The Reactions of Imidazol-2-ylidenes with the Hydrogen Atom: A Theoretical Study and Experimental Confirmation with Muonium

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Abstract: The possible radicals resulting from hydrogen atom addition to the imidazole rings of 1,3-bis-(isopropyl)-4,5-dimethylimidazol-2-ylidene (**1**) and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**2**) have been studied by means of density functional calculations (B3LYP). The calculations included solvent effects estimated via the polarized continuum model (PCM) and an empirical treatment of vibrational averaging of hyperfine constants. Addition of a hydrogen (or muonium) atom to the carbeneic carbon of 1,3-bis(isopropyl)-4,5-dimethylimidazol-2-ylidene was found to give a radical 60.46 kJ mol^{-1} more stable than the radical resulting from addition to the double bond. Estimation of the activation barriers for reaction at the two sites shows that addition at the carbeneic carbon is favored. The site of addition was confirmed experimentally using muonium (Mu), which can be considered a light isotope of hydrogen. Muon spin rotation and muon level-crossing spectroscopy were used to determine muon, ^{13}C, and ^{14}N hyperfine coupling constants (hfc's) for the radical products of addition to the two carbenes. Good agreement between the experimental and calculated hfc's confirms that Mu (and hence H) adds exclusively to the carbeneic carbon. The radicals that are produced have nonplanar radical centers with most of the unpaired electron spin density localized on the α-carbon.

1. Introduction

Carbenes (R$_2$C:) are molecules that possess a neutral dicoordinate carbon atom with six valence electrons, which results in high reactivity for these carbon centers. This high reactivity was, in part, the reason for their elusive nature. Until recently, carbenes were only observed as intermediates or trapped in an inert matrix at cryogenic temperatures.[1,2] In 1988, Bertrand produced the first stable singlet carbene, [bis(diisopropylamin)-phosphino]trimethylsilylcarbene,[3] which was soon followed by the synthesis and characterization of the first imidazol-2-ylidenes by Arduengo.[4] After these discoveries, there have been numerous studies on the reactivity and electronic structure of carbenes. Recognizing the impact that the isolation of these highly reactive molecules has had on synthetic chemistry, reviews have covered the quest for isolable carbenes,[5] main group element carbenes and carbene analogues,[6] transition metal carbene complexes and catalysts,[7,8] and main group element carbene complexes.[9]

Recently, we reported the reactivity of a stable singlet imidazol-2-ylidene with protic reagents, and in the course of these studies we identified an extremely short [C—H···O] hydrogen bond and the first [C···H—N] hydrogen bond.[10] We recognize that treatment of a carbene with a proton produces a carbocation derivative, and in principle addition of a neutral hydrogen atom instead of a proton should produce the analogous tricoordinate radical. However, reactions of imidazol-2-ylidenes with hydrogen atoms have not been reported, and this is perhaps understandable due to the difficult nature of such experiments. We initially studied the result of adding the hydrogen isotope muonium (vide infra) to 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene.[11] A single type of radical was detected, but due to the lack of symmetry in the molecule and poor signal-to-noise of the spectrum it was not possible to assign unambiguously the structure of the radical.

Even more surprising than the lack of data on hydrogen atom addition is the dearth of reports on the reactivity of stable carbenes with any free radical species.[12] However, a radical

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(12) The transfer of a hydrogen atom to a dinitroxide carbene was recently reported as part of a much larger study. The nitronyl nitroxide carbene abstracted a H atom from the solvent, and this was seen as indicative of partial radical character at the radical center, unlike the imidazole-2-ylidenes: Weiss, R.; Kraut, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 311.

Scheme 1. Possible Reactions of Stable Imidazole-type Carbenes with the Hydrogen Atom (and Its Isotope Muonium, Mu)

