

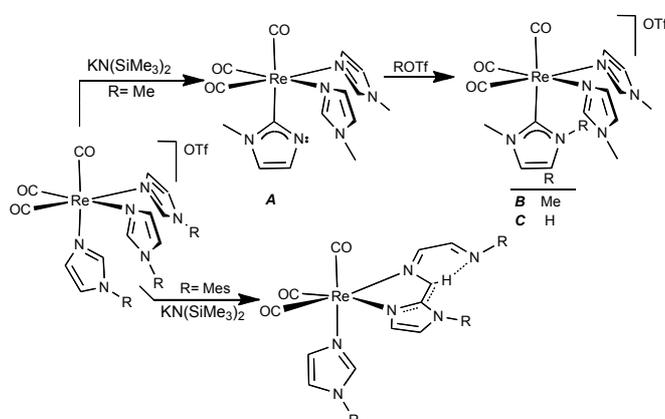
From Bis(*N*-Alkylimidazole) to Bis(NH-NHC) Complexes: A New Reactivity Pattern in Rhenium Carbonyl Complexes

Miguel A. Huertos, Julio Pérez,* Lucía Riera,* Jesús Díaz and Ramón López*

The current importance of nitrogen heterocyclic carbene (NHC) ligands in several areas of coordination chemistry and catalysis can hardly be overemphasized.^[1] The deprotonation of imidazolium salts is the prime route to NHCs; however, the study of the transformations relating imidazole and NHC ligands is still an emerging area of research. The thermodynamic preference for *N*- or *C*-coordination in imidazoles has been theoretically investigated by Crabtree and Eisenstein.^[2] Several examples of tautomerization in pyridinic ligands have been published,^[3] however apart from the work reported by Sundberg *et al.* on Ru(II) NHC complexes that were obtained in a very low yield,^[4] only a similar tautomerization in a non-chelated imidazole ligand has been proposed by Bergman and Ellman.^[5] Ruthenium- and iridium-mediated tautomerizations from NHC to imidazole ligands were reported by the groups of Whittlesey^[6] and Li^[7] respectively, whereas imidazole to NHC tautomerizations aided by chelate ring formation mediated by Ir and Ru were reported by the groups of Grotzahn^[8] and of Kuwata and Ikariya^[9] respectively. Ruiz and Perandones reported the base-promoted tautomerization of imidazole ligands to NHCs at a manganese (I) center.^[10] Our group found that the outcome of related reactions at Re^I dramatically depends on the nature of the ancillary ligands and the substituents at the nitrogen of the *N*-alkylimidazole (*N*-RIm) ligand (see below).^[11]

As previously found in our group and shown in Scheme 1, imidazol-2-yl complex **A**, the product of the deprotonation of [Re(CO)₃(*N*-MeIm)₃]OTf (*N*-MeIm = *N*-methylimidazole), can be

methylated to afford the NHC compound **B** or protonated to yield **C**, featuring an NH-NHC ligand. In contrast, employment of [Re(CO)₃(*N*-MesIm)₃]OTf (*N*-MesIm = *N*-mesitylimidazole) as precursor leads to ring opening.^[11b] Also, deprotonation of complexes with one *N*-RIm ligand and either 2,2'-bipyridine or 1,10-phenanthroline results in C-C coupling and activation of one of the pyridine rings of the diimine chelate.^[11a] This wealth of new reactivity patterns prompted us to extend our studies by investigating the deprotonation of [Re(OTf)(CO)₃(*N*-RIm)₂] complexes.



Scheme 1. Reactivity of Re^I imidazole compounds studied in our group.

Complex [Re(OTf)(CO)₃(*N*-MesIm)₂] (**1a**), prepared by reaction of [ReBr(CO)₅] and *N*-MesIm, followed by AgOTf, reacted instantaneously with the equimolar amount of KN(SiMe₃)₃ in THF (see Scheme 2). Compound **2a** could be isolated in 38 % yield from the crude reaction mixture and characterized by IR, NMR and X-ray diffraction (Figure 1a).^[12, 13] It was found to contain a *fac*-Re(CO)₃ fragment (νCO bands at 1995 and 1872 cm⁻¹ in the IR spectrum) bonded to one *N*-MesIm ligand, one imidazol-2-yl-ligand and one NH-NHC ligand, the two latter resulting from *N*-Re to *C*-Re change in the coordination mode of two *N*-MesIm ligands. The large shift to lower wavenumber values in the νCO bands (those of **1a** occur at 2033, 1925, 1897 cm⁻¹) reflects the strong σ-donor character of the C-bound heterocyclic ligands.

