Strongly Donor Metalla-N-Heterocyclic Carbenes

Javier Ruiz, a Lucía García, a Carmen Mejuto, a Marilín Vivanco, a M. Rosario Díaz b and Santiago García-Granda b

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

By choosing the appropriate coupling reactions an isocyanide ligand in complex [Fe(Cp)(CO)(CNPh)] can be transformed either into a conventional NCIC or into a metalla-N-heterocyclic carbene (MNHC), with CO and CNR ligands in the iron center being witness for the stronger electron-donating ability of the metal-containing carbenes.

Since the isolation and crystal-structure determination of the first N-heterocyclic carbene (NHC) by Arduengo and coworkers two decades ago, a vast amount of transition-metal complexes containing these types of ligands has been reported in the literature, many of them being successfully applied in homogeneous catalysis. By far, the most widely used NHCs are those based on the imidazol-2-ylidene heterocycle. The tuning of the electron-donor capability of these carbenes is crucial for the success of their catalytic applications, has been mainly accomplished by varying the substituents on the nitrogen atoms or on the carbon backbone atoms. It has been shown that several modifications of the heterocyclic skeleton itself, such as changing the location of the carbone carbon atom (mesoionic or abnormal carbenes), or the replacement of the nitrogen atoms with oxygen (oxazol-2-ylidenes), sulfur (thiazol-2-ylidenes), phosphorus (P-heterocyclic carbenes, PHCs) or carbon (cyclic (alkyl)(amino)carbenes, CAACs) atoms, strongly affect the electron-donating ability of these ligands. Only on a few occasions replacement of the carbon backbone atoms by heteroatoms such as nitrogen (A in Figure 1) or boron (B) has been reported. Recently, our group has described the synthesis of unique NHC-gold complexes containing a metal atom within the NHC skeleton (C). In the present work it has been found a new experimental protocol for the formation of metalla-N-heterocyclic carbenes (MNHCs) and proved for the first time its strong electron-donor character by comparison with classical imidazol-2-ylidenes, based on the variation of the ν(CO) and ν(CN) stretching frequencies of the ancillary carbonyl and isocyanaide ligands in the half-sandwich cationic complexes [Fe(Cp)(CO)(CNR)(L)] (L = NHC or MNHC).

Figure 1. N-heterocyclic carbenes with heteroatoms in the backbone.

The synthetic approach involves transformation of one of the isocyanide ligands of the complex [Fe(Cp)(CO)(CNPh)] into a ruthena-N-heterocyclic carbene (6) through a five-step reaction pathway implying several coupling reactions, as depicted in Scheme 1. Thus, nucleophilic addition of methylene to a xlylsisocyanide ligand of 1 readily affords the acyclic dianimocarbene (ADC) complex 2, which is converted to 3, resulting from deprotonation of the N(H)Xylyl group followed by nucleophilic attack at the adjacent isocyanide ligand, by treatment with KOH. Metallation of the remaining N(H)Me group by addition of half equivalent of [Ru(p-cym)(Cl)] in the presence of Li[N(SiMe)] leads to 4, thus reforming the isocyanide ligand after C-N bond breaking owing to the preference of the doubly deprotonated form of the ADC to bind ruthenium in a chelating manner. A substitution reaction of the chloride ligand in 4 by isocyanide, using TIPF as halogen abstractor, yields the cationic complex 5, which is finally transformed to 6 by treatment with HCl. Very likely this last reaction involves protonation of the NMe group with parallel coordination of the chloride ion to ruthenium and further nucleophilic addition of the preformed N(H)Me moiety to the ruthenium-bonded isocyanaide ligand 7. All complexes in Scheme 1 have been fully characterized by spectroscopic methods (see Supporting Information). Additionally, an X-ray crystal structure analysis has been carried out on
out for complex 6 (Figure 2).\textsuperscript{18} Note that 6 is a unique species in which an acyclic dianimocarbene complex is included in the skeleton of an N-heterocyclic carbene,\textsuperscript{3} so that the ruthenium atom formally replaces a carbon atom from the backbone in the imidazol-2-ylidine ligand (an ADC complex into an NHC!). In the $^{13}$C($^1$H) NMR spectrum both carbene carbon atoms appear in the expected low-field region (about 220 ppm), whereas the IR spectrum shows $\nu$(CO) (1975 cm$^{-1}$) and $\nu$(CN) (2114 cm$^{-1}$) bands at lower frequencies than the acyclic precursor 2 (1976 and 2130 cm$^{-1}$, respectively) reflecting the stronger donor character of the MNHC with respect to the ADC (see below).

