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Synthesis and Study of 5,5′-Bibenzimidazolylidenes and Their Bimetallic Complexes

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A new, high-yielding synthesis of 3,3′,4,4′-tetrachlorobiphenyl was developed, facilitating access to a new family of fluorescent 5,5′-bibenzimidazolium salts bearing phenyl or bulky tertiary alkyl N-substituents. Deprotonation of these salts afforded the respective 5,5′-bibenzimidazolylidenes in excellent isolated yields (≥86 %), which were characterized in the solid state and solution. Treatment of these ditopic ligands with $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) afforded bimetallic complexes composed of two Rh atoms connected through a bis(carbene) linker. Electrochemical analyses of these complexes revealed single, quasi-reversible oxidations at $E_{1/2}$ = +0.54 to +0.59 V (vs. SCE) arising from the $Rh^{I/II}$ redox couples. A bimetallic Rh carbonyl complex bearing a 5,5′-bibenzimidazolylidene was also synthesized and found to exhibit ν_{CO} signals similar to a monotopic analogue. Collectively, these results suggested that the two metal centers in the aforementioned bimetallic complexes were electronically decoupled. These observations were supported by the crystal structures of one of the 5,5′-bibenzimidazolium salts and its bis(carbene) derivative, which revealed relatively large dihedral angles of 51.2° and 47.8°, respectively, between the two aryl systems.

Introduction

The development of new molecular scaffolds capable of bridging multiple transition metals has enabled the development of organometallic and inorganic materials that exhibit a variety of novel properties.[1] Ideally, the multitopic ligands employed for such purposes should: 1) be modular, to allow fine-tuning of physical and electronic properties, 2) be easy to synthesize, and 3) have strong affinities for a wide variety of transition metals. N-Heterocyclic carbenes (NHCs),[2] such as imidazolylidenes[3] and benzimidazolylidenes,[4] satisfy all three criteria. Multiple synthetic methodologies are available that facilitate variation of the N-substituents as well as the heteroaromatic cores.[5] As a result, an impressively diverse range of derivatives has been prepared and shown to form thermally robust complexes[6] with a large number of transition metals.[2] Attention has focused primarily on the synthesis and characterization of monometallic complexes,[2] with much less emphasis on the development of multitopic NHCs that can coordinate multiple transition metals.[7]

We recently reported[8] a new class of benzobisimidazolylidenes (**1**) that feature two linearly opposed NHCs annulated to a common arene backbone.[9,10] These ditopic ligands proved to be instrumental in the preparation of new classes of bimetallic complexes[11] as well as polymeric[12] and self-assembled[13] materials. Bis(NHC)s **1** are generally prepared by deprotonation of their respective benzobisimidazolium (BBI) salts,[8] with two strategies available for the syntheses of these precursors. In the first method, formylative cyclization of 1,2,4,5-tetraaminobenzene followed by alkylation affords a tetraalkylated BBI salt. One limitation of this methodology is that only primary *N*-alkyl substituents can be installed. Although these BBIs are suitable monomers for the synthesis of poly(enetetraamine)s,[14] primary *N*-alkyl groups are generally too small to enable isolation of the respective free bis(NHC)s. This limitation was circumvented with the development of a second strategy. Four-fold aryl amination of 1,2,4,5-tetrabromo- or chlorobenzene afforded the respective tetraaminobenzenes bearing large N-substituents (R = tertiary alkyl, aryl) in excellent yields (typically >90%).[15] After subsequent formylative cyclization and deprotonation, this methodology enabled isolation of the respective stable bis(NHC)s **1**.[8] Although the physical and electronic properties of **1** can be tuned by modification of the N-substituents using the aforementioned synthetic approaches,[11] we desired methodology that would enable the incorporation of other aromatic linkers into bis(NHC) scaffolds, in particular biphenyl, leading to derivatives such as **2** (see Figure 1).

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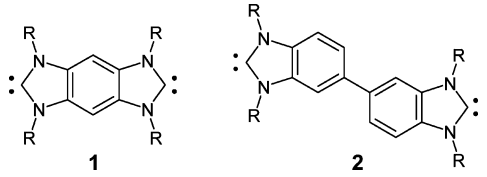


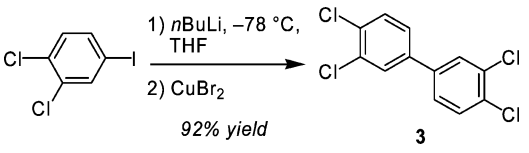
Figure 1. Structures of benzobisimidazolylidenes **1** and 5,5′-bibenzimidazolylidenes **2**.

In analogy to BBI-based compounds, formylative cyclization of 3,3′-diaminobenzidine followed by alkylation was previously shown to afford the respective 5,5′-bibenzimidazolium salts bearing primary *N*-alkyl groups in excellent yields.[12] Although deprotonation of these salts did not afford the desired free bis(NHC)s, they did yield to a new class of poly(enetetraamine)s with **2** as the repeating unit.[14] Recently, Gehrhus and Lappert reported the first example of an isolable 5,5′-bibenzimidazolylidene (**2**, R = neopentyl) by reducing the corresponding bis(thiourea) with KC_8.[10]

We envisioned that a gentler, more efficient synthesis of stable derivatives of **2** could be realized in a manner analogous to **1** through deprotonation of 5,5′-bibenzimidazolium salts featuring bulky N-substituents. Guided by our experience with **1**, we sought to develop methodology that enabled access to such salts via exhaustive aryl amination of a 3,3′,4,4′-tetrahalobiphenyl followed by formylative cyclization. Deprotonation of these salts was envisioned to afford **2** as their stable bis(NHC)s as well as bimetallic derivatives supported by this ditopic ligand. A corollary of these efforts was to explore the relationship between the geometric properties of **2** (i.e. the dihedral angles between its aryl rings) and the degree of electronic communication across the biphenyl linkage using fluorescence, electrochemical, and other spectroscopic measurements.[16]

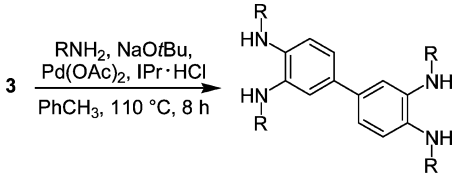
Results and Discussion

The synthesis of 3,3′,4,4′-tetrachlorobiphenyl (**3**) has been previously achieved via Suzuki–Miyaura coupling of (3,4-dichlorophenyl)boronic acid to 1,2-dichloro-4-iodobenzene.[17] Although the yield of this reaction is good (69%), the requisite boronic acid is prohibitively expensive and requires multiple steps to synthesize. We reasoned that **3** might be prepared more directly through metal-mediated, oxidative homocoupling of the respective aryllithium compound. Indeed, as shown in Scheme 1, treatment of commercially available 1,2-dichloro-4-iodobenzene with *n*BuLi at –78 °C, followed by stoichiometric $CuBr_2$, afforded **3** in 92% isolated yield.



Scheme 1. Synthesis of 3,3′,4,4′-tetrachlorobiphenyl (**3**).

With an efficient, high-yielding route to **3** developed, we shifted our efforts toward exploring the potential of this tetrahaloarene to undergo fourfold aryl amination with bulky alkyl (*tert*-butyl, *tert*-amyl and 1-adamantyl) as well as aryl (phenyl and mesityl) amines. Although tetraaminobiphenyls bearing sterically shielding *N*-substituents can be prepared by reaction of 3,3′-diaminobenzidine with RC(O)Cl followed by reduction, this route can only be used with redox inert functional groups and can only install primary alkyl *N*-substituents.[18] With **3**, however, we discovered that tertiary alkyl as well as aryl *N*-substituents could be installed using Pd-catalyzed aryl amination.[19] As summarized in Scheme 2, these reactions were performed by heating a mixture of 4.1–5.0 equiv. of an amine relative to **3** (typical $[\mathbf{3}]_0$ = 0.2 M) and a 1:2 molar ratio of $Pd(OAc)_2$/1,3-bis(2,6-diisopropylphenyl)imidazolylidene (IPr) as the pre-catalyst (2 mol-% Pd relative to **3**) in toluene at 110 °C for 12 h. The reaction mixture was then concentrated and washed with ethanol to give the desired products in modest to excellent yields (40–93%). Spectroscopic analyses of these compounds confirmed their structural assignments as 3,3′,4,4′-tetraaminobiphenyls **4**. Surprisingly, despite being connected to electron-rich arylamines, the ^{1}H NMR signals for the biphenyl protons were not significantly upfield (δ = 6.9–7.4 ppm, $CDCl_3$). Likewise, tetraaminoarenes **4** were found to be relatively stable toward oxidation. For example, ^{1}H NMR analysis of aerated $CDCl_3$ solutions of these tetraamines revealed no oxidation products, even after several days.



4a (R = *t*Bu), 93%
4b (R = *t*Am), 57%
4c (R = Ad), 40%
4d (R = Ph), 86%
4e (R = Mes), 79%

Scheme 2. Syntheses of 3,3′,4,4′-tetraaminobiphenyls (**4**).

