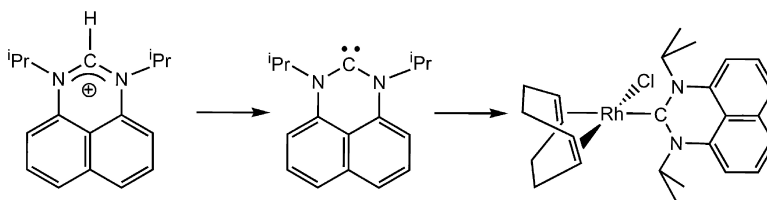


Constructing a Stable Carbene with a Novel Topology and Electronic Framework

Patrick Bazinet, Glenn P. A. Yap, and Darrin S. Richeson

J. Am. Chem. Soc., **2003**, 125 (44), 13314-13315 • DOI: 10.1021/ja0372661 • Publication Date (Web): 15 October 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 21 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



Constructing a Stable Carbene with a Novel Topology and Electronic Framework

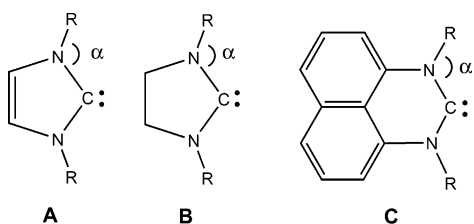
Patrick Bazinet, Glenn P. A. Yap, and Darrin S. Richeson*

Department of Chemistry and the Center for Catalysis Research and Innovation, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5, and Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received July 14, 2003; E-mail: darrin@science.uottawa.ca

The past decade has seen tremendous advances in carbene chemistry that have moved these fascinating species into the realm of isolable compounds.^{1,2} The preparation of stable, *N*-heterocyclic carbenes of type **A** and **B** represents a synthetic milestone,³ and their expeditious application as ligands for the stabilization of transition-metal compounds has been particularly successful. They are rapidly usurping the role of ubiquitous donor ligands (e.g., phosphines) in transition metal catalyzed reactions.⁴

The ylidenes **A** and **B** represent the typical architectures of stable nucleophilic singlet carbenes. These species have been largely restricted to five-membered heterocyclic rings, and the more stable unsaturated species (**A**) possess the 6π electron structure expected for aromatic systems.^{5–7} We have undertaken the design and development of new stable singlet carbenes possessing different scaffolds and electronic structures and now report on constructing novel carbenes around the perimidine core (**C**). This approach places the carbene center in a six-membered ring, which has significant implications on the steric impact of the R substituents, and leaves the divalent carbon as part of a formally seven π -electron, six-membered heterocyclic ring.⁸



The preparation of novel carbenes of type **C** begins with the reaction of *N,N'*-disubstituted diaminothalenes⁹ with triethylorthoformate in acidic solution to yield the *N,N'*-perimidinium salts (**2**) (Scheme 1). These salts can be prepared in near quantitative yields with a variety of counterions depending on the acid employed in the reaction or by ion exchange. Free, neutral carbene **3** was accessed from the perimidinium cation via clean and rapid deprotonation with $\text{LiN}(\text{SiMe}_3)_2$ and is easily crystallized from diethyl ether. Attempts to deprotonate **2** with NaO^tBu led to nucleophilic addition of the alkoxide anion and formation of **4**. Compound **4** was also cleanly generated by the addition of $^t\text{BuOH}$ to **3**.

Perhaps the clearest spectroscopic evidence identifying **3** as a carbene is the appearance of a highly deshielded ^{13}C NMR (C_6D_6) signal for the $\text{C}_{\text{carbene}}$ at δ 241.7 ppm. This chemical shift is reminiscent of the saturated species **B**, which generally appear in the range of 235–245 ppm.^{7a} For comparison, unsaturated carbenes of type **A** display $\text{C}_{\text{carbene}}$ signals further upfield in the 205–220 ppm region. A symmetrical structure for **3** was supported by a single set of ^1H NMR signals for the N-substituents.

Single-crystal X-ray diffraction analysis confirmed the monomeric structure of **3** (Figure 1). In addition to the two-coordinate environment of C(1), several features of this structure, including

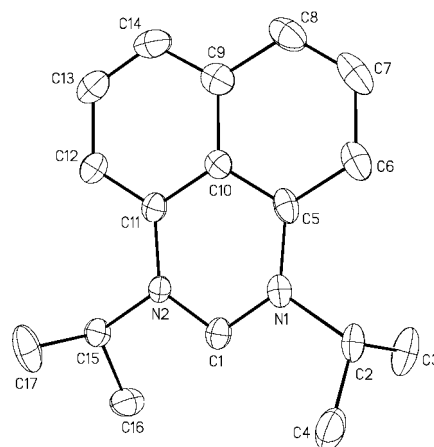
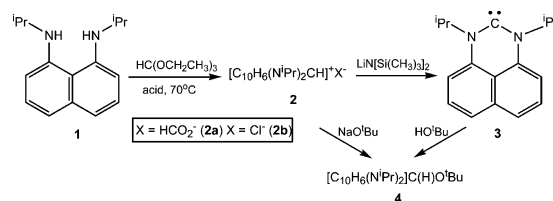


Figure 1. Thermal ellipsoid plot showing the molecular structure and atom numbering scheme for carbene **3**. Hydrogen atoms have been omitted for clarity.

