Articles

New Constrained-Geometry C_2-Symmetric Di-N-heterocyclic Carbene Ligands and Their Mono- and Dinuclear Rhodium(I) Complexes: Design, Synthesis, and Structural Analysis

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A new C_2-symmetric di-N-heterocyclic carbene (di-NHC) ligand is synthesized, and its coordination behavior with Rh(I) salts is examined. A comprehensive list is presented describing the synthesis of all chiral di-NHC ligands reported to date, including pertinent catalytic and structural features. The historical perspective indicates few structural archetypes have been investigated and more structural alternatives are needed. Accordingly, the synthesis of the diimidazolium salts [DEA-MI]$(I)_2$ (**4**) and [DEA-MBI]$(I)_2$ (**8**) (where DEA = 9,10-dihydro-11,12-ethanoanthracene; MI = methylimidazolium, and MBI = methylbenzimidazolium) are presented. When **8** is treated with 2 equiv of $KN(SiMe_3)_2$, the strained enetetramine [DEA-MBY] (**9**) is obtained and is characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The highly strained mononuclear complex [(DEA-MBY)Rh(COD)]I (**10-COD**) is obtained when **8** is treated with $KN(SiMe_3)_2$ followed by half an equivalent of $[Rh(COD)Cl]_2$. A ^1H NMR spectrum of **10-COD** revealed an unusual downfield signal at 9.26 ppm, assigned to an aliphatic bridge proton, and provides a clue as to the relative orientation of the anthracene ligand to the metal center. Ultimately, a single-crystal X-ray diffraction experiment assisted in determining the absolute solid-state structure of **10-COD**. Although an X-ray crystal structure was not obtained for the imidazole derivative [DEA-MY][Rh(COD)]I (**11-COD**), a similar structure is implied by the occurrence of a downfield signal for the bridge proton at 8.24 ppm. In addition, the dinuclear complexes [μ-DEA-MY][Rh(NBD)I]$_2$ (**12-NBD**) and [μ-DEA-MBY][Rh(COD)Cl]$_2$ (**13-COD**) are obtained. A structural comparison of the ligand precursors **2** and **7**$\cdot(HCl)_2$ and the dinuclear species **12-NBD** and **13-COD** is presented.

Introduction

Transition metal complexes supported by ligands bearing N-heterocyclic carbene (NHC) groups are emerging as effective catalysts for enantioselective and nonstereospecific organic transformations.[1] This area of research is currently exceptionally popular and is the subject of multiple reviews.[2] The allure of this ligand design[3] and catalysis is straightforward; NHC-supported complexes have the potential to promote any reaction catalyzed by traditional tertiary phosphine- and phosphite-based catalysts.[4] While the promise of similar reactivity is inviting, the promise of increased efficiency, lower toxicity, air stability, and electronic and structural diversity[5] makes NHCs a logical and smart choice for exploration. The popular and highly successful motif of chelating diphosphorous-based ligands, particularly chiral versions, prompted our investigation into chiral di-NHC ligands. Unfortunately, bidentate chiral bis-NHC-supported metal catalysts have yet to perform to the standards set by their phosphine analogues. To be fair, few ligands have been synthesized thus far, and the available structural diversity for NHCs pales in comparison to established phosphorus

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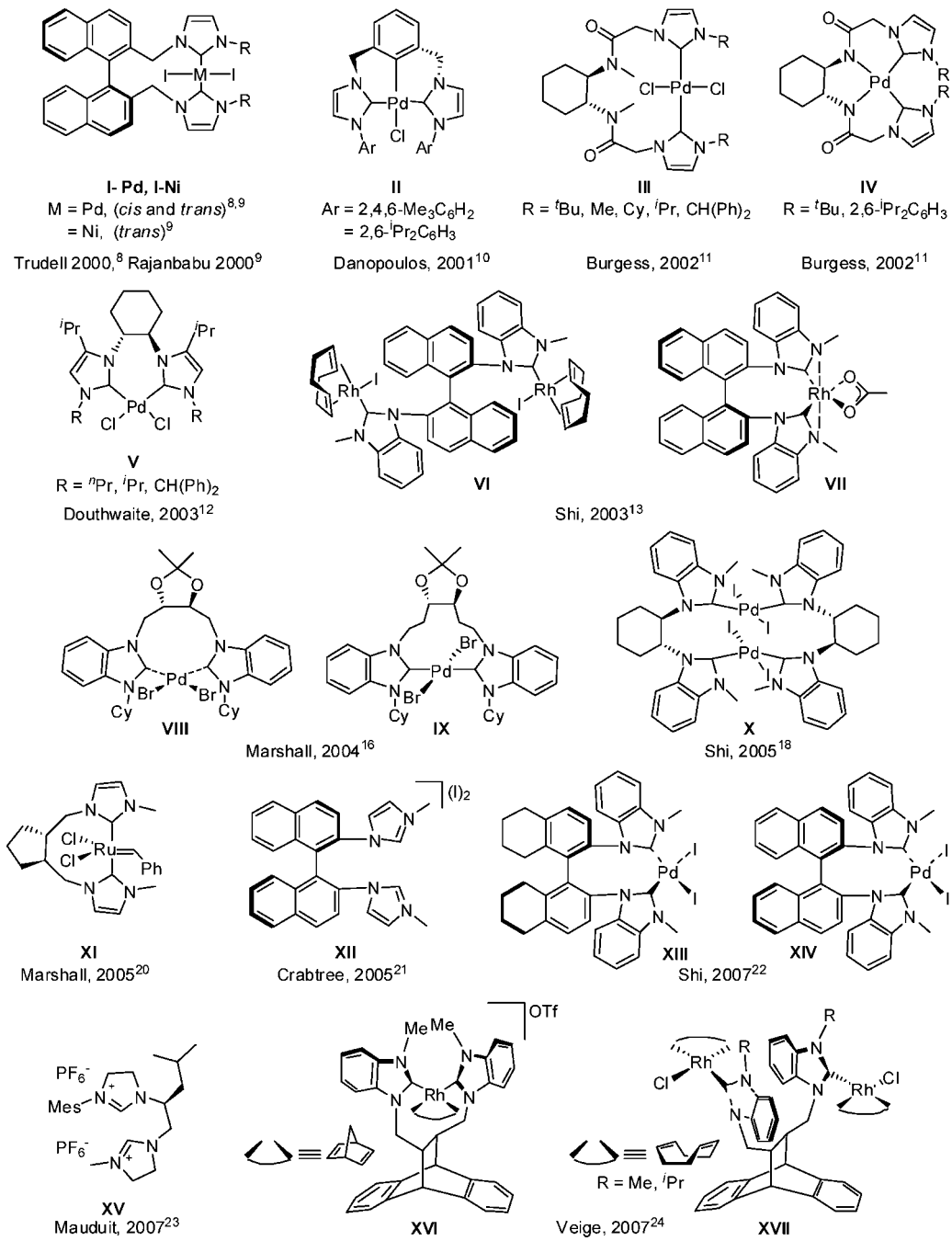
Chart 1



systems. Chart 1 contains a comprehensive list of known complexes that feature chiral ligands bearing di-NHC groups: the equivalent to ubiquitous chiral diphosphines. Not listed, but deserving of mention, are so-called chiral "hybrid" ligands containing one NHC and a pendant donating group for chelation, such as oxazoline[6] and chiral bis(acyclic diaminocarbene) complexes.[7]

The first reported use of a chiral di-NHC ligand in a catalytic reaction was **I-Pd**, where R = Mes (Mes = 2,4,6-trimethylphenyl). Trudell et al.[8] generated in situ a catalyst of unknown composition, which proved to be effective for the coupling of 4-chlorotoluene and phenylboronic acid. A racemic mixture of the ligand precursor was used and no enantioselective reactions were reported. Within months, Rajanbabu et al. reported Pd(II) and Ni(II) derivatives of the same axially chiral ligand, but R was changed to methyl.[9] Both *cis* and *trans* complexes were isolated and the first X-ray structural characterization of this class of complexes was achieved. Both *cis* and *trans* derivatives of **I-Pd** catalyze the Heck coupling of ethyl acrylate and halobenzenes.

Danopolous et al.[10] demonstrated chiral complexes such as **II** can be formed from achiral ligands, but separation of individual enantiomers was either not possible or not attempted.

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In 2002, a new architecture, incorporating 1,2-cyclohexyldiamine (**III** and **IV**) as the chiral linking group, was introduced by Burgess.[11] Complex **III** features a chelate ring containing 12 atoms, and although the amide functionality helps turn the pendant arms inward, only *trans* species are isolated. When the amide *N*-methyl is replaced with a proton, the ligand achieves a tetradentate coordination mode upon metalation featuring *cis*-NHC groups. Consequently, **IV** performs better as a catalyst in Heck reactions, although again no enantioselective reactions were reported. Douthwaite et al.[12] forced a *cis* coordination mode by building the NHC moiety directly adjacent to a 1,2-cyclohexyldiamine backbone and metalated with Pd to form **V**. The *N*-diphenylmethane derivative was crystallographically characterized and tested as a precatalyst for the asymmetric intramolecular cyclization of *N*-(2-bromophenyl)-*N*-methyl-2-(1-napthyl)propanamide. Although a 90% yield of cyclized product was achieved, only 18% enantiomeric excess was obtained.

To date, the best enantioselectivities for any reaction featuring a catalyst with a bidentate chiral di-NHC ancillary ligand were reported by Shi et al.[13] Binapthyl-bis-NHC complexes **VI** and **VII** are obtained as a mixture after metalation of the respective dibenzimidazolium salt with $[Rh(COD)Cl]_2$, but are easily separated via silica gel chromatography. Complex **VII** is an excellent precatalyst for the enantioselective hydrosilation of methyl ketones. A series of 13 different ketone substrates were reduced to form optically active secondary alcohols with overall yields that range between 82% and 96% and ee's as high as 98%. The iridium version of **VI** was also reported[14] but with no catalytic application. Later the H_8-BINAM derivative of **VII** was synthesized and found to be catalytically active in the enantioselective hydrosilylation of 3-oxo-3-arylproprionic acid and methyl or ethyl esters.[15]

A ligand design feature not to be overlooked is the accessibility of enantiopure compounds necessary for construction of the chiral linking unit. Marshal et al.[16] capitalized on naturally derived tartaric acid to form ligands containing *trans*-2,2-dimethyl-1,3-dioxalane and was able to form Pd(II) complexes **VIII** and **IX** featuring *cis* (eight-membered chelate) and *trans* (10-membered chelate) orientations, respectively. Machado and Dorta[17] have synthesized the analogous chiral diimidazole version but do not report metalation attempts or catalysis. Shi et al. revisited the 1,2-cyclohexyldiamine linking unit and were able to form dinuclear **X**, which was characterized by MALDI mass spectroscopy.[18] Dimer **X** proved to be an effective catalyst for a wide range of substrates in Suzuki−Miyaura and Heck cross-coupling reactions. Subsequently the authors also reported complex **X** will cocatalyze the homocoupling of terminal alkynes.[19]

Complex **XI** was synthesized by treating preformed Grubbs' catalyst with the corresponding di-NHC ligand precursor, but no reactivity was reported.[20] The synthesis of ligand **XII** was reported, but no complexation reactions were successful.[21] Instead, a hybrid NHC-alkoxide version was metalated with Rh(I) and Ir(I) and the enantioselective (ee's 12−60%) hydrosilylation of acetophenone was achieved. Shi et al. extended the use of di-NHC ligands derived from optically active 1,1-binapthyl-2,2′-diamine (BINAM) and the partially saturated form H_8-BINAM to oxidative kinetic resolution of secondary alcohols.[22] The Pd(II) complexes **XIII** and **XIV** were extensively screened using various bases, solvents, molecular sieves, and secondary alcohols. Excellent yields and ee's were obtained, including the demonstration of a preparative scale (1.0 g) reaction.

