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Design of Sterically Demanding, Electron-Rich Carbene Ligands with the Perimidine Scaffold

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A family of *N*,*N'*-disubstituted perimidinium cation salts were employed as precursors to persistent monomeric carbenes with novel molecular architectures and electronic structures. Depending on the substituents, reaction of these 1,3-disubstituted perimidinium cations with $LiN(SiMe_3)_2$ led either to deprotonation and generation of new carbenes or to enetetramines. In addition to spectroscopic characterization, crystallographic analysis of $C_{10}H_6(^iPrN)_2C$ (**10**), $C_{10}H_6(^iPrN)(Me_3CCH_2N)C$ (**11**), $\{C_{10}H_6[N(3,5\text{-}Me_2C_6H_3)]_2C\}_2$ (**13**), and $C_{10}H_6(^iPrN)(3,5\text{-}Me_2C_6H_3N)C$ (**14**) definitively confirmed the nature of these species. The mixed benzyl/cycloheptyl-substituted carbene $C_{10}H_6(cyclo\text{-}C_7H_{13}N)(p\text{-}MeC_6H_4CH_2N)C$ (**17**) was observed to undergo dimerization upon heating to yield both *cis* and *trans* isomers of the enetetramine $\{C_{10}H_6(cyclo\text{-}C_7H_{13}N)(p\text{-}MeC_6H_4CH_2N)C\}_2$, **(17)₂**. Rhodium complexes of these perimidine-based carbenes were accessed via reactions with either monomeric carbene or enetetramine. Spectroscopic and crystallographic analysis of these rhodium−carbene complexes revealed the sterically demanding nature of the carbene ligands, which is manifested in the observation of hindered $Rh-C_{carbene}$ bond rotation and through $\%V_{bur}$ measurements, and their exceptional electron-donating ability.

Introduction

The advent of persistent N-heterocyclic carbenes (NHCs) and the subsequent advances in carbene chemistry have moved these fascinating species into the realm of isolable, commercial compounds.[1−3] The swift application of these species in organometallic chemistry and catalysis has been a remarkable success, and NHCs are now ubiquitous in these fields. Several studies indicate that the strong σ-donor strength with negligible π-accepting ability engenders nucleophilic carbenes with similar properties to electron-rich trialkylphosphines.[4−12] In addition, NHCs have been shown to possess greater thermal stability than many phosphines.

The cyclic five-membered ylidenes **A** and **B** represent the dominant architectures of stable nucleophilic singlet carbenes. The stability of the singlet state of diaminocarbenes has been attributed to the bent structure imposed by the heterocycle, which breaks orbital degeneracy, and to orbital overlap of the empty p_π orbital on the carbene center with the nitrogen-centered lone pairs.[13] The more stable unsaturated structure of imidazol-2-ylidenes (**A**) exhibits the 6π-electron structure expected for aromatic systems. Recent reports have demonstrated that changes to the size of the heterocyclic ring can affect the donor strength and steric impact of the ligand.[14−17] Expanding on the structural and electronic diversity of this ligand class will have significant implications, and reports of novel scaffolds for stable free carbenes such as **C**,[16] **D**,[18] **E**,[14] **F**,[19] and **G**[20] have recently

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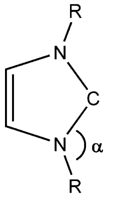
appeared. Revealing the fundamental properties of new carbenes similar to **C**−**G** is critical for the application of these species and for the design of new carbenes.



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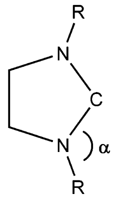

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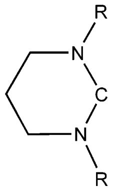

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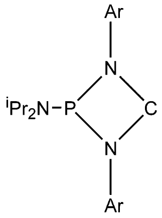

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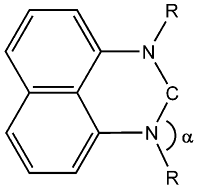

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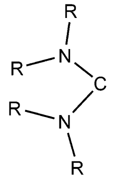

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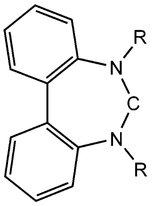


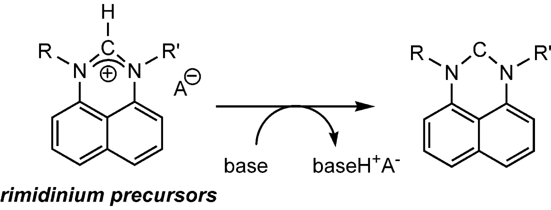
G

We were attracted to the unique framework provided by the perimidine core of **E**, where the divalent carbon is a component of an electron-rich, extended aromatic six-membered heterocyclic ring.[21] This feature modulates the donor properties of the carbene center and imposes geometric constraints on the N-substituents, influencing their steric impact. In particular, this scaffold directs the N-bound groups closer to the carbene atom, decreasing the α angle and increasing the steric pressure on both the carbene and a coordinated metal. Herein we present general synthetic avenues to **E**-type carbenes with alkyl, aryl, and mixed alkyl/aryl N-substituents. Furthermore, we provide details on the chemistry of these species with respect to their fundamental reactivity and to their ability to support catalytically relevant metal complexes.

Results and Discussion

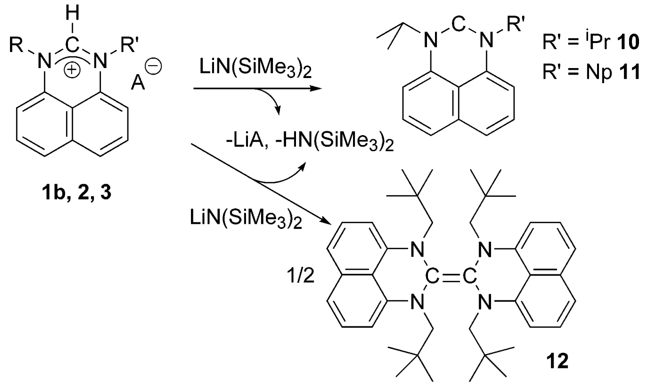
A general method for accessing persistent N-heterocyclic carbenes is the deprotonation of appropriate cationic precursors. We, therefore, targeted the direct deprotonation of 1,3-disubstituted perimidinium salts in order to generate **E**-type carbenes (Scheme 1). Synthesis of these carbene precursors first required access to appropriately N-substituted 1,8-diaminonaphthalenes, and experimental details for the preparation and characterization of these species and for the perimidinium salts are provided in the Supporting Information. The most characteristic NMR spectroscopic features of perimidinium salts **1**−**8** arise from the central HCN_2 moiety common to all compounds. For example, the nine reported perimidinium salts display a downfield ^{1}H NMR signal (δ 8.4−10.4) that integrates for a single proton with an associated ^{13}C NMR signal that appears between 148.2 and 152.6 ppm. The remaining signals for the symmetrical (**1**, **3**, and **4**) and the unsymmetrical (**2** and **5**−**8**) cations appear at appropriate chemical shifts and have integration values consistent with their formulations. Single-crystal X-ray analyses further confirmed the identities of several of these perimidinium salts, and the structural details are provided in the Supporting Information.

Scheme 1

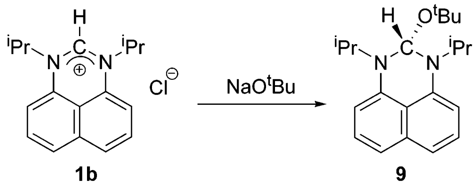


R = R' = ^{i}Pr; A$^-$ = HCO_2^- **1a**, A$^-$ = Cl$^-$ **1b**
R = ^{i}Pr, R' = Np; A$^-$ = *p*-$MeC_6H_4SO_3^-$ **2**
R = R' = Np; A$^-$ = *p*-$MeC_6H_4SO_3^-$ **3**
R = R' = 3,5-$Me_2C_6H_3$; A$^-$ = Cl$^-$ **4**
R = ^{i}Pr, R' = 3,5-$Me_2C_6H_3$; A$^-$ = *p*-$MeC_6H_4SO_3^-$ **5**
R = ^{i}Pr, R' = CH_2Ph; A$^-$ = Br$^-$ **6**
R = ^{i}Pr, R' = *p*-$CH_2C_6H_4CH_3$; A$^-$ = Br$^-$ **7**
R = *cyclo*-C_7H_{13} R' = *p*-$CH_2C_6H_4CH_3$; A$^-$ = Br$^-$ **8**

Scheme 2



Synthesis, Characterization, and Reactivity of Perimidine-Based Carbenes. Our initial efforts toward deprotonation of compounds **1**−**8** employed NaO^{t}Bu as the base. The reaction of **1b** with 1 equiv of NaO^{t}Bu lead to the isolation of the α-diamino ether **9**, rather than the free carbene (eq 1).[22] While unsaturated carbenes of type **A** can usually be generated by deprotonation of imidazolium precursors with a butoxide base, attempts to generate saturated imidazolidine-2-ylidene analogues (**B**) using alkoxides sometimes yields α-diamino ethers.[23]



(1)

We investigated the ability of bulkier, less nucleophilic bases to generate free carbene by reacting the perimidinium salt **1b** with 1 equiv of lithium hexamethyldisilazide, LiN(SiMe$_3$)$_2$ (Scheme 2). The increased solubility of the product of this reaction in nonpolar solvents was the first indication that **10** was a neutral species. The ^{1}H NMR spectrum of **10** did not display the downfield HCN_2 proton of **1b**, suggesting a successful deprotonation. The most distinctive feature characterizing this product as a free carbene is a ^{13}C NMR (C_6D_6) signal for the $C_{carbene}$ at 241.7 ppm. The downfield chemical shift for this carbon signal indicates the deshielded, electron-deficient configuration for the $C_{carbene}$ atom and is reminiscent of values obtained for the saturated species **B**, which generally appear in the range 235−245 ppm. This contrasts with the $C_{carbene}$ signals of imidazol-2-ylidenes (**A**), which appear further upfield

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[22] Details for the characterization of **9** can be found in the Supporting Information.