1: R = isopropyl   R' = methyl
2: R = mesityl   R' = H
3: R = methyl   R' = methyl
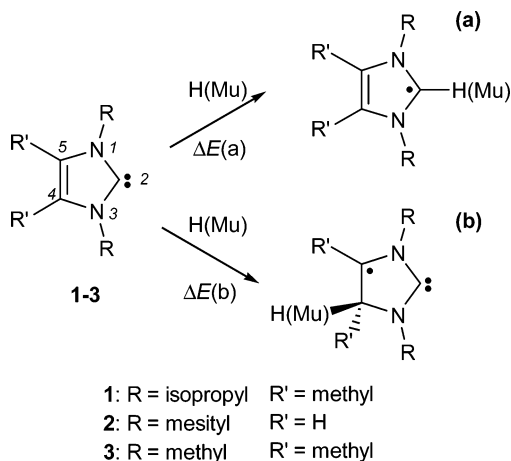
anion (which can formally be viewed as the product of the reaction between a carbene and the simplest radical, the electron) has been generated electrochemically from a stable singlet carbene and studied by electron spin resonance (ESR), cyclic voltammetry, and theoretical methods[13,14] The magnitude of the proton coupling in the ESR spectrum of the radical anion derived from 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene implies that about two-thirds of the unpaired spin density is delocalized onto one of the substituent phenyl rings. There is also a small nitrogen coupling. Thus, at most, one-fourth of the unpaired electron density remains at the nominal radical center (the original carbene). In a formal sense, the H atom adduct may be viewed as the protonated radical anion, but this cannot be used to predict the preferred site of radical attack on the carbene, which depends on both the reactivity of the various sites and the geometry of the transition state.

For imidazol-2-ylidenes, it is not obvious how the hydrogen atom will react, particularly given recent theoretical evidence for π-electron delocalization around the ring.[15,16] Thus, the addition of a hydrogen atom to carbenes **1** and **2** could occur at (a) the carbeneic carbon to produce **1a** and **2a** or (b) the alkeneic carbon to produce **1b** and **2b** (Scheme 1). The hydrogen atom might also add to the mesityl (2,4,6-trimethylphenyl) rings of carbene **2**, to give one or more of the cyclohexadienyl radicals shown in Scheme 2.

The hydrogen atom is an excellent probe of reactivity because its small size minimizes steric interference and its simple structure avoids additional electronic effects. However, H is not a common reagent for solution studies, largely because of complications inherent in its generation. Most commonly, the H atoms are produced by photolysis or radiolysis of water or other protic solvents, but this usually results in other radical species. In addition, such solvents are not compatible with imidazol-2-ylidenes. Rather than use H atoms to generate the radicals and ESR to observe them, we have used a light isotope of hydrogen called muonium (Mu = $[\mu^+, e^-]$) and detected the radicals by techniques collectively known as muon spin rotation

and resonance (μSR).[17-20] Mu is a one-electron atom whose nucleus is the positive muon; it is chemically identical to H, but has one-ninth the mass. Its usefulness as a probe of hydrogen atom chemistry is well documented.[21-23]

There are several advantages to using μSR rather than ESR: (1) Mu is formed by irradiation of a sample with positive muons, so there is no need for complicated mixtures necessary to produce H, and there are no observable side reactions. (2) Mu can be produced with the muon spins almost 100% polarized, whereas the polarization in ESR experiments is normally limited by the Boltzmann population difference (less than 0.1% polarization for X-band ESR and room temperature). (3) The muon is radioactive with a lifetime of 2.2 μs, and the positron produced in the decay is emitted preferentially along the direction of the muon spin, which provides a convenient method of monitoring the evolution of the muon spin. Muon hyperfine coupling constants (A_μ) can be measured by transverse field muon spin rotation (TF-μSR), and the hyperfine coupling constants (hfc's) for other magnetic nuclei in the radical can be determined by muon avoided level-crossing resonance (μLCR). (4) The radicals detected by μSR are formed within 10 ns of implantation of the muon, which allows for the determination of the products formed solely by Mu addition and not by rearrangements or any other process. (5) The relative signs of the hfc's can be determined by μLCR, something which is rarely possible by ESR.

Here, we present theoretical calculations on the possible radicals formed by hydrogen atom addition to the stable carbenes **1** and **2**. We have focused our efforts on the imidazol-2-ylidenes (**1**,**2**) because of their high symmetry and the availability of isotopically labeled samples. The results of the calculations were confirmed by the detection of muoniated radicals formed by addition of muonium to the carbenes.

