synthesis of Ligand Bis-Azolium Bromide Salts 1 and Hexafluorophosphate Salts 2



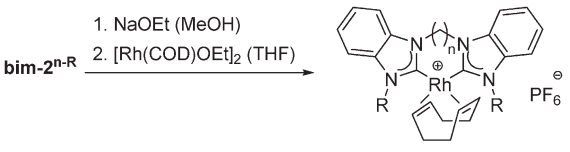
tri-1$^{1\text{-}i\text{Pr}}$ **bim-1$^{2\text{-Me}}$** **im-1$^{2\text{-Me}}$**
tri-1$^{2\text{-Me}}$ **bim-1$^{3\text{-Me}}$** **im-1$^{2\text{-}i\text{Pr}}$**
tri-1$^{2\text{-}i\text{Pr}}$ **bim-1$^{2\text{-Ph}}$** **im-1$^{2\text{-Cy}}$**
tri-1$^{2\text{-4-}i\text{PrPh}}$ **bim-1$^{3\text{-Ph}}$** **im-1$^{2\text{-Ph}}$**
tri-1$^{2\text{-Ph}}$ **bim-1$^{2\text{-}i\text{Pr}}$** **im-1$^{2\text{-Mes}}$**
tri-1$^{3\text{-}i\text{Pr}}$ **bim-1$^{3\text{-}i\text{Pr}}$**
tri-1$^{3\text{-Ph}}$

tri-2$^{1\text{-}i\text{Pr}}$ **bim-2$^{2\text{-Me}}$** **im-2$^{2\text{-Me}}$**
tri-2$^{2\text{-Me}}$ **bim-2$^{3\text{-Me}}$** **im-2$^{2\text{-}i\text{Pr}}$**
tri-2$^{2\text{-}i\text{Pr}}$ **bim-2$^{2\text{-Ph}}$** **im-2$^{2\text{-Cy}}$**
tri-2$^{2\text{-4-}i\text{PrPh}}$ **bim-2$^{3\text{-Ph}}$** **im-2$^{2\text{-Ph}}$**
tri-2$^{2\text{-Ph}}$ **bim-2$^{2\text{-}i\text{Pr}}$** **im-2$^{2\text{-Mes}}$**
tri-2$^{3\text{-}i\text{Pr}}$ **bim-2$^{3\text{-}i\text{Pr}}$**
tri-2$^{3\text{-Ph}}$

Scheme 2. Synthesis of Rh(I) Complexes 3



tri-3$^{1\text{-}i\text{Pr}}$ **im-3$^{2\text{-Me}}$**
tri-3$^{2\text{-Me}}$ **im-3$^{2\text{-}i\text{Pr}}$**
tri-3$^{2\text{-}i\text{Pr}}$ **im-3$^{2\text{-Cy}}$**
tri-3$^{2\text{-4-}i\text{PrPh}}$ **im-3$^{2\text{-Ph}}$**
tri-3$^{2\text{-Ph}}$ **im-3$^{2\text{-Mes}}$**
tri-3$^{3\text{-}i\text{Pr}}$
tri-3$^{3\text{-Ph}}$



bim-3$^{2\text{-Me}}$
bim-3$^{3\text{-Me}}$
bim-3$^{2\text{-}i\text{Pr}}$
bim-3$^{3\text{-}i\text{Pr}}$
bim-3$^{2\text{-Ph}}$
bim-3$^{3\text{-Ph}}$

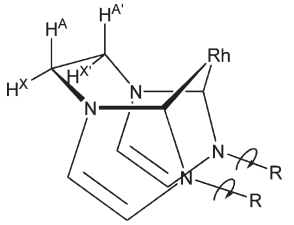


Figure 3. Boat conformation of the metallacycle.

example in Figure 4, and selected bond distances and bond angles of **tri-3$^{2\text{-Me}}$** are provided in Table 1.

Images of the molecular structures for the other complexes along with selected geometrical and crystallographic details are given in the Supporting Information.

As previously reported by Crabtree et al.,[41] a distortion of the square-planar geometry and an in-plane distortion of the NHC moiety can be observed in complexes of this type. In each complex, the rhodium atom is coordinated by two carbene carbon atoms and two η^2-bound olefin groups of the cyclooctadiene ligand that form a distorted-square-planar coordination environment. The deviation from the ideal square-planar arrangement of the ligands can be described by the tilt angle φ between plane A (through Rh1, C9, and

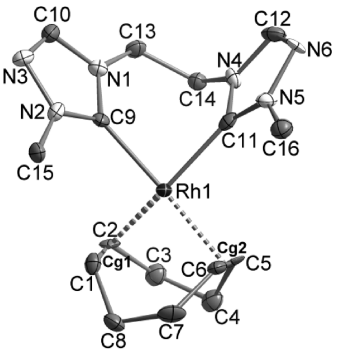


Figure 4. Molecular structure of cationic complex in **tri-3$^{2\text{-Me}}$**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.[11]

Table 1. Selected Structural Details of the Rh(I) Bis-Carbene Complex tri-3$^{2\text{-Me}}$

d(Rh−$C_{carbene}$) (Å)	2.043(7), 2.052(8)
d(Rh−C_g)[a] (Å)	2.087, 2.101
$C_{carbene}$−Rh−$C_{carbene}$ bite angle (deg)	85.0(3)
yaw distortion angle θ (deg)	1.5(5), 0.5(6)
average yaw distortion angle θ_{av} (deg)	6.0(6)
tilt angle φ (deg)	16.9
distance of C_g to plane through Rh and both $C_{carbene}$ (Å)	0.567, −0.176

[a] C_g is defined as the center of a C=C double bond in COD.

C11) and plane B (through Rh1, C_g1, and C_g2) and the distances of C_g1 and C_g2 to plane A (C_g1 and C_g2 denote the centers of the C=C double bond within the COD ligand) (Figure 5).

In accordance with the observations made by Crabtree et al. it was found that one of the Rh−C_g bonds is located within or very close to plane A (shortest distance of C_g and A: 0.003−0.368 Å), whereas the other bond deviates from it more significantly (longest distance of C_g and A: 0.115−0.648 Å).[4l] The values for φ vary from 3.7 to 19.0°. This distortion was attributed to a better overlap of the empty C_{COD}=C_{COD} π^* orbital with the occupied rhodium d_{z^2} orbital, as previously described for electron-rich d^8 ruthenium complexes.[12,4l] A correlation between the N substituents or the bridge length and the distortion was not observed. The distortions of the M−C−N bond angles (α and β) are reflected in the yaw distortion angle θ (θ = 1/2-($\alpha - \beta$)) shown in Figure 5.[4l] The values determined for θ are summarized in the Supporting Information. With the exception of **tri-3$^{3\text{-Ph}}$** (5.9(1)°), the θ values for ethylene- and propylene-bridged derivatives (2.9(2)−3.7(2) and 4.9(3)−7.5(1)°) fall within the same range as previously reported by Crabtree et al. for similar systems. The average value for θ decreases with increasing bridge length, which was proposed to be a consequence of the ring strain.[4b] It can also be seen that in all complexes the yaw distortion mainly affects one of the two M−NHC bonds, which appears to be energetically favorable.

Impact of Ligand Modification on Catalysis. The hydrosilylation of ketones or aldehydes leading to silyl ethers is a useful and experimentally relatively straightforward transformation, as protected alcohols can be produced directly from carbonyl compounds. Although several complexes containing phosphine ligands are known to be highly active catalysts,[13] they have some drawbacks such as low stability and deactivation. As the presented complexes are extremely stable to air, water, and elevated temperatures, they are expected to increase the stability of the catalytic system and do not require inert-gas conditions. The influence of ligand modifications of the synthesized bis-NHC rhodium complexes on activity and selectivity was evaluated in the hydrosilylation of 4-fluoroacetophenone with diphenylsilane to yield silyl ether **5**, as shown in Scheme 3.

In agreement with previous reports,[14] silyl enol ether **6** formed as a side product. 4-Fluoroacetophenone was used as the substrate in order to conveniently monitor the reaction progress in situ by ^{19}F NMR spectroscopy. No spectroscopic evidence for defluorination or side products other than **6** was observed. The reactions were carried out with 2 mol % catalyst at 25 °C in dichloromethane. Yields and turnover frequencies (TOFs) were determined and are summarized in Table 2. Some of the complexes were recovered and analyzed after the catalytic run and thus proved their stability under catalytic conditions.

The activities of the complexes are comparable with those of previously reported related systems. Shi et al. obtained 44% of the product in 48 h with a Rh(III) complex bearing 2,2′-bis-carbene-biphenyl ligands, using 2 mol % of catalyst in CH_2Cl_2 at room temperature.[5c] Enders et al. tested (triazolinylidene)rhodium(I) complexes as catalysts for the hydrosilylation of acetophenone with diphenylsilane using 1 mol % catalyst in THF and observed yields ranging from 60 to 90% within 4 h to 6 days.[15]

Influence of Bridge Length. The influence of the bridge length on the activity can be seen for complexes containing identical heterocycles and wingtips, differing only in bridge length (Table 3).

For complexes bearing alkyl-substituted triazole-based bis-carbenes (entries 1−3), the activity is shown to increase with decreasing bridge length, whereas in analogous aryl-substituted derivatives (entries 4 and 5) this tendency is reversed. The exact opposite trend, however, is observed for the complexes with benzimidazole-based bis-carbenes (alkyl substituted, entries 6−9, aryl substituted, entries 10 and 11). These results indicate that the influences of two different parameters cannot be treated separately but must be regarded as interdependent. No clear trend is found with regard to the selectivity.

Influence of N Substituents. Depending on the steric demand of the N substituents, the turnover frequencies (TOFs) vary considerably (Table 4).

When alkyl- (entries 1−6) and aryl-substituted (entries 7−10) complexes are compared separately, the activity and selectivity for **5** are seen to increase with steric demand of the wingtips. This implicates that the reaction pathway to **5** is favored in comparison to the competing pathway to the silyl enol ether **6** by bulky substituents.

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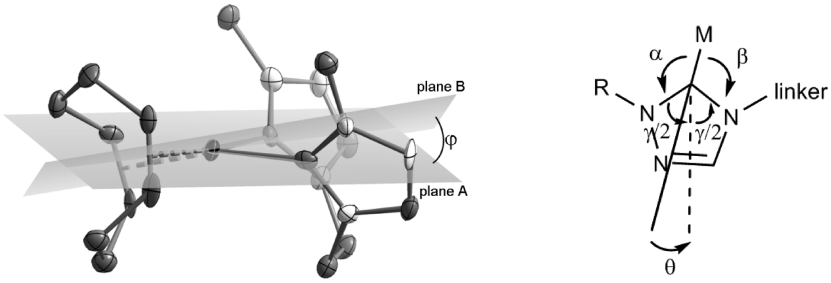

Figure 5. Tilt angle φ between planes A and B in **tri-3$^{2\text{-Me}}$** and yaw distortion angle.[11]

Scheme 3. Hydrosilylation of 4-Fluoroacetophenone with Diphenylsilane using [Rh(COD)(bisNHC)]PF_6 Complexes To Yield Silyl Ether 5 and Silyl Enol Ether 6

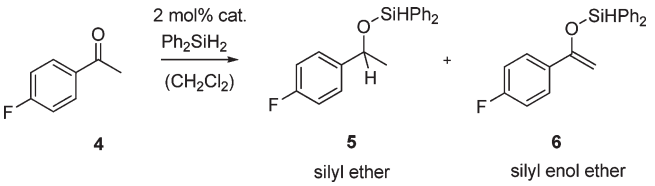

Table 2. Yields of Silyl Ether 5 and Silyl Enol Ether 6 and Turnover Frequencies for the Hydrosilylation of 4-Fluoroacetophenone with Diphenylsilane[a]

entry	complex	yield **5**/**6** (%)[b]	TOF (h^{-1})[c]
1	**tri-3$^{1\text{-}i\text{Pr}}$**	71/29	163
2	**tri-3$^{2\text{-Me}}$**	60/40	5
3	**tri-3$^{2\text{-}i\text{Pr}}$**	77/23	56
4	**tri-3$^{2\text{-4-}i\text{PrPh}}$**	80/20	25
5	**tri-3$^{2\text{-Ph}}$**	84/16	7
6	**tri-3$^{3\text{-}i\text{Pr}}$**	77/33	2
7	**tri-3$^{3\text{-Ph}}$**	80/20	60
8	**bim-3$^{2\text{-Me}}$**	66/34	70
9	**bim-3$^{3\text{-Me}}$**	74/26	100
10	**bim-3$^{2\text{-}i\text{Pr}}$**	88/12	68
11	**bim-3$^{3\text{-}i\text{Pr}}$**	77/23	140
12	**bim-3$^{2\text{-Ph}}$**	82/18	550
13	**bim-3$^{3\text{-Ph}}$**	80/20	154
14	**im-3$^{2\text{-Me}}$**	44/56	7
15	**im-3$^{2\text{-}i\text{Pr}}$**	58/42	5
16	**im-3$^{2\text{-Cy}}$**	68/32	38
17	**im-3$^{2\text{-Ph}}$**	75/25	24
18	**im-3$^{2\text{-Mes}}$**	75/25	199

[a] 2 mol % catalyst in CH_2Cl_2 at 25 °C; conversion for all experiments > 99%. [b] Yields determined by ^{19}F NMR spectroscopy. No spectroscopic evidence was found for compounds other than **4**−**6** and defluorination; thus, additional reaction pathways were excluded and no internal standard was needed. [c] TOFs were determined at the steepest slope of the kinetic curves.

