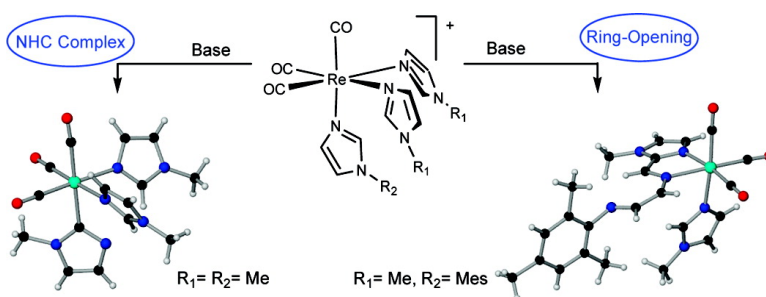


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From *N*-Alkylimidazole Ligands at a Rhenium Center: Ring Opening or Formation of NHC Complexes

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C–N bond cleavage of aromatic N-heterocycles is a challenging process that attracts much interest, partly due to its relevance to hydrodenitrogenation (HDN).¹ Metal-mediated examples involve highly reactive early transition metal fragments and usually require the presence of multiple bonds to the metal, high temperatures, and/or reductive conditions.² Recently, we have reported the first example of a facile C–N bond activation and cleavage of a pyridine (in a 2,2'-bipyridine ligand) at a rhenium organometallic center.³

Another class of aromatic N-heterocycles, namely N-heterocyclic carbenes (NHC), is arguably the type of ligands that is receiving the most attention in recent years.⁴ Tautomerization of N-heterocycles, including imidazoles, to N-heterocyclic carbenes has attracted considerable ongoing interest.⁵

Herein we report our results in the reaction of complexes *fac*-[Re(CO)₃(N-Rim)₃]⁺, a highly stable species, with a strong base, showing that one of the ligated imidazoles undergoes deprotonation under very mild conditions. The outcome of the reaction, dependent on the nature of the R group, reveals unprecedented reactivity patterns.

The reaction of [Re(CO)₃(N-Meim)₃]OTf (**1a**)⁶ with KN(SiMe₃)₂ in tetrahydrofuran (thf) at –78 °C afforded in 30 min a neutral product, **2a** (Scheme 1), as shown by a large shift to lower ν_{CO} values on the IR bands (from 2022 and 1904 cm⁻¹ to 1999 and 1878 cm⁻¹). The ¹H NMR spectrum was consistent with deprotonation of one of the three *N*-methylimidazoles and with the absence of H-scrambling between the deprotonated imidazole and the remaining two.

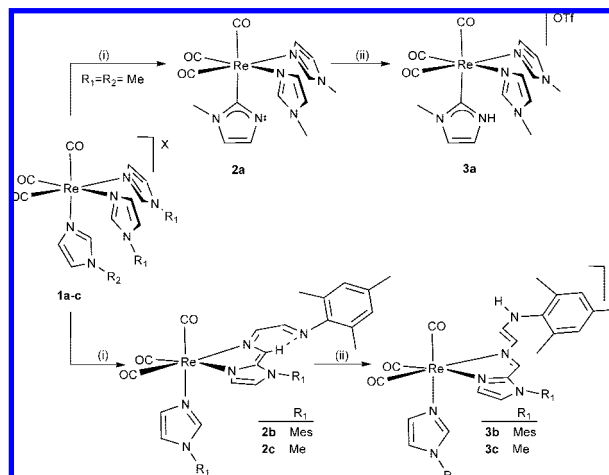
The ¹³C NMR spectrum of **2a** contains a single set of signals for the two *N*-methylimidazole ligands and two signals of different intensity for the three carbonyl ligands, reflecting the presence of a molecular mirror plane. Compared with previously known Re(I) carbonyl NHC complexes, a resonance at 182.4 ppm is assigned to the Re-bonded carbon of the NHC ligand.⁷

An X-ray determination of its structure (Figure 1a) demonstrated that **2a** features an unprecedented NHC ligand containing a nonsubstituted nitrogen. The presence of the “naked” nitrogen at the NHC ligand of **2a** was confirmed by its protonation with HOTf to afford **3a** (Scheme 1), which was spectroscopically characterized in solution⁸ and by X-ray diffraction in the solid state (Figure 1b).

The topological analysis of the Laplacian of the electron density ($\nabla^2\rho$) as obtained from Fourier maps indicated the presence of an in-plane lone pair at N2 in complex **2a** and of an N–H bond in **3a**.⁸

This reaction sequence is reminiscent of the mechanism proposed by Ruiz and Perandones for the transformation of an imidazole into an NHC ligand at a Mn(I) center,⁹ although in that case the authors could not isolate the neutral complex (analogue to **2a**), probably due to its lower stability.

Scheme 1^a



^a (i) KN(SiMe₃)₂, thf at –78 °C; (ii) HOTf or CF₃CO₂H, CH₂Cl₂ at rt.

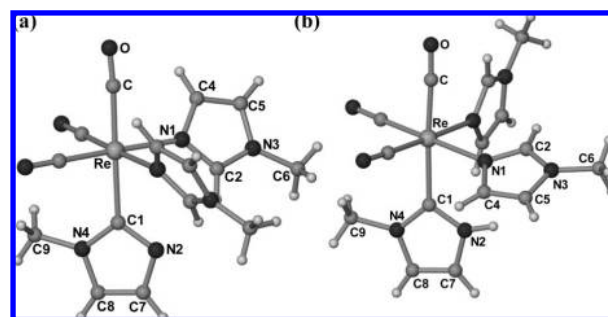


Figure 1. Molecular structures of **2a** (a) and the cation in **3a** (b).

