Carbene Ligands

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A Fischer Carbene within an Arduengo Carbene**

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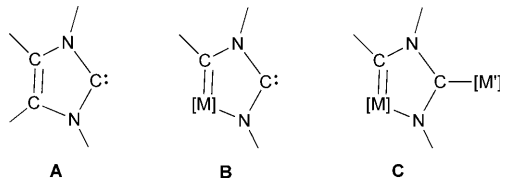
The chemistry of N-heterocyclic carbenes (NHCs) has been an intense area of research in the last several years.[1] The pioneering work by Arduengo et al.[2] and Herrmann[3] on free ligand isolation and catalytic applications of NHC metal complexes, respectively, has significantly contributed to the development of this field. There is currently a widespread interest in developing new strategies for NHC ligand design involving the replacement of the carbon atom backbone with heteroatoms.[4] Apart from the well-known triazol-2-ylidenes,[5] NHCs containing boron[4a–d] and phosphorus[4f] as heteroatoms in the N-heterocyclic skeleton have been described. However, NHCs featuring a metal atom within the heterocyclic framework, derived from the standard imidazole cycle, are still unknown.[6,7] Replacement of the carbon atom at C4 of an Arduengo carbene (Scheme 1, **A**)



Scheme 1. Arduengo carbene (**A**), and unprecedented carbene complex within an NHC skeleton (**B**) and heterometallic dicarbene derivatives (**C**). [M], [M′] = transition-metal complexes.

with a metal atom belonging to a transition-metal complex would lead to the generation of a carbene complex within the NHC skeleton (**B**), which, upon coordination of a new metallic center would give unprecedented heterometallic dicarbene derivatives (**C**).[8] This goal has been achieved as part of this study. Herein, we describe the first synthesis of an Arduengo carbene complex featuring a metal atom within the heterocyclic skeleton, which has been accomplished through an experimental approach implying transformation of an acyclic diaminocarbene complex into a NHC.

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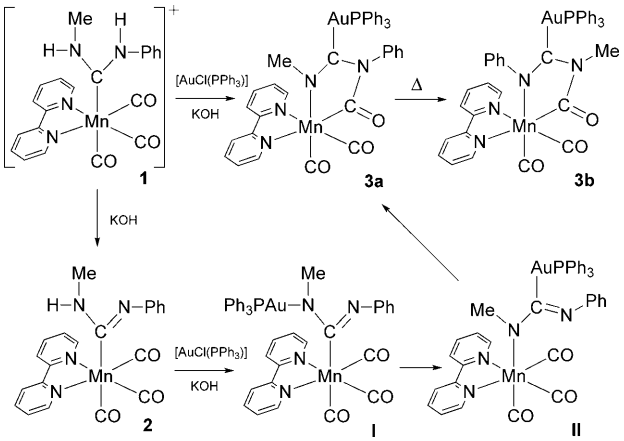
Supporting information for this article, including experimental details of the synthesis and characterization of **3a**, **3b**, **4a**, and **4b**, is available on the WWW under http://dx.doi.org/10.1002/anie.201007937.

The treatment of a solution of the cationic diaminocarbene complex *fac*-[Mn{C(NHPh)(NHMe)}(CO)$_3$(bipy)]$^+$ **1**[9] in dichloromethane with a stoichiometric amount of [AuCl(PPh$_3$)], in the presence of an excess of KOH, afforded the heterometallic Mn^I/Au^I neutral complex **3a**, which was isolated as a black solid (Scheme 2). The reaction was



Scheme 2. Formation of **3a** and **3b** through the proposed intermediates **I** and **II**.

monitored by IR spectroscopy, thus allowing observation of the formamidinyl complex **2** as a reaction intermediate. In an independent experiment we have proved that complex **2** does not react with [AuCl(PPh$_3$)] unless KOH is present. Compound **3a** was quantitatively transformed into its isomer **3b**, corresponding to the location of the NMe and NPh groups in interchanged positions, by heating a solution of the complex in THF at reflux for 20 minutes. The phosphorus spectrum of both isomers showed a singlet signal near to $\delta = 40$ ppm, which is typical for the [Au(PPh$_3$)]$^+$ fragment bonded to nucleophilic carbenes.[8b] This observation suggested that, apart from substitution of the remaining N–H proton in **2** by the isolobal [Au(PPh$_3$)]$^+$ fragment (intermediate **I**, Scheme 2),[10] a translocation process of the Mn^I and Au^I ions occurred (intermediate **II**), thus leading to the nitrogen atom being bonded to manganese and the carbene carbon atom being bonded to gold. The soft acid character of the Au^I ion, which prefers to bind a soft carbon atom instead of a hard nitrogen atom, could be the driving force for this transformation.

