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# Novel Rhodium and Iridium Complexes Coordinated to $C_3$-Symmetric Tris-NHC Ligands Based on a 1,3,5-Triphenylbenzene Core. Electronic and Catalytic Properties

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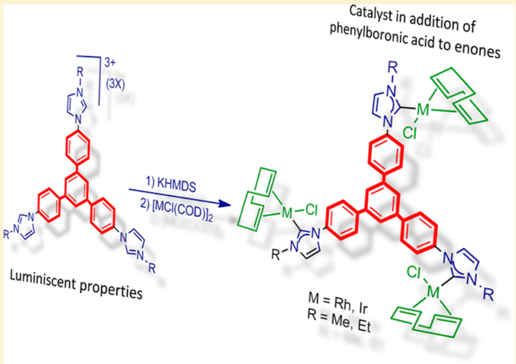
*Supporting Information*

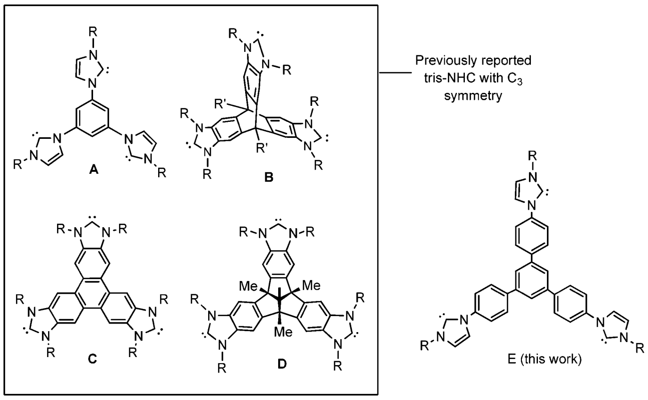
**ABSTRACT:** A series of novel tris-azolium salt precursors based on 1,3,5-triphenylbenzene have been prepared. These salts exhibit fluorescence emission in the 320−420 nm region. The coordination of these salts to $[MCl(COD)]_2$ (M = Rh, Ir) was carried out in the presence of KHMDS and allowed the formation of the corresponding tris-NHC complexes of Rh and Ir in high yield. The electronic properties of the new complexes were analyzed by means of cyclic voltammetry and IR spectroscopy of the related carbonylated species. The catalytic activity of the trirhodium complex toward the addition of arylboronic acids to cyclohexen-2-one has been evaluated and compared to the activity shown by a related monometallic complex.



## INTRODUCTION

During the past few years poly-NHCs have been object of increasing attention, because they have been demonstrated to serve as useful tools in the design of multifunctional materials.[1] A basic requirement for the development of NHC-based materials is the design of architectures with geometrically isolated carbenes,[2] because these systems are potentially useful for the preparation of organometallic polymers with unusual sensing, magnetic, optical, and catalytic properties.[2] A very interesting feature of poly-carbenes is their potential to provide heterometallic complexes that can have important applications in the design of sophisticated tandem catalytic processes.[3] Poly-NHCs have also given access to interesting supramolecular assemblies, which feature only metal−carbon bonds and generate organometallic frameworks (OMFs),[4] rather than the intensively studied metal−organic frameworks (MOFS),[5] which are typically obtained when classical Werner-type O,N-donating ligands are used. A series of interesting examples of such types of OMFs are those described by Hahn's group, in which the coordination of a $C_3$-symmetric tris-NHC (**A**; Scheme 1) allowed the formation of an interesting series of cylinder-like polynuclear structures with linearly coordinated metals such as Ag(I), Au(I), Cu(I), and Pd(II).[4i,j,6] Related to this tris-NHC ligand, the trypticene-based tris-benzoimidazolylidene (**B**)[7] and triphenylene-based imidazolylidene (**C**)[8] display rigid $D_{3h}$ symmetries, which may be applied to the generation of three-dimensional polymeric structures.[9] A $C_{3v}$-symmetrical (bowl-shaped) tribenzotriquinacene-based tris-NHC was also recently described by us (**D**).[10] While **A**, **B**, and **D** display electronically disconnected carbenes, the three carbenes in **C** are connected through the π-delocalized polyaromatic system, although the electronic communication seems to be disrupted for the metals bound to the ligand,[11] probably due to the negligible $d_{M-}p_L$ overlap as a consequence of the lack of a strong π back-donation. Despite this metal−metal disconnection, we found that the tris-carbene **C** allowed the preparation of improved trimetallic catalysts, which afforded important benefits in comparison to their monometallic analogues in several simple benchmark catalytic reactions.[8]

**Scheme 1**



On the basis of these previous findings, and aiming to introduce a new scaffold able to $C_3$ symmetrically coordinate to three different metal centers, we now report the preparation and coordination properties of the tris-NHC **E**, which is based

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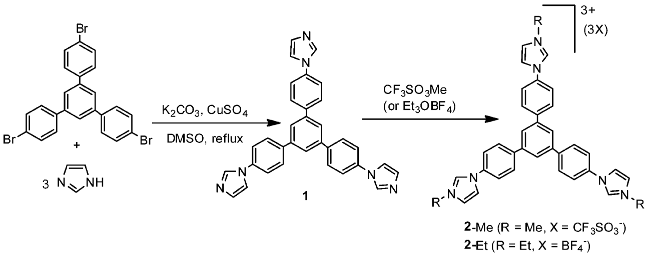
on a central 1,3,5-triphenylbenzene. We believe that this tris-NHC may be an interesting precursor to the preparation of novel supramolecular assemblies, which may also impart some interesting photophysical properties to the complexes derived due to the presence of the 1,3,5-triphenylbenzene core.[12] In fact, polyphenylenes have been the focus of attention because of their luminescence properties, and polyphenylenes derived from symmetrically trisubstituted benzenes are known to provide high quantum yield values.[13] In this work we report the coordination of **E** to rhodium and iridium and the study of the catalytic activity of the resulting complexes in the addition of boronic acids to enones.

## ■ RESULTS AND DISCUSSION

The tris-azolium salts **2**-Me and **2**-Et were obtained according to the synthetic procedure illustrated in Scheme 2. The reaction of 1,3,5-tris(4-bromophenylbenzene) with imidazole in the presence of $CuSO_4$ and $K_2CO_3$ afforded the corresponding tris-imidazolyl−triphenylene−benzene compound **1** in 65% yield. Subsequent quaternization of the tris-imidazoles with methyl trifluoromethanesulfonate and triethyloxonium tetrafluoroborate yielded the corresponding salts **2**-Me and **2**-Et, respectively.

