Synthesis and Study of the First N-Aryl Acyclic Diaminocarbene and Its Transition-Metal Complexes

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Summary: The first acyclic diaminocarbene (ADC) featuring N-aryl groups, as well as two complexes containing this ligand, (ADC)RhCl(1,5-cis,cis-cyclooctadiene) and (ADC)RhCl(CO)₂, were synthesized and characterized. Insight into controlling conformational diversity in acyclic diaminocarbenes with N-aryl groups through judicious N substitution was also explored.

N-Heterocyclic carbenes (NHCs) and their transition-metal complexes have been of interest to many in the chemical community since the 1960s.[1] However, the isolation[2] of 1,3-diadamantylimidazol-2-ylidene (**1**; Figure 1) by Arduengo and co-workers in 1991 sparked a cascade of investigations surrounding the synthesis and utility of NHCs (e.g., **2** and **3**) in numerous catalytic reactions.[3] Acyclic diaminocarbenes (ADCs) (**4**−**6**), on the other hand, have received relatively less attention.[1] Although they were discovered by Alder and co-workers over a decade ago,[4] few reports have addressed the preparation and utility of ADCs.[5] The paucity of examples is striking when one considers that these compounds are readily accessible via deprotonation of acyclic formamidinium precursors,[6] have stronger basicities than NHCs,[7] and bestow good to excellent catalytic activities upon coordination to transition metals—in some case outperforming traditional NHCs.[8]

Upon coordination to a transition metal, NHCs with bulky N-aryl substituents (e.g., **2** and **3**, which feature *N*-mesityl and *N*-2,6-diisopropylphenyl groups, respectively) often result in complexes with superior stabilities, due to protection provided
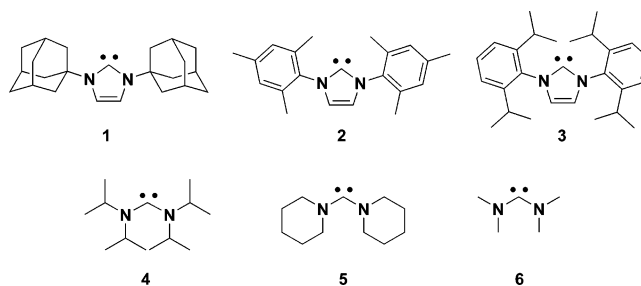

Figure 1. Representative examples of N-heterocyclic carbenes (top) and acyclic diaminocarbenes (bottom).

by steric shielding about the metal center.[9] Since ADCs generally exhibit N−C−N bond angles larger than those of their NHC analogues, additional steric protection may be expected upon complexation to an ADC possessing bulky N-aryl groups. However, to the best of our knowledge, ADCs bearing N-aryl substituents have not been prepared to date.

In 1961, Clemens and Emmons disclosed the synthesis of *N,N*′-diphenyl-*N,N*′-dimethylformamidinium tetrafluoroborate via treatment of an orthoamide with tetrafluoroboric acid.[10] Interestingly, treatment of this formamidinium salt with sodium hydride was reported to provide the corresponding *N,N*-acetal rather than a free ADC, as determined via elemental analysis. Hence, a primary objective of the study described herein was to re-examine the chemistry of N-aryl formamidinium salts to (1) determine if their respective ADCs can be synthesized using standard deprotonation protocols and (2) explore the potential of their respective ADCs to ligate transition metals.

A secondary objective of this study was to probe the feasibility of controlling the conformational diversity of ADCs as well as their respective formamidinium salts and metal complexes via sterics. As illustrated in Figure 2, the linear structure of these compounds may lead to multiple possible conformers (e.g., **A**−**C**) for systems possessing multiple, distinct N substituents.[11] Conformer **A** is analogous to common 1,3-diaryl NHCs, as the N-aryl substituents adopt a pseudo-cis orientation relative to the complexed center. Conformer **B** also features N-aryl substituents adopting a pseudo-cis orientation; however, they are now juxtaposed and opposite to the complexed center. Conformer **C** is essentially an intermediate of **A** and **B** and features pseudo-trans N-aryl substituents in a

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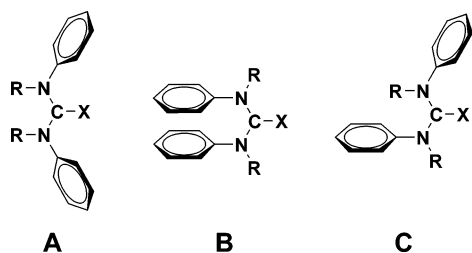
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(11) Although additional conformers are possible, they would require disrupting the planarity of the formamidine's three-center, four-π-electron system and hence were not considered.

