

A Seven-Membered N,N'-Diamidocarbene

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Condensation of N,N'-dimesitylformamidine with phthaloyl chloride afforded 1·HCl, which, upon treatment with base, afforded 2,4-dimesitylbenzo[*e*][1,3]diazepin-1,5-dione-2-ylidene (1), a seven-membered N,N'-diamidocarbene (DAC), in high yield (85%). The free DAC was used to synthesize four new, late transition metal complexes: [Rh(cod)(1)Cl] (2a) (cod = 1,5-cyclooctadiene), [Ir(cod)(1)Cl] (2b), [Rh(CO)₂(1)Cl] (3a), and [1-AuCl] (5). The Tolman electronic parameter (TEP) of 1 was calculated to be 2047 cm⁻¹ from the IR spectrum of 3a. This TEP value is approximately 10 cm⁻¹ lower than known DACs and 5 cm⁻¹ lower than known imidazol-2-ylidenes, indicating that DAC 1 is a relatively strong electron donor. Additionally, electrochemical analyses of 2a and 2b corroborated the IR data obtained on 3a and revealed $E_{1/2}$ values that were shifted cathodically by ca. 0.16 V when compared to analogous complexes supported by N-heterocyclic carbenes. The gold complex 5 was found to catalyze the hydration of phenylacetylene, affording acetophenone in yields up to 78% after 12 h at 80 °C at a catalyst loading of 2 mol %. Treatment of 1 with 2,6-dimethylphenylisocyanide afforded *N*, *N'*-diamidoketenimine 4 as a thermally robust, crystalline solid.

Introduction

Heteroatom-stabilized singlet carbenes were first described by Breslow and later by Wanzlick as reactive intermediates more than half a century ago;¹ however, the field lay fallow until Bertrand's landmark report of a stable, free carbene several decades later.² Since then, in the chemistry of these once-elusive divalent carbon species has entered a renaissance.³

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Recently, we discovered that *N*,*N'*-diamidocarbenes (DACs) **IIIa** and **IIIb** (Figure 1) also display an unusual combination of electrophilic and nucleophilic characteristics.⁷ In addition to their abilities to coordinate a range of transition metals and couple with electrophilic organic substrates (e.g., CS₂), DACs **III** were found to engage in reactions atypical of NHCs, including intramolecular C–H insertion,^{7a} coupling with isocyanides to form ketenimines,^{7b} coupling with carbon monoxide in a reversible manner,^{6b,7a,8} and activation of NH₃.^{6b} Despite forcing conditions, however, **III** was unable to activate

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Figure 1. Examples of alkyl amino carbenes I and II, N,N'-diamidocarbenes III, and seven-membered diaminocarbenes IV, V, and VI.

dihydrogen, possibly due to insufficient polarization of the H–H bond. Analogous to AACs, we reasoned that increasing the nucleophilic characteristics of DACs would expand their reactivity toward small molecules.

One method for increasing the electron donicity and, by extension,^{6a,9} the nucleophilicity of a cyclic diaminocarbene is to widen its N–C–N angle.^{9d,e,g,l,m} For example, Fallis demonstrated that seven-membered diazepine-2-ylidenes, such as **IV**, and derivatives thereof, which exhibit average N–C–N angles ranging from 113.4–116.6°,^{9e,g} are stronger electron donors than imidazolin-2-ylidenes and tetrahydropyrimidenes, whose average N–C–N angles are in the range 102–105° and 112–114°, respectively. Similarly, other seven-membered NHCs, including **V** and **VI**, have also been shown to be relatively strong nucleophiles⁹ electron donors, in some cases comparable to the cyclic alkyl amino carbenes (CAACs) **II** reported by Bertrand.¹⁰

The strong donicities observed in seven-membered NHCs may be attributed to an increase in the degree of sp-hybridization at the carbene nucleus, which results in localization of the carbene lone pair in a more diffuse orbital with greater p-character.^{4,9d,9e,9g,9l,9m} For example, seven-membered





^{*a*} Conditions: (*i*) phthaloyl chloride, Et_3N , CH_2Cl_2 , 0 °C, 1 h; (*ii*) Na-HMDS, C_6H_6 , 25 °C, 30 min. Isolated yields are indicated.

NHCs have been shown to be capable of inserting into benzylic C–H bonds, whereas smaller-ring NHCs generally do not exhibit this reactivity.^{9k} In addition to increased nucleophilicities, NHCs with wider N–C–N angles often impose steric constraints on transition metals to which they are ligated, features that have led to the development of chiral NHC-supported asymmetric catalysts^{9a–c,i,j} and novel Ru-based olefin metathesis catalysts.^{9f} Inspired by these reports, and with the aims of (1) enhancing the nucleophilicities of DACs to expand their reactivities and (2) incorporating sterically imposing DACs into catalytically active metal complexes in mind, we herein disclose the syntheses, characterization, and applications of the first seven-membered DAC.

Results and Discussion

Synthesis and Structure of DAC 1. Condensation of N, N'dimesitylformamidine with phthaloyl chloride in CH₂Cl₂, followed by solvent removal under reduced pressure and extraction of the product with toluene, afforded the desired DAC precursor 1. HCl in 88% yield (Scheme 1). 6b,7c Although consistent with the formation of a neutral chloroaminal, the ¹H NMR spectrum recorded for $1 \cdot HCl$ exhibited a NCHN resonance at $\delta = 6.41$ ppm (CDCl₃) that was upfield compared to the analogous signals observed at $\delta = 6.81$ and 6.85 ppm (CDCl₃) for the HCl adducts of IIIa and IIIb, respectively.^{6b,7c} The different chemical shifts observed may be rationalized by the disparity in ring sizes, where the larger ring in $1 \cdot HCl$ forces the N-mesityl substituents closer to the NCHN group and results in increased shielding when compared to IIIa · HCl. ¹¹ Regardless, the IR spectrum of 1·HCl revealed carbonyl stretching energies ($\nu_{CO} = 1672 \text{ cm}^{-1}$, KBr) that were in accord with the HCl adducts of DACs III (IIIa·HCl: 1682 cm^{-1} , ATR; IIIb·HCl: 1685 cm⁻¹, KBr) and consistent with $v_{\rm CO}$ exhibited by prototypical amide functional groups $(1630-1695 \text{ cm}^{-1})$.^{6b,7c}

Deprotonation of 1·HCl by NaN(SiMe₃)₂ (NaHMDS) in benzene, followed by solvent removal under reduced pressure and washing with cold hexanes, afforded the desired seven-membered DAC 1 in 85% yield as a bright yellow powder. The ¹³C NMR spectrum of 1 exhibited a signal at $\delta = 268.4$ ppm (C₆D₆, Table 1), which was assigned to the carbene nucleus and in good agreement with signals displayed by analogous seven-membered NHCs ($\delta = 255-269$ ppm),⁹ but still upfield from signals observed in the sixmembered DAC analogues IIIa and IIIb ($\delta = 278$ ppm).^{6b,7a} The observed chemical shift differences between 1 and III may result from the increased shielding due to the larger seven-membered ring, in accord with the aforementioned ¹H NMR spectroscopic data obtained for 1·HCl and III·HCl. Although at a lower energy than the ν_{CO} observed in

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⁽¹¹⁾ Despite our best efforts, we were unable to grow X-ray quality crystals of $1 \cdot \text{HCl}$.

