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Isolation of a C5-Deprotonated Imidazolium, a Crystalline "Abnormal" N-Heterocyclic Carbene

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chemical shifts are seen in partially deuterium-labeled fluxional alkyl agostic complexes (*6*).

To obtain further information about the coordination mode of the σ-methane ligand, we optimized the geometry of **$2\text{-}CH_4^+$** by using DFT, and the resulting coordination environment about the rhodium center is depicted in Fig. 4A (*21*). Calculations using the complete ligand framework showed an unsymmetrical interaction between rhodium and the methane ligand, with only one C-H bond coordinated to the metal (η^2-C,H; Fig. 4B). The η^2-C,H coordination mode calculated for **$2\text{-}CH_4^+$** is comparable to that reported by Ball and co-workers for the interaction between the 16-valence electron Cp′ReL_2 fragment and higher alkanes (vide supra) (*15*) and for other computational studies of methane complexes (*23*–*26*). A small barrier of less than 1 kcal/mol is computed for interchanging H_a and H_b and may originate from facile access to a symmetric η^2-H, H coordination mode (Fig. 4B) by the 14-valence electron (PONOP)Rh^I moiety.

Computational studies suggest that the ground state for the methane adduct, **$2\text{-}CH_4^+$**, lies ~8 kcal/mol below the ground state for the unobserved methyl hydride complex, $[(PONOP)Rh(H)CH_3]^+$ [**$2\text{-}(H)CH_3^+$**] (*21*). The rate of methane loss from **$2\text{-}CH_4^+$** was determined by ^{31}P NMR spectroscopy (*20*) and afforded an observed first-order rate constant of $1.4 \times 10^{-4} \pm 0.3 \times 10^{-4}$ s^{-1} at –87°C, corresponding to $\Delta G^{\ddagger} = 14.5 \pm 0.4$ kcal/mol (*27*). The product of methane extrusion was tentatively assigned as the rhodium(I) solvated cation, $[(PONOP)Rh(CDFCl_2)][B(Ar^F)_4]$. Free methane was detected concomitant with and roughly proportional to the formation of $[(PONOP)Rh(CDFCl_2)][B(Ar^F)_4]$. The observed barrier to methane loss is consistent with previous experimental studies of methane reductive elimination/isotopic scrambling from platinum(II) centers, which predicted a lower limit for the methane dissociation enthalpy of 9 kcal/mol (*28*).

Protonation of a rhodium(I) methyl complex at low temperature has permitted the observation and full characterization by NMR spectroscopy of a relatively long-lived σ-methane complex in solution. This methane complex is the simplest alkane analog of the now classic σ-dihydrogen complexes first reported some 25 years ago (*1*). Just as these dihydrogen species provide insight into the early stages of metal-mediated cleavage of the H-H bond, the σ-methane complex **$2\text{-}CH_4^+$** furnishes details about the weak interaction of methane with a transition metal center before C-H bond scission. Of particular interest is that **$2\text{-}CH_4^+$** is isoelectronic with Pt(II)-σ-methane complexes thought to be intermediates in Pt(II)-mediated Shilov-type oxidations of methane (*29*), the most thoroughly investigated systems for transition metal–catalyzed methane functionalization to date.

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Supporting Online Material

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Materials and Methods
SOM Text
Figs. S1 to S7
Tables S1 to S4
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Isolation of a C5-Deprotonated Imidazolium, a Crystalline "Abnormal" N-Heterocyclic Carbene

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The discovery two decades ago of metal-free stable carbenes, especially imidazol-2-ylidenes [N-heterocyclic carbenes (NHCs)], has led to numerous breakthroughs in organic and organometallic catalysis. More recently, a small range of complexes has been prepared in which alternative NHC isomers, namely imidazol-5-ylidenes (also termed abnormal NHCs or *a*NHCs, because the carbene center is no longer located between the two nitrogens), coordinate to a transition metal. Here we report the synthesis of a metal-free *a*NHC that is stable at room temperature, both in the solid state and in solution. Calculations show that the *a*NHC is more basic than its normal NHC isomer. Because the substituent at the carbon next to the carbene center is a nonbulky phenyl group, a variety of substitution patterns should be tolerated without precluding the isolation of the corresponding *a*NHC.