Manduit et al.[23] explored a series of NHC-containing chiral bidentate ligands. In one version the authors attached a second NHC unit to create the di-NHC ligand **XV**. This ligand was tested as a chiral ancillary ligand in the copper-catalyzed conjugate addition of diethylzinc to cyclohexeneone and 5-methylhex-3-en-2-one. The diimidazolium salt was used directly, and the free carbene generated in situ by deprotonation. The results were poor for the di-NHC ligand **XV** (5% ee for cyclohexeneone and 3% for 5-methylhex-3-en-2-one), but when the second imidazole is replaced with the aryl ether OMes, 80% ee is obtained with cyclohexenone.

Recently we reported the synthesis and X-ray characterization of mono- (**XVI**) and dinuclear (**XVII**) Rh(I) complexes supported by chiral di-NHC ligands based upon the *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-di(1-alkyl)benzimidazolidine-2-ylidene backbone.[24] We determined when benzimidazole-NHC groups are used, formation of the enetetramine is favorable, but as the *N*-alkyl group size is increased, a free di-NHC species is isolated. Nevertheless, metalation reactions are smooth whether the enetetramine or the free di-NHC is used.

The syntheses of six distinct structural architectures have been described since Trudell and Rajanbabu reported the first chiral di-NHC nearly eight years ago. The limited precedent makes it difficult to predict which ligand design features will work best for enantioselective induction. With this in mind, we created a rigid and highly strained di-NHC ligand and now report the synthesis and characterization of new C_2-symmetric constrained-geometry di-NHC ligands and their Rh(I) complexes. An X-ray structural comparison of imidazole and benzimidazole ligand precursors and their dinuclear Rh(I) complexes is presented. In addition, an extremely strained C_2-symmetric linked enetetramine and a C_1-symmetric mononuclear Rh(I) complex are synthesized and characterized by X-ray diffraction studies.

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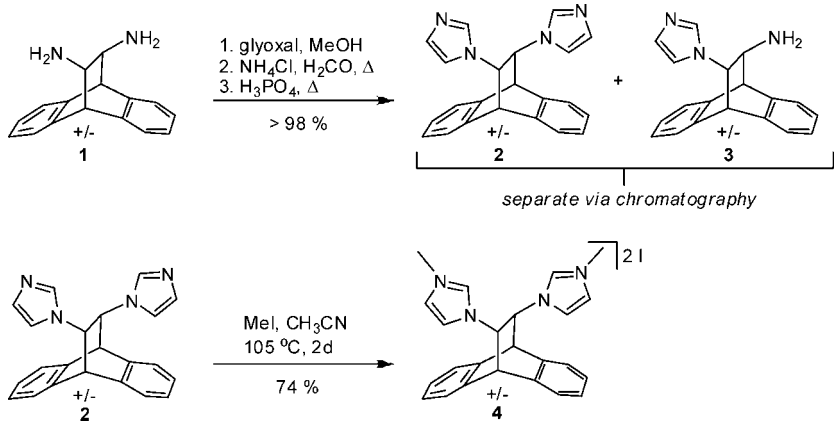
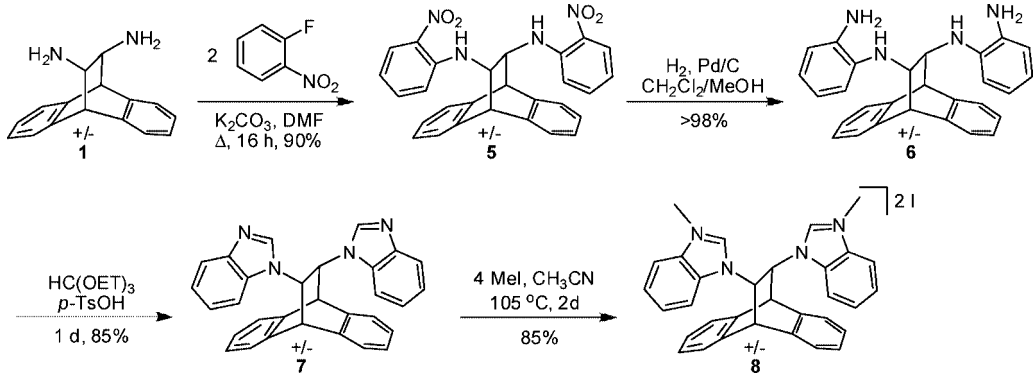
Scheme 1. Synthesis of [DEA-MI](I)$_2$ (4)



Scheme 2. Synthesis of [DEA-MBI](I)$_2$ (8)



Results and Discussion

Synthesis and Characterization of [DEA-MI](I)$_2$ (4) and [DEA-MBI](I)$_2$ (8). The diimidazolium salt [DEA-MI](I)$_2$ (**4**) is synthesized according to Scheme 1, an adaptation of a known procedure for generating monoimidazoles.[25] DEA-type ligands require assembly of the heterocycle from diamine **1**.[26] In a one-pot reaction, **1** is treated with glyoxal to form a pale yellow precipitate, which is not isolated. Solid NH_4Cl and aqueous formaldehyde are added, the mixture is refluxed for 4 h followed by addition of H_3PO_4, and the reflux is continued for an additional 12 h. After basic workup, a ^{1}H NMR spectrum indicated the presence of an equimolar mixture of the desired diimidazole **2** and imidazole-amine **3**. The products can be separated and purified by column chromatography. Douthwaite encountered a similar distribution of products when using 1,2-cyclohexyldiamine as the chiral scaffold. The mixed imidazole-amine **3** can be regarded as a potential hemilabile chiral NHC ligand whose chemistry we are currently investigating.

Diimidazolium salts are prepared by straightforward alkylation reactions. For simplicity, we chose to methylate and generate the methylimidazolium salt [DEA-MI](I)$_2$ (**4**). A ^{1}H NMR spectrum of **4** revealed a singlet at 3.82 ppm, assigned to the methyl protons. The imidazolium proton (N−CH═N) is located downfield at 8.93 ppm, and the olefinic protons of the heterocycle appear as a multiplet at 7.67 ppm and as a doublet of doublets at 6.60 ppm ($J_{HH} = J_{HH} = 1.5$ Hz). Noteworthy in the ^{13}C{^{1}H} NMR spectrum of **4** is the imidazolium carbon (N-*C*H═N), which appears downfield at 136.8 ppm.

To demonstrate versatility and to provide electronic variation, a dibenzimidazolium derivative was constructed according to Scheme 2 via a modified procedure for the conversion of a primary amine into the corresponding benzimidazole.[18] Diamine **1** is alkylated with 2 equiv of 2-fluoronitrobenzene in DMF. Upon completion, water is added slowly to precipitate bright yellow-orange dinitroamine **5**. This reaction was performed on a 15 g scale, though a larger scale is plausible. In an unoptimized reaction, **5** is reduced with H_2 (1 atm over Pd/C) to yield the tetraamine **6** after 7 days. The reaction end point is conveniently signaled by dissipation of the brilliant yellow-orange color of **5**. The dibenzimidazolium salt [DEA-MBI](I)$_2$ (**8**) is readily formed by treating **6** with triethyl orthoformate to form the neutral dibenzimidazole **7**, followed by alkylation with MeI in a sealed flask.[27] The identity of **8** was confirmed by NMR spectroscopy, HRMS, and elemental analysis. The ^{1}H NMR spectrum of **8** revealed two singlets at 3.96 and 8.85 ppm, which are assigned to the methyl and imidazolium (N-C*H*═N) protons, respectively. Consistent with Karplus's theory,[28] singlets manifest from adjacent protons on the bridge and bridgehead carbons (bridge = 5.16 ppm, bridgehead = 5.99 ppm) rather than doublets, due to a torsion angle of approximately 90°.

The diimidazole (**2**) and dibenzimidazole (**7**) are linchpin intermediates in the overall ligand synthetic route. At this stage

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(27) Enantiopure dibenzimidizole ligands were made using an analogous procedure to that used for the racemic ligand. The only notable difference is in the first step. After completion, water is added, but rather than forming a precipitate each enantiomer is isolated as a tacky solid. White solids are then obtained via flash chromatography (2:1 $CHCl_3$/pentane) and extensive drying under reduced pressure.

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Table 1. X-ray Crystallographic Structure Parameters and Refinement Data for 2, 7·(HCl)$_2$, 9, 10-COD, 12-NBD, and 13-COD