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Table 1. Selected Crystal Data and Structure Refinement Parameters for $C_{10}H_6(^iPrN)_2C$, 10, $C_{10}H_6(^iPrN)(NpN)C$, 11, $\{C[N(3,5\text{-}Me_2C_6H_3)]_2C_{10}H_6\}_2$, 13, and $C_{10}H_6(^iPrN)(3,5\text{-}Me_2C_6H_3N)C$, 14

	10	**11**	**13**	**14**
empirical formula	$C_{17}H_{20}N_2$	$C_{19}H_{24}N_2$	$C_{54}H_{48}N_4$	$C_{22}H_{22}N_2$
fw	252.35	280.40	752.96	314.42
temperature (K)	223(2)	200(2)	296(2)	170(2)
λ (Å)			0.71073	
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1$	$Pca2_1$	$P2_1/n$	$P2_1/c$
a (Å)	9.223(4)	11.1938(15)	12.4944(18)	11.985(2)
b (Å)	8.553(4)	13.9491(19)	11.4705(16)	8.6199(16)
c (Å)	10.143(5)	10.5219(14)	15.323(2)	17.383(3)
α (deg)				
β (deg)	117.04(4)		96.383(2)	101.454(3)
γ (deg)				
V (Å^3)	712.6(6)	1642.9(4)	2182.4(5)	1760.1(5)
Z	2	4	2	4
ρ(calc) (Mg/m^3)	1.176	1.134	1.146	1.187
μ (mm^{-1})	0.069	0.066	0.067	0.070
absorp corr	semiempirical from equivalents			
final R indices [$I > 2\sigma(I)$]				
R1^a	0.0759	0.0371	0.0733	0.0642
wR2^b	0.2471	0.0828	0.1849	0.1389

^{a} $R1 = \sum||F_o| - |F_c|| / \sum|F_o|$. ^{b} $wR2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $C_{10}H_6(^iPrN)_2C$, 10, $C_{10}H_6(^iPrN)(NpN)C$, 11, $\{C[N(3,5\text{-}Me_2C_6H_3)]_2C_{10}H_6\}_2$, 13, and $C_{10}H_6(^iPrN)(3,5\text{-}Me_2C_6H_3N)C$, 14

10		**11**		**13**		**14**	
Bond Lengths							
C(1)−N(1)	1.355(6)	N(1)−C(11)	1.354(3)	N(1)−C(1)	1.414(2)	N(1)−C(1)	1.356(3)
C(1)−N(2)	1.362(6)	N(1)−C(1)	1.417(3)	N(2)−C(1)	1.421(2)	N(1)−C(3)	1.418(3)
C(2)−N(1)	1.509(6)	N(1)−C(12)	1.487(3)	C(1)−C(1)A	1.336(4)	N(1)−C(17)	1.449(3)
C(5)−N(1)	1.410(6)	N(2)−C(11)	1.357(3)	N(1)−C(10)	1.400(2)	N(2)−C(1)	1.349(3)
C(11)−N(2)	1.418(6)	N(2)−C(9)	1.420(3)	N(1)−C(7)	1.437(2)	N(2)−C(11)	1.419(3)
C(15)−N(2)	1.495(5)	N(2)−C(15)	1.473(2)	N(2)−C(16)	1.418(3)	N(2)−C(20)	1.493(3)
				N(2)−C(25)	1.424(3)		
Angles							
N(1)−C(1)−N(2)	115.3(4)	N(1)−C(11)−N(2)	115.6(2)	C(10)−N(1)−C(1)	116.4(2)	C(1)−N(1)−C(3)	126.2(2)
C(1)−N(1)−C(5)	125.9(4)	C(11)−N(1)−C(1)	125.2(2)	C(10)−N(1)−C(7)	123.8(2)	C(1)−N(1)−C(17)	115.0(2)
C(1)−N(1)−C(2)	115.0(4)	C(11)−N(1)−C(12)	116.9(2)	C(1)−N(1)−C(7)	119.8(2)	C(3)−N(1)−C(17)	118.7(2)
C(5)−N(1)−C(2)	118.7(4)	C(1)−N(1)−C(12)	117.8(2)	C(1)−N(2)−C(16)	112.3(2)	C(1)−N(2)−C(11)	125.5(2)
C(1)−N(2)−C(11)	124.9(4)	C(11)−N(2)−C(9)	125.5(2)	C(1)−N(2)−C(25)	117.1(2)	C(1)−N(2)−C(20)	116.0(2)
C(1)−N(2)−C(15)	116.1(3)	C(11)−N(2)−C(15)	114.6(2)	C(16)−N(2)−C(25)	121.4(2)	C(11)−N(2)−C(20)	118.5(2)
C(11)−N(2)−C(15)	118.9(3)	C(9)−N(2)−C(15)	119.9(2)	C(1)A−C(1)−N(1)	123.0(2)	N(2)−C(1)−N(1)	115.2(2)
				N(1)−C(1)−N(2)	115.1(2)		

in the 205−220 ppm region.[24] A symmetrical structure for **10** was supported by a single set of signals for the N-^{i}Pr groups in ^{1}H NMR spectrum. In a similar fashion, the reaction of perimidinium salt **2**, possessing a combination of a secondary alkyl (^{i}Pr) and primary alkyl (Np) N-substituents, with LiN(SiMe$_3$)$_2$ proceeded smoothly to give carbene **11**. Again the most direct spectroscopic evidence for carbene formation is the appearance of the C$_{carbene}$ resonance at 247.9 ppm. Along with this observation, the ^{1}H NMR spectrum of **11** displayed a single set of resonances for the ^{i}Pr group, similar to those observed in compound **10**, and the characteristic singlets for the methylene (3.96 ppm) and methyl groups (1.04 ppm) of the Np substituent.

Figures 1 and 2 provide structural diagrams, obtained from single-crystal X-ray diffraction analysis, of carbenes **10** and **11** with data summarized in Tables 1 and 2.[25] The structure of **10** clearly features a two-coordinate environment for C(1), a planar geometry around the N atoms, and short N−C$_{carbene}$ distances with an average of 1.359(6) Å, which are consistent with a carbene structure. The longer N−C$_{naphth}$ bond lengths (average = 1.414(6) Å) suggest that the N lone pairs are more involved with bonding to C$_{carbene}$ than to the naphthyl ring. The N−C$_{carbene}$−N angle in **10** of 115.3(4)° is considerably smaller than the respective angle in the perimidinium salt **1b** of 124.4°, but larger than the analogous angles observed for isolated carbenes of type **A** and **B**, which fall in the 100−110° range. We had also anticipated a decrease in the α angle upon moving from the five-membered ring to the six-membered ring geometry. Typical values of α for structures of type **A**/**B** are 122−123°.[1,26,27] As predicted, the observed α values in **10** average 115.5(4)° and are the smallest of the three angles around the N centers. The result is an increased steric impact of the nitrogen substituents on the C$_{carbene}$ center, and this will have a concomitant effect on the reactivity of this center and of metal complexes of **10** (*vide infra*). Compound **11** displays comparable features to **10** including a planar molecular geometry, similarly short N−C$_{carbene}$ distances (average = 1.356(3) Å), an N−C$_{carbene}$−N angle of 115.6(2)°, and α-angle values of 116.9(2)° and 114.6(2)°.

All attempts at deprotonation of the symmetrically substituted 1,3-dineopentylperimidinium salt **3** yielded the enetetramine **12**,

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[24] For a summary of ^{13}C shifts for typical carbenes see: Herrmann, W. A.; Öfele, K.; Preysing, D. v.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *684*, 235.

[25] A summary of crystallographic details and tables of selected bond distance and angles are provided in the Supporting Information.

[26] Arduengo, A. J.; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027.

[27] Denk, M. K.; Thadani, A.; Hatano, K.; Lough, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2607.

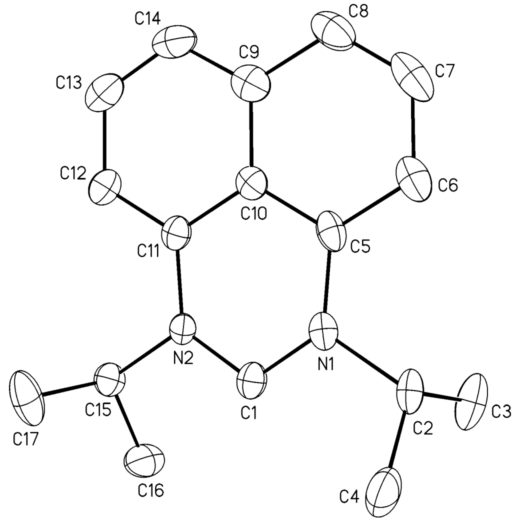


Figure 1. Molecular structure and atom-numbering scheme for carbene $C_{10}H_6(^iPrN)_2C$, **10**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.[25]

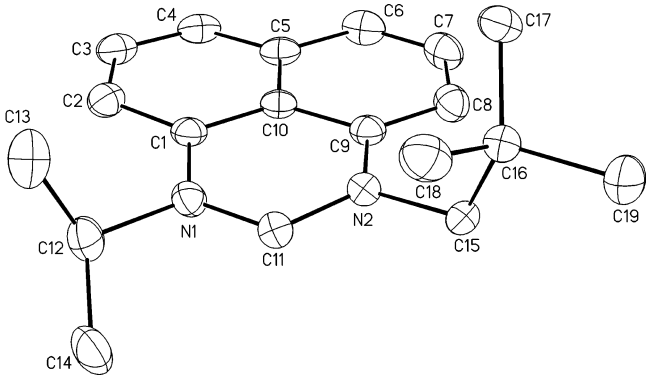


Figure 2. Molecular structure and atom-numbering scheme for carbene $C_{10}H_6(^iPrN)(Me_3CCH_2N)C$, **11**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.[25]

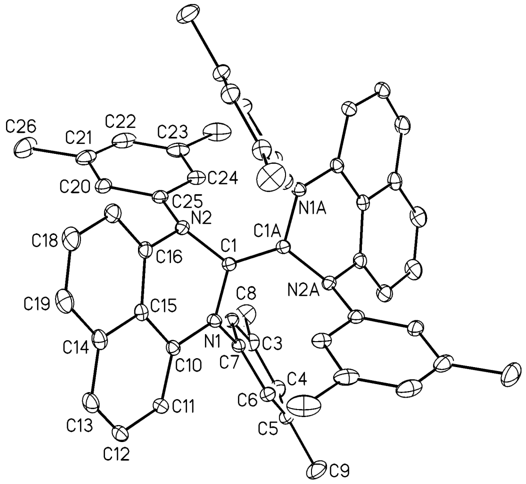
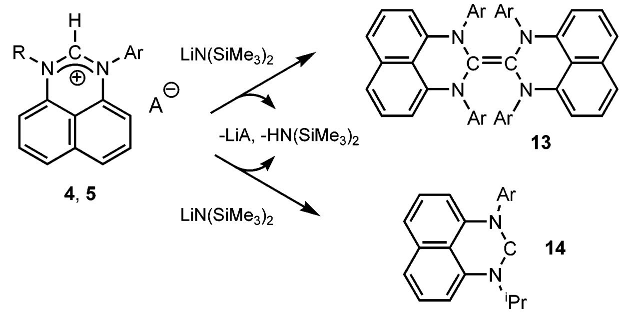


Figure 3. Molecular structure and atom-numbering scheme for the enetetramine $\{C[N(3,5\text{-}Me_2C_6H_3)]_2C_{10}H_6\}_2$, **13**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.[25]

Scheme 3



the formal dimer of the targeted carbene as shown in Scheme 2.[28] The NMR spectroscopic signatures for **12** clearly support this formulation and contrast with the spectral features observed for **10** and **11**. One particularly characteristic feature is the appearance of the methylene groups of the neopentyl substituents as a pair of diastereotopic doublets centered at 6.87 and 6.84 ppm that are considerably downfield shifted relative to the analogous group in **11**.