For decades, carbenes, which feature a neutral divalent carbon atom with two nonbonding electrons, were considered prototypical reactive intermediates (*1*). Today, thanks to the availability of stable carbenes (*2*, *3*), these molecules, especially the so-called N-heterocyclic carbenes (NHCs) (**I**) (*4*–*6*) (Fig. 1, top left), are recognized as versatile ligands for transition metal–based catalysts (*7*–*10*) and as metal-free organic catalysts in their own right (*11*–*14*). As expected, NHCs **I** usually bind metals via the carbene center (C2) to give η^1 complexes **II**. However, in 2001, Crabtree and co-workers discovered that 2-pyridylmethylimidazolium salts react with $IrH_5(PPh_3)_2$ to give **1** with the imidazole ring bound

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the "wrong way," at C5 and not at C2 (*15*, *16*) (Fig. 1, center). Since that time, a few other complexes of type **IV** featuring the so-called abnormal NHCs (*a*NHCs) (**III**) (*17*–*20*) as ligands have been prepared (*21*–*23*) (Fig. 1, top right). Experimental and theoretical data suggest that *a*NHCs **III** are even stronger electron-donor ligands than are NHCs **I**. In line with these observations, initial catalytic screening of *a*NHC metal complexes **IV** reveals promising results for the activation of unreactive bonds such as C–H and H–H (*24*–*26*). As an example, an *a*NHC palladium complex has been reported to be an efficient catalyst in the Heck olefination of aryl bromides, whereas the corresponding NHC analog is virtually inactive under identical conditions (*24*).

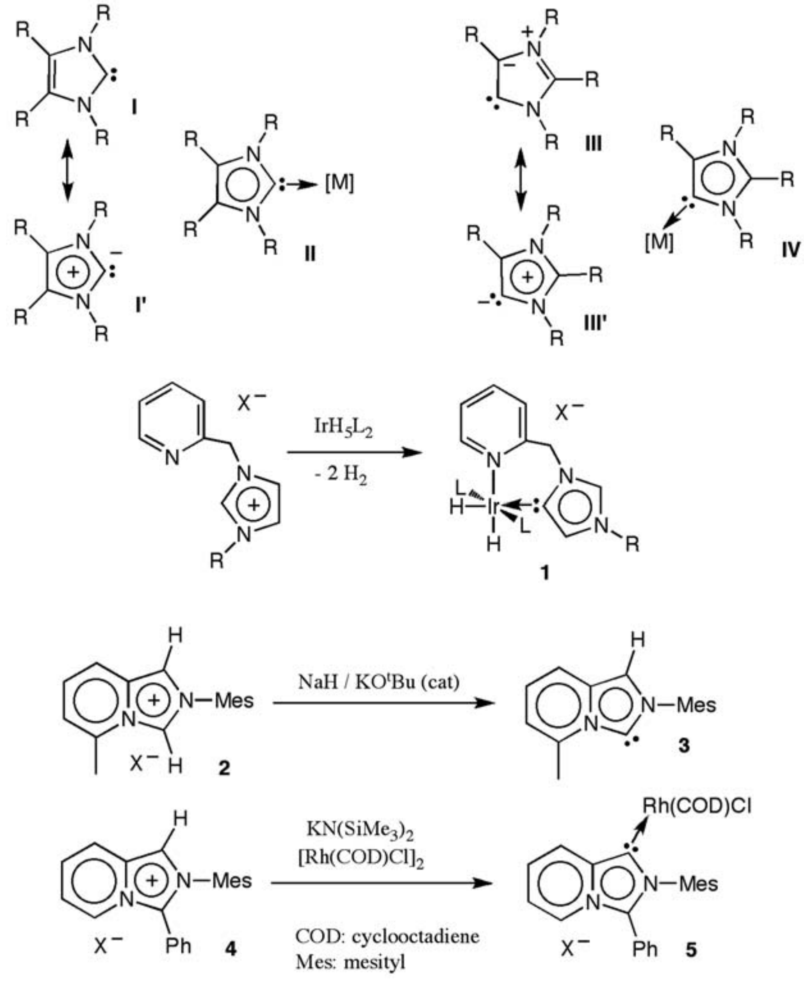

Fig. 1. (**Top**) Resonance structures for NHC (**I**/**I'**) and *a*NHC (**III**/**III'**), and their corresponding C2 and C5 metal complexes, **II** and **IV**, respectively. (**Center**) Synthesis of *a*NHC metal complex **1** by Crabtree and co-workers (*15*). (**Bottom**) Synthesis of metal-free NHC **3**, and *a*NHC metal complex **5** by Lassaletta and co-workers (*27*).

