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Selective formation of formamidines, carbodiimides and formimidates from isocyanide complexes of Mn(I) mediated by Ag₂O

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The isocyanide ligands in complexes *fac*-[Mn(CNR)(bipy)(CO)₃]⁺ are selectively transformed into formamidines, carbodiimides and formimidates upon nucleophilic addition of NH₂Me or alkoxides and subsequent treatment with Ag₂O, which promotes tautomerization or oxidation processes of the former carbene ligands.
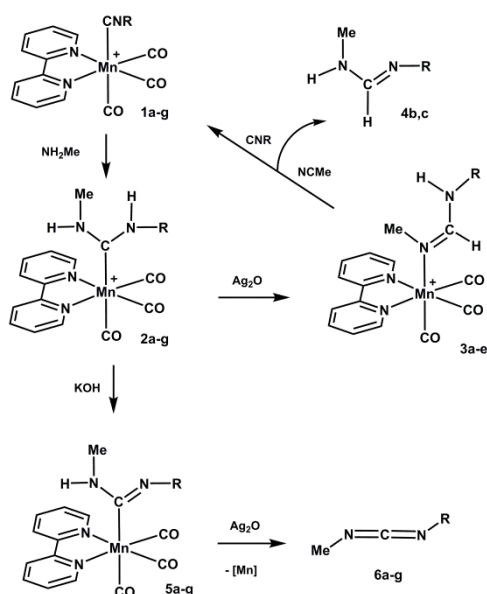
Metal complexes derived from earth-abundant and inexpensive manganese have gained increasing interest in organometallic chemistry and catalysis in the recent years.[1] In particular, manganese(I) complexes containing the cationic fragment $[Mn(bipy)(CO)_3]^+$ (bipy = 2,2'-bipyridine) have been successfully applied in several catalytic processes. Notably, complexes of formula *fac*-[MnBr(bipy)(CO)₃] and *fac*-[Mn(NCMe)(bipy)(CO)₃]⁺ are efficient electrocatalysts for CO_2 reduction to CO,[2] with the additional possibility of utilizing bulky[3] or functionalized[4] bipy ligands to improve this catalytic process. Similar rhenium(I) complexes have been used in the electrocatalytic reduction of CO_2, with the disadvantage of their high cost and the requirement of higher overpotentials.[2b,5] Selective reduction of CO_2 to either formate or CO is also accomplished by inmobilization of *fac*-[MnBr(bipy)(CO)₃] on a carbon nanotube electrode.[6] Other catalytic processes involving the $[Mn(bipy)(CO)_3]^+$ moiety include hydrogenation of CO_2 to formate and formamide[7] and dihydrogen production by reduction of trifluoroacetic acid as a proton source.[8] Some remarkable organometallic reactions promoted by the fragment $[Mn(bipy)(CO)_3]^+$ have been described by our group, and include the tautomerization of imidazoles,[9] oxazole[10] and thiazole[10] to N-heterocyclic carbenes (NHCs), the formation of NHCs by coupling of isocyanides and propargylamine[11] and the generation of unique metalla-NHCs.[12]

In relation with all the above and showing the amazing synthetic potential of the simple and easy accessible $[Mn(bipy)(CO)_3]^+$ fragment, we describe herein several reactions of isocyanide ligands occurring at the coordination sphere of manganese, mediated by silver(I) oxide, lately leading to the selective generation of a variety of organic functionalities such as formamidines, carbodiimides or formimidates.