Deprotonation of the 1,3-diarylperimidinium salt **4** with $LiN(SiMe_3)_2$ did not lead to generation of the anticipated carbene but instead yielded the enetetramine **13**, which was isolated and fully characterized via NMR spectroscopy and crystal structure analysis (Scheme 3).[25]

A structural diagram of **13** is presented in Figure 3 with crystallographic data provided in Tables 1 and 2. This reveals a molecule with a central C=C bond (1.336(4) Å) that lies on an inversion center. The two halves of the molecule are slightly twisted along this axis (N1−C1−C1A−N2A = 8.4(2)°). Interestingly, the six-membered heterocycles are not planar. Specifically, C1 deviates from the plane of the ring by approximately 0.5 Å and the observed torsion angles C10−N1−C1−N2 and C16−N2−C1−N1 are 44.0(2)° and 53.7(2)°, respectively. Furthermore, the two nitrogen centers display different environments, with N1 being planar (∑ angles 360.0(2)°) while N2 is pyramidal (∑ angles 350.8(2)°). As a result, the N2 aryl substituent projects out of the plane of the C_2N_4 core. These unusual structural features are in sharp contrast to those of enetetramines derived from dimerization of **B** or from benzimidazole-based carbenes, which typically display a larger twist angle along the C=C bond (14−21°) and have planar heterocyclic rings with two pyramidal N centers.[17,28,29]

Interestingly, deprotonation of the closely related **5** with $LiN(SiMe_3)_2$ led to formation of carbene **14** as clearly demonstrated by observation of the characteristic ^{13}C NMR resonance for the carbene carbon at 242 ppm and through X-ray diffraction analysis (Table 1).[25] The molecular structure of **14**, shown in Figure 4, confirms the two-coordinate, planar environment for the carbene center of **14** along with similar bonding parameters to carbenes **10** and **11**. Selected bond data for **14** are provided in Table 2, which revealed short $N-C_{carbene}$ distances (average = 1.352(3) Å), a relatively large $N-C_{carbene}-N$ angle (115.2(2)°), and small exocyclic $C_{carbene}-N-C$ α angles (average = 115.5(2)°).

The results obtained for the synthesis of compounds **10**−**14** suggest that successful isolation of free carbene with a perimidine scaffold requires the presence of at least one secondary alkyl N-substituent. To further explore this concept, we investigated the deprotonation of perimidinium salts **6**−**8** to yield nonsymmetric carbenes (eq 2). The reactions of **6**−**8** with 1 equiv of $LiN(SiMe_3)_2$ proceeded by clean deprotonation,

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[28] The dimerization of N-stabilized carbenes has recently been reviewed in: (a) Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schutz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896. (b) Graham, D. C.; Cavel, K. J.; Yates, B. F. *J. Phys. Org. Chem.* **2005**, *18*, 298.

[29] Cetinkaya, E.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Spyropoulos, K. *J. Chem. Soc., Perkin Trans. 1* **1992**, 561.

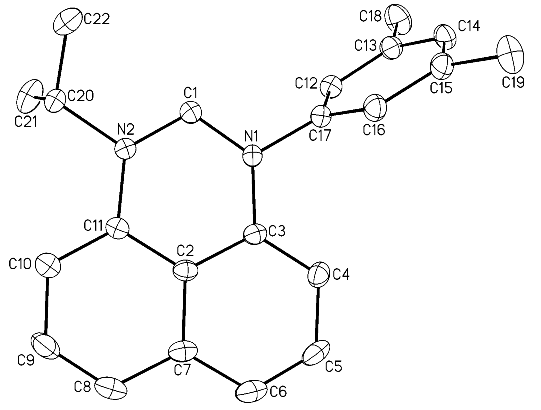
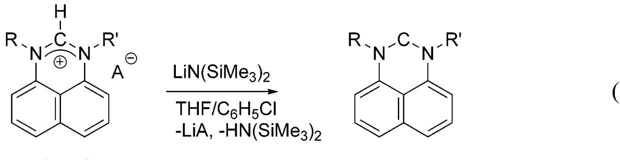


Figure 4. Molecular structure and atom-numbering scheme for the carbene $C_{10}H_6(^{i}PrN)(3,5\text{-}Me_2C_6H_3N)C$, **14**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.[25]

generating compounds **15**−**17**, which were readily identified as carbenes by the appearance of NMR spectral signatures that are comparable with compounds **10**, **11**, and **14**. For example, the ^{13}C NMR spectra of all three compounds exhibit a $C_{carbene}$ signal (**15** = 245.3 ppm, **16** = 245.1 ppm, **17** = 246.6 ppm) at chemical shifts similar to those observed for compounds **10**, **11**, and **14**. Again, these signals appear at values reminiscent of saturated carbenes with structure **B**. Importantly, the observation of singlets for the benzylic methylene groups is again consistent with our observations for the free carbenes and contrasts with the observation of a diastereotopic CH_2 group in the enetetramine **12**.

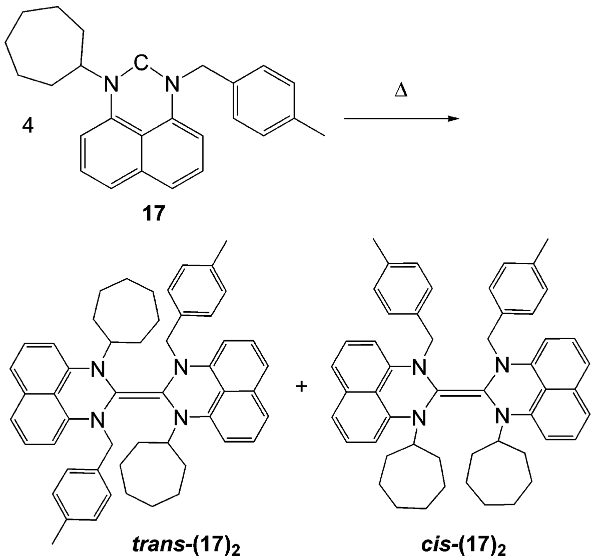


6, 7, 8

(2)

R = ^{i}Pr, R' = $CH_2C_6H_5$ **15**
R = ^{i}Pr, R' = *p*-$CH_2C_6H_4CH_3$ **16**
R = *cyclo*-C_7H_{13}, R' = *p*-$CH_2C_6H_4CH_3$ **17**

Interestingly, the ^{1}H NMR spectra of carbene **17** taken after a period of time displayed new resonances indicating its transformation into a new compound. In particular, the appearance of doublets associated with the benzylic CH_2 groups, a feature reminiscent of our observations for the neopentyl groups in compound **12**, suggested that **17** was slowly undergoing dimerization to form the enetetramine (eq 3). This transformation was monitored by dissolving a sample of **17** in C_6D_6 and observing the time evolution of its NMR spectra. The initially observed ^{1}H NMR spectrum exhibited only the signals for the carbene. This sample was then heated to 80 °C for 24 h. At the end of this period, the ^{1}H NMR spectrum of this sample displayed a diminished intensity for the singlet arising from the methylene group of the starting material at 5.29 ppm; concomitant with this observation was the appearance of four new doublets centered at 5.51, 5.22, 4.98, and 4.48 ppm, consistent with diastereotopic protons for the benzyl CH_2 moieties and corresponding to the formal dimerization of **17**. The appearance of four doublets suggested the formation of both *cis* and *trans* isomers of the product enetetramines. This sample was further heated to 80 °C for 24 h, after which time the methylene singlet for **17** in the ^{1}H NMR spectrum had completely disappeared and was replaced by the four doublets. Heating at 80 °C for an additional 24 h did not result in any further change in the ^{1}H NMR spectrum. Furthermore, the NMR spectrum did not display any additional changes over the next 13 days at room temperature.[30]



trans-**(17)$_2$** *cis*-**(17)$_2$**

(3)

We were fortunate to be able to obtain crystals of both isomers of the dimer **(17)$_2$** and were able to confirm their structural features using single-crystal X-ray diffraction (Table 3).[25] The structural diagrams obtained from these analyses are shown in Figure 5, and selected bond distances and angles are provided in Table 4. The structure of ***trans*-(17)$_2$** is analogous to dimer **13**, displaying a central C═C bond (1.348(4) Å) that lies on an inversion center with the two halves of the molecule slightly twisted along this axis (N1−C1−C1A−N2A = 9.9(2)°). Similarly, C1 deviates from the naphthyl plane by approximately 0.5 Å, and the nonplanar nature of the heterocyclic ring is further demonstrated by the torsion angles C10−N1−C1−N2 (46.5(2)°) and C16−N2−C1−N1 (−49.6(2)°). As with **13**, the two nitrogen centers in ***trans*-(17)$_2$** exhibit different geometries: one with a planar environment ($\sum$ angles for N1 = 359.8(2)°) and one that is pyramidal ($\sum$ angles for N2 = 347.8(2)°). An effect of this distortion is the projection of the cycloheptyl group on N2 out of the plane of the C_2N_4 core. Other than the obvious difference in substituent orientation, there are only slight differences between the ***cis*-(17)$_2$** and ***trans*-(17)$_2$** isomers. The C═C bond length of the *cis* isomer (1.340(5) Å) is identical to the *trans* isomer within experimental error, there is a similar twist along this bond, and the olefinic carbons again deviate from the heterocyclic planes by approximately 0.5 Å. As with both **13** and the *trans* isomer, the nitrogen centers of ***cis*-(17)$_2$** are a combination of planar (N2 and N3) and pyramidal (N1 and N4) centers. Interestingly, the two pyramidal nitrogen centers of ***cis*-(17)$_2$** bear the cycloheptyl groups as was observed in ***trans*-(17)$_2$**.