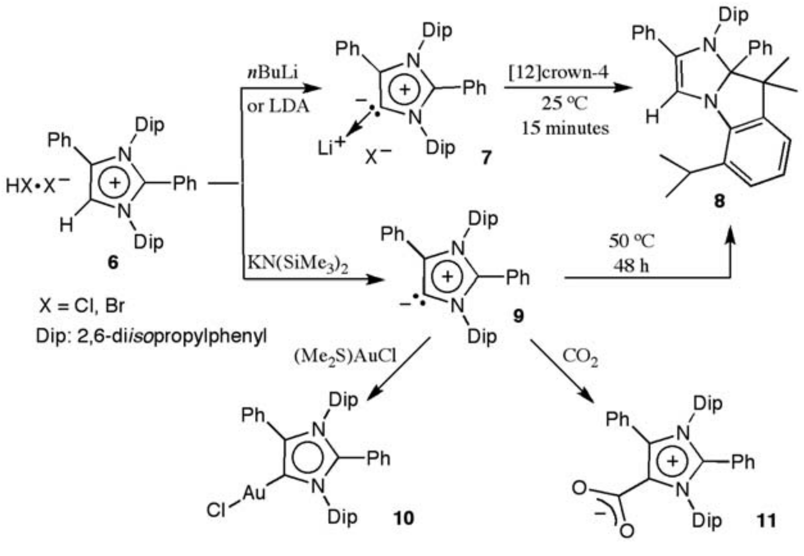

Fig. 2. Synthesis of *a*NHC lithium adduct **7,** rearrangement product **8**, free *a*NHC **9**, and its ensuing gold(I) complex **10** and CO_2-adduct **11.**

Lassaletta and co-workers (*27*) have shown that the deprotonation of imidazo[1,5-a]pyridinium salts **2** leads to free NHC **3** that can be isolated (Fig. 1, bottom). In contrast, using C2-substituted precursors, such as **4**, Lassaletta *et al.* did not observe the corresponding free *a*NHC. However, by performing the deprotonation reaction in the presence of $[Rh(COD)Cl]_2$, they were able to isolate the corresponding *a*NHC complex **5**. Because calculations predicted that the parent *a*NHC **III** (where R is equal to H) is only about 17 kcal mol^{-1} higher in energy than its NHC isomer **I** (*18*), it seemed that free *a*NHC derivatives were reasonable synthetic targets. We report here the isolation of a metal-free member of this class of heterocyclic compound.

By analogy with the classical synthetic route used to prepare NHCs, we chose imidazolium salt **6** as a precursor to the desired *a*NHC **9** (Fig. 2). The pK_a (where K_a is the acid dissociation constant) for loss of the C5-bound proton in the parent imidazolium salt (~33) (*28*) was calculated to be nine units higher than that for loss of the C2-bound proton (*29*); we therefore replaced the C2 hydrogen with a phenyl group. To offer kinetic protection to the C5 position, we appended bulky 2,6-diisopropyl-phenyl (Dip) substituents at both nitrogen atoms, as well as a second phenyl group at C4. Imidazolium salts **6** with various counterions were prepared in good yields after slight modifications to known synthetic procedures (*30*–*32*). They were fully characterized by spectroscopic methods, with a single-crystal x-ray diffraction study carried out for the bromide salt **6** (Br^-) (Fig. 3, left).

