Angewandte
Chemie

DOI: 10.1002/ange.201002879

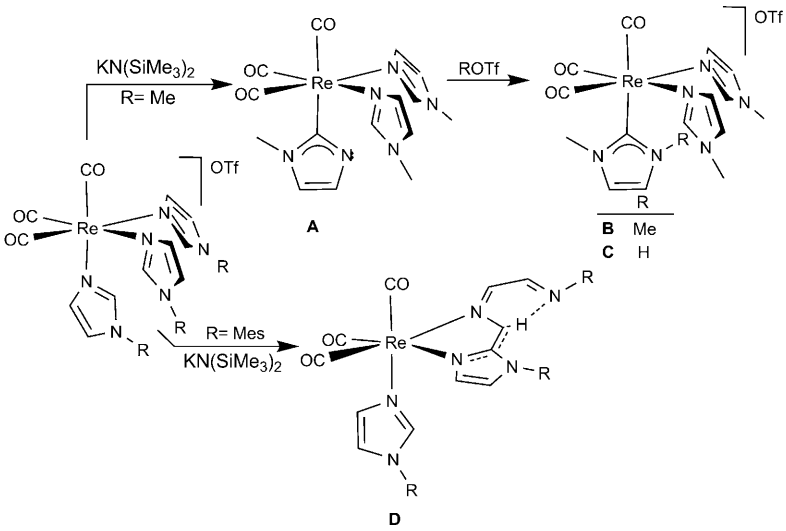
Heterocyclic Carbenes

From Bis(*N*-Alkylimidazole) to Bis(NH–NHC) 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 et al.[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 nonchelated imidazole ligand has been proposed by Bergman et al.[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 Grotjahn[8] and of Kuwata,[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 atom of the *N*-alkylimidazole (*N*-RIm) ligand (see below).[11]

As previously found by our group and shown in Scheme 1, imidazol-2-yl complex **A**, the product of the deprotonation of $[Re(CO)_3(N\text{-}MeIm)_3]OTf$ (*N*-MeIm = *N*-methylimidazole; Tf = trifluoromethanesulfonyl), can be methylated to afford the NHC compound **B** or protonated to yield **C**, which features an NH–NHC ligand. In contrast, employment of $[Re(CO)_3(N\text{-}MesIm)_3]OTf$ (*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 $[Re(OTf)(CO)_3(N\text{-}RIm)_2]$ complexes.



Scheme 1. Reactivity of the Re^I imidazole compounds studied.

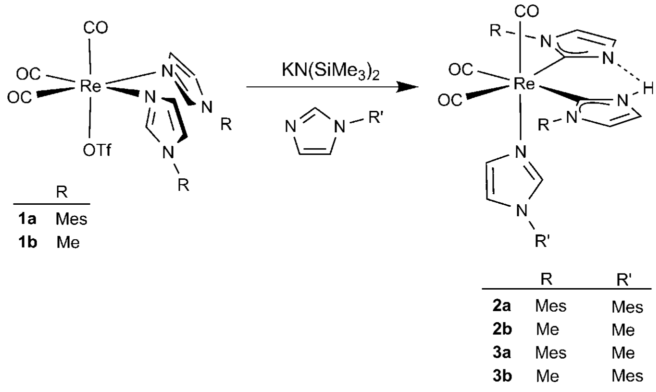
Complex $[Re(OTf)(CO)_3(N\text{-}MesIm)_2]$ (**1a**), prepared by reaction of $[ReBr(CO)_5]$ and *N*-MesIm followed by AgOTf, reacted instantaneously with an equimolar amount of $KN(SiMe_3)_2$ in THF (see Scheme 2). Compound **2a** could be isolated in 38 % yield from the crude reaction mixture and was characterized by IR spectroscopy, NMR spectroscopy, and X-ray diffraction (Figure 1 a).[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 latter two resulting from N–Re to C–Re change in the coordination mode of two *N*-MesIm ligands. The large shift to lower-

---

[*] M. A. Huertos, Dr. J. Pérez
Departamento de Química Orgánica e Inorgánica-IUQOEM
Universidad de Oviedo–CSIC
C/Julián Clavería 8, 33006 Oviedo (Spain)
E-mail: japm@uniovi.es
Dr. L. Riera
Instituto de Ciencia de Materiales de Aragón (ICMA)
Universidad de Zaragoza–CSIC
C/Pedro Cerbuna 12, 50009 Zaragoza (Spain)
E-mail: riera@unizar.es
Dr. J. Díaz
Departamento de Química Orgánica e Inorgánica
Universidad de Extremadura
Avda de la Universidad s/n, 10071 Cáceres (Spain)
Dr. R. López
Departamento de Química Física y Analítica
Universidad de Oviedo
C/Julián Clavería 8, 33006 Oviedo (Spain)
E-mail: rlopez@uniovi.es