2. Computational Methods

Theoretical calculations on the parent carbenes and the radicals resulting from Mu addition to the imidazole ring were carried out using the Gaussian 98 suite of programs.[24] The calculation of the hfc's of open shell systems has been a considerable challenge, and it is only recently that density functional theory (DFT) calculations have been successful in reproducing the geometry and magnetic properties of free radicals at moderate computational cost, relative to other appropriate methods.[25,26] Accurate calculation of the hfc's also requires inclusion of solvent effects and averaging over large amplitude modes.[27]

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Scheme 2. Structures of the Possible Hydrogen Atom Adducts of the Mesityl Ring of Carbene **2**[a]
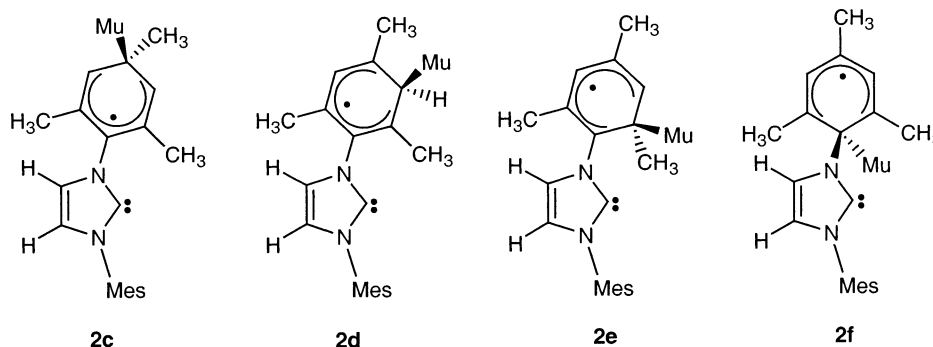
[a] For clarity, the added atom is denoted by the Mu isotope.

Geometry optimizations and calculation of hyperfine coupling constants (hfc's) were performed using the B3LYP functional,[27] which has been well validated for calculations on free radicals.[28] The geometries of molecules **1**, **1a**, and **1b** were optimized using the 6-311G** basis set, and the magnetic properties of **1a** and **1b** were found using the EPR-III basis set. Molecules **2**, **2a**, and **2b** were optimized using the 6-31G basis set, and the hyperfine coupling constants were calculated using the EPR-II basis set. The EPR-II and EPR-III basis sets have been specifically optimized for computing isotropic hfc's.[28] Solvent effects were included in the single-point calculations by using the polarized continuum model (PCM) with the solvent parameters for tetrahydrofuran ($\epsilon = 7.58$).[29]

Distinguished coordinate paths[30] for addition of Mu to the carbeneic carbon and the alkeneic carbon of **1** were obtained by optimizing the geometry for fixed distances between Mu and the site of addition. Although it has been shown previously that DFT methods have difficulty locating and estimating the transition state,[31] they are sufficient to obtain qualitative information about competing reaction paths. (Theoretical methods such as G2 or QCISD, which have been shown to produce accurate values for the reaction of H with C_2H_4,[32] proved to be too computationally expensive for the molecules in this study.) The computed values of $\langle S^2 \rangle$ ranged from 0.75 to 0.77 along the distinguished coordinate path, indicating negligible spin contamination.

The molecular geometry for each H adduct radical is also valid for the muoniated species, within the Born–Oppenheimer approximation. Similarly, electron distributions should be identical for isotopomers. However, zero-point vibrational effects are larger for normal modes involving Mu, and this can result in considerable isotope effects on vibrationally averaged hyperfine interactions. In particular, such effects have been investigated for cyclohexadienyl[33] and HC_{60}.[34] A complete treatment of vibrational averaging effects for the radicals in this study would be computationally expensive, so we have treated the vibrational motion empirically. The C–Mu bond has been estimated to be 4.9% longer than the corresponding C–H bond due to this vibrational averaging.[35] Accordingly, the C–Mu bond was artificially lengthened by this amount for the calculation of the hfc's.

For radicals **1a** and **2a**, it is also important to include the averaging due to the out-of-plane vibrational mode. The effect of this motion has been investigated extensively for planar radicals such as the methyl radical,[36] as well as for nonplanar radicals such as the fluoromethyl,[36]

cyclopropyl,[37] and oxiranyl radicals.[38] For radicals with a nonplanar radical center, the effect of vibrational averaging is to change the hfc's of the α-proton (or muon) and the α-carbon to values that correspond to a single-point calculation for a structure with a reduced out-of-plane angle as compared to the minimum energy geometry.[36] To simulate this effect, the geometries of **1a** and **2a** were optimized for several out-of-plane angles ϕ[39] between 25° and 45°, and the angular variation of the hfc's was modeled with a cubic function. The vibrationally averaged radical structure was then found empirically by adjusting ϕ to give the best agreement between the computed and experimental hfc's.