The N-H group of the NH-NHC ligand acts as hydrogen bond donor towards the un-coordinated nitrogen of the imidazol-2-yl ligand, contributing to the virtual coplanarity of the two heterocyclic ligands. A molecular mirror plane is evident from the NMR spectra of **2a**, indicating the fast (even at low temperature) H⁺ transfer between the two nitrogens, *i.e.*, the complex can be described as featuring two imidazol-2-yl ligands that share a proton. The Re-bonded carbon of these ligands occurs at 180.7 ppm in the ¹³C NMR spectrum, and the two Re-C bond distances are undistinguishable (Re-C2 2.214(10) and Re-C22 2.207(9) Å), showing the close similarity between imidazol-2-yl and NH-NHC. It could be argued that their similarity could be due to an intermediate imidazolyl-carbene character resulting from the proton being equally shared

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between both ligands. However, it should be noticed that similar Re-C distances and ^{13}C chemical shifts were also found in compounds labeled **A** and **C** in Scheme 1.^[11b,c] In a few instances imidazol-2-yl complexes were found to be stable enough so that they could be isolated, and these species and NH-NHC complexes can interconvert by H^+ -transfer reactions.^[8,9]

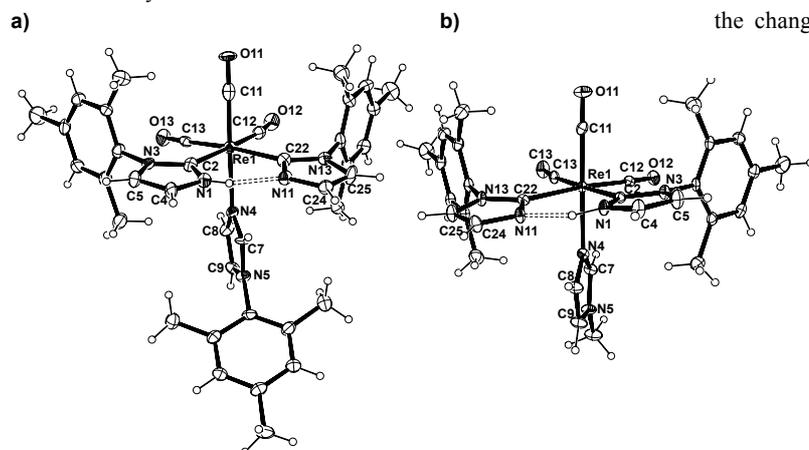
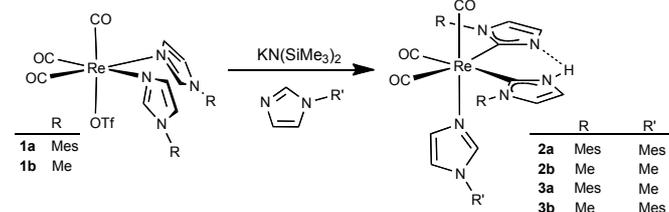


Figure 1. a) Molecular structure of **2a**. b) Molecular structure of **3a**.

The yield of **2a** increased to 86 % when its preparation was conducted in the presence of the equimolar amount of *N*-MesIm, as expected since, in its absence, part of the bis(imidazole) precursor **1a** must have acted as a sacrificial source of *N*-MesIm.^[14]



Scheme 2. Reactivity of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-RIm})_2]$ (**1a-b**) compounds.

The deprotonation of the cationic tris(*N*-mesitylimidazole) rhenium tricarbonyl complex under the same conditions led to a completely different product (compound **D** in Scheme 1). This proves that it is the neutral complex **1a**, rather than $[\text{Re}(\text{CO})_3(\text{N-MesIm})_3]\text{OTf}$ (the likely product of the reaction of **1a** with *N*-MesIm) the species that undergoes deprotonation. This is not surprising because the formation of $[\text{Re}(\text{CO})_3(\text{N-MesIm})_3]\text{OTf}$ from **1a** and *N*-MesIm could not be spectroscopically detected after two days in THF at room temperature.^[15]

The reaction of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ (**1b**) with $\text{KN}(\text{SiMe}_3)_2$ and *N*-MeIm afforded the *N*-methyl analog of **2a**, which was spectroscopically characterized. To investigate the exact fate of the entering imidazole in the product, the reactions of (a) **1a** with base