A distinguishing feature differentiating carbenes of type **A** and **B** is their propensity to form enetetramines, the formal C═C dimers of the free carbenes.[29] The more stable, unsaturated species **A** dimerize only under very specific circumstances.[31] On the other hand, the saturated carbene analogues readily form enetetramines. In fact, stable type **B** carbenes can be accessed only by shielding the carbene center with sufficiently large N-substituents to kinetically inhibit the formation of the

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[30] Dynamic dimerization of benzimidazole carbenes has been recently reported: Kamplain, J. W.; Bielawski, C. W. *Chem. Commun.* **2006**, 1727.

[31] Taton, T. A.; Chen, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1011.

Table 3. Selected Crystal Data and Structure Refinement Parameters for the *cis* and *trans* Isomers of $\{C_{10}H_6(cyclo\text{-}C_7H_{13}N)(p\text{-}MeC_6H_4CH_2N)C\}_2$, *trans*-(17)$_2$ and *cis*-(17)$_2$, $\{[1,8\text{-}(^iPrN)_2C_{10}H_6]C\}Rh(CO)_2Cl$, 18, and $\{[1,8\text{-}(^iPrN)_2C_{10}H_6]C\}Rh(COD)Cl$, 19

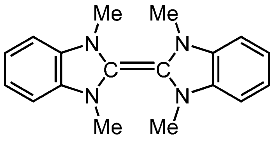
	***trans*-(17)$_2$**	***cis*-(17)$_2$**	**18**	**19**
empirical formula	$C_{104}H_{112}N_8$	$C_{52}H_{56}N_4$	$C_{22.50}H_{24}ClN_2O_2Rh$	$C_{25}H_{32}ClN_2Rh$
fw	1474.02	737.01	492.80	498.89
temperature (K)	120(2)	207(2)	150(2)	213(2)
λ (Å)			0.71073	
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	8.6140(13)	10.964(3)	10.3248(16)	10.241(2)
b (Å)	13.555(2)	11.591(4)	14.149(2)	16.129(3)
c (Å)	17.067(3)	17.429(5)	16.339(3)	14.067(3)
α (deg)	93.690(3)	91.921(6)	112.486(2)	
β (deg)	97.561(3)	97.232(6)	93.646(2)	104.722(4)
γ (deg)	97.573(3)	113.765(6)	94.078(2)	
V (Å^3)	1951.5(5)	2002.4(11)	2189.3(6)	2247.2(8)
Z	1	2	4	4
ρ(calc) (Mg/m^3)	1.254	1.222	1.495	1.475
μ (mm^{-1})	0.073	0.071	0.922	0.893
absorp corr	semiempirical from equivalents			
final R indices [$I > 2\sigma(I)$]				
R1[a]	0.0727	0.0721	0.0399	0.0724
wR2[b]	0.1822	0.1453	0.1107	0.1916

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

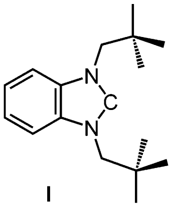
Table 4. Selected Bond Lengths [Å] and Angles [deg] for the *cis* and *trans* Isomers of $\{C_{10}H_6(cyclo\text{-}C_7H_{13}N)(p\text{-}MeC_6H_4CH_2N)C\}_2$, *trans*-(17)$_2$ and *cis*-(17)$_2$

***trans*-(17)$_2$**		***cis*-(17)$_2$**	
Bond Lengths			
N(1)−C(10)	1.393(3)	N(1)−C(1)	1.388(5)
N(1)−C(1)	1.424(3)	N(1)−C(26)	1.419(4)
N(1)−C(9)	1.469(3)	N(1)−C(11)	1.504(5)
N(2)−C(16)	1.417(3)	N(2)−C(9)	1.397(5)
N(2)−C(1)	1.431(3)	N(2)−C(26)	1.417(5)
N(2)−C(26)	1.500(3)	N(2)−C(18)	1.464(5)
C(1)−C(1)#1	1.348(4)	N(3)−C(35)	1.386(5)
		N(3)−C(52)	1.422(4)
		N(3)−C(37)	1.475(5)
		N(4)−C(52)	1.434(5)
		N(4)−C(27)	1.427(5)
		N(4)−C(45)	1.489(5)
		C(26)−C(52)	1.340(5)
Angles			
C(10)−N(1)−C(1)	116.31(17)	C(1)−N(1)−C(26)	116.5(3)
C(10)−N(1)−C(9)	121.53(18)	C(1)−N(1)−C(11)	120.7(3)
C(1)−N(1)−C(9)	121.96(17)	C(26)−N(1)−C(11)	117.6(3)
C(16)−N(2)−C(1)	112.43(17)	C(9)−N(2)−C(26)	118.7(3)
C(16)−N(2)−C(26)	116.01(17)	C(9)−N(2)−C(18)	120.7(3)
C(1)−N(2)−C(26)	119.38(17)	C(26)−N(2)−C(18)	120.2(3)
C(1)#1−C(1)−N(1)	123.6(2)	C(35)−N(3)−C(52)	116.7(3)
C(1)#1−C(1)−N(2)	120.5(2)	C(35)−N(3)−C(37)	122.0(3)
N(1)−C(1)−N(2)	115.31(17)	C(52)−N(3)−C(37)	120.8(3)
		C(52)−N(4)−C(27)	109.5(3)
		C(52)−N(4)−C(45)	119.7(3)
		C(27)−N(4)−C(45)	115.0(3)
		C(52)−C(26)−N(1)	122.1(4)
		C(52)−C(26)−N(2)	122.2(3)
		N(1)−C(26)−N(2)	115.4(3)
		C(26)−C(52)−N(3)	123.2(4)
		C(26)−C(52)−N(4)	120.2(3)
		N(3)−C(52)−N(4)	114.9(3)

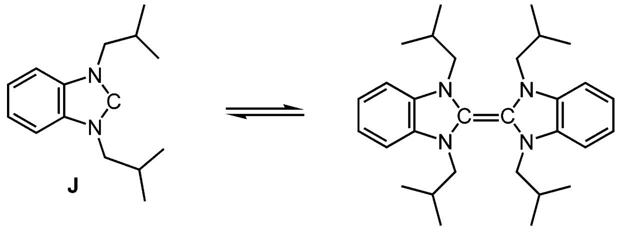
enetetramine.[27,28,32] Similarly, the dimerization behavior of benzimidazole-based carbenes is highly dependent on the steric bulk of the N-substituents.[17,31] Small N-substituents, such as methyl groups, allow the formation of the enetetramine **(H)$_2$**, whereas bulkier neopentyl groups stabilize the free carbene **I**. Intermediate sized isobutyl substituents are reported to allow for an equilibrium between the free carbene **J** and the dimer **(J)$_2$** at room temperature.



(H)$_2$



I



J

(J)$_2$

These observations have been justified through an examination of the calculated singlet−triplet energy gaps ($\Delta E_{s/t} = E_{triplet} - E_{singlet}$) for each of these species.[33−35] The magnitude of $\Delta E_{s/t}$ for type **A** carbenes has been calculated to be approximately 82 kcal/mol,[35] and using a general C═C double bond energy of 172 kcal/mol, the estimated $\Delta H_{dimerization}$ of imidazol-2-ylidenes **A** is close to zero.[36] On the other hand, type **B** carbenes are calculated to have $\Delta E_{s/t}$ values that are smaller by approximately 12 kcal/mol; these species dimerize unless sterically protected with bulky N-substituents.[35] Calculation of $\Delta E_{s/t}$ for the benzannulated analogues of **A** (e.g., **H**, **I**, and **J**) gave a value of approximately 78 kcal/mol. This value is consistent with the −13.7 ± 0.6 kcal/mol for the enthalpy of dimerization for *N*,*N*′-diethylbenzimidazol-2-ylidene and the ability to modulate the dimerization of these compounds with small steric changes to the N-substituents.[17,30] Our DFT calculation of the singlet−triplet gap of compound **10**, with the B3LYP functional using a 6-31+G(d) basis set, provided a value of $\Delta E_{s/t} = 65$ kcal/mol.[37] This suggests that perimidine carbenes should have

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(32) Hahn, F. E.; Paas, M.; Le Van, D.; Lügger, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 5243.

(33) Dixon, D. A.; Arduengo, A. J., III. *J. Phys. Chem.* **1991**, *95*, 4180.

(34) Heinemann, C.; Thiel, W. *Chem. Phys. Lett.* **1994**, *217*, 11.

(35) Cheng, M. J.; Hu, C. H. *Chem. Phys. Lett.* **2001**, *349*, 477.

(36) Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* **1986**, *90*, 998.

(37) Frisch, M. J., *et al. Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

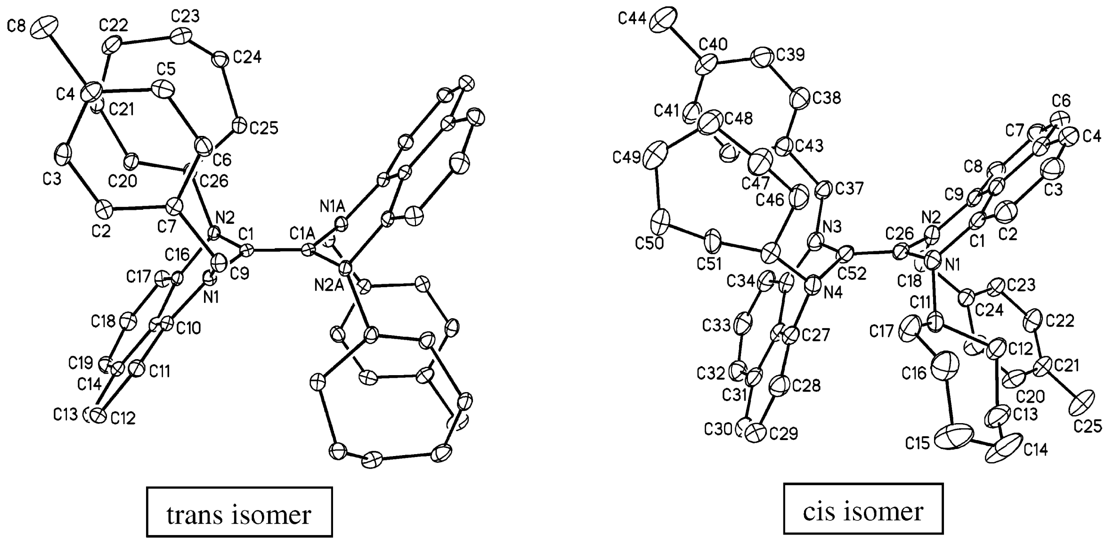
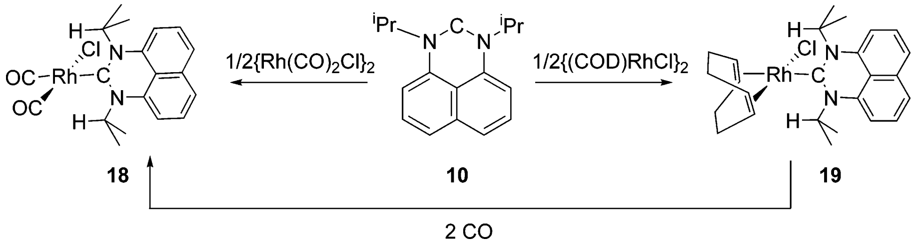


