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Basicity of a Stable Carbene, 1,3-Di-*tert*-butylimidazol-2-ylidene, in THF[1]

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Abstract: The basicity of 1,3-di-*tert*-butylimidazol-2-ylidene (**1**) was measured in THF against three hydrocarbon indicators. Both ion pairs and free ions were found and the corresponding equilibrium constants were measured. Homoconjugation was not found in either THF or DMSO. The carbene is effectively more basic in DMSO by several p*K* units, probably because of hydrogen bonding of **1**-H^+ to DMSO. Model ab initio computations are consistent with these results.

Introduction

Study of the structures and chemical reactivities of carbenes has become an active research area after Arduengo's first synthesis and isolation of stable imidazol-2-ylidene carbenes.[2] In addition to theoretical and other fundamental studies,[3] much effort has been expended to develop organometallic catalysts that contain carbenes as ligands.[4] For example, ruthenium alkylidene compounds have been used successfully as olefin metathesis catalysts.[5] Nevertheless, much of the fundamental chemistry of these carbenes is not known since they are relatively new. For example, there is only one report dealing with their basicity. The Alder group has reported the basicity of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene in dimethyl sulfoxide-d_6 (DMSO-d_6) as pK_a = 24, which makes it more basic than such strong nitrogen bases as DBN and DBU.[6] They also tried the same measurement in THF-d_8 by an NMR method and found that the carbene is able to deprotonate 9-phenylfluorene completely but not fluorene; this result suggests that the carbene is effectively more basic in DMSO than in THF. Some time later it was found that the carbenes are reactive toward halogenated and acidic solvents including DMSO.[7] [8] Thus, we considered it important to determine the basicity of carbenes more precisely in inert solvents such as THF.

Results and Discussion

Our group has developed ion pair acidity scales for the lithium and cesium salts of various hydrocarbons in THF[9] relative to a standard taken as 22.90, the ionic pK_a of fluorene per hydrogen in DMSO.[10] The relative acidities apply to the equilibria in eq 1, in which the lithium salts are solvent separated ion pairs (SSIP) and the cesium salts are contact ion pairs (CIP).

$$R^- M^+ + R'H = RH + R'^- M^+ \ (M^+ = Li^+ \text{ or } Cs^+) \quad (1)$$

More recently we have applied such ion pair acidity scales to the ion pair basicities of amines in THF. Amines are often used as base catalysts in organic synthesis under ion pairing conditions.[11] The relative ion pair basicities of amines were reported to differ substantially from the ionic values in polar solvents such as acetonitrile. We now report the basicity of the stable carbene, 1,3-di-*tert*-butylimidazol-2-ylidene (**1**), in THF using UV−vis spectroscopy. Three different indicators (**2**, **3**, and **4**) were found to equilibrate with their anions in the presence of the carbene. The λ_{max} and the concentrations of all species are listed in Table S1 (Supporting Information). We show below that both ion pairs and free ions are present at the concentrations

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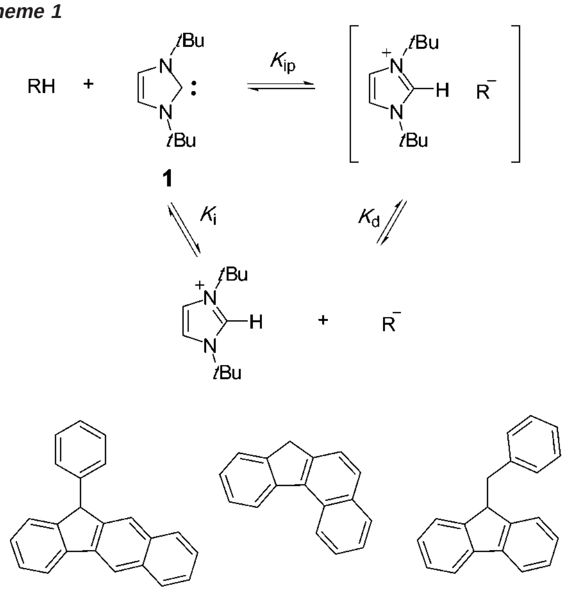
Scheme 1