### Scheme 2



**2**-Me and **2**-Et were both characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The molecular structure of **2**-Me was determined by X-ray diffractometry. Figure 1 shows the molecular structure of **2**-Me. The crystal packing shows a one-dimensional π stacking, which involves all four phenylene rings of the molecule. Although the molecule is not coplanar, the relative disposition of adjacent trisazolium molecules shows that all aromatic rings are displayed in a quasi-parallel manner.

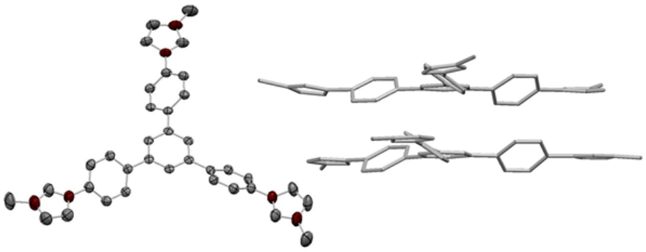


**Figure 1.** Molecular structure of **2**-Me (left) and the π stacking of two adjacent molecules (right). Hydrogen atoms and counterions ($CF_3SO_3^-$) have been omitted for clarity. Ellipsoids are given at the 50% probability level.

The introduction of the three imidazoliums into the 1,3,5-triphenylbenzene fragment affords an interesting opportunity to evaluate the photophysical changes produced in the triphenylbenzene core. Polyaromatic symmetrical cyclotrimers are known to afford favorable spectral characteristics and often yield highly emissive systems.[12b,13a] In fact, 1,3,5-triphenylbenzene possesses the highest quantum yields in comparison with other benzenes with different amounts of phenyl substituents and their different positions[12b] and therefore constitutes an excellent scaffold for the design of luminescence materials. Compounds **1**, **2**-Me, and **2**-Et all exhibit fluorescence emission in the 320−420 nm region, although the quantum yields are moderate (0.16−0.24). As can be observed from the data given in Table 1, the quaternization of **1** to afford **2**-Me or **2**-Et does not produce any significant enhancements in the quantum yields or changes in the emission maximum wavelengths, and the absorption and emission properties are comparable to those provided by 1,3,5-triphenylbenzene (entry 1). The fact that the photophysical properties of the tris-azolium molecules are maintained in comparison to those provided by triphenylbenzene may be considered as an advantage, if we take into account that the production of highly stable tricationic molecules such as **2**-Me and **2**-Et may give rise to molecules with tunable physical properties such as solubility or melting points, just by modifying the nature of the counteranion of the N substituent at the imidazole rings.

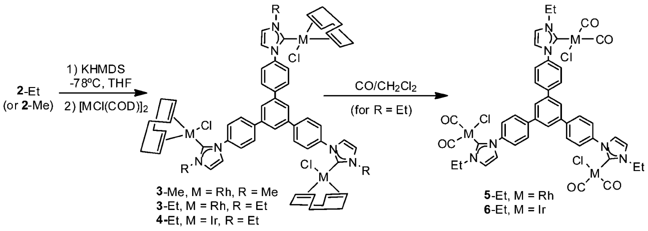
**Table 1. Photophysical Properties of 1, 2-Me, and 2-Et**

| entry | compound | $\lambda_{abs}$ (nm) (log ε)[a] | $\lambda_{em}$ (nm)[b] | $\Phi_f$[b] |
|---|---|---|---|---|
| 1[c] | 1,3,5-triphenylbenzene | 253 (4.71) | 352 | 0.29 |
| 2 | **1** | 276 (4.83) | 359 | 0.24 |
| 3 | **2**-Et | 268 (5.04) | 351 | 0.16 |
| 4 | **2**-Me | 272 (5.00) | 358 | 0.18 |

[a] Measurements were performed in MeCN under ambient conditions. Molar extinction coefficients ε were determined from Beer's law plots. [b] The emission quantum yield was measured in MeCN, with quinine bisulfate in degassed 1 N $H_2SO_4$ solution as standard ($\Phi_f$ = 0.55[14]) excited at 290 nm. [c] Values taken from ref 12b.

The deprotonation of **2**-Et with potassium bis(trimethyl)-silylamide (KHMDS) in THF, followed by the addition of $[MCl(COD)]_2$ (M = Rh, Ir), allowed the preparation of the corresponding trirhodium (**3**-Et, 42%) and triiridium (**4**-Et, 56%) tris-imidazolylidene complexes (Scheme 3). By following the same procedure, we also obtained the tris-imidazolylidene trirhodium complex **3**-Me (56%), when the tris-azolium salt **2**-Me was used. All of the new trimetallic complexes were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The $^1H$ and $^{13}C$ NMR spectra of these three new complexes reveal the 3-fold symmetry of the molecule, as exemplified by the two sharp signals assigned to the protons of the backbone of the three equivalent imidazolylidene rings observed in the $^1H$ NMR spectra and the single peaks due to the metalated carbene carbons in the $^{13}C$ NMR spectra (**3**-Et,

### Scheme 3



182.9 ppm, ${}^{1}J_{\mathrm{Rh-C}}$ = 51.3 Hz; **3**-Me, 183.8, ${}^{1}J_{\mathrm{Rh-C}}$ = 51.2 Hz; **4**-Et, 180.1 ppm).

Although we tried our best to get single crystals for the X-ray determination of the molecular structures of any of the trimetallic structures, all of our attempts failed. However, we did obtain crystals suitable for X-ray diffraction of the monorhodium complex **8**-Et, having a 1-phenyl-3-methylimidazolylidene ligand. The molecular diagram is shown in Figure 2. The molecular structure of this complex is interesting, because it can be related to the expected local molecular geometry of each of the metal fragments in the related trimetallic complex **3**-Et. The complex displays a Rh−C$_{\mathrm{carbene}}$ distance of 2.023(2) Å. The high trans influence of the NHC ligand is illustrated by the longer distance between the rhodium atom and the olefin in the position trans with relation to the NHC ligand (compare 2.195 Å for the average Rh−C distances of the olefinic carbons trans to the NHC, with an average distance of 2.103 Å between Rh and the carbons of the olefin trans to Cl).