Collectively, these results were similar to those we obtained with various 1,2,4,5-tetraaminobenzenes prepared using an analogous fourfold aryl amination methodology from tetrachloro- or tetrabromobenzene.[15] Comprehensive structural analyses of 1,2,4,5-tetraaminobenzenes analogous to **4** revealed that the nitrogen lone pairs were rotated into the planes of their respective arene rings.[15] To determine if the bisarenes **4** exhibited similar structural characteristics, single crystals of **4a** were grown by slowly cooling a saturated solution in toluene from reflux to ambient temperature and then analyzed by X-ray diffraction.[20] As shown in Figure 2, the *tert*-butyl groups on two of the nitrogen atoms were positioned above and below the planes of the arene rings with torsion angles of approximately 130°. This conformation effectively places the nitrogen lone pairs on these amino groups orthogonal to the π-systems of the

arene rings to which they are bonded. This structural arrangement attenuates the electron-donating properties typically associated with amines and explains both the unexpected NMR spectroscopic properties and the high oxidative stabilities exhibited by **4**.

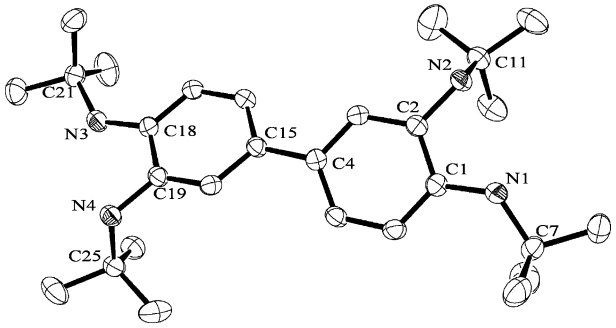
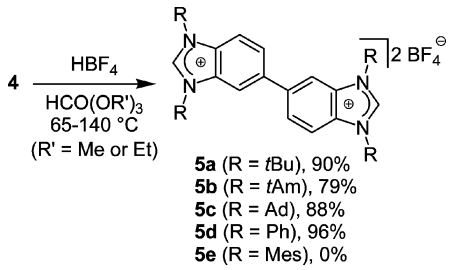


Figure 2. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **4a**. Solvent molecules and H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1, 1.376(2); N1–C7, 1.463(2); N2–C2, 1.436(2); N2–C11, 1.491(2); N3–C18, 1.379(2); N3–C21, 1.459(2); N4–C19, 1.437(2); N4–C25, 1.500(2); C4–C15, 1.480(2); C1–N1–C7, 129.90(16); C2–N2–C11, 117.00(13); C18–N3–C21, 130.05(17); C19–N4–C25, 117.44(13); C1–C2–N2–C11, 103.14(17); C2–C1–N1–C7, 10.63(16); C18–C19–N4–C25, 102.98(17); C19–C18–N3–C21, 173.47(17). The dihedral angle (ϕ) between the two benzimidazole moieties is 26.0°.

With tetraamines **4** in hand, we then pursued the synthesis of their corresponding *N*-aryl- and *N*-alkyl-5,5′-bibenzimidazolium salts (**5**). This was accomplished by treating solutions of **4** in $HC(OMe)_3$ or $HC(OEt)_3$ with excess tetrafluoroboric acid at 65–140 °C (see Scheme 3). After 24 h, the desired 5,5′-bibenzimidazolium salts (**5**) precipitated from their respective reaction mixtures, facilitating isolation in good to excellent yields (79–96%) with minimal workup. Unfortunately, **5e** failed to form under these conditions, consistent with the failure of 1,2,4,5-tetra(mesitylamino)-benzene to undergo formylative cyclization.[15] The ^1H NMR signals for the benzimidazolium protons in **5** were found between 8.9 and 10.5 ppm ([D_6]DMSO), which was within the range expected for 1,3-disubstituted benzimidazolium salts.[4,15,21] X-ray analysis of a single crystal of **5a** (obtained by slowly cooling a hot solution of DMSO saturated with this salt) revealed that the dihedral angle between the two benzimidazolium moieties was ϕ = 51.2° (structure not shown).[20]



Scheme 3. Synthesis of 5,5′-bibenzimidazolium salts (**5**).

Previous studies of BBI-based salts revealed that these compounds exhibit rich photoluminescent properties.[22] Thus, we sought to investigate the spectroscopic characteristics of their 5,5′-bibenzimidazolium analogues. The absorption spectra for **5a**–**c** were nearly indistinguishable from each other, with almost identical absorption wavelengths and extinction coefficients (see Table 1). Furthermore, the emission profiles were superimposable, with fluorescence maximizing at nearly identical wavelengths. These results are consistent with the similar electronic characteristics of the *N*-substituents in compounds **5a**–**c**: each benzimidazolium nitrogen is connected to one quaternary carbon, which itself is connected to three CH_2X moieties (where X can be a proton or hydrocarbon chain or cycle).

Table 1. Spectroscopic properties of **5**.[a]

	λ_{max} [nm]	log ε	λ_{em} [nm]	Φ
5a	292	4.24	341	0.67
5b	292	4.27	340	0.47
5c	294	4.24	342	0.88
5d	285	4.40	415	0.61

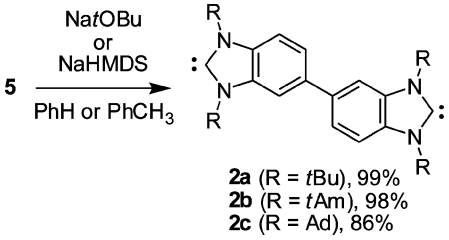
[a] Measurements were performed in DMF under ambient conditions. Molar extinction coefficients (ε, in $M^{-1}cm^{-1}$) were determined from Beer's law plots. Fluorescence quantum efficiencies (Φ) were determined relative to quinine bisulfate in 0.1 N H_2SO_4 (aq.).

Interestingly, the λ_{max} for **5a** is slightly longer than its monomeric "half" [1,3-bis(*tert*-butyl)benzimidazolium]-(BF_4) (292 nm vs. 276 nm, respectively). This is consistent with **5a** being slightly more electron deficient compared to its monomeric analogue, thus lowering the energy of the $\pi \rightarrow \pi^*$ transition. Considering that their emission wavelengths are also comparable (341 nm vs. 351 nm), we believe that similar absorption and emission processes are occurring in these two molecules, albeit with radically different quantum yields (67% vs. 0.1%). Overall, these results suggest that the exciton that forms in **5a** is localized largely on the benzimidazolium fragments, with minimal delocalization across the biphenyl linkage.

Despite the similarities among **5a**–**c**, the quantum yields for these compounds varied significantly (**5c** > **5a** > **5b**) and in accord with the identities of the *N*-substituents in these compounds. Because the excitation and emission energies of **5a**–**c** were nearly identical, the variation in quantum yields enabled us to gain greater insight into their photophysical properties than would otherwise be possible. A quantum yield is equal to the radiative decay rate divided by the sum of the radiative and non-radiative decay rates. Although a molecule can emit a photon when it relaxes from an excited state, relaxation can also be induced by intermolecular collisions or intramolecular vibrations without concomitant emission. Because 1-adamantyl is more rigid than *tert*-butyl, the former has fewer vibrational and rotational modes and thus provides fewer non-radiative decay pathways; this explains why the quantum yield of **5c** > **5a**. Similarly, because *tert*-amyl contains one more methyl group than *tert*-butyl, it has more vibrational and rotational modes available and thus the quantum yield of **5a** > **5b**.

Replacing the alkyl N-substituents with phenyl groups results in a 10 nm hypsochromic shift in absorption maximum, which can be understood by the diminished electron-releasing ability of phenyl relative to tertiary alkyl groups. Whereas **5a**–**c** show relatively small Stokes shifts (50 nm), the absorption and emission maxima for **5d** are separated by 130 nm. Given the minimal conjugation observed between the two benzimidazole fragments in **5a**–**c**, we believe that the large Stokes shift for **5d** arises from exciton delocalization onto the *N*-phenyl groups, rather than onto a neighbouring benzimidazolium group.

Upon the synthesis and characterization of 5,5′-benzimidazolium salts **5**, we then pursued the synthesis of their respective free bis(NHC)s **2**. As shown in Scheme 4, addition of two equivalents of either NaO*t*Bu or NaN(SiMe$_3$)$_2$ (NaHMDS) to **5a**–**c** afforded **2a**–**c** in excellent yields (≥86%) after filtration and removal of solvent. Diagnostic ^{13}C NMR signals for the carbene carbons were observed between δ = 220 and 230 ppm, consistent with other known annulated imidazolylidenes.[4,5,8] Deprotonation of **5d** with NaHMDS afforded a complex mixture that appears to be the expected poly(enetetraamine)[14] (formed in situ by polymerization of **2d**).[23]



Scheme 4. Synthesis of 5,5′-bibenzimidazolylidenes (**2**).

Slow cooling of a saturated solution of **2a** in refluxing toluene afforded crystals suitable for X-ray diffraction (see Figure 3).[20] The N1–C1–N2 bond angle of 104.1(2)° and the average N–C bond length of 1.372(3) Å in this structure are similar to those found in other benzimidazolylidenes.[4,5,8] Notably, the two benzimidazole moieties of this compound are more twisted (ϕ = 47.8°) relative to each other in the solid state than in the tetraamine **4a** (ϕ = 26.0°) but less than its respective bibenzimidazolium salt **5a** (ϕ = 51.2°).