Scheme 1



the planar geometry around the N atoms, and the short $\text{N}-\text{C}_{\text{carbene}}$ distances (average = 1.359(6) Å), are consistent with a carbene structure. The longer $\text{N}-\text{C}_{\text{ring}}$ bond lengths (average = 1.414(6) Å) suggest that the N lone pairs are more involved with bonding to $\text{C}_{\text{carbene}}$ than to the naphthyl ring. The $\text{N}-\text{C}_{\text{carbene}}-\text{N}$ angle in **3** of 115.3° is considerably larger than the analogous angles observed for isolated carbenes of type **A** and **B**, which fall in the 100–110° range. We 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°. As predicted, the observed value in **3** averages 115.5°, which is the smallest of the three angles around the N centers. This results in an increased steric impact of the nitrogen substituents on the $\text{C}_{\text{carbene}}$ center and a concomitant effect of the reactivity of this center and of metal complexes of **3**.

The advent of stable carbenes of type **A/B** has led to their widespread application in catalyst systems.⁴ Carbenes of type **C** will expand these efforts into new areas. The ability of **3** to stabilize catalytically relevant metal complexes is demonstrated by the reactions summarized in Scheme 2. The reaction of **3** with $[\text{Rh}(\text{COD})\text{Cl}]_2$ (COD = 1,4-cyclooctadiene) at room temperature yielded the yellow metal carbene compound **5**. Upon coordination to the Rh(I) metal center, several clear changes are observed in the

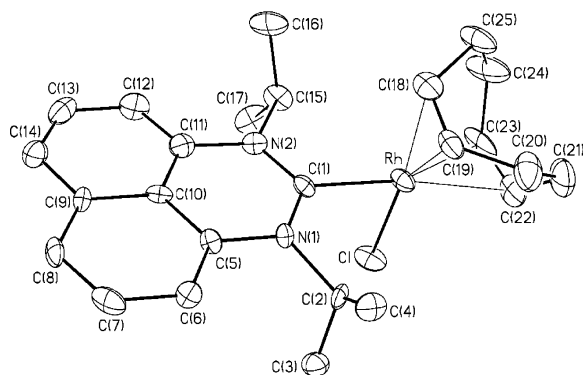
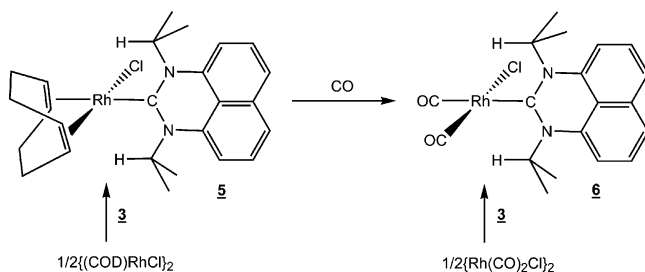


Figure 2. Thermal ellipsoid plot showing the molecular structure and atom numbering scheme for the carbene complex, (COD)RhCl[C(NⁱPr)₂C₁₀H₆], **5**. Hydrogen atoms have been omitted for clarity.

Scheme 2



NMR signatures for **3**. The ¹³C NMR signal for C_{carbene} shifts upfield to δ 213.3 ppm and appears as a doublet due to Rh coupling (¹J_{RhC} = 48.3 Hz). This value is more than 30 ppm downfield from those observed for analogous Rh(I) complexes of the unsaturated type carbenes **A** and provides evidence for an unusual environment offered by our new carbene framework.¹¹ Reminiscent of reported Rh–**A** complexes is the observation of hindered rotation of the Rh–C_{carbene} bond in **5** as evidenced by the appearance of diastereotopic methyl groups for the ³Pr substituents. A unique feature associated with **5** is a dramatic change in the ¹H NMR chemical shift for the α-protons of the NⁱPr groups. The chemical shift for these methine septets moves from δ 4.08 ppm in free **3** to 7.97 ppm for **5**. We have observed similar chemical shifts upon coordination of **3** to Ni(0) and Pd(II) and attribute this to the proximity of the NCH proton to the electron-rich metal center. This is a direct effect of the six-membered heterocyclic structure of **3** enforcing a close approach of the N-bonded groups to the metal center.

The structure of compound **5** was determined (Figure 2). The coordination of **3** to the square planar rhodium(I) center results in only very minor structural changes within the carbene group. The Rh–C_{carbene} bond distance of 2.06(1) Å is considerably longer than those reported for (COD)RhCl(**A**) (2.021(4) Å, 2.023(2) Å).^{11,12} This reflects the steric congestion that was designed into **3**.