	2	**7·(HCl)$_2$**	**9**	**10-COD**	**12-NBD**	**13-COD**
empirical formula	$C_{22}H_{18}N_4$	$C_{33.50}H_{22.50}Cl_{12.50}N_4$	$C_{64}H_{52}N_8$	$C_{41}H_{40}Cl_2IN_4Rh$	$C_{42}H_{46}I_2N_4ORh_2$	$C_{50}H_{54}Cl_6N_4Rh_2$
fw	338.40	927.20	933.14	889.48	1082.45	1129.49
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
cryst dimens (mm)	0.26 × 0.14 × 0.09	0.23 × 0.15 × 0.08	0.19 × 0.19 × 0.08	0.16 × 0.08 × 0.02	0.09 × 0.07 × 0.05	0.20 × 0.18 × 0.17
a (Å)	9.4300(11)	39.343(5)	10.5224(7)	10.7075(11)	12.8891(12)	12.4529(12)
b (Å)	9.3303(11)	11.5742(16)	38.633(3)	30.420(3)	14.6531(14)	22.822(2)
c (Å)	9.6272(12)	20.189(3)	11.9173(7)	12.1504(12)	22.462(2)	17.3074(16)
β (deg)	90.282(2)	111.910(3)	102.497(1)	112.696(2)	104.806(2)	101.420(2)
volume (Å^3)	847.04(18)	8529(2)	4729.7(5)	3651.2(6)	4101.5(7)	4821.3(8)
Z (Å)	2	8	4	4	4	4
absorp coeff (mm^{-1})	0.081	0.840	0.078	1.495	2.347	1.057
F(000)	356	3736	1968	1784	2120	2296
D_{calcd} (g/cm^3)	1.327	1.444	1.310	1.618	1.753	1.556
(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
range (deg)	2.12 to 27.50	1.85 to 23.00	1.83 to 27.50	1.34 to 27.50	1.63 to 27.50	1.50 to 27.50
completeness to θ_{max}	99.9%	98.5%	99.0%	99.1	85%	99.9%
index ranges	$-11 \le h \le 12$, $-10 \le k \le 12$, $-12 \le l \le 12$	$-43 \le h \le 36$, $-12 \le k \le 12$, $-12 \le l \le 22$	$-13 \le h \le 12$, $-50 \le k \le 48$, $-14 \le l \le 15$	$-9 \le h \le 13$, $-36 \le k \le 39$, $-15 \le l \le 15$	$-15 \le h \le 14$, $-15 \le k \le 19$, $-27 \le l \le 20$	$-13 \le h \le 16$, $-27 \le k \le 29$, $-22 \le l \le 20$
no. of reflns collected	5723	14 312	32 190	23 756	15 923	32 115
no. of indep reflns [R_{int}]	3274 [0.0323]	5862 [0.0592]	10 772 [0.0356]	8317 [0.1039]	8001 [0.0353]	11 074 [0.0691]
max., min. transmn	0.9926, 0.9793	0.9381, 0.8402	0.9930, 0.9899	0.9705, 0.8432	0.8957, 0.8365	0.8638, 0.7990
no. of data/restraints/params	3274/1/307	5862/0/336	10 772/0/651	8317/0/442	8001/0/460	11 074/0/569
final R_1 indices [$I > 2\sigma(I)$]	R1 = 0.0330, wR2 = 0.0843	R1 = 0.0827, wR2 = 0.2146	R1 = 0.0416, wR2 = 0.0943	R1 = 0.0496, wR2 = 0.0705	R1 = 0.0380, wR2 = 0.0684	R1 = 0.0354, wR2 = 0.0936
R indices (all data)	R1 = 0.0350, wR2 = 0.0855	R1 = 0.1186, wR2 = 0.2319	R1 = 0.0695, wR2 = 0.1028	R1 = 0.1158, wR2 = 0.0824	R1 = 0.0622, wR2 = 0.0746	R1 = 0.0402, wR2 = 0.0969
largest diff peak/hole (e Å^{-3})	0.178/−0.210	0.446/−0.371	0.200/−0.212	0.834/−0.608	0.581/−0.477	0.837/−1.392
goodness of fit on F^2	1.037	0.953	1.000	0.853	0.977	1.025

in the synthetic sequence, a wide variety of new ligands and steric modifications can be accessed simply by alkylation. For this reason, X-ray structural analysis was performed on the diimidazole **2** and dibenzimidazole salt **7**·(HCl)$_2$. The HCl salt **7**·(HCl)$_2$ was obtained only to assist in crystallization and is not routinely isolated. The X-ray structures of **2** and **7**·(HCl)$_2$ are presented in Figure 1, and the X-ray structure parameters and refinement statistics can be found in Table 1. The asymmetric unit of **2** contained one molecule, whereas the asymmetric unit of **7**·(HCl)$_2$ contained two independent molecules. Each compound crystallized in the monoclinic space group, but only **7**·(HCl)$_2$ possesses solid-state C_2-symmetry in which the C_2 axis bisects the C15−C16 bond and passes through the center of the dihydroanthracene fragment. Diimidazolium **2** has solid-state C_1-symmetry but exhibits C_2-symmetry in solution. The lowered symmetry is discussed further below. Aside from the obvious differences between the metric parameters of the heterocycles, the dihydroanthracene bond lengths and angles for each compound are statistically similar. For example, the bond length between C15 and C16 is 1.5579(19) and 1.544(6) Å for **2** and **7**·(HCl)$_2$, respectively. The most significant differences between the two compounds involve the orientation of the heterocycles with respect to each other and to the dihydroanthracene unit. Figure 2 displays three major differences: (1) the heterocycle torsion angles N−C15−C16−N are 99.2° and 118.8° for **2** and **7**·(HCl)$_2$, respectively; (2) the imidazolium C−H bonds of **7**·(HCl)$_2$ are directed away from each other, thereby preserving the C_2 symmetry of the ligand, whereas on **2** they are positioned on the same side; and (3) the angles between the planes created by the heterocycles are 69.4° and 114.9° for **2** and **7**·(HCl)$_2$, respectively.

The positively charged benzimidazolium rings in **7**·(HCl)$_2$ are pointed away from each other, as expected, due to repulsion. Close inspection of **2** shows the rings instead point toward each

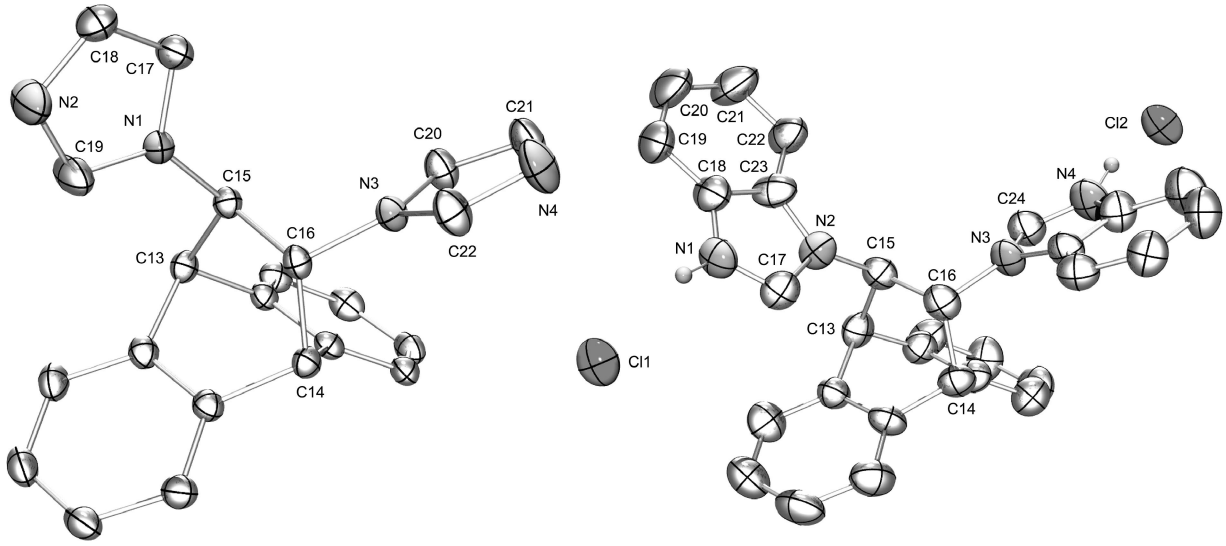


Figure 1. Molecular structure of **2** and **7**·(HCl)$_2$. Ellipsoids are drawn at the 50% probability level.

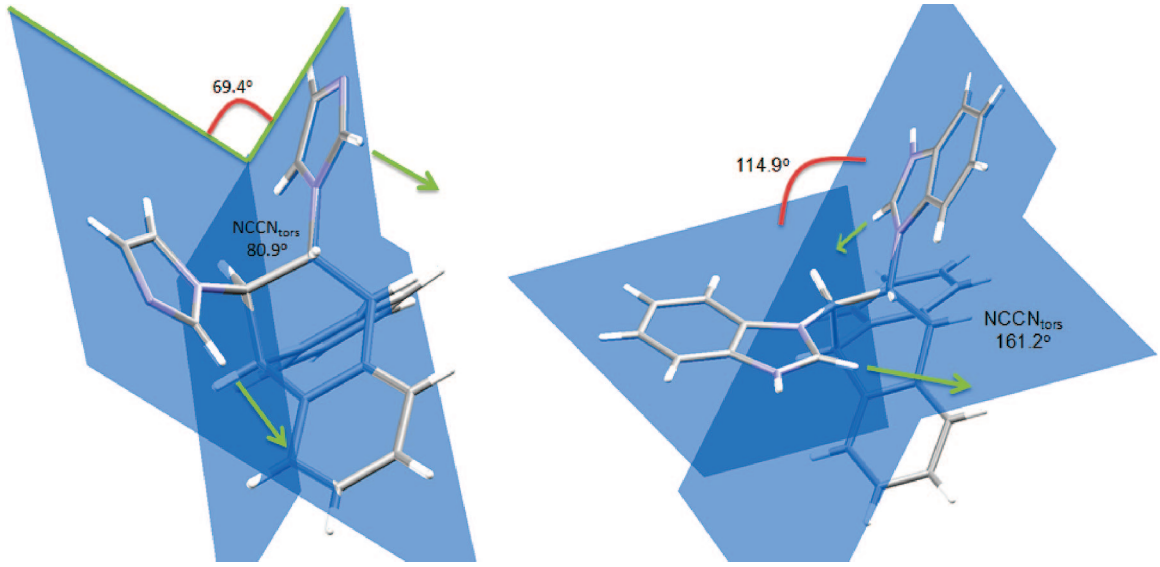
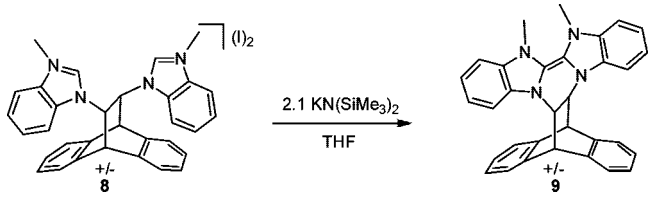


Figure 2. Molecular structures of **2** and **7**·$(HCl)_2$ depicting differences between heterocycle plane angle, orientation, and torsion angle.

Scheme 3. Synthesis of DEA-MbBY (9)

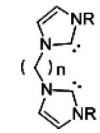


other due to beneficial N···H (2.49 Å) hydrogen bonding between adjacent compounds in the lattice. The torsion angle and planes are significantly different because the neutral and smaller imidazoles of **2** pack more efficiently and overcome detrimental strain energy associated with the lower torsion angle. In contrast, the charged rings of **7**·$(HCl)_2$ do not allow close-packing and therefore create a large torsion and wide splay angle between planes. Though these are solid-state structures and the solution-state analysis suggests free rotation for each heterocycle, the differences prelude subtle structural nuances between analogous metal-containing species to be presented below.

Synthesis and Characterization of DEA-MbBY (9). A tethered enetetramine is a convenient precursor of chelating bis-N-heterocyclic carbene complexes.[24,29] To exploit the tendency of benzimidazole-derived NHCs to preferentially form enetetramines, provided the *N*-alkyl group is not prohibitively large, **8** was treated with 2.1 equiv of $KN(SiMe_3)_2$ in THF (Scheme 3). Enetetramine **9** is isolated in 40% yield as a canary yellow solid. The absence of an imidazolium proton resonance at 8.85 ppm in the ^{1}H NMR spectrum of material obtained after 2 h indicated that either the free dicarbene or the enetetramine had formed. Conclusive evidence that only the enetetramine was synthesized is provided by $^{13}C\{^1H\}$ NMR spectroscopy. Free NHC carbons resonate within the range 205 to 245 ppm,[30] whereas enetetramine carbons are shifted well upfield.[29] The $^{13}C\{^1H\}$ NMR spectrum of **9** revealed a distinct resonance at 122.8 ppm, assigned to the newly formed double bond (N2-*C*═*C*-N2).