To explore in greater detail the degree of communication across the two benzimidazole groups in **2**, a series of bimetallic Rh complexes containing these bis(NHC)s were synthesized and studied electrochemically as well as spectroscopically.[24] Rhodium complexes **6** were prepared by adding one equivalent of **2** (generated by in situ deprotonation of **5** with NaHMDS) to one equivalent of [Rh(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene) in toluene. After stirring for 12 h at ambient temperature, the solvent was removed under reduced pressure and the resulting yellow solids were triturated with Et$_2$O to afford **6** in yields of up to 85% (see Scheme 5). The diagnostic ^{13}C signals for the ligated carbene carbon atoms were observed at 195.8–197.8 ppm, and exhibited the characteristic Rh–C splitting pattern with J = 48.6–49.6 Hz.[4,8] Unfortunately, all attempts at obtaining crystals suitable for X-ray diffraction analysis of these compounds were unsuccessful.

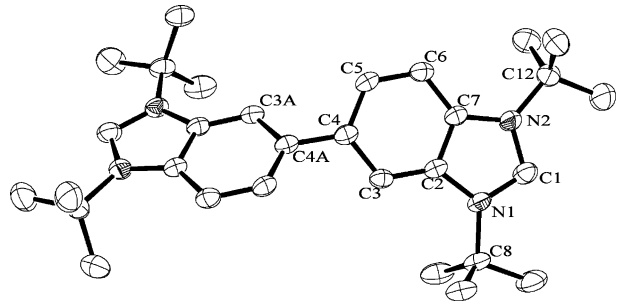
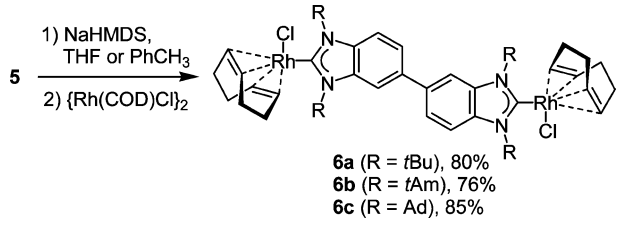


Figure 3. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **2a**. Solvent molecules and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–N1 1.372 (3), C1–N2 1.372 (3), N1–C2 1.404 (3), N2–C7 1.398(3), C2–C3 1.392 (3), C3–C4 1.396 (3), C4–C4A 1.488 (4). The dihedral angle (ϕ) between the two benzimidazole moieties is 47.8°.



Scheme 5. Synthesis of bimetallic Rh complexes containing 5,5′-bibenzimidazolylidenes (**2**).

Cyclic voltammetry of **6** in CH_2Cl_2 (for **6a**, see Figure 4, A) revealed quasi-reversible Rh$^{I/II}$ redox couples within a narrow range ($E_{1/2}$ = +0.54 to +0.59 V relative to SCE). In contrast, the Rh$^{I/II}$ couple for an *N*-ethyl analogue (**7**; see Figure 5) occurred at nearly double the potential (E_{pa} = +0.95 V), consistent with the diminished electron-donating ability of ethyl vs. tertiary alkyl groups. Furthermore, this oxidation was irreversible, presumably due to the decreased steric shielding around the metal atom. The voltammograms displayed only single metal-based redox events, indicating that the two metal centers in these complexes were electronically decoupled.[25] To test this observation, we prepared [Rh{1,3-di(*tert*-butyl)benzimidazolylidene}(COD)Cl] (**8a**) and its *N*-ethyl analogue **8b** to model the monomeric halves of **6a** and **7**, respectively. Cyclic voltammetry of **8a** revealed a single, quasi-reversible oxidation wave at $E_{1/2}$ = +0.58 V for the Rh$^{I/II}$ couple, which is nearly identical to that observed for **6a** (+0.59 V). Similarly, the Rh$^{I/II}$ oxidation potential in **8b** occurred close to that in **7** (+0.86 V vs. +0.95 V, respectively). The higher oxidation potentials observed for **6a** and **7** are consistent with the greater electron-deficient character inherent to bibenzimidazole-based systems relative to benzimidazole analogues (see above).

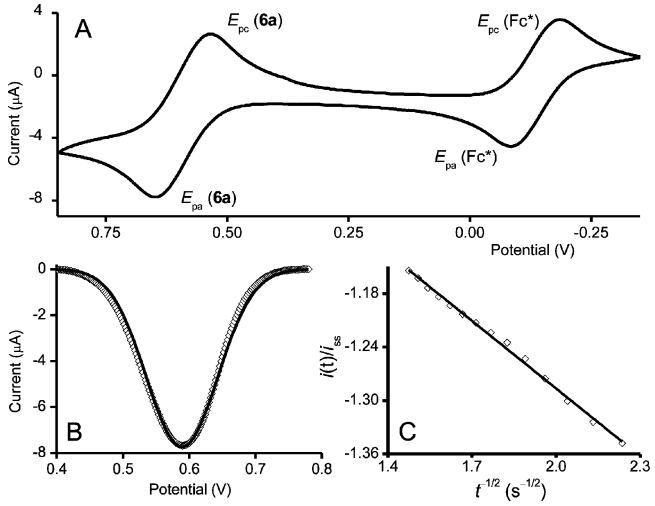


Figure 4. (A) CV of **6a** with [Fc*] as an internal standard (vs. SCE). (B) DPV of the oxidation for **6a** (✧) and single-peak deconvolution (black line). (C) Plot of $i(t)/i_{ss}$ vs. $t^{-1/2}$ data (✧) for the oxidation of **6a**. Linear fit (black line, slope = –0.25, *y*-intercept = –0.78, R^2 = 0.99) allowed determination of D_0 and *n*.

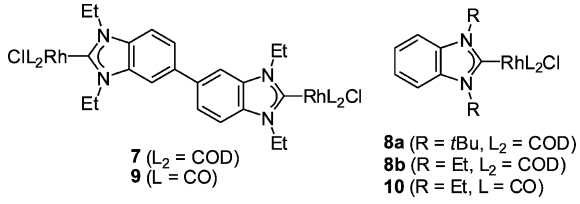


Figure 5. Structures of various Rh–NHC complexes that were synthesized and studied.

To investigate the electronic communication across the bibenzimidazolylidene linker in the aforementioned complexes in detail, we analyzed **8a** by differential pulse voltammetry (DPV) and chronoamperometry (CA). Deconvolution of the DPV data for **6a** revealed only one oxidation peak (Figure 4, B). Performing CA on **6a** using an ultramicroelectrode enabled us to measure the time-dependent and steady-state currents, $i(t)$ and i_{ss}, respectively. Dividing $i(t)$ by i_{ss} and plotting vs. $t^{-1/2}$ (Figure 4, C) allowed us to determine $D_0 = 6.9 \times 10^{-6}$ cm^2 s^{-1} and $n = 1.8$ for **6a**.[26] Similar analyses of **8a** also revealed only one oxidation peak, but with $D_0 = 2.7 \times 10^{-5}$ cm^2 s^{-1} and $n = 1.1$. These *n* values support the notion that the oxidation of **6a** is a two-electron process (comprising two independent, one-electron oxidations at each metal center) whereas that of **8a** is a one-electron process. Furthermore, the diffusion coefficients are consistent with the fact that **8a** is significantly smaller than **6a**.

We sought to complement our electrochemical evaluation of the electronic communication between the metals in **6** by incorporating ligands with diagnostic IR frequencies (i.e. carbonyls). Thus, the [Rh(COD)Cl] complexes **7** and **8b** were converted into their analogous [Rh(CO)$_2$Cl] complexes by independently pressurizing CD_2Cl_2 solutions of these complexes with carbon monoxide, followed by stirring at ambient temperature.[27] Unfortunately, the desired products **9** and **10** (observable by NMR spectroscopy) were found to decompose upon concentration (presumably through loss of CO)[28] and could not be cleanly isolated by this method. However, by allowing the solvent to evaporate under an atmosphere of carbon monoxide then triturating the crude material with pentane at –78 °C (also under carbon monoxide), complexes **9** and **10** (Figure 5) were successfully isolated in ≥ 95% yield. The *cis* and *trans* (relative to Rh) ν_{CO} bands for **9** were observed at 2003 and 2084 cm^{-1}, respectively, in solution which were similar to the analogous signals observed for its related monomeric half **10** (ν_{CO} = 2002 and 2083 cm^{-1}). Because **9** displays only two ν_{CO} bands at nearly identical energies to **10**, we conclude that the two metal centers in the former are electronically decoupled.[16] Hence, rather than viewing these complexes as ligand-bridged bimetallic species, they may be more properly viewed as dimers of monometallic benzimidazolylidene species.