Figure 5. Molecular structure and atom-numbering schemes for the two isomers of enetetramine $\{C_{10}H_6(\textit{cyclo}\text{-}C_7H_{13}N)(p\text{-}MeC_6H_4CH_2N)C\}_2$, ***trans*-(17)$_2$** and ***cis*-(17)$_2$**. For the *trans* isomer, only one of the two molecules in the asymmetric unit is shown. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.[25]

Scheme 4



a thermodynamic preference toward dimerization. Of course kinetic stabilization is not taken into account in this indirect approach to estimating propensity for dimerization. Our observations of compounds **10**−**17** suggest that kinetic stability provided by the steric impact of the N-substituents plays a significant role in the isolation of free carbenes with a perimidine framework.

Perimidine-Based Carbenes as Ligands. The advent of stable carbenes of type **A**/**B** has led to their widespread application in catalyst systems. The ability of perimidine-based carbenes to stabilize catalytically relevant metal complexes is demonstrated by the reactions summarized in Scheme 4. The reaction of **10** with $[Rh(CO)_2Cl]_2$ at room temperature yielded the pale yellow metal carbene complex **18** in 73% isolated yield. The ^{13}C NMR spectrum of **18** displays a $C_{carbene}$ resonance at 200.1 ppm (d, $^1J_{RhC} = 40.8$ Hz) along with two Rh-coupled CO resonances at 187.1 ppm ($^1J_{RhC} = 54.8$ Hz) and 183.3 ppm ($^1J_{RhC} = 74.0$ Hz), consistent with a *cis*-orientation of the carbonyl groups. The observed chemical shift for the carbene carbon in **18** is about 30 ppm downfield from the analogous Rh(I) complexes of the unsaturated carbenes of type **A** and provides evidence for an unusual environment offered by this new carbene framework.[38] Further support for the *cis*-geometry of **18** comes from the appearance of two CO stretching vibrations of similar intensity at 1989 and 2073 cm^{-1}. A consistent characteristic feature for the coordination chemistry of perimidine-based carbenes is a dramatic change in the ^1H NMR chemical shift for the α-protons of the N^iPr groups when coordinated to a metal center. The chemical shift for these methine septets moves from 4.08 ppm in free **10** to 6.72 ppm for **18**. We attribute this to the proximity of the NC*H*Me$_2$ proton to the electron-rich metal center as a direct effect of the six-membered heterocyclic structure of **10** enforcing a close approach of the N-bonded groups to the metal center.

In a similar fashion, the reaction of **10** with $[Rh(COD)Cl]_2$ (COD = 1,4-cycloocatdiene) at room temperature yields the yellow metal carbene complex **19**. The coordination of **10** to the Rh(I) metal center leads to similar changes in the NMR signatures of the carbene. The ^{13}C NMR signal for $C_{carbene}$ shifts upfield to 213.3 ppm and appears as a doublet due to Rh coupling ($^1J_{RhC} = 48.3$ Hz), and the methine septets for the ^iPr groups appear even further downfield in the ^1H NMR at 7.97 ppm. The conversion of **19** to **18** was readily achieved by room-temperature reaction with carbon monoxide.

The structures of **18** and **19** have been determined by single-crystal X-ray analyses (Table 3), and the resultant structural diagrams, which are consistent with the spectroscopic observations, are presented in Figures 6 and 7.[25] Selected structural parameters are presented in Table 5. Both are based on square-planar Rh(I) coordination geometries with a perpendicular orientation of the carbene plane. The $Rh-C_{carbene}$ bond distances of 2.090(3) and 2.06(1) Å for **18** and **19**, respectively, are considerably longer than those reported for (COD)RhCl(**A**) (2.021(4),[8] 2.023(2) Å[9]), reflecting the steric congestion that was designed into **10**.

The coordination of **10** to the square-planar rhodium(I) centers of **18** and **19** results in some minor structural changes within the carbene ligand. The average $N-C_{carbene}$ bond length became slightly shorter and the average $N-C_{carbene}-N$ angle increased by approximately three degrees to 118.9(3)° and 117.9(9)° for

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[38] Herrmann, W. A.; Köcher, C.; Goossen, L. K.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 1627.

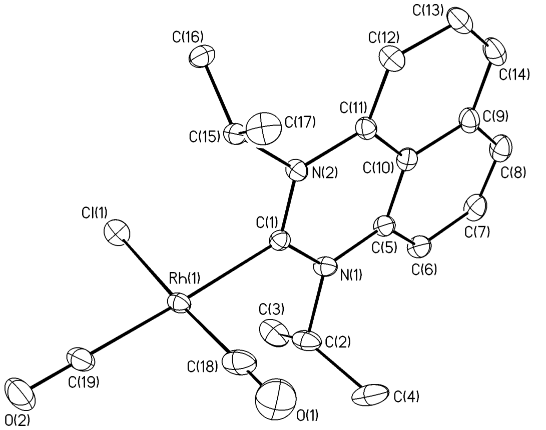


Figure 6. Molecular structure and atom-numbering scheme for one of the symmetry unique molecules of carbene complex $(CO)_2Rh\{C[1,8-(^iPrN)_2C_{10}H_6]\}Cl$, **18**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.[25]

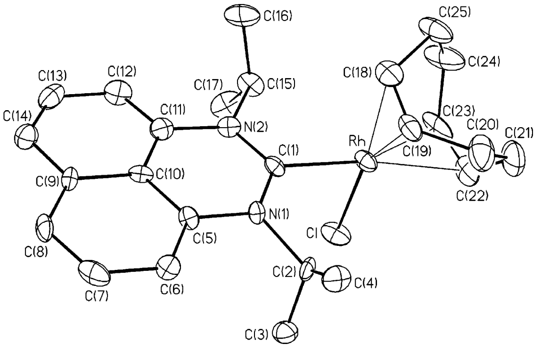


Figure 7. Molecular structure and atom-numbering scheme for the carbene complex $(COD)Rh\{C[1,8-(^iPrN)_2C_{10}H_6]\}Cl$, **19**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.[25]

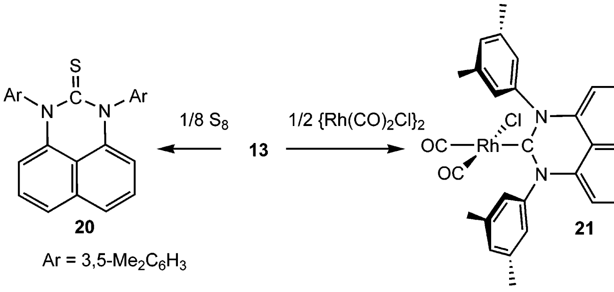
Table 5. Selected Bond Lengths [Å] and Angles [deg] for $\{[1,8-(^iPrN)_2C_{10}H_6]C\}Rh(CO)_2Cl$, 18, and $\{[1,8-(^iPrN)_2C_{10}H_6]C\}Rh(COD)Cl$, 19

18		19	
	Bond Lengths		
Rh(1)−C(1)	2.090(3)	Rh−C(1)	2.056(11)
Rh(1)−C(18)	1.876(5)	Rh−C(19)	2.113(13)
Rh(1)−C(19)	1.899(3)	Rh−C(18)	2.140(13)
Rh(1)−Cl(1)	2.3539(10)	Rh−C(23)	2.205(12)
N(1)−C(1)	1.351(4)	Rh−C(22)	2.251(13)
N(1)−C(5)	1.414(4)	Rh−Cl	2.400(3)
N(1)−C(2)	1.503(4)	N(1)−C(1)	1.366(14)
N(2)−C(1)	1.349(4)	N(1)−C(5)	1.431(13)
N(2)−C(11)	1.423(4)	N(1)−C(2)	1.519(14)
N(2)−C(15)	1.489(4)	N(2)−C(1)	1.352(14)
O(1)−C(18)	1.041(5)	N(2)−C(11)	1.436(15)
O(2)−C(19)	1.130(4)	N(2)−C(15)	1.516(14)
	Angles		
C(18)−Rh(1)−C(19)	92.27(17)	C(1)−Rh−Cl	89.4(3)
C(18)−Rh(1)−C(1)	89.64(14)	C(1)−N(1)−C(5)	123.3(9)
C(19)−Rh(1)−C(1)	177.91(14)	C(1)−N(1)−C(2)	117.2(9)
C(18)−Rh(1)−Cl(1)	177.24(12)	C(5)−N(1)−C(2)	118.9(8)
C(19)−Rh(1)−Cl(1)	90.45(12)	C(1)−N(2)−C(11)	123.7(9)
C(1)−Rh(1)−Cl(1)	87.64(8)	C(1)−N(2)−C(15)	115.8(9)
C(1)−N(1)−C(5)	122.9(3)	C(11)−N(2)−C(15)	120.3(9)
C(1)−N(1)−C(2)	116.3(3)	N(2)−C(1)−N(1)	117.9(9)
C(5)−N(1)−C(2)	120.7(2)	N(2)−C(1)−Rh	120.6(7)
C(1)−N(2)−C(11)	123.2(2)	N(1)−C(1)−Rh	121.4(8)
C(1)−N(2)−C(15)	116.8(2)		
C(11)−N(2)−C(15)	120.0(2)		
N(2)−C(1)−N(1)	118.9(3)		
N(2)−C(1)−Rh(1)	119.4(2)		
N(1)−C(1)−Rh(1)	121.7(2)		

18 and **19**, respectively. Coordination of the carbene carbon adds steric pressure to this center, and the α angles for **18** and **19** averaging 116.5(9)° are increased slightly from the 115.5(4)° observed in **10**. However, this angle remains the smallest of the three angles around the N centers.