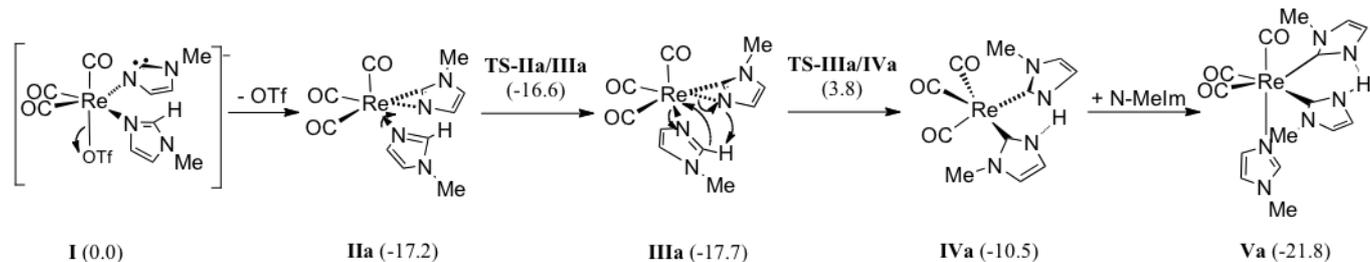
and *N*-MeIm, and (b) **1b** with base and *N*-MesIm were conducted. The products, the mixed complexes **3a** and **3b** respectively, were fully characterized by spectroscopic means, and the solid-state structure of **3a**, determined by X-ray diffraction,^[12,16] was found to be similar to that of **2a** (Figure 1b). The externally added imidazole was found to be *N*-coordinated in these complexes, suggesting that the change in the Re-N to Re-C coordination mode precedes the

coordination of the entering substituted imidazole. Indeed this reaction seemed to be quite general, and the addition of 4-dimethylaminopyridine (py^*) as external ligand similarly afforded $[\text{Re}(\text{CO})_3(\text{C-MeIm})_2(\text{py}^*)]\text{OTf}$ (**4**).^[14] To gain insight into the mechanism details a density functional theory (DFT) study was performed.^[17] A schematic view of the most favorable reaction mechanism found is shown in Scheme 3 (see also Supporting Information for alternative reaction mechanisms). The Gibbs free energy in THF solution (in parentheses) is referred to that of the deprotonated species $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ (see **I** in Scheme 3) and *N*-MeIm. The reaction starts with loss of triflate from **I** to give

intermediate **IIa** in which the Re atom is simultaneously interacting with the non-coordinated N atom and the C-2 atom of the imidazolyl ligand. All the attempts to locate the TS where the triflate anion came out failed, but the energy of this way out has to be really small considering that the new species is neutral and moreover, the potassium triflate is an insoluble salt which precipitates from the reaction media. Intermediate **IIa** undergoes a rotation of the imidazole ring around the N-Re bond through **TS-IIa/IIIa** to give the intermediate **IIIa**. **TS-IIIa/IVa** connects **IIIa** with intermediate **IVa** wherein the two heterocyclic ligands are C-bound to the Re atom. Finally, addition of *N*-MeIm leads to the formation of a rhenium imidazol-2-yl(carbene) complex **Va** without any TS. The formation of the rhenium imidazolyl-carbene complex would imply a Gibbs energy barrier in solution of 21.5 kcal/mol, consistent with the fast formation of the product experimentally observed.

A key feature of the proposed mechanism is the intermediacy of $\eta^2\text{-N,C}$ -imidazolyl complexes, which make possible ligand dissociation without going through high-energy five-coordinate species. Stable $\eta^2\text{-N,C}$ -imidazolyl complexes have been disclosed by Diaconescu *et. al.* in scandium and uranium chemistry.^[18]

The reaction of **2b** with trifluoromethanesulfonic acid (HOTf) afforded **5**, the triflate salt of the bis(NH-NHC) complex resulting from protonation at nitrogen.^[19] The shift to higher frequencies of the IR ν_{CO} bands of **5** (2012, 1913 and 1886 cm^{-1}) indicates the formation of a cationic derivative. The NMR spectra (^1H and ^{13}C NMR) showed the C_s symmetry of the molecule, and the most informative signal, at 175.0 ppm, is assigned to C carbenic atoms. An X-ray diffraction analysis (Figure 2) confirmed the proposed structure,^[12,20] the Re-C carbenic bond distances (2.183(6) and



Scheme 3. Most favorable mechanism found for the evolution of the deprotonation product of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ at B3LYP/6-31+G(d, p)(LANL2DZ + *f* for Re) theoretical level. Relative Gibbs energies ($\text{kcal}\cdot\text{mol}^{-1}$) are given in parenthesis.

2.185(5) Å) being very similar to those discussed above for **2a** and those previously reported.^[11b,c]

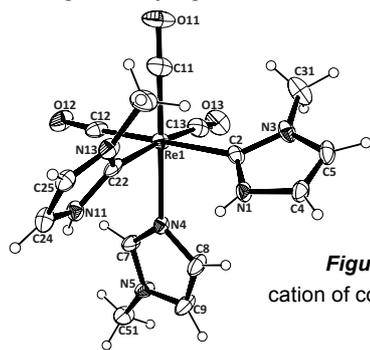


Figure 2. Molecular structure of the cation of compound **5**.