In the ν(CO) region of the IR spectra of **3a** and **3b** is revealed a pattern of bands characteristic for *cis*-dicarbonyl complexes, consisting of two strong bands at much lower frequencies than the starting complex **1**. This fact, together with the presence of a ν(C=O) band at 1580 cm^{-1}, supports the existence of a carbamoyl group in the complex, very likely

resulting from a nucleophilic attack of the imine residue of intermediate **II** to a vicinal carbonyl ligand. In addition, the ^{1}H NMR spectra shows a singlet signal for the methyl group at $\delta = 2.72$ (**3a**) and 3.42 ppm (**3b**).[11] Furthermore, the $^{13}C\{^1H\}$ NMR spectrum of **3b** clearly shows four low-field signals corresponding to carbamoyl ($\delta = 250.5$ ppm), carbonyl ($\delta =$ 227.7 and 226.0 ppm), and carbene ($\delta = 208.0$ ppm) carbon atoms. Note that intermediates **I** and **II** allow a reasonable explanation for the formation of isomer **3a** as a kinetic product, although they were not detected during the course of the reaction. Fortunately, crystals of **3a** suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution of the complex (Figure 1).[12]

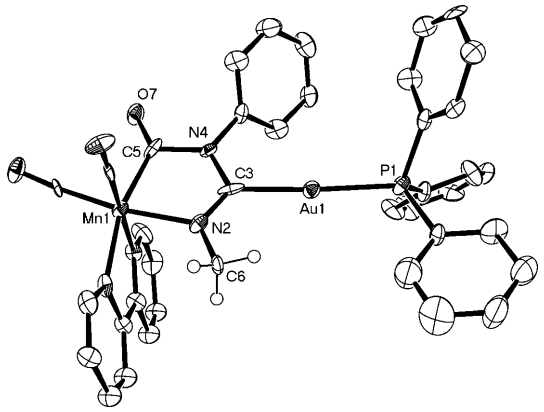
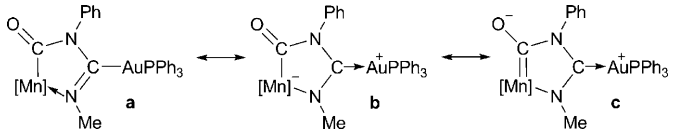


Figure 1. ORTEP drawing of the complex **3a**, shown with 50% thermal ellipsoids. Hydrogen atoms of the bipy ligand and phenyl groups are omitted for clarity. Selected interatomic bond lengths [Å] and angles [°]: Mn1–N2 2.075(15), N2–C3 1.286(20), C3–N4 1.396(20), N4–C5 1.447(20), C5–Mn1 1.967(20), C5–O7 1.260(20), C3–Au1 2.054(20), Au1–P1 2.278(5); Mn1-N2-C3 114.7(13), N2-C3-N4 115.5(17), C3-N4-C5 117.8(15), N4-C5-Mn1 110.7(12), C5-Mn1-N2 81.1(7), C3-Au1-P1 176.5(6).

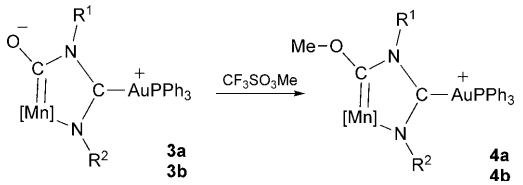
The X-ray crystal structure shows that the new diazamangana-heterocycle species formed features a carbamoyl fragment. The short C3–N2 (1.28(2) Å) and C3–N4 (1.39(2) Å) bond lengths, together with the planar geometry around N2 and N4 nitrogen atoms, indicate strong electronic delocalization within the N2-C3-N4 skeleton. Several resonance structures for the bond description in the metalaheterocycle can be drawn (Scheme 3). No doubt the formamidinyl form (**a**) should make an important contribution, but the carbene forms (**b**) and (**c**) must also be considered. In fact, the Mn1–C5 (1.96(2) Å) bond length is slightly shorter than that usually found for Mn–C single bonds (2.12 Å),[13] and the C5–O7 distance (1.26(2) Å) is lengthened from that typically encountered in acyl complexes or in amide molecules (1.21 Å),[13,14]



Scheme 3. Resonance structures for complex **3a**. [Mn] = [Mn(CO)$_2$(bipy)].

therefore supporting some contribution by the carbene-like form of the carbamoyl fragment.