![Figure 2](image1.png)

Figure 2. Molecular structure of the cationic complex 6, shown with 33% thermal ellipsoids. Hydrogen atoms (except N4-H) are omitted for clarity. Selected interatomic distances (Å) and angles (deg): C2-N1 1.315(5), C2-N3 1.410(5), C4-Ru1 2.014(4), N1-C2-N3 110.3(3), N1-Ru1-C4 75.8(2).

To compare the electronic and structural features of the new metallia-N-heterocyclic carbene with respect to classical NHCs coordinated to the same metal fragment, an isocyanide ligand of 1 has additionally been transformed into an imidazol-2-ylidene. With this aim a [3+2] coupling reaction between 1 and propargylamine has been accomplished to afford the cationic complex 7 (Scheme 2). This reaction is itself noteworthy, as this methodology to obtain NHC complexes, developed by our group,\textsuperscript{20} had never been observed with metals different from manganese.

![Scheme 2](image2.png)


The X-ray crystal structure of 7 has been determined (Figure 3), allowing a comparison of the structural parameters between 6 and 7. In both NHC and MNHC ligands the heterocycle is essentially planar. The presence of the bulky ruthenium atom in 6 causes appreciable changes in the bond distances and angles within the heterocycle with respect to those found in 7. Thus, the N1-C2-N3 angle is slightly more open in 6 (110.3(3)$^\circ$) than in 7 (105.4(6)$^\circ$), and the N1-C2 bond length is appreciably shorter in the former (1.315(5) Å versus 1.362(9) Å) indicating a strong π-donation from the ruthenium-bonded nitrogen atom (N1) to the carbene carbon atom (note that the N3-C2 distance in 6, 1.410(5) Å, is significantly longer).

Various methodologies have been described to evaluate the donor properties of NHCs:\textsuperscript{25} the most frequently used are those based on the values of the stretching frequencies of CO ligands in the complexes [Ni(CO)$_2$(NHC)],\textsuperscript{22} cis-[Rh(C)(CO)$_2$(NHC)]\textsuperscript{23} or cis-[Ir(C)(CO)$_2$(NHC)]\textsuperscript{24} (the lower the stretching frequency of CO, the stronger the donor ability of the NHC ligand).\textsuperscript{25} In our case, the availability of complexes of formula [Fe(Cp)(CO)(CN)R(L)]\textsuperscript{2+} (L = ADC, NHC or MNHC), allows a comparison of the electron-donor ability of the different carbene ligands based not only on the $\nu$(CO) frequency of the carbonyl ligand but also on the $\nu$(CN) frequency of the isocyanide ligand, which is on occasions more strongly affected by the electronic changes of the carbene ligand, as summarized in Table 1.

![Figure 3](image3.png)

Figure 3. Molecular structure of the cationic complex 7, shown with 33% thermal ellipsoids. Hydrogen atoms (except N3-H) are omitted for clarity. Selected interatomic distances (Å) and angles (deg): C2-N1 1.362(9), C2-N3 1.324(9), C4-C5 1.351(13); N1-C2-N3 110.4(6), N1-Ru1-C4 75.8(2).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$(CN)$^a$ (cm$^{-1}$)</th>
<th>$\nu$(CO)$^b$ (cm$^{-1}$)</th>
<th>$\Delta_{\text{CN}}$ (cm$^{-1}$)</th>
<th>$\Delta_{\text{CO}}$ (cm$^{-1}$)</th>
<th>$\Delta_{\text{CN}}$ + $\Delta_{\text{CO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2130</td>
<td>1976</td>
<td>2</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>2097</td>
<td>1953</td>
<td>35</td>
<td>30</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>2114</td>
<td>1963</td>
<td>18</td>
<td>20</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>2114</td>
<td>1975</td>
<td>18</td>
<td>8</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>2122</td>
<td>1980</td>
<td>3</td>
<td>3</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$^a$ cm$^{-1}$; $^b$ cm$^{-1}$</th>
<th>$^c$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_{\text{CN}} = \nu$(CN)(7) - $\nu$(CN)(n) (n = 2-8).</td>
<td>$\Delta_{\text{CO}} = \nu$(CO)(7) - $\nu$(CO)(n) (n = 2-8).</td>
</tr>
</tbody>
</table>