3. Computational Results

3.1. Geometric Structures. We have performed DFT calculations only for the radical products of H or Mu addition to the imidazole ring. Radicals **2c–f** are substituted cyclohexadienyls, a class of radicals that has been extensively studied by μSR.[21] The muon hfc's for the 1-muono-2,4,6-trimethylcyclohexadienyl and 1-muono-1,3,5-trimethylcyclohexadienyl radicals are 453.1 and 483.9 MHz,[40] respectively, and the muon hfc's for **2c–f** are expected to be of similar magnitude.

To verify the reliability of our chosen computational methods, the structures of carbenes **1** and **2** were calculated and compared to values obtained by X-ray crystallography. The geometrical values calculated for the imidazole ring of **1** are in good agreement with those in crystalline 1,3,4,5-tetramethylimidazol-2-ylidene (**3**).[41] Similarly, the calculated and experimental parameters for the imidazole ring of **2** are in good agreement.[41] We note that the DFT calculations tend to overestimate the bond lengths by 0.01–0.02 Å, on average. Given the good agreement between theory and experiment, we have concluded that the chosen computational methods are sufficient to generate accurate geometries and have used these methods to determine the minimum energy geometries of radicals **1a**, **1b**, **2a**, and **2b**.

For radicals **1a** and **2a**, the C2–N1(N3) bonds and the N1–C2–N3 angle were found to be larger than those in the parent carbene. This increase in bond lengths and angles at the radical center has been noted for the cyclopropyl and oxiranyl radicals. As is evident in Figure 1 for the case of **1a**, the radical center

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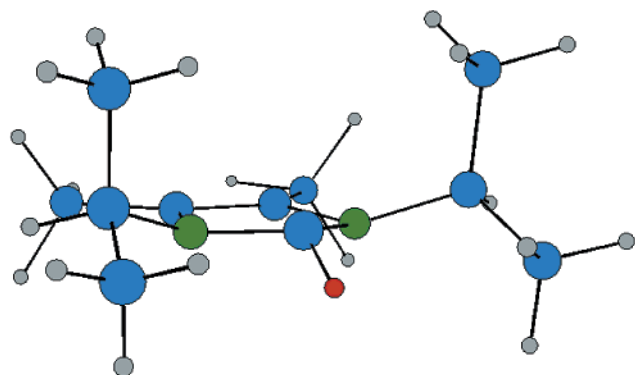
Figure 1. Optimized structure of **1a** showing the nonplanar radical center at C2. The H(Mu) adduct is colored red; the other atoms are H, gray; N, green; and C, blue.

Table 1. Selected Bond Lengths (Å) and Angles (deg) Calculated for Carbenes **1** and **2**, Their Radicals Derived from the Addition of H(Mu), and Experimental X-ray Crystallographic Data for **3**

	1a[a]	1b[a]	1[a]	3[b]	2a[c]	2b[c]	2[c]	2[b]
r(N1−C2)	1.430	1.386	1.377	1.363(1)	1.431	1.397	1.392	1.365(4)
r(N3−C2)	1.430	1.358	1.377	1.363(1)	1.431	1.367	1.392	1.371(4)
r(N1−C5)	1.418	1.414	1.415	1.394(1)	1.409	1.411	1.411	1.381(4)
r(N3−C4)	1.418	1.496	1.415	1.394(1)	1.409	1.504	1.411	1.378(4)
r(C4−C5)	1.363	1.505	1.367	1.352(2)	1.356	1.491	1.357	1.331(5)
θ(N1−C2−N3)	104.6	104.8	102.4	101.5(1)	104.0	103.6	101.2	101.4(2)
θ(C5−N1−C2)	108.6	113.8	112.8	113.47(8)	109.3	114.2	113.1	112.8(3)
θ(C2−N3−C4)	108.6	114.6	112.8	113.47(8)	109.3	115.0	113.1	112.8(3)
θ(N1−C5−C4)	108.5	106.2	106.0	105.78(5)	108.6	107.0	106.3	106.5(3)
θ(N3−C4−C5)	108.5	100.3	106.0	105.78(5)	108.6	100.2	106.3	106.5(3)

[a] Calculated values (B3LYP/6-311G**). [b] X-ray data from ref 41. [c] Calculated values (B3LYP/6-31G).

is pyramidal (out-of-plane angle 40.1° for **1a**; 41.4° for **2a**). To our knowledge, this is the first reported addition to a stable carbene that does not produce a planar tricoordinate carbon. In **1a**, the imidazole ring is no longer planar, being puckered at N1 and N3 (out-of-plane angle 23°) with the H(Mu) adduct on the side opposite to the isopropyl groups. The ring is close to planar in the case of **2a**, although this depends on the dihedral angle between the mesityl rings and the imidazole ring. In the fully optimized structure, the dihedral angle is 62°, and the ring distortion is less than 1°. If the mesityl rings are forced to be perpendicular to the imidazole ring, the out-of-plane deviation increases to 3.4°.

