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Use of an Electron-Reservoir Complex Together with Air to Generate N-Heterocyclic Carbenes

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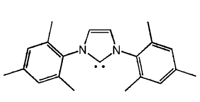
We report that the standard electron-reservoir complex [Fe^{I}Cp(η^6-C$_6$Me$_6$)], **1**,[1] can be conveniently used with air to deprotonate weak acids, via the intermediacy of superoxide radical anion $O_2^{\bullet -}$. This is exemplified here with the deprotonation of imidazolium salts, generating N-heterocyclic (NHC) carbenes. Imidazoles are universally known for their key roles in metalloenzymes, and their alkylated derivatives, imidazolium salts, have now become popular ionic liquids used for “Green Chemistry” conditions.[2] Deprotonation of these salts has been shown by Arduengo to yield isolable and relatively stable NHCs (**2** and **3**) when the heterocycle nitrogen atoms bear suitable substituents.[3]



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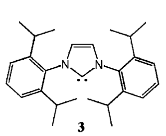

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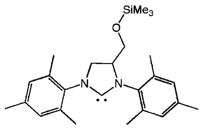

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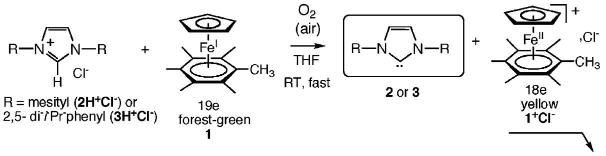
A renaissance of carbene chemistry has resulted from this discovery[4] with that of Bertrand of the stabilization of non-NHC carbenes, the first isolated carbenes.[5] In particular, NHC carbenes were introduced in catalysis in the late 90s with olefin metathesis and hetero-cross-carbon−carbon-coupling reactions.[6] The property of excellent σ-donors, non-π-acceptors of these ligands has thus brought them to the very forefront of organometallic chemistry and catalysis, especially because they can replace phosphines that are not environmentally benign. In addition to the key exceptional electronic properties and very favorable Green Chemistry aspects of NHC carbene ligands, others[7−9] have shown that they provide remarkable Grubbs-type, so-called second-generation ruthenium olefin metathesis catalysts [RuCl$_2$(=CHPh)(bis-*N*-mesityl-NHC)] and their multiple efficient derivatives.[10] More recently, Nolan has considerably developed the efficiency of a variety of C−C and C−N cross-coupling reactions (Heck, Suzuki, Stille, Sonogashira, Corriu−Kumada, Niyama, amination) of Pd complexes bearing a single NHC carbene **2** or **3**.[11]

Usually, the imidazolium salt is utilized in situ, but this does not allow for good control of the metal−carbene stoichiometry, especially because of the duality of complexation modes. Indeed, Crabtree has shown that the “normal” symmetrical coordination mode can switch to another nonsymmetrical carbene coordination.[12−14] Moreover, Nolan reported in 2004 that these two complexation modes can selectively form depending on the reaction conditions and that their reactivity behaviors in catalysis are different.[15] Therefore, it is essential to control and optimize the conditions of deprotonation of imidazolium salts to NHC carbenes viewing the central role of these ligands in catalysis.

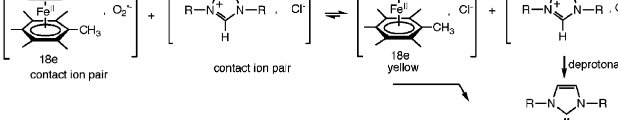
The use of **1** with O$_2$ provides a clean method for this purpose. **1** is easily available in high yields as green−black crystals upon monoelectronic reduction with Na/Hg in THF or glyme at ambient temperature of its Fe^{II} 18-electron monocationic form (**1$^+$PF$_6^-$**)[6] that can be synthesized in large scales upon heating ferrocene with the arene in the presence of aluminum chloride. Upon contact with a stoichiometric amount of **1** under ambient conditions in THF in the presence of air, **2H$^+$Cl$^-$** and **3H$^+$Cl$^-$** cleanly give high (virtually quantitative) yields of the soluble carbenes within a few seconds, visible by the quick color change from deep-green to yellow. In the meantime, the yellow salt **1$^+$Cl$^-$** precipitates. The carbenes formed in this way are characterized by ^{1}H and ^{13}C NMR when these reactions are carried out in THF-*d*$_8$ (eq 1).