All attempts to deprotonate the imidazolium tetrafluoroborate salt **6** (BF_4^-) failed. However, small anions such as Cl^- and Br^- are known to accelerate heterolytic C–H bond cleavage through hydrogen bonding, and this effect has been used with C2- and C5-unsubstituted imidazolium salts to favor metallation of C2 (with the more acidic proton) over C5 (*33*). We reasoned that with C2 protected in **6**, small anions should promote the desired deprotonation reaction at C5. Indeed, when **6** (HCl•Cl^-) was treated with two equivalents (*34*) of a lithium base such as *n*-butyllithium (*n*BuLi) or lithium diisopropylamide (LDA), the proton nuclear magnetic resonance (^1H NMR) spectrum of the resulting product showed the disappearance of the singlet at 8.7 parts per million (ppm) arising from C5(H) of **6**. In the ^{13}C NMR spectrum, the C5 carbon gives rise to a very broad resonance at 190 ppm, which is significantly downfield of the corresponding resonance for the precursor **6** (124 ppm). Although these data indicated that a deprotonation had occurred, the shape of the ^{13}C NMR signal, as well as the calculated chemical shift (*32*) for the C5 carbon of the free *a*NHC **9** (205 ppm), suggested that the new compound was the *a*NHC lithium **7**. Similar complexation has previously been observed for other singlet carbenes such as small NHCs (*35*) and bis(diisopropylamino)cyclopropenylidene (*36*, *37*); in both cases, coordination of the lithium cation was apparent from the broadening and the upfield shift of the carbene ^{13}C NMR resonance. Subsequently, we sought to sequester the lithium cation through addition of excess [12]crown-4 to a diethylether solution of **7** (where X is Br). This treatment induced a clean rearrangement to generate **8**, which was isolated in 45% yield. This product formally results from the deprotonation of an isopropyl substituent of the Dip group by the carbene center of the *a*NHC lithium adduct **7**, followed by nucleophilic addition of the resulting benzyl anion to C2. However, calculations indicated that the rearrangement of **9** into **8** is exothermic by only 6.1 kcal mol^{-1} and involves an activation barrier of 20.3 kcal mol^{-1} for the proton transfer. Therefore, we hypothesized that the observed rearrangement was catalyzed by a component of the (crown)LiBr system, and that the formation of **8** did not imply that the free *a*NHC **9** was too reactive to be isolated.

Sodium and potassium bases have proven more appropriate than lithium bases in generating free carbenes (*35*–*37*), because the corresponding carbon-heavy alkali metal bonds are more labile, which favors precipitation of the salt. When the deprotonation of imidazolium **6** ($HX{\bullet}X^-$, where X is Cl or Br) was performed with two equivalents (*34*) of potassium hexamethyldisilazide (KHMDS) in tetrahydrofuran, a clean reaction occurred, with the ^{13}C NMR spectrum of the resulting product showing a very sharp signal at 201.9 ppm. After the products were worked up, the free *a*NHC **9** was isolated as a green powder (480 mg, 68% yield), and single crystals were obtained by recrystallization from a dry hexane solution at –78°C (Fig. 3, right).

In the solid state, both the free *a*NHC **9** and the imidazolium salt **6** (Br^-) feature a fully planar ring (maximum deviation for N1–C2–N3–C4–C5–C21–C31–C41–C53 was 1.9 and 6.3 pm for **9** and **6**, respectively), confirming the delocalization of the π system. This electronic structure is corroborated by the values of the endocyclic C–N [**6**: 1.335 ± 5 to 1.409 ± 5; **9**: 1.354 ± 2 to 1.408 ± 3 Å] and C–C bond lengths [**6**: 1.351 ± 5, **9**: 1.385 ± 3 Å], which are halfway between those of single and double bonds. The carbene bond angle N1–C5–C4 for **9** [101.03 ± 17°] is more acute than the corresponding angle in the cationic precursor **6** [108.0 ± 3°]. This feature is consistent with increased *s* character of the σ lone-pair orbital on the carbene atom in **9** as compared with the $C–H^+$ bonding orbital in **6**. A similar relationship is observed in NHCs and their $NHC(H^+)$ precursors (*3*, *4*).

Calculations predict *a*NHC **9** to be 14.1 kcal mol^{-1} less stable than its isomeric normal NHC with the phenyl group bonded to C5 instead of C2. Figure 4 shows the two highest occupied molecular orbitals (HOMOs) of **9**. The HOMO (–4.403 eV) is a σ-type lone-pair orbital at C5; the HOMO-1 (–4.879 eV) is a C5–C4 π-bonding orbital, which exhibits antibonding conjugation with the π orbital of the phenyl substituent at C4. These molecular orbitals are much higher in energy than those of the isomeric NHC (–5.000 and –5.279 eV, respectively), which indicates that

