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Strongly Donor Metalla-N-Heterocyclic Carbenes

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By choosing the appropriate coupling reactions an isocyanide ligand in complex $[\text{Fe}(\text{Cp})(\text{CO})(\text{CNXyly})_2]^+$ is transformed either into a conventional NHC 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,¹ a vast amount of transition-metal complexes containing these types of ligands has been reported in the literature,² many of them being successfully applied in homogeneous catalysis.³ 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, which 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.⁴ It has been shown that several modifications of the heterocyclic skeleton itself,⁵ such as changing the location of the carbene carbon atom (mesoionic or abnormal carbenes),⁶ or the replacement of the nitrogen atoms with oxygen (oxazol-2-ylidenes),⁷ sulfur (thiazol-2-ylidenes),^{7a,8} phosphorus (P-heterocyclic carbenes, PHCs)⁹ or carbon (cyclic (alkyl)(amino)carbenes, CAACs)¹⁰ atoms, strongly affect the donor ability of these ligands. Only on a few occasions replacement of the carbon backbone atoms by heteroatoms such as nitrogen (A in Figure 1)¹¹ or boron (B)¹² has been reported.¹³

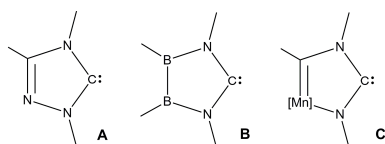
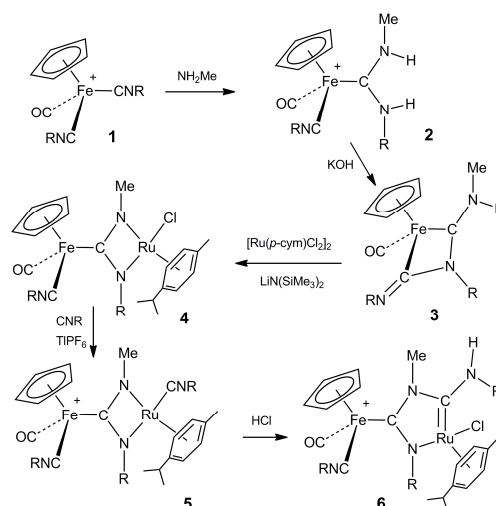


Figure 1. N-heterocyclic carbenes with heteroatoms in the backbone.

Recently, our group has described the synthesis of unique NHC-gold complexes containing a metal atom within the NHC skeleton (C).¹⁴ In the present work it has been found a new experimental protocol for the formation of metalla-N-heterocyclic carbenes (MNHCs)^{15,16} and proved for the first time its strong electron-donor character by comparison with classical imidazol-2-ylidenes, based on the variation of the $\nu(\text{CO})$ and $\nu(\text{CN})$ stretching frequencies of the ancillary carbonyl and isocyanide ligands in the half-sandwich cationic complexes $[\text{Fe}(\text{Cp})(\text{CO})(\text{CNR})(\text{L})]^+$ (L = NHC or MNHC).



Scheme 1. Formation of metalla-N-heterocyclic carbenes from a coordinated isocyanide ligand in 1. R = Xylyl.

The synthetic approach involves transformation of one of the isocyanide ligands of the complex $[\text{Fe}(\text{Cp})(\text{CO})(\text{CNXyly})_2]^+$ (1) 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 methylamine to a xylilisocyanide ligand of 1 readily affords the acyclic diaminocarbene (ADC) complex 2, which is converted to 3, resulting from deprotonation of the N(H)Xylyl group followed by nucleophilic attack to the adjacent isocyanide ligand, by treatment with KOH. Metallation of the remaining N(H)Me group by addition of half equivalent of $[\text{Ru}(p\text{-cym})\text{Cl}_2]_2$ in the presence of $\text{LiN}(\text{SiMe}_3)_2$ leads to 4, thus reforming the isocyanide 60 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 TlPF_6 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 isocyanide ligand.¹⁷

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 for complex **6** (Figure 2).¹⁸ Note that **6** is a unique species in which an acyclic diaminocarbene complex is included in the skeleton of an N-heterocyclic carbene,¹⁹ so that the ruthenium atom formally replaces a carbon atom from the backbone in the imidazol-2-ylidene ligand (an ADC complex into an NHC!). In the ¹³C{¹H} NMR spectrum both carbene carbon atoms appear in the expected low-field region (about 220 ppm), whereas the IR spectrum shows $\nu(\text{CO})$ (1975 cm^{-1}) and $\nu(\text{CN})$ (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).