We know that **1** reacts with O$_2$ to give the deep-red complex [Fe^{II}Cp(η^5-C$_6$Me$_5$CH$_2$)], **5**,[17] a base whose conjugated acid **1$^+$PF$_6^-$** has a pK_a value of 28.2 in DMSO,[18a] close to that of *t*-BuOK.



(1)

However, the reaction of **2H$^+$Cl$^-$** and **3H$^+$Cl$^-$** with **1** in the presence of air does not give the deep-red color of **5**, even transiently, but an off-white solution of the carbene. We also know that the mechanism of the reaction of **1** with O$_2$ proceeds by electron transfer from Fe^I to O$_2$ to give the transient intermediate contact ion pair [Fe^{II}Cp(η^6-C$_6$Me$_6$), $O_2^{\bullet -}$],[17] in which the $O_2^{\bullet -}$ anion[18b] deprotonates a methyl group, yielding the double-bonded exocyclic methylene. The stoichiometry is 0.25 mol O$_2$ yielding 0.5 mol H$_2$O at room temperature and 0.5 mol O$_2$ yielding 0.5 mol H$_2$O$_2$ at −78 °C. Thus, the base that deprotonates **2H$^+$Cl$^-$** and **3H$^+$Cl$^-$** in THF can be $O_2^{\bullet -}$ (whose basic properties are enhanced by the fast dismutation of HO$_2$), after fast metathetic ion exchange between the two contact ion pairs (eq 2):



(2)

Alternatively, the deprotonation of the salts **2H$^+$Cl$^-$** and **3H$^+$Cl$^-$** can be carried out using **1** and air under ambient conditions in various solvents, such as pentane, benzene, toluene, and ether, in which these salts are not soluble. Then, the deep-red color of **5** immediately appears upon contact with air, and the heterogeneous deprotonation takes place in about 5−30 min at ambient temperature, depending on the solvent (Scheme 1).

Indeed, a stoichiometric amount of **5** also deprotonates **2H$^+$Cl$^-$** and **3H$^+$Cl$^-$** quantitatively in any of these solvents or instantaneously in THF under ambient conditions, yielding the carbene and the yellow precipitate of **1$^+$Cl$^-$**.

The functionalization of NHC carbenes is useful for the derivatization of NHC carbene-containing catalysts with organic or inorganic polymers en route to supported recoverable catalysts; thus

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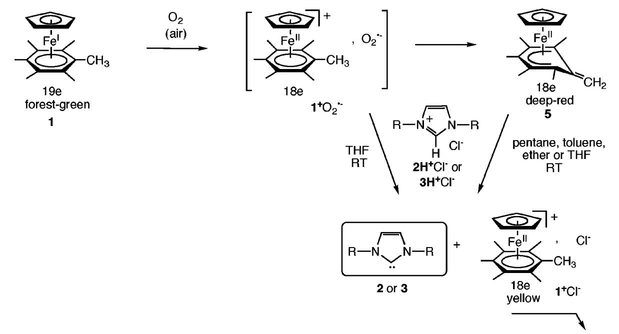
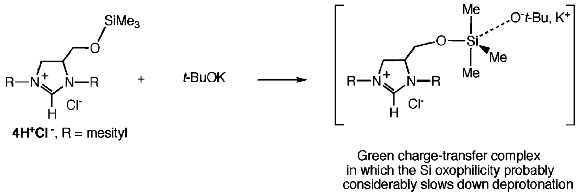
Scheme 1

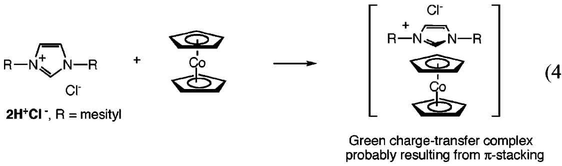


the new imidazolium salt **4H$^+$Cl$^-$** was synthesized (Supporting Information). Reaction of *t*-BuOK with **4H$^+$Cl$^-$** does not provide fast deprotonation, but development of a green color corresponding to a green charge-transfer complex (eq 3)[19] whose ^{1}H NMR peaks are close to those of the starting material, and the UV−vis spectrum is shown in Figure 1 in the Supporting Information.