One of the distinctive features for both **18** and **19** is the appearance of inequivalent methyl groups for the ^iPr moieties of the carbene ligand in both the ^{13}C and ^1H NMR spectra of these compounds. This observation is consistent with the static structures of these complexes and indicates hindered rotation around the $Rh-C_{carbene}$ bond in solution that is reminiscent of reported Rh complexes of carbenes **A** and **B**.[39] For $(CO)_2Rh(\mathbf{A})Cl$ (R = $4-CH_2C_6H_4CH_3$)[8] and $(CO)Rh(\mathbf{B})_2Cl$ (R = CH_2CH_3)[40] the rotational activation energies were estimated to be approximately 16 kcal/mol with free Rh−C rotation observed above 55 °C. In the case of **18**, NMR spectra acquired at up to 90 °C in benzene-d_6 displayed no broadening for the doublets assigned to the inequivalent methyl groups, which is consistent with a $\Delta G^{\ddagger}$ of >20 kcal/mol for M−C bond rotation. This observation supports the greater steric congestion associated with the new structural features exhibited by **10**.

Although we observed no evidence of free carbene in the NMR spectra of enetetramine **13** up to 100 °C, **13** does react with elemental sulfur to quantitatively furnish the corresponding thiourea, $C_{10}H_6(NAr)_2C{=}S$, **20**, within 4 h at 90 °C (eq 4).[41] These results prompted us to investigate the potential of **13** as a carbene synthon for the preparation of metal complexes.[42] Generally, enetetramines with *N*-aryl groups exhibit reduced reactivity compared to their alkyl analogues; however, **13** reacted cleanly with $[Rh(CO)_2Cl]_2$ in minutes at room temperature to yield the monocarbene complex *cis*-$(CO)_2Rh\{C(NAr)_2C_{10}H_6\}Cl$, **21** (eq 4).



(4)

The ^{13}C NMR spectrum of **21** displays a characteristic Rh-coupled $C_{carbene}$ resonance at 203.3 ppm (d, $^1J_{RhC}$ = 41.7 Hz), and the *cis*-geometry is supported by the appearance of two signals in the ^{13}C NMR for the CO carbon nuclei as well as through IR spectroscopy, which exhibited two CO stretching vibrations of similar intensity at 1989 and 2070 cm^{-1}. The ^1H and ^{13}C NMR spectra of **21** confirmed the presence of two inequivalent methyl groups for the $3,5-Me_2C_6H_3$ substituents. This, in combination with the appearance of 12 distinct aromatic ^{13}C signals, indicates a barrier to both $Rh-C_{carbene}$ and $N-C_{aryl}$ rotation in **21**.[8,40,41]

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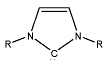
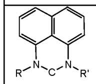
(39) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617*, 70.

(40) Doyle, M. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 679.

(41) The cif file for **20** can be found in the Supporting Information.

(42) For reviews on the use of enetetramines in the synthesis of metal−carbene complexes see: Lappert, M. F. *J. Organomet. Chem.* **2005**, *690*, 5467. Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185.

Table 6. Steric Parameter %V_{bur} Calculated for Selected Carbenes and PR_3 Ligands

Ligand		
Formula	Substituents	%V_{bur}[a]
	R = 4-methylphenyl (ITol)	23[b]
	R = 2,4,6-trimethylphenyl (IMes)	26[b]
	R = 2,6-diisopropylphenyl (IPr)	29[b]
	R = adamantyl (IAd)	37[b]
PR_3	R = phenyl (PPh_3)	27[b]
	R = cyclohexyl (PCy_3)	32[b]
	R = R' = isopropyl (**10**)	29[c]
	R= isopropyl, R' = neopentyl (**11**)	28[c]
	R= isopropyl R' = 3,5-$Me_2C_6H_3$ (**14**)	30[c]
	R = R' = 3,5-$Me_2C_6H_3$	30[c]

[a] Fixed M−L = 2.00 Å and sphere radius of 3 Å. [b] Values from ref 43. [c] This report.

Carbene ligands have a more unsymmetrical steric profile than tertiary phosphine ligands, and in order to quantify the steric features associated with perimidine-based carbenes ligands, we applied a model recently reported by Cavallo and Nolan for the measurement of "percent buried volume" or %V_{bur}.[43−46] These measurements have been employed to estimate the steric demands for carbenes possessing structures **A** and **B** and to allow comparisons of these species with tertiary phosphine ligands. Essentially, this measurement involves calculating the volume occupied by a ligand relative to the volume of a sphere centered on a metal center. The volume of the sphere that is occupied by the atoms of a ligand, the %V_{bur} value, provides a measure of steric bulk. The bulkier a ligand, the larger will be the amount of the sphere that is occupied by the ligand and the greater the magnitude of %V_{bur}.

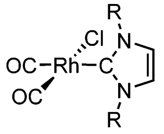
In order to obtain comparable estimates of the steric demands for carbenes **10**, **11**, and **14** and the diaryl carbene of complex **21**, we employed complex **18** and the DFT-optimized geometries of the $(CO)_2Rh(carbene)Cl$ analogues as starting points.[47] Since the values of %V_{bur} will depend on the ligand−metal distance and on the metal-centered sphere, the measurements were carried out with the $M-C_{carbene}$ distance fixed to 2.00 Å and a sphere with a 3 Å radius. The resulting %V_{bur} values are presented in Table 6 along with values for some imidazol-2-ylidenes and phosphine ligands. With an average %V_{bur} value of 29, the perimidine-based carbenes are more sterically demanding than PPh_3 and similar to the common IMes and IPr ligands. The fact that the steric impact of the relatively small ^iPr groups in **10**, **11**, and **14** is comparable to the 2,6-diisopropylphenyl substituents in IPr is a direct result of the unique framework provided by the perimidine scaffold.

Table 7. Carbonyl Stretching Frequencies for Mono(carbene)bis(carbonyl)chlororhodium(I) Complexes H−K, 18, and 21

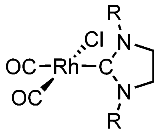
compound	ν_{CO} (cm^{-1})
K[5]	2076, 2006
L (R = Mes)[5]	2081, 1996
L (R = Ph)[a]	2085, 2004
L (R = Me)[a]	2090, 2005
M[5]	2057, 1984
N[b]	2093, 2001
18	2073, 1989
21	2070, 1989

[a] Doyle, M. J.; Lappert, M. F.; Pye, P. L.; Terreros, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2355. [b] Bitterwolf, T. E.; Kline, D. L.; Linehan, J. C.; Yonker, C. R.; Addleman, R. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2692.

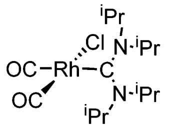
One of the fundamental properties of NHCs is a strong electron donor ability that rivals that of trialkylphosphines. A systematic comparison of ν_{CO} values for a series of $(CO)_3Ni(carbene)$ complexes confirmed that NHC ligands with structures **A** and **B** are better donors than tertiary phosphines and that the difference in donor properties between the saturated and unsaturated analogues is small.[46] Furthermore, this study revealed that saturated NHC ligands were slightly less electron-donating than their unsaturated analogues, bringing into question the common assumption that saturated NHC ligands are more electron-donating and that, for this reason, metal complexes incorporating them perform better in catalysis. A comparison of the ν_{CO} values obtained for **18** and **21** with reported *cis*-$(CO)_2Rh(L)Cl$ compounds **K**−**N** is presented in Table 7. These data confirm that the carbene ligands are better donors than PMe_3. Furthermore, a comparison of the ν_{CO} values obtained for **18** and **21** with the carbene complexes **K**, **L**[48] (R = Me, Ph), and **M**[5] indicates that **10** and its *N*,*N'*-diaryl analogue are stronger electron donors than carbenes of type **A** and **B** but weaker than the acyclic carbene $C(N^iPr_2)_2$.



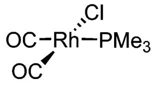
K



L



M



N

Conclusion

Our efforts to design carbene ligands possessing unique structural and electronic properties led to the preparation of a series of symmetric and unsymmetric 1,3-disubstituted perimidinium salts possessing a combination of primary, secondary, or aryl groups, which were employed as precursors to perimidine-based carbenes. The nature of the products obtained from the deprotonation of these perimidinium salts exhibited a significant dependence on the identity of the nitrogen substituents and suggests that steric bulk plays an important role in stabilizing perimidine-based carbenes relative to formation of enetetramine. This balance was further supported by the

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(43) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407.

(44) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815.

(45) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485.

(46) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Peterson, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322.

(47) Optimizations were carried out using the B3LYP functional and the LANL2DZ basis set with the Gaussian 03 program. The optimization results are provided in the Supporting Information.

(48) Doyle, M. J.; Lappert, M. F.; Pye, P. L.; Terreros, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2355.

observed dimerization of **17** to form both the *cis*- and *trans*-enetetramine species.

Perimidine-based carbenes display ^{13}C NMR resonances for the $C_{carbene}$ center that are upfield from acyclic diamino carbenes, but downfield compared to typical imidazole- and imidazolidine-based NHCs. Combined with the observation of enetetramine formation, these results suggest that carbenes with structure **E** possess reactive properties that are closer to those of saturated NHCs rather than the more stable unsaturated analogues. The relatively small value obtained for the singlet−triplet gap of **10** (65 kcal/mol) is again consistent with a more reactive carbene.

The synthesis and characterization of rhodium complexes bearing perimidine-based carbene ligands establishes the fundamental properties and applicability of these species as ligands in organometallic chemistry. Spectroscopic observations support the sterically demanding nature of these ligands both through the substantial downfield shift of the ^{i}Pr methine protons and the hindered rotation of the Rh−$C_{carbene}$ bond. Further support for the steric demand of these carbenes is provided through the calculated $\%V_{Bur}$ values, which are comparable to the IPr carbene ligand.

The donor properties of the perimidine-based carbenes were investigated by comparison of the ν_{CO} stretching frequencies of compounds **18** and **21** to the reported values for analogous compounds. The results indicate that the perimidine-based carbenes are stronger electron donors than PMe_3 and carbenes of type **A** and **B** but weaker than the acyclic carbene $C(N^{i}Pr_2)_2$.