Figure 2. Three unique conformers of N,N′-diaryl-N,N′-dialkyl-formamidiniums (X = H), acyclic diaminocarbenes (X = lone pair), and organometallic complexes (X = transition metal). R = alkyl group.
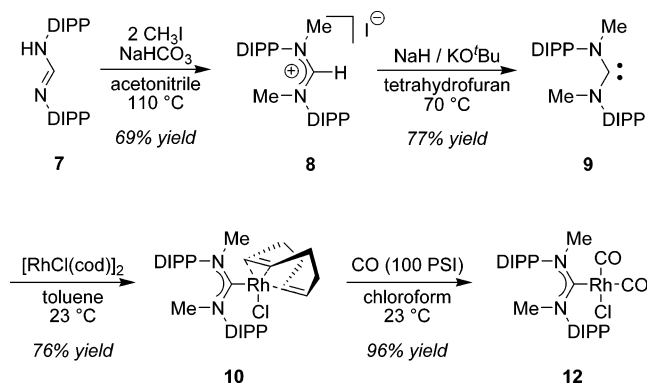

Figure 3. Synthesis of an N-aryl acyclic diaminocarbene and its transition-metal complexes.

diametrically opposed orientation about the diaminocarbene linkage. Since the ground-state geometries exhibited by these compounds will depend on which conformation minimizes unfavorable steric interactions, we envisioned that the relative sizes of the N-aryl and N-alkyl groups may be varied to favor one conformer over another. Such ability may ultimately open new opportunities for fine-tuning steric environments in organometallic complexes formed with ADCs and lead to new methods for controlling catalytic reactions. Hence, we also explored the potential of controlling the ground-state conformations exhibited by ADCs, as well as their respective formamidinium salts and transition-metal complexes, through judicious N substitution.

The synthesis of a N,N′-diaryl ADC as well as its transition-metal complexes is summarized in Figure 3. Alkylation of *N,N′*-bis(2,6-diisopropylphenyl)formamidine (**7**) with 2 equiv of methyl iodide in acetonitrile under mildly basic conditions afforded the formamidinium iodide **8** in 69% isolated yield. The *N*-methyl groups of **8** appeared to be inequivalent, as two distinct singlets were found at δ 3.59 and 2.69 ppm in its ^{1}H NMR spectrum (DMSO-d_6). Similarly, methine proton signals attributed to the 2,6-diisopropylphenyl (DIPP) substituents appeared as two distinct septets centered at 3.00 and 2.80 ppm.[12] These data suggested that **8** adopted a pseudo-trans conformation analogous to **C** (Figure 2). This was a surprising result, as a conformation that maximized the distance between the bulky

DIPP substituents (i.e., conformer **A**) was expected. For example, the reported ^{1}H NMR chemical shifts for *N,N′*-di-*tert*-butyl-*N,N′*-dimethylformamidinium triflate and *N,N′*-dicyclo-hexyl-*N,N′*-diethylformamidinium triflate, which also feature two large and two small groups on each nitrogen atom, are consistent with these compounds adopting a conformation analogous to **A**.[6]

To obtain additional support for this structural assignment, a quality crystal was obtained by slow diffusion of diethyl ether into a saturated methylene chloride solution of **8** and analyzed via X-ray crystallography; selected crystal data are summarized in Table 1. The ORTEP diagram shown in Figure 4 indicated that the solid-state structure of **8** was superficially similar to conformer **C**, featuring N-aryl substituents in a pseudo-trans orientation. The N–C–N bond angle (129.6°) and C–N bond lengths (1.319 and 1.317 Å) of **8** were comparable with those in various tetraalkylformamidinium salts reported by Alder as precursors to ADCs.[6] However, distinguishable features of **8** include its relatively narrow C–N–C–N dihedral angles of 0.7 and 1.6°, indicative of nearly coplanar *N*-DIPP and methyl groups. For comparison, the same dihedral angles in known[6] formamidinium salts with bulky N-alkyl substituents range between 10.6 and 22.5°. Close inspection of **8** provides an explanation for this difference: the *N*-DIPP groups adopted conformations perpendicular to the N–C–N plane, which provided ample space for the juxtaposed *N*-methyl group and effectively relieved an otherwise sterically congested 1,3-interaction (see below for additional discussion of this phenomenon). Furthermore, the ^{1}H NMR signal attributed to this methyl group was found relatively upfield (δ 2.69 ppm), which suggested that it may be participating in a CH–π interaction[13] with the arene face of the adjoining *N*-DIPP group.