One of the fundamental chemical properties of diheteroatom-stabilized carbenes is their strong electron-donor ability. In general, saturated **B**-type carbenes are more electron donating than their unsaturated analogues **A**, and both of these species are stronger donors than trialkylphosphines. To assess the electron-donating ability of carbene **3**, we prepared the Rh(I) dicarbonyl species **6** by the reaction of **3** with [Rh(CO)₂Cl]₂ or by replacement of the COD ligand of **5** with CO (Scheme 2). The NMR spectra for **6** display a C_{carbene} resonance at δ 200.1 (d, ¹J_{RhC} = 40.8 Hz) and diastereotopic methyl groups for the ³Pr moieties. The *cis*-geometry for **6** is supported by the appearance of two ¹³C NMR signals for the CO carbons and by IR spectroscopy, which shows two CO stretching vibrations of similar intensity at 1985 and 2073 cm⁻¹.

The values of ν_{CO} can be used to gauge the donor ability of a ligand, and comparison of the values obtained for **6** with the saturated carbene complexes *cis*-(CO)₂RhCl(**B**)¹³ (R = Me, Et, Ph) and *cis*-(CO)₂RhCl(C(NⁱPr)₂)¹⁴ indicates that **3** is a stronger electron donor than carbenes of type **B** but weaker than the acyclic carbene C(NⁱPr)₂. The appearance of diastereotopic methyl signals for the ³Pr groups in the ¹H NMR spectrum of **6** indicates hindered rotation around the Rh–C_{carbene} bond.¹⁵ For (CO)₂Rh(**A**)Cl (R = 4-CH₂C₆H₄CH₃)¹⁶ and CORh(**B**)₂Cl (R = CH₂CH₃),¹⁷ the rotational activation energies are approximately 16 kcal/mol, and free rotation is observed above 55 °C. In the case of **6**, NMR spectra acquired at up to +90 °C in benzene-*d*₆ show no broadening for the doublets assigned to diastereotopic methyl peaks consistent with a Δ*G*[‡] of >20 kcal/mol for M–C bond rotation. This observation supports the greater steric congestion associated with the new structural features exhibited by **3**.

This report demonstrates that rational changes can be applied to the preparation of novel stable carbenes exhibiting increased steric impact and electron-donating ability. These properties manifest themselves by yielding sterically encumbered metal-carbene complexes. The novel electronic framework gives rise to a nucleophilic carbene center capable of acting as a strong σ-donor ligand. These features should enable perimidine-based carbenes of type **C** to provide steric protection and electronic activation to coordinatively unsaturated metal complexes that are vital intermediates in a myriad of catalytic transformations.

Acknowledgment. This work was supported by NSERC. P.B. is the recipient of an NSERC Postgraduate Scholarship.

Supporting Information Available: Summary of spectral data for compounds **2**–**6** and structural data for complexes **3** and **5** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) *Carbene chemistry: from fleeting intermediates to powerful reagents*; Bertrand, G., Ed.; Marcel Dekker: New York, 2002. *Carbenes*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1973 and 1975; Vols. 1 and 2.
- (2) Bourissou, D.; Guerret, O.; Gabbay, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
- (3) (a) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.
- (4) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.
- (5) For the report of an annulated carbene (benzimidazol-2-ylidenes), see: Liu, Y.; Lindner, P. E.; Lemal, D. M. *J. Am. Chem. Soc.* **1999**, *121*, 10626. Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 541.
- (6) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039.
- (7) Six-membered ring carbene are reported in: (a) Alder, R. W.; Blake, M. E.; Bortolotti, C.; Bufali, S.; Butts, C. P.; Linehan, E.; Oliva, J. M.; Orpen, A. G.; Quayle, M. *J. Chem. Commun.* **1999**, 241. (b) Guillen, F.; Winn, C. L.; Alexakis, A. *Tetrahedron: Asymmetry* **2001**, *12*, 2083.
- (8) *Handbook of Heterocyclic Chemistry*, 2nd ed.; Katritzky, A. R., Pozharskii, A. F., Eds.; Pergamon: New York, 2000.
- (9) We have prepared these species with a variety of alkyl and aromatic substituents including R = ⁱPr, cyclo-C₃H₉, cyclo-C₆H₁₁, 3,5-(CH₃)₂C₆H₃, 4-[(CH₃)₃C]C₆H₄ which will be described in a full report of this work.
- (10) O. Arduengo, A. J.; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027. Denk, M. K.; Thadani, A.; Hatano, K.; Lough, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2607.
- (11) Herrmann, W. A.; Köcher, C.; Goossen, L. K.; Artus, G. R. *J. Chem.-Eur. J.* **1996**, *2*, 1627.
- (12) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C. *Chem.-Eur. J.* **1996**, *2*, 772.
- (13) Doyle, M. J.; Lappert, M. F.; Pye, P. L.; Terreros, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2355.
- (14) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219.
- (15) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2000**, *617*, 70.
- (16) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.
- (17) Doyle, M. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 679.

JA0372661