Ph-2,3-BF (**2**) 3,4-BF (**3**) BnFl (**4**)

used, yet the λ_{max} values are essentially constant over this range. Accordingly, the extinction coefficients of the Li salts were used for the calculation of the concentrations of the anion moieties as in our earlier amine basicity study. These λ_{max} values are 3−5 nm shorter than those of the SSIP lithium salts. Similar results were found for those amines whose protonated forms are delocalized cations.

The reaction of the carbene with the indicator hydrocarbon produces first an ion pair between the protonated carbene, **1**-H$^+$, and the indicator anion with an equilibrium constant $K_{ip.}$ The ion pair dissociates to the free ions with an equilibrium constant K_d (Scheme 1). In treating the data, however, it is convenient to consider both species as directly equilibrating with the reactants, that is, the free ions in equilibrium with the carbene and hydrocarbons with equilibrium constant K_i ($=K_{ip}K_d$). Since the spectra measure both the ion pair and free indicator anion, the measured anion moiety, expressed with curly brackets as $\{R^-\}$, is given by eq 2.

$$\{R^-\} = [\text{ion pair}] + [\text{free ion}] = K_{ip}[\text{RH}][\text{carbene}] + (K_i[\text{RH}][\text{carbene}])^{1/2} \quad (2)$$

Figure 1 shows plots of $\{R^-\}$ vs ([RH][carbene])$^{1/2}$ for all three indicator hydrocarbons. The plots are smooth second-order polynomials ($R^2 > 0.98$) for which straightforward curve-fittings yield the corresponding equilibrium constants as summarized in Table 1. The resulting K_d values are of the order of 10^{-5} M, which is similar to the values for SSIP Li salts obtained from conductivity measurements.[12] This agreement is evidence for the validity of this method.

From the K_{ip} and K_d values obtained, the concentrations of ion pairs and free ions were calculated and are listed in Table S1. They are of comparable magnitude in the dilute solutions used, but of course, the ion pairs are much more important at synthesis concentrations.

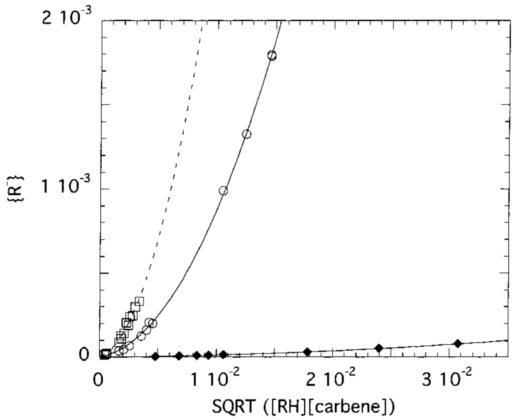


Figure 1. Plot of ([RH][carbene])$^{1/2}$ vs $\{R^-\}$. The regression lines shown are $(0.0212 \pm 0.0093)x + (24.17 \pm 3.47)x^2$ ($R^2 = 0.980$) for Ph-2,3-BF (□); $(0.0111 \pm 0.0019)x + (7.68 \pm 0.15)x^2$ ($R^2 = 0.999$) for 3,4-BF (○); and $(0.000499 \pm 0.000036)x + (0.066 \pm 0.0015)x^2$ ($R^2 = 0.9996$) for BnBF (◆).

