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^{13}C NMR Spectroscopy of "Arduengo-type" Carbenes and Their Derivatives

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1. Introduction

Since the isolation and crystallographic characterization of the first stable N-heterocyclic carbene in early 1991,[1] nucleophilic diaminocarbenes (also known as "Arduengo-type" carbenes) and their analogues have emerged as a powerful class of carbon-based ligands with broad applications in metal-based catalytic reactions.[2−12] The main reason for their success in catalysis is their superior properties as ligands in comparison with their phosphine counterparts.[11,13−18] In addition, carbene organocatalysis has emerged as an extremely fruitful area of research in synthetic organic chemistry. The benzoin condensation, the Stetter reaction, transformations involving homoenolates, 1,2-additions, transesterifications, and ring opening polymerizations are among the many reactions promoted by nucleophilic carbenes. Several excellent reviews, chapters, and books highlighting the recent progress of nucleophilic carbenes in metal-based catalysis and organocatalysis are available.[7,9,11−16,19−24]

Significant efforts have been made to better understand the unique properties associated with the free nucleophilic carbenes using a wide range of experimental techniques. X-ray diffraction,[1,25] neutron diffraction,[26,27] photoelectron spectroscopy,[28] cyclic voltammetry,[29−34] NMR spectroscopy, and IR spectroscopy[10,35−40] are among the experimental techniques employed in these studies. The experimental methods have been complemented by theoretical investigations, which have become extremely important because they enable the study of a great number of related systems, a task that would be difficult or sometimes impossible to achieve experimentally. Density functional theory and molecular orbital theory have been employed for the study of these intriguing species.[26−28,41−49]

ESR spectroscopy has been successfully used to provide information about the electronic environment of triplet carbenes and was critical in the determination of the structure of the ground state of the simplest carbene, CH_2.[50−56] On the other hand, solid- and liquid-state NMR spectroscopies are highly reliable techniques for providing structural and electronic information about the closed-shell nucleophilic carbenes. This review highlights the use of ^{13}C NMR spectroscopy as an analytical tool for the study and characterization of this powerful class of carbon-based ligands.

2. Cyclic Carbenes and Their Metal Complexes

2.1. Nonfused Diaminocarbenes

The cyclic diaminocarbenes represent the dominant architecture of stable nucleophilic singlet carbenes reported to date. Their exceptional stability arises from the combined π-donating and σ-withdrawing properties of the neighboring nitrogen atoms.[25−28,57−59] These mesomeric and inductive effects formally preserve the electronic neutrality of the carbene center by an electronic push−pull mechanism and lead to an increase in the singlet−triplet gap thereby stabilizing the singlet over the more reactive triplet state. These effects also make the nominally vacant π orbital on the C less available for reactions so as to increase not only the thermodynamic stability of the singlet but also its kinetic stability. Steric effects also contribute to the stability of the diaminocarbenes, but to a smaller extent.[25,57,58] A more detailed overview of the electronic properties of diaminocarbenes can be found in two excellent reviews.[14,17]

One of the most popular methods for the synthesis of diaminocarbenes is deprotonation of the corresponding azolium salts with strong bases (Scheme 1).[1] These reactions are characterized by the disappearance of the signal due to the acidic azolium H2 proton in the ^{1}H NMR spectrum and, in the ^{13}C NMR spectrum, the appearance of a signal due to carbenic N*C*N (C2), significantly downfield from that of the corresponding azolium N*C*N carbon. The ^{13}C NMR data for the most commonly used symmetric substituted diaminocarbenes **1**−**29** and their corresponding azolium salts **30**−**49**, where available, are summarized in Table 1.

The five-membered unsaturated diaminocarbenes, imidazol-2-ylidenes, are the most studied carbenes. Strong downfield shifts of ca. 75−88 ppm are observed for C2 in imidazol-2-ylidenes **1**−**16** (δ = 206−220 ppm)[1,25,26,28,62,64,67−70,81] compared with the corresponding imidazolium salts **30**−**38**.[1,26,60,61,63,65,67,82−84] The high downfield shifts of the

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Daniela Tapu was born in Roman, Romania. In 1998, she obtained her undergraduate degree in chemistry from Alexandru Ioan Cuza University, Romania. She studied for a year at the Technische Universität Braunschweig, Germany, as a Socrates scholar. She received her Master's degree in 2000 from Alexandru Ioan Cuza University. She moved to Tuscaloosa, Alabama, to pursue graduate studies with Professor A. J. Arduengo, III, at the University of Alabama. During graduate school, she held Atotech and University of Alabama Graduate Council Fellowships. In 2005, she graduated with her Ph.D. in Organic/Organometallic Chemistry. After graduation, she joined the Chemistry and Biochemistry department at Kennesaw State University where she is currently an Assistant Professor. Her research interests are in the area of nucleophilic polycyclic aromatic carbenes and catalysis.

David A. Dixon was born in Houston, Texas, in 1949 and received his B.S. in chemistry from Caltech (1971) and his Ph.D. in physical chemistry from Harvard University in 1976. He was a Junior Fellow, Society of Fellows, Harvard University, 1975−1977. After 6 years on the faculty at the University of Minnesota, he joined Dupont Central Research and Development at the Experimental Station where he spent 12 years ending as a Research Fellow. In 1995, he became the Associate Director for Theory, Modeling and Simulation in the William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory. In January, 2004, he joined the Department Chemistry, University of Alabama, where he is currently the Robert Ramsay Chair. His main research interest is the use of numerical simulation techniques combining electronic structure theory and high performance computing to solve chemical problems. He has received a number of awards including a Sloan Fellowship, a Camille and Henry Dreyfus Teacher-Scholar fellowship, the 1989 ACS Leo Hendrik Baekeland Award, and the 2003 ACS Award for Creative Work in Fluorine Chemistry. He is a Fellow of the American Association for the Advancement of Science and the American Physical Society.

carbenic center are consistent with expectations based on the analysis of the carbene shielding tensors.[46] The substituents on nitrogen exert little influence on the chemical shift.

In the solid state, the chemical shift of a given ^{13}C depends on the orientation of the electronic distribution relative to the applied magnetic field. In a polycrystalline or amorphous

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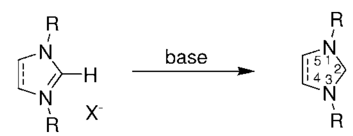
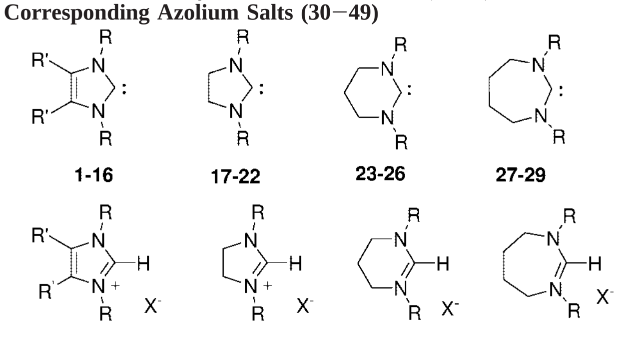
Scheme 1



material, this ^{13}C will yield a broad "powder" spectrum corresponding to the range of chemical shifts associated with the possible orientations. In solution, the molecules are rapidly tumbling on the NMR time scale leading to all possible molecular orientations in the magnetic field. It is the average value of all of these shifts that gives rise to the isotropic chemical shift in solution. The underlying anisotropy of the chemical shift is characterized by the chemical shielding tensor, a 3×3 matrix, which can be diagonalized to yield the three principal components along an appropriate set of axes. These principal elements constitute a source of information regarding the electronic environment associated with the carbene carbon. The tensor is composed of both a diamagnetic component and a paramagnetic component and the analysis of these components can provide further insight into the electronic structure of the carbene.