[**] Financial support from the Ministerio de Ciencia e Innovación (MICINN, No. CTQ2009-12366) and Principado de Asturias (No. IB08-104) is gratefully acknowledged. NHC = N-heterocyclic carbene.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002879.



	R
1a	Mes
1b	Me

	R	R'
2a	Mes	Mes
2b	Me	Me
3a	Mes	Me
3b	Me	Mes

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

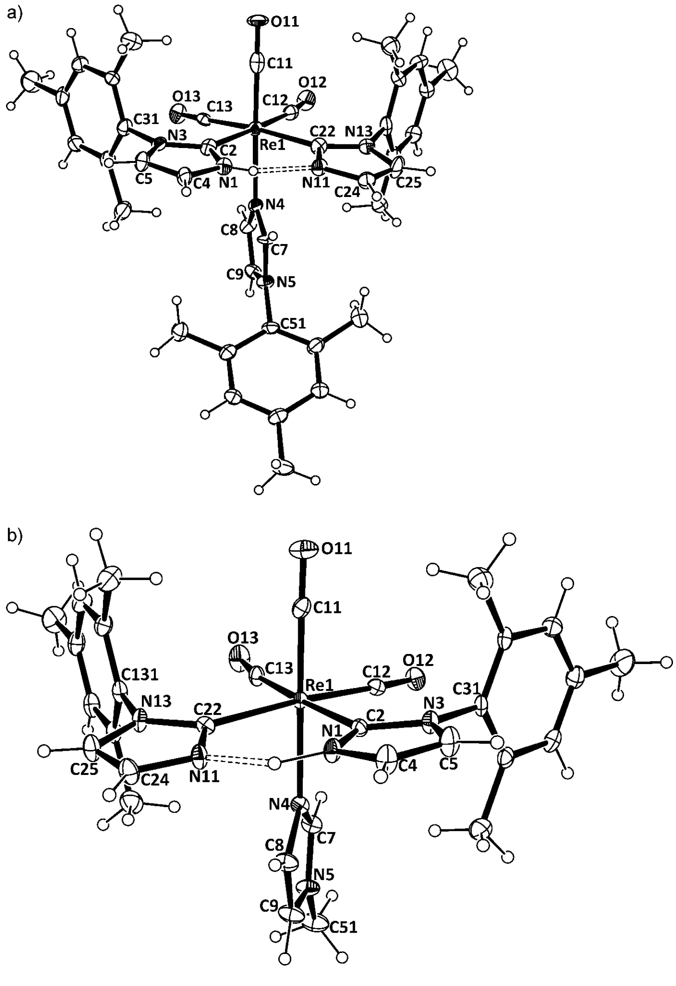


Figure 1. Molecular structures of a) **2a** and b) **3a** (thermal ellipsoids set at 30% probability).

wavenumber values in the νCO bands (those of **1a** occur at 2033, 1925, and 1897 cm^{-1}) reflects the strong σ-donor character of the C-bound heterocyclic ligands.

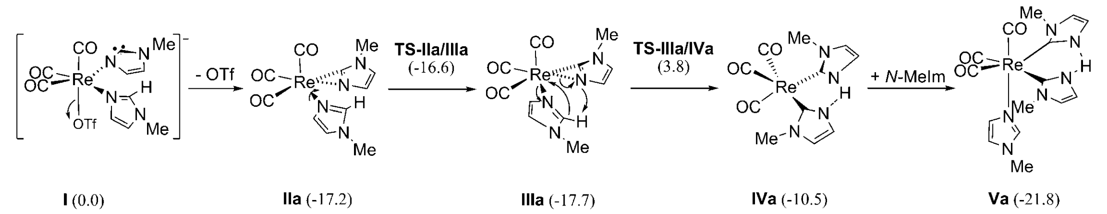
The NH group of the NH–NHC ligand acts as a hydrogen-bond donor towards the uncoordinated nitrogen atom of the imidazol-2-yl ligand, and contributes to the virtual coplanarity of the two heterocyclic ligands. A molecular mirror plane is evident from the ^{1}H and ^{13}C NMR spectra of **2a**, thus indicating the fast (even at low temperature) H$^+$ transfer between the two nitrogen atoms, that is, the complex can be described as featuring two imidazol-2-yl ligands that share a proton. The Re-bonded carbon atom of these ligands occurs at $\delta = 180.7$ ppm in the ^{13}C NMR spectrum, and the two Re–C bond lengths are undistinguishable (Re–C2 2.214(10) and Re–C22 2.207(9) Å), which shows the close similarity between imidazol-2-yl and NH–NHC ligands. It could be argued that their similarity is the result of an intermediate imidazolyl carbene character resulting from the proton being equally shared between both ligands. However, it should be noted that similar Re–C distances and ^{13}C chemical shifts were also found in compounds **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]