Treatment of formamidinium **8** with sodium hydride in a tetrahydrofuran solution heated to 70 °C afforded the free ADC **9**, which was isolated in 77% yield after the sodium iodide byproduct was precipitated from toluene and removed by filtration. The diagnostic ^{13}C NMR chemical shift of the carbene

Table 1. Selected Crystal Data

	8	10	15
CCDC no.	653951	653949	653950
empirical formula	$C_{27}H_{41}N_2I\cdot$ H_2O	$C_{35}H_{52}ClN_2$-Rh	$C_{33}H_{35}N_4O_4$-Br$\cdot$1.5C_4H_8O
formula wt	538.53	639.15	739.72
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1$	$C2/c$
a, Å	10.6234(3)	9.6720(2)	32.8293(5)
b, Å	10.8976(4)	17.9370(5)	8.9223(1)
c, Å	13.5789(5)	10.5920(3)	25.9432(6)
α, deg	103.3480(15)	90	90
β, deg	103.8380(18)	116.4921(12)	95.8360(10)
γ, deg	106.6460(17)	90	90
V, Å^3	1384.63(8)	1644.62(7)	7559.7(2)
T, K	293(2)	153(2)	153(2)
Z	2	2	8
D_{calcd}, Mg/m^3	1.292	1.291	1.300
cryst size (mm)	0.15 × 0.13 × 0.05	0.20 × 0.18 × 0.09	0.31 × 0.20 × 0.17
no. of rflns collected	9787	7171	21397
no. of indep rflns	6299	7171	8419
R1, wR2 ($I >$ $2\sigma(I)$)	0.0434, 0.0953	0.0685, 0.1464	0.0466, 0.1021
goodness of fit	1.064	1.114	1.093

(12) The barrier to rotation about the C–N bonds in tetraisopropylformamidinium triflate and bis(diisopropylamino)carbene (**4**) was determined by VT-NMR spectroscopy to be about 13 kcal/mol.[4] However, the analogous barriers in **8** and **9** appear to be considerably higher. For example, heating a DMSO-d_6 solution of **8** to 130 °C resulted in less than 0.1 ppm changes in key chemical shifts, as determined by variable-temperature ^{1}H NMR spectroscopy. For in-depth analyses of C–N bond rotations in ADCs, see: (a) Tafipolsky, M.; Scherer, W.; Öfele, K.; Artus, G.; Pedersen, B.; Herrmann, W. A.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865. (b) Alder, R. W.; Blake, M. E.; Olivia, J. M. *J. Phys. Chem. A* **1999**, *103*, 11200.

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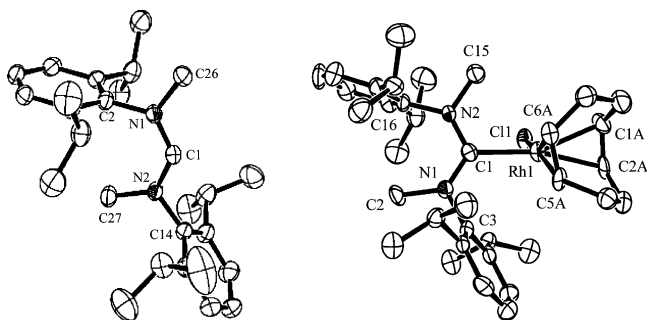
Figure 4. ORTEP diagrams of formamidinium **8** (left) and Rh complex **10** (right). Displacement ellipsoids were drawn at the 50% probability level. Hydrogen atoms, counterions, and solvent molecules have been omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) for **8**: N1−C1, 1.319-(4); N2−C1, 1.319(4); N2−C1−N1, 129.6(3); C26−N1−C1−N2, −179.5(3); C27−N2−C1−N1, 0.6(5); C14−N2−C1−N1, −179.7-(3); C2−N1−C1−N2, 1.7(5). Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) for **10**: Rh1−C1, 2.086(8); Rh1−C6A, 2.100(9); Rh−C5A, 2.128(9); Rh1−C1A, 2.179(7); Rh1−C2A, 2.187(8); Rh1−Cl1, 2.405(2); N1−C1, 1.341(8); N2−C1, 1.364(9); C1−Rh1−Cl1, 88.7(2); N1−C1−N2, 119.5(6); C2−N1−C1−N2, −4.9(11); C16−N2−C1−N1, 0.4(1); C15−N2−C1−N1, 175.6(6); C3−N1−C1−N2, 168.8(6).