Broad powder patterns are problematic in terms of having low signal-to-noise and poor resolution due to overlap with other ^{13}C sites in the molecule. Magic-angle spinning (MAS) is often used to average the powder pattern in order to produce an isotropic spectrum, with attendant loss of the information contained in the anisotropic pattern. If MAS is carried out at a spinning rate less than the frequency spread of the powder pattern, a sharp peak is produced at the isotropic chemical shift together with a manifold of sharp spinning sidebands whose intensities reflect the profile of the chemical shift anisotropy. Herzfeld−Berger analysis of the spinning sideband intensities permits reconstruction of the powder pattern and determination of the three principal components of the carbon chemical shielding tensor.[85] Just such an approach was taken in a solid-state MAS study of carbene **2**;[46] the C-13 cross-polarization magnetic-angle spinning (^{13}C CP/MAS) spectrum of **2** (7.05 T magnetic field

Table 1. Chemical Shifts (in ppm) for Five-, Six- and Seven-Membered Cyclic Diaminocarbenes (1−29) and Their Corresponding Azolium Salts (30−49)



1-16, 17-22, 23-26, 27-29, 30-38, 39-42, 43-46, 47-49

carbene	R[h]	R′	δC2	Azolium salt (X)	δC2
1[25]	Me	H	215.2[b]	**30**[60] (I)	137.2[g]
2[25]	Me	Me	213.7[b]	**31**[61] (Cl)	135.0[e]
3[26]	CD_3	CD_3	212.5[b]	**32**[26] (Cl)	135.0[e]
4[62]	*i*-Pr	H	210.5[a]	**33**[63]	132.5[g]
5[64]	*i*-Pr	Me	206.8[c]		
6[28]	*t*-Bu	H	213.2[b]	**34**[65] (Cl)	132.7[e]
7[66]	Np	H	217[a]		
8[1]	Ad	H	211.4[b]	**35**[1,65] (Cl)	132.1[e]
9[67]	Cy	H	210.1[b]	**36**[67] (Cl)	134.9[d]
10[68]	Ph	Ph	219.6[b]		
11[25]	mes	H	219.7[b]	**37**[65] (Cl)	134.8[e]
12[69]	mes	Cl	219.9[a]		
13[25]	tol	H	215.8[b]		
14[25]	ClPh	H	216.3[b]		
15[70]	dipp	H	220.6[a]	**38**[65] (Cl)	132.2[e]
16[70]	dipp	Cl	220.6[a]		
17[71]	Me		239.8[a]		
18[71]	Et		237.7[a]	**39**[72] (I)	156.7[d]
19[71]	*i*-Pr		236.8[a]		
20[71,73,74]	*t*-Bu		238.2[a]	**40**[74] (Cl)	153.5[e]
21[70,75]	mes		243.8[a]	**41**[70] (Cl)	160.2[e]
22[70]	dipp		244.0[a]	**42**[70] (Cl)	160.0[e]
23[76]	Me		242.7[c]	**43**[77] (I)	154.4[f]
24[64]	*i*-Pr		236.1[c]	**44**[78] (Br)	151.5[d]
25[79]	mes		244.9[a]	**45**[79] (BF_4)	154.0[d]
26[79]	dipp		245.1[a]	**46**[79] (BF_4)	153.1[d]
27[80]	Cy		251.2[a]	**47**[80] (PF_6)	156.4[d]
28[79]	mes		257.3[a]	**48**[79] (BF_4)	158.2[d]
29[79]	dipp		260.2[a]	**49**[79] (BF_4)	157.3[d]

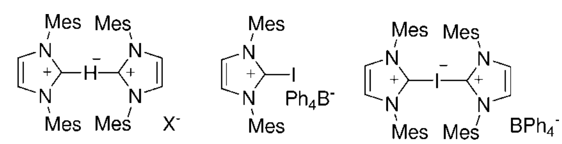
[a] In d_6-benzene. [b] In d_8-tetrahydrofurane (THF). [c] In d_8-toluene. [d] In d_3-chloroform. [e] In d_6-dimethylsulfoxide (DMSO). [f] In d_6-acetone. [g] In d_2-water. [h] Abbreviations: ad = 1-adamantyl, dipp = 2,6-diisopropylphenyl, mes = mesityl, tol = 4-methylphenyl, ClPh = *p*-chlorophenyl, Np = neopentyl.

strength, 293 K) spinning at 1.8 kHz revealed the isotropic shifts of each carbon (including C2 at 209.6 ppm) and the sidebands of C2 (occurring at integer multiples of the spin rate to either side of the isotropic peak) over a spectral width of approximately 300 ppm. Such a large frequency spread is indicative of a large chemical shielding anisotropy for this site. Analysis of the sideband intensities led to the absolute chemical shift tensor elements $\sigma_{11} = -184(20)$ ppm, $\sigma_{22} = 9(18)$ ppm, and $\sigma_{33} = 104(15)$ ppm (estimated errors in parentheses). The calculations described in section 2.1.1 were used to assign the components of the chemical shift tensor to a molecular axis system.

The singlet−triplet gap becomes smaller upon saturation of the C−C bond, since five-center six-electron π-delocalization as a stabilizing factor is no longer possible.[71,75] These changes in the electronic structure of the imidazole ring can easily be detected using NMR spectroscopy. The imidazolin-2-ylidenes **17**−**22** (the saturated version of imidazol-2-ylidenes) show resonances for the carbene center further downfield, between 236 and 244 ppm, consistent with a higher anisotropy at the carbene center due to a lower population of the carbene p_π-orbital.[70,71,74,75] A comparison of identical substituted imidazol- and imidazolin-2-ylidenes (e.g., **1** vs **17**, **4** vs **19**, etc.) reveals that saturation of the imidazole ring produces a downfield shift of the carbene carbon that ranges between 23 and 26 ppm.

More than 40 years ago, Wanzlick noted that saturated carbenes dimerize rapidly to the corresponding olefins if the substituents on the nitrogen atoms allow this geometrically,[86] an observation that was only much later confirmed.[71] Carbenes **17**−**19** persist in solution (−20 °C), but slowly dimerize at room temperature to give the corresponding olefins. By dimerization, the resonance of the former carbene center shifts upfield to 129.6 ppm (**17** dimer), 125.6 ppm (**18** dimer), and 124.3 ppm (**19** dimer), an upfield shift of over 106 ppm in comparison to the free carbenes.[71]

Arduengo et al. studied the reaction of 1,3-dimesitylimidazol-2-ylidene (**11**) with the corresponding imidazolium salt **37**. They observed the formation of a linear three-center−four-electron C−H−C hydrogen bridge.[87] The resonance for C2 of the bis(carbene)-proton systems (**50** and **51**) is ∼175 ppm, the average of the C2 resonances of carbene **11** and imidazolium ion **37**. Such averaged NMR resonances are observed even for non-1:1 ratios of carbene/imidazolium salt, an indication of rapid proton exchange on the NMR time scale.[87] Unlike these proton systems, the structurally related bis(carbene)−I(1+) complex **53** exhibits the resonance for the former carbene carbons at 155.2 ppm. This value is different than the average resonances (163.5 ppm) for the free carbene **11** (219.7 ppm) and the 2-iodoimidazolium ion **52** (107.09 ppm), and it is the result of a less dynamic behavior of iodanide **53**. If an excess of carbene **11** is added to a deuterated THF solution of **53**, separate resonances are observed for the carbene and **53**, a reflection of a slow exchange on the NMR time scale with the symmetric structure **53**.[88]



50 X = PF_6
51 X = CF_3SO_3
52
53

Cyclic diaminocarbenes derived from six- and seven-membered rings are also known, and the ^{13}C NMR shifts of their carbene centers fall between 236 and 245 ppm for **23**−**26**[64,76,79] and 251 and 260 ppm for **27**−**29**.[79,80] The large downfield shift of C2 of the seven-membered ring carbenes is comparable with those displayed by acyclic aminocarbenes (see section 3). The deshielding of the carbene centers of six- and seven-membered diaminocarbenes was ascribed to the higher triplet contribution to the electronic structure of these carbenes when compared with the five-membered cyclic carbenes.[79] The smaller singlet−triplet gap is likely the result of a less effective electron donation from the nitrogen atoms into the p_π orbital of the carbene center, an assumption supported by the values calculated by Alder for the singlet−triplet (S−T) gap of five-, six-, and seven-membered ring carbenes (301.2, 258.9, and 210.7 kJ mol^{-1}, respectively).[89] The best calculation of the S−T gap in **2** is 360.2 kJ mol^{-1} at 0 K at the CCSD(T)/CBS (complete basis set) level.[48]

Carbene complexes of almost any main-group element and transition metal in a wide variety of oxidation states are known to date.[11,14,17,90] The ^{13}C shift of the former carbenic center is substantially shielded in all these adducts and provides a sensitive probe for complexation. The intensity of this resonance is usually weak, since the C2 carbon is a quaternary center and in some cases has not been observed.[91−99] An analysis of the ^{13}C chemical shifts of carbene−metal complexes spanning a wide range of metals has shown an upfield shift for the carbenoid carbon that correlates well with the Lewis acidity of the metal (e.g., H > Be ≈ Al > Mg ≈ Ti), as postulated by Herrmann et al.[100] Indeed, a free carbene lacking electronic donation toward a Lewis acid has a very low field signal reflecting the availability of an excess of electron density at the carbene carbon. On complexation, the electronic density is partially transferred to the Lewis acid by σ-donation, which results in a displacement of the chemical shift to higher field. The upfield shift for C2 in the corresponding adducts of carbenes **1**−**16** relative to the free species suggests that the imidazole moiety experiences a degree of delocalization that is intermediate between that of the free carbene and the fully delocalized carbenium ion. In addition, both the resonances for C4(5) and the protons at these positions are downfield from those of the same nuclei in the free carbenes. The H4(5) resonances are particularly sensitive indicators of the positive charge and delocalization of the imidazole ring.[101−103] Complexes derived from imidazolin-2-ylidenes **17**−**22** show significant downfield chemical shifts of the former carbenic carbon in comparison with their unsaturated analogues (e.g., ($\mathbf{15}$)$_2$Ni vs ($\mathbf{22}$)$_2$Ni with δ 193.8 and 211.2, respectively).[104] Although large, this difference tracks extremely well with the observed difference in the chemical shifts of the free carbenes. The most upfield resonance reported so far for the C2 center for a cyclic diaminocarbene adduct is 46.54 ppm in the (**2**)Eu(thd)$_3$ complex (thd = 2,2,6,6-tetramethylheptane-3,5-dionato).[91] This unusual value was attributed to the large lanthanide shift[91] due to the strong anisotropy of europium. Examples of ^{13}C NMR spectroscopic data for selected metal complexes derived from cyclic diaminocarbenes are presented in Table 2.