Table 1. Equilibrium Constants at 25 °C Obtained from Plots of $\{R^-\}$ vs ([RH][carbene])$^{1/2}$ and Comparison of pK Values with pK_{Li}

	K_{ip}	K_d	K_i	pK_{Li}[a]	pK_{ip}	pK_i
Ph-2,3-BF	24.17	1.87E-05	4.52E-04	17.84	−1.38	3.34
3,4-BF	7.68	1.58E-05	1.21E-04	19.29	−0.59[b]	4.22[b]
BnFl	0.0656	3.79E-06	2.49E-07	21.36	1.18	6.60

[a] Reference 8b. [b] Per-hydrogen basis, statistical correction applied (+0.3).

Scheme 2

$$\text{RH} + \mathbf{1} + \mathbf{1} \xrightleftharpoons{K_{ip}} [\mathbf{1}\text{-H-}\mathbf{1}^+\ R^-] \xrightleftharpoons{K_d} \mathbf{1}\text{-H-}\mathbf{1}^+ + R^- \quad (3)$$

$$\{R^-\} = K_{ip}\ [\text{RH}][\text{carbene}]^2 + (K_i\ [\text{RH}][\text{carbene}]^2)^{1/2}$$

Scheme 3

$$\text{RH} + \mathbf{1} \xrightleftharpoons{K_{ip}} [\mathbf{1}\text{-H}^+\ R^-] \xrightleftharpoons{\mathbf{1}} \mathbf{1}\text{-H-}\mathbf{1}^+ + R^- \quad (4)$$

$$\{R^-\} = K_{ip}\ [\text{RH}][\text{carbene}] + (K_i\ [\text{RH}][\text{carbene}]^2)^{1/2} \qquad \text{eq 4}$$

Arduengo et al. have reported a crystal structure of a carbene hydrogen bonded to its conjugate acid with C−H−C hydrogen bonding.[13] The rapid proton transfers between carbenes such as **1** and their conjugate acids on the NMR time scale in THF suggests that such homoconjugation might apply in the equilibria in Scheme 1. Two possibilities are that homoconjugation occurs both in the ion pair and in the free ion (Scheme 2) or that it applies to the free ion alone (Scheme 3). The corresponding equations for $\{R^-\}$ are 3 and 4, respectively.

Neither equation provides a satisfactory fit to the data: negative equilibrium constants result. Scheme 2 and eq 3 were found to apply to some amines (for example, DMAP) in THF.[14] Homoconjugation, therefore, does apply to some cases but it appears to be negligible for the carbene **1** and its conjugate acid in THF, at least at the low concentrations involved in our experiments.

If the pK_a values were known for the indicator hydrocarbons in THF then the pK_i in Table 1 would provide a value for pK_a for **1**-H$^+$ in THF. These pK_a values are not known but since the dissociation constants of the SSIP lithium salts are ap-

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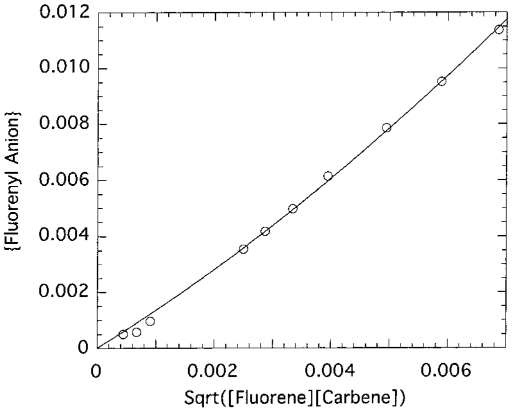

Figure 2. Plot of {fluorenyl anion} vs ([RH][carbene])$^{1/2}$ for fluorene and **1** in DMSO at 25 °C. The regression curve shown is $(1.30 \pm 0.05)x + (54.36 \pm 9.45)x^2$; $R^2 = 0.998$. Calculated $K_d = 0.031$ M, $K_i = 1.68$, and $K_{ip} = 54$ M^{-1}.

proximately constant for the indicator hydrocarbons, differences in the ion pair pK_{Li} are equal to the differences in pK_a.[12] Accordingly, pK_{Li} − pK_i in Table 1 should be approximately constant and it is. The resulting value, 14.9 ± 0.1, has no other fundamental significance but does demonstrate the self-consistency of the experiments.

