N-Heterocyclic Carbenes

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Generating and Trapping Metalla-N-Heterocyclic Carbenes**

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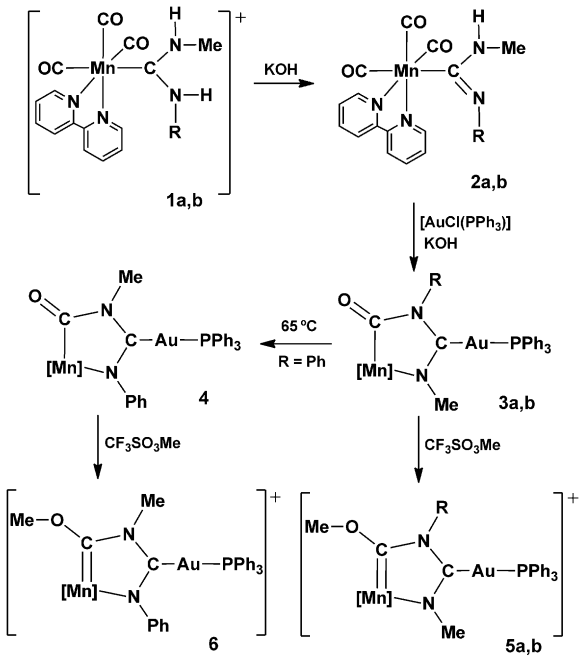
In memory of Oscar V. Quinzani

Abstract: *By means of a combined experimental and theoretical approach, the electronic features and chemical behavior of metalla-N-heterocyclic carbenes (MNHCs, N-heterocyclic carbenes containing a metal atom within the heterocyclic skeleton) have been established and compared with those of classical NHCs. MNHCs are strongly basic (proton affinity and pK_a values around 290 kcal mol^{-1} and 36, respectively) with a narrow singlet–triplet gap (around 23 kcal mol^{-1}). MNHCs can be generated from the corresponding metalla-imidazolium salts and trapped by addition of transition-metal complexes affording the corresponding heterodimetallic dicarbene derivatives, which can serve as carbene transfer agents.*

In view of the interest in and wide applicability of N-heterocyclic carbenes (NHCs),[1] many variations in the NHC architecture compared to classical imidazol-2-ylidenes have been developed. These structural variations aim to modify and tune the steric and electronic properties of the ligands[2] for their application in transition-metal complexes and catalysis. Notably, many of these investigations have led to NHCs with increased donor strength and involve changes in the heterocyclic skeleton. For example, the heterocyclic ring has been expanded from five- to six- or seven-membered NHCs[3] and the location of the carbene carbon atom has been changed (to form mesoionic or abnormal carbenes).[4] Additionally, one or two of the nitrogen atoms can be replaced with either phosphorus atoms (to form P-heterocyclic carbenes (PHCs)[5] and cyclic carbodiphosphoranes (CCDPs)[6]) or carbon atoms (forming cyclic (alkyl)(amino)carbenes (CAACs),[7] cyclic (amino)ylidic carbenes (N-YHC),[8] and cyclic bent allenes (CBAs)[9]).

In this regard, in the search for a new class of tunable electron-rich cyclic carbenes we have recently described the synthesis of hetero-dimetallic complexes bearing NHCs that contain a metal atom within the heterocycle skeleton (metalla-N-heterocyclic carbenes, MNHCs),[10] resulting from the formal replacement of a backbone carbon atom with a transition-metal atom.[11] The synthetic method (Scheme 1) implies double deprotonation of an acyclic diaminocarbene ligand in carbonyl manganese(I) complexes (**1a**,**b**), transmetalation of the carbene carbon atom from



Scheme 1. Generation of MNHC complexes **5a** (R = Ph), **5b** (R = Me), and **6**. [Mn] = [Mn(bipy)(CO)$_2$].

manganese to the gold center, and nucleophilic attack of a nitrogen atom to a carbonyl ligand to firstly isolate the carbamoyl derivatives **3a**, **3b**, and **4**. A further treatment with methyl triflate yields the corresponding complexes **5a**, **5b**, and **6**,[12] which are adducts of neutral MNHCs with the cationic fragment $[Au(PPh_3)]^+$.

