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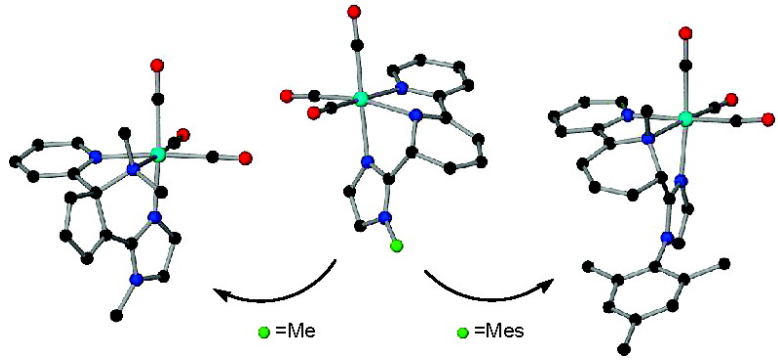

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Pyridine Ring Opening at Room Temperature at a Rhenium Tricarbonyl Bipyridine Complex

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The cleavage of the C−N bond of pyridine derivatives is a challenging task, and the homogeneous, metal-mediated C−N bond cleavage of pyridines has been accomplished only with a few, highly reactive early transition metal complexes.[1]

Bipy and phen have been known for more than one century. These ligands form very stable, five-membered chelate rings with transition metals. Complexes containing *fac*-$Re(CO)_3(N{-}N)$ (N−N = bipy or phen) fragments are particularly stable and have been widely used in bioinorganic chemistry,[2] supramolecular chemistry,[3] and catalysis of CO_2 reduction[4] among other areas. Activation of their bipy or phen ligands remains very rare,[5] and cleavage of their pyridine C−N bonds is unknown. Herein we disclose an activation of bipy and phen ligands at $Re(CO)_3(N{-}N)$ fragments which, for the bipy complex, ends in C−N cleavage of one of the pyridine rings.

The compound $[Re(CO)_3(MeIm)(bipy)]OTf$ (**1a**) was prepared by reaction of $[Re(OTf)(CO)_3(bipy)]$[6] with *N*-methylimidazole. When **1a** was treated with $KN(SiMe_3)_2$ in THF at −78°, a neutral product was formed, as evidenced by shifts in the IR spectra to lower ν(CO) values, which was too unstable for isolation. The addition of MeOTf (excess) in CH_2Cl_2 afforded a mixture from which the triflate salt **4** could be isolated.

Compound **4** was fully characterized, including an X-ray structural determination (see Figure 1). The cationic complex consists of a *fac*-$Re^I(CO)_3$ fragment bonded to the three nitrogen atoms of a tridentate ligand. The latter can be described as a central cyclopentadienyl bridgehead group and three different N-donor arms: an *N*-methylimidazole, a pyridine, and a dimethylamine. The most striking feature of this structure is the fact that, in the overall reaction, one of the pyridine rings of the bipy chelate underwent nitrogen extrusion to afford a 2,4-cyclopentadienyldimethylamine unit. The facts that no similar transformation was known, that pyridine C−N bond cleavage took place under very mild conditions, and that the starting metal complex is an easily available, very stable species prompted us to further study this reaction.

Thus, when $[Re(CO)_3(MesIm)(bipy)]OTf$ (**1c**), the mesitylimidazole analogue of **1a**, was allowed to react with $KN(SiMe_3)_2$ (Scheme 1), the neutral product **2c** was stable enough for isolation. The IR showed ν(CO) bands at 2005, 1893, and 1886 cm^{-1}, consistent with the formation of a neutral compound. The ^1H and ^{13}C NMR spectra of **2c** featured distinct signals for every nucleus of the bipy moiety and for each of the three methyl groups of the mesityl substituent. The three carbonyl ligands appeared also as three singlets in the ^{13}C NMR spectrum. These features reflect the asymmetry of the molecule of **2c** and therefore indicate that the reaction involved a transformation of the bipy ligand. The X-ray determination of the structure of

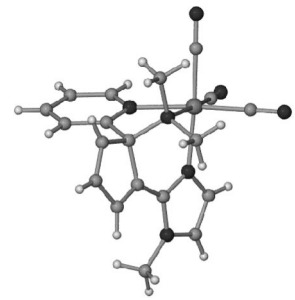

Figure 1. Molecular structure of the cation present in **4**.

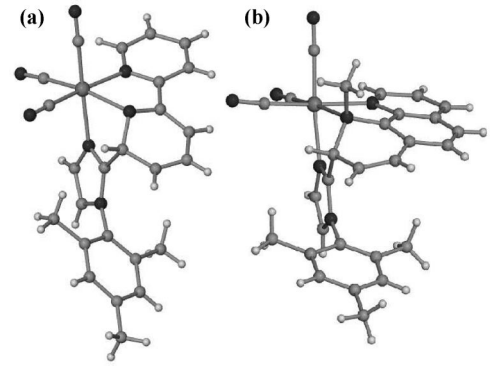

Figure 2. Molecular structure of **2c** (a) and the cation of **3d** (b).