A plot of pK_{ip} in Table 1 vs pK_{Li} for the corresponding indicators gives a linear fit with a slope of 0.74 ± 0.08, a value similar to that, 0.75, reported earlier for similar equilibria between DBU and indicator hydrocarbons.[11] The compressed sensitivity for pK_{ip} results from changing of the dissociation constant, K_d. The more basic indicators have tighter ion pairs and smaller K_d values; the same effect occurs with the cesium contact ion pair indicator salts.[12] This plot gives p$K_{ip} = 0$ for p$K_{Li} = 20$, which puts a lithium salt of this pK_{Li} and the carbene **1** at the same level of effective basicity, a level several pK units less basic than that reported in DMSO solution. That is, in THF the carbene is as basic as the lithium salt of a compound having an "ion pair pK" of 20 on our lithium scale. To the extent that this type of comparison is appropriate the carbene is effectively relatively less basic than in DMSO. One possible explanation for such a difference is that homoconjugation could be occurring for the carbene in DMSO; such homocojugation has been demonstrated for some amines in acetonitrile solution.[15] To test this possibility we applied the method of eqs 2−4 to DMSO solution.

From the UV−vis spectra we found that fluorene is deprotonated when similar amounts of carbene are present as previously reported.[6] The reported extinction coefficients[16] in DMSO were used for the calculation of the concentration of {R$^-$}. The UV−vis spectra for the anion decreased and generated unknown peaks to a significant extent after 1 day. This observation shows that there is ongoing reaction and gradual decomposition. Thus, the spectral measurements were limited to a 2−3 h period. The resulting experimental points (Table S2, Supporting Information) do not fit either eq 3 or eq 4 but do fit eq 2 well (Figure 2). Accordingly, we find no evidence for homoconjugation of the protonated carbene in either THF or DMSO. The derived pK_a for **1**-H$^+$ in DMSO is 22.7. This value is appreciably lower than the value of 24 reported for a close analogue of **1**.[6] We note in Table 1 also the significant ion pairing found in DMSO; Olmstead and Bordwell have also reported a number of salts that ion pair appreciably in DMSO.[17] Thus, we suggest that Alder et al.[6] measured both ion pair and free ion as their anionic species, which would lead to a pK_a that is too high. For example, combining the ion pair and free ion concentrations in our DMSO experiment gives a "pK_a" of 23.04, which is significantly higher than that for free ions alone. At the higher concentrations of a NMR measurement this value would be expected to be still higher; nevertheless, the two carbenes are different structures and even the corrected pK_a could well be different.

Even with the corrected values, the carbene **1** is still effectively somewhat more basic in DMSO than in THF. The most likely explanation is the following. It is well-known that hydrocarbons with delocalized carbanions have comparable pK_a values in water and in DMSO; neither the hydrocarbon acid nor the delocalized conjugate base is significantly stabilized by hydrogen bonding. Hydroxylic acids, however, are generally less acidic in DMSO than in water; in water, both acid and conjugate base are stabilized by hydrogen bonding but in DMSO only the hydroxylic acid is so stabilized. Similarly, the protonated carbene **1**-H$^+$ can be stabilized by hydrogen bonding in DMSO but not the carbene itself.

Theory

One of the remaining questions concerns the structure of the ion pair: is it a type of charge-transfer complex with the two ring systems parallel or is the central CH of **1**-H$^+$ directed toward the anionic ring system? This question was addressed with the help of ab initio computations of a model system, protonated 2,5-dimethylimidazole, **5**-H$^+$**,** and cyclopentadienyl anion. Ab initio calculations, RHF 6-31+G*, were carried out with PC Spartan[18] and Gaussian98.[19] All energies and coordinates for the imidazolium complexes are summarized in Table S3 (Supporting Information). The energies are summarized in Table 2. Stationary points were characterized by frequency calculations.