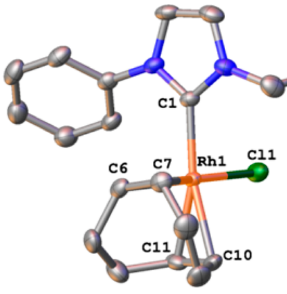


**Figure 2.** Molecular diagram of complex **8**-Et. Ellipsoids are given at the 50% probability level. Hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−C(1) 2.023(2), Rh(1)−Cl(1) 2.382(6), Rh(1)−C(7) 2.099(2), Rh(1)−C(6) 2.105(2), Rh(1)−C(10) 2.208(2); C(1)−Rh(1)−Cl(1) 88.47(6).

In order to get information about the electron-donating character of the tri-NHC ligand, we carbonylated complexes **3**-Et and **4**-Et and obtained the corresponding hexacarbonylated complexes **5**-Et (Rh) and **6**-Et (Ir), which were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The infrared stretching frequencies of the carbonyl ligands in the rhodium and iridium complexes (**5**-Et, 2072, 1991 cm$^{-1}$; **6**-Et, 2061 and 1975 cm$^{-1}$) allowed us to estimate a Tolman electronic parameter (TEP) of 2045 cm$^{-1}$ for the tris-NHC ligand, by using the well-accepted correlations.[15]

The photophysical properties of **3**−**6** were also studied but, unlike the imidazolium salts, exhibited negligible fluorescence emission. This fluorescence quenching is attributed to the heavy-atom perturbation,[16] where singlet excited state population decreases due to intersystem crossing, an effect that is commonly observed for other NHC complexes of rhodium and iridium.[16b,17]

In order to determine if there is any measurable electronic communication between the metals across the polyaromatic ligand, we performed cyclic voltammetric studies of complexes **3**-Et and **4**-Et. Both species showed irreversible waves, probably due to the low steric shielding about the metal, as has been previously proposed.[16] For comparative purposes, we compared the results provided by these two trimetallic complexes with those of their monometallic analogues **8**-Et and **9**-Et, which were specifically made in the present work for this purpose. As can be seen from the cyclic voltammetric (CV) diagrams shown by the two iridium complexes **4**-Et and **9**-Et (Figure 3), they both display similar oxidation waves, at the same half-wave potential ($E_{1/2}$ = 0.67 V). This result indicates that both ligands (the tri-NHC ligand in **4**-Et and the mono-NHC in **9**-Et) provide similar electron densities to the metal, and thus we can estimate a similar electron-donating power.[18] By comparing the curves from the differencial pulse voltammetry (DPV) analysis generated for **4**-Et and **9**-Et, it can be established that there is no detectable broadening of the signal provided by the trimetallic complex, in comparison to that generated by the monometallic complex, and thus it becomes evident that the trimetallic complex **4**-Et contains three iridium fragments that are essentially decoupled.

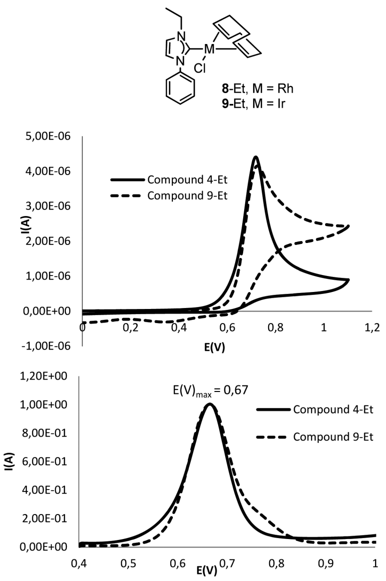
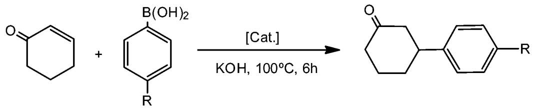


**Figure 3.** CV plots (top) and relevant DPV sections (bottom) of complexes **4**-Et and **9**-Et (1 mM in dry $CH_2Cl_2$ with 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte, 50 mV s$^{-1}$ scan rate, Fc$^+$/Fc used as internal standard with $E_{1/2}$(Fc/Fc$^+$) = 0.44 V vs SCE).

The fact that the three metal centers in **3**-Et and **4**-Et are essentially electronically disconnected suggests that the ligand may be used to support different metal fragments without detriment to their potential catalytic properties and thus should constitute a good opportunity to study cooperative effects. Also, the fact that the mono-NHC ligand in **8**-Et and **9**-Et provides stereoelectronic properties almost identical with those offered by the tri-NHC ligand in **3**-Et and **4**-Et gives us an excellent opportunity to compare the catalytic activities provided by the trimetallic complexes and their monometallic analogues. For the determination of the catalytic properties of the complexes, we decided to evaluate the rhodium-catalyzed addition of arylboronic acids to $\alpha,\beta$-unsaturated ketones,[19] a process for which several Rh$^{\mathrm{I}}$−NHC complexes have afforded excellent activities and chemoselectivities.[19a,20] For our catalytic experiments, we decided to study the arylation of cyclohexen-2-one with several arylboronic acids and compared the activity of **3**-Et and **8**-Et, using catalyst loadings of 0.2 and 0.066 mol %, respectively, which actually provide the same amount of metal load. As can be observed from the data given in Table 2, the reactions provided higher conversions when they were carried out in toluene than in a THF/$H_2O$ mixture. This result is rather surprising, if we take into account that this reaction is generally performed in the presence of water,[19e] and the

Table 2. 1,4-Addition of Arylboronic Acids to Cyclohex-2-one[a]



| entry | [cat.] (mol %) | solvent | R | cat. | conversn (%)[b] |
|---|---|---|---|---|---|
| 1 | 0.066 | THF/$H_2O$ | H | **3**-Et | 56 (45) |
| 2 | 0.2 | THF/$H_2O$ | H | **8**-Et | 58 (46) |
| 3 | 0.066 | THF/$H_2O$ | Me | **3**-Et | 63 (53) |
| 4 | 0.2 | THF/$H_2O$ | Me | **8**-Et | 74 (50) |
| 5 | 0.066 | toluene | H | **3**-Et | 100 (91) |
| 6 | $6.6 \times 10^{-3}$ | toluene | H | **3**-Et | 71 (68) |
| 7 | 0.2 | toluene | H | **8**-Et | 96 (90) |
| 8 | 0.02 | toluene | H | **8**-Et | 61 (48) |
| 9 | 0.066 | toluene | Me | **3**-Et | 85 (69) |
| 10 | 0.2 | toluene | Me | **8**-Et | 69 (55) |
| 11[c] | 0.066 | toluene | OMe | **3**-Et | 48 (16) |
| 12[c] | 0.2 | toluene | OMe | **8**-Et | 47 (14) |