Table 3. Influence of the Bridge Length: Selected Yields of Silyl Ether 5 and Silyl Enol Ether 6 and Turnover Frequencies for the Hydrosilylation of 4-Fluoroacetophenone with Diphenylsilane

entry	complex	yield **5**/**6** (%)	TOF (h^{-1})
1	**tri-3$^{1\text{-}i\text{Pr}}$**	71/29	163
2	**tri-3$^{2\text{-}i\text{Pr}}$**	77/23	56
3	**tri-3$^{3\text{-}i\text{Pr}}$**	77/33	2
4	**tri-3$^{2\text{-Ph}}$**	84/16	7
5	**tri-3$^{3\text{-Ph}}$**	80/20	60
6	**bim-3$^{2\text{-Me}}$**	66/34	70
7	**bim-3$^{3\text{-Me}}$**	74/26	100
8	**bim-3$^{2\text{-}i\text{Pr}}$**	88/12	68
9	**bim-3$^{3\text{-}i\text{Pr}}$**	77/23	140
10	**bim-3$^{2\text{-Ph}}$**	82/18	550
11	**bim-3$^{3\text{-Ph}}$**	80/20	154

Table 4. Influence of the N Substituent: Selected Yields of Silyl Ether 5 and Silyl Enol Ether 6 and TOFs for the Hydrosilylation of 4-Fluoroacetophenone with Diphenylsilane

entry	complex	yield **5**/**6** (%)	TOF (h^{-1})
1	**tri-3$^{2\text{-Me}}$**	60/40	5
2	**tri-3$^{2\text{-}i\text{Pr}}$**	77/23	56
3	**bim-3$^{3\text{-Me}}$**	74/26	100
4	**bim-3$^{3\text{-}i\text{Pr}}$**	77/23	140
5	**im-3$^{2\text{-Me}}$**	44/56	7
6	**im-3$^{2\text{-Cy}}$**	68/32	38
7	**tri-3$^{2\text{-Ph}}$**	84/16	7
8	**tri-3$^{2\text{-4-}i\text{PrPh}}$**	80/20	25
9	**im-3$^{2\text{-Ph}}$**	75/25	24
10	**im-3$^{2\text{-Mes}}$**	75/25	199

Table 5. Influence of the Heterocycle: Selected Yields of Silyl Ether 5 and Silyl Enol Ether 6 and TOFs for the Hydrosilylation of 4-Fluoroacetophenone with Diphenylsilane

entry	complex	yield **5**/**6** (%)	TOF (h^{-1})
1	**tri-3$^{2\text{-Me}}$**	60/40	5
2	**bim-3$^{2\text{-Me}}$**	66/34	70
3	**im-3$^{2\text{-Me}}$**	44/56	7
4	**tri-3$^{2\text{-}i\text{Pr}}$**	77/23	56
5	**bim-3$^{2\text{-}i\text{Pr}}$**	88/12	68
6	**im-3$^{2\text{-}i\text{Pr}}$**	58/42	5
7	**tri-3$^{2\text{-Ph}}$**	84/16	7
8	**bim-3$^{2\text{-Ph}}$**	82/18	550
9	**im-3$^{2\text{-Ph}}$**	75/25	24

Influence of Heterocycle. In order to study the influence of the different heterocycles, the activities and selectivities of complexes with the same N substituents (Me, *i*Pr, Ph) and bridge length ($n = 2$) are compared. Table 5 shows the TOFs and yields of silyl ether **5** for the three sets of complexes.

According to these data, the benzimidazole-based systems are the most active and, except for **3$^{2\text{-Ph}}$**, also the most selective catalysts, whereas the imidazole-based systems are the least selective catalysts in all cases.

It is apparent that the benzimidazole systems offer the most favorable electronic properties for achieving high activity and selectivity.

Conclusion

In summary, synthetic routes to novel triazole-, benzimidazole- and imidazole-based bis-carbene ligands and derived rhodium(I) complexes are described. The complexes were analyzed by elemental analysis and mass spectrometry and structurally characterized in solution by NMR spectroscopy and by X-ray crystallography. All compounds are shown to be catalytically active for the hydrosilylation of 4-fluoroacetophenone with diphenylsilane. The systematic study of a

variety of bis-carbene ligand systems reveals that the interplay of heterocycle, bridge length and N substituents has to be considered when designing an appropriate catalyst for a certain application. Sterically demanding substituents and benzimidazole-based bis-carbene ligands with short bridge lengths seem to be favorable for the hydrosilylation with Rh(I) bis-carbene complexes. Additional mechanistic studies are currently under way to allow a deeper understanding of the observed results and the prediction of the modifications necessary to enhance the catalyst activity and selectivity, including applications for asymmetric hydrosilylation.

Experimental Section

General Remarks. The synthesis of the metal complexes was carried out using standard Schlenk techniques under an argon atmosphere. Solvents were dried and degassed by standard methods prior to use.[16] The term filtration refers to filtration via cannula and a Whatman GF/B filter. Elemental analyses were carried out by the Microanalytical Laboratory of the Technische Universität München. Mass spectra were acquired by the Technische Universität München Mass Spectrometry Laboratory using a Finnigan MAT 90 spectrometer equipped with a FAB ionization chamber. NMR spectra were recorded on a JEOL-JMX-GX 400 MHz or Bruker Avance DPX 400 spectrometer. NMR multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; sept, septet; m, multiplet; br, broad signal. Coupling constants *J* are given in Hz. The spectra were referenced to residual ^{1}H and $^{13}C\{^{1}H\}$ signals of the solvents.[17] If not otherwise mentioned, all reagents were purchased from commercial sources and used without further purification.

Di-1,2,4-triazolium Salts. 1-Phenyl-1*H*-1,2,4-triazole,[18] 1-(4-isopropylphenyl)-1*H*-1,2,4-triazole,[18] 1-isopropyl-1*H*-1,2,4-triazole,[19] and 1-methyl-1*H*-1,2,4-triazole[20] were prepared according to previously reported literature methods. The ditriazolium bromide and hexafluorophosphate salts were obtained by following a previously reported procedure.[4b,6a]

1-(4-Isopropylphenyl)-1*H*-1,2,4-triazole. (4-Isopropylphenyl)-hydrazine hydrochloride (3.44 g, 1.85 mol) was added to a solution of *s*-triazine (1.0 g, 12.3 mmol) in ethanol (10 mL). The mixture was refluxed for 12 h before the precipitating ammonium chloride was removed by filtration, leaving a red filtrate. The solvent was removed in vacuo to yield a dark brown oil which was purified by vacuum distillation at 150 °C and 10^{-2} mbar. Yield: 1.91 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (d, ^{3}J = 7.04 Hz, 6H, CH_3CH), 2.96 (sept, ^{3}J = 7.04 Hz, 1H, CH$_3$C*H*), 7.34 (d, 2H, *m*-C*H*), 7.57 (d, 2H, *o*-C*H*), 8.08 (s, 1H, NC*H*N), 8.51 (s, 1H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, $CDCl_3$): δ 23.9 (*C*H$_3$CH), 33.8 (CH$_3$*C*H), 120.2 (*m*-*C*H), 127.7 (*o*-*C*H), 134.9 (C_{quart}), 140.7 (N*C*HN), 149.3 (C_{quart}), 152.3 (N*C*HN).

General Procedure for the Synthesis of Di-1,2,4-triazolium Dibromide. 1-R-1*H*-1,2,4-triazole (10 mmol), dibromoalkane (5 mmol), and 2 mL of THF were heated for 12 h at 80 °C in an ACE pressure tube with a volume of 35 mL. The precipitate was isolated by filtration, washed three times with 5 mL of diethyl ether, and dried under reduced pressure to obtain the pure product in form of a colorless solid.

1,1′-Diisopropyl-4,4′-methylenedi-1,2,4-triazolium Dibromide (tri-1$^{1\text{-}i\text{Pr}}$). Yield: 1.72 g (87%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.53 (d, ^{3}J = 6.4 Hz, 12H, CH_3CH), 4.90 (sept, ^{3}J = 6.4 Hz, 2H, CH$_3$C*H*), 6.91 (s, 2H, NCH_2), 9.59 (s, 2H, NC*H*N), 10.69 (s, 2H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, DMSO-d_6): δ 21.0 (*C*H$_3$), 44.3 (NCH$_2$), 55.1 (CH$_3$*C*H), 141.5 (N*C*HN), 144.4 (N*C*HN).

1,1′-Bis(4-isopropylphenyl)-4,4′-ethylenedi-1,2,4-triazolium Dibromide (tri-1$^{2\text{-}i\text{Pr}}$). Yield: 1.52 g (54%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.24 (d, ^{3}J = 6.6 Hz, 12H, CH_3CH), 3.02 (sept, 2H, ^{3}J = 6.6 Hz, CH$_3$C*H*), 5.04 (s, 4H, NCH_2), 7.58 (d, 4H, *m*-C*H*), 7.81 (d, 4H, *o*-C*H*), 9.46 (s, 2H, NC*H*N), 11.02 (s, 2H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, DMSO-d_6): δ 23.6 (*C*H$_3$CH), 33.1 (CH$_3$*C*H), 46.8 (N*C*H$_2$), 120.7 (*m*-*C*H), 128.0 (*o*-*C*H), 132.8 (C_{quat}), 141.6 (N*C*HN), 145.1 (N*C*HN), 151.4 (C_{quat}).

1,1′-Diphenyl-4,4′-ethylenedi-1,2,4-triazolium Dibromide (tri-1$^{2\text{-}Ph}$). Yield: 1.94 g (81%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.06 (s, 4H, NCH_2), 7.65 (m, 2H, *p*-C*H*), 7.73 (m, 4H, *m*-C*H*), 7.92 (m, 4H, *o*-C*H*), 9.50 (s, 2H, NC*H*N), 11.12 (d, 2H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, DMSO-d_6): δ 46.8 (N*C*H$_2$), 120.6 (*m*-*C*H), 130.3 (*o*-*C*H), 130.7 (*p*-*C*H), 134.8 (C_{quat}), 142.0 (N*C*HN), 145.2 (N*C*HN).

1,1′-Diisopropyl-4,4′-propylenedi-1,2,4-triazolium Dibromide (tri-1$^{3\text{-}i\text{Pr}}$). Yield: 2.08 g (98%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.54 (d, ^{3}J = 6.8 Hz, 12H, CH_3), 2.59 (t, 2H, NCH$_2$-CH_2CH$_2$N), 4.38 (t, 4H, NCH_2), 4.82 (sept, ^{3}J = 6.8 Hz, 2H, CH$_3$C*H*), 9.35 (s, 2H, NC*H*N), 10.41 (s, 2H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, DMSO-d_6): δ 21.0 (*C*H$_3$), 28.3 (NCH$_2$-*C*H$_2$CH$_2$N), 44.3 (N*C*H$_2$), 55.1 (*C*HCH$_3$), 141.5 (N*C*HN), 144.4 (N*C*HN).

1,1′-Diphenyl-4,4′-propylenedi-1,2,4-triazolium Dibromide (tri-1$^{3\text{-}Ph}$). Yield: 1.65 g (67%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.72 (qu, 2H, NCH$_2$CH_2CH$_2$N), 4.52 (t, 4H, NCH_2), 7.67 (m, 2H, *p*-C*H*), 7.73 (m, 4H, *m*-C*H*), 7.96 (m, 4H, *o*-C*H*), 9.54 (s, 2H, NC*H*N), 11.10 (s, 2H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (100.53 MHz, DMSO-d_6): δ 28.3 (NCH$_2$CH_2CH$_2$N), 44.8 (N*C*H$_2$), 120.7 (*m*-*C*H), 130.3 (*o*-*C*H), 130.7 (*p*-*C*H), 135.0 (C_{quat}), 141.9 (N*C*HN), 145.2 (N*C*HN).

General Synthesis for Di-1,2,4-triazolium Bis(hexafluorophosphate) Salts. A solution of ditriazolium dibromide (5 mmol) in water (15 mL) was added to a solution of potassium hexafluorophosphate (10 mmol) in water (10 mL). The precipitate was isolated by filtration, washed with diethyl ether (three times with 5 mL), and dried in vacuo overnight, yielding the colorless solid product.