When compound [Re(CO)₃(N-Mesim)₃]OTf (**1b**), the mesityl analogue of **1a**, synthesized by reaction of [Re(OTf)(CO)₅] with 3 equiv of *N*-Mesim in refluxing toluene,⁸ was treated with KN(SiMe₃)₂ at low temperature, IR monitoring indicated the generation of the neutral product **2b** (Scheme 1). Its ¹H NMR spectrum showed the asymmetry of the molecule (three different mesityl groups could be observed) and the formation of a ring-opened *N*-Mesim product. The reaction implies the deprotonation of a CH central group of an *N*-MesIm ligand and the intramolecular attack of the so generated carbenate onto a neighbor NCHN moiety, leading to C–C coupling and ring opening. In the ¹H NMR the signal assigned to the C–H central group occurs at 9.29 ppm. This downfield chemical shift suggests interaction of this group with the terminal nitrogen of the ring-opened product. In the ¹³C NMR of **2b**, the three inequivalent carbonyl groups appeared as three singlets at 199.0, 198.0, and 195.1 ppm.

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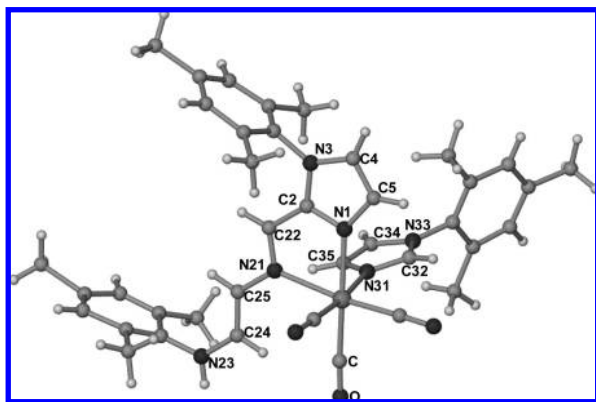


Figure 2. Molecular structure of the cation present in **3b**.

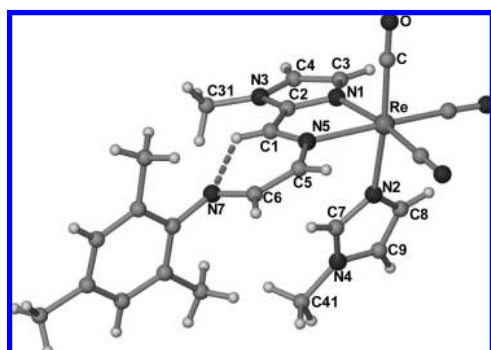


Figure 3. Molecular structure of **2c**.

The reaction of **2b** with HOTf gives, in 30 min at room temperature, in good yield (67%), compound **3b** as the only product of the reaction. Its spectroscopic data⁸ agree with the formulation shown in Scheme 1, and the solid state structure showed the ring opening of one of the N-Mesim ligands (see Figure 2) and that the site of protonation was the amido-like nitrogen (N23 in Figure 2), leading now to a *transoid* unit. The distances and angles indicated significant delocalization involving the acyclic moiety from N1 to N23.

The only previous example of metal-mediated ring opening of an imidazole ligand involved a very reactive Sc(III) complex and required heating at 70 °C for several hours.¹⁰

The results discussed above show that the kind of product obtained in the deprotonation reactions is dramatically dependent on the substituents on the N-Rim ligands. With this in mind we decided to explore the reaction of KN(SiMe₃)₂ with the “mixed” compound [Re(CO)₃(NMeim)₂(NMesim)]BAR₄ (**1c**).⁸

The reaction, carried out in thf at −78 °C, yielded immediately the neutral species **2c** (Scheme 1, ν_{CO} IR change from 2026 and 1909 cm^{−1} to 2013 and 1901 cm^{−1}). The comparison of the ¹H and ¹³C NMR spectra with those of **2b** showed the formation of a ring-opened product. The structure of **2c**, determined by X-ray diffraction (Figure 3), shows the C–C coupling between a deprotonated N-Meim and the N-Mesim ligand, which, as a result, undergoes ring opening. The amido-like nitrogen N7 forms a relatively strong hydrogen bond with the C1–H group (N⋯C=

2.851 Å and N–H⋯C= 122.4°), resulting in a *cis* configuration for the olefin, as proposed above for compound **2b**.

The reaction of **2c** with HOTf in toluene at room temperature afforded compound **3c** as a single product in 71% yield. Its IR ν_{CO} values (2031, 1929, and 1912 cm^{−1}) confirm the presence of a cationic *fac*-{Re(CO)₃} complex, and the broad doublet at 6.11 ppm in the ¹H NMR shows that the protonation occurred at the nitrogen atom to form a product like **3b** (see above). The structure, determined by X-ray diffraction, confirmed the formulation given for compound **3c**.⁸

In summary, we have shown that the deprotonation of an N-alkylimidazole bonded to a *fac*-{Re(CO)₃} fragment generates highly reactive species, which can lead to C–C coupling and ring opening or to the formation of rhenium NHC complexes. Extension of this chemistry to other metal fragments and to other aromatic heterocycles is currently under way in our laboratory.

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Supporting Information Available: Crystallographic data of **1b**, **1c**, **2c**, **3b**, and **3c** and synthesis of **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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