The structure of racemic **9** was confirmed by single-crystal X-ray crystallography and is presented in Figure 3. Two independent molecules possessing the same stereochemistry are found in the asymmetric unit and are related to the opposite enantiomer via an inversion center. Only one molecule is presented in Figure 3, but the metric parameters are similar for all like species. For example, the C═C double bond for each independent molecule is 1.3426(19) and 1.3416(19) Å, similar to that observed previously for a derivative featuring a two-carbon expanded ring.[24] All four nitrogen atoms are pyramidalized ($\angle C-N-C_{av} = 116.07(13)°$), indicating significant loss of aromaticity, and representative of an sp^3-hybridized nitrogen. In viewing the molecule from the top (Figure 3, right) it is clear the methyl groups are bent out of the plane created by the four nitrogen atoms. The benzimidazole groups are nearly coplanar, separated by only 15°, and the dihedral angles N3−C25═C17−N1 and N4−C25═C17−N2 are 13.71° and 7.82°, respectively. The six-membered "cyclohexene" connection is preferred compared to the free dicarbene, but metalation via carbon−carbon double-bond scission is expected to proceed smoothly, considering the obvious strain. In addition, rearomatization of the benzimidazole should make metalation thermodynamically favorable.

Table 2. Correlation of Ligand Structural Features and Resulting Complex Composition

n	R	counterion	complex	ligand
1 or 2	*n*-butyl	PF_6	bridging 2:1	
≥3	*n*-butyl	PF_6	chelate	
1	*tert*-butyl	PF_6	chelate	
≥2	*tert*-butyl	PF_6	chelate	
3	*i*-Pr	PF_6	mixture[a]	

[a] A mixture of bridging and chelate complexes are formed in a 7:4 ratio.

Recent studies by Crabtree et al.[31] relate linker length and *N*-alkyl size to the preference of di-NHC ligands to form chelate complexes over bridging 2:1 (metal:bis-NHC) complexes. Their findings are summarized in Table 2. These results suggest both the constrained di-NHC ligands (**4** and **8**), with a linker $n = 2$ and small *N*-methyl substituent, should favor a bridged 2:1

(29) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185–214.
(30) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91.
(31) (a) Leung, C. H.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2006**, *25*, 6099–6107. (b) Mata, J. A.; Chianese, A. R.; Miecznikowski, J. R.; Poyatos, M.; Peris, E.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 1253–1263.

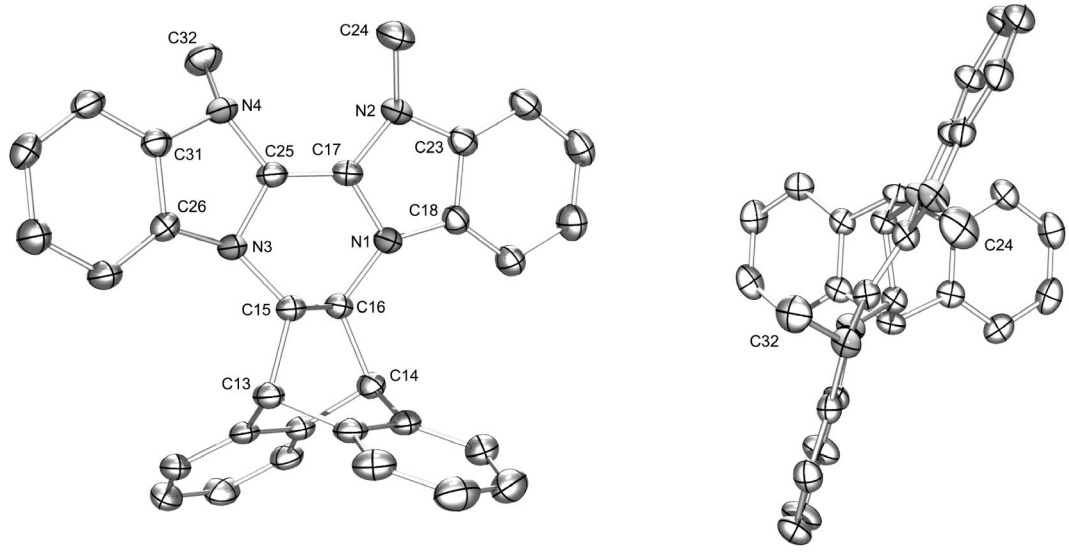


Figure 3. Molecular structure of **9** from a side-on (left) and top view (right) perspective. Ellipsoids are drawn at the 50% probability level.

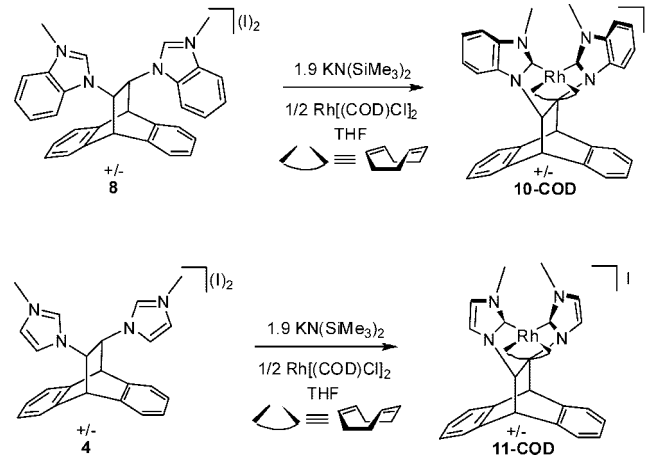
complex. Crabtree asserts that, because NHC ligands do not tend to reversibly dissociate from a metal center, the kinetic product (bridging 2:1 complex for $n = 1$ or 2) is formed unless transmetalation reagents are utilized.[32] However, the monometallic chelating species [DEA-MBY][Rh(COD)]I (**10-COD**) and [DEA-MY][Rh(COD)]I (**11-COD**) were synthesized in 53% and 87% isolated yield, respectively, without the use of a transmetalation reagent.

Synthesis and Characterization of [(DEA-MBY)Rh(COD)]I (10-COD) and [(DEA-MY)Rh(COD)]I (11-COD). Treatment of the dibenzimidazolium salt **8**, at −35 °C, with 1.9 equiv of $KN(TMS)_2$ followed by 0.5 equiv of $[Rh(COD)Cl]_2$ in THF, resulted in precipitation of crystalline yellow **10-COD** in 53% yield. The absolute assignment of each proton and carbon is accomplished by one- and two-dimensional NMR techniques. It is clear the mononuclear complex possesses C_1 symmetry in solution. The low symmetry is demonstrated by nonequivalent methyl resonances observed at 4.46 and 3.95 ppm. Before X-ray structural studies were complete, the geometry and orientation of the rhodium metal center relative to the anthracene backbone was predicted by a single ^{1}H NMR resonance.

A distinct doublet, attributed to the aliphatic proton in the bridge positions, is observed downfield at 9.26 ppm ($J_{HH} = 10$ Hz). Its identity was confirmed by an NOE spectrum. This proton typically resonates between 2 and 5 ppm, and its preternatural location led us to predict the rhodium center must be in close proximity, achievable only if the complex is oriented as depicted in Scheme 4. The formation of chelate species **10-COD**, rather than a bridging 2:1 complex, does not conflict with Crabtree's study. As stated previously, deprotonation of **8** results in formation of enetetramine **9**, thereby positioning the two heterocycle moieties in close proximity, akin to a transmetalation reagent. Although the mechanism of metalation is not yet understood, the proximity of the heterocycles surely plays an important role in the formation of chelating complex **10-COD**.

Confirmation of the identity and orientation of **10-COD** is obtained with a single crystal X-ray diffraction experiment. Figure 4 displays the solid-state structure of **10-COD**, and refinement data can be found in Table 1. The C_1-symmetric

Scheme 4. Synthesis of [(DEA-MBY)Rh(COD)]I (10-COD) and [(DEA-MY)Rh(COD)]I (11-COD)



complex is comprised of a slightly distorted square-planar Rh(I) ion chelated by COD and the di-NHC. M−carbene bond lengths of 2.033(4) and 2.051(5) Å for C23−Rh1 and C31−Rh, respectively, compare favorably to those in the dinuclear and mononuclear species of the DEAM derivatives previously reported.[24] The constrained ligand forces a small bite angle between the NHC groups and the Rh ion (∠C23−Rh1−C31 = 84.14(17)°). The most remarkable feature of the structure is that, upon chelation, the benzimidazole rings force the torsion angle N1−C15−C16−N3 to contract to a miniscule 69°. In accordance with the ^{1}H NMR resonance at 9.26 ppm for H16, a close Rh−C16 interaction is evident (d(Rh1−C16) ≈ 3.03 Å), although crystallographic data do not warrant the assignment of an agostic interaction. Instead, the rhodium center is fortuitously placed above H16 due to the natural twist of the molecule.

Synthesis of chelate **11-COD** from imidazolium salt **4** is accomplished using the same procedure as described for **10-COD**. Complex **11-COD** is obtained as a yellow powder in 87% yield. Although X-ray quality crystals were not obtained, the compound has been characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. The C_1-symmetry is evidenced clearly by nonequivalent methyl resonances at 4.03 and 3.64 ppm. The downfield aliphatic proton in the bridge position resonates at

(32) Crabtree, R. H. *J. Organomet. Chem.* **2006**, *691*, 3146–3150.

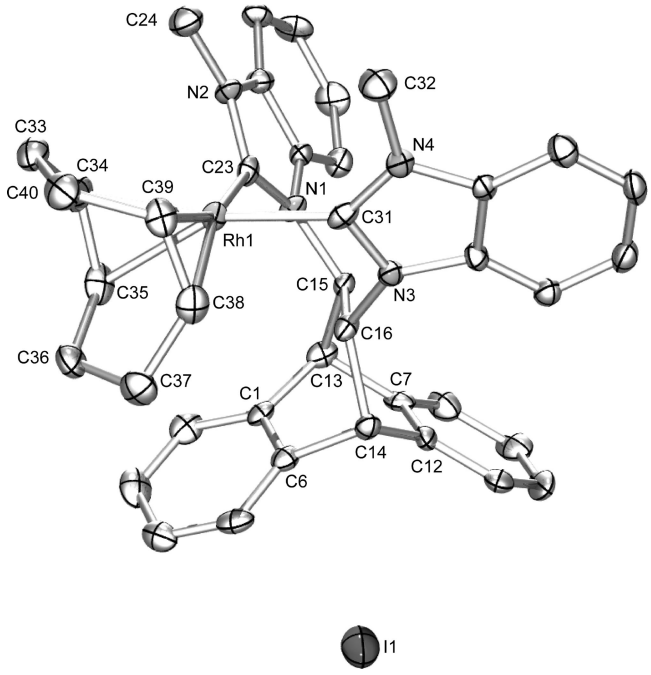


Figure 4. Molecular structure of [(DEA-MBY)Rh(COD)]I (**10-COD**) with ellipsoids drawn at the 50% probability level.