1,1′-Diisopropyl-4,4′-methylenedi-1,2,4-triazolium Bis(hexafluorophosphate) (tri-2$^{1\text{-}i\text{Pr}}$). Yield: 2.32 g (88%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.53 (d, ^{3}J = 6.6 Hz, 12H, CH_3CH), 4.93 (sept, ^{3}J = 6.6 Hz, 2H, CH$_3$C*H*), 6.74 (s, 2H, NCH_2), 9.36 (s, 2H, NC*H*N), 10.29 (s, 2H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, DMSO-d_6): δ 21.1 (*C*H$_3$), 54.9 (N*C*H$_2$), 55.6 (CH$_3$*C*H), 142.2 (N*C*HN), 144.8 (N*C*HN). MS (FAB): *m*/*z* (%) 380.8 (36.7) $[M + PF_6]^+$, 234.9 (100) $[M]^{2+}$. Anal. Calcd for $C_{11}H_{20}F_{12}N_6P_2$ (526.10): C, 25.11: H, 3.83; N, 15.97. Found: C, 24.99: H, 3.88; N, 15.95.

1,1′-Dimethyl-4,4′-ethylenedi-1,2,4-triazolium Bis(hexafluorophosphate) (tri-2$^{2\text{-}Me}$). Yield: 2.20 g (91%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.10 (s, 6H, CH_3), 4.78 (s, 4H, NCH_2), 9.06 (s, 2H, NC*H*N), 9.94 (s, 2H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, DMSO-d_6): δ 38.7 (*C*H$_3$), 46.5 (N*C*H$_2$), 143.1 (N*C*HN), 144.5 (N*C*HN). MS (FAB): *m*/*z* (%) 338.8 (17.4) $[M + PF_6]^+$, 191.7 (100) $[M]^{2+}$. Anal. Calcd for $C_8H_{14}F_{12}N_6P_2$ (484.06): C, 19.85: H, 2.91; N, 17.36. Found: C, 19.58: H, 2.92; N, 16.70.

1,1′-Diisopropyl-4,4′-ethylenedi-1,2,4-triazolium Bis(hexafluorophosphate) (tri-2$^{2\text{-}i\text{Pr}}$). Yield: 1.57 g (84%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.52 (d, ^{3}J = 6.6 Hz, 12H, CH_3), 4.75 (s, 4H, NCH_2), 4.84 (sept, ^{3}J = 6.6 Hz, 2H, CH$_3$C*H*), 9.11 (s, 2H, NC*H*N), 10.08 (s, 2H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, DMSO-d_6): δ 21.1 (*C*H$_3$), 46.5 (N*C*H$_2$), 55.3 (*C*HCH$_3$), 141.7 (N*C*HN), 144.7 (N*C*HN). MS (FAB): *m*/*z* (%) 394.8 (59.9) $[M + PF_6]^+$, 248.9 (100) $[M]^{2+}$. Anal. Calcd for $C_{12}H_{22}F_{12}N_6P_2$ (540.12): C, 26.68, H, 4.10; N, 15.56. Found: C, 26.51: H, 4.01; N, 15.40.

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1,1′-Bis(4-isopropylphenyl)-4,4′-ethylenedi-1,2,4-triazolium Bis(hexafluorophosphate) (tri-$2^{2\text{-}4\text{-}i\text{Pr}Ph}$). Yield: 2.60 g (96%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.24 (d, ^3J = 6.6 Hz, 12H, CH_3CH), 3.02 (sept, 2H, ^3J = 6.6 Hz, CH$_3$CH), 5.02 (s, 4H, NCH_2), 7.59 (m, 4H, *m*-CH), 7.81 (m, 4H, *o*-CH), 9.44 (s, 2H, NCHN), 10.97 (s, 2H, NCHN). ^{13}C{^{1}H} NMR (100.5 MHz, DMSO-d_6): δ 23.6 (*C*H$_3$CH), 33.1 (CH$_3$*C*H), 46.8 (N*C*H$_2$), 120.7 (*m*-*C*H), 128.0 (*o*-*C*H), 132.8 (C_{quat}), 141.6 (N*C*HN), 145.1 (N*C*HN), 151.4 (C_{quat}). MS (FAB): *m*/*z* (%) 547.1 (5.9) [M + PF$_6$]$^+$, 401.0 (100) [M]$^{2+}$. Anal. Calcd for $C_{24}H_{30}F_{12}N_6P_2$ (692.18): C, 41.63: H, 4.37; N, 12.14. Found: C, 41.54: H, 4.55; N, 12.20.

1,1′-Diphenyl-4,4′-ethylenedi-1,2,4-triazolium Bis(hexafluorophosphate) (tri-$2^{2\text{-}Ph}$). Yield: 2.37 g (78%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.99 (s, 4H, NCH_2), 7.67 (m, 2H, *p*-CH), 7.74 (m, 4H, *m*-CH), 7.90 (m, 4H, *o*-CH), 9.42 (s, 2H, NCHN), 10.92 (s, 2H, NCHN). ^{13}C{^{1}H} NMR (100.5 MHz, DMSO-d_6): δ 46.8 (N*C*H$_2$), 120.5 (*m*-*C*H), 130.2 (*o*-*C*H), 130.7 (*p*-*C*H), 134.7 (C_{quat}), 141.9 (N*C*HN), 145.2 (N*C*HN). MS (FAB): *m*/*z* (%) 459.8 (100) [M + PF$_6$]$^+$. Anal. Calcd for $C_{18}H_{18}F_{12}N_6P_2$ (608.09): C, 35.54: H, 2.98; N, 13.82. Found: C, 35.85: H, 2.84; N, 13.53.

1,1′-Diisopropyl-4,4′-propylenedi-1,2,4-triazolium Bis(hexafluorophosphate) (tri-$2^{3\text{-}i\text{Pr}}$). Yield: 2.69 g (97%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.57 (d, ^3J = 6.6 Hz, 12H, CH_3), 2.53 (t, 2H, NCH$_2$CH_2CH$_2$N), 4.34 (t, 4H, NCH_2), 4.86 (sept, ^3J = 6.6 Hz, 2H, CH$_3$CH), 9.24 (s, 2H, NCHN), 10.16 (s, 2H, NCHN). ^{13}C{^{1}H} NMR (100.5 MHz, DMSO-d_6): δ 21.1 (*C*H$_3$), 28.3 (NCH$_2$*C*H$_2$CH$_2$N), 44.3 (N*C*H$_2$), 55.1 (*C*HCH$_3$), 141.3 (N*C*HN), 144.5 (N*C*HN). MS (FAB): *m*/*z* (%) 408.8 (46.9) [M + PF$_6$]$^+$, 262.9 (100) [M]$^{2+}$. Anal. Calcd for $C_{13}H_{24}F_{12}N_6P_2$ (554.14): C, 28.17: H, 4.36; N, 15.16. Found: C, 27.98; H, 4.37; N, 15.03.

1,1′-Diphenyl-4,4′-propylenedi-1,2,4-triazolium Bis(hexafluorophosphate) (tri-$2^{3\text{-}Ph}$). Yield: 2.55 g (82%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.65 (t, 2H, NCH$_2$CH_2CH$_2$N), 4.48 (t, 4H, NCH_2), 7.68 (t, 2H, *p*-CH), 7.75 (t, 4H, *m*-CH), 7.94 (d, 4H, *o*-CH), 9.46 (s, 2H, NCH), 10.94 (s, 2H, NCH). ^{13}C{^{1}H} NMR (100.53 MHz, DMSO-d_6): δ 28.1 (NCH$_2$*C*H$_2$CH$_2$N), 44.5 (N*C*H$_2$), 120.5 (*m*-*C*H), 130.2 (*o*-*C*H), 130.6 (*p*-*C*H), 134.8 (C_{quat}), 141.7 (N*C*HN), 145.0 (N*C*HN). MS (FAB): *m*/*z* (%) 476.8 (69.3) [M + PF$_6$]$^+$, 330.9 (100) [M]$^{2+}$. Anal. Calcd for $C_{19}H_{20}F_{12}N_6P_2$ (622.11): C, 36.67: H, 3.24; N, 13.50. Found: C, 36.82; H, 2.99; N, 13.28.

Dibenzimidazolium Salts. Methylbenzimidazole was synthesized according to the literature procedure[21] or was obtained from a commercial source and sublimated (90 °C @ 10^{-2} mbar) prior to use. Isopropylbenzimidazole[5a] and phenylbenzimidazole[22] were synthesized according to literature procedures. Isopropylbenzimidazole was distilled (bp 136−137 °C @ 2.0 mbar, 106 °C @ 0.2 mbar) to yield a colorless oil. Phenylbenzimidazole was purified by extraction with hot pentane to yield a white solid.

General Synthesis for 1,1′-Disubstituted 3,3′-Alkyl-Bridged Dibenzimidazolium Salts[9]. To a solution of the N-substituted benzimidazole (20 mmol) in 5 mL of THF in an ACE pressure tube was added dibromoalkane (10 mmol), and the mixture was heated for 72 h at 120 °C. The solution was filtered off, and the precipitate was washed with 2 × 5 mL of THF, recrystallized from methanol, and dried in vacuo to yield a white powder. Thereafter, an exchange of the anion from Br$^-$ to PF$_6^-$ was performed.

1,1′-Dimethyl-3,3′-methylenedibenzimidazolium Dibromide (bim-$1^{1\text{-}Me}$). Yield: 4.29 (89%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.16 (s, 6H, CH_3), 7.55 (s, 2H, NCH_2N), 7.76 (m, 4H, CH_{arom}), 8.09 (d, 2H, CH_{arom}), 8.44 (d, 2H, CH_{arom}), 10.41 (s, 2H, NCHN). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 34.6 (*C*H$_3$), 55.4 (N*C*H$_2$N), 114.3, 114.7, 127.7, 128.0 (*C*H$_{arom}$), 130.8, 132.3 (C$_{tert}$), 144.8 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 356.8 (7) [M − Br]$^+$, 277.2 (100) [M − Br$_2$]$^+$, 173.1 (16) [M − C$_8$H$_9$Br$_2$N$_2$]$^+$, 153.2 (100) [M − Br]$^{2+}$.

1,1′-Dimethyl-3,3′-ethylenedibenzimidazolium Dibromide (bim-$1^{2\text{-}Me}$). Yield: 3.38 g (75%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.10 (s, 6H, CH_3), 5.15 (s, 4H, CH_2CH_2), 7.62 (t, 2H, CH_{arom}), 7.67 (t, 2H, CH_{arom}), 7.93 (d, 2H, CH_{arom}), 8.03 (d, 2H, CH_{arom}), 9.88 (s, 2H, NCHN). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 34.0 (*C*H$_3$), 46.1 (*C*H$_2$CH$_2$), 113.6, 114.3, 127.2, 127.3 (*C*H$_{arom}$), 131.4, 132.3 (C$_{tert}$), 144.0 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 371.0 (7) [M − Br]$^+$, 291.1 (100) [M − Br$_2$]$^+$, 173.1 (16) [M − C$_8$H$_9$Br$_2$N$_2$]$^+$, 153.2 (100) [M − Br]$^{2+}$.

1,1′-Dimethyl-3,3′-propylenedibenzimidazolium Dibromide (bim-$1^{3\text{-}Me}$). Yield: 4.52 g (97%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.61 (q, 2H, NCH$_2$CH_2CH$_2$N), 4.09 (s, 6H, CH_3), 4.72 (t, J = 7.1, 4H, NCH_2CH$_2$CH_2N), 7.78−7.62 (m, 4H, CH_{arom}), 8.08 (dd, J = 8.3, 33.2, 4H, CH_{arom}), 9.90 (s, 2H, NCHN). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 28.7 (CH$_2$*C*H$_2$CH$_2$), 33.9 (*C*H$_3$), 44.5 (*C*H$_2$CH$_2$*C*H$_2$), 114.2, 127.0, 127.1 (*C*H$_{arom}$), 131.5, 132.4 (C$_{tert}$), 143.5 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 385.0 (12) [M − Br]$^+$, 305.0 (15) [M − Br$_2$]$^+$, 173.1 (16) [M − C$_8$H$_9$Br$_2$N$_2$]$^+$, 153.2 (100) [M − Br]$^{2+}$. Anal. Calcd for $C_{19}H_{22}Br_2N_4$: C, 48.95; H, 4.76; N, 12.02. Found: C, 48.90; H, 5.00; N, 11.81.