This report demonstrates that rational changes can be applied to the preparation of novel stable carbenes exhibiting increased steric impact and electron-donating ability derived from the perimidine scaffold and that these properties manifest themselves in the behavior of the metal−carbene complexes. Our future efforts are directed at exploiting the unique features of these metal complexes in a myriad of catalytic transformations.

Experimental Section

General Procedures. Unless otherwise noted, all manipulations were carried out in either a nitrogen filled glovebox or under nitrogen using standard Schlenk techniques. Reaction solvents were sparged with nitrogen, then dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated benzene, chloroform, and dimethylsulfoxide were purchased from Aldrich Chemical Co. Deuterated benzene was dried by vacuum transfer from potassium. $LiN(SiMe_3)_2$ was purchased from Aldrich Chemical Co. and purified by crystallization from cold hexane. ^{1}H and ^{13}C NMR spectra were run on either a Varian Gemini-200, a Bruker 300 MHz, or a Bruker 500 MHz spectrometer using the residual protons of the deuterated solvent for reference. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, ON, or in the Department of Chemistry at the University of Ottawa on a Perkin-Elmer PE CHN 4000 elemental analysis system.

Preparation of 1,3-(^{i}Pr)$_2$-perimidin-2-ylidene, $C_{10}H_6(^{i}PrN)_2C$ (10). Compound **1b** (0.40 g, 1.4 mmol) in 20 mL of 1:1 chlorobenzene/THF was added to a solution of $LiN(SiMe_3)_2$ (0.232 g, 1.4 mmol) in 4 mL of 1:1 chlorobenzene/THF at room temperature. The reaction was stirred overnight, and the volatiles were removed under vacuum. This solid was extracted with 15 mL of toluene followed by filtration. The filtrate was evaporated under vacuum to afford a white powder, which was purified by crystallizing from an ether solution at −25 °C (0.160 g, 46% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 7.12 (m, 4H, CH), 6.29 (dd, 2H, CH), 4.08 (sept, 2H, $HCMe_2$), 1.41 (d, 12H, CH_3). ^{13}C NMR (300 MHz, C_6D_6): δ 241.7 (NCN), 136.0, 133.7, 128.0, 122.7, 119.4, 102.9 (C_{arom}), 51.5 ($CHMe_2$), 22.3 (CH_3). Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.55; H, 8.01; N, 10.84

Synthesis of 1-Isopropyl-3-neopentylperimidin-2-ylidene, $C_{10}H_6(^{i}PrN)(NpN)C$ (11). Compound **2** (0.185 g, 1.10 mmol) in 15 mL of anhydrous chlorobenzene was added to a solution of $LiN(SiMe_3)_2$ (0.500 g, 1.10 mmol) in 10 mL of anhydrous chlorobenzene. The reaction was stirred for 2 days, and the volatiles were removed under vacuum. The solid was extracted with 15 mL of toluene followed by filtration. The filtrate was evaporated under vacuum to afford a pale orange, sticky solid, which was purified by crystallizing from hexane to give a pale beige solid (0.20 g, 64%). ^{1}H NMR (200 MHz, 298 K, C_6D_6): δ 7.12 (m, 4H, CH), 6.51 (m, 1H, CH), 6.40 (m, 1H, CH), 4.10 (sept, 1H, CHMe$_2$), 3.96 (s, 2H, CH_2), 1.46 (d, 6H, CH_3), 1.04 (s, 9H, CH_3). ^{13}C NMR (200 MHz, 298 K, C_6D_6): δ 247.9 (NCN), 136.0, 135.0, 133.7, 128.3, 127.6, 119.7, 119.4, 104.9, 102.9 (C_{arom}), 64.2 ($CH_2C(CH_3)_3$), 51.1 ($CH(CH_3)_2$), 29.0 ($CH_2C(CH_3)_3$), 22.3 ($CH(CH_3)_2$). Anal. Calcd for $C_{19}H_{24}N_2$: C, 81.38; H, 8.63; N, 9.99. Found: C, 80.94; H, 8.97; N, 9.61.

Preparation of Enetetramine ($C[N\{[CH_2C(CH_3)_3]\}_2C_{10}H_6)_2$ (12). Compound **3** (0.500 g, 1.10 mmol) in 20 mL of anhydrous chlorobenzene was added to a solution of $LiN(SiMe_3)_2$ (0.185 g, 1.10 mmol) in 10 mL of anhydrous chlorobenzene. The reaction was stirred 18 h, and the volatiles were removed under vacuum. This solid was extracted with 15 mL of toluene followed by filtration. The filtrate was evaporated under vacuum to afford a green, sticky solid, which was purified by crystallizing from hexane to give a pale beige solid (0.120 g, 71%). ^{1}H NMR (200 MHz, 298 K, C_6D_6): δ 7.27 (m, 4H, CH), 6.86 (m, 2H, CH), 6.87 (d, 2H, CH_2), 6.84 (d, 2H, CH_2), 0.866 (s, 18H, CH_3). ^{13}C NMR (200 MHz, 298 K, C_6D_6): δ 145.7, 136.2, 132.0, 128.3, 126.7, 119.2, 107.3, 61.3 ($CH_2C(CH_3)_3$), 34.0 ($CH_2C(CH_3)_3$), 29.2 ($CH_2C(CH_3)_3$). Anal. Calcd for $C_{21}H_{28}N_2$: C, 81.77; H, 9.15; N, 9.08. Found: C, 82.15; H, 9.42; N, 9.09.

Preparation of Enetetramine $\{C[N(3,5\text{-}Me_2C_6H_3)]_2C_{10}H_6\}_2$ (13). Compound **4** (0.76 g, 1.84 mmol) in 15 mL of $ClCH_2CH_2Cl$ was added to a solution of $LiN(SiMe_3)_2$ (0.31 g, 1.84 mmol) in 15 mL of $ClCH_2CH_2Cl$. The reaction was stirred 6 h, and the volatiles were removed under vacuum to afford a white residue. This solid was extracted with 15 mL of toluene followed by filtration. The filtrate was evaporated under vacuum to afford a white powder (0.53 g, 76.5%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.30 (d, 2H, CH), 7.12 (d, 2H, CH), 6.88 (d, 4H, CH), 6.78, (d, 2H, CH), 6.49 (s, 2H, CH), 1.87 (s, 12H, CH_3). ^{13}C NMR (300 MHz, C_6D_6): 147.1,-139.2, 139.0, 135.5, 128.3, 127.3, 126.1, 121.5, 120.5, 120.1, 113.4, 21.3 (CH_3). Anal. Calcd for $C_{54}H_{48}N_4$: C, 86.13; H, 6.43; N, 7.44. Found: C, 85.94; H, 6.26; N, 7.18.

Preparation of 1-(3,5-Dimethylphenyl)-3-isopropylperimidin-1-ylidene, $C_{10}H_6(^{i}PrN)(3,5\text{-}Me_2C_6H_3N)C$ (14). To a solution of **5** (0.26 g, 0.53 mmol) in 15 mL of chlorobenzene was added a solution of $LiN(SiMe_3)_2$ (0.10 g, 0.53 mmol) in 15 mL of chlorobenzene. The reaction was stirred at room temperature for 6 h, and the volatiles were removed under vacuum to afford a white residue. This solid was extracted with 15 mL of toluene followed by filtration. The filtrate was evaporated under vacuum to afford a white powder. This solid was redissolved in 8 mL of ether and stored at −30 °C to give a white solid (0.16 g, 95%). ^{1}H NMR (300 MHz, C_6D_6): 7.20−6.90 (m, 6H, CH), 6.7 (s, 1H, CH), 6.35 (t, 1H, CH), 6.25 (d, 1H, CH), 4.15 (sept, 1H, CH), 2.01 (s, 6H, CH_3),1.42 (d, 6H, CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): 242.0 (NCN), 137.8, 135.9, 135.6, 133.7, 129.1, 128.2, 127.8, 126.0, 122.2, 120.0, 119.9, 106.0, 103.5 (C_{arom}), 51.7 (CH), 22.5 (CH_3), 21.2 (CH_3). Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.36; H, 6.89; N, 8.56.

Preparation of 1-^{i}Pr-3-$CH_2C_6H_5$-perimidin-2-ylidene, $C_{10}H_6(^{i}PrN)(BnN)C$ (15). Perimidinium bromide **6** (1.0 g, 2.6 mmol) was dissolved in 30 mL of 1:1 chlorobenzene/THF, then added to

$LiN(SiMe_3)_2$ (0.43 g, 2.6 mmol) also dissolved in 30 mL of 1:1 chlorobenzene/THF. The reaction was stirred for 6 h, and the solvent was removed under vacuum. The product, a pale brown viscous liquid, was isolated by extraction with toluene and drying under vacuum (0.76 g, 2.5 mmol, 96%). ^1H NMR (300 MHz, C_6D_6): δ 7.28 (d, 2H, CH), 6.98−7.14 (m, 6H, CH), 6.87 (t, 1H, CH), 6.34−6.39 (m, 1H, CH), 6.28 (dd, 1H, CH), 5.27 (s, 2H, CH_2), 4.12 (sept, 1H, $CHMe_2$), 1.49 (d, 6H, CH_3). ^{13}C NMR (300 MHz, C_6D_6): δ 245.3 (N_2C_{carb}), 137.8, 135.7, 133.6, 133.3, 128.8, 128.0, 127.4, 126.8, 122.5, 120.0, 119.8, 105.2, 103.5 (C_{arom}), 61.0 (CH_2), 51.4 (CH), 22.6 (CH_3). Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 83.68; H, 6.48; N, 9.71.

Preparation of 1-^{i}Pr-3-*p*-$CH_2C_6H_4CH_3$-perimidin-2-ylidene, $C_{10}H_6(^iPrN)(CH_3C_6H_4CH_2N)C$ (16). Perimidinium bromide **7** (0.74 g, 1.9 mmol) was dissolved in 30 mL of 1:1 chlorobenzene/THF, then added to $LiN(SiMe_3)_2$ (0.31 g, 1.9 mmol) also dissolved in 30 mL of 1:1 chlorobenzene/THF. The reaction was stirred for 6 h, and the solvent was removed under vacuum. The product, a viscous liquid, was isolated by extraction with toluene and drying under vacuum (0.52 g, 1.7 mmol, 87%). ^1H NMR (300 MHz, C_6D_6): δ 7.25 (d, 2H, CH), 7.09−7.15 (m, 2H, CH), 7.05 (d, 1H, CH), 6.88−6.95 (m, 3H, CH), 6.32−6.39 (m, 2H, CH), 5.29 (s, 2H, CH_2), 4.13 (sept, 1H, $CHMe_2$), 2.02 (s, 3H, CH_3) 1.51 (d, 6H, CH_3). ^{13}C NMR (300 MHz, C_6D_6): δ 245.1 (N_2C_{carb}), 136.7, 135.7, 134.7, 133.7, 133.3, 129.6, 128.0, 126.9, 125.6, 120.0 119.8, 105.2, 103.6 (C_{arom}), 60.8 (CH_2), 51.4 (br, CH), 22.5 (CH_3), 21.0 (CH_3). Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.92; H, 7.35; N, 8.59.