atom was found at δ 248.9 ppm (C_6D_6), in accordance with other known[4,5d] ADCs (236.8−255.5 ppm).[14] Similar to the case for **8**, ADC **9** exhibited two distinct singlets at 3.54 and 2.34 ppm in its ^{1}H NMR spectrum (C_6D_6) and two distinguishable multiplets centered at 3.42 ppm, attributed to diastereotopic methyl and methine protons, respectively. Likewise, the relatively large upfield *N*-methyl signal was consistent with a CH−π interaction, as observed in the ^{1}H NMR spectrum of formamidinium **8**. Hence, the ADC **9** also appeared to adopt a conformation analogous to **C**. Unfortunately, all attempts to obtain quality crystals of this carbene were unsuccessful, which thwarted assessment of its structure using X-ray crystallography.

To identify the structure of **9** and to probe for any conformational changes upon coordination to a transition metal, a Rh complex containing this ligand was synthesized. Addition of **9** to a toluene solution of [Rh(cod)Cl]$_2$ (cod = 1,5-*cis,cis*-cyclooctadiene) afforded Rh complex **10** as a yellow solid in 76% isolated yield. The complex was found to be soluble in methylene chloride, ethyl acetate, diethyl ether, and pentanes and stable to air, moisture, and silica gel media used for chromatographic purification. The ^{1}H NMR spectrum (C_6D_6) of complex **10** suggested that the coordinated ADC ligand maintained its relatively desymmetrized conformation when bound to a transition metal, as two singlets, attributable to the *N*-methyl groups, were observed at 4.59 and 2.49 ppm. Additionally, four distinct DIPP methine protons were observed: two of the methine protons appeared as complex but distinguishable multiplets centered at 4.54 ppm, while the remaining two exhibited distinct septets at 3.14 and 2.82 ppm.

To determine the structure of complex **10**, X-ray-quality crystals were grown by slow diffusion of pentane into a saturated methylene chloride solution; selected crystal data are summarized in Table 1. As shown in Figure 4, the ORTEP diagram of Rh complex **10** revealed that the N-aryl groups on the ADC

ligand adopted a pseudo-trans conformation about the diaminocarbene linkage consistent with the solution assignments of free ADC **9** and formamidinium **8**. As a result of the complex's apparent C_1 symmetry, the *N*-DIPP and *N*-methyl substituents were positioned in unique chemical environments, which corroborated the aforementioned NMR spectroscopic data. Relative to formamidinium salt **8**, Rh complex **10** exhibited a contracted N−C−N angle (119.5°) and longer N−C bond lengths (1.341 and 1.364 Å), which may reflect increased steric interactions between the N substituents and the complexed transition metal. Comparison of tetraisopropylformamidinium triflate with (bis(diisopropylamino)carbene)(cod)RhCl (**11**, structure not shown) revealed similar structural changes.[7c] However, the Rh−$C_{carbene}$ bond length observed in **10** (2.086 Å) was slightly longer than the analogous bond in **11** (2.041 Å). To compensate for the diminished ADC−metal interaction, relatively short trans Rh−C_{cod} bond lengths were observed (compare 2.187 and 2.178 Å for **10** vs 2.203 and 2.247 Å for **11**).