Table 1. Summary	of Spectroscopic,	Structural, and	Electrochemical Data
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	1	2a	2b	3a	4	5
¹³ C NMR (ppm) ^a	268.4	244.0	230.3	222.6	88.9, 184.1 ^d	202.1
$\nu_{\rm CO} (\rm cm^{-1})^{b}$ $E_{\rm VCO} (\rm V)^{c}$	1681	1669 + 0.84	1676 + 0.84	1699, 2002, 2070 ^e	1663, 1675	1715
$E_{\rm pa}({\rm V})^c$		1 0.04	0.04	+ 1.27		
N-C-N (deg) M-C (Å)	122.6(2)	119.7(5) 2.051(6)	119.7(4) 2.043(4)	122.9(3) 2.093(3)	118.05(14)	123.4(2) 2.002(3)
av C _{acvl} =O (Å)	1.209	1.211	1.210	1.202	1.221	1.204
av N-C _{carbene} (Å)	1.354	1.366	1.381	1.355	1.435	1.355
av N-C _{acyl} (Å)	1.423	1.431	1.416	1.430	1.384	1.449

 a13 C NMR spectra were obtained in C₆D₆ (1 and 4) or CD₂Cl₂ (2, 3, and 5), and the listed value corresponds to the carbene nucleus in the respective compound or complex. b IR data obtained in KBr matrices. c Electrochemical analyses were obtained in dry CH₂Cl₂ with 0.1 M *n*Bu₄NPF₆ electrolyte using a 100 mV s⁻¹ scan rate and referenced to saturated calomel electrode (SCE). d The first and second values correspond to the carbenoid (*C*CN) and ketenoid (*C*CN) signals, respectively. e The three values represent the DAC and the Rh *trans*- and *cis*-carbonyl groups, respectively.

known DACs (1709–1714 cm⁻¹, KBr),^{6b,7a} the IR spectrum of 1 revealed a $\nu_{\rm CO}$ at 1681 cm⁻¹ (KBr), which was consistent with the $\nu_{\rm CO}$ values typically displayed by amides.

To obtain additional structural information, single crystals of **1** were grown from a saturated C_6D_6 solution and subjected to an X-ray diffraction analysis. As shown in Figure 2, the N-C-N angle measured in **1** (122.6(2)°) was significantly wider than the analogous angle measured in **IIIa** (114.83(19)°)^{6b} and nearly 2° more obtuse than the widest N-C-N angle for any NHC reported to date (1,3-neopentylferrocenophan-2-ylidene: 120.5°).¹² In addition, the obtuse N-C-N angle observed in the solid-state structure of **1** supported the aforementioned ¹³C NMR data, which indicated that the carbene nucleus was effectively more shielded when compared to its six-membered analogue (i.e., **IIIa**).

Coordination Chemistry and Assessment of the Ligand Donating Properties of DAC 1. Upon the synthesis and characterization of 1, its coordination chemistry was explored. Initial efforts were directed toward the preparation of the M(cod)(1)Cl and $M(CO)_2(1)Cl$ complexes (cod = 1,5-cyclooctadiene; M = Rh or Ir), because related complexes containing NHCs are often stable and have been used to compare to other ligands reported in the literature.¹³ As shown in Scheme 2, combination of DAC 1 with 0.5 molar equiv of $[Rh(cod)(Cl)]_2$ in toluene resulted in the precipitation of 2a, which was isolated via filtration in 61% yield as a brick red solid. The ¹H NMR spectrum of **2a** displayed signals at δ = 7.14 and 6.99 ppm as well as δ = 2.59, 2.39, and 2.16 ppm (CD₂Cl₂), which were assigned to inequivalent mesityl aryl-CH and methyl groups, respectively. Consistent with other [Rh(cod)Cl] complexes supported by seven-membered NHCs, the inequivalency of the mesityl substituents observed in 2a was presumably due to increased steric encumbrance at the carbene nucleus imposed by $1.^{9d,e,g,l,m}$ In support of



Figure 2. ORTEP representation of 1, rendered using POV-ray, with 50% thermal ellipsoids and H atoms and solvent molecules omitted for clarity. Distances (Å) and angles (deg): C1-N1, 1.3536(17); N1-C2, 1.423(2); C2-O1, 1.209(2); N1-C1-N1A, 122.6(2); C1-N1-C2, 136.35(13); N1-C2-O1, 117.43(14).

this assessment, a ¹³C NMR signal assigned to the carbene nucleus was observed at $\delta = 243.9$ ppm (¹ $J_{Rh-C} = 47.98$ Hz; CD₂Cl₂), a value upfield from the analogous signal exhibited by free DAC **1** (268.7 ppm, C₆D₆) and downfield by approximately 20 ppm from the analogous signals exhibited by known [Rh(cod)Cl] complexes supported by NHCs ($\delta = 180.6-225.8$ ppm; $J_{RhC} = 41-76$ Hz).^{9g,13a,13c,13d,14} However, the low-field signal assigned to the carbenoid nucleus in **2a** is consistent with the analogous signal displayed by a [Rh(cod)Cl] complex supported by **IIIa** ($\delta = 245.2$ ppm; d, ¹ $J_{Rh-C} = 49.1$ Hz; CDCl₃).^{7c} The IR spectrum of **2a** revealed a $\nu_{CO} = 1669$ cm⁻¹

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Scheme 2. Synthesis of 2 and 3^a



^{*a*}Conditions: (*i*) [M(cod)Cl]₂, C₇H₈, 25 °C, 16 h; (*ii*) 1 atm CO(g), CH₂Cl₂, 25 °C, 30 min. M = Rh or Ir. Isolated yields where applicable are indicated.

(KBr), a lower energy compared to the analogous signal exhibited by [Rh(cod)(IIIa)Cl]) ($\nu_{CO} = 1719 \text{ cm}^{-1}$; KBr), reflecting the greater amide-like character in the former.^{7c}

Crystals of 2a suitable for X-ray diffraction analysis were obtained by vapor diffusion of *n*-pentane into a saturated CH₂Cl₂ solution. As shown in Figure 3, the DAC ligand occupied a coordination site cis to the chloride ligand and was nearly orthogonal to the metal-ligand plane (dihedral angle = $84.7(5)^{\circ}$), features that are consistent with the solid-state structures of known NHC-Rh(cod)Cl complexes.^{9g,13a,13c,13d,14} In contrast to previously reported sevenmembered NHC-supported [M(cod)Cl] complexes, which feature large C_{Ar} -N···N- C_{Ar} torsion angles α (see Scheme 4) of 15.9-46.0°, ^{9d,e,g,l,m} the α measured in the solid-state structure of 2a was 9.8°.¹⁵ This relatively acute angle was surprising given the obtuse N-C-N angle observed in the solidstate structure of 1. As such, we reasoned that the steric congestion about the carbene nucleus was not significantly increased upon coordination to the rhodium center, particularly when compared to known seven-membered NHCsupported [Rh(cod)Cl] complexes.^{9d,e,g,l,m} Regardless, the N-C-N angle measured for $2a (119.7(5)^\circ)$ agreed well with analogous angles measured in known seven-membered NHCsupported [M(cod)Cl] complexes (118.7-122.3°).9d,g,l,m To investigate the steric properties of 1 further, its percent buried volume $(\% V_{bur})^{16}$ was calculated from the solid-state structure of 2a and compared to analogous complexes. Using the method developed by Cavallo, 16b,c the % V_{bur} of 1 was calculated^{16d} at 41.2%, which is significantly greater than the analogous values reported for 1,3-dimesitylimidazol-2-ylidene $(33.5\%)^{16a}$ and DAC IIIa $(38.4\%)^{7c}$ as well as the sevenmembered NHC IV (40.6%; Ar = mesityl).^{9g}

As noted above, 2a (M = Rh) precipitated during the course of its synthesis, which facilitated its isolation. The Ir congener 2b, however, could not be isolated cleanly under similar conditions, and its formation was concomitant with an unidentified decomposition product. It was empirically determined that the purity and isolated yield of the desired product significantly improved when the metalation reaction was conducted in the absence of light.¹⁷ In particular, if the metalation reaction was carried out using toluene



Figure 3. ORTEP representation of **2a**, rendered using POV-ray, with 50% thermal ellipsoids and H atoms and solvent molecules omitted for clarity. Relevant distances (Å) and angles (deg): C1–Rh1 2.051(6), Rh1–Cl1 2.3822(17), N1–Cl 1.375(7), N2–Cl 1.356(7), N1–C2 1.433(7), N2–C5 1.429(7), C2–O1 1.208(7), C5–O2 1.214(7), N1–C1–N2 119.7(5), C1–N1–C2 132.7(5), C1–N2–C5 132.6(5), N1–C2–O1 117.6(6), N2–C5–O2 118.7(6).