[a] Conditions: cyclohexen-2-one (0.5 mmol), KOH (0.09 mmol), $ArB(OH)_2$ (0.6 mmol), dry solvent. [b] Conversions determined by gas chromatography (GC), using anisole as internal standard. Percent yields are given in parentheses. [c] Using 2,4,6-trimethylphenol as standard.

examples in which dry toluene are used have been regarded as rare and are only promoted when OH groups are forming part of the ancillary ligands,[19a,20a] which is not our case. Also, we did not find it necessary to add any type of additive to the reaction mixture in order to improve the catalytic outcome. Regardless of the type of solvent used, the two catalysts afforded very similar reaction outcomes, therefore suggesting that the higher nanolocal concentration provided by the trimetallic complex (dendrimer effect)[21] did not have any significant effect on its activity or that for any other reason the trimetallic nature of **3**-Et provides any improvements in comparison to its monometallic analogue. The representation of the reaction profiles for the reaction between phenylboronic acid and cyclohexen-2-one (Figure 4) also gives a good illustration of the similar behavior of the two catalysts, where it is clearly observed that the activity of the two catalysts is quasi-identical along the reaction course. This observation is interesting and may be related to our previous observations in which the use of π-extended polyaromatic-based di- and tri-NHC ligands did produce significant improvements in the catalytic activities of their related complexes, in comparison to their monometallic analogues.[8,22] For this situation, we tentatively attributed the catalytic benefits to a potential π stacking between the substrates and polyaromatic π-extended ligand, a situation that may not be reproduced in this new case, in which the NHC ligands are π disconnected from the polyaromatic core. It is also interesting to mention that, for the reactions carried out at catalyst loadings of $6.6 \times 10^{-3}$ and 0.02 mol % for **3**-Et and **8**-Et, respectively (entries 11 and 12), the yields obtained after 6 h are moderately high, therefore illustrating the activity of the catalyst.

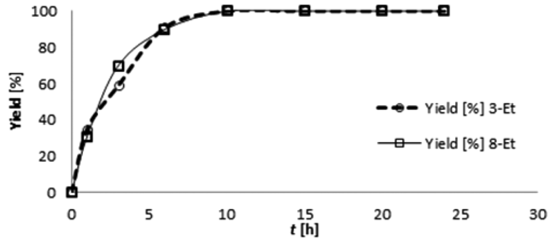


**Figure 4.** Time course for the addition of phenylboronic acid to cyclohexen-2-one. Reactions were carried out in toluene at 100 °C, with 0.06 (**3**-Et) or 0.2 mol % (**8**-Et) catalyst load. Yields were determined by GC, using anisole as standard.

We did observe a side reaction implying the deborylation of the arylboronic acid, and this justifies the differences found between conversions and yields for most of the catalytic reactions that we studied. This observation is more relevant for the case of the use of 4-methoxyphenylboronic acid, for which the formation of anisole is the dominant process (entries 11 and 12).

## ■ CONCLUSIONS

In summary, we have prepared a series of rhodium and iridium complexes with a new tris-NHC ligand based on a triphenylbenzene core, which we have spectroscopically characterized. The electron-donating character of the ligand has been established by means of IR spectroscopy of the corresponding hexacarbonylated iridium compound and by cyclic voltammetric studies of the rhodium and iridium cyclooctadiene derivatives. As observed by the electrochemical studies, the three metals do not show any detectable electronic communication. The preliminary catalytic studies on the rhodium-catalyzed addition of boronic acids to cyclohexen-2-one showed that the activity of the trirhodium complex **3**-Et is similar to that shown by its monometallic analogue **8**-Et, thus suggesting that there is no type of catalytic cooperativity.

The new ligand provides a new motif for designing novel polymetallic architectures, in which not only can discrete trimetallic structures be obtained but also supramolecular assemblies in which the photophysical properties of the triphenylbenzene core can be combined with the properties derived from the introduction of a variety of metal fragments. Studies on the preparation of these types of macromolecular compounds with this and other related systems with extended polyphenylene branches are currently underway.

## ■ EXPERIMENTAL SECTION

**General Methods.** All operations were carried out under a nitrogen atmosphere unless otherwise stated using standard Schlenk techniques. Solvents were dried using a solvent purification system (MBraun SPS). All reagents were used as received from commercial suppliers. NMR spectra were recorded on Varian Mercury 300 and Varian NMR System 500 MHz spectrometers and referenced ($^1H$, $^{13}C$) as follows: DMSO-$d_6$ (δ 2.50, 39.52), $CD_3OD$ (δ 3.31, 49.00), $CD_3CN$ (δ 1.94, 1.32), $CDCl_3$ (δ 7.26, 77.16). Electrospray mass spectra (ESIMS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Accurate mass measurements were performed by use of a Q-TOF premier mass spectrometer with electrospray source (Waters, Manchester, U.K.) operating at a resolution of ca. 16000 (fwhm). Elemental analyses were carried out on a EuroEA3000 Eurovector Analyzer.

**Electrochemistry.** Electrochemical studies were carried out by using an Autolab Model PGSTAT101 potentiostat, using a three-electrode cell. The cell was equipped with platinum working and counter electrodes, as well as a silver-wire reference electrode. In all experiments, $[NBu_4][PF_6]$ (0.1 M in dry $CH_2Cl_2$) was used as the supporting electrolyte with an analyte concentration of approximately 1 mM. Measurements were performed at 50 and 100 mV $s^{-1}$ scan rates. All redox potentials were referenced to the $Fc^+/Fc$ couple as internal standard with $E_{1/2}(Fc/Fc^+ \text{ vs SCE}) = +0.44$ V.

**General Spectroscopic Considerations.** UV−visible absorption spectra were recorded on a Varian Cary 300 BIO spectrophotometer using $CH_3CN$ under ambient conditions. Emission spectra were recorded on a modular Horiba FluoroLog-3 spectrofluorometer employing degassed $CH_3CN$. Extinction coefficients ($\varepsilon$) were determined from Beer's law measurements using $4 \times 10^{-6}$−$4 \times 10^{-9}$ M concentrations of the analyte. Quantum yields were determined relative to quinine bisulfate in degassed 1 N sulfuric acid solution as standard ($\Phi_f = 0.27$),[13] with excitation at 290 nm.