As we have previously described, the reaction of *fac*-[Mn(CNR)(bipy)(CO)₃]⁺ (**1a**, R = phenyl; **1b**, R = 2-naphthyl; **1c**, R = 4-methoxyphenyl; **1d**, R = methyl; **1e**, R = benzyl; **1f**, R = 2,6-xylyl; **1g**, R = 2-chloro-6-methylphenyl) with NH₂Me leads to the formation of the diaminocarbene complexes *fac*-[Mn{CNHR(NHMe)}(bipy)(CO)₃]⁺ (**2a-g**) after a few minutes of stirring at room temperature.[13] Now we have found that the diaminocarbene ligands in these complexes can be selectively converted to formamidines or carbodiimides, depending on the reaction conditions (Scheme 1). Thus, the treatment of dichloromethane solutions of complexes **2** with Ag₂O, which acts as a catalyst, leads to quantitative isomerization of the carbene ligand to the corresponding formamidine, yielding complexes **3**.[14] Tentatively, this process might involve some interaction of the Ag(I) ion with the carbene carbon atom of **2**, which is reminiscent of the heterometallic Mn(I)/Au(I) carbene intermediates we have found in homogeneous conditions for the transfer of carbene ligands from Mn(I) to Au(I).[15] This reaction works pretty well with a variety of alkylic or arylic substituents (R =Ph, 2-Naph 4-MeOPh, Me , Bn; complexes **2a-e**); however, with more sterically demanding substituents such as 2-6-xylyl or 2-Cl-6-MePh (complexes **2f** and **2g**), the above isomerization reaction does not occur. In similar conditions, addition of Cu₂O instead of Ag₂O leaves the diaminocarbene complexes unchanged. Other metal oxides of variable nature, such as V₂O₅, ZnO, MgO or CuO do not induce any reaction either. Complexes **3a-e** were characterized by spectroscopic methods. The IR spectra reflect the reduced donor capability of formamidines as ligands compared to their diaminocarbene precursors, showing ν(CO) bands at higher frequencies. Complexes **3a-d** are isolated as a mixture of isomers, resulting

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Scheme 1. Generation of diaminocarbene complexes **2a-g** and their selective transformation into formamidine and carbodiimide functionalities induced by Ag$_2$O.

from the formation of two formamidine tautomers, which forces coordination of this molecule either through the NMe group (showed in Scheme 1) or through the NR moiety (see details in the Supplementary Information). In the case of **3e** (R = Bn), the ^{1}H NMR spectrum of the reaction mixture showed the formation of a sole isomer, for which, after crystallization, an X-ray diffraction study was undertaken. The structure of the molecular cation (Figure 1) shows coordination of the formamidine through the NMe group. The C2-N1 (1.332(2) Å) and C2-N3 (1.294(3) Å) bond lengths are intermediate between single and double bond, reflecting π-delocalization of the lone pair of the N1 nitrogen atom along the NCN skeleton.