8.23 ppm, which is upfield relative to compound **10-COD**. Presumably the rhodium ion rests farther away from the bridge proton in **11-COD**, resulting in the upfield shift. This may be due to a more relaxed configuration created by the smaller imidazole heterocycles.

The imidazole moieties of ligand **4** make it more closely related, relative to benzimidazolium **8**, to the compounds studied by Crabtree (Table 2). Presumably, deprotonation of **4** forms a free di-NHC intermediate, unrestrained except by the rigid ethanoanthracene backbone. Although the rigid backbone may play a significant role in chelate formation, on the basis of Crabtree's assertions a significant amount of bridging 2:1 compound should be formed.

Synthesis and Characterization of [μ-DEA-MY][Rh(NBD)I]$_2$ (12-NBD) and [μ-DEA-MBY][Rh(COD)Cl]$_2$ (13-COD). The bimetallic complexes [μ-DEA-MY][Rh(NBD)I]$_2$ (**12-NBD**) and [μ-DEA-MY][Rh(COD)Cl]$_2$ (**13-COD**) are synthesized in THF by first treating **4** and **8** with KN(SiMe$_3$)$_2$ to generate the corresponding enetetramine and free di-NHC in situ, respectively, followed by addition of metal substrate. The complexes are obtained as mixtures with the corresponding mononuclear species, which complicated analysis. Attempts to separate these mixtures by column chromatography were not successful. The molecular structures of **12-NBD** and **13-COD** were confirmed by single-crystal X-ray crystallography and are presented in Figure 5. Each complex features a ligand that binds two separate distorted square-planar rhodium centers via a Rh−carbene bond. The coordination spheres are completed by a halide (Cl^-, **12-NBD**; I^-, **13-COD**) and a chelating diene. As expected, in **12-NBD** the average bond distance between the Rh and alkene carbons opposite the Rh-NHC (d(Rh−$C_{transNHC}$) = 2.2125(6) Å) is elongated by 0.116(6) Å compared to those opposite the I^- (d(Rh−C_{transI}) = 2.097(6) Å). Despite the differences in σ-donor strength of benzimidazolidynes versus imidazolidynes, a similar difference (0.109(6) Å) is observed for the Rh−alkene bond in complex **13-COD**. In fact, the average Rh−NHC bond lengths between **12-NBD** (d(Rh−NHC_{av} = 2.018(4) Å) and **13-COD** (d(Rh−NHC_{av} = 2.007(3) Å) differ only by 0.011(5) Å. Unfortunately, the variations in *trans* influences of Cl^- versus I^- and NBD versus COD preclude a meaningful comparison.

Figure 6 provides an additional perspective of complexes **12-NBD** and **13-COD** and highlights their similarities and differences. Unlike the comparison of **2** and **7**·(HCl)$_2$ in Figure 2, these two species are both neutral, resulting in similar angles between the planes of the heterocyclic rings (**12-NBD**; 88.7°; **13-COD**; 82.9°). Within **12-NBD**, the rhodium iodide bonds are divergent and preserve the ligand C_2-symmetry, whereas in **13-COD** the solid-state symmetry is broken by rotation of one Rh−Cl bond inward. The inward rotation results in a 3.33 Å separation between Cl1 and the centroid of the heterocycle. Although packing forces cannot be ruled out, a beneficial interaction between the chloride lone pairs and the π-orbitals of the heterocycle is plausible. These structural studies again emphasize the ability of the anthracene backbone to accommodate significant structural changes to the periphery of the molecule, such as the inward rotation of the Rh−Cl bond. The dihydroethanoanthracene scaffold was specifically chosen to provide a rigid configuration, at least more rigid than Douthwaite's cyclohexane derivatives.[12] The ability to expand and contract the bridge dihedral angle when needed is not necessarily detrimental.

Conclusions

This report establishes the synthesis of two new C_2-symmetric chelating di-N-heterocyclic carbene ligands based upon a *trans*-ethanoanthracene backbone, and their mono- and bimetallic Rh(I) complexes. These ligands add to a growing, but still limited, library of chiral di-NHC ligands. The major modification to the previously reported DEAM[24] ligand set is direct attachment of the NHC unit to the anthracene backbone by removal of a methylene group. This was designed to create a more constrained geometry evident in the X-ray crystal structure of **10-COD**. The NCCN dihedral angle along the bridge of the anthracene unit is contracted severely to 69°. In addition, the strain forces the rhodium ion to rest in close proximity to an aliphatic bridge proton, causing a severe downfield shift in the ^{1}H NMR spectrum (9.26 ppm for **10-COD** and 8.24 ppm for **11-COD**). Although the backbone anthracene unit is expected to instill increased rigidity over cyclohexyl versions,[12] examination of the NCCN dihedral angles shows a variation from 69° for **10-COD** to 118° for **7**·(HCl)$_2$. This suggests some flexibility may be available when coordination sphere contractions/expansions occur during catalysis.

Experimental Section

General Comments. Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glovebox techniques. Glassware was oven-dried before use. Pentane, toluene, diethyl ether (Et_2O), tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were dried using a GlassContours drying column. C_6D_6 (Cambridge Isotopes) was dried over sodium-benzophenone ketyl and distilled or vacuum transferred and stored over 4 Å molecular sieves. $CDCl_3$ (Cambridge Isotopes) was dried over calcium hydride, distilled or vacuum transferred, and stored over 4 Å molecular sieves. Bis-norbornadiene rhodium(I) tetrafluoroborate [Rh(NBD)$_2$][BF_4] and chloro(1,5-cyclooctadiene)rhodium(I) dimer [Rh(COD)Cl]$_2$ were purchased from Strem Chemicals and used without further purification. 1-Methylbenzimidazole was purchased from Sigma-Aldrich and used without further purification. KN(SiMe$_3$)$_2$ was purchased from Fisher Scientific and used without further purification. NMR spectra were

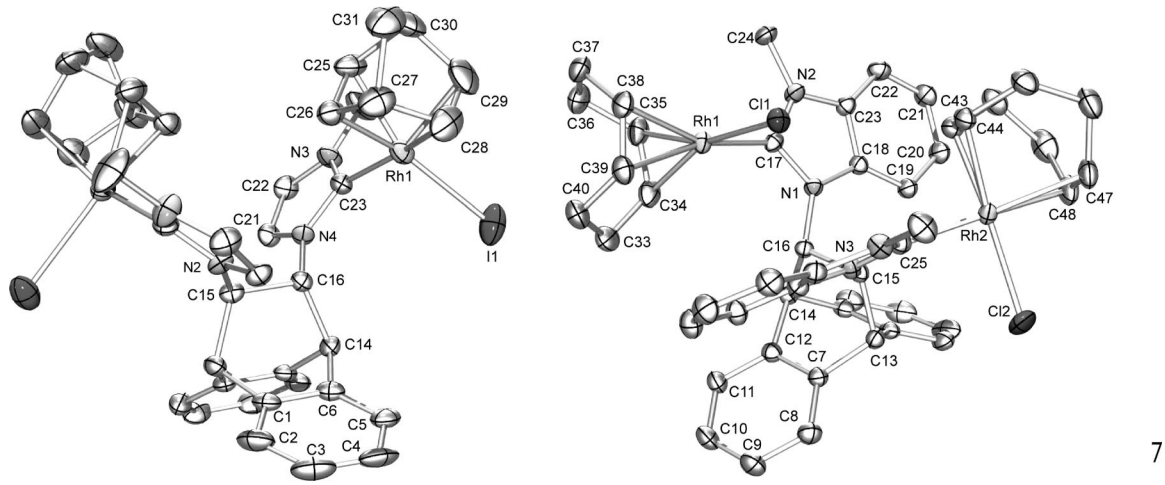


Figure 5. Molecular structure of **12-NBD** and **13-COD**. Ellipsoids are drawn at the 50% probability level.

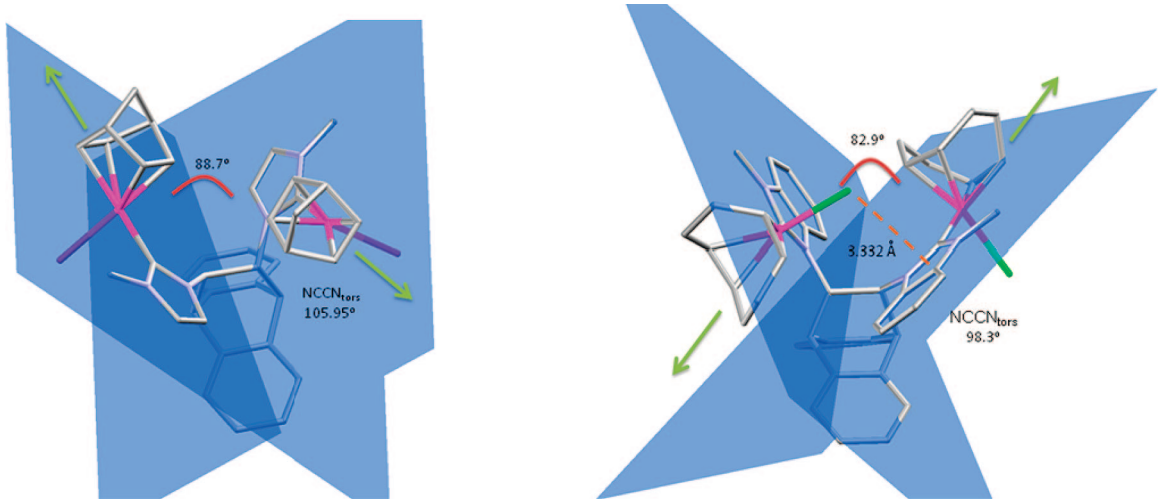
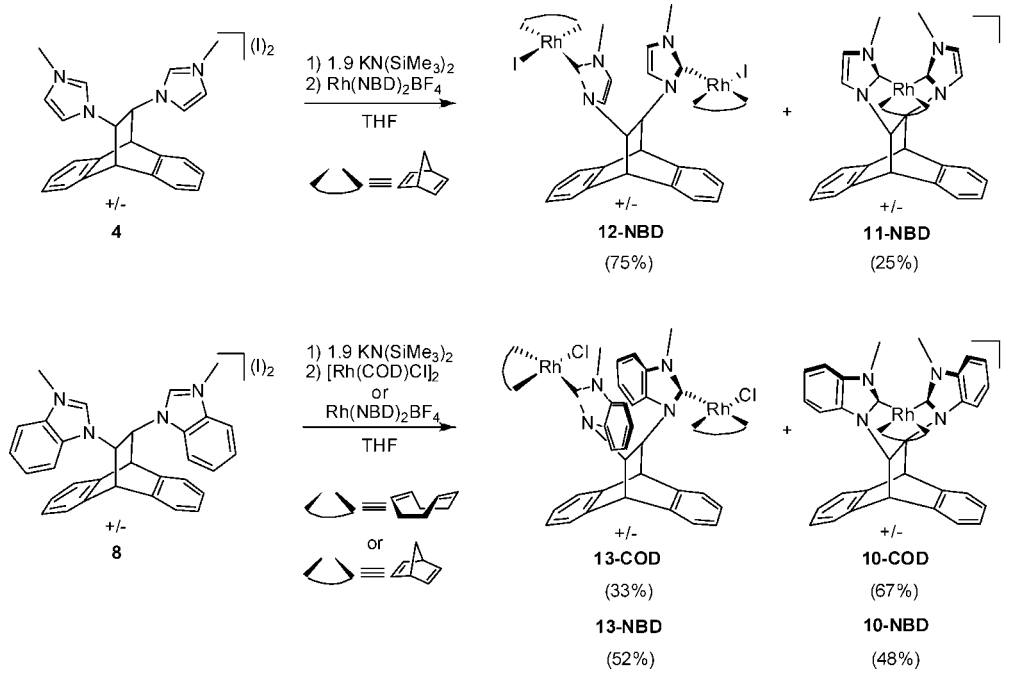