**Synthesis of Compound 1.** A round-bottomed flask was loaded with 1,3,5-tris(4-bromophenylbenzene) (1 g, 1.84 mmol), $K_2CO_3$ (1.25 g, 9.05 mmol), imidazole (0.75 g, 11.02 mmol), and $CuSO_4$ (0.005 g, 0.03 mmol). DMSO (5 mL) was added, and the reaction mixture was heated to 185 °C for 2 days. Then the solvent was removed by distillation. The crude mixture was redissolved in methylene chloride and the solution washed with water. The resulting organic solution was dried with $MgSO_4$, and the solvent was removed under vacuum to give a yellow solid: yield 0.60 g (64.6%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 7.94 (s, 3H, NC*H*N), 7.82 (m, 9H, $CH_{Imid}$, $CH_{Ar}$), 7.55 (d, $J$ = 6.6 Hz, 6H, $CH_{Ar}$), 7.36 (s, 3H, $CH_{Ar}$), 7.26 (s, 3H, $CH_{Imid}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 141.59 ($C_{Ar}$), 140.09 ($C_{Ar}$), 137.14 ($C_{Ar}$), 135.69 ($C_{Imid}$), 130.79 ($C_{Imid}$), 128.91 ($C_{Ar}$), 125.43 ($C_{Imid}$), 122.02 ($C_{Ar}$), 118.29 ($C_{Ar}$). Electrospray MS (20 V, $m/z$): 253.3 $[M + 2H]^{2+}$. Anal. Calcd for $C_{33}H_{24}N_6 \cdot 2H_2O$: C, 73.3; H, 5.2; N, 15.5. Found C, 73.3; H, 3.9; N, 15.4. Mp: 148 °C. Dec pt: 243 °C.

**Synthesis of Compound 2-Et.** Triethyloxonium tetrafluoroborate (0.844 g, 4.44 mmol) was placed in a Schlenk tube containing a solution of 1,3,5-tris(4-imidazolylphenyl)benzene (0.5 g, 0.99 mmol) in dry methylene chloride (30 mL). Instantaneously, a white precipitate crashed out. The solid was filtered and washed with hexane and MeOH to yield 0.462 g of a white powder (54.7%). $^1H$ NMR (300 MHz, DMSO-$d_6$): $\delta$ (ppm) 9.86 (s, 3H, NC*H*N), 8.41 (d, $J$ = 8.4 Hz, 3H, $CH_{Ar}$), 8.29–8.15 (m, 9H, $CH_{Imid}$, $CH_{Ar}$), 8.10 (d, $J$ = 8.1 Hz, 3H, $CH_{Imid}$), 7.96 (d, $J$ = 8.4 Hz, 6H, $CH_{Ar}$), 4.33 (q, $J$ = 7.3 Hz, 6H, $CH_2$), 1.55 (t, $J$ = 7.3 Hz, 9H, $CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-$d_6$): $\delta$ (ppm) 140.88 ($C_{Ar}$), 140.20 ($C_{Ar}$), 135.10 ($C_{Ar}$), 134.42 ($C_{Ar}$), 128.96 ($C_{Ar}$), 125.37 ($C_{Ar}$), 123.04 ($C_{Imid}$), 122.18 ($C_{Ar}$), 121.14 ($C_{Imid}$), 44.84 ($CH_2$), 14.81 ($CH_3$). Electrospray MS (20 V, $m/z$): 196.9 $[M]^{3+}$, 339.3 $[M + BF_4]^{2+}$. Anal. Calcd for $C_{39}H_{39}N_6B_3F_{12} \cdot 2H_2O$: C, 52.7; H, 4.9; N, 9.5. Found: C, 52.8; H, 5.1; N, 9.5. Dec pt: 174 °C

**Synthesis of Compound 2-Me.** Methyl trifluoromethanesulfonate (143 $\mu$L 1.31 mmol) was placed in a Schlenk tube containing a solution of 1,3,5-tris(4-imidazolylphenyl)benzene (0.2 g, 0.40 mmol) in 1,2-dichloroethane (10 mL). The solution was heated to 100 °C overnight. An oily precipitate was obtained after evaporating the solvent. MeOH was added to dissolve the oily crude product, and the addition of hexane gave a light brown solid: yield 0.264 g (71.9%). $^1H$ NMR (300 MHz, $CD_3OD$): $\delta$ (ppm) 9.52 (s, 3H, NC*H*N), 8.12–8.05 (m, 12H, $CH_{Imid}$, $CH_{Ar}$), 7.88–7.81 (m, 9H, $CH_{Imid}$, $CH_{Ar}$), 4.08 (s, 9H, $CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CD_3CN$): $\delta$ (ppm) 142.80 ($C_{Ar}$), 141.56 ($C_{Ar}$), 136.31 ($C_{Ar}$), 135.35 ($C_{Ar}$), 130.08 ($C_{Ar}$), 126.78 ($C_{Ar}$), 125.34 ($C_{Imid}$), 123.64 ($C_{Ar}$), 122.42 ($C_{Imid}$), 37.16 ($CH_3$). Electrospray MS (20 V, $m/z$): 183.2 $[M]^{3+}$. Anal. Calcd for $C_{39}H_{33}N_6S_3O_9F_9.H_2O$: C, 46.2; H, 3.5; N, 8.3. Found: C, 46.2; H, 4.5; N, 7.9. Dec pt: 184 °C.

