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# Spectroscopic Distinction of Different Carbon Bases: An Insight from Theory

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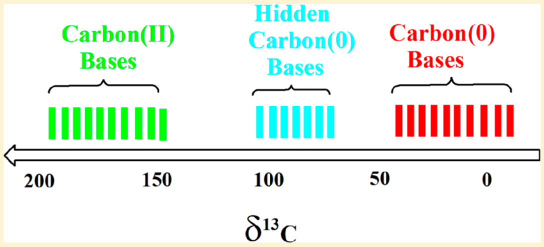
*Supporting Information*

**ABSTRACT:** Spectroscopic differentiation based on the $^{13}C$ NMR chemical shift of the parent and protonated derivatives of carbon(II) and carbon(0) bases has been proposed. The $^{13}C$ chemical shift of the central carbon atom of carbenes in their parent and protonated forms will experience more downfield shift, whereas the central carbon atom of carbones will experience a lesser downfield shift; such shifts for compounds that possess "hidden" carbon(0) characteristics will lie between these two extremes. The $^{13}C$ chemical shifts of the protonated derivatives are solely dependent on the out-of-plane $p_\pi$ occupancies of the central carbon atom. This difference arises due to their unique difference in bonding and may provide an easier distinction between these two classes of compounds.



Carbon is usually known to employ all of the valence electrons in bonding. A rather unusual bonding situation where only two of its valence electrons are involved, such as in carbenes, $CR_2$, is isolated and experimentally well-characterized.[1−9] This bonding situation in carbenes results in retention of the remaining two electrons in the same orbital to form a lone pair (singlet carbenes); they may occupy different orbitals with opposite spins to form excited singlet states (open-shell singlet), or they may occupy different orbitals with the same spin (triplet carbenes). Although the parent carbene $CH_2$ has a triplet ground state,[10,11] stable singlet carbenes containing a lone pair of electrons are also known.[1−9] On the other hand, some experimentally known[12−22] carbon compounds are also expected[23] to reveal another unique bonding situation. A recent electronic structure study[23] has revealed that it is also possible for the central carbon atom of such compounds[12−22] to use none of its valence electrons, thereby forming stable divalent carbon(0) compounds, carbones ($CL_2$). This bonding situation, which is described as donor−acceptor-type, $L \rightarrow C \leftarrow L$,[23] results in the retention of two lone pairs at the central carbon, unlike carbene, which contains a single lone pair. It is this difference in the nature of bonding that is responsible for the different reactivity shown by carbenes and carbones. For example, due to the presence of two lone pairs in carbones, their first and, more precisely, second proton affinities are quite high compared to those of carbenes, which have only one lone pair. This has been used as a decisive indicator to distinguish carbenes from carbones.[24a,b] A similar distinction for carbon can also be made for the heavier group-14 elements,[24c,d] which were supported by the recent synthesis of first stable silylones[24e,f] and germylones.[24g−i] Other reactivity parameters, such as complexation with one and two molecules of AuCl to distinguish carbenes from carbones, have also been proposed.[25] We have recently shown that both carbenes and carbones may show very high values of second proton affinity as well as bond dissociation energies for *gem*-dimetalation.[26] Thus, their reactivity becomes blurred when subjected to electrophilic attack. However, unlike carbones, carbenes are ambiphilic in nature owing to the presence of a $\sigma$ symmetric lone pair and a vacant p orbital concentrated on the central carbon atom ($C_c$). Thus, they may show different reactivity when subjected to nucleophilic attack. This reactivity difference had been proposed as another criterion to distinguish these two classes of compounds.[26]

Herein, we propose a spectroscopic distinction between these two classes of compounds (Scheme 1) based on $^{13}C$ NMR chemical shielding of the parent compounds and their protonated derivatives. Recently, Bertrand and co-workers have experimentally shown that $^{31}P$ chemical shifts of the carbene−phosphinidene adducts are very good indicators of the $\pi$ acidity of carbenes,[27] which has been substantiated theoretically by us.[28] Thus, it appears that the spectroscopic parameters may not only provide insight toward understanding the ligating abilities but also be useful in distinguishing different carbon bases. Moreover, these spectroscopic parameters are very easy to accumulate experimentally because many carbenes,[1−9] carbones,[12−22] and their protonated derivatives are already known.[1−9,12−22,27]

Calculations[29] predict that values of $^{13}C$ shifts of the parent and protonated derivatives of carbenes and carbones indeed provide a quantitative difference between these two classes of compounds. Due to the presence of an extra lone pair, there is a larger concentration of electron density at $C_c$ of carbone than at