Figure 4. Illustration describing torsion angle α .

as a solvent at room temperature in a foil-wrapped vial, the ¹H NMR spectrum (CD₂Cl₂) of the crude reaction mixture obtained after 16 h revealed the formation of **2b** as the major product (with ca. 90% purity; 85% isolated yield).

The NMR spectral data recorded for 2b were nearly identical to that obtained for 2a, and inequivalent ¹H NMR resonances assigned to the mesityl substituents were observed ($\delta = 7.14$ and 6.99 ppm for the aryl-CH groups and $\delta = 2.59$, 2.39, and 2.16 ppm for the methyl protons; CD₂Cl₂). Similar to the conclusions derived when [Ir(cod)-(IIIb)Cl] ($\delta = 231.3$ ppm, C₆D₆)^{7a} was analyzed by ¹³C NMR spectroscopy, the signal assigned to the carbene nucleus in 2b $(\delta = 230.3 \text{ ppm}, \text{CD}_2\text{Cl}_2)$ resonated downfield from analogous signals exhibited by NHC-supported [Ir(cod)Cl] complexes $(\delta = 179.6 - 208.2 \text{ ppm})$, likely due to the electron-withdrawing nature of the carbonyl groups of the respective DAC ligands.^{9g,13a,13c,13d,14} The IR spectrum of **2b** exhibited a $v_{\rm CO} = 1676 \text{ cm}^{-1}$ (KBr), which was consistent with the signal measured for 2a, but at a lower frequency than that exhibited by [Ir(cod)(IIIb)Cl] ($\nu_{CO} = 1711 \text{ cm}^{-1}$), again correlating with the greater amide-like character of the seven-membered NHC in the former.7a

⁽¹⁵⁾ The torsion angle α is $\sim 0^{\circ}$ in the X-ray crystal structures of known seven-membered NHCs as well as DAC 1.^{9d,e,g,l,m}

^{(16) (}a) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 841–861. (b) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, 1759–1766. (c) http://www.molnac. unisa.it/OMtools/sambvca.php. (d) The %V_{Bur} values were calculated with Bondi radii scaled by 1.17, 3.5 Å radius of the sphere, and a $M-C_{carbene}$ distance of 2.00 Å.

⁽¹⁷⁾ For an example of an Ir(I) complex that was shown to decompose photochemically see: Dahlenburg, L.; Ernst, M.; Dartiguenave, M.; Dartiguenave, Y. J. Organomet. Chem. **1993**, 463, C8–C10.

Article

Crystals of 2b that were suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of n-pentane into a saturated CH₂Cl₂ solution. As shown in Figure 5, complex 2b was found to be isostructural with 2a, where the DAC ligand in the former was oriented orthogonal to the Ir-square plane (dihedral angle = $85.6(3)^\circ$) and a nearly linear (8.0°) torsion angle α was observed. Additionally, the N-C-N angle measured in the solid-state structure of **2b** (119.7(7)°) was nearly identical to that measured in **2a** $(119.7(5)^{\circ})$, both of which were in accord with analogous metal complexes containing seven-membered NHCs (118.7-122.3°).9d,e,g,l,m From these crystallographic data, we concluded that a significant amount of steric strain was not enforced to the carbene upon metalation of 1, as evidenced by the relatively acute N-C-N (compared to 1) and acute α angles measured in the aforementioned solid-state structures of 2a and 2b.

To gauge the donicity of DAC 1 in greater detail, efforts were directed toward converting the aforementioned [M(cod)(1)Cl] complexes into their corresponding dicarbonyl complexes. The Rh dicarbonyl complex 3a was prepared in excellent yield (98%) by sparging a CH₂Cl₂ solution of **2a** with CO(g) for 30 min (Scheme 2). Complex 3a was found to be stable at room temperature for extended periods of time,¹⁸ which facilitated its characterization. Single crystals were obtained by slow vapor diffusion of n-pentane into a saturated CH₂Cl₂ solution and subjected to an X-ray diffraction analysis, thus enabling more detailed structural confirmation. As shown in Figure 6, the square-planar geometry of the Rh center in 3a was conserved upon carbonylation, with the DAC oriented perpendicular to the metal-ligand plane (dihedral angle = $89.2(2)^{\circ}$). Consistent with **2a** and **2b**, the steric constraint enforced on the carbene in 3a was not significant when compared to other seven-membered NHCs, as evidenced by the linear torsion angle α observed (0.0°).

Upon synthesis and solid-state characterization of 3a, efforts shifted toward examining this complex using a variety of spectroscopic and electrochemical techniques. The ¹³C NMR signal attributed to the carbene nucleus in 3a was observed at $\delta = 222.6$ ppm (${}^{1}J_{\text{Rh-C}} = 43.6$ Hz, CD₂Cl₂), a value intermediate of the analogous signals observed for 2a ($\delta =$ 244.9 ppm, ${}^{1}J_{Rh-C} = 47.98$ Hz; CD₂Cl₂) and other NHCsupported [Rh(CO)₂Cl] complexes ($\delta = 186.2-206.2$ ppm, ${}^{1}J_{Rh-C} = 37.7-53.8$ Hz, CD₂Cl₂).^{9d,g,i,14} The relatively downfield chemical shift exhibited by the carbene nucleus in 3a compared to its NHC analogues may be attributed to the electron-withdrawing carbonyl groups. In contrast, the ¹³C NMR signals assigned to the CO ligands in **3a** were observed at $\delta = 186.0$ ppm (${}^{1}J_{Rh-C} = 55.4$ Hz) and 182.7 ppm (${}^{1}J_{Rh-C} = 76.6$ Hz), and were in agreement with those recorded for other NHC complexes containing seven-membered NHCs and DACs ($\delta = 184.0-188.2 \text{ ppm}$, ${}^{1}J_{\text{Rh-C}} = 42.3-54.7 \text{ Hz}$ and $\delta = 182.0-184.9 \text{ ppm}$, ${}^{1}J_{\text{Rh-C}} = 72.7-75.5 \text{ Hz}$, respectively). Collectively, these data suggested to us that while the DAC ligand exhibited a downfield-shifted ¹³C NMR resonance for the carbene nucleus, it did not sufficiently perturb the metal's electron density to alter the ¹³C NMR resonances attributed to the carbonyl ligands and was more akin to known seven-membered carbenes in this regard.9d,g,i,14



Figure 5. ORTEP representation of **2b**, rendered using POV-ray, with 50% thermal ellipsoids and H atoms omitted for clarity. Relevant distances (Å) and angles (deg): C1–Ir1 2.043(4), Ir1–Cl1 2.3807(12), N1–C1 1.375(6), N2–C1 1.387(5), N1–C2 1.422(6), N2–C5 1.409(6), C2–O1 1.209(6), C5–O2 1.211(6), N1–C1–N2 119.7(4), C1–N1–C2 132.5(4), C1–N2–C5 132.8(4), N1–C2–O1 117.5(4), N2–C5–O2 118.4(4).