The yield of **2a** increased to 86% when its preparation was conducted in the presence of an 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]

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 the [Re(CO)$_3$(*N*-MesIm)$_3$]OTf species (the likely product of the reaction of **1a** with *N*-MesIm) that undergoes deprotonation. This is not surprising because the formation of [Re(CO)$_3$(*N*-MesIm)$_3$]OTf from **1a** and *N*-MesIm could not be spectroscopically detected after two days in THF at room temperature.[15]

The reaction of [Re(OTf)(CO)$_3$(*N*-MeIm)$_2$] (**1b**) with KN(SiMe$_3$)$_3$ and *N*-MeIm afforded the *N*-methyl analogue 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, which suggests that the change in the N–Re to C–Re 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 [Re(CO)$_3$(*C*-MeIm)$_2$(py*)]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 is shown in Scheme 3 (see also the Supporting Information for alternative reaction mechanisms). The Gibbs free energy in THF solution (in parentheses) is referred to that of the deprotonated species [Re(OTf)(CO)$_3$(*N*-MeIm)$_2$]$^-$ (see **I** in Scheme 3) and *N*-MeIm. The reaction starts with the loss of triflate from **I** to give intermediate **IIa**, in which the Re atom is simultaneously



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

interacting with the noncoordinated N atom and the C2 atom of the imidazolyl ligand. All attempts to locate the transition state (TS) where the triflate anion came out failed, but the energy of this route has to be really small considering that the new species is neutral; moreover, potassium triflate is an insoluble salt that precipitates from the reaction medium. 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 to **IVa** 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^{-1}, consistent with the fast formation of the product experimentally observed.

A key feature of the proposed mechanism is the intermediacy of η^2-N,C-imidazolyl complexes, which make possible ligand dissociation without going through high-energy five-coordinate species. Stable η^2-N,C-imidazolyl complexes have been disclosed by Monreal and Diaconescu 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 νCO bands of **5** (2012, 1913, and 1886 cm^{-1}) indicates the formation of a cationic derivative. The NMR spectra (^{1}H and ^{13}C NMR) showed the C_s symmetry of the molecule, and the most informative signal at 175.0 ppm is assigned to carbenic C atoms. An X-ray diffraction analysis (Figure 2) confirmed the proposed structure,[12,20] the Re–C carbenic bond distances (2.183(6) and 2.185(5) Å) being very similar to those discussed above for **2a** and those previously reported.[11b,c]

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 N–Re to C–Re rearrangement of two imidazole ligands. Notably, when the deprotonation reactions of a) the tris(*N*-MesIm) compound or b) the triflato complex **1a** are carried out in the presence of free *N*-MesIm, 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 latter 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.

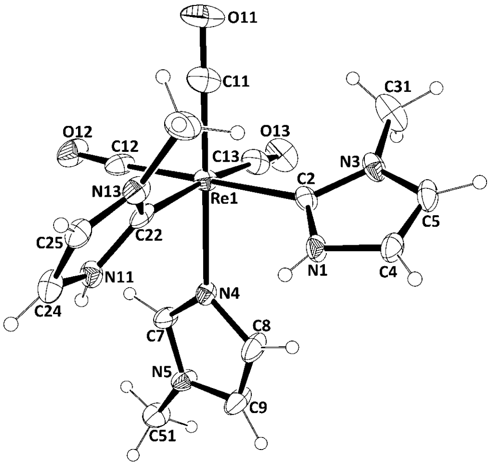


Figure 2. Molecular structure of the cation of compound **5** (thermal ellipsoids set at 30% probability).

