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On the interactions of *N*,*N*′-bismesitylimidazolin-2-yl and alcohols

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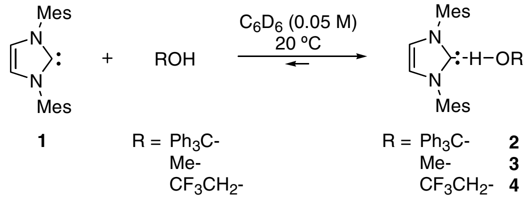
Abstract

The interaction of *N*,*N*′-bismesitylimidazolin-2-yl (IMes) with alcohols is discussed. NMR spectroscopy and X-ray crystallography were used to examine the influence of solvent and alcohol on this interaction. The stabilizing effect of these interactions may be used for the storage of nitrogen–heterocyclic carbenes (NHCs) since removal of the volatiles liberates the NHC.

Since their successful isolation in 1991 by Arduengo,[1] stable imidazole based singlet carbenes have grown from a unique discovery to a practical reagent in various chemical applications. Much of the early work focused on the properties of carbenes as ligands in the coordination sphere of metals.[2] There has been growing attention to the catalytic properties of heteroatom–stabilized carbenes.[3] We disclosed that *N*,*N*′-bismesitylimidazolin-2-yl (IMesNHC, **1**) is an effective catalyst for the amidation of unactivated esters with amino alcohols.[4] During the course of our mechanistic study, we identified a hydrogen bond interaction between **1** and hydroxyl protons. In this Letter we expand on our earlier findings regarding this interaction (Scheme 1).

The current study concerns the influence of the alcohol involved in this hydrogen bond interaction in addition to the effect of solvation. We reported the solution studies of IMes with a variety of alcohols.[4] In addition to a series of NMR studies, we also identified the first X-ray structure of a carbene–alcohol hydrogen bond complex. It is interesting to compare the X-ray structure of IMes–HOMe with the more labile X-ray structure of IMes–HOCPh$_3$ (Fig. 1).[5] The solid-state structure of complex **2** revealed a distorted hydrogen bond between the hydroxyl proton and the carbene. Hydrogen bond formation is expected to relax the N1–C2–N3 bond angle of the carbene toward an imidazolium ion. It could then be reasoned that the degree of proton transfer (i.e., strength of the hydrogen bond) would be reflected in the N1–C2–N3 bond angle of



Scheme 1. Hydrogen bond interaction between IMes and alcohols. Mes = 2,4,6-trimethylphenyl.

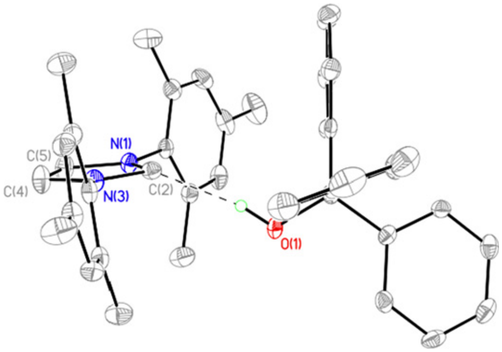


Fig. 1. Thermal ellipsoid representation of complex **2**.

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the carbene. The N1–C2–N3 bond angle of the carbene moiety in **2** is 101.9(2)°, which is closer to the observed angle in the free carbene (101.4°)[1a] than the imidazolium chloride (108.6°).[6] This angle is however smaller than that of the methanol complex **3** at 102.53(16)°.[4] Interestingly, in the triphenylmethanol complex **2** the hydrogen atom is 0.84(3) Å below the imidazolinyl azaheterocycle plane, a non-optimal orientation for hydrogen bond interaction with the carbene lone pair (Fig. 1, ~26° from planarity).[7] The length of the hydrogen bond interaction in IMes–triphenylmethanol complex (**2**) was found to be 2.856(3) Å that is slightly longer than the corresponding hydrogen bond interaction (2.832(2) Å) in the methanol complex **3**[4] by 0.02 Å.