Conclusions

We have developed a new, highly efficient synthesis of 3,3′,4,4′-tetrachlorobiphenyl (**3**) from commercially available starting materials. Subsequent Pd-catalyzed coupling of bulky alkyl or arylamines, followed by formylative cyclization, afforded a new class of highly fluorescent bibenzimidazolium salts (**5**). The *N*-alkyl variants of these salts displayed identical absorption and emission energies with increasing quantum yields correlating to increasing rigidity of the N-substituent (1-adamantyl > *tert*-butyl > *tert*-amyl). Although the emission from these salts appears localized primarily on each benzimidazolium moiety, that from the *N*-phenyl analogue suggests delocalization onto its N-substituents. Deprotonation of these salts afforded the respective bis(NHC)s **2** in high isolated yields. Treatment of these ditopic ligands with [Rh(COD)Cl]$_2$ afforded the expected bimetallic complexes, which exhibited only single, metal-based redox processes. Furthermore, comparison of the cyclic voltammograms of these bimetallic complexes to models of their monometallic "halves" revealed $Rh^{I/II}$ redox processes at similar potentials. Likewise, the ν_{CO} values observed for a related bimetallic carbonyl complex were found at frequencies similar to a monometallic model. Collectively, the results from our fluorescence, electrochemical, and spectroscopic experiments have demonstrated that Rh metal centers ligated to 5,5′-bibenzimidazolylidenes are largely electronically decoupled. As such, bimetallic complexes supported by the ditopic bis(NHC)s described herein hold potential for use as bifunctional catalysts[9d,29] as well as connectable components in the emerging fields of nano- and molecular electronics.[30]

Experimental Section

General Procedures: Unless otherwise noted, all manipulations were performed using standard Schlenk techniques under nitrogen or in a nitrogen-filled glove box. THF was distilled from Na/benzo-

phenone under nitrogen. Toluene was distilled from CaH_2 and degassed by three consecutive freeze-pump-thaw cycles. All other chemicals were used as received. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz DirectDrive spectrometer and were referenced to residual protio solvent. ^{13}C NMR spectra were routinely run with broadband decoupling. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual solvent as an internal standard [^1H: $CDCl_3$, 7.24 ppm; C_6D_6, 7.15 ppm; [D_6]-DMSO, 2.49 ppm; $C_6D_5CD_3$, 2.09 ppm; CD_2Cl_2, 5.32 ppm; ^{13}C: $CDCl_3$, 77.0 ppm; C_6D_6, 128.0 ppm; [D_6]DMSO, 39.5 ppm; $C_6D_5CD_3$, 20.4 ppm; CD_2Cl_2, 53.8 ppm]. ^{19}F NMR spectra were also run on a Varian 400 MHz DirectDrive spectrometer and referenced to an external standard (^{19}F: $CFCl_3$, 0 ppm). To quantify the extent of the anion metathesis reactions, a known quantity of 1,2-dibromo-4,5-difluorobenzene (δ = –136.3 ppm) was added as an internal standard. In all cases, the reactions were found to proceed in >99% conversion. Infrared spectra were recorded using a Perkin–Elmer Spectrum BX FT-IR spectrometer in a solution cell equipped with CaF_2 windows. Melting points were determined under ambient atmosphere and are uncorrected. High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E or a Karatos MS9 instrument and are reported as *m*/*z* (%).

UV/Vis absorption and fluorescence emission spectra were recorded with a Perkin–Elmer Lambda 35 spectrophotometer and a PTI QuantaMaster 4 L fluorimeter, respectively. All measurements were made with matched 6Q Spectrosil quartz cuvettes (Starna) with 1-cm path lengths and 3.0 mL of sample solution volumes. Beer's law measurements were performed using 10, 20, 30 and 40 μM sample concentrations. Emission spectra were acquired using 1.0 μM solutions of fluorophore. Quantum yields were determined relative to 1.0 μM quinine sulfate in 0.1 *N* H_2SO_4.[31] All measurements were performed in DMF under ambient conditions.

Electrochemical experiments were conducted using CH Instruments Electrochemical Workstations (series 630C and 700B) using a gas-tight three-electrode cell under nitrogen. The electrochemical cell contained platinum working and counter electrodes and a silver wire as a quasi-reference electrode. Chronoamperometric experiments were performed using a 15 μm Pt ultramicroelectrode as the working electrode. Quasi-reversibility for **6a** was confirmed by scan-rate independence from 50 mV/s to 1 V/s. All measurements were performed in dry CH_2Cl_2 using 1 mM analyte, 0.1 M [tetra-*n*-butylammonium](PF_6) as the electrolyte, and decamethylferrocene [Fc*] as the internal standard ($[Fc^*]^{0/+}$ = –0.13 V vs. SCE).[26,32] The potentials listed in the manuscript and experimental section were determined at 100 mV/s scan-rates and adjusted to SCE.

3,3′,4,4′-Tetrachlorobiphenyl (3): A 25 mL round-bottomed flask was charged with 1,2-dichloro-4-iodobenzene (100 mg, 0.366 mmol) and a stir bar, and then placed under nitrogen. After dry THF (1.5 mL) was introduced into the flask via syringe, the resulting solution was cooled to –78 °C using a dry ice/acetone bath. *n*BuLi (2.2 M in hexanes, 0.18 mL, 0.403 mmol) was then added dropwise over 30 min. The resulting reaction mixture was then stirred at –78 °C for an additional 30 min. $CuBr_2$ (81.7 mg, 0.366 mmol) was then added in a single portion and the resulting mixture was stirred for 3 h at –78 °C. Afterward, the mixture was quenched with an aqueous solution saturated with NH_4Cl and the organic material was extracted with hexanes (3 × 50 mL). The resultant organic extracts were then combined and dried with $MgSO_4$. Residual solvent was removed using a rotary evaporator under reduced pressure. The residual solids were collected by filtration, washed with ethanol, and dried under vacuum to afford 49 mg (92% yield) of the desired compound as white powder. Spectroscopic data was in accord with literature values.[17] M.p. 172–175 °C. ^1H NMR ($CDCl_3$): δ = 7.60 (d, *J* = 2.2 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 7.35 (dd, *J* = 8.4, 2.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.7, 133.2, 132.5, 131.0, 128.8, 126.1 ppm. HRMS: $[M + H]^+$ calcd. for $C_{12}H_7Cl_4$: 290.9302; found 290.9303.

1,1′,3,3′-Tetra(*tert*-butyl)-3,3′-diaminobenzidine (4a): In a 30-mL vial, a mixture of $Pd(OAc)_2$ (4.9 mg, 0.022 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (19 mg, 0.045 mmol), NaO*t*Bu (5.0 mg, 0.052 mmol), and toluene (2 mL) was stirred for 15 min. Afterward, 3,3′,4,4′-tetrachlorobiphenyl (**3**) (500 mg, 1.71 mmol), *tert*-butylamine (626 mg, 8.56 mmol), NaO*t*Bu (675 mg, 7.02 mmol), and toluene (6.6 mL) were added. The resulting mixture was then sealed and stirred at 110 °C for 12 h. The cooled reaction mixture was filtered and then concentrated under reduced pressure. After washing the residual solids with excess ethanol, they were dried under high vacuum to afford 700 mg (93% yield) of the desired product as white powder; m.p. 148–151 °C. ^1H NMR ($CDCl_3$): δ = 7.09 (d, *J* = 2.0 Hz, 2 H), 6.94 (dd, *J* = 8.2, 2.2 Hz, 2 H), 6.89 (d, *J* = 8.2 Hz, 2 H), 3.65 (s, 4 H), 1.31 (s, 18 H), 1.29 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.8, 136.8, 134.0, 120.9, 118.1, 52.0, 51.9, 30.0, 29.9 ppm. HRMS: $[M + H]^+$ calcd. for $C_{28}H_{47}N_4$: 439.3798; found 439.3795.

1,1′,3,3′-Tetra(*tert*-amyl)-3,3′-diaminobenzidine (4b): Using a procedure analogous to one used to prepare **4a**, **3** (200 mg, 0.685 mmol) and *tert*-amylamine (298 mg, 3.42 mmol) afforded 193 mg (57% yield) of the desired compound as white powder; m.p. 94–98 °C. ^1H NMR ($CDCl_3$): δ = 7.05 (d, *J* = 2.2 Hz, 2 H), 6.90 (dd, *J* = 8.2, 2.2 Hz, 2 H), 6.85 (d, *J* = 8.2 Hz, 2 H), 3.64 (s, 4 H), 1.65 (q, *J* = 7.6 Hz, 4 H), 1.62 (q, *J* = 7.4 Hz, 4 H), 1.22 (s, 12 H), 1.19 (s, 12 H), 0.92 (t, *J* = 7.4 Hz, 12 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.9, 136.6, 133.9, 120.6, 118.1, 117.8, 54.5, 54.3, 35.0, 34.9, 27.2, 27.1, 8.7 ppm. HRMS: $[M + H]^+$ calcd. for $C_{32}H_{55}N_4$: 495.4415; found 495.4421.

1,1′,3,3′-Tetra(1-adamantyl)-3,3′-diaminobenzidine (4c): In a manner analogous to the procedure used to prepare **4a**, **3** (300 mg, 1.03 mmol) and 1-adamantylamine (873 mg, 4.16 mmol) afforded 309 mg (40% yield) of the desired compound as a white powder. Note that one minor modification to the workup procedure was employed: after cooling and filtering the reaction mixture, the residual solids were rinsed with toluene and extracted with $CHCl_3$. The combined extracts were then concentrated under reduced pressure to obtain the desired product; m.p. 316–319 °C. ^1H NMR ($CDCl_3$): δ = 7.14 (s, 2 H), 6.94 (d, *J* = 8.1 Hz, 2 H), 6.91 (d, *J* = 8.1 Hz, 2 H), 3.64 (s, 4 H), 2.07 (br., 12 H), 1.91 (br., 12 H), 1.86 (br., 12 H), 1.64 (br., 24 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.6, 135.6, 134.3, 122.8, 119.3, 117.9, 52.7, 43.3, 36.6, 29.8 ppm. HRMS: $[M + H]^+$ calcd. for $C_{52}H_{71}N_4$: 751.5663; found 751.5973.