Figure 6. Molecular structures of **12-NBD** and **13-COD** depicting differences between imidazole plane angle, orientation, and torsion angle.

obtained on Varian INOVA 500 MHz, Varian Mercury broad band 300 MHz, or Varian Mercury 300 MHz spectrometers. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C{^{1}H} NMR spectra, the residual protio solvent peak was referenced as an internal reference. Mass spectrometry was performed at the in-house facility of the Department of Chemistry at the University of Florida. Elemental analyses were performed at either the in-house facility of the Department of Chemistry at the University of Florida or Complete Analysis Laboratory Inc., Parsippany, NJ.

Synthesis of 1,1′-(9,10-Dihydro-9,10-ethanoanthracene-11,12-diyl)di(1*H*-imidazole) (2) and 12-(1*H*-imidazol-1-yl)-9,10-dihydro-9,10-ethanoanthracene-11-amine (3). To a solution of diamine **1** (3.05 g, 12.9 mmol) in MeOH (20 mL) was added glyoxal (3.0 mL of 40% aqueous solution, 2 equiv, 25.8 mmol). The resulting solution immediately turned bright yellow and became warm, and a light yellow precipitate formed. The mixture was stirred for 16 h. Additional MeOH (20 mL) was added, followed by solid NH_4Cl (2.76 g, 4 equiv, 51.7 mmol) and formaldehyde (3.85 mL of 37% solution in water, 4 equiv, 51.7 mmol). The resulting mixture turned dark orange and was heated at reflux for 4 h. H_3PO_4 (3.54 mL of 85% solution in water, 4 equiv, 51.7 mL) was added slowly, and the resulting mixture was heated at reflux for 16 h. The mixture was cooled to room temperature and volatiles were removed. Dichloromethane was added and the mixture was basified to pH 14 with 10% NaOH solution. The organic extract was dried over $MgSO_4$, filtered, and concentrated to an orange solid (3.63 g) consisting of an approximately 1:1 ratio of **2**:**3**. Diimidazole **2** was separated from **3** by flash column chromatography on 300 g of silica gel, using 5% MeOH in $CHCl_3$ as eluent (R_f of **2** = 0.28 and R_f of **3** = 0.23 in 9:1 $CHCl_3$/MeOH) to afford **2** as a white solid (1.27 g, 30%) and **3** as a white solid (725 mg, 20%). **2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.49−7.46 (m, 2H, ArH), 7.35−7.24 (m, 6H, ArH), 7.09 (dd, 2H, J = 1.1 Hz, N−C*H*═NCH═CH), 6.92 (dd, 2H, J = 1.1 Hz, N-CH═NC*H*═CH), 6.18 (dd, 2H, J = 1.1 Hz, N-CH═NCH═C*H*) 4.50 (4H, overlapping singlets for bridge and bridgehead CH's). ^{13}C NMR (75.3 MHz, $CDCl_3$) δ (ppm): 140.4 (N-*C*H═N), 138.2 and 136.2 (*C*═*C*), 129.8 (*C* aromatic), 127.7 (*C* aromatic, overlapping signals), 126.6 (*C* aromatic), 124.3 (N-CH═NCH═*C*H), 117.1 (N-CH═N*C*H═CH), 64.7 (N-*C*H-CH-C═), 50.8 (N-CH-*C*H−C═). HRMS: (CIP-CI) calcd (found) for $C_{22}H_{19}N_4$ $(M + H)^+$ 339.1610 (339.1649). **3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.43−7.36 (m, 3H, ArH), 7.27−7.21 (m, 3H, ArH), 7.17−7.15 (m, 2H, ArH), 7.12 (dd, 1H, J = 1.2 Hz, N-C*H*═N), 6.88 (dd, 1H, J = 1.2 Hz, N-C*H*═NCH═CH), 6.14 (dd, 1H, J = 1.2 Hz N-CH═NC*H*═CH), 4.29 (d, 1H, J = 2.4 Hz, NH_2CHC*H*N), 4.20 (d, 1H, J = 2.4 Hz, NCHC*H* bridgehead), 3.90 (dd, 1H, J = 3.6, 2.4 Hz, NH_2C*H*CHN), 3.30 (dd, 1H, J = 3.7, 3.0 Hz, NH_2CHC*H* bridgehead), 1.48 (2H, NH_2). ^{13}C NMR (75.3 MHz, $CDCl_3$) δ (ppm): 141.7, 140.4, 138.7, and 138.1 (*C*═*C*), 136.4 (N-*C*H═N), 129.1 (C aromatic), 127.03 (C aromatic), 126.9 (C aromatic), 126.8 (C aromatic), 126.7 (C aromatic), 126.5 (C aromatic), 126.2 (C aromatic), 124.1 (C aromatic), 124.04

Scheme 5. Synthesis of [μ-DEA-MY][Rh(NBD)I]$_2$ (12-NBD) and [μ-DEA-MBY][Rh(COD)Cl]$_2$ (13-COD)



(C aromatic), 117.7 (C aromatic), 67.4 (NH_2CH *C*HN), 60.0 (NH_2*C*HCHN), 53.3 (NCH*C*H bridgehead), 51.6 (NH_2*C*HCH bridgehead). HRMS: (DIP-CI) calcd (found) for $C_{19}H_{18}N_3$ $(M + H)^+$ 288.1501 (288.1496).

Synthesis of 1,1′-(9,10-Dihydro-9,10-ethanoanthracene-11,12-diyl)di(3-methyl-1*H*-imidazol-3-ium) diiodide, [DEA-MI](I)$_2$ (4). Diimidazole **2** (940 mg, 2.78 mmol) was dissolved in anhydrous MeCN (15 mL) in a glass ampule fitted with a sealable Teflon stopcock. MeI (700 μL, 4 equiv, 11.1 mmol) was added, and the flask was evacuated then sealed under vacuum. The flask was shielded from light and was heated in a sand bath at 105 °C for 48 h. The mixture was cooled to room temperature, and the precipitate was filtered and washed with cold MeCN to yield **2** as a beige solid (1.24 g, 72%). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 8.93 (s, 2H, N-C*H*=N), 7.68 (dd, 2H, J = 1.7 Hz, ImH), 7.61 (d, 2H, J = 6.9 Hz, ArH), 7.41−7.35 (m, 4H, ArH), 7.30−7.25 (m, 2H, ArH), 6.60 (dd, 2H, J = 1.7 Hz, ImH), 5.48 (s, 2H, bridge CH), 5.05 (s, 2H, bridgehead CH), 3.82 (s, 6H, NCH_3). ^{13}C NMR (75.3 MHz, DMSO-d_6) δ (ppm): 139.1 and 137.3 (*C*=*C*), 136.7 (N-*C*H=N), 127.6 (C aromatic), 127.5 (C aromatic), 126.3 (C aromatic), 125.5 (C aromatic), 123.6 (N-CH=NCH=*C*H), 119.7 (N-CH=N*C*H=CH), 63.0 (N-*C*H-CH-C=), 48.3 (N-CH-*C*H−C=), 36.1 (N *C*H_3). HRMS: (FIA-ESI) calcd (found) for $C_{24}H_{24}IN_4$ $(M - I)^+$ 495.1040 (495.1040).

Synthesis of *N*,*N*′-Bis(2-nitrophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-diamine (5). To a solution of **1** (6.43 g, 27.2 mmol) in anhydrous DMF (50 mL) was added anhydrous K_2CO_3 (8.3 g, 2.2 equiv, 60 mmol) and 2-fluoronitrobenzene (6.0 mL, 2.1 equiv, 57 mmol). The resulting bright orange mixture was heated at 60 °C for 18 h. The mixture was cooled to ambient temperature, and water (100 mL) was added. The resulting bright orange precipitate (13.3 g, >98%) was isolated by filtration and was washed with water. Dinitro **5** was purified further by stirring in hot EtOH (10 mL/g) for 20 min. After cooling to 0 °C the orange solid was filtered and finally washed with cold EtOH. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.13 (dd, 2H, J = 8.6 Hz, 1.5 Hz, NO_2-C=C*H*), 7.82 (br d, 2H, J = 8.5 Hz, N*H*), 7.44−7.35 (m, 4H, ArH), 7.33−7.23 (m, 4H, ArH), 6.85 (dd, 2H, J = 8.7 Hz, 0.9 Hz, ArH), 6.64 (ddd, 2H, J = 8.5, 7.1, 1.1 Hz, ArH), 4.49 (d, 2H, J = 2.8 Hz, bridgehead CH), 3.83 (br m, 2H, bridge CH). ^{13}C NMR (75.3 MHz, $CDCl_3$) δ (ppm): 143.8 (NH-*C*=), 139.6 and 138.7 (*C*=*C*), 136.5 (NH-C=*C*H-), 132.7 (NO_2-*C*=), 127.6 (C aromatic), 127.5 (C aromatic), 127.2 (C aromatic), 126.2 (C aromatic), 124.9 (NO_2-C=*C*HCHCH), 116.5 (NO_2−C=CH*C*HCH), 114.8 (NO_2−C=CHCH*C*H), 61.4 (HN-*C*H-CH-C=), 49.3 (HN-CH-*C*H−C=). HRMS (MMI-TOF): calcd (found) for $C_{28}H_{22}N_4O_4Na$ $(M + Na)^+$ 501.1533 (501.1527).