Received: May 12, 2010
Published online: July 29, 2010

Keywords: carbene ligands · density functional calculations · nitrogen heterocycles · protonation · rhenium

---

[1] a) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; c) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; d) special issue on recent developments in the organometallic chemistry of N-heterocyclic carbenes (edited by R. H. Crabtree): *Coord. Chem. Rev.* **2007**, *251*, 595–896.

[2] G. Sini, O. Eisenstein, R. H. Crabtree, *Inorg. Chem.* **2002**, *41*, 602–604.

[3] G. Song, Y. Su, R. A. Periana, R. H. Crabtree, K. Han, H. Zhang, X. Li, *Angew. Chem.* **2010**, *122*, 924–929; *Angew. Chem. Int. Ed.* **2010**, *49*, 912–917, and references therein.

[4] R. J. Sundberg, R. F. Bryan, I. F. Taylor, Jr., H. Taube, *J. Am. Chem. Soc.* **1974**, *96*, 381–392.

[5] a) K. L. Tan, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2002**, *124*, 3202 – 3203; b) J. C. Lewis, S. H. Wiedemann, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2004**, *6*, 35 – 38.

[6] S. Burling, M. F. Mahon, R. E. Powell, M. K. Whittlesey, J. M. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 13702 – 13703.

[7] X. Wang, H. Chen, X. Li, *Organometallics* **2007**, *26*, 4684 – 4687.

[8] V. Miranda-Soto, D. B. Grotjahn, A. G. DiPasquale, A. L. Rheingold, *J. Am. Chem. Soc.* **2008**, *130*, 13200 – 13201.

[9] K. Araki, S. Kuwata, T. Ikariya, *Organometallics* **2008**, *27*, 2176 – 2178.

[10] J. Ruiz, B. F. Perandones, *J. Am. Chem. Soc.* **2007**, *129*, 9298 – 9299.

[11] a) M. A. Huertos, J. Pérez, L. Riera, *J. Am. Chem. Soc.* **2008**, *130*, 5662 – 5663; b) M. A. Huertos, J. Pérez, L. Riera, A. Menéndez-Velázquez, *J. Am. Chem. Soc.* **2008**, *130*, 13530 – 13531; c) M. A. Huertos, J. Pérez, L. Riera, J. Díaz, R. López, *Chem. Eur. J.* **2010**, *16*, 8495 – 8507.

[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**: $C_{46}H_{49}N_6O_3Re$, $M=920.11$, orthorhombic, $Pbca$, $a=19.2434(3)$, $b=15.2881(2)$, $c=28.6367(5)$ Å, $\alpha=90$, $\beta=90$, $\gamma=90°$, 150(2) K, $V=8424.8(2)$ Å^3, $Z=8$; 29800 reflections measured, 8171 independent ($R_{int}=0.1176$); $R_1=0.0699$, $wR_2=0.1435$ (all data).

[14] See the Supporting Information for further experimental details.

[15] On the other hand, starting materials **1a** and **1b** are obtained as pure species that have been fully characterized, including by X-ray diffraction for compound **1a** (see the Supporting Information).

[16] Selected crystallographic data for **3a**: $C_{35}H_{38}N_6O_3Re$, $M=776.91$, monoclinic, $C2/c$, $a=21.6583(6)$, $b=15.1624(5)$, $c=21.1537(5)$ Å, $\alpha=90$, $\beta=106.518(2)$, $\gamma=90°$, 150(1) K, $V=6660.0(3)$ Å^3, $Z=8$; 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 Gaussian 03 (Revision D.01), M. J. Frisch et al., Gaussian, Inc., Pittsburgh, PA, **2004**. See the Supporting Information for details and complete reference.

[18] M. J. Monreal, P. L. Diaconescu, *J. Am. Chem. Soc.* **2010**, *132*, 7676 – 7683, and references 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**: $C_{16}H_{18}F_3N_6O_6ReS$, $M=665.62$, triclinic, $P\bar{1}$, $a=7.428(5)$, $b=12.332(5)$, $c=12.392(5)$ Å, $\alpha=94.329(5)$, $\beta=95.113(5)$, $\gamma=98.155(5)°$, 150(1) K, $V=1114.7(10)$ Å^3, $Z=2$; 16691 reflections measured, 4372 independent ($wR_{int}=0.0484$); $R_1=0.0331$, $wR_2=0.0729$ (all data).