1,1′,3,3′-Tetraphenyl-3,3′-diaminobenzidine (4d): In a manner analogous to the procedure used to prepare **4a**, **3** (500 mg, 1.71 mmol) and aniline (646 mg, 6.94 mmol) afforded 763 mg (86% yield) of the desired compound as a brown powder; m.p. 160–163 °C. ^1H NMR ($CDCl_3$): δ = 7.38 (d, *J* = 2.2 Hz, 2 H), 7.32 (s, 2 H), 7.30 (s, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 7.14 (m, 8 H), 7.08 (dd, *J* = 8.4, 2.2 Hz, 2 H), 6.96 (m, 8 H), 6.74 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 143.8, 143.7, 135.6, 135.0, 133.9, 129.4, 129.3, 121.2, 120.6, 120.3, 118.4, 117.3, 117.2 ppm. HRMS: $[M + H]^+$ calcd. for $C_{36}H_{31}N_4$: 519.2533; found 519.2543.

[1,1′,3,3′-Tetra(*tert*-butyl)-5,5′-bibenzimidazolium](BF_4)$_2$ (5a): A mixture of **4a** (700 mg, 1.59 mmol), HBF_4 (1.08 mL, 50% in Et_2O), and trimethyl orthoformate (20 mL) was heated at 65 °C for 24 h. Afterward, precipitated solids were collected by filtration, washed

with THF, and then dried under vacuum to afford 786 mg (90% yield) of the desired compound as a white powder; m.p. 224–248 °C (dec.). ^{1}H NMR ([D$_6$]DMSO): δ = 8.87 (s, 2 H), 8.42 (d, J = 8.9 Hz, 2 H), 8.39 (s, 2 H), 7.97 (d, J = 8.9 Hz, 2 H), 1.86 (s, 18 H), 1.86 (s, 18 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 139.0, 137.1, 131.0, 130.1, 125.7, 117.5, 116.2, 61.9, 61.7, 40.1, 40.0, 35.1, 35.0, 29.2, 29.1 ppm. ^{19}F NMR ([D$_6$]DMSO): δ = –148.2, –148.3 ppm. HRMS: [M]$^{2+}$ calcd. for $C_{30}H_{44}N_4$: 230.1782; found 230.1778. UV/Vis: λ_{max} = 292 nm, $\varepsilon = 1.74 \times 10^4$ M^{-1} cm^{-1}. Fluorescence: λ_{em} = 341 nm, Φ = 0.67.

[1,1′,3,3′-Tetra(*tert*-amyl)-5,5′-bibenzimidazolium](BF$_4$)$_2$ (5b): Using a procedure analogous to one used to prepare **5a**, **4b** (375 mg, 0.76 mmol) afforded 360 mg (79% yield) of the desired compound as a beige solid; m.p. 219–222 °C (dec.). ^{1}H NMR ([D$_6$]-DMSO): δ = 8.90 (s, 2 H), 8.46 (d, J = 8.8 Hz, 2 H), 8.44 (d, J = 1.4 Hz, 2 H), 7.99 (dd, J = 8.8, 1.4 Hz, 2 H), 2.24 (q, J = 7.0 Hz, 4 H), 2.23 (q, J = 6.8 Hz, 4 H), 1.87 (s, 12 H), 1.85 (s, 12 H), 0.69 (t, J = 7.4 Hz, 6 H), 0.68 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 140.5, 137.7, 131.4, 130.6, 127.0, 166.9, 115.4, 64.9, 64.7, 31.8, 26.1, 26.0, 8.1, 7.9 ppm. ^{19}F NMR ([D$_6$]DMSO): δ = –148.2, –148.3 ppm. HRMS: [M]$^{2+}$ calcd. for $C_{34}H_{52}N_4$: 258.2088; found 258.2091. UV/Vis: λ_{max} = 292 nm, $\varepsilon = 1.86 \times 10^4$ M^{-1} cm^{-1}. Fluorescence: λ_{em} = 340 nm, Φ = 0.47.

[1,1′,3,3′-Tetra(1-adamantyl)-5,5′-bibenzimidazolium](BF$_4$)$_2$ (5c): Using a procedure analogous to one used to prepare **5a**, **4c** (100 mg, 0.133 mmol) afforded 113 mg (88% yield) of the desired compound as a beige solid; m.p. 347–352 °C (dec.). ^{1}H NMR ([D$_6$]-DMSO): δ = 8.89 (s, 2 H), 8.55 (d, J = 8.9 Hz, 2 H), 8.47 (d, J = 1.2 Hz, 2 H), 7.97 (d, J = 8.9, 1.4 Hz, 2 H), 2.51 (br., 12 H), 2.46 (br., 12 H), 2.32 (br., 6 H), 2.28 (br., 6 H), 1.88–1.78 (br., 24 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 139.1, 137.2, 131.0, 130.1, 125.8, 117.6, 116.3, 61.9, 61.7, 35.1, 29.2, 29.1 ppm. ^{19}F NMR ([D$_6$]-DMSO): δ = –148.2, –148.3 ppm. HRMS: [M]$^{2+}$ calcd. for $C_{54}H_{68}N_4$: 386.2721; found 386.2717. UV/Vis: λ_{max} = 294 nm, $\varepsilon = 1.74 \times 10^4$ M^{-1} cm^{-1}. Fluorescence: λ_{em} = 342 nm, Φ = 0.88.

[1,1′,3,3′-Tetraphenyl-5,5′-bibenzimidazolium](BF$_4$)$_2$ (5d): Using a procedure analogous to one used to prepare **5a**, combination of **4d** (500 mg, 0.96 mmol) and triethyl orthoformate (20 mL) at 140 °C for 24 h afforded 648 mg (96% yield) of the desired compound as a beige solid; m.p. 296–300 °C (dec.). ^{1}H NMR ([D$_6$]DMSO): δ = 10.48 (s, 2 H), 8.20 (s, 2 H), 8.18 (d, J = 8.6 Hz, 2 H), 8.02 (d, J = 8.8 Hz, 2 H), 7.95 (m, 8 H), 7.77 (m, 12 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 143.9, 138.7, 133.0, 132.9, 131.7, 131.1, 130.9, 130.8, 130.5, 130.4, 127.9, 125.4, 125.3, 114.5, 112.7 ppm. ^{19}F NMR ([D$_6$]-DMSO): δ = –148.2, –148.3 ppm. HRMS: [M]$^{2+}$ calcd. for $C_{38}H_{28}N_4$: 270.1155; found 270.1152. UV/Vis: λ_{max} = 285 nm, $\varepsilon = 2.51 \times 10^4$ M^{-1} cm^{-1}. Fluorescence: λ_{em} = 415 nm, Φ = 0.61.

1,1′,3,3′-Tetra(*tert*-butyl)-5,5′-bibenzimidazolylidene (2a): In a 5-mL vial, a suspension of bibenzimidazolium salt **5a** (20.9 mg, 0.0328 mmol), NaO*t*Bu (6.5 mg, 0.067 mmol) and benzene (1 mL) was stirred at ambient temperature for 10 h. The reaction mixture was then filtered through a 0.4 μm PTFE filter and concentrated under reduced pressure to afford 14.9 mg (99% yield) of the desired compound as a beige powder; m.p. 222 °C. ^{1}H NMR (C_6D_6): δ = 7.96 (s, 2 H), 7.49 (d, J = 8.7 Hz, 2 H), 7.42 (d, J = 8.7 Hz, 2 H), 1.79 (s, 12 H), 1.78 (s, 12 H) ppm. ^{13}C NMR (C_6D_6): δ = 224.0, 136.3, 135.2, 134.8, 120.8, 114.4, 113.7, 59.1, 59.0, 32.9 ppm. HRMS: [M + H]$^+$ calcd. for $C_{30}H_{43}N_4$: 459.3488; found 459.3486.

1,1′,3,3′-Tetra(*tert*-amyl)-5,5′-bibenzimidazolylidene (2b): In a manner analogous to the procedure used to prepare **2a**, **5b** (20.5 mg, 0.030 mmol) and NaHMDS (11.1 mg, 0.0605 mmol) afforded 14.9 mg (98% yield) of the desired compound as a yellow solid; m.p. 219 °C. ^{1}H NMR (C_6D_6): δ = 7.97 (s, 2 H), 7.50 (d, J = 8.2 Hz, 2 H), 7.41 (dd, J = 8.5, 1.7 Hz, 2 H), 2.09 (q, J = 7.5 Hz, 4 H), 2.04 (q, J = 7.5 Hz, 4 H), 1.82 (s, 12 H), 1.81 (s, 12 H), 0.75 (t, J = 7.5 Hz, 6 H), 0.74 (t, J = 7.5 Hz, 6 H) ppm. ^{13}C NMR (C_6D_6): δ = 228.1, 136.7, 135.4, 135.1, 120.7, 113.8, 113.1, 60.3, 60.2, 33.8, 33.7, 29.0, 28.9, 8.5 ppm. HRMS: [M + H]$^+$ calcd. for $C_{34}H_{51}N_4$: 515.4114; found 515.4103.

1,1′,3,3′-Tetra(1-adamantyl)-5,5′-bibenzimidazolylidene (2c): In a manner analogous to the procedure used to prepare **2a**, **5c** (30.0 mg, 0.032 mmol), NaHMDS (11.9 mg, 0.0649 mmol) and toluene (1 mL) afforded 23.2 mg (86% yield) of the desired compound as a white solid; m.p. 344 °C. ^{1}H NMR ($C_6D_5CD_3$): δ = 8.17 (d, J = 1.5 Hz, 2 H), 7.73 (d, J = 8.4 Hz, 2 H), 7.53 (dd, J = 8.4, 1.6 Hz, 2 H), 2.65 (br., 12 H), 2.60 (br., 12 H), 2.14 (br., 12 H), 1.76–1.67 (m, 24 H) ppm. ^{13}C NMR ($C_6D_5CD_3$): δ = 225.9, 136.5, 134.9, 134.7, 119.8, 114.4, 113.7, 58.4, 58.3, 43.6, 43.5, 37.1, 37.0, 30.6, 30.5 ppm. HRMS: [M + H]$^+$ calcd. for $C_{54}H_{67}N_4$: 771.5367; found 771.5366.