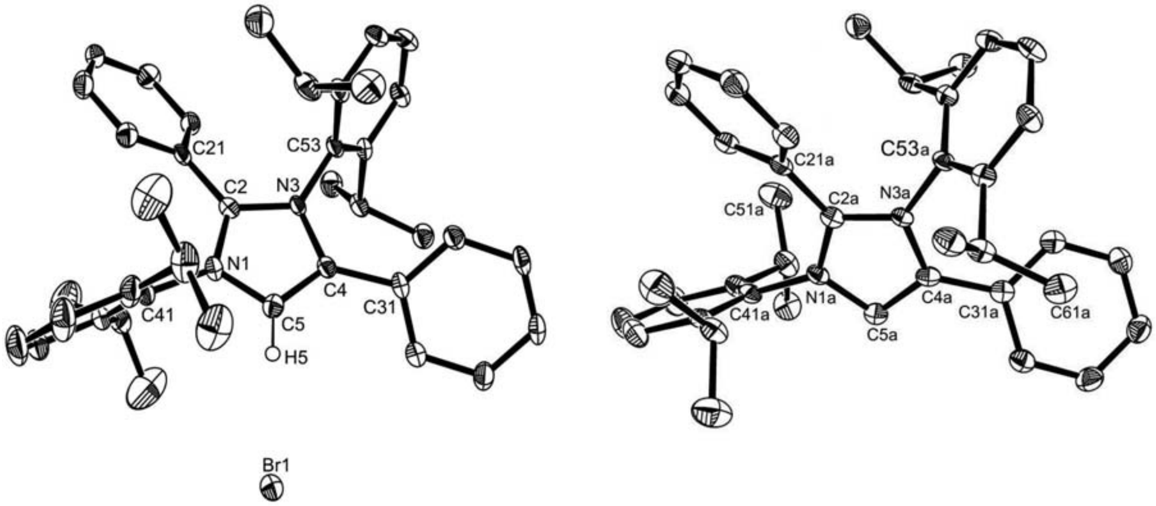

Fig. 3. Molecular views (50% thermal ellipsoids are shown) of imidazolium bromide **6** (Br^-) (left) and *a*NHC **9** (right) in the solid state (for clarity, H atoms are omitted, except for the ring hydrogen). Bond lengths and angles for **6** (Br^-) are as follows: C5–N1, 1.368 ± 4 Å; N1–C2, 1.334 ± 4 Å; C2–N3, 1.363 ± 4 Å; N3–C4, 1.408 ± 4 Å; C4–C5, 1.355 ± 5 Å; N1–C5–C4, 108.0 ± 3°; C5–C4–N3, 106.0 ± 3°; C4–N3–C2, 108.8 ± 3°; N3–C2–N1, 106.9 ± 3°; C2–N1–C5, 110.4 ± 3°. Bond lengths and angles for **9** are as follows: C5a–N1a, 1.417 ± 2 Å; N1a–C2a, 1.357 ± 2 Å; C2a–N3a, 1.345 ± 2 Å; N3a–C4a, 1.412 ± 3 Å; C4a–C5a, 1.383 ± 3 Å; N1a–C5a–C4a, 101.03 ± 17°; C5a–C4a–N3a, 111.01 ± 16°; C4a–N3a–C2a, 107.97 ± 15°; N3a–C2a–N1a, 106.25 ± 16°; C2a–N1a–C5a, 113.72 ± 15°.