The structures of **1b** and **2b** were found to be considerably different from those of the parent carbenes. The C4−C5 and C4−N3 bonds are significantly longer, while the N3−C4−C5 angle is smaller, due to the change in bonding at the site of addition. The differences in the geometrical parameters extend a considerable distance from the site of addition. The N1−C2−N3 angle is also slightly larger in the radicals. The geometrical parameters for the carbenes **1** and **2** and the radicals **1a**, **1b**, **2a**, and **2b** are reported in Table 1.

3.2. Energetics. To validate our thermochemical calculations, we have investigated the reaction of H with triplet methylene. Our calculations (UB3LYP/6-311G**) show that the addition reaction is exothermic (−492.1 kJ mol⁻¹), in good agreement with literature values.[42] Similar calculations were performed for the addition of a hydrogen atom to either the carbeneic carbon or the double bond of **1**. In both cases, the reaction is exothermic (−182.7 and −122.3 kJ mol⁻¹, respectively), with radical **1a**

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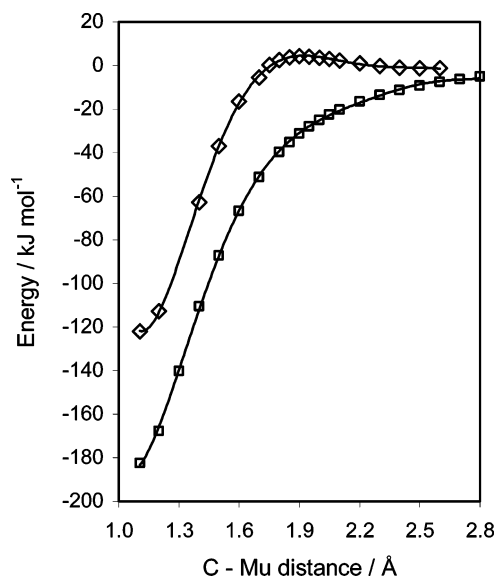
Figure 2. Distinguished coordinate reaction paths for H addition to the carbeneic (□) and alkeneic carbons (◇) of **1**.

(addition to the carbeneic site) favored. The same result was found for carbene **2**: the carbeneic site is favored over the double bond (the energies of reaction are −213.8 and −134.6 kJ mol⁻¹, respectively).

The distinguished coordinate paths for addition at the two sites are shown in Figure 2. There is a discernible transition state for addition to the double bond, with a C−Mu distance of ~1.92 Å and an activation barrier of 4.5 kJ mol⁻¹. This value is similar to the barrier for the H + C₂H₄ reaction.[32] There is no clear transition state for reaction at the carbene site (C2). While it is known that DFT methods have difficulty in locating transition states, the fact that one was located for addition to the double bond at C5 suggests that the lack of a transition state is not due to problems with the theoretical model but actually reflects the behavior of the system. The nonexistent activation barrier for reaction at the carbeneic carbon suggests that this should be the dominant pathway. We therefore expect that **1a** will be the major radical product for H(Mu) addition to **1**, and **2a** in the case of carbene **2**.

3.3. Hyperfine Coupling Constants. The results of calculations on **1a** indicate that the majority of the unpaired spin density (74.9%) is localized on the α-carbon (C2), with 9.3% on each of the adjacent nitrogens and a small amount of negative spin density (−1.2%) on carbons 4 and 5. In **1b**, most of the unpaired spin density is localized on C4 (83.3%), with a small amount of delocalization into the N1−C2−N3 fragment (7.3%, 7.8%, and 6.3%, respectively).

Single-point calculations performed on the minimum energy geometry of **2a** show a small (4.4%) but significant amount of unpaired spin density delocalized onto the mesityl rings. This occurs because the optimized structure of **2a** has the mesityl rings at an angle of 61.9° to the N1−C2−N3 plane, resulting in a small overlap of the π-system of the mesityl ring with the imidazole ring. Torsional oscillations of the mesityl rings at room temperature should make this overlap intermittent and greatly reduce the spin delocalization, resulting in a higher measured hfc than that calculated for a fixed geometry. X-ray crystallography of **2** shows that the average position of the mesityl rings is perpendicular to the imidazole rings, and it would be reasonable to expect the same for **2a**. We have