The IR spectrum of 3a revealed two distinct carbonyl stretching frequencies at $v_{\rm CO} = 2070$ and 2002 cm^{-1} (KBr), which were assigned to the *trans*- and *cis*-carbonyl moieties, respectively.¹⁹ These values correlated well with other known NHC-rhodium carbonyl complexes (*trans*: 2057–2093 cm⁻¹, *cis*: 1984–2006 cm⁻¹).^{9d,g,i,14} Using methods developed by Plenio and Nolan,^{13a,b,f} the average $\nu_{\rm CO}$ (2036 cm⁻¹) was used to calculate a Tolman electronic parameter (TEP) of 2048 cm⁻¹ for DAC 1. This value was in agreement with the TEP (2051 cm⁻¹) calculated for 1 from 3b ($\nu_{\rm CO} = 2066$ and 1984 cm⁻¹; average $\nu_{\rm CO} = 2025$ cm⁻¹), which was prepared in situ (by treating 2b with CO(g) in the absence of light). On the basis of these calculated TEP values, DAC 1 appeared to be a stronger donor than IIIa (TEP = 2055 cm^{-1})^{7c} as well as 1,3-dimesitylimidazol-2-ylidene (IMes) and its saturated analogue 1,3-dimesitylimidazolin-2-ylidene (SIMes) (TEP = 2050.7 and 2051.5 cm⁻¹, respectively),^{14b} but not as strong as II (TEP = 2041 cm⁻¹)^{10a} or other known seven-membered NHCs (e.g., IV: TEP = 2043 cm⁻¹).^{9d} These results could be considered surprising given that the electron-withdrawing carbonyl groups should decrease the carbene donicity; however, the observed donicity for 1 supported our hypothesis that increasing the DAC ring size from six to seven atoms increased its ligand donicity and, by extension, its nucleophilicity (vide infra).6a,20

⁽¹⁸⁾ Over a period of approximately 2 days, **3a** was found to change from pale yellow to dark green. Although the identity of this discolored species was not identified, subsequent treatment with CO resulted in reformation of the desired [Rh(CO)₂(1)Cl] complex (**3a**).

⁽¹⁹⁾ Because there is no symmetry operation that exchanges the two carbonyl ligands in $(NHC)MX(CO)_2$ -type complexes, there is no projection operator that mediates combination. Hence, the carbonyl ligands cannot be coupled and must be energetically independent. For similar reasons, the use of symmetric/asymmetric nomenclature to describe these complexes is not advised.

^{(20) (}a) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239–2246. (b) Herrmann, W. A.; Mihalios, D.; Ofele, K.; Kiprof, P.; Belmedjahed, F. *Chem. Ber. Recl.* **1992**, *125*, 1795–1799.



Figure 6. ORTEP representation of **3a**, rendered using POV-ray, with 50% thermal ellipsoids and H atoms omitted for clarity. Relevant distances (Å) and angles (deg): C1–Rh1 2.093(3), Rh1–Cl1 2.3420(10), Rh1–Cl0 1.883(4), Rh1–Cl1 1.846(4), C10–O3 1.113(5), C11–O4 1.117(5), N1–C1 1.355(2), N1–C2 1.430(3), C2–O1 1.202(3), N1–C1–N2 122.9(3), C1–N1–C2 133.1(2), N1–C2–O1 117.6(2).

Despite its widespread use in organometallic chemistry for the pseudoquantification of NHC electron-donating ability, the synthesis of [(NHC)M(CO)₂Cl] complexes and measurement of their respective $\nu_{\rm CO}$ values is an indirect measure of NHC donicity.²¹ Moreover, the measured NHC donicity via the determination of its TEP can be influenced by transdirecting ligands, whereby the carbonyl trans to the ligand of interest will experience a weakening of the metal-carbon bond (and thus attenuation of π -back-bonding), independent of the electron-richness of the metal. To complement the IR spectroscopic analyses and to circumvent the inherent limitations thereof, we performed cyclic voltammetry (CV) of the [M(cod)Cl] complexes supported by 1 (see Figure 7 and Table 1). The $Rh^{I/II}$ couple in **2a** was measured at 0.84 V vs SCE,²² which is below the range of values previously observed in NHC-supported [Rh(cod)Cl] complexes (ca. +1.0 V).¹⁴ Similarly, the Ir^{1/II} couple in **2b** was also measured at 0.84 V and was within the range of values previously observed in NHC-supported [Ir(cod)Cl] complexes (0.65-0.92 V).²³ Replacing the cod ligand with two carbonyl ligands afforded a significant anodic shift in the Rh^{I/II} and Ir^{I/II} oxidation potentials in complexes 3a and 3b (the latter was prepared in situ by bubbling CO(g) into the electrochemical cell after obtaining the CV for **2b**).²⁴ The carbonyl complexes exhibited irreversible oxidation processes ($E_{pa} = 1.27$ and 1.90 V for 3a and 3b, respectively) but were within the range

Scheme 3. Synthesis of Diamidoketenimine 4^a



^{*a*} Conditions: (*i*) C=N-2,6-(Me)₂-C₆H₃, C₇H₈, 25 °C, 4 h. Isolated yield indicated.

of values observed for other NHC-supported $[M(CO)_2Cl]$ complexes (0.88–1.16 V).^{14b} Regardless, we concluded from the collective electrochemical data that the coordination of 1 to a transition metal renders the metal more electron rich when compared to analogous complexes supported by sixmembered analogues III, a result consistent with the former being a relatively stronger electron donor.

Exploring the Reactivity of DAC 1: Applications in Small-Molecule Activation. Having evaluated the ligand donicity of 1 and finding that this carbene is a stronger donor than previously reported DACs, we next turned our attention to utilizing 1 to activate small molecules. Recent results from our group have shown that DACs are effective at engaging in coupling reactions with nucleophilic substrates such as organic isocyanides.^{6b,7b} Indeed, these coupling reactions have led to the synthesis and characterization of the first N,N'-diamidoketenimines, which are thermally robust and crystalline materials. Given that DACs react with nucleophilic isocyanides, whereas more typical imidazol-2-ylidenes do not, we believe that the enhanced electrophilicities of DACs makes them susceptible to nucleophilic attack.^{6b,7b}

To test whether 1 engaged in comparable nonvlidenetype reactivities, we explored its reaction with an organic isocyanide. As shown in Scheme 3, treatment of a toluene solution of 1 with 2,6-dimethylphenylisocyanide resulted in a color change from bright orange to yellow, and the desired N,N'-diamidoketenimine 4 was obtained in excellent yield (92%) upon removal of the solvent after 4 h. The ¹H NMR spectrum of 4 revealed the resonances expected for the desired product. Whereas the signal corresponding to the methyl groups at the 2,6-positions for the isocyanide aryl group appeared as a sharp singlet ($\delta = 1.84$ ppm; C₆D₆), the mesityl methyl groups resonated as broad signals (δ = 2.02-2.29 ppm; C₆D₆), indicative of steric congestion about the ketenimine fragment. Additionally, the ¹³C NMR spectrum of **4** revealed diagnostic signals at $\delta = 88.90$ and 184.07 ppm (C_6D_6), which were assigned to the carbenoid (CCN) and ketenoid (CCN) nuclei of diamidoketenimines, respectively.^{6b,7b} The IR spectrum of 4 exhibited a signal at 2015 cm⁻¹, as expected for the ketenimine stretching mode ($\nu_{C=C=N}$, KBr), as well as bands at 1675 and 1663 cm⁻¹, which were assigned to the amide carbonyl stretching modes.