Synthesis of *N*,*N*′-Bis(2-aminophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-diamine (6). To a solution of **5** (13.0 g, 27.2 mmol) in CH_2Cl_2 (100 mL) and MeOH (40 mL) was added Pd/C (10 wt %, 50% wet; 4.0 g). The resulting mixture was stirred under H_2 (1 atm balloon) for 7 days, with daily replenishing of the H_2 in the balloon and periodic additions of approximately 100 mg of fresh Pd/C. After 7 days the mixture was filtered through Celite to remove Pd/C and the filtrate was concentrated to yield **6** as a brown solid (11.3 g, 99%). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.47−7.44 (m, 2H, ArH), 7.22−7.10 (m, 6H, ArH), 6.69−6.46 (m, 8H, ArH), 4.50 (br s, 2H, N*H*), 4.45 (br s, 4H, N H_2), 4.12 (d, 2H, J = 7 Hz, bridgehead CH), 3.64 (d, 2H, J = 7 Hz, bridge CH). ^{13}C NMR (75.3 MHz, DMSO-d_6) δ (ppm): 142.4 and 139.9 (*C*=*C*), 135.5 (NH_2-*C*=), 134.5 (NH-*C*=), 126.3 (C aromatic), 126.0 (C aromatic), 125.9 (C aromatic), 123.8 (C aromatic), 117.6 (NH_2-C=*C*HCHCH), 117.3 (NH_2-C=CH *C*HCH), 114.5 (NH-C=*C*H-), 111.1 (NH_2-C=CHCH*C*H), 60.3 (HN-*C*H-CH-C=), 47.5 (HN-CH-*C*H-C=). HRMS (DIP-CI): calcd (found) for $C_{28}H_{27}N_4$ $(M + H)^+$ 419.2236 (419.2212).

Synthesis of 1,1′-(9,10-Dihydro-9,10-ethanoanthracene-11,12-diyl)di(1*H*-benzimidazole) (7). To a solution of **6** (1.18 g, 2.82 mmol) in anhydrous $HC(OEt)_3$ (30 mL) was added *para*-toluenesulfonic acid monohydrate (110 mg, 0.2 equiv, 0.56 mmol). The resulting mixture was stirred at room temperature for 48 h and then filtered. Hexanes was added to the filtrate, resulting in precipitation of a pale yellow solid. The solid was filtered and washed with hexanes. Dibenzimidazole **7** was obtained in 83% yield (1.02 g). Some $HC(OEt)_3$ is retained as an impurity but is removed during the synthesis of **8**. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.75−7.72 (m, 2H, ArH), 7.58 (d, 2H, J = 7.2 Hz, ArH), 7.38 (ddd, 2H, J = 7.1 Hz, 7.0 Hz, 2.1 Hz, ArH), 7.31−7.22 (m, 4H, ArH), 7.20 (s, 2H, N-C*H*=N), 7.14−7.08 (m, 2H, ArH), 6.86−6.83 (m, 2H, ArH), 5.11−5.10 (m, 2H, bridge CH), 4.66 (br s, 2H, bridgehead CH). ^{13}C NMR (75.3 MHz, $CDCl_3$) δ (ppm): 143.1 (N-*C*=*C*-N), 140.4 and 138.5 (C aromatic), 139.7 (*N*=CH-N), 133.8 (C aromatic),

128.4 (C aromatic), 128.3 (C aromatic), 127.0 (C aromatic), 124.9 (C aromatic), 123.7 and 123.1 (N-CCH*C*H*C*HCHC-N), 120.7 and 109.3 (N-C*C*HCHCH*C*HC-N), 62.2 (N-*C*H-CH-C═), 50.6 (N-CH-*C*H-C═). HRMS (FIA-ESI): calcd (found) for $C_{30}H_{23}N_4$ $(M + H)^+$ 439.1917 (439.1917).

Synthesis of 1,1-(9,10-Dihydro-9,10-ethanoanthracene-11,12-diyl)di(3-methyl-1*H*-benzimidazol-3-ium) Diiodide (8). Dibenzimidazole **7** (530 mg, 1.21 mmol) was dissolved in anhydrous MeCN (5.0 mL) in a glass ampule fitted with a sealable Teflon stopcock. MeI (300 μL, 4 equiv, 4.84 mmol) was added, and the vessel was evacuated and sealed. The flask was shielded from light and heated in a sand bath at 105 °C for 48 h. The mixture was cooled to room temperature, and the solid was filtered and washed with cold MeCN to afford **8** as a light beige powder (630 mg, 72% yield). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 8.85 (s, 2H, N-C*H*═N), 8.05−8.01 (m, 2H, Me-NCC*H*), 7.89−7.85 (m, 4H, ArH), 7.76−7.67 (m, 4H, ArH), 7.47 (ddd, 2H, J = 7.5, 7.5, and 1.2 Hz, ArH), 7.27 (ddd, 2H, J = 7.5, 7.5, and 1.2 Hz, ArH), 7.18 (d, 2H, J = 7 Hz, ArH), 5.99 (s, 2H, bridge CH), 5.16 (s, 2H, bridgehead CH), 3.96 (s, 6H, NCH_3). ^{13}C NMR (75.3 MHz, DMSO-d_6) δ (ppm): 140.5 (*N*═*C*H-N), 138.5 and 137.5 (*C*═*C*), 131.3 and 130.6 (N-*C*═*C*-N), 127.8 (C aromatic), 127.7 (C aromatic), 126.8 (C aromatic), 126.8 (C aromatic), 126.6 (C aromatic), 126.2 (C aromatic), 114.2 and 113.7 (N-C*C*HCHCH *C*HC-N), 61.3 (N-*C*H-CH-C═), 48.0 (N-CH-*C*H−C═), 33.8 (N-*C*H_3). HRMS (ESI-FTICR): calcd (found) for $C_{32}H_{28}IN_4$ $(M - I)^+$ 595.1353 (595.1272).

Synthesis of the (±)-*trans*-9,10-Dihydro-9,10-ethanoanthracene-9,10-(1-methyl)bibenzimidazole), [(DEA-MbBY] (9). KN(TMS)$_2$ (116 mg 0.58 mmol) in 5 mL of dry THF was added dropwise to a 10 mL THF solution of **8** (200 mg, 0.27mmol). The reaction was allowed to stir at room temperature for 3 h and then filtered. Solvent was removed from the filtrate in vacuo to produce a yellow powder. Excess base was extracted by washing the yellow precipitate with Et_2O (10 mL) to afford **9** as a yellow solid (53 mg, 40% yield). ^{1}H NMR (300 MHz, C_6D_6) δ (ppm): 6.95 (m, 12 H, ArH), 6.77 (dt, J = 7.5, 1.1 Hz, 2 H, ArH), 6.39 (dd, J = 7.5, 1.0 Hz, 2 H, ArH), 4.95 (s, 2 H, bridgehead CH), 3.40 (s, 2 H, bridgehead CH) 2.63 (s, 6 H, NC H_3). ^{13}C NMR (75.3 MHz, C_6D_6) δ ppm: 145.5 and 138.3 (CH*C*═*C*CH), 144.0 and 139.3 (N-*C*═*C*-N), 127.4 (C aromatic), 127.0 (C aromatic), 126.4 (C aromatic), 123.9 (C aromatic), 122.8 (*C*═*C*), 121.5 (C aromatic), 119.8 (C aromatic), 109.1 and 106.9 (NC*C*HCHCH*C*HCN), 66.0 (N-CH-*C*H-C═), 46.7 (N-*C*H-CH-C═), 36.3 (N *C*H_3). MS(DIP-CI): calc for [$C_{32}H_{26}N_4$] m/z 466.5564 [M^+], found m/z 466.2157.

Synthesis of the (±)-Rhodium(I) *trans*-9,10-Dihydro-9,10-ethanoanthracene-9,10-bis(1-methylbenzimidazolidine-2-ylidene Cyclooctadiene Iodide, [(DEA-MBY)Rh(COD)]I (10-COD). Dibenzimidazolium salt **8** (100 mg, 0.14 mmol) was suspended in 5 mL of THF and stirred overnight. At −35 °C, KN(TMS)$_2$ (53 mg, 0.26 mmol) in 3 mL of THF was added dropwise to the salt suspension and allowed to warm to room temperature and stir for 1 h. After cooling the solution to −35 °C, [Rh(COD)Cl]$_2$ (34 mg, 0.07mmol) in 3 mL of THF was then added dropwise to the reaction and allowed to stir for 1 h at room temperature. The reaction mixture was cooled at −35 °C overnight, and the resulting solid was filtered and washed wit Et_2O to provide [(DEA-MBY)Rh(COD)]I (**10-COD**) as a yellow powder (59 mg, 53% yield). ^{1}H NMR (499 MHz, CD_3Cl) δ ppm: 9.26 (d, J = 10.0 Hz, 1 H, L), 7.81 (d, J = 7.0 Hz, 1 H, D), 7.72 (d, J = 7.1 Hz, 1 H, A), 7.63 (d, J = 7.3 Hz, 1 H, H), 7.48−7.55 (m, 3 H, T, Q, C), 7.42−7.47 (m, 1 H, B), 7.36−7.42 (m, 2 H, S, R), 7.29−7.36 (m, 3 H, P, G, E), 7.15−7.25 (m, 2 H, O, F), 7.01−7.07 (m, 1 H, N), 6.95 (d, J = 8.2 Hz, 1 H, M), 5.19 (s, 1 H, I), 5.16 (s, 1 H, J), 5.10−5.15 (m, 1 H, COD-CH), 4.52−4.59 (m, 1 H, COD-CH), 4.46 (s, 3 H, V), 4.37 (dd, J = 9.9, J = 0.7 Hz, 1 H, K), 4.26−4.33 (m, 1 H, COD-CH), 3.95 (s, 3 H, U), 3.80−3.87 (m, 1 H, COD-CH), 2.60−2.79 (m, 2 H, COD), 2.26−2.35 (m, 1 H, COD), 2.21−2.26 (m, 2 H, COD), 2.12−2.21 (m, 1 H, COD), 1.69−1.79 (m, 1 H, COD), 1.24−1.37 (m, 1 H, COD). ^{13}C NMR (75.3 MHz, CD_3Cl) δ (ppm): 193.6 (d, J_{RhC} = 54.1 Hz, Y or Z), 191.4 (d, J_{RhC} = 52.4 Hz, Y or Z), 146.7 (C aromatic), 144.1 (C aromatic), 138.4 (C aromatic), 136.6 (C aromatic), 136.0 (C aromatic), 135.7 (C aromatic), 135.6 (C aromatic), 131.4 (C aromatic), 131.3 (C aromatic), 128.1 (C aromatic), 127.9 (C aromatic), 127.5C aromatic), 135.6 (C aromatic), 131.4 (C aromatic), 131.3 (C aromatic), 127.3 (C aromatic), 127.2 (C aromatic), 126.8 (C aromatic), 124.5 (C aromatic), 123.9 (C aromatic), 123.9 (C aromatic), 123.6 (C aromatic), 123.4 (C aromatic), 121.9 (C aromatic), 111.4 (s, NC*C*HCHCHCHCN), 111.2 (s, NC*C*HCHCH-CHCN), 111.1 (s, NC*C*HCHCHCHCN), 110.3 (s, NC*C*HCHCH-CHCN), 94.0 (C, d, J = 8.3 Hz, COD-*C*H), 91.4 (C, d, J_{RhC} = 7.7 Hz, COD-*C*H), 90.7 (C, d, J_{RhC} = 7.2 Hz, COD-*C*H), 89.8 (C, d, J_{RhC} = 7.7 Hz, COD-*C*H), 65.7 (s, CH*C*HN), 62.1 (s, CH*C*HN), 49.0 (s, C*C*HC), 47.8 (s, C *C*HC), 39.4 (s, N*C*H_3), 35.5 (s, N*C*H_3), 30.7 (s, COD-*C*H_2), 30.5 (s, COD-*C*H_2), 30.4 (s, COD-*C*H_2), 29.5 (s, COD-*C*H_2). Anal. Calc for $C_{40}H_{38}N_4IRh$ plus one molecule CH_3Cl: C, 55.36; H, 4.53; N, 6.30. Found: C, 55.06; H, 4.56; N, 6.17.