Preparation of 1-^{c}Hep-3-*p*-$CH_2C_6H_4CH_3$-perimidin-2-ylidene, $C_{10}H_6(c\text{-}C_7H_{13}N)(CH_3C_6H_4CH_2N)C$ (17). Perimidinium bromide **8** (0.535 g, 1.2 mmol) was dissolved in 10 mL of 1:1 chlorobenzene/THF and added to $LiN(SiMe_3)_2$ (0.20 g, 1.2 mmol) also dissolved in 15 mL of 1:1 chlorobenzene/THF. The reaction was stirred for 6 h, and the solvent was removed under vacuum. The product, an off-white solid, was isolated by extraction with hexane and drying under vacuum (0.408 g, 92%). ^1H NMR (500 MHz, C_6D_6): δ 7.26 (d, 2H, CH), 7.11−7.17 (m, 2H, CH), 7.04 (d, 1H, CH), 6.91−6.94 (m, 3H, CH), 6.51 (br, 1H, CH), 6.34 (d, 1H, CH), 5.29 (s, 2H, CH_2), 4.05 (br, 1H, CH), 2.38 (m, 2H, CH_2), 2.19 (br, 2H, CH_2), 2.03 (s, 3H, CH_3), 1.77 (br, 2H, CH_2), 1.56 (br, 4H, CH_2), 1.42 (br, 2H, CH_2). ^{13}C NMR (500 MHz, C_6D_6): δ 246.6 (N_2C_{carb}), 136.7, 135.8, 134.8, 133.8, 133.3, 129.8, 128.4, 127.8, 126.9, 122.7, 119.9, 119.8, 105.1, 103.3 (C_{arom}), 61.25 (CH), 60.8 (CH_2), 35.5 (br, CH_2), 28.2 (br, CH_2), 25.4 (br, CH_2), 21.0 (CH_3). Anal. Calcd for $C_{26}H_{28}N_2$: C, 84.74; H, 7.66; N, 7.60. Found: C, 84.46; H, 7.78; N, 7.40.

Spectroscopic Observation of Formation of $(17)_2$. In a glovebox, a sample of **17** was dissolved in C_6D_6 and placed in a Teflon-capped NMR tube. An initial ^1H NMR spectrum confirmed the sample to be carbene **17**. The NMR sample was then heated to 80 °C for 24 h followed by further heating to 80 °C for 24 h. A ^1H NMR spectrum of this sample confirmed the transformation of the starting material, and the following ^1H NMR was obtained: δ 7.6−6.6 (br m, 20H, CH), 5.51 (d, 1H, NCH_2), 5.22 (d, 1H, NCH_2), 4.98 (d, 1H, NCH_2), 4.48 (d, 1H, NCH_2), 3.25 (br m, 2H, NCH), 2.04 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.70−0.80 (br m, 24H, CH_2). Heating for an additional 24 h did not result in any further change in the ^1H NMR spectrum. We were able to isolate a sample of one of the components of this mixture and obtain the following NMR spectra. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.37−6.87 (m, 18H, CH), 6.60 (d, 2H, CH), 5.21 (d, 2H, CH_2), 5.06(d, 2H, CH_2), 3.19 (br, 2H, NCH), 2.22 (s, 6H, CH_3), 1.85 (br, 2H, CH_2), 1.28 (br m, 18H, CH_2) 1.01 (br m, 4H, CH_2). ^{13}C NMR (300 MHz, CD_2Cl_2): δ 143.3, 143.0, 137.0, 136.7, 135.9, 132.5, 129.3, 128.2, 127.1, 126.9, 121.3, 119.9, 116.8, 115.1, 104.4, 67.4 (CH_2), 52.6 (N−CH), 37.2 (CH_2), 34.5 (CH_2), 32.9 (CH_2), 28.6 (CH_2), 27.8 (CH_2), 25.3 (CH_2), 25.0 (CH_3).

Preparation of $\{[1,8\text{-}(^iPrN)_2C_{10}H_6]C\}Rh(CO)_2Cl$ (18). In a nitrogen-filled glovebox a round-bottom flask was charged with $[Rh(CO)_2Cl]_2$ (0.081 g, 0.208 mmol), 10 mL of toluene, and a stir bar. To this solution was added dropwise carbene **10** (0.115 g, 0.456 mmol), predissolved in 10 mL of toluene. The solution turned a more pale yellow color. The reaction was stirred for 1 h, then all volatiles were removed under vacuum. The crude product was washed with 20 mL of hexanes to remove any uncoordinated carbene and then dried under vacuum (0.135 g, 73% yield). ^1H NMR (300 MHz, C_6D_6): δ 7.00 (d, 2H, CH), 6.86 (t, 2H, CH), 6.72 (sept, 2H, $HCMe_2$), 6.50 (d, 2H, CH), 1.49 (d, 6H, CH_3), 1.25 (d, 6H, CH_3) ^{13}C NMR (300 MHz, C_6D_6): δ 200.1 (d, $^1J_{RhC}$ = 40.8 Hz, $C_{carb}Rh$), 187.1 (d, $^1J_{RhC}$ = 54.8 Hz, OCRh), 183.3 (d, $^1J_{RhC}$ = 74.0 Hz, OCRh), 136.0, 131.8, 127.0, 123.7, 121.6, 108.4 (C_{arom}), 62.2 (s, $CHMe_2$), 17.7 (s, CH_3), 17.2 (s, CH_3). IR: ν_{CO} (cm^{-1}) = 2073, 1989. Anal. Calcd for $C_{19}H_{20}N_2O_2ClRh$: C, 51.08; H, 4.51; N, 6.27. Found: C, 51.42; H, 4.83; N, 5.99.

Preparation of $\{[1,8\text{-}(^iPrN)_2C_{10}H_6]C\}Rh(COD)Cl$ (19). In a nitrogen-filled glovebox a round-bottom flask was charged with $[(COD)RhCl]_2$ (0.100 g, 0.2 mmol), 10 mL of toluene, and a stir bar. To this solution was added dropwise carbene **10** (0.104 g, 0.4 mmol), predissolved in 10 mL of toluene. The solution turned to a more pale yellow color. The reaction was stirred for 1 h, then all volatiles were removed under vacuum. The crude product was washed with 2−4 mL of ether to remove any uncoordinated carbene and then dried under vacuum (0.110 g, 55% yield). ^1H NMR (300 MHz, C_6D_6): δ 7.97 (sept, 2H, $HCMe_2$), 7.04 (d, 2H, CH), 6.96 (t, 2H, CH), 6.62 (d, 2H, CH), 5.35 (m, 2H, CH_{cod}), 3.47 (m, 2H, CH_{cod}), 2.24 (m, 4H, $(CH_2)_{cod}$), 1.78 (m, 4H, $(CH_2)_{cod}$), 1.75 (d, 6H, CH_3), 1.54 (d, 6H, CH_3). ^{13}C NMR (300 MHz, C_6D_6): δ 213.3 (d, $^1J_{RhC}$ = 48.3 Hz, $C_{carb}Rh$), 136.1, 132.4, 127.0, 123.4, 120.8, 107.4, 95.9 (d, $^1J_{RhC}$ = 7.2 Hz, CH_{cod}), 69.0 (d, $^1J_{RhC}$ = 14.1 Hz, CH_{cod}), 61.1 (s, $CHMe_2$), 32.9 (s, $(CH_2)_{cod}$), 29.2 (s, $(CH_2)_{cod}$), 20.4 (s, CH_3), 17.7 (s, CH_3). Anal. Calcd for $C_{25}H_{32}ClN_2Rh$: C, 60.19; H, 6.47; N, 5.62. Found: C, 59.78; H, 6.56; N, 5.86.

Preparation of $(CO)_2Rh\{C[N(3,5\text{-}Me_2C_6H_3)]_2C_{10}H_6\}Cl$ (21). In a nitrogen-filled glovebox a round-bottom flask was charged with $[Rh(CO)_2Cl]_2$ (0.027 g, 0.069 mmol), 10 mL of toluene, and a stir bar. Compound **13** (0.052 g, 0.069 mmol) dissolved in 15 mL of toluene was added to this solution. The reaction was stirred for 20 min, then all volatiles were removed under vacuum. The crude product was washed with ether and dried under vacuum to yield a yellow solid (0.055 g, 70% yield). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.48 (d, 4H, CH), 7.20 (m, 4H, CH), 7.00, (s, 2H, CH), 6.10 (d, 2H, CH), 2.42 (s, 6H, CH_3), 2.40(s, 6H, CH_3). ^{13}C (300 MHz, CD_2Cl_2): δ 203.3 (NCN, d, J_{Rh-C} = 41.65 Hz), 187.2 (CO, d, J_{Rh-C} = 54.47 Hz), 183.1 (CO, d, J_{Rh-C} = 76.36 Hz), 140.8, 140.5, 140.4, 137.1,134.6, 131.0, 128.0, 126.0, 124.5, 122.2, 120.6, 108.2 (C_{arom}), 21.5(CH_3), 21.40 (CH_3). IR: ν_{CO} (cm^{-1}) = 2070, 1989. Anal. Calcd for $C_{29}H_{24}ClN_2O_2Rh$: C, 61.01; H, 4.24; N, 4.91. Found: C, 61.38; H, 4.52; N, 5.19.

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Supporting Information Available: Experimental details for synthesis and characterization of the perimidinium salts **1**−**8** and compound **9**. Optimization results for the Rh structures used in the %V_{bur} calculations and a complete citation to ref 37. Crystallographic files (cif) for compounds **1a**, **1b**, **2**, **4**, **6**, **10**, **11**, **13**, **14**, ***trans*-(17)$_2$**, ***cis*-(17)$_2$**, **18**, **19**, and **20**. Tables of selected crystallographic data for **10**, **11**, **13**, **14**, ***trans*-(17)$_2$**, ***cis*-(17)$_2$**, **18**, and **19**. This material is available free of charge on the Internet at http://pubs.acs.org.

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