**Synthesis of Compound 3-Et.** In a Schlenk tube containing a solution of **2**-Et (0.100 g, 0.12 mmol) and $[RhCl(COD)]_2$ (0.087 g, 0.18 mmol) in THF (15 mL) at −78 °C was added dropwise a solution of KHMDS (0.5 M in toluene, 774 $\mu$L, 0.39 mmol). The mixture was stirred overnight at room temperature. After removal of the volatiles, the crude solid was dissolved in methylene chloride and purified by column chromatography using silica gel. Using $CH_2Cl_2$/acetone mixtures, an orange product was obtained: yield: 87 mg (55.8%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 8.39 (d, $J$ = 8.4 Hz, 6H, $CH_{Ar}$), 7.96 (m, 9H, $CH_{Imid}$, $CH_{Ar}$), 7.30 (s, 3H, $CH_{Ar}$), 7.06 (d, $J$ = 2.0 Hz, 3H, $CH_{Imid}$), 5.14 (m, 3H, $CH_{COD}$), 4.98 (m, 3H, $CH_{COD}$), 4.78 (m, 6H, $CH_2$), 3.28 (br s, 3H, $CH_{COD}$), 2.67 (br s, 3H, $CH_{COD}$), 2.36 (m, 12H, $CH_{2\,COD}$), 2.17 (m, 12H, $CH_{2\,COD}$), 1.86 (m, 9H, $CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) $\delta$ 182.88 (d, $J$ = 51.3 Hz, Rh-$C_{carbene}$), 141.91 ($C_{Ar}$), 140.32 ($C_{Ar}$), 140.15 ($C_{Ar}$), 127.74 ($C_{Ar}$), 125.40 ($C_{Ar}$), 125.30 ($C_{Ar}$), 121.57 ($C_{Imid}$), 120.64 ($C_{Imid}$), 97.92 ($CH_{COD}$), 68.94 ($CH_{COD}$), 68.75 ($CH_{COD}$), 68.46 ($CH_{COD}$), 68.27 ($CH_{COD}$), 46.57 ($CH_2$), 33.46 ($CH_{2\,COD}$), 32.02 ($CH_{2\,COD}$), 29.82 ($CH_{2\,COD}$), 29.18 ($CH_{2\,COD}$), 28.61 ($CH_{2\,COD}$), 16.21 ($CH_3$). Electrospray MS (20 V, $m/z$): 648.8 $[M - 2Cl + MeCN]^{2+}$. Anal. Calcd for $C_{63}H_{72}N_6Rh_3Cl_3 \cdot 2H_2O \cdot CH_2Cl_2$: C, 53.0; H, 5.4; N, 5.8. Found: C, 53.0; H, 6.0; N, 5.6.

**Synthesis of Compound 3-Me.** In a Schlenk tube containing a solution of **2**-Me (0.100 g, 0.10 mmol) and $[RhCl(COD)]_2$ (0.074 g, 0.15 mmol) in THF (15 mL) at −78 °C was added dropwise a solution of KHMDS (0.5 M in toluene, 662 $\mu$L, 0.33 mmol). The mixture was stirred overnight at room temperature. After removal of the volatiles, the crude solid was dissolved in $CH_2Cl_2$ and purified by column chromatography using silica gel. An orange product was obtained: yield 72 mg (56.3%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 8.38 (d, $J$ = 8.5 Hz, 6H, $CH_{Ar}$), 7.93 (m, 9H, $CH_{Imid}$, $CH_{Ar}$), 7.25 (s, 3H, $CH_{Ar}$), 7.02 (d, $J$ = 2.0 Hz, 3H, $CH_{Imid}$), 5.06 (m, 3H, $CH_{COD}$), 4.24 (s, 9H, $CH_3$), 3.29 (br s, 3H, $CH_{COD}$), 2.64 (br s, 3H, $CH_{COD}$), 2.36–2.17 (m, 12H, $CH_{2\,COD}$), 1.61 (m, 12H, $CH_{2\,COD}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) $\delta$ 183.81 (d, $J$ = 51.2 Hz, Rh-$C_{carbene}$), 141.93 ($C_{Ar}$), 140.42 ($C_{Ar}$), 140.03 ($C_{Ar}$), 127.78 ($C_{Ar}$), 125.44 ($C_{Ar}$), 125.26 ($C_{Ar}$), 122.98 ($C_{Imid}$), 121.23 ($C_{Imid}$), 98.26 ($CH_{COD}$), 68.65 ($CH_{COD}$), 68.46 ($CH_{COD}$), 68.29 ($CH_{COD}$), 68.10 ($CH_{COD}$), 53.99 ($CH_3$), 38.63 ($CH_{2\,COD}$), 32.07 ($CH_{2\,COD}$), 31.02 ($CH_{2\,COD}$), 29.43 ($CH_{2\,COD}$), 28.68 ($CH_{2\,COD}$). Electrospray MS (20 V, $m/z$): 627.7 $[M - 2Cl + MeCN]^{2+}$. Satisfactory microanalytical data could not be obtained, due to halide scrambling.

**Synthesis of Compound 4-Et.** A solution of KHMDS (0,5 M in toluene, 774 $\mu$L, 0.39 mmol) was added dropwise into a Schlenk tube containing a solution of **2**-Et (0.10 g, 0.12 mmol) and $[IrCl(COD)]_2$ (0.12 g, 0.18 mmol) in THF (15 mL) at −78 °C. The mixture was stirred overnight at room temperature. After removal of the volatiles, the crude mixture was dissolved in $CH_2Cl_2$ and purified by column chromatography using silica gel ($CH_2Cl_2$/acetone), to give an orange product: yield: 79 mg (42.2%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 8.20 (d, $J$ = 8.4 Hz, 6H, $CH_{Ar}$), 7.92–7.83 (m, 9H, $CH_{Imid}$, $CH_{Ar}$), 7.23 (d, $J$ = 1.9 Hz, 3H, $CH_{Ar}$), 7.06 (d, $J$ = 2.0 Hz, 3H, $CH_{Imid}$), 4.72–4.51 (m, 12H, $CH_{Ar}$, $CH_2$), 2.89 (m, 3H, $CH_{COD}$), 2.34–2.14 (m, 12H, $CH_{2\,COD}$), 1.91–1.84 (m, 3H, $CH_{COD}$), 1.61–1.47 (m, 21H, $CH_{2\,COD}$, $CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) $\delta$ 180.30 (Ir−$C_{carbene}$), 141.95 ($C_{Ar}$), 140.28 ($C_{Ar}$), 139.97 ($C_{Ar}$), 127.57 ($C_{Ar}$), 125.79 ($C_{Ar}$), 125.39 ($C_{Ar}$), 121.40 ($C_{Imid}$), 120.39 ($C_{Imid}$), 84.26 ($CH_{COD}$), 83.82 ($CH_{COD}$), 68.60 ($CH_{COD}$), 52.32 ($CH_{COD}$), 52.19 ($CH_{COD}$), 46.36 ($CH_2$), 34.08 ($CH_{2\,COD}$), 32.78 ($CH_{2\,COD}$), 29.83 ($CH_{2\,COD}$), 29.60 ($CH_{2\,COD}$), 29.45 ($CH_{2\,COD}$), 27.92 ($CH_{2\,COD}$), 16.06 ($CH_3$). Electrospray MS (20 V, $m/z$): 783.2 $[M - 2Cl + MeCN]^{2+}$. Anal. Calcd for $C_{63}H_{72}N_6Ir_3Cl_3 \cdot 2H_2O \cdot 2CH_2Cl_2$: C, 43.3; H, 4.5; N, 4.7. Found: C, 43.0; H, 3.3; N, 4.5.