2c (Figure 2a) demonstrated the presence of a bond between the C(2) carbon of the imidazole moiety and C(3) of bipy. As a result, the latter has become an sp^3-hybridized carbon, and the aromaticity of the pyridine ring was lost. In solution, this is reflected in a large upfield shift of three of the signals of the bipy in ^1H NMR (at 4.87, 5.52, and 6.34 ppm) and ^{13}C NMR (70.1 ppm for the sp^3 C). The nitrogen atom adjacent to the pyridine carbon that underwent the coupling is now part of an amido ligand. The phenanthroline analogue of **1c**, $[Re(CO)_3(MesIm)(phen)]OTf$ (**1d**), reacted with $KN(SiMe_3)_2$ in a similar way, affording complex **2d**, whose spectral features indicate isostructurality with **2c**. The reactions of **2c**,**d** with the equimolar amounts of MeOTf in CH_2Cl_2 afforded stable products **3c**,**d** (Scheme 1), which were spectroscopically characterized; in addition, the structure of **3d** was determined by X-ray diffraction (Figure 2b). The results showed that methylation at nitrogen transformed the amido-like nitrogen of **2c**,**d** into an amine ligand in the cationic complexes of **3c**,**d**. Compounds **3c**,**d** did not further react with MeOTf.

In view of the results with the mesitylimidazole complexes discussed above, we returned our attention to the transformation from **1a** to **4**, trying to find out if species akin to **2c** and **3c**

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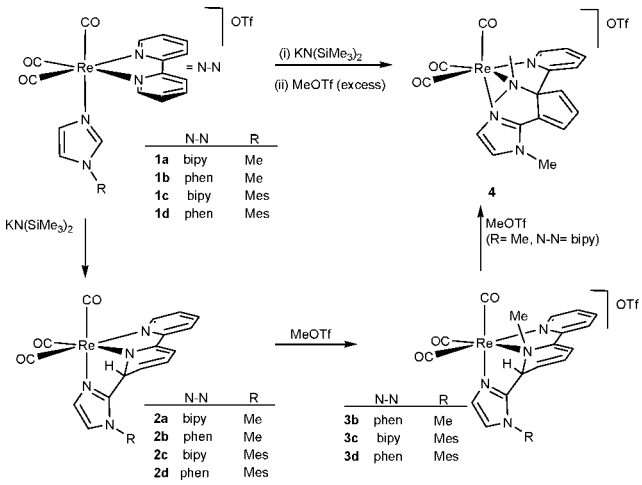
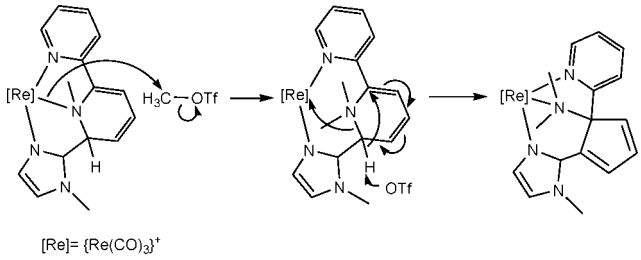
Scheme 1



Scheme 2



could be involved as intermediates. The putative neutral product of the deprotonation of **1a** displayed IR ν(CO) bands (2005, 1892, and 1884 cm^{-1}) almost identical to those of **2c**. Furthermore, its ^1H NMR spectrum displayed three signals in the range of 4.96−5.53 ppm, attributable to the dearomatized bipy hydrogens, very similar to those observed for **2c** (see above). As mentioned before, reaction of the methylimidazole-derived intermediate **2a** with MeOTf produced **4**. Using a single equivalent of MeOTf did not allow the isolation of a stable product. However, when the analogue methylimidazole phen complex [Re(CO)$_3$(MeIm)(phen)]OTf (**1b**) was deprotonated and the resulting intermediate was treated with MeOTf, the monomethylated compound **3b** could be isolated. Its spectroscopic characterization indicated a structure like those of **3c**,**d**. Compound **3b** did not react with a second equivalent of MeOTf, suggesting that the central aromatic ring of phen is an obstacle for the rearrangement that ends in nitrogen extrusion.

The results discussed above suggest that the latter step in the transformation from the *N*-methylimidazole bipyridine compound **1a** to the N-extruded compound **4** is a second at-nitrogen methylation of a compound like **3c**. In the absence of mechanistic evidence, Scheme 2 shows a rationale for the observed transformation.

In the previously known C−N activation processes referred to in the introductory paragraph, the initial coordination of pyridine in a κ^2(C,N) fashion to the early transition metal center disrupts pyridine aromaticity. In contrast, in our system, pyridine dearomatization, along with generation of a highly nucleophilic amido nitrogen (which will undergo subsequent methylation), results from intramolecular attack of the carbeniate anion generated by deprotonation of the imidazole ligand.

The C−C coupling between the C-deprotonated imidazole and bipy stands in contrast with the reactivity reported in 2007 by Ruiz and Perandones.[7] These authors found that deprotonation of *N*-alkylimidazoles in Mn(CO)$_3$(bipy) complexes similar to **1a** afforded, after subsequent reprotonation, a C-coordinated N-heterocyclic carbene ligand. Our findings show that moving from manganese to rhenium results in that the putative carbeniate intermediate would attack the adjacent bipy or phen ligand, presumably because the cleavage of the Re−N bond is more difficult than that of Mn−N.

In summary, we have found that treatment of [Re(CO)$_3$(MeIm)(bipy)]OTf (**1a**) with the base KN(SiMe$_3$)$_2$ deprotonates the imidazole C2−H, and the so formed carbeniate attacks C3 of the bipyridine ligand. The consequence is the loss of aromaticity of the affected ring, which becomes an amide ligand. Two successive methylations of the latter cleave the C−N bonds of the ring, resulting in formation of an N-ligated cyclopentadienyldimethylamine group. Since *fac*-Re(CO)$_3$(N−N) fragments are usually very inert, these results lead us to think that carbeniates similarly generated by deprotonation of an *N*-alkylimidazole ligand could be used for coupling reactions with electrophilic ligands other than bipy and phen. Studies along this line are currently underway in our laboratory and will be reported in due course.

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Supporting Information Available: Crystallographic data of **2c**, **3d**, and **4** and synthesis of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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