We also studied the formation of a complex between IMes (**1**) and 2,2,2-trifluoroethanol (TFE) to examine electronic effects on such carbene alcohol complexes. This alcohol was expected to be a better proton donor due to the increased acidity[8] of TFE compared to other alcohols we had examined. We obtained high quality crystals from toluene solutions containing an equal molar ratio of IMes (**1**) and TFE. Indeed, the X-ray structure of these crystals clearly illustrated a complete proton transfer to afford an imidazolium ion derivative (Fig. 2). Interestingly, rather than a 2,2,2-trifluoroethoxide counter ion another molecule of **1** was bound to the C_2-proton of the imidazolium ion. The 2,2,2-trifluoroethoxide was stabilized by a hydrogen bond interaction with a TFE molecule (Fig. 2). Analysis of the structure suggests a hydrogen bond interaction between the 2,2,2-trifluoroethoxide and the C4-proton of the imidazolin-2-yl fragment while TFE is engaged in a hydrogen bond interaction with the C4-proton of the imidazolium ion in the crystal structure.

A carbene–imidazolium interaction was also observed in the solid state by Arduengo[6] when a 1:1 mixture of **1** and **1·HPF$_6$** (or **1** and **1·HOTf**) was allowed to crystallize. Interestingly, in these structures the C2-carbon of the two heterocycles exhibited an averaged ^{13}C NMR resonance at 175 ppm, midway between the resonances expected for a carbene and an imidazolium ion.[6] Interestingly, in our studies of the IMes–TFE (1:1) solution in benzene (0.5 M in C_6D_6 at 20 °C) we observe a downfield ^{13}C NMR resonance for the C2-carbon at 194.7 ppm which is closer to the free carbene (219.4 ppm 0.5 M in C_6D_6 at 20 °C).[4] Additionally, all other carbon resonances save those related to the methyl groups appear as two unequal resonances. These appear as a broad minor resonance blending into a sharp major resonance in the ^{13}C NMR spectra. Using variable temperature NMR we observed that at 70 °C in C_6D_6 (0.5 M), all signals appear to sharpen, however not all pair of carbon resonances coalesce.[9] Importantly, upon cooling the sample from 70 °C (after extended heating, >12 h) to 20 °C there was no decomposition, providing spectra identical to those obtained prior to heating. Interestingly, we also examined the ^{1}H NMR of the IMes–TFE (1:1) solution in benzene and observed a significant dependence as a function of TFE equivalents (from 1.0 to 5.0 equiv).[10] Cumulatively, our observations suggest a dynamic equilibrium in the solution involving multiple species (Scheme 2) only one of which is seen in the crystal structure shown in Figure 2.

The observation with TFE described above and the effect of solvation paralleled those of IMes (**1**) in protic solvents. Dissolution of IMes (**1**) in MeOD-d_4 led to deuterium incorporation at C4/5 of the azaheterocycle (96.5% at 0.5 M in MeOD-d_4 at 20 °C).[4,11] A residual protium resonance at 8.13 ppm is similar to the C2-imidazolium chloride signal for the C2-H (8.10 ppm). The ^{13}C NMR resonances corresponding to the C4/5 in methanolic solution of IMes were found at 126 ppm as a triplet ($J_{CD} = 32$ Hz), similar to the imidazolium chloride salt (126 ppm). The resonance corresponding to the C2 in this methanolic solution of IMes was at 139.9 ppm as a broad singlet[12] and not in the region observed for IMes–HOMe (1:1) in aprotic solvent (i.e., ~200 ppm).[4] These results indicate that the dissolution of IMes in methanol provides a solvated imidazolium methoxide in contrast to the hydrogen bonded complex seen in aprotic solvents.[4]