Starting with **5**-H$^+$ in a plane perpendicular to the Cp plane and with the central C−H pointing at the center of the Cp ring gave a second-order saddle point with the distance between the ring center and the H of **5**-H$^+$ of 2.089 Å. Relaxing this structure led to a transition structure, **6A** (one imaginary frequency), 0.11 kcal mol^{-1} lower in energy with the C−H of **5**-H$^+$ pointing to the center of a CC bond in Cp at a distance of 2.210 Å (Figure 3). Starting with a charge-transfer type structure with the **5**-H$^+$ and Cp rings parallel and separated by 2.95 Å led to another transition structure, **6B** (Figure 3), in which the central CH bond

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Table 2. Computed Energies at RHF/6-31+G* (Zero-Point Energies Are Uncorrected)

	E, au	ZPE, kcal mol^{-1}
Cp-	−192.208 655	52.98
carbene, **5**	−302.848 178	85.49
protonated carbene, **5**-H$^+$	−303.276 741	94.73
protonated carbene-Cp$^-$, **6A**	−495.628 927	149.15[a]
protonated carbene-Cp$^-$, **6B**	−495.628 960	149.12[a]
DMSO	−551.545 088	53.76
Me$_2$O	−154.069 429	53.93
7	−606.150 052	181.12
8	−854.854 930	149.39
9	−457.362 979	149.58

[a] One imaginary frequency.

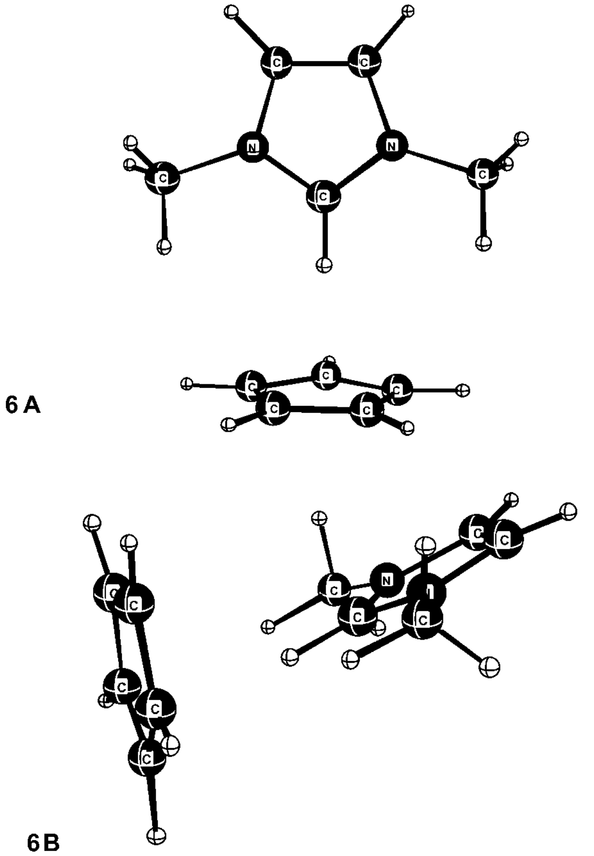

Figure 3. Optimized geometries of two complexes of **5**-H$^+$ and cyclopentadienyl anion, **6A** and **6B**.

of **5**-H$^+$ points to a carbon in Cp with a distance of 2.141 Å and the ring planes at an angle of 117.8°. Transition structure **6B** in Figure 3 is lower than **6A** by only 0.015 kcal mol^{-1} and is less stable than cyclopentadiene plus carbene by 10.6 kcal mol^{-1}. That is, the computations indicate that in the gas phase the model carbene is too weakly basic to abstract a proton from cyclopentadiene, but the results do suggest that the ion pair structure has the central C−H of the protonated carbene pointing toward the indicator anion rather than a π-type structure.