Table 2. Dependence of Selected Hyperfine Constants in **1a** and **2a** on the Out-of-Plane Angle (ϕ)

	1a			2a		
ϕ	A_μ/MHz	A_C/MHz	A_N/MHz	A_μ/MHz	A_C/MHz	A_N/MHz
25°	83.54	81.76	9.69	69.22	142.42	9.62
30°	161.74	99.05	8.76	157.00	166.98	10.20
35°	240.50	117.69	8.18	244.53	190.96	10.55
40°	318.70	136.00	7.97	330.36	215.59	10.59
45°	393.85	152.28	7.97	411.87	233.83	10.63

Table 3. Calculated Hyperfine Constants[a] (MHz) and Energies of Reaction[b] (kJ mol^{-1}) for the Possible Radicals Formed by Mu Addition to Carbene **1**, and the Hyperfine Constants Determined Experimentally

	1a[c,d]	1a[c,e]	1b[c]	expt.
$A_\mu{}^f$	278.8	246.4[g]	401.0	246.4
A_C(C2)	+136.0	+119.0	7.4	+139.6
A_N(N1)	+8.3	+9.2	+0.5	+13.7
A_N(N3)	$=A_N$(N1)	$=A_N$(N1)	+4.0	
A_p(CH₃C5)			+53.1[h]	(+82.9)[i]
ΔE	−182.7		−122.3	

[a] Proton hfc's for isopropyl substituents are not reported. [b] $\Delta E = E(\text{radical}) - [E(\text{H}) + E(\text{carbene})]$. [c] B3LYP/6-311G**//B3LYP/EPR-III. [d] Minimum energy structure. [e] $\phi = 35.3°$ to simulate vibrational averaging. [f] $A_\mu = A_p(\gamma_\mu/\gamma_p)$. [g] Optimized to equal the experimental value. [h] Average proton hfc in methyl group. [i] Rejected alternative assignment.

Table 4. Calculated Hyperfine Constants[a] (MHz) and Energies of Reaction[b] (kJ mol^{-1}) for the Possible Radicals Formed by Mu Addition to Carbene **2**, and the Hyperfine Constants Determined Experimentally

	2a[c,d]	2a[c,e]	2b[c]	expt.
$A_\mu{}^f$	340.0	286.7[g]	401.0	286.7
A_C(C2)	+220.0	+202.9	+5.0	
A_N(N1)	+10.6	+10.6	+0.9	+13.0
A_N(N3)	$=A_N$(N1)	$=A_N$(N1)	+3.6	
A_p(HC4)			+138.3	(+94.5)[h]
A_p(HC5)			−43.6	
ΔE	−213.8		−134.6	

[a] Proton hfc's for mesityl substituents are not reported. [b] $\Delta E = E(\text{radical}) - [E(\text{H}) + E(\text{carbene})]$. [c] B3LYP/6-31G// B3LYP/EPR-II. [d] Minimum energy structure. [e] $\phi = 37.2°$ to simulate vibrational averaging. [f] $A_\mu = A_p(\gamma_\mu/\gamma_p)$. [g] Optimized to equal the experimental value. [h] Rejected alternative assignment.

modeled this by reoptimizing the structure of **2a** with the mesityl rings fixed perpendicular to the N1−C2−N3 plane. This resulted in negligible spin density on the mesityl rings and a larger muon hfc.

The hfc's of the muon and the α-carbon (C2) in **1a** and **2a** were found to depend very strongly on the out-of-plane angle ϕ,[39] whereas the ^{14}N hfc is not greatly affected (Table 2). Thus, accurate prediction of hfc's at a given temperature would require calculation of the effect of vibrational averaging. Because a full vibrational analysis is beyond our present computational capability, we have resorted to an empirical procedure to simulate the effect of vibrational averaging: The value of ϕ was adjusted for each radical so that the calculated muon hfc's agree with those determined by experiment (see below). Tables 3 and 4 list the calculated hfc's for the energy minimum and vibrationally averaged radical structures.

