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

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In relation with all the above and showing the amazing synthetic potential of the simple and easy accessible \([\text{Mn(bipy)}]^{+}\) 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 \(\text{fac-Mn(CNR)(bipy)(CO)}\) with Ag₂O, which acts as a catalyst, leads to quantitative isomerization of the carbene ligand to the corresponding formamidine, yielding complexes \(1\) after a few minutes of stirring at room temperature. Now we have found that the formamidine 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 \(3\). Tentatively, this process might involve some interaction of the Ag⁺ 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). This reaction works pretty well with a variety of alkylic or arylc substituents (R = Ph, 2-Naph 4-MeOPh, Me, Bn; complexes \(2a-e\); however, with more sterically demanding substituents such as 2-6-xyl 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 dianinocarbene 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 dianinocarbene precursors, showing ν(CO) bands at higher frequencies. Complexes \(3a-d\) are isolated as a mixture of isomers, resulting

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**Notes:**

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from the formation of two formamidine tautomers, which forces coordination of this molecule either through the NMe group (shown 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(NCMelimide)(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 dichloromethane as solvent (Scheme 1). The new carbodiimides were immediately detected by recording the IR spectrum of the reaction mixture, which showed a characteristic υ(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

\[
\text{MnCl(bipy)(CO)$_3$}.
\]

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 formamidinilide 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, 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.

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, which 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 υ(CO) bands in each reaction path (see ESI). In the $^{13}$C($^1$H) NMR spectra, significant changes are also observed in the chemical
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 the naphthyl derivative 10b (Scheme 2). Reaction of 1a with sodium ethoxide proceeds similarly, allowing for the obtention of the corresponding alkoxyaminocarbenes 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 carbens 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), 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 diamino carbocenes, formamidines, carbodiimides, alkoxyamincarbones 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.

**Scheme 2.** Reaction pathway for the formation of alkoxyaminocarben complex 8a,b and their tautomerization to formimidate derivatives mediated by Ag$_2$O.

**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).

**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).
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Conflicts of interest
There are no conflicts to declare.

Notes and references


14 We have already described the synthesis of 3a and 3d as intermediates in the formation of metalla-N-heterocyclic carbenes, see reference 12b.