**Synthesis of Compound 5-Et.** CO gas was bubbled through a solution of **3**-Et in dichloromethane (10 mL) at 0 °C for 30 min. The solution was concentrated by evaporation of the solvent under reduced pressure. Addition of hexanes allowed the precipitation of **5**-Et as a yellow solid: yield 59 mg (89.6%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 7.92–7.87 (m, 15H, $CH_{Ar}$), 7.36 (br s, 3H, $CH_{Imid}$), 7.20 (br s, 3H, $CH_{Imid}$), 4.98 (br s, 6H, $CH_2$), 1.61 (s, 9H, $CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 185.61 (d, $J$ = 54.3 Hz, Rh-$C_{carbene}$), 182.17 (d, $J$ = 74.7 Hz, Rh-CO), 173.91 (d, $J$ = 43.6 Hz, Rh-CO), 141.05 ($C_{Ar}$), 140.96 ($C_{Ar}$), 139.20 ($C_{Ar}$), 127.98 ($C_{Ar}$), 125.80 ($C_{Ar}$), 125.41 ($C_{Ar}$), 122.68 ($C_{Imid}$), 121.62 ($C_{Imid}$), 46.79 ($CH_2$), 15.99 ($CH_3$). Electrospray MS (20 V, $m/z$): 1188.8 $[M - CO - Cl + 2MeCN]^+$, 1106.8 $[M - CO - Cl]^+$. Anal. Calcd for $C_{45}H_{36}N_6Rh_3Cl_3O_6 \cdot 2H_2O$: C, 44.8; H, 3.3; N, 6.8. Found: C, 44.4; H, 3.8; N, 6.8; IR ($cm^{-1}$): 2072, 1991; TEP 2045.

**Synthesis of Compound 6-Et.** CO was bubbled through a solution of **4**-Et in dichloromethane (10 mL) at 0 °C for 30 min. The solution was concentrated by evaporation of the solvent under reduced pressure. A yellow precipitate was obtained after addition of hexanes to the resulting solution: yield 78 mg (86.5%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 7.90 (br s, 3H, $CH_{Ar}$), 7.84 (br s, 12H, $CH_{Ar}$), 7.32 (br s, 3H, $CH_{Imid}$), 7.21 (br s, 3H, $CH_{Imid}$), 4.52 (br s, 6H, $CH_2$), 1.59 (s, 9H, $CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 181.12 (Ir-$C_{carbene}$), 173.28 (Ir-CO), 167.81 (Ir-CO), 141.43 ($C_{Ar}$), 141.32 ($C_{Ar}$), 139.09 ($C_{Ar}$), 128.14 ($C_{Ar}$), 126.68 ($C_{Ar}$), 125.76 ($C_{Ar}$), 122.84 ($C_{Imid}$), 121.43 ($C_{Imid}$), 46.87 ($CH_2$), 16.04 ($CH_3$). Electrospray MS (20 V, $m/z$): 1506.9 $[M - 3Cl - 3CO + 6MeCN]^+$. IR ($cm^{-1}$): 2061, 1975; TEP 2045 $cm^{-1}$. Satisfactory microanalytical data could not be obtained, due to halide scrambling.

**Synthesis of Compound 7-Et.** Triethyloxonium tetrafluoroborate (0.450 g, 2.37 mmol) was placed in a Schlenk tube containing a solution of 1-phenylimidazole (200 $\mu$L, 1.60 mmol) in dry methylene chloride (10 mL) at room temperature. After 30 min, the solvent was removed, affording an oil that was broken by hexane addition to give a white powder: yield 0.332 g (80.7%). $^1$H NMR (300 MHz, $CD_3CN$): $\delta$ (ppm) 8.95 (s, 1H, NC*H*N), 7.78 (t, $J$ = 1.8 Hz, 1H, $CH_{Imid}$), 7.69−7.56 (m, 6H, $CH_{Imid}$, $CH_{Ar}$), 4.31 (q, $J$ = 7.3 Hz, 2H, $CH_2$), 1.55 (t, $J$ = 7.3 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CD_3CN$): $\delta$ (ppm) 135.83 ($C_{Ar}$),135.26 ($C_{Ar}$), 131.18 ($C_{Ar}$), 131.06 ($C_{Ar}$), 123.79 (NCHN), 123.25 ($C_{Imid}$), 122.56 ($C_{Imid}$), 46.27 ($CH_2$), 15.18 ($CH_3$). Electrospray MS (20 V, $m/z$): 173.0 $[M]^+$. Anal. Calcd for $C_{11}H_{13}N_2BF_4$: C, 50.8; H, 5.0; N, 10.8. Found: C, 50.0; H, 4.7; N, 10.6.

**Synthesis of Compound 8-Et.** In a Schlenk tube containing a solution of **7**-Et (0.100 g, 0.38 mmol) and $[RhCl(COD)]_2$ (0.095 g, 0.19 mmol) in THF (15 mL) at −78 °C was added dropwise a solution of KHMDS (0.5 M in toluene, 845 $\mu$L, 0.42 mmol). The mixture was stirred overnight at room temperature. After removal of the volatiles, the crude solid was dissolved in methylene chloride and purified by column chromatography using a $CH_2Cl_2$/acetone mixture to give a yellow solid: yield 0.142 g (88.8%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 8.18−8.15 (m, 2H, $CH_{Ar}$), 7.56−7.44 (m, 3H, $CH_{Ar}$), 7.14 (d, $J$ = 1.9 Hz, 1H, $CH_{Imid}$), 7.01 (d, $J$ = 1.9 Hz, 1H, $CH_{Imid}$), 5.08 (m, 1H, $CH_{COD}$), 4.93 (m, 1H, $CH_{COD}$), 4.82−4.67 (m, 2H, $CH_2$), 3.21 (m, 1H, $CH_{COD}$), 2.54 (m, 1H, $CH_{COD}$), 1.81−1.77 (m, 4H, $CH_{COD}$), 1.62−1.57 (m, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 182.58 (d, $J$ = 51.2 Hz, Rh−$C_{carbene}$), 140.37 ($C_{Ar}$), 128.78 ($C_{Ar}$), 127.79 ($C_{Ar}$), 124.74 ($C_{Ar}$), 121.43 ($C_{Imid}$), 120.30 ($C_{Imid}$), 97.68 ($CH_{COD}$), 97.59 ($CH_{COD}$), 97.53 ($CH_{COD}$), 97.44 ($CH_{COD}$), 68.58 (d, $J$ = 14.3 Hz, Rh−$C_{COD}$), 68.05 (d, $J$ = 14.3 Hz, Rh−$C_{COD}$) ($CH_{2\ COD}$), 46.32 ($CH_2$), 33.38 ($CH_{2\ COD}$), 31.65 ($CH_{2\ COD}$), 28.92 ($CH_{2\ COD}$), 28.37 ($CH_{2\ COD}$), 16.01 ($CH_3$). Electrospray MS (20 V, $m/z$): 383.2 [M − Cl], 424.2 $[M - Cl + MeCN]^+$. Anal. Calcd for $C_{19}H_{24}N_2RhCl$: C, 54.5; H, 5.8; N, 6.7. Found: C, 53.3; H, 6.7; N, 6.9.