Synthesis of the (±)-Rhodium(I) *trans*-9,10-Dihydro-9,10-ethanoanthracene-9,10-bis(1-methylimidazolidine-2-ylidene) Cyclooctadiene Iodide, [(DEA-MY)(COD)]I (11-COD). Diimidazolium salt **4** (100 mg, 0.16 mmol) was suspended in 3 mL of dry THF and stirred overnight. At −35 °C, KN(TMS)$_2$ (61 mg, 0.31 mmol) in 3 mL of dry THF was added dropwise to the salt suspension and allowed to stir at room temperature for 1.5 h. At −35 °C a solution [Rh(COD)Cl]$_2$ (40 mg, 0.08 mmol) in 3 mL of dry THF was added dropwise to the salt suspension and allowed to stir for 1.5 h. A precipitate formed that was filtered and washed with diethyl ether to afford **11-COD** as a yellow powder (99 mg, 87% yield). ^{1}H NMR (299 MHz, CD_3Cl) δ (ppm): 8.23 (dd, J = 7.5, J = 1.0 Hz, L), 7.84 (d, J = 1.7 Hz, NC*H*═CHN), 7.74 (1 H, dd, J = 6.4, J = 1.8 Hz, CCHC*H*CHCHC), 7.58 (1 H, dd, J = 6.4, 2.1 Hz, CCHC*H*CHCHC), 7.52 (1 H, dd, J = 7.1, J = 1.1 Hz, CCHCHC*H*CHC), 7.46 (1 H, dd, J = 6.9, J = 1.0 Hz, CCHCH-C*H*CHC), 7.11−7.39 (overlapping signals, 5 H, ArH and NC*H*═CHN), 6.96 (d, J = 2.0 Hz, 1 H, NCH═C*H*N), 6.69 (d, J = 1.7 Hz, 1 H, NCH═C*H*N), 5.17 (d, J = 1.1 Hz, 1 H, NCHC*H*C), 4.87 (d, J = 0.6 Hz, 1H, NCHC*H*C), 4.87 (overlapping signal, 1 H, COD-C*H*), 4.15 (m, 1 H, COD-C*H*), 4.03 (s, 3 H, R), 3.73 (m, 2 H, COD-C*H*), 3.64 (s, 3 H, Q), 3.62 (overlapping signal, dd, J = 1.4 Hz, 1 H, K), 2.44−2.66 (m, 1 H, COD-CH$_2$), 2.18−2.41 (m, 2 H, COD-CH$_2$), 1.98−2.17 (m, 1 H, COD-CH$_2$), 1.69−1.98 (m, 3 H, COD-CH$_2$), 1.47−1.68 (m, 1 H, COD-CH$_2$). ^{13}C NMR (75.3 MHz, CD_3Cl) δ (ppm): 180.1 (1 C, d, J_{RhC} = 54.7 Hz, N*C*N), 179.3 (1 C, d, J_{RhC} = 52.7 Hz, N*C*N), 143.8 (T), 142.6 (V), 136.9 (U), 136.1 (S), 128.7 (C aromatic), 127.8 (C aromatic), 127.7 (C aromatic), 127.5 (C aromatic), 127.2 (C aromatic), 126.9 (C aromatic), 125.1 (C aromatic), 125.0 (N*C*HCHN), 124.7 (N*C*HCHN), 123.7 (NC>H*C*HN), 122.4 (C aromatic), 115.9 (NCH*C*HN), 92.6 (1 C, d, J_{RhC} = 8.6 Hz, COD-C*H*), 88.3 (1 C, d, J_{RhC} = 7.4 Hz, COD-C*H*), 88.0 (1 C, d, J_{RhC} = 8.3 Hz, COD-C*H*), 85.8 (1 C, d, J_{RhC} = 7.4 Hz, COD-C*H*), 66.5 (s, CH*C*HN), 63.7 (s, CH*C*HN), 48.5 (s, C*C*HC), 47.6 (s, C*C*HC), 40.8 (s, N*C*H_3), 37.5 (s, N*C*H_3), 32.5 (s, COD-*C*H_2), 31.8 (s, COD-*C*H_2), 29.0 (s, COD-*C*H_2), 28.0 (s, COD-*C*H_2). Anal. Calc for $C_{32}H_{34}N_4IRh$: C, 54.56; H, 4.86; N, 7.95. Found: C, 54.47; H, 4.72; N, 8.25.

Synthesis of (±)-[μ-DEA-MY][Rh(NBD)I]$_2$ (12-NBD) as a Mixture with 11-NBD. At −35 °C, KN(TMS)$_2$ (46 mg, 0.23 mmol) in 3 mL of dry THF was added dropwise to a 3 mL suspension of **4** (76 mg, 0.12 mmol) in THF. The reaction mixture was then stirred for 45 min while warming to room temperature. After cooling the mixture to −35 °C, it was added dropwise to cold a 3 mL THF solution of [Rh(NBD)$_2$]BF_4 (100 mg, 0.27 mmol). This mixture was allowed to stir at room temperature for 2.5 h before the solvent

was removed in vacuo. The resulting residue was triturated with Et_2O (2 × 3 mL) and pentanes (2 × 3 mL). After drying overnight, the residue was taken up in pentanes, filtered, and then washed with Et_2O and extracted into benzene. The solvent was removed, producing a yellow-orange solid (53 mg). A ^{1}H NMR spectrum of the solid revealed 25 mol % of **11** was present as an impurity that could not be removed. ^{1}H NMR (299 MHz, C_6D_6) δ (ppm): 7.85 (2 H, d, J_{HH} = 7.1 Hz, A), 6.86−7.11 (6 H, m, B, C, D), 6.41 (2 H, s, G), 5.91 (2 H, d, J_{HH} = 1.7 Hz, H), 5.77 (2 H, d, J_{HH} = 1.7 Hz, I), 5.48 (2 H, s, F), 5.19 (2 H, br s, NBD-CH), 5.05 (2 H, br s, NBD-CH), 3.38 (2 H, br s, NBD-CH), 3.28 (6 H, s, J), 3.12 (2 H, d, J_{HH} = 2.3 Hz, NBD-CHC*H*CH) 2.89 (2 H, br s, NBD-CH) 1.64 (2 H, d, J_{HH} = 2.5 Hz, NBD-CHC*H*CH) 0.96 (4 H, m, NBD-CH_2).

Synthesis of (±)-[μ-DEA-MBY][Rh(COD)Cl]$_2$ (13-COD) as a Mixture with 10-COD. Dibenzimidazolium salt **8** (54 mg, 0.07 mmol), KN(TMS)$_2$ (28 mg, 0.14 mmol), and [Rh(COD)Cl]$_2$ (44 mg, 0.09 mmol) were weighed into separate 20 mL vials and suspended in 3 mL of dry THF. After the reagents were cooled to −35 °C, the KN(TMS)$_2$ solution was added dropwise to the salt suspension. The reaction mixture was allowed to warm to room temperature for 45 min before being cooled again to −35 °C. The reaction mixture was then added dropwise to the cold [Rh(COD)Cl]$_2$ suspension, then allowed to warm to room temperature and stir for 1 h. The solvent was removed in vacuo, and the residue was triturated with Et_2O (2 × 3 mL) and pentane (2 × 3 mL). The residue was taken up in pentanes and filtered, washed with Et_2O, and extracted into benzene. A yellow-orange solid was obtained upon solvent removal. The solid material consisted of ∼33% **13-COD** and 67% **10-COD**. The mixture obtained prevented meaningful assignment of NMR spectral signals. To remedy this problem, the analogous **13**-NBD was synthesized in hopes of generating a larger percentage of the dinuclear species.

Synthesis of 13-NBD. Dibenzimidazolium salt **8** (53 mg, 0.07 mmol), KN(TMS)$_2$ (28 mg, 0.14 mmol), and [Rh(NBD)$_2$]BF_4 (60 mg, 0.16 mmol) were weighed into separate 20 mL vials and suspended in 3 mL of dry THF. The reagents were cooled to −35 °C, and KN(TMS)$_2$ was added dropwise to the salt suspension, which was stirred at room temperature for 45 min and cooled again to −35 °C. The reaction mixture was then added dropwise to the cold [Rh(NBD)$_2$]BF_4 suspension and allowed to warm, stirring at room temperature for 1 h. The solvent was removed in vacuo, and the residue was triturated with Et_2O (2 × 3 mL) and pentane (2 × 3 mL). The residue was then taken up in pentanes and filtered, washed with Et_2O, and extracted with benzene. A yellow-orange precipitate (41 mg) was produced upon solvent removal, which consisted of 48% **10-NBD**. ^{1}H NMR (299 MHz, C_6D_6) δ (ppm): 8.09 (2 H, d, J_{HH} = 7.4 Hz, D and E), 7.80 (2 H, s), 7.04−7.10 (2 H, m, ArH), 6.63−6.83 (10 H, m, ArH), 6.49−6.56 (2 H, m, ArH), 5.98 (2H, s, L and H), 5.70 (2 H, s, J and I), 5.25 (2 H, t, J_{HH} = 4.0 Hz, NBD-*H*C═CH), 4.81 (2 H, t, J_{HH} = 4.0 Hz, NBD-*H*C═CH), 4.41(2H, m, NBD-HC═C*H*), 3.62 (2H, m, NBD-HC═C*H*), 3.56 (6 H, br s, R), 3.04 (2H, m, NBD-CHC*H*CH), 1.52 (2H, m, NBD-CHC*H*CH), 0.74 (2 H, d, J_{HH} = 8.5 Hz, NBD-*H*CH), 0.60 (1 H, d, J_{HH} = 8.2 Hz, NBD-HC*H*).

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Supporting Information Available: Crystallographic data tables, experimental protocols, and ^{1}H and ^{13}C NMR. This material can be found free of charge via the Internet at http://pubs.acs.org.

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