Among metallocene−carbene complexes of alkaline earth metals (**2**)MCp$_2$* (M = Mg, Ca, Sr, Ba), as one moves down the group, the C2 resonance shifts downfield from 185.7 ppm (**54**) to 196.2 ppm (**55**), to 198.2 ppm (**56**), and to 203.5 ppm (**57**).[105] It was suggested that the bonding of the metal to carbon loses covalent character and becomes weaker as the metal center becomes larger and more electropositive. For the barium adduct, the chemical shift of the coordinated carbene is the most “carbene like”, being only 17.5 ppm upfield of the carbene resonance of **2**. The ^{13}C resonance of the carbene carbon in the related zinc complex **58** occurs at 174.4 ppm and is the highest resonance for the C2 center of these complexes, but the hapticity of the Cp* ligand is also modified (η^1 vs η^3).[105] Similar trends were observed for biscarbene complexes **59** and **60**[105] and the amido-bridged dimers **61**−**69** ({(carbene)M(μ[N(SiMe$_3$)$_2$]}$_2$, M = Li, Na, K) that display an increased downfield shift of the former carbene center by complexation with a heavier cation.[64,106] It was noted that the chemical shift of the carbene center for the latter complexes is sensitive not only to the nature of the coordinated cation but also to the amount of the alkali metal species present in solution. Exceptions to the above trend were also encountered. For example, phosphorus adduct **70** has a higher chemical shift than the arsenic adduct **71** (161.4 vs 158.3 ppm),[92] even though analogous adducts **72** and **73** display an opposite ordering.[107]

Interestingly, different trends were observed when the chemical shifts of the C2 center of identical substituted complexes of elements in the same transition metal triad were compared. Complexes of type [(carbene)M(CO)$_5$] (M = Cr, Mo, W) (**74**−**85**),[108−114] *cis*[(carbene)$_2$M(CO)$_4$] (M = Cr, Mo, W) (**86**−**91**),[108,110,111] *trans*[(carbene)$_2$M(CO)$_4$] (M = Mo, W) (**92**, **93**),[110,111] [(carbene)M(COD)Cl] (M = Rh, Ir) (**94**−**113**),[10,34,36,78,80,115−126] [(carbene)M(CO)$_2$X] (M = Rh, Ir) (**114**−**117**),[36,80,118] [(carbene)M(η^3allyl)Cl] (M = Ni, Pd) (**118**−**129**),[127−133] and [(carbene)M(dvtms)] (M = Pd, Pt and dvtms = divinyltetramethylsiloxane) (**130**−**135**)[117,134−138] show upfield shifts of the carbene center upon the replacement of a lighter by a heavier metal. A different trend was observed for a number of group 11 transition metal complexes of type [(carbene)MCl] (M = Cu, Ag, Au) (**136**−**155**), where silver complexes display the most deshielded C2 resonance, followed by complexes of copper and gold.[139−151] Similar downfield shifts were observed going from copper to silver in the cationic complexes [(carbene)$_2$M]$^+$ (**156**−**162**).[124,144,152−155] The complexes [(carbene)$_2$MCl$_4$] (M = Ti, Zr, Hf) (**163**−**167**)[62,156] [(carbene)$_2$MX$_2$] (M = Ni, Pd) (**168**−**173**),[126,157−162] and [(carbene)$_2$M] (M = Ni, Pd, Pt) (**174**−**181**)[101,128,163−165] also display interesting patterns.

Consistent with Herrmann’s hypothesis,[100] work by Baker et al. showed that the chemical shifts of carbene carbons vary widely with different ancillary ligands, correlating well with the σ-donor ability of the coligand.[168] They noted, in complexes of the type [(**6**)AuX] (**182**−**190**), that the weakest σ-donor ligand of the series, nitrate, shows the most upfield shift (δ = 156.3 ppm) of the carbenic carbon, whereas the strongest σ-donor ligand, methyl, shows the most downfield shift (δ = 198.7 ppm), presumably as a result of both a larger *trans* influence and a decreased Lewis acidity of the metal going from the weakest to the strongest σ-donor ancillary ligand. The authors also found a correlation between the chemical shift of the carbene carbon and C2−M bond distance (Figure 1).[168] A similar dependence (with slight differences) was observed for rhodium complexes [(**1**)Rh(COD)X] where X = Cl, Br, I, SCN, SeCN, NCO, and N$_3$.[115,126]

The Lewis acidity of the metal is sensitive to the changes in the oxidation state of the metal, and as a result, these changes have an influence on the chemical shift of the carbenic carbon. Raubenheimer et al. have noted chemical shift variations of ca. 30−40 ppm for the carbene carbon resonance on oxidations of [(**1**)$_2$Au]$^+$ to [(**1**)$_2$AuX$_2$]$^+$ (**191** and **192** vs **193**−**195**).[173] Variations of 25−38 ppm as a result of the increase of the metal oxidation state were observed by de Frémont et al. between the neutral [(carbene)AuBr] complexes **196**−**200** and [(carbene)AuBr$_3$] complexes **201**−**207**.[170] Similar dependencies were observed for complexes of other metals (nickel, palladium, silver, platinum, copper, etc.).[101,134,138,158,159,164,174]

A recent review by Garrison and Youngs focused on the synthesis, characterization, and uses of silver N-heterocyclic carbenes.[4] The authors have made compilations of the characteristic chemical shifts for a large number of silver complexes. The C2 chemical shifts fall over a fairly wide range (163.2−218 ppm), consistent with the observed trend for the free carbenes. Complex **157** was the first reported homoleptic carbene−silver complex.[152] This complex exhibits couplings of the silver nucleus with all of the centers

Table 2. Chemical Shifts (in ppm) and Coupling Constants (in Hz) of Carbenoid Center for Selected Main Group and Transition Metal Complexes