[{Rh(COD)Cl}$_2$(2a)] (6a): A 30-mL vial was charged with **5a** (107 mg, 0.168 mmol), NaHMDS (62.9 mg, 0.343 mmol) and a Teflon®-coated stirbar. THF (10 mL) was then added and the slurry was stirred at ambient temperature for 20 min. The resulting cloudy light brown solution was filtered through a 0.4 μm PTFE filter to give a solution of **2a**. [Rh(COD)Cl]$_2$ (82.7 mg, 0.168 mmol) was then added to the solution of freshly generated **2a** and the mixture was stirred at ambient temperature for 12 h. THF was then removed and the resulting yellow solid was triturated with diethyl ether (3 × 20 mL) and dried under vacuum to afford 127 mg (80% yield) of the desired product as a light yellow powder. ^{1}H NMR ($CDCl_3$): δ = 7.79 (d, J = 1.3 Hz, 2 H), 7.75 (d, J = 8.7 Hz, 2 H), 7.34 (dd, J = 1.3, 8.7 Hz, 2 H), 5.01 (br., 4 H), 2.99 (br., 4 H), approx. 2.41 (m, 8 H), 2.40 (d, 36 H), 1.76 (m, 8 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 196.1 (d, J = 48.6 Hz), 136.1, 134.9, 134.4, 120.7, 114.8, 113.7, 93.4, 67.6, 67.4, 60.5, 32.3, 32.2, 28.6 ppm. HRMS: [M – Cl]$^+$ calcd. for $C_{46}H_{66}ClN_4Rh_2$: 915.3090; found 915.3081. $E_{1/2}$ (Rh$^{I/II}$) = +0.59 V (quasi-reversible).

[{Rh(COD)Cl}$_2$(2b)] (6b): A 5 mL vial was charged with **5b** (22 mg, 0.043 mmol), [Rh(COD)Cl]$_2$ (21.1 mg, 0.0428 mmol), THF (2 mL), and a Teflon®-coated stirbar and then stirred at ambient temperature for 12 h. After removal of the solvent, the resulting yellow solid was triturated with diethyl ether (3 × 10 mL) and then dried under vacuum to give 32.7 mg (76% yield) of the desired product as a light yellow powder. ^{1}H NMR ($CDCl_3$): δ = 7.82 (s, 2 H), 7.77 (d, J = 8.5 Hz, 2 H), 7.32 (d, J = 8.5 Hz, 2 H), 5.02 (br., 4 H), 3.10 (br., 12 H), 2.96 (br., 4 H), 2.71 (m, 4 H), 2.43 (m, 8 H), 2.19 (s, 6 H), 2.15 (s, 6 H), 1.77 (m, 12 H), 0.59 (t, J = 6.8 Hz, 12 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 197.8 (d, J = 49.4 Hz), 136.1, 134.9, 134.3, 120.8, 114.4, 113.2, 93.2, 67.5, 63.7, 34.6, 32.2, 31.8, 29.1, 29.0, 28.6, 8.5 ppm. HRMS: [M – 2Cl]$^{2+}$ calcd. for $C_{46}H_{66}N_4Rh_2$: 468.2010; found 468.2006. $E_{1/2}$ (Rh$^{I/II}$) = +0.59 V (quasi-reversible).

[{Rh(COD)Cl}$_2$(2c)] (6c): A 30-mL vial was charged with **5c** (100 mg, 0.106 mmol), NaHMDS (40 mg, 0.22 mmol) and a Teflon®-coated stirbar. Toluene (25 mL) was then added and the resulting mixture was stirred at ambient temperature for 45 min. The resulting cloudy, light brown mixture was then filtered through a 0.4 μm PTFE filter to afford a solution of **2c**. [Rh(COD)Cl]$_2$ (98 mg, 0.21 mmol) was added to the solution of freshly generated **2c** and the resulting mixture was stirred at ambient temperature for 12 h. Toluene was then removed and the resulting brown solid was triturated with diethyl ether (3 × 20 mL). Drying the residual solids under vacuum afforded 120 mg (85% yield) of the desired product

as a light yellow powder. ^{1}H NMR ($CDCl_3$): δ = 7.81 (s, 2 H), 7.77 (d, J = 8.5 Hz, 2 H), 7.32 (d, J = 8.5 Hz, 2 H), 4.99 (br., 4 H), 3.50 (m, 12 H), 3.02 (m, 16 H), 2.42 (br., 24 H), 1.90 (m, 35 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 195.8 (d, J = 49.6 Hz), 135.7, 134.6, 133.6, 120.0, 115.6, 114.2, 92.4, 67.5, 62.4, 62.3, 43.0, 36.5, 36.4, 32.4, 32.3, 30.4, 28.8, 28.7 ppm. HRMS: $[M - 2Cl]^{2+}$ calcd. for $C_{70}H_{90}N_4Rh_2$: 596.2628; found 596.2632. $E_{1/2}$ ($Rh^{I/II}$) = +0.54 V (quasi-reversible).

[1,1′,3,3′-Tetraethyl-5,5′-bibenzimidazolium](BF$_4$)$_2$: A 30-mL vial was charged with [1,1′,3,3′-tetraethyl-5,5′-bibenzimidazolium](Br)$_2$[14] (202 mg, 0.398 mmol), dry CH_3CN (5 mL), triethyloxonium tetrafluoroborate (182 mg, 0.956 mmol) and a stir bar.[33] The reaction mixture was stirred at ambient temperature for 12 h. Excess triethyloxonium tetrafluoroborate was quenched by adding ethanol (2 mL) followed by stirring for an additional 2 h. The resulting solution was poured into excess ether and white solids (186.1 mg, 85%) were collected by vacuum filtration. ^{1}H NMR ([D$_6$]DMSO): δ = 9.82 (s, 2 H), 8.52 (s, 2 H), 8.23 (d, J = 8.7 Hz, 2 H), 8.18 (d, J = 8.7 Hz, 2 H), 4.57 (m, 8 H), 1.58 (m, 12 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 142.5, 137.6, 131.8, 130.8, 126.2, 114.3, 112.2, 42.2, 42.1, 14.3 ppm. ^{19}F NMR ([D$_6$]DMSO): δ = –148.2, –148.3 ppm. HRMS: $[M]^{2+}$ calcd. for $C_{22}H_{28}N_4$: 174.1155; found 174.1152. UV/Vis: λ_{max} = 297 nm, $\varepsilon = 1.39 \times 10^4$ M^{-1} cm^{-1}. Fluorescence: λ_{em} = 347 nm, Φ = 0.83.

[{Rh(COD)Cl}$_2${1,1′,3,3′-tetraethyl-5,5′-bibenzimidazolylidene}] (7): A 30-mL vial was charged with [1,1′,3,3′-tetraethyl-5,5′-bibenzimidazolium](BF$_4$)$_2$ (110 mg, 0.211 mmol), KOtBu (49.7 mg, 0.443 mmol), [Rh(COD)Cl]$_2$ (104 mg, 0.211 mmol), THF (3 mL), and a Teflon®-coated stirbar. The resulting slurry was then stirred at ambient temperature for 12 h. This produced a yellow solution which was filtered through a 0.4 μm PTFE filter. The filtrate was concentrated to afford 178 mg (98% yield) of the desired product as pale yellow powder. ^{1}H NMR ($CDCl_3$): δ = 7.37 (m, 6 H), 5.14 (br., 4 H), 5.08 (m, 4 H), 4.84 (m, 4 H), 3.37 (br., 4 H), 2.45 (m, 8 H), 2.00 (m, 8 H), 1.64 (m, 12 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 196.7 (d, J = 50.7 Hz), 135.9, 135.1, 133.9, 122.2, 122.1, 110.1, 108.8, 108.7, 100.2, 68.7, 68.6, 43.7, 43.6, 32.9, 28.8, 15.1, 15.0 ppm. HRMS: $[M - Cl]^+$ calcd. for $C_{38}H_{50}ClN_4Rh_2$: 803.1832; found 803.1829. E_{pa} ($Rh^{I/II}$) = +0.95 V (irreversible).

[1,3-Bis(*tert*-butyl)benzimidazolium](BF$_4$): A 5-mL vial was charged with [1,3-bis(*tert*-butyl)benzimidazolium](Cl)[34] (41.8 mg, 0.157 mmol), dry CH_3CN (3 mL), triethyloxonium tetrafluoroborate (41.7 mg, 0.219 mmol) and a stir bar.[33] The reaction mixture was stirred at ambient temperature for 12 h. Excess triethyloxonium tetrafluoroborate was quenched by adding ethanol (2 mL) followed by stirring for an additional 2 h. The resulting solution was concentrated and washed with methanol (3 mL) to afford 47.6 mg (95% yield) of the desired compound as a white powder. ^{1}H NMR ([D$_6$]-DMSO): δ = 8.84 (s, 1 H), 8.31 (dd, J = 6.34, 3.17 Hz, 2 H), 7.64 (dd, J = 6.34, 3.17 Hz, 2 H), 1.81 (s, 18 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 138.7, 130.9, 125.8, 116.6, 60.9, 28.1 ppm. ^{19}F NMR ([D$_6$]-DMSO): δ = –148.2, –148.3 ppm. HRMS: $[M]^+$ calcd. for $C_{15}H_{23}N_2$: 231.1859; found 231.1856. UV/Vis: λ_{max} = 276 nm, $\varepsilon = 6.98 \times 10^3$ M^{-1} cm^{-1}. Fluorescence: λ_{em} = 351 nm, $\Phi = 1.1 \times 10^{-3}$.