Complex 7 features the highest $\nu$(CN) and $\nu$(CO) values so that its imidazol-2-ylidene ligand can be considered the weakest electron-donor in this series, and was taken as a reference for measuring the decrease of the $\nu$(CN) and $\nu$(CO) stretching frequencies in the different complexes ($\Delta_{\text{CN}}$ and $\Delta_{\text{CO}}$, Table 1) and hence the relative donor character of the corresponding carbene ligands. Thus, the MNHC ligand in complex 6 is considerably more donating than the NHC ligand in 7 with a total decrease in the stretching frequencies of CO and CNR ligands ($\Delta_{\text{CN}} + \Delta_{\text{CO}}$) of 26 cm$^{-1}$. Note that changing the substituents on a nitrogen atom of the NHC affects the electron richness of the NHC ligand only to a minor extent (complex 8 in Scheme 2, $\Delta_{\text{CN}} + \Delta_{\text{CO}} = 10$ cm$^{-1}$) compared to the introduction of a metal atom into the heterocycle (complex 6). On the other hand, the carbene ligands in complexes 4 and 5, which can be considered as four-membered metallia-N-heterocyclic carbene, feature the highest donor character, singularly complex 4 ($\Delta_{\text{CN}} + \Delta_{\text{CO}} = 65$ cm$^{-1}$) that contains an anionic chloride ligand bonded to ruthenium instead of a neutral isocyanide ligand as in 5 ($\Delta_{\text{CN}} + \Delta_{\text{CO}} = 38$ cm$^{-1}$). This illustrates the feasibility of tuning the electronic properties.
of the MNHCs by modifying the coordination environment of the metal atom in the metallacycle.

To summarize, it has been described herein a new experimental approach for the construction of N-heterocyclic carbones containing a metal atom within the heterocyclic skeleton (metalλ-N-heterocyclic carbones, MNHCs) and shown their enhanced electron-donor character compared with classical NHCs, based on the measure of the stretching frequencies of CO and CNR ligands in the complexes [Fe(Cp)(CO)(CNR)(L)] (L = NHC or MNHC). The isolation of free MNHCs, which would allow access to a new generation of tunable electron-rich MNHC complexes, remains as an intellectual and experimental challenge.

This work was supported by the Spanish Ministerio de Economía y Competitividad (Project CTQ2012-32239).

Notes and references

14 a) In fact, in an independent experimental we have demonstrated that the reaction time for the generation of complexes 5 can be considerably shortened by depyrotonation of the first formed Ni(II)Me moiety with KOH, which facilitates the nucleophilic attack to the adjacent isoxyanide ligand, and further protonation with NH4PF6. For intramolecular nucleophilic attack of primary amines at coordinated isoxanides see: b) F. E. Hahn, V. Langenhanh, N. Meier, T. Lügger and W. P. Fehlhammer, Chem. Eur. J. 2003, 9, 704; c) F. E. Hahn, V. Langenhanh and T. Pape, Chem. Commun. 2005, 5390; d) A. Flores-Figueroa, T. Pape, K. Feldmann and E. H. Hahn, Chem. Commun. 2010, 46, 324.
15 Preliminary X-ray diffraction data confirm the proposed structure for 5.
16 A related dimetallacyclic complex of palladium(II) bearing a formamidinyl moiety has been described recently: A. G. Tskhovrebov, K. V. Luzyanin, M. F. Dolgushin, M. F. C. Guedes da Silva, A. J. L. Pombeiro and V. Y. Kukushkin, Organometallics 2011, 30, 3362.
18 For a review see reference 2a.