metal complexes[j]		δC2 (J)	metal complexes[j]		δC2 (J)
54[105]	(**2**)$MgCp^*_2$	185.7[a]	**131**[134]	(**11**)Pt(dvtms)	184.2[d]
55[105]	(**2**)$CaCp^*_2$	196.2[a]	**132**[136,138]	(**12**)Pd(dvtms)	191.9[b]
56[105]	(**2**)$SrCp^*_2$	198.2[a]	**133**[135]	(**13**)Pt(dvtms)	188.0[d]
57[105]	(**2**)$BaCp^*_2$	203.5[a]	**134**[136,138]	(**15**)Pd(dvtms)	200.8[b]
58[105]	(**2**)$Zn(\eta^1Cp^*)_2$	174.4[a]	**135**[134]	(**15**)Pt(dvtms)	186.4[d]
59[105]	$(\mathbf{2})_2SrCp^*_2$	203.7[a]	**136**[141]	(**2**)AgCl	177.6[g]
60[105]	$(\mathbf{2})_2BaCp^*_2$	208.8[a]	**137**[140]	(**2**)AuCl	168.4[g]
61[64]	$[(\mathbf{5})Li(N(SiMe_3)_2)]_2$	195.7[c]	**138**[150]	(**8**)CuBr	172.1[d]
62[64]	$[(\mathbf{5})Na(N(SiMe_3)_2)]_2$	196.4[c]	**139**	(**8**)AgCl	173.8[g]
63[64]	$[(\mathbf{5})K(N(SiMe_3)_2)]_2$	201.1[c]	**140**[140]	(**8**)AuCl	166.3[g]
64[106]	$[(\mathbf{23})Li(N(SiMe_3)_2)]_2$	219.4[i]	**141**[142]	(**9**)CuCl	174.2[f]
65[106]	$[(\mathbf{23})Na(N(SiMe_3)_2)]_2$	224.9[i]	**142**[141]	(**9**)AgCl	179.1[d]
66[106]	$[(\mathbf{23})K(N(SiMe_3)_2)]_2$	241.0[i]	**143**[139,140]	(**9**)AuCl	166.1[d]
67[64]	$[(\mathbf{24})K(N(SiMe_3)_2)]_2$	226.7[c]	**144**[144,147]	(**11**)CuCl	178.7[d]
68[64]	$[(\mathbf{24})Li(N(SiMe_3)_2)]_2$	216.8[c]	**145**[141,149]	(**11**)AgCl	185.0[d] ($^1J_{AgC}$ = 270/234)
69[64]	$[(\mathbf{24})Na(N(SiMe_3)_2)]_2$	221.3[c]	**146**[140]	(**11**)AuCl	173.4[d]
70[92]	(**12**)PF_5	161.4[b] ($^1J_{PC}$ = 290.6)	**147**[145,151]	(**15**)CuCl	182.3[a]
71[92]	(**12**)AsF_5	158.3[b]	**148**[141]	(**15**)AgCl	184.6[d] ($^1J_{AgC}$ = 271/253)
72[107]	(**11**)PPh	170.0 [b] ($^1J_{PC}$ = 102.8)	**149**[140]	(**15**)AuCl	175.1[g]
73[107]	(**11**)AsPh	174.3[a]	**150**[143]	(**21**)CuCl	202.8[d]
74[113]	(**1**)$Cr(CO)_5$	188.3[h]	**151**[141,148]	(**21**)AgCl	207.5[d] ($^1J_{AgC}$ = 256/222)
75[113]	(**1**)$Mo(CO)_5$	186.5[h]	**152**[140,141]	(**21**)AuCl	195.0[d]
76[113]	(**1**)$W(CO)_5$	178.5[h]	**153**[144]	(**22**)CuCl	204.3[d]
77[114]	(**2**)$Cr(CO)_5$	186.6 [i]	**154**[141]	(**22**)AgCl	207.7[g] ($^1J_{AgC}$ = 253/219)
78[114]	(**2**)$Mo(CO)_5$	183.5[i]	**155**[140,146]	(**22**)AuCl	196.1[d]
79[114]	(**2**)$W(CO)_5$	175.8[i]	**156**[152]	$(\mathbf{11})_2Cu][CF_3SO_3]$	178.24[b]
80[108]	(**17**)$Cr(CO)_5$	219.6[a]	**157**[152]	$[(\mathbf{11})_2Ag][CF_3SO_3]$	183.6 ($^1J_{AgC}$ = 188/208.6)
81[111]	(**17**)$Mo(CO)_5$	215.1[a]	**158**[166]	(**15**)$2Cu][BF_4]$	177.4[d]
82[110]	(**17**)$W(CO)_5$	206.6[a]	**159**[124]	$[(\mathbf{15})_2Ag][PF_6]$	183.6 ($^1J_{AgC}$ = 183/211)
83[108,109,112]	(**18**)$Cr(CO)_5$	217.6[a]	**160**[153]	$[(\mathbf{18})_2Cu][BF_4]$	197.0[d]
84[111]	(**18**)$Mo(CO)_5$	213.3[a]	**161**[153]	$[(\mathbf{18})_2Ag][BF_4]$	202.5[d] ($^1J_{AgC}$ = 168/192)
85[110]	(**18**)$W(CO)_5$	205.4[a] ($^1J_{WC}$ = 94.6)	**162**[153−155]	$[(\mathbf{18})_2Au]Cl$	203.8[d]
86[108,167]	*cis*$(\mathbf{17})_2Cr(CO)_4$	226.9[g]	**163**[156]	$(\mathbf{1})_2TiCl_4$	180.7[h]
87[111]	*cis*$(\mathbf{17})_2Mo(CO)_4$	222.9[d]	**164**[156]	$(\mathbf{1})_2ZrCl_4$	178.2[h]
88[110]	*cis*$(\mathbf{17})_2W(CO)_4$	211.4[g]	**165**[156]	$(\mathbf{1})_2HfCl_4$	176.2[h]
89[108]	*cis*$(\mathbf{18})_2Cr(CO)_4$	226.9[g]	**166**[62]	$(\mathbf{4})_2ZrCl_4$	181.8[g]
90[111]	*cis*$(\mathbf{18})_2Mo(CO)_4$	220.2[g]	**167**[62]	$(\mathbf{4})_2HfCl_4$	189.1[g]
91[110]	*cis*$(\mathbf{18})_2W(CO)_4$	213.6[g]	**168**[158]	$(\mathbf{1})_2NiI_2$	173.9[d]
92[111]	*trans*$(\mathbf{17})_2Mo(CO)_4$	225.3[g]	**169**[126,162]	$(\mathbf{1})_2PdI_2$	168.2[d]
93[110]	*trans*$(\mathbf{17})_2W(CO)_4$	215.4[g]	**170**[160]	$(\mathbf{2})_2NiI_2$	169.4[g]
94[10,115,126]	(**1**)Rh(COD)Cl	182.6[d] ($^1J_{RhC}$ = 51.1)	**171**[160]	$(\mathbf{2})_2PdI_2$	158.9[e]
95[122,126]	(**1**)Ir(COD)Cl	176.6[d]	**172**[159]	$(\mathbf{15})_2NiCl_2$	168.4[d]
96[10,115]	(**1**)Rh(COD)I	182.4[f] ($^1J_{RhC}$ = 48.6)	**173**[157]	$(\mathbf{15})_2PdCl_2$	172.5[d]
97[120,121]	(**1**)Ir(COD)I	180.4[g]	**174**[163]	$(\mathbf{6})_2Ni$	191.1[a]
98[125]	(**4**)Rh(COD)Cl	179.9[d] ($^1J_{RhC}$ = 50.8)	**175**[163,164]	$(\mathbf{6})_2Pd$	194.5[a]
99[125]	(**4**)Ir(COD)Cl	177.9[d]	**176**[163]	$(\mathbf{6})_2Pt$	193.9 ($^1J_{PtC}$ = 1257)
100[125]	(**6**)Rh(COD)Cl	177.9[d]	**177**[101]	$(\mathbf{11})_2Ni$	193.22[a]
101[118,125]	(**6**)Ir(COD)Cl	179.9[d]	**178**[164]	$(\mathbf{11})_2Pd$	186.2[a]
102[125]	(**8**)Rh(COD)Cl	183.0[e]	**179**[101]	$(\mathbf{11})_2Pt$	197.5[a] ($^1J_{PtC}$ = 1218)
103[118]	(**8**)Ir(COD)Cl	179.1[d]	**180**[128]	$(\mathbf{22})_2Ni$	211.2[a]
104[122,123]	(**11**)Rh(COD)Cl	183.5[d] ($^1J_{RhC}$ = 52.5)	**181**[165]	$(\mathbf{22})_2Pd$	218.5[a]
105[118,119]	(**11**)Ir(COD)Cl	180.9[d]	**182**[168]	(**6**)$AuONO_2$	156.3[d]
106[124]	(**15**)Rh(COD)Cl	187.7 ($^1J_{RhC}$ = 53)	**183**[168,169]	(**6**)AuCl	167.6[h]
107[118]	(**15**)Ir(COD)Cl	182.6[d]	**184**[168,170]	(**6**)AuBr	172.4[d]
108[36]	(**21**)Rh(COD)Cl	212[d] ($^1J_{RhC}$ = 48.1)	**185**[168]	(**6**)Au(SCN)	174.7[d]
109[36,118]	(**21**)Ir(COD)Cl	207.4[d]	**186**[168]	(**6**)Au(SeCN)	177.3[d]
110[78,117]	(**25**)Rh(COD)Cl	210.8[d] ($^1J_{RhC}$ = 53)	**187**[168]	(**6**)AuI	179.9[d]
111[116]	(**25**)Ir(COD)Cl	191.4[b]	**188**[168]	(**6**)Au(CN)	181.5[d]
112[80]	(**27**)Rh(COD)Cl	215.3[g] ($^1J_{RhC}$ = 43.7)	**189**[169]	(**6**)Au(CCH)	187.9[b]
113[80]	(**27**)Ir(COD)Cl	208.3[d]	**190**[168]	(**6**)AuMe	198.7
114[36]	(**21**)$Rh(CO)_2Cl$	205.7 ($^1J_{RhC}$ = 41)	**191**[171]	$[(\mathbf{1})_2Au]Br$	183.3[e]
115[118]	(**21**)$Ir(CO)_2Cl$	201.9[d]	**192**[172]	$[(\mathbf{1})_2Au][OTf]$	185.7[e]
116[80]	(**27**)$Rh(CO)_2Cl$	206.2[d] ($^1J_{RhC}$ = 37.7)	**193**[173]	*trans*$[(\mathbf{1})_2AuCl_2]^+$	154.5[d]
117[80]	(**27**)$Ir(CO)_2Cl$	200.5[c]	**194**[173]	*trans*$[(\mathbf{1})_2AuBr_2]^+$	154.1[d]
118[128,130]	(**6**)$Ni(\eta^3allyl)Cl$	179.93[a]	**195**[173]	*trans*$[(\mathbf{1})_2AuI_2]^+$	145.6[d]
119[131]	(**6**)$Pd(\eta^3allyl)Cl$	179.255[a]	**196**[170]	(**8**)AuBr	170.2[d]
120[130]	(**8**))$Ni(\eta^3allyl)Cl$	179.01[a]	**197**[170]	(**11**)AuBr	176.7[d]
121[133]	(**8**)$Pd(\eta^3allyl)Cl$	175.6[g]	**198**[170]	(**15**)AuBr	179.0[d]
122[128]	(**9**)$Ni(\eta^3allyl)Cl$	180.84[a]	**199**[170]	(**21**)AuBr	198.1[d]
123[133]	(**9**)$Pd((\eta^3allyl)Cl$	178[g]	**200**[170]	(**22**)AuBr	199.0[d]
124[128]	(**11**)$Ni(\eta^3allyl)Cl$	186.2[a]	**201**[170]	(**6**)$AuBr_3$	134.2[d]
125[131,133]	(**11**)$Pd(\eta^3allyl)Cl$	185.68[a]	**202**[170]	(**8**)$AuBr_3$	132.9[d]
126[127]	(**15**)$Ni(\eta^3allyl)Cl$	188.8[a]	**203**[170]	(**9**)$AuBr_3$	136.8[d]
127[133]	(**15**)$Pd(\eta^3allyl)Cl$	188.53[a]	**204**[170]	(**11**)$AuBr_3$	144.4[d]
128[128]	(**22**)$Ni(\eta^3allyl)Cl$	218.41[a]	**205**[170]	(**15**)$AuBr_3$	146.2[d]
129[131−133]	(**22**)$Pd(\eta^3allyl)Cl$	215.385[a]	**206**[170]	(**21**)$AuBr_3$	172.3[d]
130[136−138]	(**11**)Pd(dvtms)	199.3[b]	**207**[170]	(**22**)$AuBr_3$	174.1[d]

[a] In d_6-benzene. [b] In d_8-THF. [c] In d_8-toluene. [d] In d_3-chloroform. [e] In d_6-DMSO. [f] In d_6-acetone. [g] In d_2-methylene chloride. [h] In d_3-acetonitrile. [i] Solvent not reported. [j] Abbreviations: dvtms = divinyltetramethylsiloxane.