1,1′-Diisopropyl-3,3′-methylenedibenzimidazolium Dibromide (bim-$1^{1\text{-}i\text{Pr}}$). Yield: 2.66 g (54%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.68 (d, 12H, CH(CH_3)$_2$), 5.13 (sept, 2H, CH(CH$_3$)$_2$), 7.78−7.22 (m, 4H, CH_{arom}), 8.21 (d,2H, CH_{arom}), 8.46 (d,2H, CH_{arom}), 10.70 (s, 2H, NCHN). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 22.1 (CH(*C*H$_3$)$_2$), 45.6 (N*C*H$_2$N), 51.8 (*C*H(CH$_3$)$_2$), 114.2, 115.1, 127.6, 128.1 (*C*H$_{arom}$), 131.0, 131.4 (C$_{tert}$), 143.5 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 419.1 (15) and 427.1 (17) [M − Br]$^+$, 348.2 (22) and 347.2 (5) [M − 2Br − H]$^+$, 174.2 (100) [M − 2Br]$^{2+}$. Anal. Calcd for $C_{21}H_{26}Br_2N_4$: C, 51.03; H, 5.30; N, 11.34. Found: C, 51.04; H, 5.28; N, 10.98.

1,1′-Diisopropyl-3,3′-ethylenedibenzimidazolium Dibromide (bim-$1^{2\text{-}i\text{Pr}}$). Yield: 3.88 g (77%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.53 (d, 12H, CH(CH_3)$_2$), 5.07 (sept, 2H, CH(CH$_3$)$_2$), 7.66−7.59 (m, 4H, CH$_{arom}$), 7.79 (d, 2H, CH$_{arom}$), 8.10 (d, 2H, CH$_{arom}$), 9.84 (s, 2H, NCHN). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 22.0 (CH(*C*H$_3$)$_2$), 45.4 (NCH$_2$CH$_2$N), 51.8 (*C*H(CH$_3$)$_2$), 114.2, 115.2, 127.6, 128.0 (*C*H$_{arom}$), 131.1, 131.6 (C$_{tert}$), 141.5 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 427.0 (17) and 429.0 (16) [M − Br]$^+$, 347.1 (28) [M − Br$_2$ − H]$^+$, 305.2 (100) and 306.2 (20) [M − Br$_2$ − C$_3$H$_7$]$^+$, 263.2 (33) [M − Br$_2$ − (C$_3$H$_7$) + H], 174.1 (53) [M − Br]$^{2+}$.

1,1′-Diisopropyl-3,3′-propylenedibenzimidazolium Dibromide (bim-$1^{3\text{-}i\text{Pr}}$). Yield: 3.64 g (70%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.41 (d, 12H, CH(CH_3)$_2$), 3.35 (q, 2H, CH$_2$CH_2CH$_2$), 4.53 (t, 4H, CH_2CH$_2$CH_2), 4.85 (sept, 2H, CH(CH$_3$)$_2$), 7.49 (m, 4H, CH_{arom}), 7.96 (m, 4H, CH_{arom}), 9.92 (s, 2H, NCHN). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 22.1 (CH(*C*H$_3$)$_2$), 28.5 (CH$_2$*C*H$_2$CH$_2$), 44.7 (*C*H$_2$CH$_2$*C*H$_2$), 51.2 (*C*H(CH$_3$)$_2$), 114.2, 114.7, 127.2, 127.3 (*C*H$_{arom}$), 131.1, 131.9 (C$_{tert}$), 141.3 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 443.1 (23) and 441.0 (21) [M − Br]$^+$, 181.2 (100) [M − Br − H]$^{2+}$.

1,1′-Diphenyl-3,3′-methylenedibenzimidazolium Dibromide (bim-$1^{1\text{-}Ph}$). Yield: 1.17 g (21%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.71 (s, 2H, NCH_2N), 7.76−7.92 (m, 16H, CH_{arom}), 8.65 (d, 2H, CH_{arom}), 10.88 (s, 1H, NCHN). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 55.1 (N*C*H$_2$N), 113.9, 114.1, 125.1, 127.9, 128.0, 130.6, 130.7 (*C*H$_{arom}$), 130.8 (C$_{tert}$), 131.0 (*C*H$_{arom}$), 132.8 (C$_{tert}$), 144.7 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 481.1 (2) [M − Br]$^+$, 401.4 and 402.4 (17) [M − Br$_2$ − H]$^+$.

1,1′-Diphenyl-3,3′-ethylenedibenzimidazolium Dibromide (bim-$1^{2\text{-}Ph}$). Yield: 3.80 g (64%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.37 (s, 4H, CH_2CH_2), 7.73−7.89 (m, 16H, CH_{arom}), 8.16

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(d, 2H, CH_{arom}), 10.47 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 45.7 (CH_2CH_2), 113.5, 113.7, 125.0, 127.2, 127.8, 130.5, 130.7 (*C*H$_{arom}$), 130.9 (C$_{tert}$), 131.1 (C$_{tert}$), 132.9 (C$_{tert,Ph}$), 143.4 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 417 (100) and 418 (30) and 419 (12) $[M - 2Br - H]^+$.

1,1′-Diphenyl-3,3′-propylenedibenzimidazolium Dibromide (bim-1$^{3\text{-Ph}}$). Yield: 5.47 g (93%). ^1H NMR (400 MHz, DMSO-d_6): δ 2.85 (q, 2H, $CH_2CH_2CH_2$), 4.89 (t, 4H, $CH_2CH_2CH_2$), 7.72−7.80 (m, 16H, CH_{arom}), 8.30 (m, 2H, CH_{arom}), 10.38 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 27.7 ($CH_2CH_2CH_2$), 44.3 ($CH_2CH_2CH_2$), 113.6, 114.1, 125.2, 127.0, 127.6, 130.4, 130.5 (CH$_{arom}$), 131.1, 131.3 (C$_{tert}$), 133.1 (C$_{tert,Ph}$), 142.7 (NCHN). HPLC-MS (ESI): *m*/*z* (%) 509.0 (17) and 511.0 (4) $[M - Br]^+$, 429.1 (28) $[M - Br_2 - H]^+$.

General Synthesis for 1,1′-Substituted 3,3′-Alkyl-Bridged Dibenzimidazolium Hexafluorophosphate Salts. The azolium bromide salt (10 mmol) was dissolved in 10 mL of warm water and transferred via cannula to a solution of KPF_6 (20 mmol) in 5 mL of water, and a white precipitate formed. The mixture was cooled for 5 h at 4 °C and filtered off. The residue was dried in vacuo to yield a white powder.

1,1′-Dimethyl-3,3′-methylenedibenzimidazolium Bis(hexafluorophosphate) (bim-2$^{1\text{-Me}}$). Yield: 3.52 (62%). ^1H NMR (400 MHz, DMSO-d_6): δ 4.14 (s, 6H, CH_3), 7.40 (s, 2H, CH_2), 7.75 (m, 4H, CH_{arom}), 8.08 (d, 2H, CH_{arom}), 8.34 (d, 2H, CH_{arom}), 10.12 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 34.3 (*C*H$_3$), 55.4 (*C*H$_2$), 114.1, 114.6, 127.7, 128.1 (*C*H$_{arom}$), 130.8, 132.4 (C$_{tert}$), 144.8 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 422.9 (49) and 424.0 (12) $[M - PF_6]^+$, 277.1 (100) $[M - 2PF_6 - H]^+$. Anal. Calcd for $C_{17}H_{18}F_{12}N_4P_2$: C, 35.93; H, 3.19; N, 9.86. Found: C, 36.20; H, 3.23; N, 9.69.

1,1′-Dimethyl-3,3′-ethylenedibenzimidazolium Bis(hexafluorophosphate) (bim-2$^{2\text{-Me}}$). Yield: 3.55 g (61%). ^1H NMR (400 MHz, DMSO-d_6): δ 4.05 (s, 6H, CH_3), 5.08 (s, 4H, NCH_2-CH_2N), 7.71 (m, 4H, CH_{arom}), 7.90 (d, 2H, CH_{arom}), 8.04 (d, 2H, CH_{arom}), 9.57 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 33.9 (*C*H$_3$), 46.1 (CH_2CH_2), 113.5, 114.3, 127.3, 127.4 (*C*H$_{arom}$), 131.4, 132.3 (C$_{tert}$), 143.9 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 437.1 (42) and 438.1 (8) $[M - PF_6]^+$, 291.2 (35) and 292.2 (7) $[M - 2PF_6 - H]^+$, 146.2 $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{18}H_{20}F_{12}N_4P_2$: C, 37.13; H, 3.46; N, 9.62. Found: C, 37.47; H, 3.42; N, 9.51.

1,1′-Dimethyl-3,3′-propylenedibenzimidazolium Bis(hexafluorophosphate) (bim-2$^{3\text{-Me}}$). Yield: 4.30 g (72%). ^1H NMR (400 MHz, DMSO-d_6): δ 2.60 (q, 2H, J = 7.2), 4.66 (t, 4H, J = 7.2), 4.08 (s, 6H), 7.62−7.83 (m, 4H, CH$_{arom}$), 7.95−8.15 (m, 4H, CH$_{arom}$), 9.68 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 28.6 ($CH_2CH_2CH_2$), 33.9 (*C*H$_3$), 44.4 ($CH_2CH_2CH_2$), 114.0, 114.2, 127.1, 127.2 (*C*H$_{arom}$), 131.4, 132.4 (C$_{tert}$), 143.4 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 451.9 (28) $[M - PF_6]^+$, 305.1 (22) $[M - 2PF_6 - H]^+$. Anal. Calcd for $C_{19}H_{22}F_{12}N_4P_2$: C, 38.27; H, 3.72; N, 9.40. Found: C, 37.95; H, 3.52; N, 9.60.

1,1′-Diisopropyl-3,3′-methylenedibenzimidazolium Bis(hexafluorophosphate) (bim-2$^{1\text{-}i\text{Pr}}$). Yield: 2.81 g (45%). ^1H NMR (400 MHz, DMSO-d_6): δ 1.68 (d, 12H, CH(CH_3)$_2$), 5.13 (sept, 2H, C*H*(CH$_3$)$_2$), 7.29 (s, 2H, NCH_2N), 7.76−7.85 (m, 4H, CH_{arom}), 8.20 (d, 2H, CH_{arom}), 8.41 (d, 2H, CH_{arom}), 10.31 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 22.0 (CH(*C*H$_3$)$_2$), 51.9 (NCH_2N), 55.7 (*C*H(CH$_3$)$_2$), 114.1, 115.1, 127.7, 128.2 (*C*H$_{arom}$), 131.0, 131.4 (C$_{tert}$), 143.3 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 479.0 (47) and 480.0 (8) and 481.0 (2) $[M - PF_6]^+$, 333.2 (100) and 334.2 (24) and 335.4 (3) $[M - PF_6 - H]^+$, 291.1 (34) and 292.2 (4) $[M - PF_6 - C_3H_7]^+$.

1,1′-Diisopropyl-3,3′-ethylenedibenzimidazolium Bis(hexafluorophosphate) (bim-2$^{2\text{-}i\text{Pr}}$). Yield: 4.00 g (63%). ^1H NMR (400 MHz, DMSO-d_6): δ 1.54 (d, 12H, CH(CH_3)$_2$), 5.02 (sept, 2H, C*H*(CH$_3$)$_2$), 5.06 (s, 4H, NCH_2CH_2N), 7.60−7.66 (m, 4H, CH_{arom}), 7.79 (d, 2H, CH_{arom}), 8.10 (d, 2H, CH_{arom}), 9.79 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 22.0 (CH(*C*H$_3$)$_2$, 46.4 (NCH_2*C*H$_2$N), 51.2 (*C*H(CH$_3$)$_2$), 113.3, 114.7, 127.3, 127.4 (*C*H$_{arom}$), 130.9, 131.8 (C$_{tert}$), 141.9 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 493.2 (90) and 494.2 (23) and 495.2 (2) $[M - PF_6]^+$, 347.2 (28) and 348.2 (8) $[M - 2PF_6 - H]^+$, 305.3 (50) and 306.2 (10)) $[M - 2PF_6 - (C_3H_7)]$, 174.2 (100) $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{22}H_{28}F_{12}N_4P_2$: C, 41.39; H, 4.42; N, 8.78. Found: C, 41.49; H, 4.45; N, 8.54.

1,1′-Diisopropyl-3,3′-propylenedibenzimidazolium Bis(hexafluorophosphate) (bim-2$^{3\text{-}i\text{Pr}}$). Yield: 4.89 g (75%). ^1H NMR (400 MHz, DMSO-d_6): δ 1.62 (d, 12H, CH(CH_3)$_2$), 2.78 (q, 2H, $CH_2CH_2CH_2$), 4.65 (s, 4H, $CH_2CH_2CH_2$), 5.06 (sept, 2H, C*H*(CH$_3$)$_2$), 7.70−7.74 (m, 4H, CH_{arom}), 8.09 (d, 2H, CH_{arom}), 8.15 (d, 2H, CH_{arom}), 9.78 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 22.0 (CH(*C*H$_3$)$_2$), 28.5 ($CH_2CH_2CH_2$), 44.7 ($CH_2CH_2CH_2$), 51.2 (*C*H(CH$_3$)$_2$), 114.2, 114.7, 127.2, 127.3 (*C*H$_{arom}$), 131.1, 131.9 (C$_{tert}$), 141.3 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 507.1 (94) and 508.1 (27) $[M - PF_6]^+$, 361.1 (49) and 362.1 (11) $[M - 2PF_6 - H]^+$, 319.3 (58) and 320.2 (11) $[M - 2PF_6 - (C_3H_7)]$, 181.2 (100) $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{23}H_{30}F_{12}N_4P_2$: C, 42.34; H, 4.63; N, 8.59. Found: C, 42.30; H, 4.56; N, 8.72.