In summary, the overall formation of **5** from **1b** involves, besides the substitution of OTf by the entering imidazole, the formation of two new Re-C bonds at the expense of the two Re-N bonds. Deprotonation of a coordinated *N*-MeIm ligand in [Re(CO)₃(*N*-MeIm)₃]OTf followed by protonation of the resulting imidazol-2-yl ligand affords an NHC complex (see Scheme 1). The present formation of the bis(carbene) complex from the bis(imidazole) precursor is not just twice that process, because the addition of only one equivalent of base triggers the Re-N to Re-C rearrangement of two imidazole ligands. It is noteworthy that when the deprotonation reactions of a) the tris(*N*-MeIm) compound, or b) the triflate complex **1a** in the presence of free *N*-MeIm, the components of the reactant mixture are the same, whereas different isomers are obtained as products. The formation of the ring-opening product in the former case or the imidazolyl-carbene in the later shows again the extreme sensitivity of the reaction course to the exact nature and number of the ligands. Further studies on the deprotonation of rhenium imidazole complexes with different sets of ligands are in progress.

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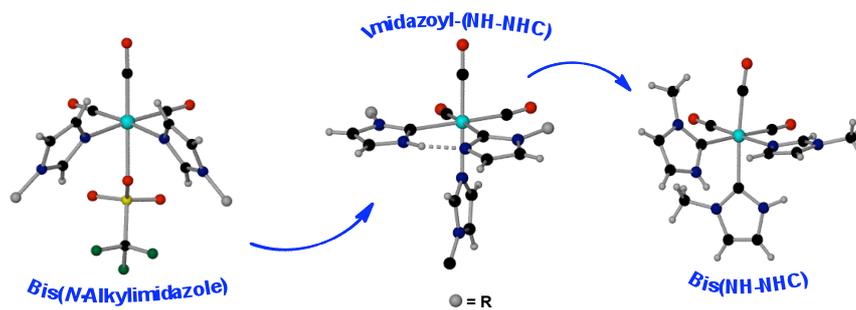
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- [12] CCDC 776191 (**1a**), 776192 (**2a**), 776193 (**3a**) and 776195 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [13] Selected crystallographic data for **2a**: C₄₆H₄₉N₆O₃Re, *M* = 920.11, orthorhombic, *Pbca*, *a* = 19.2434(3) Å, *b* = 15.2881(2) Å, *c* = 28.6367(5) Å, α = 90°, β = 90°, γ = 90°, 150(2) K, *V* = 8424.8(2) Å³, *Z* = 8. 29800 reflections measured, 8171 independent (*R*_{int} = 0.1176). *R*₁ = 0.0699, *wR*₂ = 0.1435 (all data).
- [14] For further experimental details see Supporting Information.
- [15] On the other hand, starting materials **1a-b** are obtained as pure species that have been fully characterized, including by X-ray diffraction for compound **1a** (see Supporting Information).
- [16] Selected crystallographic data for **3a**: C₃₅H₃₈N₆O₃Re, *M* = 776.91, monoclinic, *C2/c*, *a* = 21.6583(6) Å, *b* = 15.1624(5) Å, *c* = 21.1537(5) Å, α = 90°, β = 106.518(2)°, γ = 90°, 150(1) K, *V* = 6660.0(3) Å³, *Z* = 8. 28086 reflections measured, 6837 independent (*wR*_{int} = 0.0516). *R*₁ = 0.0323, *wR*₂ = 0.0712 (all data).
- [17] Quantum chemical computations were carried out with the Gaussian 03 (M. J. Frisch, et al. Gaussian 03, revision D.01; Gaussian, Inc.: Pittsburgh, PA, 2004), see Supporting Information for details and complete reference.
- [18] M. J. Monreal, P. L. Diaconescu, *J. Am. Chem. Soc.* **2010**, *Article ASAP*, DOI: 10.1021/ja9109715 and referents therein.
- [19] An example of a rhenium bis(NHC) complex has been recently prepared by a different method, see: O. Hiltner, E. Herrdtweck, M. Drees, W. A. Herrmann, F. E. Kühn, *Eur. J. Inorg. Chem.* **2009**, 1825-1831.
- [20] Selected crystallographic data for **5**: C₁₆H₁₈F₃N₆O₆ReS, *M* = 665.62, triclinic, *P-1*, *a* = 7.428(5) Å, *b* = 12.332(5) Å, *c* = 12.392(5) Å, α = 94.329(5)°, β = 95.113(5)°, γ = 98.155(5)°, 150(1) K, *V* = 1114.7(10) Å³, *Z* = 2. 16691 reflections measured, 4372 independent (*wR*_{int} = 0.0484). *R*₁ = 0.0331, *wR*₂ = 0.0729 (all data).

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Two birds, one stone: A deprotonation-protonation sequence using only one molar-equivalent of base and acid transforms two *N*-alkylimidazoles into NHC ligands.