(3)

We notice that other electron-rich reagents, such as cobaltocene, also give a blue−green charge-transfer complex upon reaction with **2H$^+$Cl$^-$** or **4H$^+$Cl$^-$** (eq 4; see the UV−vis spectrum in the Supporting Information).

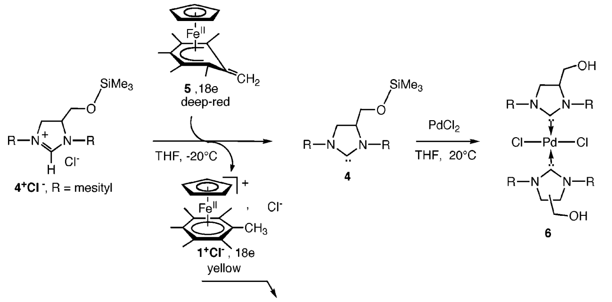


(4)

No reduction occurs because such an electron transfer between the donor and the imidazolium acceptor is strongly endergonic (by 1.3 V), the reduction potential of imidazolium salts being extremely negative.[20] Clyburne pointed out that monoelectronic reduction of the imidazolium salts **2H$^+$Cl$^-$** provides the carbene. The reduction potential value of the salts is so negative, however (−2.68 V vs ferrocenium/ferrocene), that only the extremely strong reductant potassium metal (excess) in refluxing THF can be used,[20] which limits the possible scale and compatibility with side functional groups and the presence of reagents in situ. It is well-known that carbenes have a rich chemistry,[4] thus a deprotonation method removing the chemical used for deprotonation is advisable.

Deprotonation of **4H$^+$Cl$^-$** is best carried out using **5** at −20 °C in ether and yields **4**. The reaction is now very convenient because it proceeds with precipitation of the salt **1$^+$Cl$^-$** of the protonated acidic form **1$^+$** of the base **5** at ambient or sub-ambient conditions. Indeed, the stability of **4** is much lower and its air sensitivity is higher than those of **2** and **3** due to the absence of the conjugated double bond in **4**. The ^{1}H NMR spectrum of **4** shows the shielding of all the aromatic and NHC protons and disappearance of the NC*H*N proton as expected, and reaction of **4** with PdCl$_2$ gives the new biscarbene Pd complex **6** (analogous to Nolan's biscarbene Pd complex obtained with **2**[15]), whose MALDI TOF mass spectrum presents the molecular peak corresponding to [M]$^+$ at 851 mu (Scheme 2).

Scheme 2



In conclusion, this study shows the first use of an electron-reservoir complex and air for clean deprotonation. Efficient deprotonation of the imidazolium salts **2H$^+$Cl$^-$** and **3H$^+$Cl$^-$** to the stable carbenes **2** and **3** best proceeds under ambient conditions using the electron-reservoir complex **1** and air in a variety of solvents, whereas the reaction of **1** with air to give the base **5** should be carried out in THF before deprotonation of **4H$^+$Cl$^-$** in order to take into account the sensitivity to air of the functional carbene **4**. Thus, this study is the first one demonstrating that **5** is a very useful neutral base whose acidic form is removed from the reaction medium (thus recyclable) after deprotonation by precipitation. This use of **5** is essential, when the deprotonation yields a fragile species, and can potentially be generalized to many other systems.

Note Added after ASAP Publication. Production error published previous revision of Supporting Information March 18, 2006; Editor approved at acceptance Supporting Information published April 4, 2006.

Supporting Information Available: Syntheses and NMR spectra of **2**−**4** and **6**, and UV−vis spectra of the colored charge-transfer products of donors with **4H$^+$Cl$^-$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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