[Rh{1,3-Bis(*tert*-butyl)benzimidazolylidene}(COD)Cl] (8a): A 5-mL vial was charged with [1,3-bis(*tert*-butyl)benzimidazolium](Cl)[34] (110 mg, 0.412 mmol), NaHMDS (83.1 mg, 0.453 mmol), [Rh(COD)Cl]$_2$ (102 mg, 0.206 mmol), THF (4 mL), and a Teflon®-coated stirbar. The resulting slurry was then stirred at ambient temperature for 12 h. This produced a yellow solution that was filtered through a 0.4 μm PTFE filter. After removal of solvent, the crude product was purified by flash chromatography (silica gel, 70% EtOAc/30% hexanes as eluent) and then dried to afford 96.2 mg (42% yield) of the desired product as pale yellow powder. ^{1}H NMR ($CDCl_3$): δ = 7.67 (dd, J = 6.26, 3.13 Hz 2 H), 7.13 (dd, J = 6.26, 3.13 Hz 2 H), 4.98 (br., 2 H), 2.97 (br., 2 H), 2.42 (m, 4 H), 2.36 (s, 18 H), 1.74 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 194.4 (d, J = 49.4 Hz), 135.4, 120.8, 114.7, 93.1, 93.0, 67.5, 67.3, 60.3, 32.2, 32.1, 28.6 ppm. HRMS: $[M - Cl]^+$ calcd. for $C_{23}H_{34}N_2Rh$: 441.1775; found 441.1772. $E_{1/2}$ ($Rh^{I/II}$) = +0.58 V (quasi-reversible).

[1,3-Diethylbenzimidazolium](Br): A 30-mL vial was charged with benzimidazole (416 mg, 3.52 mmol), $NaHCO_3$ (607 mg, 7.22 mmol), acetonitrile (5 mL), and a stir bar. The vial was then sealed and the resulting reaction mixture was stirred at 90 °C for 1 h. After cooling to ambient temperature, bromoethane (1.6 mL, 21 mmol) was added. The resulting mixture was stirred at 90 °C for 12 h. After cooling to ambient temperature, precipitated NaBr was removed by vacuum filtration and the filtrate was concentrated to afford 792.3 mg (>99% yield) of the desired product as a white powder. ^{1}H NMR ([D$_6$]DMSO): δ = 10.0 (s, 1 H), 8.09 (dd, J = 6.31, 3.08 Hz, 2 H), 7.66 (dd, J = 6.31, 3.08 Hz, 2 H), 4.54 (q, J = 7.34 Hz, 4 H), 1.53 (t, J = 7.34 Hz, 6 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 141.7, 130.9, 126.4, 113.6, 42.0, 14.2 ppm. HRMS: $[M]^+$ calcd. for $C_{11}H_{15}N_2$: 175.1227; found 175.1230.

[1,3-Diethylbenzimidazolium](BF$_4$): A 30-mL vial was charged with [1,3-diethylbenzimidazolium](Br) (291 mg, 1.29 mmol), dry CH_3CN (5 mL), triethyloxonium tetrafluoroborate (295 mg, 1.55 mmol) and a stir bar.[33] The reaction mixture was stirred at ambient temperature for 12 h. Excess triethyloxonium tetrafluoroborate was quenched by adding ethanol (2 mL) followed by stirring for an additional 2 h. The resulting solution was concentrated and washed with methanol (3 mL) to afford 187 mg (92% yield) of the desired product as a white powder. ^{1}H NMR ([D$_6$]DMSO): δ = 9.74 (s, 1 H), 8.08 (dd, J = 6.31, 3.08 Hz, 2 H), 7.69 (dd, J = 6.31, 3.08 Hz, 2 H), 4.50 (q, J = 7.34 Hz, 4 H), 1.53 (t, J = 7.34 Hz, 6 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 141.6, 131.0, 126.5, 113.6, 42.0, 14.2 ppm. ^{19}F NMR ([D$_6$]DMSO): δ = –148.3 ppm. HRMS: $[M]^+$ calcd. for $C_{11}H_{15}N_2$: 175.1232; found 175.1230. UV/Vis: λ_{max} = 277 nm, $\varepsilon = 6.28 \times 10^3$ M^{-1} cm^{-1}. Fluorescence: none detectable, possibly due to extremely low Φ, insufficient Stokes shift, or both.

[Rh(1,3-Diethylbenzimidazolylidene)(COD)Cl] (8b): A 30-mL vial was charged with [1,3-diethylbenzimidazolium](BF$_4$) (99.7 mg, 0.380 mmol), KOtBu (47.0 mg, 0.419 mmol), [Rh(COD)Cl]$_2$ (93.8 mg, 0.190 mmol), THF (3 mL), and a Teflon®-coated stirbar. The resulting slurry was then stirred at ambient temperature for 12 h. The resulting yellow solution was filtered through a 0.4 μm PTFE filter and concentrated to give 158.8 mg (99% yield) of the desired product as yellow powder. ^{1}H NMR ($CDCl_3$): δ = 7.29 (dd, J = 5.81, 3.08 Hz, 2 H), 7.18 (dd, J = 5.81, 3.08 Hz, 2 H), 5.11 (br., 2 H), 5.02 (m, 2 H), 4.77 (m, 2 H), 3.34 (br., 2 H), 2.43 (m, 4 H), 1.98 (m, 4 H), 1.60 (t, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 195.1 (d, J = 50.7 Hz), 134.4, 122.1, 109.8, 99.9, 99.8, 68.6, 68.5, 43.5, 32.8, 28.7, 14.9 ppm. HRMS: $[M - Cl]^+$ calcd. for $C_{19}H_{26}N_2Rh$: 385.1141; found 385.1146. E_{pa} ($Rh^{I/II}$) = +0.86 V (irreversible).

[{Rh(CO)$_2$Cl}$_2${1,1′,3,3′-tetraethyl-5,5′-bibenzimidazolylidene}] (9): A solution of **7** (20 mg, 0.024 mmol) and CH_2Cl_2 (2 mL) was stirred under CO (balloon) with slow purging until the solvent was evaporated. The resulting yellow solid was then washed with pentane (3 × 3 mL) at –78 °C under an atmosphere of CO. Removal of the residual pentane under vacuum afforded 16.9 mg (96% yield) of the desired product as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ = 7.67 (d, J = 1.54 Hz, 2 H), 7.64 (dd, J = 8.44, 1.54 Hz, 2 H), 7.58

(d, J = 8.44 Hz, 2 H), 4.73 (m, 8 H), 1.60 (t, J = 7.26 Hz, 6 H), 1.59 (t, J = 7.26 Hz, 6 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 186.2 (d, J = 53.7 Hz), 186.0 (d, J = 42.9 Hz), 183.0 (d, J = 73.8 Hz), 137.1, 135.0, 133.9, 123.9, 111.5, 110.0, 44.4, 44.3, 15.1, 15.0 ppm. IR (CaF_2, CD_2Cl_2): $\tilde{\nu}$ = 2084 (*trans* ν_{CO}), 2003 (*cis* ν_{CO}) cm^{-1}. HRMS: $[M - Cl]^+$ calcd. for $C_{26}H_{26}ClN_4O_4Rh_2$: 698.9753; found 698.9747. E_{pa} ($Rh^{I/II}$) = +1.16 V (irreversible).

[Rh(1,3-Diethylbenzimidazolylidene)(CO)$_2$Cl] (10): A solution of **8b** (30 mg, 0.071 mmol) and CH_2Cl_2 (3 mL) was stirred under slight pressure of CO (balloon) with slow purging until the solvent was evaporated. The resulting yellow solid was then washed with pentane (3 × 3 mL) at –78 °C under CO. Removal of the residual pentane under vacuum afforded 26.0 mg (>99% yield) of the desired product as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ = 7.49 (dd, J = 5.81, 3.08 Hz, 2 H), 7.37 (dd, J = 5.81, 3.08 Hz, 2 H), 4.67 (m, 4 H), 1.55 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 186.2 (d, J = 53.8 Hz), 184.5 (d, J = 42.3 Hz), 183.1 (d, J = 73.8 Hz), 134.3, 123.7, 111.1, 44.2, 14.9 ppm. HRMS: $[M - Cl]^+$ calcd. for $C_{13}H_{14}N_2O_2Rh$: 333.0109; found 333.0105. IR (CaF_2, CD_2Cl_2): $\tilde{\nu}$ = 2083 (*trans* ν_{CO}), 2002 (*cis* ν_{CO}) cm^{-1}. E_{pa} ($Rh^{I/II}$) = +0.88 V (irreversible).

Supporting Information (see also the footnote on the first page of this article): NMR spectra and cyclic voltammograms.

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[1] a) P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69–72; b) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–907; c) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759–771.

[2] For excellent reviews, see: a) W. A. Herrmann, K. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2163–2187; b) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91; c) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239–2246; d) M. F. Lappert, *J. Organomet. Chem.* **2005**, *690*, 5467–5473; e) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.

[3] a) A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363; b) A. J. Arduengo III, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.* **1997**, *119*, 12742–12749; c) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913–921.