To gain insight into the electronic properties of this new type of carbenes and develop synthetic strategies, we have now performed theoretical calculations supporting the existence of free strongly nucleophilic MNHCs, featuring a notably high proton affinity (PA). In parallel, and most importantly, we have found an experimental approach to generate the corresponding azolium salts $[MNHC\text{-}H]^+[CF_3SO_3]^-$ which were used as a source for trapping MNHCs with a variety of metal fragments.

DFT calculations were carried out on carbenes **7a**, **7b**, and **8**, formed upon removal of the cation $[Au(PPh_3)]^+$ in

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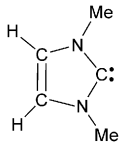
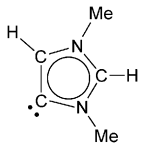
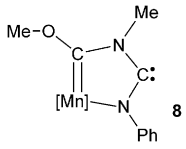
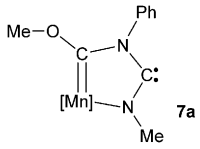
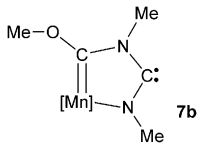
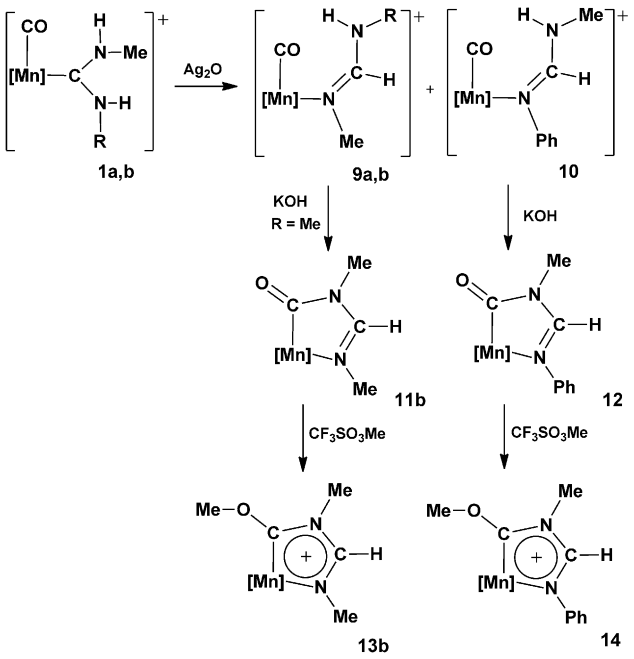
Table 1: Calculated values for proton affinity (PA), pK_a, and the singlet–triplet energy gap (Δ_{ST}) for carbenes **7a**, **7b**, and **8**, and for normal and abnormal NHCs.

Entry		PA (kcal mol^{-1})	pK_a	Δ_{ST} (kcal mol^{-1})
1		258.3	27.4	84.9
2		278.4	33.0	60.2
3	 **8**	289.6	35.0	26.5
4	 **7a**	292.6	36.3	23.5
5	 **7b**	290.8	37.1	23.2

complexes **5a**, **5b** and **6**, respectively, and on their corresponding metalla-azolium cations [MNHC-H]$^+$. As shown in Table 1, these MNHCs are singlet in the ground state, but the singlet–triplet gap is much smaller than for classical NHCs (imidazol-2-ylidenes; Table 1 entry 1)[13] or abnormal NHCs (entry 2)[13a,b] and is similar to the acyclic alkyl amino carbenes described by Bertrand and co-workers (26 kcal mol^{-1}).[14] Curiously, the average $C_{carbene}$–N bond lengths in **7a**, **7b**, and **8** (1.37 Å) are nearly identical to those found in NHCs.[1e] Similarly, the average C–N bond lengths in the cations [MNHC-H]$^+$ (1.32 Å) are comparable to those found in imidazolium salts.[1e] Naturally, both C–N distances are appreciably different from each other owing to the presence of the metal center bonded to the nitrogen atom N1 (for details see Supporting Information). The N–$C_{carbene}$–N bond angles are wider in these MNHCs (108°) and their cations [MNHC-H]$^+$ (118°) than in classical NHCs (102°) and imidazolium cations (around 110°), once again because of the distortion created by the bulky (compared with carbon) manganese atom within the heterocycle.