1,1′-Diphenyl-3,3′-methylenedibenzimidazolium Bis(hexafluorophosphate) (bim-2$^{1\text{-Ph}}$). Yield: 6.44 g (93%). ^1H NMR (400 MHz, DMSO-d_6): δ 7.67 (s, 2H, NCH_2N), 7.67 (s, 2H, NCH_2N), 7.80−7.93 (m, 16H, CH_{arom}), 8.63 (d, 2H, CH_{arom}), 10.81 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 55.6 (NCH_2N), 114.6, 118.1, 125.7, 128.6, 128.7, 130.7, 131.7 (*C*H$_{arom}$), 132.7 (C$_{tert}$), 133.3 (*C*H$_{arom}$), 135.3 (C$_{tert}$), 145.1 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 494.9 (17) and 496.9 (15) $[M - PF_6]^+$, 415.1 (94) and 416.1 (34) $[M - 2PF_6 - H]^+$, 339.3 (39) $[M - 2PF_6 - C_6H_5]^+$, 221.2 (100) $[M - 2PF_6 - C_{13}H_{11}N_2]^+$. Anal. Calcd for $C_{27}H_{22}F_{12}N_4P_2$: C, 46.83; H, 3.20; N, 8.09. Found: C, 46.43; H, 3.12; N, 7.86.

1,1′-Diphenyl-3,3′-ethylenedibenzimidazolium Bis(hexafluorophosphate) (bim-2$^{2\text{-Ph}}$). Yield: 5.44 g (77%). ^1H NMR (400 MHz, DMSO-d_6): δ 5.26 (s, 4H, CH_2CH_2), 7.73−7.90 (m, 16H, CH_{arom}), 8.11 (d, 2H, CH_{arom}), 10.19 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 46.3 (CH_2CH_2), 114.0, 114.4, 125.5, 127.9, 128.4, (*C*H$_{arom}$), 131.1 (C$_{tert}$), 131.4 (*C*H$_{arom}$), 131.6 (C$_{tert}$), 133.5 (C$_{tert,Ph}$), 144.0 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 417 (100) and 418 (30) and 419 (12) $[M - 2PF_6 - H]^+$. Anal. Calcd for $C_{28}H_{28}F_{12}P_2N_4$: C, 47.60; H, 3.42; N, 7.93. Found: C, 47.28; H, 3.38; N, 7.90.

1,1′-Diphenyl-3,3′-propylenedibenzimidazolium Bis(hexafluorophosphate) (bim-2$^{3\text{-Ph}}$). Yield: 4.97 g (69%). ^1H NMR (400 MHz, DMSO-d_6): δ 2.81 (q, 2H, $CH_2CH_2CH_2$), 4.81 (t, 4H, $CH_2CH_2CH_2$), 7.74−7.92 (m, 16H, CH_{arom}), 8.23 (m, 2H, CH_{arom}), 10.20 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 28.0 ($CH_2CH_2CH_2$), 44.8 ($CH_2CH_2CH_2$), 114.2, 114.5, 125.7, 127.7, 128.2, 131.0, 131.2 (*C*H$_{arom}$), 131.7, 131.8 (C$_{tert}$), 133.7 (C$_{tert,Ph}$), 143.3 (N*C*HN). HPLC-MS (ESI): *m*/*z* (%) 575.0 (35) $[M - PF_6]^+$, 430 (8) $[M - 2PF_6]^+$, 430 (19) $[M - 2PF_6 - H]^+$, 215 (100) $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{29}H_{26}F_{12}P_2N_4$: C, 48.34; H, 3.64; N, 7.78. Found: C, 47.98; H, 3.48; N, 7.69.

Diimidazolium Salts. The N-substituted imidazoles and the imidazolium salts **im-1$^{2\text{-Me}}$** and **im-3$^{2\text{-}i\text{Pr}}$** were synthesized according to known literature procedures.[23,9]

General Synthesis of the Diimidazolium Bromides. A mixture of the N-substituted imidazole (50 mmol), 1,2-dibromoethane (25 mmol), and THF (5 mL) was heated in an ACE pressure tube (35 mL) at 120 °C for 48 h. The resulting colorless precipitate was collected by filtration, washed with THF (3 × 5 mL), and dried in vacuo.

1,1′-Dicyclohexyl-3,3′-ethylenediimidazolium Dibromide (im-1$^{2\text{-Cy}}$). Yield: 88%. ^1H NMR (DMSO-d_6): δ 1.16−1.23 (m, 2H, cy-*H*), 1.33−1.42 (m, 4H, cy-*H*), 1.60−1.82 (m, 10H, cy-*H*), 2.05

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(m, 4H, cy-*H*), 4.30 (m, 2H, cy-*H*), 4.76 (s, 4H, NCH_2), 7.70 (s, 2H, NC*H*), 7.93 (s, 2H, NC*H*), 9.40 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 24.3 (s, cy-*C*3/*C*4/*C*5), 32.3 (s, cy-*C*2/*C*6), 48.4 (s, cy-*C*1), 58.7 (s, NCH_2), 121.2 (s, NCH), 122.5 (s, NCH), 135.5 (s, NCHN). MS (FAB): m/z (%) 407 (16) $[M + Br]^+$, 327 (21) $[M]^{2+}$, 177 (100) $[M -$ cyclohexylimidazole$]^{2+}$.

1,1′-Diphenyl-3,3′-ethylenediimidazolium Dibromide (im-1$^{2\text{-Ph}}$). Yield: 78%. ^1H NMR (DMSO-d_6): δ 4.98 (s, 4H, NCH_2), 7.60 (t, $^3J_{HH}$ = 7.7 Hz, 2H, ar-*H*4), 7.67 (t, $^3J_{HH}$ = 7.7 Hz, 4H, ar-*H*3/*H*5), 7.82 (d, $^3J_{HH}$ = 7.7 Hz, 4H, ar-*H*2/*H*6), 8.04 (s, 2H, NC*H*), 8.38 (s, 2H, NC*H*), 10.13 (s, 2H, NC*H*N) . $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 48.7 (s, NCH_2), 121.2 (s, NCH), 121.8 (s, ar-*C*2/*C*6), 123.5 (s, NCH), 129.8 (s, ar-*C*4), 130.1 (s, ar-*C*3/*C*5), 134.7 (s, ar-*C*1), 136.3 (s, NCHN).

1,1′-Dimesityl-3,3′-ethylenediimidazolium Dibromide (im-1$^{2\text{-Mes}}$). Yield: 86%. ^1H NMR (DMSO-d_6): δ 1.99 (s, 12H, ar-CH_3), 2.33 (s, 6H, ar-CH_3), 5.05 (s, 4H, NCH_2), 7.15 (s, 4H, ar-*H*3/*H*5), 8.01 (s, 2H, NC*H*), 8.13 (s, 2H, NC*H*), 9.65 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 17.0 (s, ar-*C*H_3), 20.6 (s, ar-*C*H_3), 48.5 (s, NCH_2), 123.3 (s, NCH), 124.2 (s, NCH), 129.3 (s, ar-*C*3/*C*5), 130.9 (s, ar-*C*1), 134.2 (s, ar-*C*2/*C*6), 138.1 (s, ar-*C*4), 140.4 (s, NCHN). MS (FAB): *m*/*z* (%) 479 (11) $[M + Br]^+$, 399 (20) $[M]^{2+}$, 213 (100) $[M -$ mesitylimidazole$]^{2+}$.

Synthesis of the Diimidazolium Bis(hexafluorophosphates).[4b] A solution of diimidazolium dibromide (7.7 mmol) in water (15 mL) was added to a solution of potassium hexafluorophosphate (2.9 g, 15 mmol) in water (50 mL). The resulting precipitate was isolated by filtration, washed with diethyl ether (3 × 5 mL), and dried in vacuo overnight to yield **im-2$^{2\text{-R}}$** in the form of a colorless solid.

1,1′-Diisopropyl-3,3′-ethylenediimidazolium Bis(hexafluorophosphate) (im-2$^{2\text{-}i\text{Pr}}$). Yield: 80%. ^1H NMR (DMSO-d_6): δ 1.61 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CHCH_3), 4.81 (sp, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*CH$_3$), 5.02 (s, 4H, NCH_2), 7.74 (s, 2H, NC*H*), 7.90 (s, 2H, NC*H*), 9.29 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 22.8 (s, CH*C*H$_3$), 49.8 (s, NCH_2), 54.5 (s, *C*HCH$_3$), 122.4 (s, NCH), 123.9 (s, NCH), 136.5 (s, NCHN). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −143.6 (sp, $^1J_{PF}$ = 707.4 Hz, *P*F$_6$). MS (FAB): *m*/*z* (%) 393 (100) $[M + PF_6]^+$, 247 (68) $[M]^{2+}$. Anal. Calcd for $C_{14}H_{24}F_{12}N_4P_2$ (538.30): C, 31.24; H, 4.49; N, 10.41. Found: C, 31.13; H, 4.43; N, 9.84.

1,1′-Diphenyl-3,3′-ethylenediimidazolium Bis(hexafluorophosphate) (im-2$^{2\text{-Ph}}$). Yield: 91%. ^1H NMR (DMSO-d_6): δ 4.83 (s, 4H, NCH_2), 7.61 (t, $^3J_{HH}$ = 7.7 Hz, 2H, ar-*H*4), 7.69 (t, $^3J_{HH}$ = 7.7 Hz, 4H, ar-*H*3/*H*5), 7.83 (d, $^3J_{HH}$ = 7.7 Hz, 4H, ar-*H*2/*H*6), 7.90 (s, 2H, NC*H*), 8.35 (s, 2H, NC*H*), 9.80 (s, 2H, NC*H*N) . $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 48.9 (s, NCH_2), 121.5 (s, NCH), 121.8 (s, ar-*C*2/*C*6), 123.4 (s, NCH), 130.0 (s, ar-*C*4), 130.2 (s, ar-*C*3/*C*5), 134.6 (s, ar-*C*1), 136.1 (s, NCHN). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −143.5 (sp, $^1J_{PF}$ = 710.9 Hz, *P*F$_6$). Anal. Calcd for $C_{20}H_{20}F_{12}N_4P_2$ (606.33): C, 39.62; H, 3.32; N, 9.24. Found: C, 39.26; H, 2.99; N, 8.95.

1,1′-Dicyclohexyl-3,3′-ethylenediimidazolium Bis(hexafluorophosphate) (im-2$^{2\text{-Cy}}$). Yield: 72%. ^1H NMR (acetone-d_6): δ 1.23−1.34 (m, 2H, cy-*H*), 1.43−1.54 (m, 4H, cy-*H*), 1.70−1.92 (m, 10H, cy-*H*), 2.24 (m, 4H, cy-*H*), 4.45 (m, 2H, cy-*H*), 4.99 (s, 4H, NCH_2), 7.69 (s, 2H, NC*H*), 7.90 (s, 2H, NC*H*), 9.02 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 25.4 (s, cy-*C*4), 25.6 (s, cy-*C*3/*C*5), 33.7 (s, cy-*C*2/*C*6), 50.0 (s, cy-*C*1), 61.0 (s, NCH_2), 122.7 (s, NCH), 123.7 (s, NCH), 136.1 (s, NCHN). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −143.6 (sp, $^1J_{PF}$ = 709.2 Hz, *P*F$_6$). MS (FAB): *m*/*z* (%) 473 (29) $[M + PF_6]^+$, 327 (27) $[M]^{2+}$, 177 (100) $[M -$ cyclohexylimidazole$]^{2+}$.

1,1′-Dimesityl-3,3′-ethylenediimidazolium Bis(hexafluorophosphate) (im-2$^{2\text{-Mes}}$). Yield: 91%. ^1H NMR (acetone-d_6): δ 1.98 (s, 12H, ar-CH_3), 2.33 (s, 6H, ar-CH_3), 4.97 (s, 4H, NCH_2), 7.15 (s, 4H, ar-*H*3/*H*5), 8.00 (s, 2H, NC*H*), 8.05 (s, 2H, NC*H*), 9.49 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 17.0 (s, ar-CH_3), 20.6 (s, ar-CH_3), 48.7 (s, NCH_2), 123.3 (s, NCH), 124.4 (s, NCH), 129.4 (s, ar-*C*3/*C*5), 130.9 (s, ar-*C*1), 134.2 (s, ar-*C*2/*C*6), 138.0 (s, ar-*C*4), 140.5 (s, NCHN). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −144.0 (sp, $^1J_{PF}$ = 709.2 Hz, *P*F$_6$). MS (FAB): *m*/*z* (%) 545 (9) $[M + PF_6]^+$, 399 (15) $[M]^{2+}$, 213 (100) $[M -$ mesitylimidazole$]^{2+}$. Anal. Calcd for $C_{26}H_{32}F_{12}N_4P_2$ (690.49): C, 45.23; H, 4.67; N, 8.11. Found: C, 45.87; H, 5.00; N, 8.11.