**Synthesis of Compound 9-Et.** In a Schlenk containing a solution of **7**-Et (0.100 g, 0.38 mmol) and $[IrCl(COD)]_2$ (129 mg, 0.18 mmol) in THF (15 mL) at −78 °C was added dropwise a solution of KHMDS (0.5 M in toluene, 980 $\mu$L, 0.49 mmol). The mixture was stirred overnight at room temperature. After removal of the volatiles, the crude product was dissolved in methylene chloride and purified by column chromatography using silica gel ($CH_2Cl_2$/acetone), to give a yellow solid: yield 0.130 g (59.4%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 8.01−7.98 (m, 2H, $CH_{Ar}$), 7.49−7.41 (m, 3H, $CH_{Ar}$), 7.14 (d, $J$ = 1.9 Hz, 1H, $CH_{Imid}$), 7.01 (d, $J$ = 1.9 Hz, 1H, $CH_{Imid}$), 4.71−4.46 (m, 4H, $CH_{2\ COD}$, $CH_2$), 2.84 (m, 1H, $CH_{COD}$), 2.25−2.11 (m, 4H, $CH_{2\ COD}$), 1.95−1.83 (m, 1H, $CH_{COD}$), 1.58−1.49 (m, 6H, $CH_{2\ COD}$, $CH_3$), 1.39−1.20 (m, 1H, $CH_{2\ COD}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 180.08 (Ir−$C_{carbene}$), 140.26 ($C_{Ar}$), 128.69 ($C_{Ar}$), 127.81 ($C_{Ar}$), 125.31 ($C_{Ar}$), 121.43 ($C_{Imid}$), 120.17 ($C_{Imid}$), 84.03 ($CH_{COD}$), 83.37 ($CH_{COD}$), 52.09 ($CH_{COD}$), 51.99 ($CH_{COD}$), 46.23 ($CH_2$), 34.11 ($CH_{2\ COD}$), 32.55 ($CH_{2\ COD}$), 29.50 ($CH_{2\ COD}$), 29.35 ($CH_{2\ COD}$), 16.19 ($CH_3$). Electrospray MS (20 V, $m/z$): 514.1 $[M - Cl + MeCN]^+$. Anal. Calcd for $C_{19}H_{24}N_2IrCl\cdot{}^1/_2C_6H_{14}\cdot H_2O$: C, 46.4; H, 5.8; N, 4.9. Found: C, 46.1; H, 6.5; N, 5.5.

**General Procedure for Addition of Arylboronic Acids to Cyclohex-2-enone.** In a 50 mL high-pressure Schlenk tube, catalyst (0.2−0.02 mol %), 2-cyclohexen-1-one (0.5 mmol), arylboronic acid (0.6 mmol), KOH (0.09 mmol) ,and dry toluene (2 mL) were placed. The mixture was stirred and heated to 100 °C for 6 h. The reaction yields were calculated by GC, using anisole as internal standard.

**X-ray Diffraction Studies.** Crystals suitable for X-ray studies of compounds **2**-Me were obtained by slow diffusion of ether into a solution of the complex in MeOH. Crystals suitable for X-ray studies of compound **8**-Et were obtained by slow diffusion of hexane into a solution of the complex in $CHCl_3$. Diffraction data were collected on a Agilent SuperNova diffractometer equipped with an Altas CCD detector using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Single crystals were mounted on a MicroMount polymer tip (MiteGen) in a random orientation. The crystals were kept at 200 K during data collection. The structures were solved by direct methods in SHELXS-97[23] and refined by the full-matrix method based on $F^2$ with the program SHELXL-97 using the OLEX software package.[23,24]

*Crystal data and structure refinement details for compound **2**-Me:* $C_{150}H_{132}F_{18}N_{24}O_{18}S_6$ ($M_r$ = 515.52), trigonal, space group $R\bar{3}$ (No. 148), $a$ = 34.2772(14) Å, $c$ = 14.1208(6) Å, $V$ = 14368.1(13) Å$^3$, $Z$ = 3, $T$ = 293(2) K, $\mu$(Cu K$\alpha$) = 1.294 mm$^{-1}$, $D_{calc}$ = 1.072 g/mm$^3$, 13623 reflections measured ($6.932 \leq 2\theta \leq 121.99$), 4812 unique reflections ($R_{int}$ = 0.0285, $R_\sigma$ = 0.0274), which were used in all calculations. Final R1 = 0.0765 ($I > 2\sigma(I)$) and wR2 = 0.2626 (all data).

*Crystal data and structure refinement details for complex **8**-Et:* $C_{24}HN_7ClRh$ ($M_r$ = 418.77), monoclinic, space group $P2_1/a$ (No. 14), $a$ = 10.1941(3) Å, $b$ = 17.6476(4) Å, $c$ = 10.3104(3) Å, $\beta$ = 101.886(3)°, $V$ = 1815.08(8) Å$^3$, $Z$ = 4, $T$ = 200.00(10) K, $\mu$(Mo K$\alpha$) = 1.089 mm$^{-1}$, $D_{calc}$ = 1.5324 g/mm$^3$, 39071 reflections measured ($5.62 \leq 2\theta \leq 58.84$), 4737 unique reflections ($R_{int}$ = 0.0605, $R_\sigma$ = 0.0323), which were used in all calculations. Final R1 = 0.0270 ($I \geq 2\sigma(I)$) and wR2 = 0.0648 (all data).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Figures, tables, and CIF files giving information regarding the preparation and characterization of the new complexes, including high-resolution mass spectrometry, NMR, UV/vis, FTIR and Raman spectroscopy, and X-ray crystallographic data for **2**-Me and **8**-Et. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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