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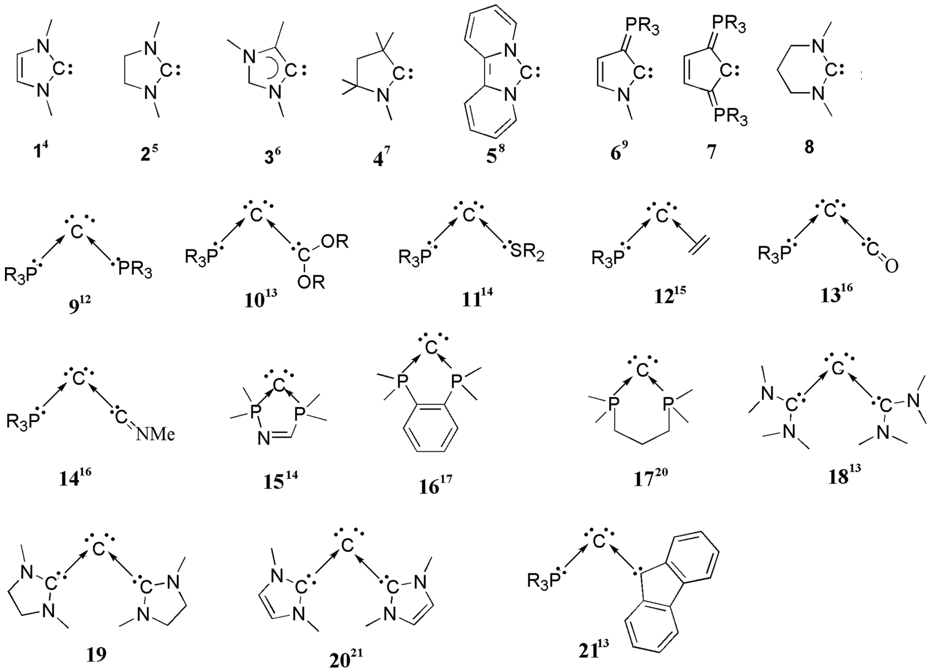
Scheme 1. Selected Divalent Carbon(II)/Carbon(0) Compounds Considered for This Study



carbenes. This, in turn, should result in a more downfield shift of the $^{13}C$ NMR signal for carbenes. Table 1 collects the $^{13}C$ NMR shifts of the parent molecules. The calculated values of $^{13}C$ NMR shifts are in reasonable agreement with the available experimental data.[7,8,13,21,34]

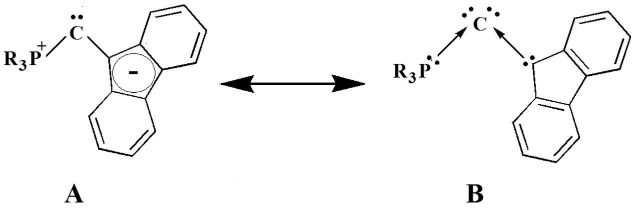
It is evident from Table 1 that the $^{13}C$ NMR shifts of carbenes **1**−**8** are more downfield compared to carbones **9**−**20**. However, with an increase in $\pi$ donation ability of the carbenes as in **5**−**7**, the $^{13}C$ NMR shifts move to slightly higher field. This might be due to the presence of more electron density at $C_c$ of **5**−**7**. Previous studies[26,35] suggest that these compounds may be considered to be "hidden" carbon(0) compounds, due to their ability for both $\sigma$ and $\pi$ donation. Surprisingly, the $^{13}C$ shift of **4** is significantly downfield, which may be traced not only to the presence of *only* one N atom closer to the carbenic center but also to the absence of any electronic delocalization from other ring atoms, thereby rendering the carbenic center electron-deficient. Although compound **21** may be thought to show the properties of carbon(0) compounds, as revealed by the following resonance forms,[13] its experimental as well as calculated $^{13}C$ NMR shift[13] clearly establishes its carbene characteristics (resonance form **A**, Scheme 2). Thus, the calculated values of the $^{13}C$ NMR shift of carbenes are found to be more downfield compared to those for carbones and provide us a unique distinction between these two classes of compounds.