The complexed carbene atom in Rh complex **10** displayed a chemical shift at δ 211.6 ppm ($J_{C−Rh}$ = 45.6 Hz) in its ^{13}C NMR spectrum (CDCl$_3$). This large downfield shift has been attributed to strong σ-donating abilities coupled with limited π-back-bonding capabilities inherent to ADCs.[7c] To determine the relative electron-donating ability of ADC **10**, Rh carbonyl complex **12** was synthesized as shown in Figure 3 and compared with (**4**)RhCl(CO)$_2$ (**13**, structure not shown),[7c] an analogous complex containing bis(diisopropylamino)carbene. IR spectroscopy (KBr) revealed that the carbonyl stretching frequencies exhibited by **12** (ν_{CO} 2068 and 1984 cm^{-1}) were higher than those of **13** (2056 and 1984 cm^{-1}),[7c] suggesting that ADC **10** was relatively less basic than a tetraalkyl analogue.

The aforementioned results indicated that formamidinium **8**, ADC **9**, and Rh complex **10** favor a conformation that places the *N*-DIPP substituents in a pseudo-trans orientation (i.e., **C**). Analysis of the three possible conformers shown in Figure 2 in terms of 1,3-allylic strain[15] (or $A^{1,3}$ strain) provided a rationale for this preference. Adoption of conformers analogous to **A** or **B** by **8**−**10** necessitates relatively high energy 1,3-dimethyl or 1,3-di-DIPP interactions, respectively. In contrast, the rotated *N*-DIPP groups in conformer **C** opens space for the juxtaposed *N*-methyl group, which effectively minimizes unfavorable 1,3-interactions in this orientation. The crystal structures of **8** and **10** support this hypothesis, as *N*-methyl groups were found inserted into pockets created by the diisopropyl groups on the N-aryl substituents. Furthermore, as noted above, development of CH−π interactions between *N*-methyl and adjoining *N*-DIPP groups may additionally bias adoption of conformer **C** in **8**−**10**.

With these concepts in mind, subsequent efforts were focused on evaluating the potential of obtaining *N*,*N*′-diarylformamidiniums that adopt a conformation analogous to either **A** or **B** by changing the size of the N-substituents. As shown in eq 1,
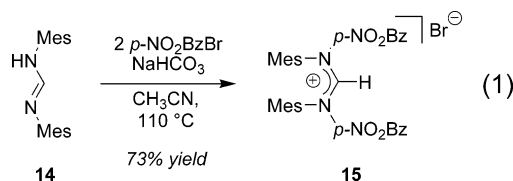
treatment of *N*,*N*′-dimesitylformamidine (**14**) with 2 equiv of *p*-nitrobenzyl bromide[16] in acetonitrile under mildly basic

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(14) ADC **9** did not appear to dimerize to its respective enetetraamine, even after prolonged standing in solution. For excellent, comprehensive analyses of diaminocarbene dimerizations, see: (a) Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schütz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896. (b) Alder, R. W.; Blake, M. E.; Chaker, L.; Paolini, F. P. V. *Chem. Commun.* **2004**, 2172.

(15) For reviews on the concept of 1,3-allylic strain, see: (a) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841. (b) Johnson, F. *Chem. Rev.* **1968**, *68*, 375.
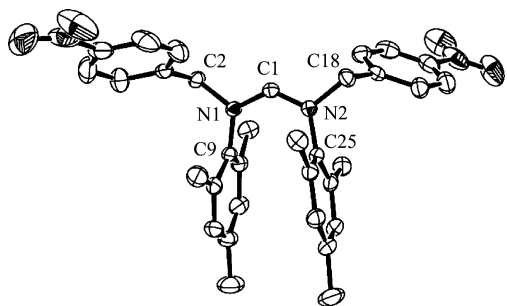
Figure 5. ORTEP diagram of formamidinium **15**. Displacement ellipsoids were scaled to the 50% probability level. Hydrogen atoms, counterions, and solvent molecules have been omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): N1−C1, 1.321(3); N2−C1, 1.321(3); N1−C1−N2, 129.7-(2); C9−N1−C1−N2, −13.2(4); C25−N2−C1−N1, −11.8(4); C18−N2−C1−N1, −178.6(2), C2−N1−C1−N2, 177.0(2).

conditions afforded formamidinium bromide **15** in 73% isolated yield.[17] Inspection of the ^{1}H NMR spectrum (CDCl$_3$) showed predominantly[18] a single resonance attributed to the methylene groups at 5.45 ppm, consistent with pseudo-cis conformations analogous to **A** and **B**. Compound **15** was tentatively assigned the latter structure after signals attributed to the aryl protons on the *N*-mesityl groups were found relatively upfield (6.43 ppm, CDCl$_3$), indicative of a $\pi-\pi$ interaction.