Whereas X-ray diffraction analysis confirmed the structure of **4** (see Figure 8), a torsion angle $\alpha = 44.5^{\circ}$ was measured, which deviated significantly from the analogous angles measured in the solid-state structures of the Rh and Ir complexes **2a**, **2b**, and **3a** ($\alpha = 9.8^{\circ}$, 8.0°, and 0.0°, respectively). The disparity in the torsion angles may be explained by the C1–E distance (where E = a carbon atom or a metal atom). In the case of **4**, the C1–C2 distance was measured to be 1.323(2) Å (consistent with the formation of a C=C double bond of a ketenimine),^{6b,7b} which is nearly 0.8 Å shorter than

⁽²¹⁾ For efforts detailing the use of ¹³C NMR spectroscopy to determine NHC donor strength see: Huynh, H. V.; Han, Y.; Jothibasu, R.; Yang, J. A. *Organometallics* **2009**, *28*, 5395–5404.

⁽²²⁾ All potentials were referenced to SCE.

 ^{(23) (}a) Tennyson, A. G.; Rosen, E. L.; Collins, M. S.; Lynch, V. M.;
 Bielawski, C. W. *Inorg. Chem.* 2009, *48*, 6924–6933. (b) Leuthäusser, S.;
 Schwarz, D.; Plenio, H. *Chem.*—*Eur. J.* 2007, *13*, 7195–7203.

⁽²⁴⁾ The electrochemical analysis of 3b was obtained *in situ*, as we were unable to isolate this complex without decomposition.



Figure 7. CVs of (A) [Rh(cod)(1)Cl] (2a); (B) [Rh(CO)₂(1)Cl] (3a); (C) [Ir(cod)(1)Cl] (2b); and (D) [Ir(CO)₂(1)Cl] (3b). Electrochemical analyses were obtained in dry CH₂Cl₂ with 0.1 M nBu_4NPF_6 electrolyte using a 100 mV s⁻¹ scan rate and referenced to saturated calomel electrode (SCE) by shifting (Fc*)^{0/+} to -0.057 V.²⁵.



Figure 8. ORTEP representation of **4**, rendered using POV-ray, with 50% thermal ellipsoids and H atoms and solvent molecules omitted for clarity. Relevant distances (Å) and angles (deg): C1–N1 1.429(2), C1–N2 1.440(2), C1–C2 1.323(2), C2–N3 1.217(2), N1–C3 1.375(2), N2–C6 1.392(2), C3–O1 1.224(2), C6–O2 1.218(2), N1–C1–N2 118.05(14), C1–C2–N3 165.52(17), C1–N1–C3 119.58(14), C1–N2–C6 119.61(14), N1–C3–O1 122.50(15), N2–C6–O2 120.99(16).

the analogous distances observed in the solid-state structures of **2a**, **2b**, and **3a** (C1–Rh1 = 2.051(6) Å, C1–Ir1 = 2.043(4) Å, and C1–Rh1 = 2.093(3) Å, respectively). Thus, a more obtuse torsion angle α may be required to alleviate steric congestion in the ketenimine. Regardless, the NCO fragments in **4** exhibited short N–C_{acyl} distances concomitant with long C_{acyl}–O distances (N1–C3 = 1.375(2) Å, C3–O1 = 1.224(2) Å, N2–C6 = 1.392(2) Å, C6–O2 = 1.218(2) Å) and were consistent with the IR data, which indicated that these groups are characteristic of prototypical amides.

Because carbon monoxide (CO) is isolobal to isocyanides, we next investigated whether 1 could react with CO to generate the respective N,N'-diamidoketene (structure not shown).^{6b,7a,8} Upon bubbling CO through a C₆D₆ (or C₇H₈) solution of 1, an instantaneous color change from dark orangered to yellow was observed. This color change was unexpected, as we have previously found that N,N'-diamidoketenes (prepared from **III**) are typically blue to purple.^{6b,7a} Regardless, an IR spectrum recorded for a toluene solution of DAC **1** treated with CO(g) revealed stretching frequencies at 2112 and 1729 cm⁻¹, which were consistent with the $\nu_{C=C=O}$ and $\nu_{C=O}$ stretching modes, respectively, measured for the ketene obtained from **IIIa** (2092 and 1681 cm⁻¹).^{6b} Although ¹H NMR analysis of the aforementioned reaction was also promising (broad signals were observed at $\delta = 7.92$, 7.75, 6.99, and 2.22 ppm; C₆D₆), attempts to isolate the desired product were unsuccessful.

In addition to exploring the ability of 1 to couple to an isonitrile and CO, efforts were also directed toward activating NH_3 and H_2 . Unlike the aforementioned results obtained with CO, our preliminary experiments, which involved treating solutions of 1 with NH_3 or H_2 , resulted predominately in the formation of unidentified decomposition products, even under forcing conditions (elevated temperatures and pressures of H_2 as high as 1000 psi). Collectively, these results suggested to us that while DAC 1 exhibited ylidene and carbene-like reactivities, the carbene or its adducts also engaged in reactions that led to decomposition, an indicator of a loss of controlled reactivity.

Exploring the Potential for DAC 1 to Support Catalytically Active Complexes. Given that DAC 1 exhibited a unique set of steric and electronic properties when compared to known seven-membered diaminocarbenes as well as other DACs, efforts shifted toward investigating its use as a ligand in a catalytically active NHC complex. Preliminary efforts were directed toward gold complexes supported by NHCs, such as IPr-AuCl (IPr = 1,3-(2,6-diisopropylphenyl)imidazol-2ylidene), which have recently been shown to catalyze a variety of chemical reactions, ranging from the hydration of alkynes to the carboxylation of arenes.²⁶ As shown in Scheme 4, treatment of a solution of 1 in toluene with stoichiometric

⁽²⁵⁾ Noviandri, I.; Brown, K. N.; Fleming, D. S.; Gulyas, P. T.; Lay, P. A.; Masters, A. F.; Phillips, L. J. Phys. Chem. B 1999, 103, 6713–6722.

Scheme 4. Synthesis of DAC Gold(I) Chloride Complex 5^{a}



^{*a*} Conditions: (*i*) THT–AuCl (THT = tetrahydrothiophene), C_7H_8 , 25 °C, 2 h. Isolated yield indicated.

[Au(THT)Cl] (THT = tetrahydrothiophene) resulted in the immediate precipitation of the desired DAC-AuCl complex (5) in near-quantitative yield as a pale yellow solid. Complex 5 was found to be thermally stable (mp 216-220 °C, dec) and could be stored and manipulated under ambient conditions without detriment. In contrast to the aforementioned Rh and Ir complexes containing 1, the ¹H NMR spectrum of 5 (CD₂Cl₂) exhibited equivalent mesityl substituents in solution at 25 °C, indicating relatively minimal steric congestion at the carbene nucleus. Upon coordination of [AuCl], the ¹³C NMR signal assigned to the carbene nucleus significantly shifted upfield from $\delta = 268.4$ ppm (C₆D₆) in 1 to 202 ppm (CD_2Cl_2) in 5, consistent with analogous signals observed in other known NHC-supported AuCl complexes ($\delta = 166$ – 195 ppm).²⁷ To confirm the structure of 5, single crystals suitable for an X-ray diffraction analysis were obtained by slow evaporation of a saturated CH₂Cl₂ solution. As shown in Figure 9, the solid-state structure of 5 was found to be isostructural with reported NHC-supported [AuCl] complexes, with a nearly linear C_{DAC}-Au-Cl angle (179.29(8)°) and C-Au and Au-Cl distances (2.002(3) and 2.2828(7) Å, respectively) that were within range (1.942-1.998 and 2.275-2.306 Å).²⁷