To model the role of solvation we compared structures with **5** hydrogen-bonded to the model carbene **5**-H$^+$ (**7**, homoconjugation) and to DMSO, **8**, and dimethyl ether (as a simple model of THF), **9**. In the homoconjugation model, **7**, the C−H−C hydrogen bond is linear (180.00°) and two CH bond lengths are 1.082 and 2.314 Å. These values can be compared to those in the crystal structure (mesityl group instead of methyl, 172.5°, 1.159, and 2.026 Å, respectively).[13] The complexation energy, −15.8 kcal mol^{-1}, is between the values for dimethyl ether and **5**-H$^+$ (**9**, −10.5 kcal mol^{-1}) and for DMSO and **5**-H$^+$ (**8**, −20.8 kcal mol^{-1}). The stronger hydrogen bond to DMSO in **8** compared to dimethyl ether in **9** is also reflected in the two O···H bond lengths, 1.966 and 2.057 Å, respectively. The computational results thus model the experimental findings that there is no homoconjugation in DMSO and the greater basicity of the carbene in DMSO compared to THF.

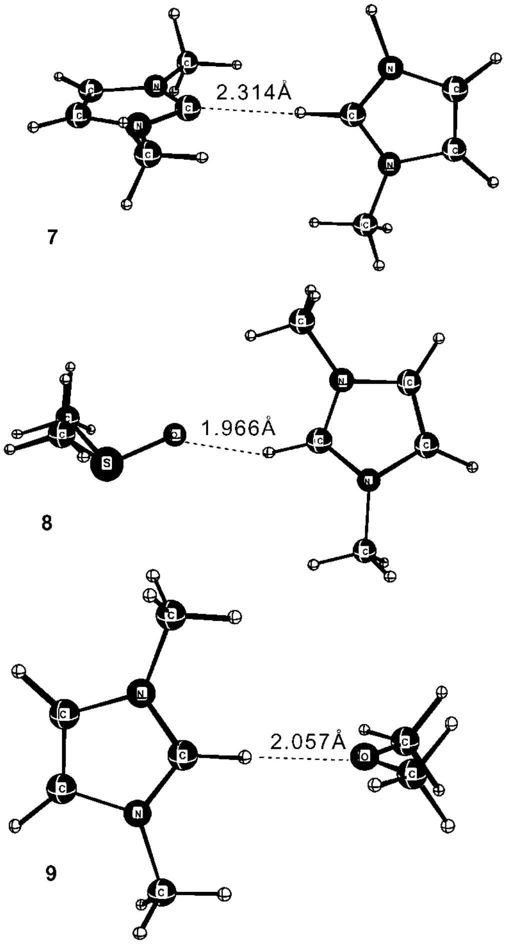

Figure 4. Hydrogen-bonded complexes of **5**-H$^+$ with **5** (**7**), dimethyl sulfoxide (**8**), and dimethyl ether (**9**).

Conclusions

The stable carbene, 1,3-di-*tert*-butylimidazol-2-ylidene (**1**), was found to be more basic than any of the amines we have studied. An accurate value of the effective basicity of the carbene in THF has been obtained. A method was demonstrated for deducing the dissociation constant of ion pairs to free ions from UV−vis data as an alternative to conductivity measurement. We have also developed methods for determining whether homoconjugation is important. These new methods are now being applied in our continuing study of the ion pair basicity of amines.

Experimental Section

The carbene, 1,3-di-*tert*-butylimidazol-2-ylidene (**1**), was a generous gift from Professor Arduengo. The indicators were available from our previous studies. Solutions of the indicator and the carbene were prepared in a glovebox and spectroscopic measurements were made at 25 °C using the glovebox−spectrometer system described previously.[20] The experimental results are reported in Tables S1 and S2 (Supporting Information) and plotted in Figures 1 and 2.

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank Professor A. J. Arduengo for his generous gift of compound **1**.

Supporting Information Available: Tables of experimental data and computational results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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