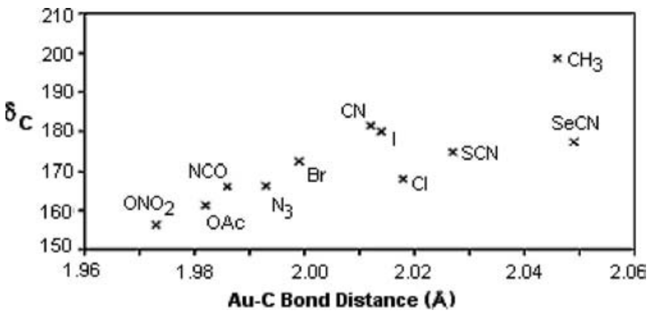


Figure 1. ^{13}C NMR chemical shift of the Au−C2 carbon (δ, ppm) vs Au−C2 bond distance. Reprinted from ref 168 by permission of The Royal Society of Chemistry.

in the imidazole ring. The coupling constants $J_{^{109/107}Ag-^{13}C}$ were resolved (208.6 and 188 Hz, respectively), and they reflect the magnetogyric ratio for these nuclei.[152] Similar couplings were observed for other carbene−silver complexes, and they are indicative of relatively strong metal−carbon bonds, which translates into none or only a slow exchange of the carbene moiety between silver atoms (at least on an NMR time scale).[152] The coupling constants (J_{AgC}) of the neutral complexes [(carbene)AgX][79,141] are, in general, 50−60 Hz greater than those in the corresponding ionic complexes [(carbene)$_2$Ag]X (Table 3).[175,79,124] A significant number of silver complexes show no splitting[141,176] or no resonance for C2.[78] Lin and co-workers explained the absence of a splitting pattern for the carbenic carbon as being the result of the fluxional behavior of silver complexes on the NMR time scale as proposed in Scheme 2.[177] The transfer of a carbene and bromide between the cation and anion in an ion pair is likely to take place through a carbene and bromide bridge to form two neutral [(carbene)AgBr] species. It was observed that the addition of chloride slows down this dynamic behavior.[178] While the absence of the C2 resonance is not fully understood, poor relaxation of the quaternary carbon or fast exchange could be important contributing factors.

Fairly large one-bond coupling constants are typical for the metal complexes of the N-heterocyclic carbenes. Some representative examples of other one-bond coupling constants of the carbene center to different elements such as silver, rhodium, boron, phosphorus, yttrium, tungsten, platinum, and mercury are summarized in Tables 2 and 3. The magnitude of J_{Pt-C} was used by Nolan's group to characterize the electronic environment of compounds of type *cis*[(carbene)PtCl$_2$(dmso)] (carbene = **11**, **15**, **293**, **21**, and **22**).[179] Because the coupling constants between two nuclei are directly related to the electron density present in the σ orbital of the bond, the authors observed that the trend in the J values (**15** > **11** > **293** > **22** > **21**) correlates well with the σ-donor strength of the carbene, which in turn determines the electronic density of the metal and its π-backbonding ability.[179]

2.1.1. Computational Predictions of Carbene−NMR Chemical Shifts

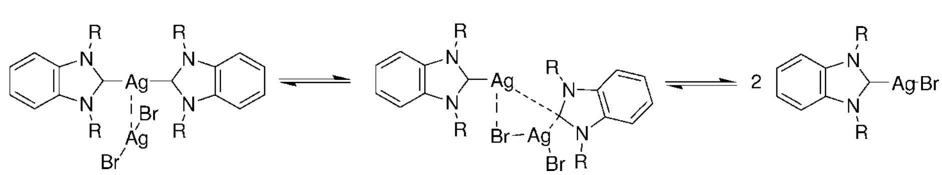
The prediction of NMR shielding tensors by *ab initio* electronic structure methods[193−196] has grown significantly as various research groups have developed methods to deal with the gauge invariance problem and the introduction of electron correlation. Early work in the prediction of shielding constants noted the problem with gauge invariance and addressed it by employing the largest possible basis sets.[197] Modern work in this field began with the paper of Ditchfield in 1972,[198,199] who introduced the concept of using a local gauge origin in place of the origin of the external magnetic vector potential. This method is called the gauge invariant atomic orbital (GIAO) method but was really not employed extensively because of the computational expense. The idea was to expand the wave function in terms of gauge-transformed atomic orbitals, which significantly reduces the size of the basis set. By formulating this in terms of modern second derivative theory, Pulay and co-workers showed how to make the problem more computationally tractable.[200] Before the second derivative formulation of GIAO, the next major step in the prediction of shielding constants after Ditchfield's work was taken by Kutzelnigg[201,202] who intro-

Table 3. One-Bond Coupling Constants (in Hz) and Chemical Shifts (in ppm) for Carbenic Carbon in Selected Metal Complexes

	metal complexes[j]	^1J (δC2)		metal complexes[j]	^1J (δC2)
208[79]	(**25**)AgCl	J_{AgC} = 228/260 (205.9)[g]	**223**[92]	(**12**)PF$_5$	J_{PC} = 291 (161.4)[b]
209[79]	(**26**)AgBr	J_{AgC} = 224/257 (207.5)[d]	**224**[107]	(**21**)PPh	J_{PC} = 87 (184.3)[b]
210[79]	(**28**)AgBr	J_{AgC} = 226/261 (218.4)[d]	**225**[180]	(**1**)Y[N(SiHMe$_2$)$_2$]$_3$	J_{YC} = 50 (190.3)[a]
211[181]	[(**5**)$_2$Ag][BF$_4$]	J_{AgC} = 195/195 (172.2)[d]	**226**[91]	(**2**)Y(tmhd)$_3$	J_{YC} = 33 (194.3)[a]
212[81]	[(**7**)$_2$Ag][BF$_4$]	J_{AgC} = 186/214 (181.9)	**227**[182−185]	*trans*[(**1**)$_2$W(CO)$_4$]	J_{WC} = 88 (183.1)[f]
213[79]	[(**21**)$_2$Ag][AgBr$_2$]	J_{AgC} = 167/193 (207.0)[d]	**228**[182−185]	*cis*[(**1**)$_2$W(CO)$_4$]	J_{WC} = 93 (187.1)[f]
214[79]	[(**25**)$_2$Ag][AgBr$_2$]	J_{AgC} = 174/201 (204.5)[d]	**229**[153]	*cis*[(**18**)W(CO)$_4$(PPh$_3$)]	J_{WC} = 94 (214.1)
215[79]	[(**25**)$_2$Ag][Pd$_2$Cl$_6$]$_{1/2}$	J_{AgC} = 174/201 (205.8)[g]	**230**[67]	(**9**)W(CO)$_5$	J_{WC} = 99 (176.4)[d]
216[79]	[(**28**)$_2$Ag][BF$_4$]	J_{AgC} = 178/205 (215.4)[d]	**231**[134,186]	(**6**)Pt(dvtms)	J_{PtC} = 1361 (181.2)[d]
217[187]	(**2**)BH$_3$	J_{BC} = 52 (167.3)[c]	**232**[134,188]	(**9**)Pt(dvtms)	J_{PtC} = 1350 (180.0)[d]
218[187]	(**5**)BH$_3$	J_{BC} = 55 (166.9)[c]	**233**[189]	*trans*[(**17**)PtCl$_2$(AsEt$_3$)]	J_{PtC} = 1074 (188.6)[h]
219[92]	(**12**)BF$_3$	J_{BC} = 78 (162.8)[a]	**234**[189]	*cis*[(**17**)PtCl$_2$(AsEt$_3$)]	J_{PtC} = 756 (175.1)[h]
220[190]	(**10**)PF$_4$Ph	J_{PC} = 306 (164.7)[b]	**235**[153,154]	(**18**)PtCl$_2$(CO)	J_{PtC} = 1125 (166.5)
221[191]	(**11**)P(BH$_3$)$_2$Ph	J_{PC} = 32 (152.3)[g]	**236**[192]	[(**1**)$_2$Hg]Cl$_2$	J_{HgC} = 2741 (178.2)[e]
222[107]	(**11**)PPh	J_{PC} = 103 (170.0)[b]			

[a] In d_6-benzene. [b] In d_8-THF. [c] In d_8-toluene. [d] In d_3-chloroform. [e] In d_4-methanol. [f] In d_6-acetone. [g] In d_2-methylene chloride. [h] In 75% d_3-chloroform + 20%C$_6$F$_6$ + 5% TMS. [i] Solvent not reported. [j] Abbreviations: tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionato-O,O′; dvtms = divinyltetramethylsiloxane.