Upon the synthesis and characterization of 5, efforts then shifted toward studying its catalytic activity. To explore the potential of 5 as a viable catalyst for the hydration of terminal alkynes in a manner similar to other known complexes,^{26f,g} the hydration of phenylacetylene in the presence of 2 mol % of 5 under a variety of conditions was explored (see eq 1). Using a previously reported procedure, 1 mmol of phenylacetylene in methanol (2.5 mL) was treated with solid 5 (0.02 mmol) followed by the addition of water (2.5 mL).^{26f} The resulting solution was then heated to 80 °C in a 40 mL Teflon-capped vial for 3 h. A ¹H NMR spectrum (CD₂Cl₂) of the crude reaction mixture recorded after removal of solvent revealed the formation of the desired product, albeit in low yield (\sim 36%), which was accompanied with starting material and a minor amount ($\sim 2\%$) of an unidentified product (presumably due to catalyst decomposition, as the formation of a gold mirror was observed). To explore conditions that resulted in minimal catalyst decomposition, the hydration reaction was repeated at various temperatures. Although



Figure 9. ORTEP representation of **5**, rendered using POV-ray, with 50% thermal ellipsoids and H atoms omitted for clarity. Relevant distances (Å) and angles (deg): C1–Au1 2.002(3), Au1–Cl1 2.2828(7), N1–Cl 1.358(4), N2–Cl 1.352(4), N1–C2 1.443(4), N2–C5 1.454(4), C2–Ol 1.205(4), C5–O2 1.203(4), C1–Au1–Cl1 179.29(8), N1–Cl–N2 123.4(2), C1–N1–C2 132.4(2), C1–N2–C5 132.2(2), N1–C2–Ol 117.7(3), N2–C5–O2 118.2(3).

negligible formation of acetophenone (<5% yield by gas chromatography) was observed at temperatures at or below 25 °C and catalyst decomposition was observed at temperatures above 40 °C, the best results were obtained when the reaction was performed at 80 °C for 12 h, which afforded acetophenone in good yield (78%).

$$\underbrace{ \begin{array}{c} \hline \\ \hline \\ \end{array}} \underbrace{ \begin{array}{c} 5 (2 \text{ mol } \%) \\ \hline \\ MeOH / H_2O \\ 25 - 80 \text{ °C} \end{array}} \underbrace{ \begin{array}{c} O \\ \hline \\ \end{array}} (1)$$

Conclusions

In summary, we have synthesized and characterized the first example of a seven-membered N,N'-diamidocarbene (1). X-ray crystallographic analysis revealed that this carbene contained the widest N-C-N angle (122.6(2)°) reported to date as well as a large calculated $\% V_{bur}$ (41.2%). However, various Rh and Ir metal complexes supported by 1 exhibited acute torsion angles ($\alpha < 10^{\circ}$), which are atypical for analogous complexes supported by seven-membered NHCs and may reflect minimal steric constraint being enforced on the carbene upon metalation. Electrochemical and IR spectroscopic analyses of 2a, 2b, and 3a revealed that DAC 1 is a stronger electron donor than six-membered analogues (III) as well as IMes and SIMes. While coupling of 1 to 2,6-dimethylphenylisocyanide afforded the N,N'diamidoketenimine 4 as a thermally robust, crystalline compound, treatment of 1 with CO, NH₃, or H₂ resulted in the formation of decomposition products. Hence, the unique steric and electronic properties inherent to DAC 1 appeared to result in a loss of controlled reactivity toward many small molecules. Conversely, DAC 1 was successfully used to support a catalytically active Au(I) complex, which was shown to facilitate the hydration of phenylacetylene to acetophenone in good yield. We conclude from these studies that modulating the ring size effectively alters orbital hybridization at the carbene nucleus and the attendant singlet-triplet gap, and

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^{(27) (}a) de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411–2418. (b) Gaillard, S.; Slawin, A. M. Z.; Bonura, A. T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2010**, *29*, 394–402.

that the ring size of cyclic carbenes is an important variable to consider in determining carbene character and reactivity (i.e., ylidene vs carbene). As such, new discoveries may result from further detailed investigations of the structure reactivity relationship of cyclic carbenes as a function of their ring size.

Experimental Section

General Considerations. All procedures were performed using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glovebox unless otherwise noted. N,N'-Dimesitylformamidine was synthesized using previously reported procedures.²⁸ Phthaloyl chloride and 2,4,6-trimethylaniline were obtained from TCI America and used as received. Triethylorthoformate and 2,6-dimethylphenylisocyanide were purchased from Alfa Aesar and used as received. Sodium bis-(trimethylsilyl)amide (NaHMDS) was purchased from ACROS and used as received. [Rh(cod)Cl]₂ and [Ir(cod)Cl]₂ were obtained from Strem Chemical and used as received. THT-AuCl (THT = tetrahydrothiophene) was prepared as previously described.²⁹ Benzene was dried over molecular sieves and distilled prior to use. Dichloromethane (CH₂Cl₂), hexanes, and toluene were dried and degassed by a Vacuum Atmospheres Company solvent purification system and stored over molecular sieves in a nitrogen-filled glovebox. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FTIR spectrophotometer. UV-visible spectra were recorded using a Perkin-Elmer Lambda 35 UV/vis spectrophotometer. High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E instrument (CI). NMR spectra were recorded on Varian UNITY+ 300, Varian Mercury 400, and Varian INOVA 500 spectrometers. Chemical shifts (δ) are given in ppm and are referenced to the residual solvent (¹H: CDCl₃, 7.24 ppm; C₆D₆, 7.15 ppm; C₇D₈, 2.09 ppm; ¹³C: CDCl₃, 77.0 ppm; C₆D₆, 128.0 ppm, C₇D₈, 128.3 ppm). Elemental analyses were performed at Midwest Microlab, LLC (Indianapolis, IN). Melting points were obtained using a Mel-Temp apparatus and are uncorrected.

Electrochemistry. Electrochemical experiments were conducted on CH Instruments electrochemical workstations (series 660D) using a gastight, three-electrode cell under an atmosphere of dry nitrogen. The electrochemical cells employed were equipped with gold working, tungsten counter-, and silver quasi-reference electrodes. Measurements were performed in dry CH₂Cl₂ with 0.1 M *n*Bu₄NPF₆ electrolyte and decamethylferrocene (Fc^{*}) internal standard. Data deconvolution and fitting were performed with the Origin 8.0 software package. All reported potentials were determined at 100 mV s⁻¹ scan rate and referenced to saturated calomel electrode (SCE) by shifting (Fc^{*})^{0/+} to -0.057 V (CH₂Cl₂).²⁵

Crystallography. All crystallographic measurements were carried out on a Rigaku Mini CCD area detector diffractometer using graphite-monochromated Mo K α radiation ($\alpha = 0.71073$ Å) at 150 K using an Oxford Cryostream low-temperature device. A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using DENZO-SMN.³⁰ The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinements on F_2 using the SHELXTL/PC package (version 5.1)³¹ allowed location of the remaining non-hydrogen

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atoms. Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for $1 \cdot (C_6H_6)$, $2a \cdot (CH_2Cl_2)$, 2b, 3a, $4 \cdot (C_6H_6)$, and 6 and were assigned as 782378, 782379, 782380, 782381, 782383, and 782382, respectively.