Table 1. $^{13}C$ Chemical Shifts of Carbenes and Carbones Calculated at the PBE1PBE/6-311++G*//PBE1PBE/6-31+G* Level of Theory[a]

| molecule | $\delta^{13}C$ | molecule | $\delta^{13}C$ |
|---|---|---|---|
| **1** | 214.9<br>*215.2*[34] | **12** | 13.3 |
| **2** | 236.1<br>*239.8*[34] | **13** | −3.4 |
| **3** | 196.4 | **14** | 29.8 |
| **4** | 314.5<br>*304.2*[7] | **15** | 20.5 |
| **5** | 200.3<br>*196.4*[8] | **16** | 21.9 |
| **6** | 218.4 | **17** | 14.5 |
| **7** | 208.9 | **18** | 163.0<br>*136.0*[21] |
| **8** | 231.9<br>*242.7*[34] | **19** | 124.4 |
| **9** | 18.1 | **20** | 107.3<br>*110.2*[21] |
| **10** | 72.7 | **21** | 197.4<br>*198.8*[13] |
| **11** | 40.1 | | |

[a] Experimental values are shown in italics. Values of $^{13}C$ shifts are calculated using the relationship $\delta$ = (intercept − $\sigma$)/(−slope), where intercept and slope were obtained from the plot of calculated isotropic value ($\sigma$) versus the experimental chemical shift. For details, see Supporting Information.

Scheme 2. Resonating Forms of 21 Showing the Carbene (Form A) and Carbone (Form B) Characteristics



We then turned our attention to investigate whether or not such a trend will be followed in their protonated derivatives. In general, carbene has a single lone pair of electrons at $C_c$, which after donation to a proton (Scheme 3) becomes electron-deficient. As a result, the $^{13}C$ NMR shift of $C_c$ in protonated carbenes will have a downfield shift. However, $C_c$ of carbones will not have such a downfield shift in their protonated form as

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**Scheme 3. Bonding Situation in the Protonated Derivatives of Carbenes and Carbones**

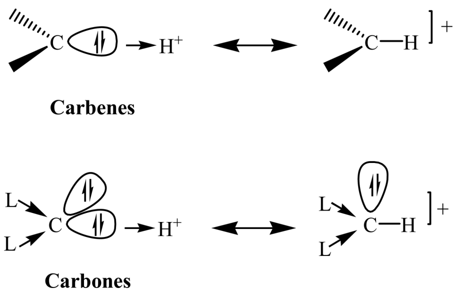

**Table 2. $^{13}C$ Chemical Shifts of the Protonated Derivatives of Carbenes and Carbones Calculated at the PBE1PBE/6-311++G*//PBE1PBE/6-31+G* Level of Theory[a]**

| molecule | $\delta^{13}C$ | occ ($p_\pi$) | molecule | $\delta^{13}C$ | occ ($p_\pi$) |
|---|---|---|---|---|---|
| **1** | 133.8<br>*137.2*[34] | 0.94 | **12** | 17.7 | 1.22 |
| **2** | 153.3<br>*156.7*[34] | 0.80 | **13** | 20.5 | 1.43 |
| **3** | 196.3 | 1.05 | **14** | 33.7 | 1.34 |
| **4** | 186.5<br>*192.2*[34] | 0.70 | **15** | 9.2 | 1.67 |
| **5** | 111.4<br>*116.0*[8] | 1.11 | **16** | 7.6 | 1.66 |
| **6** | 127.6 | 1.02 | **17** | 8.1 | 1.67 |
| **7** | 117.2 | 1.06 | **18** | 80.0 | 1.29 |
| **8** | 149.0<br>*154.4*[34] | 0.82 | **19** | 60.2 | 1.34 |
| **9** | 11.4 | 1.70 | **20** | 53.7 | 1.37 |
| **10** | 53.0 | 1.41 | **21** | 90.8 | 1.20 |
| **11** | 21.7 | 1.68 | | | |

[a] Out-of-plane $p_\pi$ occupancy [Occ($p_\pi$)] at the central carbon atom is also tabulated. Experimental values are shown in italics. Values of $^{13}C$ are calculated using the relationship $\delta = (\text{intercept} - \sigma)/(-\text{slope})$, where intercept and slope were obtained from the plot of calculated isotropic value ($\sigma$) versus the experimental chemical shift. For details, see Supporting Information.