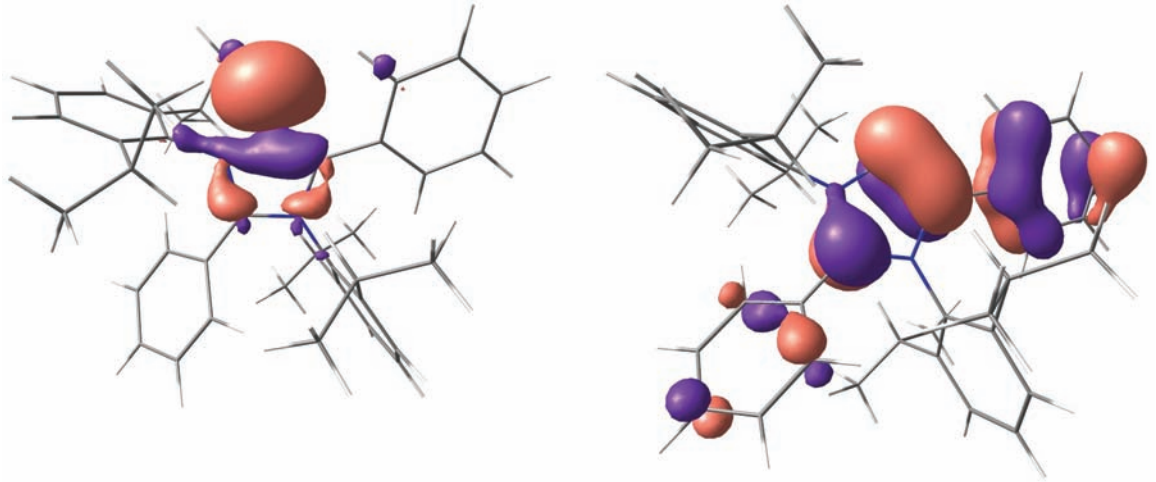

Fig. 4. Plot of the calculated two highest-lying occupied orbitals HOMO (left) and HOMO-1 (right) of the *a*NHC **9**.

*a*NHCs are more basic than NHCs. Indeed, calculations predict that the first (287.0 kcal mol^{-1}) and second (144.6 kcal mol^{-1}) proton affinity of *a*NHC **9** are significantly higher than those of normal NHCs (229.9 to 270.6 and 38.9 to 106.5 kcal mol^{-1}, respectively) (*38*).

Although abnormal NHC **9** is sensitive to air and quantitatively rearranges to **8** upon heating in benzene at 50°C for 48 hours, it is stable at room temperature for a few days both in the solid state (melting point: decomposition at 65°C) and in solution (*39*). The availability of stable *a*NHCs not only provides easy access to a variety of transition-metal complexes, but also allows for their use as organocatalysts. As a proof of concept (*40–43*), (*a*NHC)AuCl complex **10** and (*a*NHC)-CO_2 adduct **11** have been prepared in 79 and 95% isolated yields by simply reacting **9** with chloro(dimethylsulfide)gold(I) and CO_2, respectively (Fig. 2).

Because the substituent at the C4 of **9** is a nonbulky benzene ring, a variety of substitution patterns should be tolerated without precluding isolation of the corresponding *a*NHC. The substituent at C4 is in conjugation with the carbene center, which opens the possibility of substantially modulating the electronic character of the ring system.

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Supporting Online Material

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Materials and Methods
References

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Carbenes As Catalysts for Transformations of Organometallic Iron Complexes

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Compared with the enormous arsenal of catalysts used to produce organic compounds, complementary species that are able to mediate sophisticated organometallic transformations are virtually nonexistent. We found that stable N-heterocyclic carbenes (NHCs) can mediate unusual organometallic transformations in solution at room temperature. Depending on the choice of NHC initiator, stoichiometric or catalytic reactions of bis(cyclooctatetraene)iron [$Fe(COT)_2$] ensue. The stoichiometric reaction leads to the isolation of a previously unknown mixed-valent species, featuring distinct and directly bonded Fe(0) and Fe(I) centers. In the catalytic process, three iron atoms are fused to afford the tri-iron cluster $Fe_3(COT)_3$, which is a hydrocarbon analog of Dewar's classic $Fe_3(CO)_{12}$ complex. The key step in both of these processes is proposed to involve the NHC's ability to induce metal–metal bond formation. These NHC-mediated reactions provide a foundation on which to develop future organometallic transformations that are catalyzed by organic species.

Carbenes are compounds with a neutral divalent carbon atom that feature either two singly occupied nonbonding orbitals (a triplet state) or a lone pair and an accessible vacant orbital (a singlet state). With only six electrons in its valence shell, the carbene center defies the octet rule, and for many years, carbenes were considered to be prototypical reactive intermediates (*1*). The view that carbenes could exist only as transient species was shattered in the late 1980s and early 1990s by the isolation of singlet phosphinosilyl (*2*) and N-heterocyclic carbenes (NHCs) (*3*), respectively, that were able to be bottled. These pioneering studies paved the way for the current revolution in carbene chemistry, which has rapidly developed over the past two decades (*4–7*). Although fundamental interest has contributed, the primary driving force for the explosion of research in this area is that NHCs and related species (*8*, *9*) have great synthetic utility.

Acting as strong electron donors, such species readily bind other molecules (*10–13*). Two of the best-known exploitations of this property are the

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