Synthesis of 1.HCl. Phthaloyl chloride (2.00 g, 9.85 mmol, 1.05 equiv) was added dropwise to a stirred solution of N,N'dimesitylformamidine (2.63 g, 9.38 mmol) and triethylamine (2.00 mL, 14.1 mmol, 1.50 equiv) in CH₂Cl₂ (100 mL) at 0 °C. The solution was stirred at 0 °C for 1 h, whereupon the volatiles were removed under reduced pressure. The resulting solid was taken up into toluene (100 mL), inducing the precipitation of triethylammonium chloride, which was then removed via filtration over a plug of dry Celite. After removal of the solvent under reduced pressure, the residue was washed with hexanes $(3 \times 50 \text{ mL})$. Subsequent drying of the residual solid under reduced pressure afforded the desired compound as an off-white solid (3.69 g, 88.1% yield). m.p.: 158-160 °C (dec). ¹H NMR (CDCl₃, 400.27 MHz): δ 2.13 (br s, 12H, Mes-o-CH₃), 2.26 (s, 6H, Mes-p-CH₃), 6.41 (s, 1H, NCHN), 6.90 (s, 4H, Ar-CH), 7.75 (m, 2H, Ar-CH), 8.11 (m, 2H, Ar-CH). ¹³C NMR (CDCl₃, 75.47 MHz): δ 19.28 (br s), 20.86, 85.33 (N-CHCl-N), 130.19, 130.92 132.40, 132.73, 135.51, 137.15, 138.64, 167.97 (C=O). IR (KBr): $\nu_{\rm CO} = 1672$ cm^{-1} . HRMS: [M]⁺ calcd for C₂₇H₂₇N₂O₂Cl: 446.1761, found 446.1757. Anal. Calcd for C₂₇H₂₇N₂O₂Cl: C, 72.55; H, 6.09; N, 6.27. Found: C, 72.49; H, 6.27; N, 6.17.

Synthesis of 1. A 20 mL vial was charged with 1 · HCl (250 mg, 0.561 mmol), NaHMDS (105 mg, 0.560 mmol), benzene (15 mL), and a stir bar. The solution was stirred at 25 °C for 30 min and then filtered through a PTFE filter. After removing the residual solvent under reduced pressure, the solid residue was washed with cold hexanes, decanted, and then dried under vacuum to afford the desired product as a yellow solid (195 mg, 84.9% yield). Single crystals suitable for an X-ray diffraction analysis were grown from a concentrated solution of 1 in C_6D_6 . m.p.: $75-77 \ ^{\circ}C$ (dec). ¹H NMR (C₆D₆, 400.27 MHz): δ 2.13 (s, 12H, Mes-o-CH₃), 2.14 (s, 6H, Mes-p-CH₃), 6.79 (s, 4H, Ar-CH) 7.02 (m, 2H, Ar-CH), 8.14 (m, 2H, Ar-CH). ¹³C NMR (C₆D₆, 75.47 MHz): δ 18.34, 20.94, 129.53, 130.49, 132.57, 133.82, 133.99, 136.69, 143.79, 165.56 (C=O), 268.42 (NCN). IR (KBr): $\nu_{CO} =$ 1681 cm^{-1} . HRMS: $[M + H]^+$ calcd for $C_{27}H_{27}N_2O_2 411.2073$, found 411.2069.

Synthesis of [Rh(cod)(1)Cl] (2a). A 20 mL vial was charged with a toluene (5 mL) solution of 1 (104 mg, 0.252 mmol) and a stir bar. To this solution was added a toluene solution (5 mL) of [Rh(cod)Cl]₂ (62.0 mg, 0.126 mmol). The color of the latter changed from bright orange to deep red upon mixing, and the resulting solution was stirred at 25 °C for 16 h. During the course of the reaction a red precipitate formed, which was isolated via decantation of the supernatant solution, washed with hexanes $(3 \times 5 \text{ mL})$, and dried under reduced pressure to afford the desired product (45.1 mg). The hexanes washes were added to the toluene mother liquor, and the combined solution was concentrated to dryness. The resulting residue was dissolved in dichloromethane (2 mL) and precipitated into a solution of hexanes (20 mL) under sonication. The precipitated solid was isolated via decantation, washed with hexanes $(3 \times 5 \text{ mL})$, and dried to afford the desired product as a brick-red solid (55.9 mg, combined yield: 101 mg, 61.2%). Single crystals suitable for an X-ray diffraction analysis were grown by slow vapor diffusion of *n*-pentane into a CH₂Cl₂ solution saturated with 2a. m.p.: 176-178 °C. ¹H NMR (CD₂Cl₂, 400.28 MHz): δ 1.38-1.52 (br s, 5H, COD-CH₂), 1.64–1.74 (br s, 3H, COD-CH₂), 2.16 (s, 6H, Mes-CH₃), 2.39 (s, 6H, Mes-CH₃), 2.59 (s, 6H, Mes-CH₃), 2.80-2.84 (br s, 2H, COD-CH), 4.58-4.64 (br s, 2H, COD-CH), 7.00 (s, 2H, Mes-CH), 7.14 (s, 2H, Mes-CH), 7.81-7.84 ¹³C NMR (m, 2H, Ar-CH), 7.91–7.94 (m, 2H, Ar-CH). (CD₂Cl₂, 125.59 MHz): δ 19.99, 21.01, 21.54, 27.79, 32.06, 75.34

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(d, ${}^{1}J_{\rm Rh-C} = 13.7$ Hz), 98.77 (d, ${}^{1}J_{\rm Rh-C} = 6.9$ Hz), 128.94, 130.65, 130.87, 131.64, 134.23, 136.80, 137.30, 139.20, 140.49, 166.81 (*CO*), 166.83 (*CO*), 243.95 (d, ${}^{1}J_{\rm Rh-C} = 47.98$ Hz, N*C*N). IR (KBr): $\nu_{\rm CO} = 1669$, 1718 cm⁻¹. HRMS: [M]⁺ calcd for C₃₅H₃₈N₂O₂ClRh 656.1677, found 656.1667. Anal. Calcd for C₃₅H₃₈N₂O₂ClRh: C, 63.98; H, 5.83; N, 4.26. Found: C, 63.62; H, 5.96; N, 3.95.

Synthesis of [Ir(cod)(1)Cl] (2b). A 20 mL vial wrapped in aluminum foil was charged with a toluene (5 mL) solution of 1 (47.6 mg, 0.116 mmol) and a stir bar. To this solution was added a toluene solution (5 mL) of [Ir(cod)Cl]₂ (39.0 mg, 0.0580 mmol). The resulting solution was stirred in the dark at 25 °C for 16 h. The resulting dark red solution was then transferred to a round-bottom flask that was wrapped in aluminum foil, and the solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane (1 mL) and added dropwise to *n*-pentane (35 mL) under sonication, which resulted in the precipitation of a dark orange solid. The solid was isolated by filtration, dissolved in dichloromethane (1 mL), and added dropwise to a sonicated solution of hexanes (35 mL), which resulted in the precipitation of the desired product as a redbrown solid, which was isolated by filtration (36.7 mg) The n-pentane and hexanes washes were combined and concentrated under reduced pressure. To the residue was added hexanes (40 mL), and the resulting suspension was sonicated for 1 h. The precipitated solid was collected via filtration and dried to yield an additional crop of the desired product as a red-brown solid (37.0 mg; combined yield: 73.7 mg, 84.8%). Single crystals suitable for an X-ray diffraction analysis were grown by slow vapor diffusion of n-pentane into a CH₂Cl₂ solution saturated with **2b**. m.p.: 205–208 °C (dec). ¹H NMR (CD₂Cl₂, 400.28 MHz): δ 1.31-1.42 (br s, 4H, COD-CH₂), 1.50-1.62 (br s, 4H, COD-CH₂), 2.21 (s, 6H, Mes-CH₃), 2.36 (s, 6H, Mes-CH₃), 2.43 (s, 6H, Mes-CH₃), 2.56-2.58 (br m, 2H, COD-CH), 4.39-4.41 (br m, 2H, COD-CH), 6.98 (s, 2H, Mes-CH), 7.05 (s, 2H, Mes-CH), 7.80-7.84 (br m, 2H, Ar-CH), 7.90-7.93 (br m, 2H, Ar-CH). ¹³C NMR (CD₂Cl₂), 125.59 MHz): δ 20.11, 20.99, 21.36, 27.94, 33.19, 60.27, 87.62, 128.69, 130.59, 130.60, 131.82, 134.12, 136.58, 137.04, 139.10, 139.86, 167.85 (CO), 230.27 (NCN). IR (KBr): $\nu_{CO} = 1676 \text{ cm}^{-1}$. HRMS: $[M - Cl]^+$ calcd for $C_{35}H_{38}$ -N2O2Ir 711.25570, found 711.25594. Anal. Calcd for C35.5H39-N₂O₂Cl₂Ir (**2b** • 0.5 CH₂Cl₂): C, 54.05; H, 4.98; N, 3.55. Found: C, 53.97; H, 5.41; N, 3.19.