(16) To bias the reaction to favor the desired tetrasubstituted product, a more electrophilic benzylating agent (i.e., *p*-nitrobenzyl bromide) was required. Treatment of *N,N′*-dimesitylformamidine (**14**) with benzyl bromide under a variety of conditions (temperature, solvent, etc.) resulted in a mixture of mono- and dialkylated salts, which proved too difficult to cleanly separate. Low reactivities of di- and trisubstituted formamidines have been documented; see: (a) Reference 6. (b) Wicherink, S. C.; Scheerlen, J. W.; Nivard, R. J. F. *Synthesis* **1977**, 273.

(17) Treatment of *N,N′*-dimesitylformamidine (**14**) with methyl iodide under mildly basic conditions afforded *N,N′*-dimesityl-*N,N′*-dimethylfor-mamidinium iodide (**16**, structure not shown). ^{1}H NMR spectroscopy (DMSO-d_6) indicated that this salt exhibited a pseudo-trans orientation (analogous to conformer **C**), as two distinct singlets, attributable to its *N*-methyl groups, were found at δ 3.50 and 2.63 ppm. Interestingly, known[16b] *N,N′*-diphenyl-*N,N′*-dimethylformamidinium iodide, which features relatively small N-aryl substituents, appeared to exist in solution as an approximately 1:1 mixture of two different conformers. The ^{1}H NMR spectrum (DMSO-d_6) of this salt revealed two singlets at δ 8.83 and 8.64 ppm and three singlets at 3.68, 3.61, and 2.84 ppm, which were attributed to unique formamidinium and *N*-methyl groups, respectively. Although unambiguous assignment of the conformational mixture has been elusive (i.e., either **A** or **B** in combination with **C** is possible), these results underscored the need to reduce the size of the N-aryl groups while increasing the size of N-alkyl groups to drive conformational changes in these tetrasubstituted formamidine systems.

(18) The relative ratio of pseudo-cis to pseudo-trans conformers was found to be 87:13 by ^{1}H NMR spectroscopy (CDCl$_3$).

To ascertain the structure of **15**, a quality crystal suitable for X-ray analysis was obtained by slow evaporation of a saturated tetrahydrofuran solution; selected crystal data are summarized in Table 1. The ORTEP diagram shown in Figure 5 revealed that this compound adopted a conformation analogous to **B**, where the N-aryl groups were juxtaposed in a pseudo-cis orientation. The N−C−N bond angle (129.7°), C−N bond lengths (1.321 Å), and absolute C−N−C−N dihedral angles (13.2 and 11.8°) were consistent with known[6] tetrasubstituted formamidinium salts. Furthermore, the distance between the centroids of the mesityl groups was found to be 3.531 Å, in accord with a favorable $\pi-\pi$ interaction. Considering the conformation of formamidinium **8** did not change upon deprotonation (to obtain ADC **9**) or upon coordination to a transition metal (i.e., Rh complex **10**), we predict formamidinium **15** will also maintain its conformation upon derivatization. Efforts toward synthesizing the respective ADC and related metal complexes are underway.

In conclusion, the first N-aryl acyclic diaminocarbene (ADC), *N,N′*-bis(2,6-diisopropylphenyl)-*N,N′*-dimethyldiaminocar-bene, has been synthesized from its respective formamidinium precursor. This ADC was found to coordinate to Rh(I), facilitating the synthesis of two new organometallic complexes containing this ligand. In each of these compounds, the N-aryl groups were found to adopt a distally opposed, pseudo-trans orientation about the diaminocarbene linkage. In contrast, the N-aryl groups in *N,N′*-dimesityl-*N,N′*-bis(*p*-nitrobenzyl)forma-midinium bromide were found to adopt a juxtaposed, pseudo-cis orientation. Collectively, these results indicate that the ground state conformations of N,N′-diaryl-N,N′-dialkylformamidine-based systems can be judiciously controlled through sterics. Efforts toward developing catalytically active organometallic complexes containing conformationally tunable ADC ligands are in progress and will be reported in due course.

Supporting Information Available: Experimental procedures, NMR spectra, and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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