The coordinated formamidines can be liberated from the metal center by heating under reflux acetonitrile solution of the corresponding complexes, as exemplified with the obtention of formamidines **4b** and **4c** (Scheme 1). The workup includes separation of the formamidine from the crude reaction mixture by extraction with diethyl ether. The remaining manganese complex *fac*-[Mn(NCMe)(bipy)(CO)$_3$]$^+$ can be further transformed into the starting complexes **1b,c** by reaction with isocyanide, which allows recycling of these metal complexes.
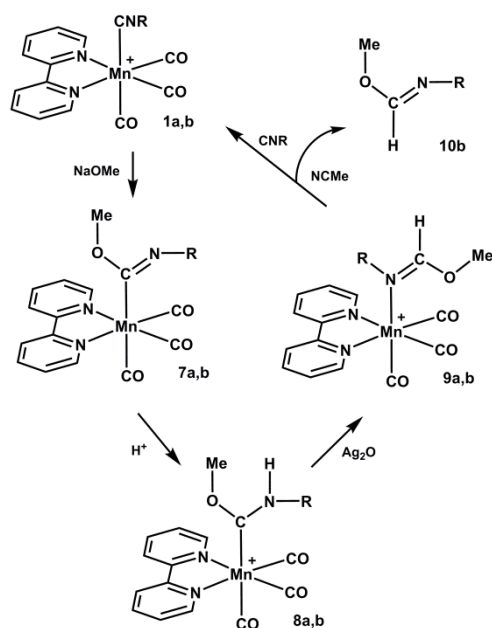
If the diaminocarbene complexes **2a-g** are previously transformed into the formamidinile derivatives **5a-g** by deprotonation (these were detected by IR spectroscopy but not isolated), the treatment with Ag$_2$O produces the oxidation of the formamidinile ligand affording the unsymmetrically substituted carbodiimides **6** within a few minutes of stirring at room temperature in dichoromethane as solvent (Scheme 1). The new carbodiimides were immediately detected by recording the IR spectrum of the reaction mixture, which showed a characteristic ν(N=C=N) band at around 2140 cm^{-1}, and were conveniently isolated as colorless oils after workup. A silver mirror was formed as a by-product together with a carbonyl manganese complex which was identified as
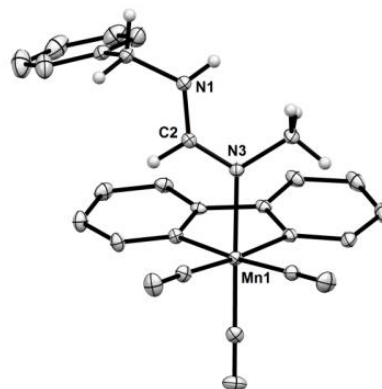
Figure 1. A view of the structure of the cationic complex **3e** with thermal ellipsoids set at 30% probability. Hydrogen atoms of phenyl and bipy groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1-N3 2.0769(16), N3-C2 1.294(3), C2-N1 1.332(2); N1-C2-N3 127.6(2).
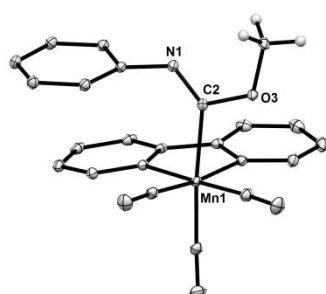
fac-[MnCl(bipy)(CO)$_3$]. Interestingly, there are not steric restrictions in the formation of the carbodiimide products, so that isocyanide ligands with encumbered aryl substituents are also transformed into carbodiimides, in contrast to that occurring with the above commented tautomerization of diaminocarbenes to formamidines. However, the dialkyl carbodiimides **6d,e** could not be obtained, owing to the extreme propensity of the corresponding dialkyl formamidinile complexes to protonation, producing the diaminocarbene complexes **2d,e** (and subsequently the formamidine derivatives **3d,e**) before the oxidation process had taken place. The selective formation of formamidines or carbodiimides starting from the same manganese(I) diaminocarbene complexes promoted by Ag$_2$O is noteworthy. In this regard, it must be emphasized the important contribution of Angelici on gold metal-catalyzed reactions of isocyanides with primary amines and oxygen to give carbodiimides,[16] which is in sharp contrast with the early results of Parks and Balch describing the formation of formamidines by substitution reactions from gold(I) diaminocarbene complexes.[17]

Under the activation of the rather stable [Mn(bipy)(CO)$_3$]$^+$ fragment, the isocyanide ligands can also be transformed into formimidates upon reaction with sodium methoxide. The whole reaction pathway starting from **1a,b** is depicted in Scheme 2 and involves firstly nucleophilic attack of the alkoxide to the coordinated isocyanide ligand, affording the neutral complexes **7a,b**. These are further protonated at the imine group by treatment with HBF$_4$ to give the alkoxyaminocarbene derivatives **8a,b**, wich are finally converted to their formimidate isomers **9a,b** by treatment with Ag$_2$O, in a similar way as diaminocarbene complexes are transformed into formamidine derivatives. Interestingly, the [Mn(bipy)(CO)$_3$]$^+$ fragment is not only stable enough to allow these transformations, but also behaves as an exceptional witness to monitory all the reaction sequence by IR spectroscopy in solution, with clear changes in the ν(CO) bands in each reaction path (see ESI). In the ^{13}C{^{1}H} NMR spectra, significant changes are also observed in the chemical
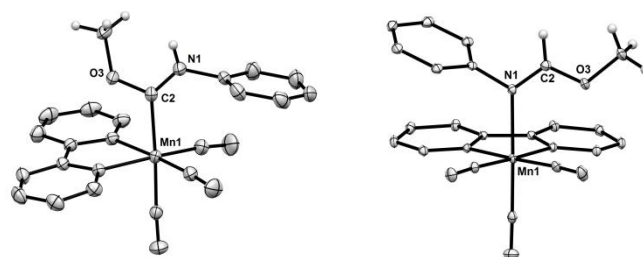
Scheme 2. Reaction pathway for the formation of alkoxyaminocarbene complexes **8a,b** and their tautomerization to formimidate derivates mediated by Ag$_2$O.