General Synthesis for 1,2,4-Triazolium-Based Rhodium Complexes.[10]**.** NaH (12.16 mg, 0.51 mmol) was dissolved in ethanol (5 mL) and slowly added to a suspension of $[RhCl(COD)]_2$ (50.0 mg, 0.10 mmol) in ethanol (5 mL). The reaction mixture was stirred for 30 min at room temperature before the di-1,2,4-triazolium bis(hexafluorophosphate) salt (0.21 mmol) was added. After the mixture was stirred for 16 h at 40 °C, the solvent was reduced in vacuo. The remaining solid was dissolved in dichloromethane, this solution was filtered, and then the solvent was removed under reduced pressure to obtain the pure product. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a solution of the corresponding complex in dichloromethane.

(η^4-1,5-Cyclooctadiene)(1,1′-diisopropyl-4,4′-methyleneditriazoline-5,5′-diylidene)rhodium(I) Hexafluorophosphate (tri-3$^{1\text{-}i\text{Pr}}$). Yield: 101.4 mg (86%). ^1H NMR (400 MHz, DCM): δ 1.38, 1.46 (d, ^3J = 6.6 Hz, 6H, CH_3), 2.10 (m, 4H, COD_{allyl}), 2.34 (m, 2H, COD_{allyl}), 2.56 (br, 2H, COD_{allyl}), 4.75 (sept, ^3J = 6.6 Hz, 2H, CH$_3$C*H*), 4.86 (br, 4H, COD_{vinyl}), 6.37, 6.55 (d, ^2J = 13.1 Hz, 4H, NCH_2N), 8.44 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100.5 MHz, DCM): δ 22.8, 23.1 (*C*H$_3$), 30.8, 30.9 (COD_{allyl}), 55.0 (CH$_3$*C*H), 59.1 (NCH_2), 89.7 (d, $^1J_{Rh-C}$ = 7.6 Hz, COD_{vinyl}), 94.3 (d, $^1J_{Rh-C}$ = 8.4 Hz, COD_{vinyl}), 142.3 (NCHN), 179.8 (d, $^1J_{Rh-C}$ = 51.2 Hz, carbene). ^{31}P NMR (161.8 MHz, DCM): δ −143.6 (sept). MS (FAB): *m*/*z* (%) 444.7 (8.2) $[M]^+$, 336.7 (100) $[M -$ COD$]^+$. Anal. Calcd for $C_{19}H_{30}F_6N_6PRh$ (590.35): C, 38.66: H, 5.12; N, 14.24. Found: C, 38.55: H, 5.27; N, 14.31.

(η^4-1,5-Cyclooctadiene)(1,1′-dimethyl-4,4′-ethyleneditriazoline-5,5′-diylidene)rhodium(I) Hexafluorophosphate (tri-3$^{2\text{-Me}}$). Yield: 101.2 mg (91%). ^1H NMR (400 MHz, DCM): δ 2.25 (m, 2H, COD_{allyl}), 2.36 (m, 4H, COD_{allyl}), 2.52 (m, 2H, COD_{allyl}), 3.98 (s, 6H, CH_3), 4.68−4.80 (m, 6H, NCH_2, COD_{vinyl}), 5.42 (m, 2H, NCH_2), 8.11 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100.5 MHz, DCM): δ 30.8, 30.9 (COD_{allyl}), 40.5 (CH$_3$), 45.6 (NCH_2), 90.6 (d, $^1J_{Rh-C}$ = 7.6 Hz, COD_{vinyl}), 93.1 (d, $^1J_{Rh-C}$ = 7.6 Hz, COD_{vinyl}), 144.3 (NCHN), 181.9 (d, $^1J_{Rh-C}$ = 51.2 Hz, carbene). ^{31}P NMR (161.8 MHz, DCM): δ −143.8 (sept). MS (FAB): *m*/*z* (%) 402.5 (100) $[M]^+$, 294.6 (35.0) $[M -$ COD$]^+$. Anal. Calcd for $C_{16}H_{24}F_6N_6PRh$ (548.29): C, 35.05: H, 4.41; N, 15.33. Found: C, 34.81: H, 4.68; N, 15.52.

(η^4-1,5-Cyclooctadiene)(1,1′-diisopropyl-4,4′-ethyleneditriazoline-5,5′-diylidene)rhodium(I) Hexafluorophosphate (tri-3$^{2\text{-}i\text{Pr}}$). Yield: 109.4 mg (89%). ^1H NMR (400 MHz, DCM): δ 1.36 (d, 6H, CH_3), 1.47 (d, 6H, CH_3), 2.21−2.56 (m, 8H, COD_{allyl}), 4.62 (br, 2H, COD_{vinyl}), 4.73 (m, 4H, NCH_2, COD_{vinyl}), 4.97 (sept, 2H, CH$_3$C*H*), 5.45 (m, 2H, NCH_2), 8.14 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100.5 MHz, DCM): δ 23.0 (*C*H$_3$), 30.9 (COD_{allyl}), 45.7 (NCH_2), 55.6 (CH$_3$*C*H), 90.0 (d, $^1J_{Rh-C}$ = 6.9 Hz, COD_{vinyl}), 92.8 (d, $^1J_{Rh-C}$ = 8.4 Hz, COD_{vinyl}), 144.5 (NCHN), 180.0 (d, $^1J_{Rh-C}$ = 50.5 Hz, carbene). ^{31}P NMR (161.8 MHz, DCM): δ −143.7 (sept). MS (FAB): *m*/*z* (%) 458.6 (100) $[M]^+$, 350.6 (68.1) $[M -$ COD$]^+$ Anal. Calcd for $C_{20}H_{32}F_6N_6PRh$ (604.38): C, 39.75: H, 5.34; N, 13.91. Found: C, 40.13: H, 5.43; N, 13.42.

(η^4-1,5-Cyclooctadiene)(1,1′-bis(4-isopropylphenyl)-4,4′-ethyleneditriazoline-5,5′-diylidene)rhodium(I) Hexafluorophosphate (tri-3$^{2\text{-4-}i\text{PrPh}}$). Yield: 122.0 mg (80%). ^1H NMR (400 MHz, DCM): δ 1.34 (d, ^3J = 7.04 Hz, 12H, CH_3), 1.93 (br, 8H, COD_{allyl}), 3.06 (sept, ^3J = 7.04 Hz, 2H, CH$_3$C*H*), 3.77 (br, 2H, COD_{vinyl}), 4.53 (br, 2H, COD_{vinyl}), 4.90 (m, 2H, NCH_2), 5.71 (m, 2H, NCH_2), 7.41−8.00 (m, 8H, aryl), 8.39 (s, 2H, NC*H*N). $^{13}C\{^1H\}$ NMR (100.5 MHz, DCM): δ 24.1 (*C*H$_3$), 30.4, 30.8 (COD_{allyl}), 34.4 (CH$_3$*C*H), 46.8 (NCH_2), 90.9 (d, $^1J_{Rh-C}$ = 7.7 Hz, COD_{vinyl}), 93.0 (d, $^1J_{Rh-C}$ = 8.4 Hz, COD_{vinyl}), 124.3, 127.4, 137.2, 144.5 (aryl), 151.4 (NCHN), 181.5 (d,

$^1J_{Rh-C}$ = 51.2 Hz, carbene); ^{31}P NMR (161.8 MHz, DCM): δ −143.7 (sept). MS (FAB): *m*/*z* (%) 610.7 (35.1) $[M]^+$, 502.7 (100) $[M - COD]^+$. Anal. Calcd for $C_{32}H_{40}F_6N_6PRh$ (756.57): C, 50.80: H, 5.33; N, 11.11. Found: C, 50.57: H, 5.42; N, 10.93.

(η^4-1,5-Cyclooctadiene)(1,1′-diphenyl-4,4′-ethyleneditriazoline-5,5′-diylidene)rhodium(I) Hexafluorophosphate (tri-3$^{2\text{-Ph}}$). Yield: 127.6 mg (94%). ^{1}H NMR (400 MHz, DCM): δ 1.96 (m, 4H, COD_{allyl}), 2.03−2.12 (m, 2H, COD_{allyl}), 2.33−2.26 (m, 2H, COD_{allyl}), 3.81 (br, 2H, COD_{vinyl}), 4.57 (br, 2H, COD_{vinyl}), 4.92 (m, 2H, NCH_2), 5.74 (m, 2H, NCH_2), 7.59 (m, 6H, aryl), 8.14−8.17 (m, 4H, aryl), 8.42 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (100.5 MHz, DCM): δ 30.4, 30.7 (COD_{allyl}), 46.8 (N*C*H$_2$), 91.0 (d, $^1J_{Rh-C}$ = 6.9 Hz, COD_{vinyl}), 93.4 ($^1J_{Rh-C}$ = 8.5 Hz, COD_{vinyl}), 124.2, 129.5, 130.0, 139.4 (aryl), 144.6 (N*C*HN), 181.7 (d, $^1J_{Rh-C}$ = 52 Hz, carbene). ^{31}P NMR (161.8 MHz, DCM): δ −143.7 (sept). MS (FAB): *m*/*z* (%) 526.5 (100) $[M]^+$, 418.5 (87.3) $[M - COD]^+$. Anal. Calcd for $C_{26}H_{28}F_6N_6PRh$ (672.42): C, 46.44; H, 4.20; N, 12.50. Found: C, 46.01: H, 4.67; N, 12.12.

(η^4-1,5-Cyclooctadiene)(1,1′-diisopropyl-4,4′-propyleneditriazoline-5,5′-diylidene)rhodium(I) Hexafluorophosphate (tri-3$^{3\text{-}i\text{Pr}}$). Yield: 122.5 mg (98%). ^{1}H NMR (400 MHz, DCM): δ 1.47 (d, 12H, CH_3), 2.25−2.36 (m, 5H, COD_{allyl}, NCH$_2$CH_2CH$_2$N), 2.42−2.54 (m, 4H, COD_{allyl}), 2.62 (m, 1H, NCH$_2$CH_2CH$_2$N), 4.48−4.60 (m, 6H, NCH_2, COD_{vinyl}), 4.86 (m, 2H, NCH_2), 5.10 (sept, 2H, CH$_3$C*H*), 8.05 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (100.5 MHz, DCM): δ 22.6, 24.2 (*C*H$_3$), 30.8, 31.0 (COD_{allyl}), 33.1 (NCH$_2$*C*H$_2$CH$_2$N), 50.3 (N*C*H$_2$), 55.3 (CH$_3$*C*H), 91.0 (d, $^1J_{Rh-C}$ = 7.7 Hz, COD_{vinyl}), 92.4 (d, $^1J_{Rh-C}$ = 7.7 Hz, COD_{vinyl}), 144.6 (N*C*HN), 182.6 (d, $^1J_{Rh-C}$ = 52.0 Hz, carbene). ^{31}P NMR (161.8 MHz, DCM): δ −143.8 (sept). MS (FAB): *m*/*z* (%) 474.7 (100) $[M]^+$, 364.7 (48.8) $[M - COD]^+$. Anal. Calcd for $C_{21}H_{34}F_6N_6PRh$ (618.42): C, 40.79: H, 5.54; N, 13.59. Found: C, 40.74: H, 6.00; N, 13.10.

(η^4-1,5-Cyclooctadiene)(1,1′-phenyl-4,4′-propyleneditriazoline-5,5′-diylidene)rhodium(I) Hexafluorophosphate (tri-3$^{3\text{-Ph}}$). Yield: 138.1 mg (99.2%). ^{1}H NMR (400 MHz, DCM): δ 2.13−2.28 (m, 7H, COD_{allyl}, NCH$_2$CH_2CH$_2$N), 2.56 (br, 2H, COD_{allyl}), 2.83 (br, 1H, NCH$_2$CH_2CH$_2$N), 4.36 (br, 2H, COD_{vinyl}), 4.63 (br, 2H, COD_{vinyl}), 4.71 (m, 2H, NCH_2), 5.18 (m, 2H, NCH_2), 7.26 (m, 4H, aryl), 7.40 (m, 2H, aryl), 7.82 (m, 4H, aryl), 8.27 (s, 2H, NC*H*N). ^{13}C{^{1}H} NMR (100.5 MHz, DCM): δ 30.4, 31.0 (COD_{allyl}), 33.3 (NCH$_2$*C*H$_2$CH$_2$N), 51.1 (N*C*H$_2$), 91.2 (d, $^1J_{Rh-C}$ = 7.7 Hz, COD_{vinyl}), 93.3 (d, $^1J_{Rh-C}$ = 8.4 Hz, COD_{vinyl}), 123.8, 129.4, 129.5, 138.8 (aryl), 144.4 (N*C*HN), 185.1 (d, $^1J_{Rh-C}$ = 51.2 Hz, carbene). ^{31}P NMR (161.8 MHz, DCM): δ −143.8 (sept). MS (FAB): *m*/*z* (%) 540.3 (100) $[M]^+$, 432.4 (73.7) $[M - COD]^+$. Anal. Calcd for $C_{27}H_{30}F_6N_6PRh$ (686.45): C, 47.24: H, 4.41; N, 12.24. Found: C, 47.33: H, 4.33; N, 11.68.