Scheme 2



duced the use of localized molecular orbitals (LMOs) to alleviate the gauge problem. Localized orbitals are obtained by a unitary transformation of the canonical orbitals under some criteria. The most common criteria are those of Edmiston, Ruedenberg, and Boys.[203−205] By taking the centroid of charge of the LMO as the origin, one can assign the same gauge factor to each of the atomic orbitals in the LMO; this method is known as the individual gauge localized orbital (IGLO) method. This is, in principle, simpler than the GIAO method in which gauge factors for each atomic orbital in a molecular orbital have different phases. Hansen and Bouman[206] then introduced the localized orbital/local origin (LORG) method about 5 years later. Although the LORG method was derived by a very different approach, it was shown to be very similar to the IGLO method.[207] During the 1980s and early 1990s, careful experimental measurements yielded accurate chemical shifts of atoms in free gas phase molecules, which provides a means of testing the theoretical methods.[208]

The original electronic structure work for the prediction of chemical shifts was done mostly at the Hartree−Fock level. With the development of exchange−correlation functionals that could be broadly applied to a wide range of molecular systems in the late 1980s, coupled with software advances, density functional theory (DFT) has become a common tool in chemistry and has been broadly applied to the prediction of molecular properties. The first calculations of NMR shielding constants were reported at the uncoupled DFT (UDFT) level.[209−214] In the original work, there was no special choice of the gauge origin.[209−211] Friedrich et al.[212] reported GIAO calculations at the LCAO-Xα level with a minimal basis set. Salahub and co-workers[213] reported uncoupled DFT calculations in the individual gauge origin for canonical MO (IGMO) and IGLO approaches. Salahub and co-workers subsequently developed an approximate coupled DFT approach.[214]

A critical issue with the first calculations on the chemical shielding tensor for a carbene was the need to introduce some amount of electron correlation as well as having a computationally efficient method. This is because of the well-known computational issues with the prediction of the singlet−triplet gap in CH_2. The issue is the potential need to include a coupling of the in-plane lone pair on the carbene C with the out-of-plane empty p orbital.[53] It was decided that DFT was an appropriate approach because one could introduce some component of electron correlation. The initial approach was to use the LORG treatment of the gauge invariance issue. The derivation at the DFT level for the LORG treatment of the gauge invariance based on perturbation theory is now provided. An expression for the magnetic shielding tensor σ, which can be expressed as the second derivative of the energy is

$$\boldsymbol{\sigma}^{\mathrm{C}} = \left(\frac{\partial^2 E}{\partial \boldsymbol{\mu} \partial \mathbf{B}}\right)_{\boldsymbol{\mu}=0,\mathbf{B}=0} \tag{1}$$

where $\boldsymbol{\mu}$ is the magnetic moment of a nucleus and $\mathbf{B}$ is an external magnetic field; $\boldsymbol{\sigma}$ is a 3 × 3 tensor that is not symmetric, and $\boldsymbol{\mu}$ and $\mathbf{B}$ are vectors. The Kohn−Sham equations for an unperturbed system are

$$F_0\varphi_{i0} = \varepsilon_0\varphi_{i0} \tag{2}$$

where φ_i is a molecular orbital, ε_i is an eigenvalue, and F is the Kohn−Sham operator. The "0" subscript emphasizes that this equation is solved in the absence of the field $\mathbf{B}$. The Kohn−Sham operator is given by

$$F = -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}} + V_{\mathrm{C}} + V_{\mathrm{XC}} \tag{3}$$

where the first gradient squared term is the kinetic energy of the electrons, V_{ext} is the external potential due to the nuclei (the electron−nuclear attraction), V_C is the electronic Coulomb repulsion, and V_{XC} is the potential due to exchange−correlation effects. Perturbation theory[194] can be used to make the following expansion in powers of the perturbation parameter λ:

$$h = h_0 + i\lambda h_1 + \lambda^2 h_2 + ... \tag{4}$$

where h is the one-electron Hamiltonian with

$$h_1 = \frac{e}{2mci}(\mathbf{B} \times r)\cdot\mathbf{p} \tag{5}$$

and

$$h_2 = \frac{e^2}{8mc^2}(\mathrm{B} \times r)^2 \tag{6}$$

where $\mathbf{B}$ is the magnetic field and $\mathbf{p}$ is the momentum operator. Because the first-order pertubation is complex, we introduce the factor of i to make h real. Both the orbitals and the energy can be expanded in terms of λ such that

$$\varphi_i = \varphi_{i0} + i\lambda\varphi_{i1} + \lambda^2\varphi_{i2} + ... \tag{7}$$

and

$$E = E_0 + i\lambda E_1 + \lambda^2 E_2 + ... \tag{8}$$

This allows the expansion of eq 3 as

$$F = F_0 + i\lambda F_1 + \lambda^2 F_2 + ... \tag{9}$$

At this point, one sets $\lambda = 1$ to obtain

$$\varphi_i = \varphi_{i0} + i\varphi_{i1} + \varphi_{i2} + ... \tag{7a}$$

and

$$F = F_0 + iF_1 + F_2 + ... \tag{9a}$$

The first-order molecular orbitals, φ_{k1}, may be written in terms of the unperturbed orbitals as

$$\varphi_{k1} = \sum_i \varphi_{i0} C_{kj}^{(1)} \tag{10}$$

and $C_{ia}^{(1)}$ can be calculated from the coupled equations

$$\langle\varepsilon_i - \varepsilon_a\rangle C_{ia}^{(1)} = F_{ia}^{(1)} \tag{11}$$

For the shielding tensor, only eq 11 needs to be solved for the so-called "off-diagonal" blocks of $F^{(1)}$. In this notation, the subscripts i, j, k, etc. refer to occupied and a, b, c, etc. to virtual (unoccupied) molecular orbitals. The first-order change in the Kohn−Sham operator is further given by

$$F_{ia}^{(1)} = h_{ia}^{(1)} + \langle \varphi_i | V_{XC}^{(1)} | \varphi_a \rangle \quad (12)$$

where $h_{ia}^{(1)}$ (from the operator given in eq 5) is defined in atomic units as

$$h_{ia}^{(1)} = -\frac{1}{2}\langle \varphi_{i0} | r \times \nabla | \varphi_{a0} \rangle \quad (13)$$

and discussion of the expression for the first-order change in the exchange−correlation potential, $V_{XC}^{(1)}$ is deferred. By using the terms defined above, it is now possible to provide an expression for the magnetic shielding tensor from eq 1. The tensor on center C is given by

$$\boldsymbol{\sigma}^{C}(G) = \frac{1}{2c^2}\sum_i \left\langle \varphi_{i0} \middle| (r-G)\cdot\frac{(r-C)}{|r-C|^3} I - (r-G)\cdot\frac{(r-C)}{|r-C|^3} \middle| \varphi_{i0} \right\rangle - \frac{1}{c^2}\sum_{ia}\left\langle \varphi_{a0} \middle| \frac{(r-C)}{|r-C|^3} \times \nabla \middle| \varphi_{i0} \right\rangle C_{ia}^{(1)} \quad (14)$$

where G is the gauge origin of the system. Equation 14 is correct to second order. However, to evaluate this expression, one needs to solve for the first-order change in the wave function, that is, the $C_{ia}^{(1)}$ from eq 11. This would normally be a time-consuming process, since the terms arising from $V_{XC}^{(1)}$ complicate the expression and generally require an iterative solution. In the present approach, an approximate expression can be obtained by setting $V_{XC}^{(1)}$ to zero. This is justified because the expansion of the density in terms of the magnetic field has no first-order contribution and the contribution from $V_{XC}^{(1)}$ is expected to be small.[213] The neglect of this term leads to the so-called "uncoupled" formalism. In this case, $C_{ia}^{(1)}$ is readily evaluated by dividing the expression for $h^{(1)}$ in eq 10 by the appropriate difference of eigenvalues, $(\varepsilon_i - \varepsilon_a)$.