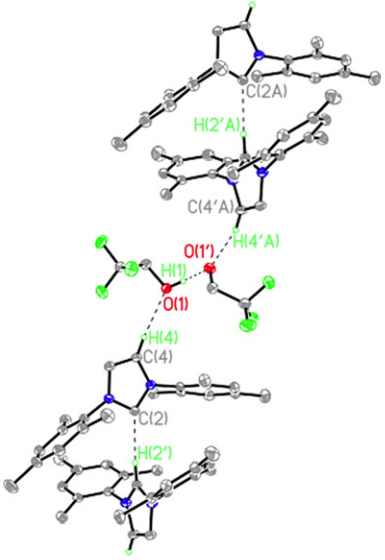
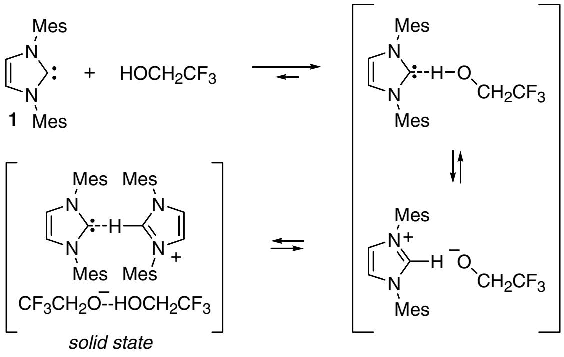
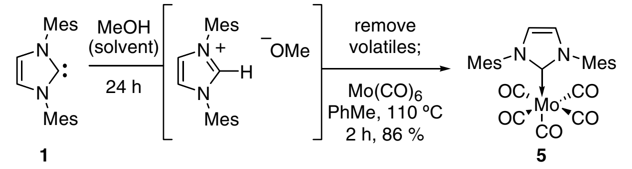


Fig. 2. Thermal ellipsoid representation of the crystal obtained from IMes and TFE. Atoms labeled with an A after the atom name are generated from the parent atom by the symmetry operator $x + 1$, y, z.



Scheme 2.



Scheme 3. Synthesis of complex **5** from methanolic IMes.

Given the stability of imidazolium salts we sought to investigate the chemistry of IMes dissolved in MeOD-d_4. A solution of IMes in methanol (0.05 M) persisted unchanged for six weeks at −10 °C under an argon atmosphere by NMR. A methanolic solution of IMes (as the solvated imidazolium methoxide) is also more resistant to hydrolytic decomposition. Addition of deionized and degassed water (1.0 equiv) to a solution of IMes in MeOD-d_4 (0.05 M, 20 °C) did not lead to decomposition over 24 h. Notably, rapid decomposition (<5 min) was observed when deionized and degassed water (1.0 equiv) was added to a solution of IMes in C_6D_6 (0.05 M, 20 °C). The solvated imidazolium methoxide mentioned above is resistant to hydrolytic decomposition even upon the addition of large excess of water (30.0 equiv) over 1 week.[13]

The protium/deuterium exchange at C4/5-carbons of the solvated imidazolium methoxide samples described above hinted at a reversible access to the free carbene. This is due to the observation that while such protium/deuterium exchange is very rapid in the case of the carbene structure, it is significantly slower in methanolic solution of imidazolium chloride. Indeed, the IMes–MeOH complex was accessible after removal of the excess methanol and was used in complex formation with $Mo(CO)_6$ to give IMes·$Mo(CO)_5$ **5** in 86% yield (Scheme 3).[14] These observations suggest an alternative means for the storage of carbenes alongside the formation of BEt_3 adducts[14] and Ag-complexes.[15]

The strength and nature of the hydrogen bond interaction between IMes (as a representative NHC) and alcohols are greatly sensitive to the solvent and the particular alcohol. The more sterically congested the alcohol, the weaker the interaction with the carbene. A more acidic alcohol leads to greater involvement of imidazolium alkoxides in equilibriums with other hydrogen bond complexes. Dissolution of IMes in methanol leads to the formation of a solvated imidazolium methoxide. Evaporation of the volatiles and desolvation of robust imidazolium alkoxide solutions return the carbene–alcohol (1:1) complex that may be used in organometallic complex formation or used directly in transformations employing them as catalysts.

Acknowledgments

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