[4] a) F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931–1935; b) F. E. Hahn, M. Foth, *J. Organomet. Chem.* **1999**, *585*, 241–245; c) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem. Int. Ed.* **2000**, *39*, 541–544; d) F. E. Hahn, V. Langenhahn, N. Meier, T. Lügger, W. P. Fehlhammer, *Chem. Eur. J.* **2003**, *9*, 704–712; e) F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. Le Van, *Angew. Chem. Int. Ed.* **2005**, *44*, 3759–3763; f) F. E. Hahn, *Angew. Chem. Int. Ed.* **2006**, *45*, 1348–1352; g) O. Kühl, S. Saravanakumar, F. Ullah, M. K. Kindermann, P. G. Jones, M. Köckerling, J. Heinicke, *Polyhedron* **2008**, *27*, 2825–2832.

[5] For selected examples, see: a) D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1021–1023; b) R. W. Alder, P. R. Allen, M. Murray, A. G. Orpen, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1121–1123; c) A. J. Arduengo III, J. R. Goerlich, W. J. Marshall, *Liebigs Ann. Recl.* **1997**, 365–374; d) R. Weiss, S. Reichel, M. Handke, F. Hampel, *Angew. Chem. Int. Ed.* **1998**, *37*, 344–347; e) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **2000**, 3094–3099; f) G. Altenhoff, R. Goddard, C. Lehmann, F. Gloris, *J. Am. Chem. Soc.* **2004**, *126*, 15195–15201; g) C. Burstein, C. W. Lehmann, F. Glorius, *Tetrahedron* **2005**, *61*, 6207–6217; h) C. Präsang, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2005**, *127*, 10182–10183; i) A. J. Arduengo III, D. Tapu, W. J. Marshall, *J. Am. Chem. Soc.* **2005**, *127*, 16400–16401; j) T. Sajoto, P. I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau, M. E. Thompson, R. J. Holmes, S. R. Forrest, *Inorg. Chem.* **2005**, *44*, 7992–8003; k) S. Saravanakumar, K. M. Kindermann, J. Heinicke, M. Köckerling, *Chem. Commun.* **2006**, 640–642; l) S. Saravankumar, A. I. Oprea, M. K. Kindermann, P. G. Jones, J. Heinicke, *Chem. Eur. J.* **2006**, *12*, 3143–3154; m) D. M. Khramov, E. L. Rosen, V. M. Lynch, C. W. Bielawski, *Angew. Chem. Int. Ed.* **2008**, *47*, 2267–2270; n) Y. Ma, S. Wei, J. Lan, J. Wang, R. Xie, J. You, *J. Org. Chem.* **2008**, *73*, 8256–8264; o) D. Tapu, C. Owens, D. VanDerveer, K. Gwaltney, *Organometallics* **2009**, *28*, 270–276.

[6] N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem.* **2005**, *10*, 1815–1828; N. M. Scott, H. Clavier, P. Mahjoor, E. D. Stevens, S. P. Nolan, *Organometallics* **2008**, *27*, 3181–3186.

[7] For selected examples of bimetallic complexes formed between transition metals and (non-rigid) bis(NHC)s connected through saturated linkers, see: a) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 772–780; b) R. S. Simons, P. Custer, C. A. Tessier, W. J. Youngs, *Organometallics* **2003**, *22*, 1979–1982; c) F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, *Organometallics* **2005**, *24*, 6458–6463; d) T. Chen, X.-G. Liu, M. Shi, *Tetrahedron* **2007**, *63*, 4874–4880.

[8] D. M. Khramov, A. J. Boydston, C. W. Bielawski, *Angew. Chem. Int. Ed.* **2006**, *45*, 6186–6189.

[9] For examples of other classes of linearly opposed bis(NHC)s ligated to transition metals, see: a) O. Guerret, S. Solé, H. Gornitzka, M. Teichert, G. Trinquier, G. Bertrand, *J. Am. Chem. Soc.* **1997**, *119*, 6668–6669; b) W. Li, Ph. D. Thesis, University of Alabama, Tuscaloosa (USA), **2004**; c) E. Mas-Marzá, J. A. Mata, E. Peris, *Angew. Chem. Int. Ed.* **2007**, *46*, 3729–3731; d) A. Zanardi, R. Coberán, J. A. Mata, E. Peris, *Organometallics* **2008**, *27*, 3570–3576.

[10] B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1383–1386.

[11] A. J. Boydston, C. W. Bielawski, *Dalton Trans.* **2006**, 4073–4077.

[12] A. J. Boydston, K. A. Williams, C. W. Bielawski, *J. Am. Chem. Soc.* **2005**, *127*, 12496–12497.

[13] F. E. Hahn, C. Radloff, T. Pape, A. Hepp, *Organometallics* **2008**, *27*, 6408–6410.

[14] J. W. Kamplain, C. W. Bielawski, *Chem. Commun.* **2006**, 1727–1729.

[15] D. M. Khramov, A. J. Boydston, C. W. Bielawski, *Org. Lett.* **2006**, *8*, 1831–1834.

[16] Albrecht and co-workers recently reported weak to moderate coupling in bimetallic Fe and Ru derivatives of **1**, see: L. Mercs, A. Neels, M. Albrecht, *Dalton Trans.* **2008**, 5570–5576.

[17] I. Kania-Korwel, S. Parkin, L. W. Robertson, H. J. Lehmler, *Chemosphere* **2004**, *56*, 735–744.

[18] M. Hmadeh, H. Traboulsi, M. Elhabiri, P. Braunstein, A.-M. Albrecht-Gary, O. Siri, *Tetrahedron* **2008**, *64*, 6522–6529.

[19] a) J. P. Wolfe, S. Wagaw, J.-F. Marcox, S. L. Buchwald, *Acc. Chem. Res.* **1998**, *31*, 805–818; b) J. F. Hartwig, *Angew. Chem. Int. Ed.* **1998**, *37*, 2046–2067.

[20] CCDC-709265 (for **2a**), -709266 (for **4a**), and -709264 (for **5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] A. J. Boydston, D. M. Khramov, C. W. Bielawski, *Tetrahedron Lett.* **2006**, *47*, 5123–5125.

[22] a) A. J. Boydston, C. S. Pecinovsky, S. T. Chao, C. W. Bielawski, *J. Am. Chem. Soc.* **2007**, *129*, 14550–14551; b) A. J. Boydston, P. D. Vu, O. L. Dykhno, V. Chang, A. R. Wyatt II, A. S. Stockett, E. T. Ritschdorff, J. B. Shear, C. W. Bielawski, *J. Am. Chem. Soc.* **2008**, *130*, 3143–3156.
[23] This material displayed signals characteristic of tetraaminoethylenes at δ = 100–110 ppm in its ^{13}C NMR spectrum ([D_8]-THF) and at $\tilde{\nu}$ = 1600 cm^{-1} (br) in its IR spectrum (KBr); see: a) ref.[14]; b) Z. Shi, R. P. Thummel, *J. Org. Chem.* **1995**, *60*, 5935–5945; c) J. W. Kamplain, V. M. Lynch, C. W. Bielawski, *Org. Lett.* **2007**, *9*, 5401–5404. Further characterization of this material is underway.
[24] For examples of the evaluation of electronic coupling in other types of bimetallic Rh complexes, see: a) W. Kaim, R. Reinhardt, J. Fiedler, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2493–2495; b) W. Kaim, S. Berger, S. Greulich, R. Reinhardt, J. Fiedler, *J. Organomet. Chem.* **1999**, *582*, 153–159; c) S. Berger, T. Scheiring, J. Fiedler, W. Kaim, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2409–2417.
[25] P. Zanello, *Inorganic Electrochemistry Theory, Practice and Application*, The Royal Society of Chemistry: Cambridge, UK, **2003**, p. 178.
[26] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., John Wiley & Sons, Inc., Hoboken, **2001**.
[27] Unfortunately, complexes **6a**–**c** failed to undergo carbonylation, even under forcing conditions (e.g., high CO pressure and elevated temperatures). These results are consistent with the reversibility of their oxidations: steric shielding around the metal may prevent both ligand coordination and associative disproportionation.
[28] M. D. Sanderson, J. W. Kamplain, C. W. Bielawski, *J. Am. Chem. Soc.* **2006**, *128*, 16514–16515.
[29] A. Ajamian, J. L. Gleason, *Angew. Chem. Int. Ed.* **2004**, *43*, 3754–3760; J. M. Lee, Y. Na, H. Han, S. Chang, *Chem. Soc. Rev.* **2004**, *33*, 302–312; D. E. Fogg, E. N. dos Santos, *Coord. Chem. Rev.* **2004**, *248*, 2365–2379.
[30] N. Robertson, C. A. McGowan, *Chem. Soc. Rev.* **2003**, *32*, 96–103.
[31] J. H. Brannon, D. Magde, *J. Phys. Chem.* **1978**, *82*, 705–709.
[32] R. L. Cordiner, D. Corcoran, D. S. Yufit, A. E. Goeta, J. A. Howard, P. J. Low, *Dalton Trans.* **2003**, 3541–3549.
[33] a) S. Gischig, A. Togni, *Organometallics* **2004**, *23*, 2479–2487; b) P. D. Vu, A. J. Boydston, C. W. Bielawski, *Green Chem.* **2007**, *9*, 1158–1159.
[34] D. M. Khramov, C. W. Bielawski, *J. Org. Chem.* **2007**, *72*, 9407–9417.

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