4. μSR Experiments

The carbenes 1,3-bis(isopropyl)-4,5-dimethylimidazol-2-ylidene[43] (**1**) and 1,3-dimesityl-imidazol-2-ylidene[41] (**2**) were prepared following the literature procedures. A ^{13}C-labeled

(43) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.
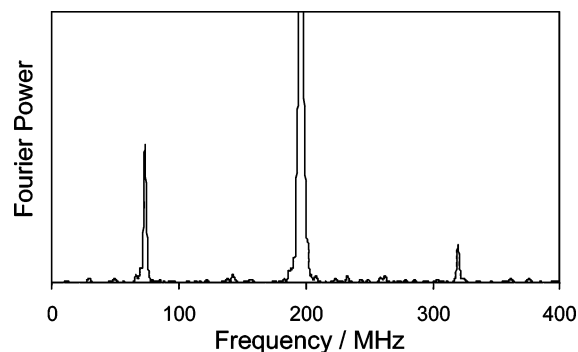
Figure 3. Transverse field μSR spectrum at 14.4 kG from **1** in THF at 298 K. The pair of peaks at ca. 73 and 320 MHz is due to a muoniated radical.

sample of **1** (40% enriched at C2) was prepared starting from ^{13}CS$_2$. The samples used for μSR consisted of a 1 M solution of **1** in THF and a 0.5 M solution of **2** in THF. Prior to muon irradiation, the solutions were subjected to several freeze−pump−thaw cycles to remove any dissolved oxygen and then sealed in nonmagnetic stainless steel cells. The cells are designed such that the muon beam (nominal momentum 28 MeV/c) passes with negligible loss through the 0.025 mm thick stainless steel foil window but stops completely in the sample. The temperature of the sample was maintained by circulating fluid from a constant-temperature bath through the sample mount, which was surrounded by vacuum. The experiments were performed at the M20 beam line of the TRIUMF cyclotron facility in Vancouver, B.C., using the HELIOS μSR spectrometer. Details of the apparatus and the muon spectroscopic techniques are available in greater detail elsewhere.[44,45]

Muon hyperfine coupling constants were determined by transverse field muon spin rotation (TF-μSR). An example is shown in Figure 3, which shows the effect of muon irradiation of **1** at 298 K. Only one type of radical was found, as is evident from the characteristic pair of frequencies above and below the muon Larmor frequency. The difference between these two radical precession frequencies is a direct measure of the muon hfc:

$$A_\mu = \nu_{R1} - \nu_{R2} \qquad (1)$$

The muon hfc for the radical produced from **1** was found to be $A_\mu = 246.43 \pm 0.02$ MHz. A similar experiment on carbene **2** yielded a single radical with muon hfc $A_\mu = 286.69 \pm 0.07$ MHz at 298 K.

Hyperfine coupling constants for other nuclei in the radicals were determined by muon avoided level-crossing resonance. In this technique, each magnetic nucleus (characterized by a hyperfine constant A_k) gives rise to a resonance at a value of the magnetic field determined primarily by the difference between A_μ and A_k:

$$B_{\text{res}} = \frac{1}{2}\left[\frac{A_\mu - A_k}{\gamma_\mu - \gamma_k} - \frac{A_\mu{}^2 - 2MA_k{}^2}{\gamma_e(A_\mu - A_k)}\right] \qquad (2)$$

where M is the z-component of the total spin of the unpaired

(44) Percival, P. W.; Brodovitch, J.-C.; Leung, S.-K.; Yu, D.; Kiefl, R. F.; Luke, G. M.; Venkateswaran, K.; Cox, S. F. J. *Chem. Phys.* **1988**, *127*, 137.
(45) Percival, P. W.; Addison-Jones, B.; Brodovitch, J.-C.; Ghandi, K.; Schüth, J. *Can. J. Chem.* **1999**, *77*, 326.
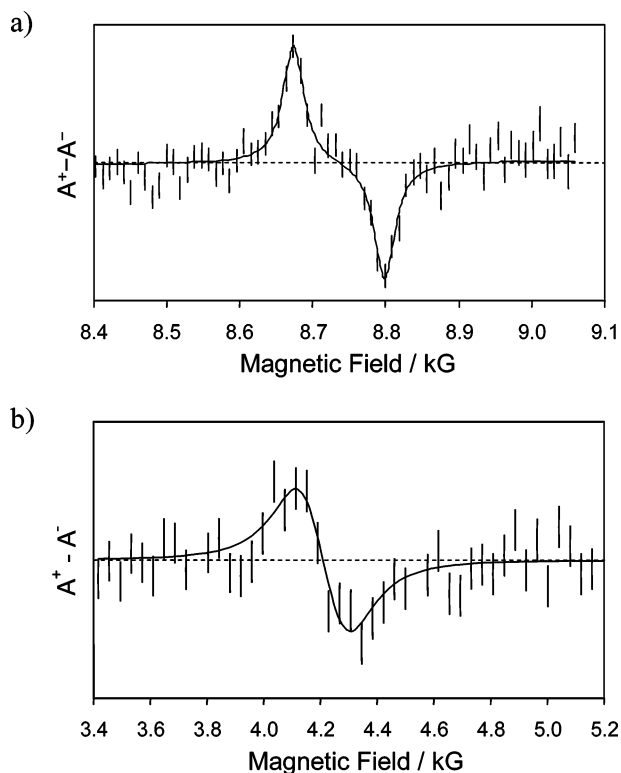
a)

b)