Figure 3. A view of the structure of the cationic complex **8a** (left) and its tautomer derivative **9a** (right) with thermal ellipsoids set at 30% probability. Hydrogen atoms of phenyl and bipy groups are omitted for clarity. Selected bond lengths (Å) and angles (°): **8a** Mn1-C2 2.057(2), O3-C2 1.326(2), C2-N1 1.310(2); N1-C2-O3 115.5(2). **9a** Mn1-N1 2.1087(19), O3-C2 1.323(3), C2-N1 1.273(3); N1-C2-O3 120.4(2).

the naphthyl derivative **10b** (Scheme 2). Reaction of **1a** with sodium ethoxide proceeds similarly, allowing for the obtention of the corresponding alkoxyaminocarbene and formimidate derivatives (see ESI).

The ability of Ag$_2$O to transform diaminocarbene ligands to formamidines in manganese(I) complexes was extended to cyclic carbenes with similar results. As showed in Scheme 3, the Mn(I)-NHC complex **11** is easily converted to the imidazole complex **12** by treatment with Ag$_2$O simply by stirring at room temperature in CH$_2$Cl$_2$. As we had already described the acid/base-promoted tautomerization of 1-phenylimidazole to the corresponding NHC (Scheme 3),[9] the present result completes a totally reversible transformation between these two tautomeric forms in the coordination sphere of manganese. Note that metal-assisted tautomerization reactions of imidazoles[9,18] and other azaheterocycles[10,19] to NHCs have been intensely investigated in the last years and that, in occasions, coordinated-NHCs can also be converted to imidazoles.[20] However, to our knowledge, this is the first time that this transformation is found to be reversible.

To conclude, we have shown herein that [Mn(bipy)(CO)$_3$]$^+$ containing earth-abundant manganese is an excellent metallic fragment to induce transformations of isocyanides into a variety of organic functionalities such as diaminocarbenes, formamidines, carbodiimides, alkoxyaminocarbenes and formimidates, upon treatment with bases such as primary amines and alkoxides, and with the singular contribution of Ag$_2$O as an isomerization or oxidation reagent.

shift of the central carbon atom of the N-C-O skeleton, going from about 203 ppm (**7a,b**) to 239 ppm (**8a,b**) and finally 170 ppm (**9a,b**). For complexes **7a**, **8a** and **9a** an X-ray diffraction study was undertaken (see Figures 2 and 3, together with selected bond distances and angles), which definitively confirmed the structure of these species. Note that the relative disposition of the phenyl and methyl substituents at the N1 and O3 atoms is maintained on going from **7a** to **8a**. In the case of **8a**, the ^{1}H NMR spectrum shows the presence of two conformers (approximate ratio 92:8) very likely arising from the absence of free rotation around the carbon-nitrogen bond of the carbene ligand, which is in accordance with the rather short C2-N1 bond length (1.310(2) Å). Most probably the structure in Figure 3 corresponds to the major isomer. Free formimidates can be obtained in a similar way as described above for formamidines, as exemplified with the isolation of

Figure 2. A view of the structure of complex **7a** with thermal ellipsoids set at 30% probability. Hydrogen atoms of phenyl and bipy groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1-C2 2.0809(12), O3-C2 1.3836(15), C2-N1 1.2767(16); N1-C2-O3 115.0(1).
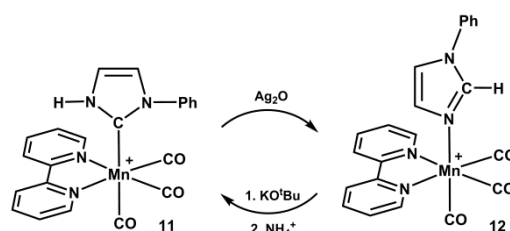

Scheme 3. Reversible tautomerization of 1-phenylimidazole to the corresponding protic NHC coordinated to the fragment [Mn(bipy)(CO)$_3$]$^+$.

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Conflicts of interest

There are no conflicts to declare.

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