The treatment of the gauge problem that arises from using a finite-basis set is now considered. Following a procedure to implement the IGLO and LORG methods similar to that described by Handy and co-workers,[207] the density functional expression for the magnetic tensor can be obtained. For the LORG treatment of gauge invariance, the change in the magnetic shielding due to the change in the localized origins, $\mathbf{R}_\alpha$, from the origin θ is

$$\boldsymbol{\sigma}^{C}(\mathbf{R}_\alpha) - \boldsymbol{\sigma}^{C}(\theta) = -\frac{1}{2c^2}\sum_i \left\langle \varphi_i \middle| \mathbf{R}_\alpha\cdot\frac{(r-C)}{|r-C|^3} I - \mathbf{R}_\alpha\cdot\frac{(r-C)}{|r-C|^3} \middle| \varphi_i \right\rangle + \frac{1}{c^2}\sum_{ij}\left\langle \varphi_i \middle| \frac{(r-C)}{|r-C|^3} \times \nabla \middle| \varphi_j \right\rangle \cdot \langle \varphi i | \mathbf{R}_\alpha \times r | \varphi_j \rangle + \frac{1}{c^2}\sum_{ia}\left\langle \varphi_i \middle| \frac{(r-C)}{|r-C|^3} \times \nabla \middle| \varphi_a \right\rangle C_{ia}^{(1)} \quad (15)$$

This expression equals zero if one uses a complete basis set. The shielding tensor at atom C in a system can be expressed as

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^{C}(C) + [\boldsymbol{\sigma}^{C}(\mathbf{R}_\alpha) - \boldsymbol{\sigma}^{C}(\theta)] \quad (16)$$

Therefore, from eqs 11, 14, 15, and 16, for the LORG choice of origin, the expression for magnetic shielding tensor $\boldsymbol{\sigma}^{C}$ is given by

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^{C} = \frac{1}{2c^2}\sum_i \langle \varphi_i | (r-C)\cdot(r-C) I - (r-C)(r-C) | \varphi_i \rangle \frac{1}{|r-C|^3} - \frac{1}{2c^2}\sum_{ia}\left\langle \varphi_a \middle| \frac{(r-C)\times\nabla}{|r-C|^3} \middle| \varphi_i \right\rangle \beta_{ia} - \frac{1}{2c^2}\sum_i \langle \varphi_i | \mathbf{R}_i\cdot(r-C) I - \mathbf{R}_i\cdot(r-C) | \varphi_i \rangle \frac{1}{|r-C|^3} + \frac{1}{c^2}\sum_{ij}\left\langle \varphi_i \middle| \frac{(r-C)\times\nabla}{|r-C|^3} \middle| \varphi_j \right\rangle \langle \varphi_j | R_i \times \nabla | \varphi_i \rangle \quad (17)$$

where

$$\beta_{ia} = \langle \varphi_i | (r-C) \times \nabla - (\mathbf{R}_i \times \nabla) | \varphi_a \rangle \frac{1}{(\varepsilon_a - \varepsilon_i)} \quad (18)$$

Following Hansen and Bouman,[206,215] the gauge origin $\mathbf{R}_i$ is set at the centroid of the LMO when it is not directly bonded to atom C, the reference atom; if it is directly bonded to atom C, $\mathbf{R}_i$ is set at the atomic center.

The initial implementation of this formalism, which was done specifically for the carbenes, was in the program DGauss[216−218] which employs Gaussian basis sets. Localized molecular orbitals were calculated following the Boys criteria[204,205] and the Edmiston−Ruedenberg procedure[203] for actually obtaining the LMOs was used.[219] An implementation of the IGLO approach in DGauss was also done. Comparison of these approaches for CH_4, C_2H_2, and C_2H_4 show that one should be able to predict these values within about 10 ppm (Table 4).

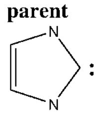
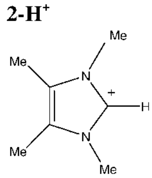
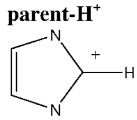
There are a number of issues that must be addressed in the prediction of NMR chemical shifts. A molecular geometry is needed. The NMR chemical shifts are not too sensitive to the optimized geometry but differences in ^{13}C shifts on the order of a few parts per million can easily arise due to the specific molecular geometry. The experimental values are vibrational averages, whereas the computational result corresponds to a fixed geometry at 0 K. For NMR chemical shift calculations, one may also not be able to use a model compound because all of the substituents may need to be present to provide the best comparison with experiment. A computational electronic structure method must be chosen, and today, this is usually DFT with the B3LYP exchange−correlation functional.[220,221] The implementation of B3LYP in the commonly used Gaussian codes has been described.[222] Once the electronic structure method is chosen, one often has to choose a basis set because most molecular calculations of NMR chemical shifts are done with Gaussian-based orbitals rather than plane waves or fully numerical apparaoches. A number of the calculations on carbene chemical shifts have been performed with the 6-31G* basis set. This basis set, although it does work well for a number of organic molecules,[223] is not guaranteed to predict reliable NMR

Table 4. Absolute NMR Shielding Constants (ppm) Calculated at the ULDFT/IGLO and ULDFT/LORG levels

molecule	IGLO/opt[a]	LORG/opt[a]	IGLO/expt[b]	LORG/expt[b]	expt[d]
CH_4	199.5	199.5	200.8	200.8	195.1
C_2H_2	122.3	118.2	115.4	110.6	117.2
C_2H_4	54.7	55.3	52.7	53.3	64.5

[a] Chemical shift at the DFT optimized geometry. [b] Chemical shift at the experimental geometry. [d] Experimental data were taken from refs 213 and 214.

Table 5. DFT Calculations of the Absolute Chemical Shift, σ_{iso}, and the Chemical Shift Tensor Components, σ_{ii}, for Singlet Carbenes as a Function of Method

Molecule	Method	σ_{iso}	σ_{11}	σ_{22}	σ_{33}
CH_2	LDA/TZVP/IGLO	-1853.5	-5298.7	-461.4	199.7
	LDA/TZVP/ LORG	-1807.2	-5155.3	-461.4	195.2
	B3LYP/TZP/GIAO	-1244.9	-3588.9	-354.7	208.9
	BP86/TZP/GIAO	-1135.1	-3249.4	-364.8	208.9
	PW91/TZP/GIAO	-1244.3	-3567.7	-375.2	209.9
	PBE/TZP/GIAO	-1265.3	-3628.6	-377.4	210.2
	B3LYP/6-31G*/GIAO	-1154.1	-3377.7	-284.8	200.3
CF_2	LDA/TZVP/IGLO	-114.1	-436.9	29.0	65.7
	LDA/TZVP/ LORG	-130.5	-446.7	15.6	39.5
	B3LYP/TZP/GIAO	-144.4	-459.5	8.7	17.7
	BP86/TZP/GIAO	-127.2	-407.7	8.7	17.3
	PW91/TZP/GIAO	-132.0	-417.9	6.7	15.2
	PBE/TZP/GIAO	-130.7	-415.5	7.0	16.4
	B3LYP/6-31G*/GIAO	-104.5	-387.7	34.3	39.9
1	B3LYP/TZP/GIAO	-54.3	-252.4	-11.4	100.8
	BP86/TZP/GIAO	-40.1	-219.1	-3.6	102.4
	PW91/TZP/GIAO	-42.5	-224.9	-5.1	102.5
	PBE/TZP/GIAO	-40.8	-221.9	-3.8	103.3
	B3LYP/6-31G*/GIAO	-22.9	-209.5	19.4	121.2
2	LDA/TZVP/IGLO	-12.8	-213.3	4.1	170.3
	LDA/TZVP/ LORG	-22.3	-234.3	5.1	162.4
	B3LYP/TZP/GIAO	-48.8	-234.7	-9.8	98.0
	BP86/TZP/GIAO	-35.4	-201.7	-2.9	98.3
	PW91/TZP/GIAO	-37.6	-206.5	-4.2	97.9
	PBE/TZP/GIAO	-35.8	-203.6	-2.9	98.9
	B3LYP/6-31G*/GIAO	-21.4	-200.5	18.3	117.9
	Expt: CP/MAS	-23.2	-184 (20)	9 (18)	104 (15)
parent	LDA/TZVP/IGLO	-2.4	-158.2	13.3	137.6
	LDA/TZVP/ LORG	-10.4	-174.0	14.0	128.9
	B3LYP/TZP/GIAO	-47.3	-283.8	-8.0	149.8
	BP86/TZP/GIAO	-33.3	-250.9	-1.5	152.4
	PW91/TZP/GIAO	-36.0	-256.4	-3.0	151.4
	PBE/TZP/GIAO	-34.3	-253.4	-1.9	152.5
	B3LYP/6-31G*/GIAO	-17.7	-240.0	23.9	162.9
2-H$^+$	LDA/TZVP/IGLO	66.9	34.2	15.1	151.4
	LDA/TZVP/ LORG	60.6	131.0	0.0	147.9
	B3LYP/TZP/GIAO	46.4	46.6	-11.6	104.2
	BP86/TZP/GIAO	52.4	54.7	-1.2	103.7
	PW91/TZP/GIAO	51.6	54.2	-2.2	102.8
	PBE/TZP/GIAO	52.7	55.3	-0.7	103.6
	B3LYP/6-31G*/GIAO	64.6	64.4	12.1	117.4
	Expt: CP/MAS	49.4	45 (11)	7 (11)	94(11)
parent-H$^+$	LDA/TZVP/IGLO	65.2	68.8	8.9	117.9
	LDA/TZVP/ LORG	59.4	51.8	9.6	116.7
	B3LYP/TZP/GIAO	46.6	14.6	-9.2	134.3
	BP86/TZP/GIAO	52.7	23.4	0.6	134.2
	PW91/TZP/GIAO	51.7	22.4	-0.8	133.6
	PBE/TZP/GIAO	52.8	23.6	0.6	134.3
	B3LYP/6-31G*/GIAO	66.2	37.9	17.6	143.2

chemical shifts, and the Ahlrichs polarized triple-ζ basis sets[224] or the IGLO optimized basis sets[193,194] are recommended. Although one may get reasonable agreement with experiment with an inadequate basis set, this does not imply that the results are necessarily better than those obtained at a higher level. The chemical shifts for the set of compounds **1**, **2**, and the parent with R = R′ = H from the reaction in Scheme 1 have been predicted, as well as those of protonated **2** and protonated parent. The calculated chemical shifts are given in Table 5 with the various components as a function of exchange−correlation functional (PW91,[225,226] BP86,[227,228] PBE[229,230]) and basis set. The results show that it is difficult to predict the chemical shift for the carbene center to within about 30 ppm. Although the B3LYP/6-31G* calculations give good agreement with experiment; improvement of the basis set shows that the results move away from experiment.