there will be another lone pair still available even after protonation. Table 2 collects the $^{13}C$ chemical shifts of the protonated derivatives of carbenes and carbones and the occupancy of the out-of-plane $p_\pi$ orbital of $C_c$, respectively. The calculated NMR chemical shifts are in very good agreement with the experimental values.[8,34] It is evident from Table 2 that the carbenic centers in their protonated form have much fewer out-of-plane $p_\pi$ occupancies. As a result, the $^{13}C$ chemical shifts of $C_c$ will experience a downfield shift. On the other hand, $C_c$ of protonated carbones has a higher out-of-plane $p_\pi$ occupancy, and consequently, they will not experience a downfield shift larger than that in carbenes. For example, the ranges of $^{13}C$ chemical shifts in the protonated derivatives of **1**–**4** and **8**, which are clearly divalent carbon(II) species, have much greater positive values, indicating a higher downfield shift. However, $C_c$ of the protonated forms of **5**–**7** experience a lower downfield shift. This might be due to the presence of some degree of "hidden" carbon(0) characteristics in them.[35] The difference in $^{13}C$ chemical shifts in the protonated derivatives of carbenes and carbones becomes distinct from **9** onward, a well-established carbon(0) species.[12,23] The values of $^{13}C$ shifts are significantly downfield for **9**–**21** compared to those for **1**–**8**. We obtained an excellent correlation between the out-of-plane $p_\pi$ occupancy at the central carbon atom and $^{13}C$ chemical shifts ($R^2 = 0.96$, omitting the points corresponding to **3** and **12**, Figure 1). Carbenes have lower $p_\pi$ occupancy and more downfield shifts, whereas carbones have higher $p_\pi$ occupancy and lesser downfield shifts. It should be noted that a correlation between the $p_\pi$ occupancy at $C_c$ and $^{13}C$ chemical shifts for the parent compounds should not be drawn as the total electron density at $C_c$ will have a contribution from the in-plane lone pair, as well.

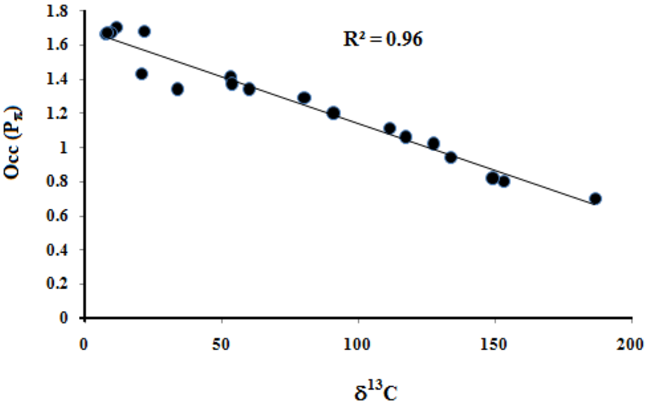

**Figure 1.** Correlation plot between $\delta^{13}C$ and out-of-plane $p_\pi$ occupancy of the central carbon atom of the protonated derivatives.

In summary, quantum chemical calculations provide a spectroscopic distinction between the divalent carbon(II) and carbon(0) species, which may be easily verified by experimental means. The $^{13}C$ chemical shift of the central carbon atom of both parent carbenes and their protonated forms will experience a more downfield shift than the C(0) compounds. This difference arises due to their unique difference in bonding. The central carbon atom of carbenes will become more electron-deficient in their protonated form, while carbones will be less electron-deficient due to the presence of another out-of-plane lone pair at the central carbon atom. This is evidenced by the good correlation between the $p_\pi$ occupancy and the $^{13}C$ chemical shifts of the central carbon atom in their protonated form. Thus, we feel that this spectroscopic approach may be safely used for distinguishing these two classes of carbon bases.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Cartesian coordinates of the optimized geometries of the parent compounds and their protonated derivatives. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01056.

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### Notes

The authors declare no competing financial interest.

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(29) Geometry optimization of all the molecules in the gas phase was carried out without any symmetry constraint using the hybrid PBE1PBE exchange-correlational functional.[30] We used the 6-31+G(d) basis set for all atoms. Frequency calculations were performed at the same level of theory to characterize the nature of the stationary points. All structures were found to be minimum in the potential energy surface with real frequencies. For the calculation of $^{13}$C NMR shifts, calculated isotropic values (in the gas phase) were plotted (see Supporting Information) against the experimental values. The values of the intercept and slope obtained from this plot are used to calculate the chemical shift of the compounds using the relationship $\delta = (\text{intercept} - \sigma)/(-\text{slope})$, where $\delta$ is the computed chemical shift and $\sigma$ is the computed isotropic value.[31] Isotropic $^{13}$C chemical shifts were calculated in the gas phase using a higher basis set, 6-311++G*, on the 6-31+G* optimized geometries. All chemical shifts were calculated using the gauge-independent atomic orbital scheme implemented in the Gaussian03 suite of programs.[32] The nature of bonding has been analyzed using the natural bond orbital[33] method at the PBE1PBE/6-311++G*//PBE1PBE/6-31+G* level of theory.

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