Cyclooctadiene Rhodium Ethoxide Dimer [Rh(COD)OEt]$_2$. [Rh(COD)Cl]$_2$ (1 g) was stirred in a 1 M solution of NaOEt in MeOH at room temperature overnight. The color of the precipitate changed from orange to yellow. The reaction mixture was filtered and the remaining residue washed with cold MeOH and Et$_2$O. Yield: 98%.

General Synthesis of Benzimidazole-Based Rhodium Complexes.[10,4b]. The dibenzimidazolium salt (0.50 mmol) was stirred for approximately 30 min with 1 mL of a 1 M solution of NaOEt in MeOH. [Rh(COD)OEt]$_2$ (0.25 mmol) was dissolved in 5 mL of THF and the clear, yellow solution added via a Teflon cannula to the dibenzimidazolium salt mixture. The mixture was stirred for 2−5 h at room temperature, while a color change of the reaction mixture from the white dibenzimidazolium salt to a yellow complex was observed. The solvent was removed in vacuo, and the yellow residue was extracted several times with dichloromethane until a white residue remained. To the extract was added 8 mL of ethanol, and the solvent was reduced in vacuo to a volume of about 1−2 mL to furnish a yellow precipitate. The mixture was cooled to −35 °C for 2−3 h and the remaining solvent filtered off. The yellow precipitate was washed with cold Et$_2$O (2−3 mL) and dried in vacuo.

(η^4-1,5-Cyclooctadiene)(1,1′-dimethyl-3,3′-ethylenedibenzimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (bim-3$^{2\text{-Me}}$). Yield: 290.9 mg (90%). ^{1}H NMR (400 MHz, DCM-d_2): δ 2.35 (dm, 4H, COD_{allyl}), 2.53 (dm, 4H, COD_{allyl}), 4.08 (s, 6H, CH$_3$), 4.81 (br, 4H, COD_{vinyl}), 4.88 (m, 2H, CH_2), 5.88 (m, 2H, CH_2), 7.28 (m, 6H, CH_{arom}), 7.44 (m, 2H, CH_{arom}). ^{13}C{^{1}H} NMR (100 MHz, DCM-d_2): δ 30.5, 31.1 (COD_{allyl}), 50.8 (*C*H$_2$*C*H$_2$) 54.5 (*C*H$_3$), 90.6, 90.7, 93.0, 93.1 (COD_{vinyl}), 109.6, 109.9, 123.4, 123.6 (*C*H$_{arom}$), 134.7, 135.1 (C$_{tert}$), 192.0 (N*C*N, d, $^1J_{Rh-C}$ = 51.5 Hz). HPLC-MS (ESI): *m*/*z* (%) 501.2 (58) and 502.2 (20) and 503.2 (2) $[M - PF_6]^+$, 393.3 (26) and 394.4 (6) $[M - PF_6 - COD]^+$. MS (FAB): *m*/*z* (%) 500.5 (100.0), 501.5 (31.4), 502.5 (4.4), 392.5 (45.4). Anal. Calcd for $C_{26}H_{30}F_6N_4PRh$: C, 48.31; H, 4.68; N, 8.67. Found: C, 44.92; H, 4.39; N, 8.39.

(η^4-1,5-Cyclooctadiene)(1,1′-dimethyl-3,3′-propylenedibenzimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (bim-3$^{3\text{-Me}}$). Yield: 290.6 mg (88%). ^{1}H NMR (400 MHz, DCM-d_2): δ 2.38 (m, 4H, COD_{allyl}), 2.64 (m, 4H, COD_{allyl}), 4.20 (s, 6H, CH_3), 4.74 (br, 4H, COD_{vinyl}), 4.78 (m, 2H, CH$_2$CH_2CH$_2$), 5.30 (m, 4H, CH_2CH$_2$CH_2), 7.22−7.29 (m, 8H, CH_{arom}). ^{13}C{^{1}H} NMR (100 MHz, DCM-d_2): δ 23.6 (*C*H$_3$) 30.5, 30.7, (COD_{allyl}), 36.3 (CH$_2$*C*H$_2$CH$_2$), 45.3 (CH$_2$*C*H$_2$CH$_2$), 49.5 (*C*H$_3$), 91.5, 92.0, 92.1, 92.3 (COD_{vinyl}), 109.3, 109.9, 123.0, 123.2 (*C*H$_{arom}$), 134.5, 135.0 (C$_{tert}$), 194.6 (N*C*N, d, $^1J_{Rh-C}$ = 52.3 Hz). HPLC-MS (ESI): *m*/*z* (%) 515.3 (100) and 516.3 (29) and 517.3 (4) $[M - PF_6]^+$, 407.3 (38) $[M - PF_6 - C_8H_{12}]^+$. MS (FAB): *m*/*z* (%) 514.6 (100.0), 515.6 (31.6), 516.5 (4.5), 406.6 (26.6), 274.7 (27.8). Anal. Calcd: C, 49.10; H, 4.88; N, 8.48. Found: C, 48.81; H, 4.91; N, 8.39.

(η^4-1,5-Cyclooctadiene)(1,1′-diisopropyl-3,3′-ethylenedibenzimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (bim-3$^{2\text{-}i\text{Pr}}$). Yield: 298.6 mg (85%). ^{1}H NMR (400 MHz, DCM-d_2): δ 2.31 (dm, 4H, COD_{allyl}), 2.52 (dm, 4H, COD_{allyl}), 4.67 (br, 2H, COD_{vinyl}), 4.81 (br, 2H, COD_{vinyl}), 4.90 (m, 2H, CH_2), 5.54 (sept, 2H, C*H*(CH$_3$)$_2$), 5.94 (m, 2H, CH_2), 7.24 (m, 4H, CH_{arom}), 7.49 (m, 4H, CH_{arom}). ^{13}C{^{1}H} NMR (100 MHz, DCM-d_2): δ 21.4, 21.9 (*C*H$_3$), 30.2, 30.5 (COD_{allyl}), 44.5 (CH$_2$CH$_2$), 51.0 (*C*H(CH$_3$)$_2$), 89.6, 89.8, 92.7, 92.8 (COD_{vinyl}), 110.2, 112.2, 123.4, 123.0, 123.4 (*C*H$_{arom}$), 132.1, 136.2 (C$_{tert}$), 190.2 (N*C*N, d, $^1J_{Rh-C}$ = 52.3 Hz). HPLC-MS (ESI): *m*/*z* (%) 557.1 (20) and 558.2 (7) and 559.1(1) $[M - PF_6]^+$, 449.3 (100) and 450.3 (23) and 451.2 (3) $[M - PF_6 - COD]^+$. MS (FAB): *m*/*z* (%) 556.5 (100.0), 557.6 (34.4), 558.6 (5.6), 448.6 (72.2), 364.5 (17.2). Anal. Calcd: C, 51.29; H, 5.45; N, 7.98. Found: C, 50.98; H, 5.24; N, 7.64.

(η^4-1,5-Cyclooctadiene)(1,1′-diisopropyl-3,3′-propylenedibenzimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (bim-3$^{3\text{-}i\text{Pr}}$). Yield: 315.2 mg (88%). ^{1}H NMR (400 MHz, DCM-d_2): δ 2.07−2.87 (m, 8H, COD_{allyl}), 4.67 (br, 4H, COD_{vinyl}), 4.78 (m, 2H, CH_2), 5.32 (m, 2H, CH_2), 5.63 (sept, 2H, C*H*(CH$_3$)$_2$), 7.22 (m, 4H, CH$_{arom}$), 7.29 (m, 2H, CH_{arom}), 7.49 (m, 2H, CH_{arom}). ^{13}C{^{1}H} NMR (100 MHz, DCM-d_2): δ 22.3, 22.8 (*C*H$_3$), 30.4, 30.7 (COD_{allyl}), 37.1 (CH$_2$*C*H$_2$CH$_2$) 50.8 (*C*H-(CH$_3$)$_2$), 54.5, (*C*H$_2$*C*H$_2$*C*H$_2$), 90.15, 90.22, 92.0, 92.12 (COD_{vinyl}), 122.65, 112.40, 122.65, 123.15 (*C*H$_{arom}$), 132.1, 136.4 (C$_{tert}$), 193.2 (N*C*N, d, $^1J_{Rh-C}$ = 53.8 Hz). HPLC-MS (ESI): *m*/*z* (%) 571 (18) and 572 (5) $[M - PF_6]^+$, 463 (100) $[M - PF_6 - C_8H_{12}]^+$. MS (FAB): *m*/*z* (%) 570.5 (100.0), 571.5 (36.4), 572.5 (6.0), 462.5 (88.1), 302.6 (56.6). Anal. Calcd: C, 51.96; H, 5.63; N, 7.82; F, 15.91; P, 4.32; Rh, 14.36. Found: C, 51.46; H, 5.74; N, 7.75.

(η^4-1,5-Cyclooctadiene)(1,1′-diphenyl-3,3′-ethylenedibenzimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (bim-3$^{2\text{-Ph}}$). Yield: 377.5 mg (98%). ^{1}H NMR (400 MHz, DCM-d_2): δ 1.46, 1.74, 2.00, 2.32 each (m, 2H, COD_{allyl}), 3.71 (br, 2H, COD_{vinyl}), 4.70 (br, 2H, COD_{vinyl}), 5.11 (m, 2H, CH_2CH_2), 6.13 (m, 2H, CH_2CH_2), 7.20 (m, 2H, Ph−CH_{arom}), 7.28 (m, 2H, Ph−CH_{arom}), 7.44 (m, 2H, Ph−CH_{arom}), 7.62 (m, 4H, bim-CH_{arom}), 7.66 (m, 4H, Ph-CH_{arom}), 7.73 (m, 4H, bim-CH_{arom}). ^{13}C{^{1}H} NMR (100 MHz, DCM-d_2): δ 30.3, 31.0 (COD_{allyl}),

45.8 (CH_2CH_2), 90.6, 90.7, 92.1, 92.2 (COD_{vinyl}), 110.6, 111.5, 124.5, 124.9, 127.2, 130.3, 130.5, 135.1, 136.2, 138.2 (CH_{arom}), 191.2 (NCN, d, $^1J_{Rh-C}$ = 53.4 Hz). HPLC-MS (ESI): *m/z* (%) 625.2 (30) and 626.2 (12) and 627.3 (3) $[M - PF_6]^+$, 557.9 (100) and 558.8 (28) $[M - PF_6 - COD + H_3CCN]^{\bullet+}$, 517.6 (30) and 518.5 (9) $[M - PF_6 - COD]^+$. MS (FAB): *m/z* (%) 624.3 (62.1), 625.4 (25.5), 626.4 (5.17), 516.4 (100), 321.5 (9.5). Anal. Calcd: C, 56.11; H, 4.45; N, 7.27. Found: C, 55.14; H, 4.42; N, 7.34.

(η^4-1,5-Cyclooctadiene)(1,1′-diphenyl-3,3′-propylenedibenzimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (bim-$3^{3\text{-Ph}}$). Yield: 306.0 mg (78%). ^{1}H NMR (400 MHz, DCM-d_2): δ 1.87 (m, 2H, COD_{allyl}), 1.97 (m, 2H, COD_{allyl}), 2.20 (m, 2H, COD_{allyl}), 2.55 (m, 2H, COD_{allyl}), 4.10 (s, 2H, COD_{vinyl}), 4.69 (s, 2H, COD_{vinyl}), 4.97 (m, 2H, $CH_2CH_2CH_2$), 5.56 (m, 4H, $CH_2CH_2CH_2$), 7.14 (m, 2H, CH_{arom}), 7.21 (m, 2H, CH_{arom}), 7.32 (m, 2H, CH_{arom}), 7.45 (m, 10H, CH_{arom}), 7.56 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (100 MHz, DCM-d_2): δ 29.2, 29.8, 30.3 (COD_{allyl}), 39.6 ($CH_2CH_2CH_2$), 54.3 ($CH_2CH_2CH_2$), 90.2, 90.3, 91.7, 91.8 (COD_{vinyl}), 109.8, 111.5, 123.6, 124.0, 126.6, 129.5, 129.8, 134.8, 135.8, 137.0 (CH_{arom}), 195.2 (NCN, d, $^1J_{Rh-C}$ = 55.3 Hz). HPLC-MS (ESI): *m/z* (%) 639.1 (33) and 640.1 (13) and 641.1 (2) $[M - PF_6]^+$, 571.6 (62) $[M - PF_6 - COD + H_3CCN]^+$, 531.3 (100) and 532.3 (27) and 533.2 (4) $[M - PF_6 - COD]^+$. MS (FAB): *m/z* (%) 638.4 (80.7), 639.4 (35.2), 640.4 (7.0), 530.5 (100), 336.6 (33.1). Anal. Calcd: C, 56.64; H, 4.62; N, 7.14. Found: C, 55.21; H, 4.68; N, 6.72.