Synthesis of [Rh(CO)₂(1)Cl] (3a). Carbon monoxide (CO) was bubbled through a solution of 1-Rh(cod)Cl (40.0 mg, 0.0611 mmol) in dichloromethane (5 mL) until the solvent had evaporated. The remaining light yellow residue was then dissolved in dichloromethane (0.5 mL) and added dropwise to a rapidly stirring solution of hexanes (20 mL), which resulted in the precipitation of a pale yellow solid. The solid was isolated via decantation of the supernatant solution, washed with hexanes $(3 \times 5 \text{ mL})$, and dried under reduced pressure to afford the desired product as a pale yellow solid (35.4 mg, 0.0591 mmol, 96.3% yield). Single crystals suitable for an X-ray diffraction analysis were grown by slow vapor diffusion of n-pentane into a CH₂Cl₂ solution saturated with 3a. m.p.: 113-115 °C (dec). ¹H NMR (CD₂Cl₂, 400.27 MHz): δ 2.18 (s, 6H, Mes-CH₃), 2.37 (s, 12H, Mes-CH₃), 6.98 (s, 2H, Mes-CH), 7.04 (s, 2H, Mes-CH), 7.90–7.94 (m, 2H, Ar-CH), 7.99–8.21 (m, 2H, Ar-CH). ¹³C NMR (CD₂Cl₂, 125.59 MHz): δ 19.13, 20.18, 21.20, 129.59, 130.10,

130.36, 131.48, 135.57, 135.67, 135.83, 135.88, 139.91, 140.63, 167.60 (ligand-CO), 167.62 (ligand-CO), 182.73 (d, ${}^{1}J_{Rh-C} =$ 76.61 Hz, Rh-CO), 185.95 (d, ${}^{1}J_{Rh-C} =$ 55.39 Hz, Rh-CO), 222.56 (d, ${}^{1}J_{Rh-C} =$ 43.58 Hz, NCN). IR (KBr): $\nu_{CO} =$ 1699, 2002, 2070 cm⁻¹. HRMS: [M – Cl]⁺ calcd for C₂₉H₂₆N₂O₄Rh 569.0948, found 569.0941. Anal. Calcd for C₂₉H₂₆N₂O₄ClRh: C, 57.58; H, 4.33; N, 4.63. Found: C, 57.55; H, 4.50; N, 4.59.

Synthesis of 4. An 8 mL vial was charged with toluene (5 mL), 2,6-dimethylphenylisocyanide (31.5 mg, 0.242 mmol), 1 (100 mg, 0.244 mmol), and a stir bar. The resulting mixture was stirred at 25 °C for 4 h. Removal of the residual solvent under reduced pressure afforded the desired product as a yellow solid (120 mg, 92.3% yield). Slow evaporation of a benzene solution of 4 afforded crystals suitable for X-ray diffraction analysis. m.p.: 164-166 °C. ¹H NMR (C₆D₆, 400.27 MHz): δ 1.84 (s, 6H, Ar-(CH₃)₂), 2.02 (s, 6H, Mes-*p*-CH₃), 2.00-2.28 (br s, 12H, Mes-o-CH3), 6.59-6.62 (m, 6H, Ar-CH), 6.69-6.72 (m, 1H, Ar-CH), 7.14 (m, 2H, Ar-CH), 8.31 (m, 2H, Ar-CH). ¹³C NMR (C₆D₆, 75.47 MHz): δ 18.76, 19.58 (br s), 20.75, 88.90 (CCN), 128.73, 129.03, 129.95 (br s), 131.42, 131.85, 133.75, 134.70, 137.43, 138.35, 170.30 (CO), 184.07 (CCN). IR (KBr): $\nu_{C=N} =$ 2015 cm^{-1} ; $\nu_{CO} = 1675$, 1663 cm^{-1} . HRMS: [M]⁺ calcd for $C_{36}H_{35}$ -N₃O₂ 541.2729, found 541.2733. Anal. Calcd for C₃₅H₃₆N₃O₂: C, 79.82; H, 6.51; N, 7.76. Found: C, 79.85; H, 6.62; N, 7.65.

Synthesis of [1-AuCl] (5). A vial was charged with a toluene (3 mL) solution of 1 (63.4 mg, 0.154 mmol) and a stir bar. To this solution was added a toluene suspension (3 mL) of THT-AuCl (THT = tetrahydrothiophene) (50.0 mg, 0.154 mmol). The latter solution changed color from bright orange to pale yellow (with some THT-AuCl present as a solid) upon mixing. Upon stirring, a yellow precipitate formed, resulting in a yellow suspension, which was stirred for 2 h at 25 °C. The precipitated product was then isolated via decantation of the supernatant solution. The resulting pale yellow solid was washed with hexanes $(3 \times 5 \text{ mL})$ and dried under reduced pressure to afford the desired product as a pale yellow powder (94.9 mg, 95.8%). Single crystals suitable for an X-ray diffraction analysis were grown by slow evaporation of a CH₂Cl₂ solution saturated with 7. m.p.: 216–220 °C (dec). ¹H NMR (CD₂Cl₂, 400.28 MHz): δ 2.21 (s, 12H, Mes-CH₃), 2.39 (s, 6H, Mes-CH₃), 7.08 (s, 4H, Mes-CH), 7.94–7.99 (m, 2H, Ar-CH), 8.08–8.13 (m, 2H, Ar-CH). ¹³C NMR (CD₂Cl₂, 125.59 MHz): δ 19.50, 21.27, 130.00, 130.25, 131.91, 134.68, 135.93, 140.22, 141.66, 167.69 (CO), 202.10 (NCN). IR (KBr): $\nu_{CO} = 1715$, 1729 cm⁻¹. HRMS: [M]⁺ calcd for C₂₇H₂₆N₂O₂ClAu 642.1348, found 642.1350. Anal. Calcd for $C_{27.5}H_{27}N_2O_2Cl_2Au$ (5.0.5CH₂Cl₂): C, 48.19; H, 3.97; N, 4.09. Found: C, 47.75; H, 3.95; N, 4.00.

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Supporting Information Available: X-ray crystallographic data in CIF format for compounds **1**, **2a**, **2b**, **3a**, **4**, and **5** as well as crystal tables and NMR spectra are available free of charge via the Internet at http://pubs.acs.org.