To evaluate the basicity of these new MNHCs, proton affinities (PA) of **7a**, **7b**, and **8** and pK_a values of their corresponding metalla-azolium cations [MNHC-H]$^+$ were calculated and compared with other known heterocyclic carbenes (Table 1).[15] Interestingly, the PA values of **7a**, **7b**, and **8** (around 290 kcal mol^{-1}) are much higher than for classical imidazol-2-ylidenes (258 kcal mol^{-1}; entry 1)[15,13a,16] and are greater than those of abnormal NHCs (278 kcal mol^{-1}; entry 2),[13a] indicating their strong basic character. Analogously, the pK_a values of **7a**, **7b**, and **8** (around 36) are higher than the pK_a of the conjugated acid of abnormal NHCs (33),[17] indicating once again the strong basicity of the MNHCs.

Once the existence and electronic properties of MNHCs **7a**, **7b**, and **8** were theoretically established, we looked for experimental procedures aimed at generating and trapping these unprecedented carbenes. The starting target compounds for these systems were their corresponding metalla-imidazolium salts [MNHC-H]$^+$[CF_3SO_3]$^-$. The assumed translocation process of the Au^I and Mn^I ions that allows formation of complexes **5a**, **5b**, and **6** (Scheme 1) prompted us to developed an experimental approach to transform the diaminocarbene complexes **1a** and **1b** to their corresponding formamidine tautomers. This was cleanly and quantitatively accomplished by treatment of dichloromethane solutions of **1a** or **1b** with Ag_2O which acts as a catalyst (Scheme 2). When starting material **1a** (R = Ph) was employed, two isomer complexes were formed in an approximate 1:1 ratio, containing either a C=NMe (**9a**) or a C=NPh (**10**) imine group bonded to the manganese center. Obviously, from the symmetrically-substituted diaminocarbene complex **1b** (R = Me) as starting material, the *N*,*N*′-dimethylformamidine complex **9b** was obtained as the only product (see the Supporting Information for full characterization data). Note, this metal-induced carbene–imine tautomerization is the opposite to that usually found with N-heterocyclic carbenes, which sometimes are formed through the metal-promoted tautomerization of imidazoles or other related cyclic imine ligands.[18] Under strong basic conditions (i.e. treatment with KOH), the cationic complexes **9b** and **10** are converted into neutral *cis*-dicarbonyl complexes **11b** and **12**, respectively (Scheme 2). This reaction involves deprotonation of the remaining N–H

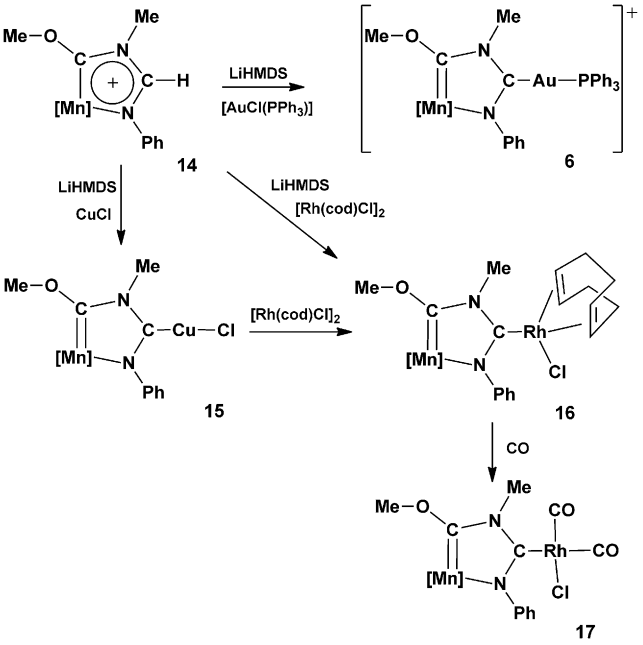


Scheme 2. Ag_2O-catalyzed tautomerization of diaminocarbene ligands to formamidine derivatives and the formation of metalla-imidazolium cations **13b** and **14**. [Mn] = [Mn(bipy)(CO)$_2$].