Imidazole-Based Rhodium Complexes. A solution of sodium hydride (12.7 mg, 0.51 mmol) in ethanol (5 mL) was slowly added to a suspension of $[RhCl(COD)]_2$ (50.0 mg, 0.10 mmol) in ethanol (5 mL). The reaction mixture was stirred for 30 min at room temperature before **im-$2^{2\text{-R}}$** (0.20 mmol) was added. After the mixture was stirred for 72 h in the case of **im-$3^{2\text{-Me}}$**, **im-$3^{2\text{-}i\text{Pr}}$**, and **im-$3^{2\text{-Cy}}$** and 16 h in the case of **im-$3^{2\text{-Ph}}$** and **im-$3^{2\text{-Mes}}$** at 50 °C, the solvent was removed under reduced pressure. The product was extracted with dichloromethane (3 × 5 mL). The obtained solutions were combined and filtered, and the solvent was removed in vacuo. The solid residue was washed with pentane (3 × 5 mL) and dried under reduced pressure to obtain **im-$3^{2\text{-R}}$** in the form of a yellow solid.

(η^4-1,5-Cyclooctadiene)(1,1′-dimethyl-3,3′-ethylenediimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (im-$3^{2\text{-Me}}$). Yield: 95%. ^{1}H NMR (CD_2Cl_2): δ 2.14−2.20 (m, 2H, COD-CH_2), 2.22−2.28 (m, 2H, COD-CH_2), 2.34−2.37 (m, 2H, COD-CH_2), 2.43−2.50 (m, 2H, COD-CH_2), 3.82 (s, 6H, NCH_3), 4.41 (m, 2H, NCHH), 4.61 (s, 4H, COD-CH), 5.51 (m, 2H, NCHH), 6.83 (d, $^3J_{HH}$ = 2.1 Hz, 2H, NCH), 6.97 (d, $^3J_{HH}$ = 2.1 Hz, 2H, NCH). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 31.1 (s, COD-CH_2), 31.3 (s, COD-CH_2), 38.5 (s, NCH_3), 48.5 (s, NCH_2), 88.0 (d, $^1J_{RhC}$ = 8.5 Hz, COD-CH), 90.5 (d, $^1J_{RhC}$ = 8.5 Hz, COD-CH), 123.6 (s, NCH), 180.8 (d, $^1J_{RhC}$ = 52.3 Hz, NCN). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −143.6 (sp, $^1J_{PF}$ = 707.4 Hz, PF_6). MS (FAB): *m/z* (%) 401 (100) $[M]^+$.

(η^4-1,5-Cyclooctadiene)(1,1′-diisopropyl-3,3′-ethylenediimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (im-$3^{2\text{-}i\text{Pr}}$). Yield: 95%. ^{1}H NMR (CD_2Cl_2): δ 1.31 (d, $^3J_{HH}$ = 7.1 Hz, 6H, $CHCH_3$), 1.42 (d, $^3J_{HH}$ = 7.1 Hz, 6H, $CHCH_3$), 2.12−2.18 (m, 2H, COD-CH_2), 2.21−2.27 (m, 2H, COD-CH_2), 2.33−2.40 (m, 2H, COD-CH_2), 2.42−2.51 (m, 2H, COD-CH_2), 4.40−4.48 (m, 4H, NCHH/COD-CH), 4.62 (s, 2H, COD-CH), 4.97 (sp, $^3J_{HH}$ = 7.1 Hz, 2H, $CHCH_3$), 5.56 (m, 2H, NCHH), 6.89 (d, $^3J_{HH}$ = 1.6 Hz, 2H, NCH), 7.04 (d, $^3J_{HH}$ = 1.6 Hz, 2H, NCH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 24.0 (s, $CHCH_3$), 24.1 (s, $CHCH_3$), 30.9 (s, COD-CH_2), 31.0 (s, COD-CH_2), 48.2 (s, NCH_2), 50.6 (s, $CHCH_3$), 87.5 (d, $^1J_{RhC}$ = 7.7 Hz, COD-CH), 90.6 (d, $^1J_{RhC}$ = 8.5 Hz, COD-CH), 117.4 (s, NCH), 123.6 (s, NCH), 178.5 (d, $^1J_{RhC}$ = 52.3 Hz, NCN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.8 (sp, $^1J_{PF}$ = 710.9 Hz, PF_6). MS (FAB): *m/z* (%) 457 (100) $[M]^+$, 349 (87) $[M - COD]^+$. Anal. Calcd for $C_{22}H_{34}F_6N_4PRh$ (602.40): C, 43.86; H, 5.69; N, 9.30. Found: C, 44.22; H, 5.86; N, 8.76.

(η^4-1,5-Cyclooctadiene)(1,1′-dicyclohexyl-3,3′-ethylenediimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (im-$3^{2\text{-Cy}}$). Yield: 97%. ^{1}H NMR (CD_2Cl_2): δ 1.40−1.50 (m, 8H, cy-H), 1.71−1.79 (m, 4H, cy-H), 1.87−1.96 (m, 8H, cy-H), 2.12−2.19 (m, 2H, COD-CH_2), 2.25−2.31 (m, 2H, COD-CH_2), 2.33−2.40 (m, 2H, COD-CH_2), 2.43−2.51 (m, 2H, COD-CH_2), 4.40−4.47 (m, 4H, COD-CH/NCHH), 4.53−4.62 (m, 4H, COD-CH/cy-H), 5.53 (m, 2H, NCHH), 6.86 (d, $^3J_{HH}$ = 1.9 Hz, 2H, NCH), 7.02 (d, $^3J_{HH}$ = 1.9 Hz, 2H, NCH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 25.4 (s, cy-C), 26.1 (s, cy-C), 26.4 (s, cy-C), 31.0 (s, COD-CH_2), 31.1 (s, COD-CH_2), 34.9 (s, cy-C), 35.3 (s, cy-C), 48.2 (s, cy-C), 61.6 (s, NCH_2), 87.6 (d, $^1J_{RhC}$ = 7.7 Hz, COD-CH), 90.6 (d, $^1J_{RhC}$ = 8.5 Hz, COD-CH), 118.1 (s, NCH), 123.3 (s, NCH), 178.6 (d, $^1J_{RhC}$ = 52.3 Hz, NCN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.8 (sp, $^1J_{PF}$ = 710.9 Hz, PF_6). MS (FAB): *m/z* (%) 537 (84) $[M]^+$, 427 (100) $[M - COD]^+$. Anal. Calcd for $C_{28}H_{42}F_6N_4PRh$ (682.53): C, 49.27; H, 6.20; N, 8.21. Found: C, 48.97; H, 6.37; N, 8.06.

(η^4-1,5-Cyclooctadiene)(1,1′-diphenyl-3,3′-ethylenediimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (im-$3^{2\text{-Ph}}$). Yield: 95%. ^{1}H NMR (CD_2Cl_2): δ 1.55−1.74 (m, 4H, COD-CH_2), 1.90−1.96 (m, 2H, COD-CH_2), 2.19−2.28 (m, 2H, COD-CH_2), 3.47 (s, 2H, COD-CH), 4.42 (s, 2H, COD-CH), 4.65 (m, 2H, NCHH), 5.79 (m, 2H, NCHH), 7.24 (d, $^3J_{HH}$ = 1.7 Hz, 2H, NCH), 7.28 (d, $^3J_{HH}$ = 1.7 Hz, 2H, NCH), 7.51−7.56 (m, 6H, ar-H), 7.79−7.82 (m, 4H, ar-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 30.3 (s, COD-CH_2), 30.9 (s, COD-CH_2), 49.2 (s, NCH_2), 88.2 (d, $^1J_{RhC}$ = 7.7 Hz, COD-CH), 90.4 (d, $^1J_{RhC}$ = 9.2 Hz, COD-CH), 123.1 (s, NCH), 123.4 (s, NCH), 125.2 (s, ar-C), 129.5 (s, ar-C), 129.6 (s, ar-C), 140.1 (s, ar-C), 179.6 (d, $^1J_{RhC}$ = 52.3 Hz, NCN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.8 (sp, $^1J_{PF}$ = 710.9 Hz, PF_6). MS (FAB): *m/z* (%) 524 (80) $[M]^+$, 416 (100) $[M - COD]^+$.

(η^4-1,5-Cyclooctadiene)(1,1′-dimesityl-3,3′-ethylenediimidazoline-2,2′-diylidene)rhodium(I) Hexafluorophosphate (im-$3^{2\text{-Mes}}$). Yield: 96%. ^{1}H NMR (CD_2Cl_2): δ 1.51 (m, 2H, COD-CH_2), 1.69 (m, 2H, COD-CH_2), 1.83 (s, 6H, ar-CH_3), 1.86 (s, 6H, ar-CH_3), 2.18 (m, 2H, COD-CH_2), 2.33 (s, 6H, ar-CH_3), 2.36 (m, 2H, COD-CH_2), 3.61 (s, 2H, COD-CH), 4.48 (s, 2H, COD-CH), 4.66 (m, 2H, NCHH), 5.82 (m, 2H, NCHH), 6.85 (d, $^3J_{HH}$ = 1.7 Hz, 2H, NCH), 6.91 (s, 2H, ar-H), 6.93 (s, 2H, ar-H), 7.28 (d, $^3J_{HH}$ = 1.7 Hz, 2H, NCH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.8 (s, ar-CH_3), 19.7 (s, ar-CH_3), 21.1 (s, ar-CH_3), 30.7 (s, COD-CH_2), 31.2 (s, COD-CH_2), 49.7 (s, NCH_2), 86.9 (d, $^1J_{RhC}$ = 7.7 Hz, COD-CH), 89.2 (d, $^1J_{RhC}$ = 9.2 Hz, COD-CH), 122.7 (s, NCH), 125.3 (s, NCH), 129.3 (s, ar-C), 129.4 (s, ar-C), 135.6 (s, ar-C), 136.3 (s, ar-C), 136.5 (s, ar-C), 139.8 (s, ar-C), 179.1 (d, $^1J_{RhC}$ = 53.0 Hz, NCN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.8 (sp, $^1J_{PF}$ = 710.9 Hz, PF_6). MS (FAB): *m/z* (%) 609 (68) $[M]^+$, 501 (100) $[M - COD]^+$. Anal. Calcd for $C_{34}H_{42}F_6N_4PRh$ (754.59): C, 54.12; H, 5.61; N, 7.42. Found: C, 54.46; H, 5.81; N, 7.00.

Acknowledgment. Dr. Karl Öfele, Prof. Dr. Peter Härter, and Dr. Evangeline Tosh are gratefully acknowledged for helpful discussions. This work was generously supported by the Margarete Ammon Stiftung (Ph.D. grant for S.K.U.R.) and the *Wacker AG* (Ph.D. grant for P.G. and M.P.H.). S.K.U.R., P.G., and M.P.H. performed the majority of the experiments and data analysis. E.H. and B.B. collected and analyzed the X-ray data. F.E.K. and W.A.H. designed and supervised the research. The paper was written by S.K.U.R., P.G., M.H., B.B., and F.E.K., and all authors discussed the results and commented on the paper.

Supporting Information Available: Tables and figures giving crystallographic details and Diamond plots of all crystal structures and CIF files giving crystallographic data for all X-ray studies.

This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for all structures reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-776289 (**tri-3$^{2\text{-Me}}$**), CCDC-776288 (**tri-3$^{2-4\text{-iPrPh}}$**), CCDC-776290 (**tri-3$^{2\text{-Ph}}$**), CCDC-776292 (**tri-3$^{3\text{-iPr}}$**), CCDC-776291 (**tri-3$^{3\text{-Ph}}$**), CCDC-776280 (**bim-3$^{2\text{-Me}}$**), CCDC-776282 (**bim-3$^{2\text{-}i\text{Pr}}$**), CCDC-776281 (**bim-3$^{2\text{-Ph}}$**), CCDC-776285 (**im-3$^{2\text{-Me}}$**), CCDC-776284 (**im-3$^{2\text{-Cy}}$**), CCDC-776287 (**im-3$^{2\text{-Ph}}$**), and CCDC-776286 (**im-3$^{2\text{-Mes}}$**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).