In accordance with the above interpretation, **3a** and **3b** can be alkylated at the carbamoyl oxygen atom in a similar manner as acyl complexes are transformed into Fischer carbenes.[15] This transformation is achieved by treatment with methyl triflate, thus yielding the cationic complexes **4a** and **4b**, respectively (Scheme 4).[16] The reaction proceeds



Scheme 4. Formation of the mixed Fischer/Arduengo carbene complexes **4a** and **4b. 3a**, **4a**: $R^1 = Ph$, $R^2 = Me$; **3b**, **4b**: $R^1 = Me$, $R^2 = Ph$. [Mn] = [Mn(CO)$_2$(bipy)].

readily with a strong change in the color of the solution from black to red and, after appropriate work-up, compounds **4a** and **4b** were isolated as air-sensitive red solids. In the ν(CO) region of the IR spectra of **4a** and **4b** is revealed two strong bands at higher frequencies than their neutral precursors. The most significant signals in the $^{13}C\{^1H\}$ NMR spectra are those corresponding to the manganese-bonded and gold-bonded carbene carbon atoms (around $\delta = 278$ and 213 ppm, respectively). The structure of **4a** was unambiguously established by single-crystal X-ray analysis (Figure 2),[12] thus allowing a comparison with its neutral precursor **3a**.

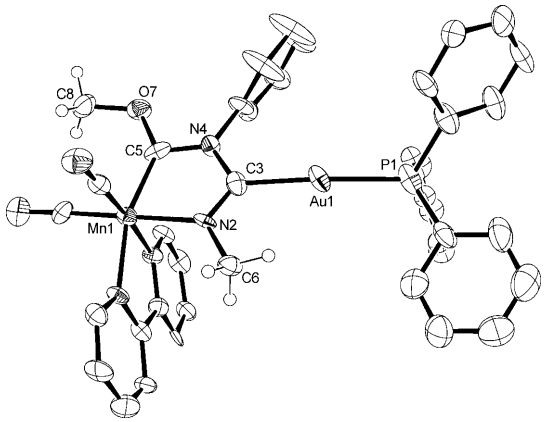


Figure 2. ORTEP drawing of the cationic complex **4a**, shown with 50% thermal ellipsoids. Hydrogen atoms of the bipy ligand and phenyl groups are omitted for clarity. Selected interatomic bond lengths [Å] and angles [°]: Mn1–N2 2.049(7), N2–C3 1.292(11), C3–N4 1.387(11), N4–C5 1.355(12), C5–Mn1 1.925(10), C5–O7 1.343(10), C3–Au1 2.066(9), Au1–P1 2.220(3); Mn1-N2-C3 115.4(6), N2-C3-N4 113.9(8), C3-N4-C5 116.0(8), N4-C5-Mn1 115.8(6), C5-Mn1-N2 78.0(4), C3-Au1-P1 171.8(21), N4-C5-O7 108.6(8), C5-O7-C8 119.9(8), Mn1-C5-O7 135.6(8).

The methoxy substituent of **4a** displays an *anti*-disposition with respect to the bridging N–Ph group, which is very likely

due to steric reasons. The Mn1–C5 bond length (1.92(1) Å) is slightly shortened with respect to the corresponding distance in **3a**, and is in the range of those usually found in Fischer carbenes of Mn^{I}.[17] The difference between the C3–N2 and C3–N4 bond lengths is slightly smaller in **4a** (0.09 Å) than in **3a** (0.11 Å. However, this difference is still more pronounced than that usually found in unsymmetrically substituted NHCs,[18] naturally owing to the special electronic influence of the metal atom within the heterocycle, which forces a stronger π-donation from N2 than from N4 to the carbene carbon atom C3.

In summary, we have found an experimental approach to transform acyclic diaminocarbene complexes into N-heterocyclic carbenes containing a transition-metal atom within the heterocyclic skeleton. In this way, an unprecedented bonding arrangement for carbene complexes, consisting of the placement of a Fischer carbene as part of an Arduengo carbene backbone, was achieved. Studies aimed at generating other metal-containing NHC ligands are currently in progress.

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[12] CCDC 740746 (**3a**) and 804379 (**4a**) contain the suplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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