group and subsequent nucleophilic attack of the resulting formamidinate on a vicinal carbonyl ligand. The spectroscopic data are consistent with the proposed formulations for these new carbamoyl derivatives. Additionally, for compound **12** a single-crystal X-ray diffraction study has been undertaken (see the Supporting Information).[19]

To complete the formation of the metalla-imidazolium cations, compounds **11b** and **12** were alkylated at the carbamoyl oxygen atom by reaction with methyl triflate (Scheme 2), affording the salts [**13b**](CF_3SO_3) and [**14**]-(CF_3SO_3), respectively, which were isolated as microcrystalline red solids. It is worth noting that [**13b**](CF_3SO_3) and [**14**](CF_3SO_3) are soluble in water, in addition to in most common organic solvents, such as CH_2Cl_2 or THF, as occurs with classical imidazolium salts. The crystal structure of [**14**](CF_3SO_3) has been determined by single-crystal X-ray crystallography. A view of the metalla-imidazolium cation **14** is shown in Figure 1, together with that of its corresponding gold metallated counterpart **6**.[19] Notably, the structural parameters of **14** are very similar to those found from DFT calculations for molecule [**8-H**]$^+$.

In the absence of any trapping agent, all attempts to spectroscopically detect the MNHC **8** upon treatment of [**14**](CF_3SO_3) with several bases (LiHMDS, BuLi, NaH, or KO*t*Bu; LiHMDS = lithium hexamethyl disilazide) even at low temperature were unsuccessful owing to its instability. However, when the deprotonation reaction of the metalla-imidazolium cation **14** was carried out in the presence of a variety of transition-metal compounds, such as [AuCl-(PPh_3)], CuCl, and [Rh(cod)Cl]$_2$ (cod = 1,5-cyclooctadiene), the corresponding metal adducts of carbene **8** (complexes **6**, **15**, and **16**, respectively; see Scheme 3) were obtained and



Scheme 3. Formation of transition-metal complexes **6**, **15**, **16**, and **17**, each containing the MNHC **8**, from the metalla-imidazolium cation **14**. [Mn] = [Mn(bipy)(CO)$_2$].

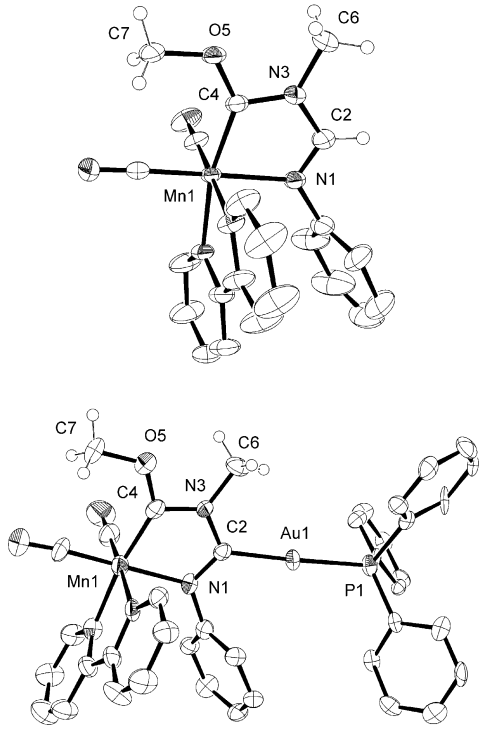


Figure 1. Molecular structure of the cationic complexes **14** (top) and **6** (bottom), shown with thermal ellipsoids set at 50% probability. Hydrogen atoms (except C2-H and those of the methyl groups) are omitted for clarity. Selected bond lengths [Å] and angles [°] in **14**: Mn1–N1 2.068(2), N1–C2 1.277(4), C2–N3 1.374(4), N3–C4 1.376(4), C4–Mn1 1.920(3), C4–O5 1.326(3); Mn1-N1-C2 113.2(2), N1-C2-N3 117.3(3), C2-N3-C4 114.5(3), N3-C4-Mn1 115.9(2), C4-Mn1-N1 78.81(11). **6**: Mn1–N1 2.072(9), N1–C2 1.306(13), C2–N3 1.373(13), N3–C4 1.403(14), C4–Mn1 1.910(12), C4–O5 1.347(13), Au1–C2 2.050(11), Au1–P1 2.285(3); Mn1-N1-C2 115.3(7), N1-C2-N3 113.7(10), C2-N3-C4 115.9(10), N3-C4-Mn1 115.6(8), C4-Mn1-N1 78.5(4), C2-Au1-P1 177.5(3).