Figure 4. μLCR spectra from **1** in THF at 298 K displaying (a) the ^{14}N resonance and (b) the ^{13}C resonance in a 40% enriched sample.

electron, the muon, and the nucleus involved in the level crossing, and γ_e, γ_μ, and γ_k refer to the magnetogyric ratios of the electron, muon, and other nucleus, respectively.

A single resonance was found in the μLCR spectrum obtained from **1** (Figure 4a). The field position, 8736.44 ± 1.24 G, corresponds to either ^{14}N nuclei with $A_N = +13.73 \pm 0.04$ MHz or protons with $A_p = +82.88 \pm 0.03$ MHz. An additional resonance was found at 4359.94 ± 8.54 G for the ^{13}C-labeled sample of **1** (Figure 4b). This is undoubtedly due to the ^{13}C nucleus (C2) and corresponds to $A_C = +139.64 \pm 0.21$ MHz.

A single, weak resonance was found in the μLCR spectrum obtained by muon irradiation of carbene **2** at 298 K. In principle, the resonance field position, 10276.62 ± 3.14 G, could be due to either ^{14}N nuclei with $A_N = +13.01 \pm 0.10$ MHz or protons with $A_p = +94.53 \pm 0.08$ MHz.

5. Discussion

By comparing the experimentally determined hfc's to the calculated values for **1a** and **1b** (Table 3) and **2a** and **2b** (Table 4), we could see that the radical spectra should be assigned to structures **1a** and **2a**. Vibrational averaging can easily account for the difference between the muon hfc's and the calculated values for the energy minimum structures. The experimental and predicted values of the nitrogen hfc's are in reasonable agreement, whereas the alternative assignment of the relevant μLCR signals gives proton hfc's which are completely unacceptable. Finally, the ^{13}C resonance observed for **1** can only

arise from **1a**. Given the general agreement between measured and predicted hfc's, as well as the relative energies of the possible radicals, we conclude that Mu adds exclusively to the carbeneic carbon.

If the calculated muon hfc's are optimized to match the measured values by adjusting the configuration at the radical center, the out-of-plane angles ϕ found for structures **1a** and **2a** are 35.3° and 37.2°, respectively. These values are 12% and 10% less than for the energy minimum structures, consistent with expectations based on other radicals[36-38] and the effects of temperature and the light mass of the muon.

The calculations reported in Tables 3 and 4 underestimate the nitrogen hfc's. The prediction for **2a** is in better agreement with experiment than **1a**, and this is likely a consequence of the restrictions imposed on the mesityl rings of **2a** in our calculations. Thus, when the mesityl ring is fixed perpendicular to the imidazole ring, the configuration of the nitrogen atoms is almost planar (the angle between the N1−mesityl bond and the C2−N1−C5 plane is only 0.8°, as compared to 3.4° in the minimum energy geometry). The planar geometry promotes π-electron delocalization and the consequent increase in the nitrogen hfc. In contrast, the nitrogen geometry in the minimum energy configuration of **1a** is very pyramidal (23°). We therefore speculate that vibrational averaging results in a more planar configuration, leading to the increased nitrogen hfc.

6. Summary

The geometries, spin density distributions, and hfc's for the possible radicals resulting from the addition of a hydrogen isotope to a stable singlet carbene have been studied by density functional calculations. The calculated hfc's were compared to those obtained by TF-μSR/μLCR experiments. The results show that H (or Mu) adds exclusively to the carbeneic carbon rather than the double bond in imidazol-2-ylidenes. The resulting radicals have nonplanar radical centers with the majority of the unpaired spin density localized on the α-carbon. Vibrational averaging and solvent effects must be included to calculate accurate hfc's. Future experiments on these molecules are aimed at understanding the effect of isotopic substitution on the vibrational motion and will be accomplished by measuring the temperature dependence of the hfc's and theoretical modeling of the large amplitude vibrations.

Supporting Information Available: Additional spectra and the optimized Cartesian coordinates of all molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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