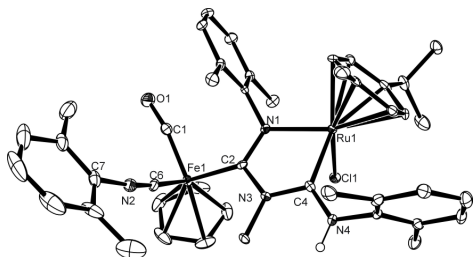
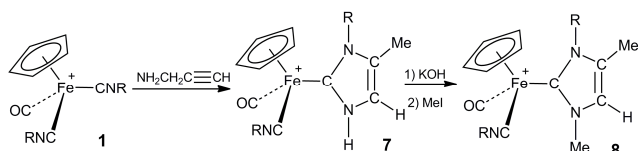


Figure 2. Molecular structure of the cationic complex **6**, shown with 33% thermal ellipsoids. Hydrogen atoms (except N4-H) are omitted for clarity. Selected interatomic distances (Å) and angles (deg): C2-N1 1.315(5), C2-N3 1.410(5), C4-Ru1 2.014(4); N1-C2-N3 110.3(3), N1-Ru1-C4 75.8(2).

To compare the electronic and structural features of the new metalla-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,²⁰ had never been observed with metals different from manganese.



Scheme 2. Formation of complex **7** by a [3+2] coupling reaction of propargylamine and isocyanide, and its derivatization to **8**. R = Xylyl.

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)°) than in **7** (105.4(6)°), 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;²¹ the most frequently used are those based on the values of the stretching frequencies of CO ligands in

the complexes $[\text{Ni}(\text{CO})_3(\text{NHC})]$,²² *cis*- $[\text{Rh}(\text{Cl})(\text{CO})_2(\text{NHC})]$ ²³ or *cis*- $[\text{Ir}(\text{Cl})(\text{CO})_2(\text{NHC})]$ ²⁴ (the lower the stretching frequency of CO, the stronger the donor ability of the NHC ligand).²⁵ In our case, the availability of complexes of formula $[\text{Fe}(\text{Cp})(\text{CO})(\text{CNR})(\text{L})]^+$ (L = ADC, NHC or MNHC), allows a comparison of the electron-donor ability of the different carbene ligands based not only on the $\nu(\text{CO})$ frequency of the carbonyl ligand but also on the $\nu(\text{CN})$ 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.

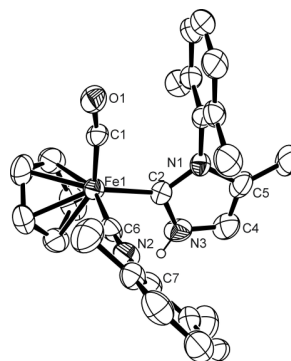


Figure 3. Molecular structure of the cationic complex **7**, shown with 33% thermal ellipsoids. Hydrogen atoms (except N3-H) are omitted for clarity. Selected interatomic distances (Å) and angles (deg): C2-N1 1.362(9), C2-N3 1.324(9), C4-C5 1.351(13); N1-C2-N3 105.4(6), N1-C5-C4 105.7(8).

Table 1. IR data of the carbene complexes **2-8** in THF.

Complex	$\nu(\text{CN})$ ^[a]	$\nu(\text{CO})$ ^[a]	$\Delta_{(\text{CN})}$ ^[b]	$\Delta_{(\text{CO})}$ ^[c]	$\Delta_{(\text{CN})} + \Delta_{(\text{CO})}$
2	2130	1976	2	7	9
4	2097	1953	35	30	65
5	2114	1963	18	20	38
6	2114	1975	18	8	26
7	2132	1983	0	0	0
8	2125	1980	7	3	10

[a] cm^{-1} . [b] $\Delta_{(\text{CN})} = \nu(\text{CN})(\mathbf{7}) - \nu(\text{CN})(\mathbf{n})$ ($\mathbf{n} = \mathbf{2-8}$). [c] $\Delta_{(\text{CO})} = \nu(\text{CO})(\mathbf{7}) - \nu(\text{CO})(\mathbf{n})$ ($\mathbf{n} = \mathbf{2-8}$).

Complex **7** features the highest $\nu(\text{CN})$ and $\nu(\text{CO})$ 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 $\nu(\text{CN})$ and $\nu(\text{CO})$ stretching frequencies in the different complexes ($\Delta_{(\text{CN})}$ and $\Delta_{(\text{CO})}$, Table 1) and hence the relative donor character of the corresponding carbenes. 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, $\Delta_{(\text{CN})} + \Delta_{(\text{CO})} = 10 \text{ cm}^{-1}$) 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 metalla-N-heterocyclic carbenes, feature the highest donor character, singularly complex **4** ($\Delta_{(\text{CN})} + \Delta_{(\text{CO})} = 65 \text{ cm}^{-1}$) that contains an anionic chloride ligand bonded to ruthenium instead of a neutral isocyanide ligand as in **5** ($\Delta_{(\text{CN})} + \Delta_{(\text{CO})} = 38 \text{ cm}^{-1}$). 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 carbenes containing a metal atom within the heterocyclic skeleton (metalla-N-heterocyclic carbenes, 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 $[\text{Fe}(\text{Cp})(\text{CO})(\text{CNR})(\text{L})]^+$ (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.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and analytical and spectroscopic data in pdf format. CCDC reference numbers 951024 (6) and 951023 (7). See DOI: 10.1039/b000000x/

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