fully spectroscopically characterized. Additionally, the structure of **15** has been determined by X-ray crystallography (Figure 2).[19] In the $^{13}C\{^1H\}$ NMR spectra, a resonance signal attributable to the newly formed carbene carbon atom is detected as expected in the downfield region of the spectrum, appearing at $\delta = 212.9$ ppm for **15** and at $\delta = 220.4$ ppm for **16** (d, $^1J_{RhC} = 46.9$ Hz). Naturally, the signal due to the endocyclic Fischer carbene C atom at very high frequency (around $\delta =$ 275 ppm) is maintained. It is worth noting that the MNHC–Cu^I compound **15** can serve as a carbene transfer reagent, showing a similar behavior to that found with classical NHC–Cu^I[20] or NHC–Ag^I[21] derivatives. As a preliminary example, the reaction of **15** with [Rh(cod)Cl]$_2$ was carried out to readily afford the MNHC–Rh^I complex **16**.

By bubbling CO through a solution of **16** in THF, complex *cis*-[RhCl(CO)$_2$(MNHC)] (**17**; Scheme 3) was readily formed. The FTIR spectrum of **17** features ν(CO) bands at 2062 and 1986 cm^{-1} (average value 2024 cm^{-1}), which accounts for a Tolman electronic parameter (TEP) of 2039 cm^{-1}. This value is low in comparison with most known imidazol-2-ylidene ligands,[2] showing once again the strong electron-donating character of MNHCs.

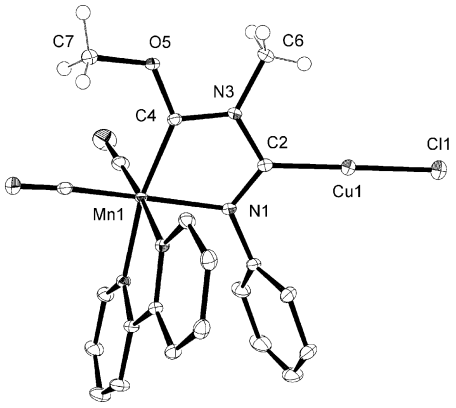


Figure 2. Molecular structure of the neutral complex **15**, shown with thermal ellipsoids set at 50% probability. Hydrogen atoms (except those of the methyl groups) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn1–N1 2.0607(9), N1–C2 1.3036(14), C2–N3 1.4032(14), N3–C4 1.3658(14), C4–Mn1 1.9309(10), C4–O5 1.3369(13), Cu1–C2 1.9074(11), Cu1–Cl1 2.1102(3); Mn1-N1-C2 117.48(7), N1-C2-N3 111.11(9), C2-N3-C4 117.16(9), N3-C4-Mn1 116.21(7), C4-Mn1-N1 77.54(4), C2-Cu1-Cl1 178.52(4).

In summary, we have found an experimental procedure for generating and trapping metalla-N-heterocyclic carbenes following a synthetic approach that involves a unique metal-catalyzed tautomerization reaction of diaminocarbene ligands to formamidines. From this work the electronic features and chemical behavior of MNHCs have been established: a) DFT calculations and TEP values show that MNHCs are stronger bases than many classical NHCs, b) MNHCs can be generated from the corresponding azolium cations ([MNHC-H]$^+$) and form complexes with a variety of transition metals, and c) MNHCs can easily undergo transmetalation reactions. The possibility of tuning the donor strength of MNHCs by modifying the ancillary ligands, oxidation state, and nature of the endocyclic metal atom is now being explored in our laboratory.

Keywords: carbene ligands · density functional calculations · manganese · N-heterocyclic carbenes · rhodium

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