An important test of the computational approach is the ability to predict not only the chemical shift but also the chemical shift tensor, which defines the anisotropy of the shift. The chemical shift tensor as a function of computational method is given in Table 5 for CH_2, CF_2, **1**, **2**, and the product in Scheme 1 with R = R′ = H, the so-called parent carbene. The orientation of the chemical shift tensor at the carbene center is shown in Figure 2. The results show that for the Arduengo carbenes, the tensor component, σ_{22}, along the direction of the carbene lone pair is almost zero. The most shielded component of the tensor, σ_{33}, is oriented perpendicular to the molecular plane along the nominally vacant p orbital in the simplest Lewis dot structure for the carbene. The strongly deshielded tensor component, σ_{11}, is normal to the other two components and is oriented in the plane of the ring in part toward the nitrogen atoms. The absolute value for σ_{11} is substantially larger than that for the other two components. The effects of the methyl substituents at N are to decrease the value of σ_{33} relative to the parent. The effects of Me substitution on the other two components is much smaller. The effect of methyl substitution on the ring carbons involved in the C=C bond is not

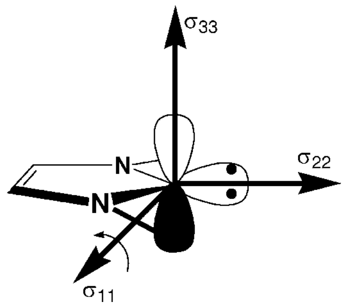


Figure 2. Components of chemical shielding tensor at the carbene center in **2**. Reprinted and modified with permission from ref 244. Copyright 1999 American Chemical Society.

large. The predicted chemical shifts of the model carbene CF_2 shows similar behavior. The strongly deshielded component is σ_{11}, and σ_{22} is near zero. The most shielded component is again σ_{33}, but its absolute value is much smaller than that for the other two components. It should be noted that CF_2 is a ground-state singlet with a large singlet−triplet splitting. CH_2 is a ground-state triplet with a well-known coupling of the carbene lone pair with the vacant out-of-plane p orbital in the singlet. The σ_{11} component in singlet CH_2 is highly deshielded, and the σ_{22} becomes more deshielded as well.

The chemical shift tensor is composed of a paramagnetic component and a diamagnetic component. The diamagnetic components exhibit an orientation dependence at the LDA/LORG level but do not show much of an orientation dependence at the GIAO level as shown in Table 6. The diamagnetic components are all positive and in the more recent calculations decrease in the order $\sigma_{11,d} > \sigma_{22,d} > \sigma_{33,d}$. The paramagnetic component is of opposite sign and shows a larger variation. The values in terms of absolute values follow the same trend as the diamagnetic components so $\sigma_{11,p} < \sigma_{22,p} < \sigma_{33,p}$. The changes in the paramagnetic components are larger than those in the diamagnetic components to give the predicted pattern for the shifts. It is useful to note that the paramagnetic and diamagnetic components almost cancel for σ_{22}.

The paramagnetic contributions correlate in part with the energy of the n → π* transition at the carbene center.[46,231] The perturbation expansion (eqs 17 and 18) shows that the angular momentum operator introduces a coupling of occupied and unoccupied orbitals. For a low-energy transition, as found in the destabilized singlet CH_2 ($^1A_1 \rightarrow {}^1B_1$, ∼1.1 eV), electron density is readily moved from the n lone pair to the out of plane p orbital, effectively creating an electric field. For simplicity, the 11, 22, and 33 directions are labeled as *x*, *y*, and *z*, and thus the electrons move from the lone pair along *y* to the vacant orbital along *z*. Following the right-hand rule, this creates a magnetic vector perpendicular to the *yz* plane leading to a paramagnetic component in the *x* (11) direction. The largest change in density creating the

Table 6. DFT Calculations of the Paramagnetic, $\sigma_{ii,p}$, and Diamagnetic, $\sigma_{ii,d}$, Components of the Chemical Shift Tensor for Singlet Carbenes as a Function of Method

molecule	method	$\sigma_{11,p}$	$\sigma_{22,p}$	$\sigma_{33,p}$	$\sigma_{11,d}$	$\sigma_{22,d}$	$\sigma_{33,d}$
CH_2	LDA/TZVP/LORG	−5431.6	−732.3	−99.3	276.4	270.9	294.5
	B3LYP/TZP/GIAO	−3844.3	−600.9	−39.1	255.5	246.2	248.0
	BP86/TZP/GIAO	−3504.9	−611.5	−39.2	255.4	246.7	248.1
	PW91/TZP/GIAO	−3823.1	−621.7	−38.0	255.4	246.5	247.9
	PBE/TZP/GIAO	−3884.0	−623.8	−37.6	255.3	246.4	247.8
	B3LYP/6-31G*/GIAO	−3633.0	−531.9	−47.8	255.3	247.1	248.0
CF_2	LDA/TZVP/LORG	−711.1	−333.2	−300.5	264.3	348.9	340.0
	B3LYP/TZP/GIAO	−719.0	−242.1	−203.9	259.5	250.9	221.5
	BP86/TZP/GIAO	−668.2	−243.6	−205.4	260.5	252.3	222.7
	PW91/TZP/GIAO	−678.1	−245.4	−206.9	260.2	252.2	222.1
	PBE/TZP/GIAO	−675.7	−245.1	−205.7	260.2	252.2	222.1
	B3LYP/6-31G*/GIAO	−648.8	−217.1	−184.8	261.1	251.4	224.7
1	B3LYP/TZP/GIAO	−526.3	−265.9	−135.4	273.9	254.6	236.2
	BP86/TZP/GIAO	−494.7	−259.3	−135.1	275.6	255.8	237.6
	PW91/TZP/GIAO	−501.1	−261.0	−136.4	276.1	255.9	238.9
	PBE/TZP/GIAO	−498.0	−259.9	−135.8	276.1	256.0	239.1
	B3LYP/6-31G*/GIAO	−479.3	−237.5	−118.4	269.8	256.9	239.6
2	LDA/TZVP/LORG	−441.0	−405.9	−262.0	267.0	419.9	390.9
	B3LYP/TZP/GIAO	−512.5	−265.6	−135.5	277.7	255.8	233.5
	BP86/TZP/GIAO	−481.0	−259.9	−136.6	279.2	257.1	234.9
	PW91/TZP/GIAO	−486.3	−261.4	−138.4	279.7	257.2	236.3
	PBE/TZP/GIAO	−483.4	−260.2	−137.9	279.8	257.3	236.8
	B3LYP/6-31G*/GIAO	−472.0	−240.2	−122.1	271.5	258.5	240.0
parent	B3LYP/TZP/GIAO	−554.4	−261.3	−81.8	270.7	253.3	231.6
	BP86/TZP/GIAO	−522.5	−255.8	−79.7	271.6	254.3	232.1
	PW91/TZP/GIAO	−528.8	−257.5	−82.8	272.3	254.5	234.2
	PBE/TZP/GIAO	−525.8	−256.4	−81.7	272.4	254.5	234.3
	B3LYP/6-31G*/GIAO	−507.2	−231.0	−73.4	267.2	255.0	236.3
2-H^+	LDA/TZVP/LORG	−264.5	−413.7	−323.1	316.3	423.5	439.8
	B3LYP/TZP/GIAO	−227.4	−277.7	−148.3	273.9	266.1	252.5
	BP86/TZP/GIAO	−220.1	−268.4	−149.2	274.8	267.2	252.9
	PW91/TZP/GIAO	−220.0	−269.5	−150.5	274.2	267.3	253.3
	PBE/TZP/GIAO	−219.0	−268.2	−150.1	274.3	267.5	253.7
	B3LYP/6-31G*/GIAO	−206.3	−253.8	−130.4	270.8	265.9	247.8
Parent-H^+	B3LYP/TZP/GIAO	−252.5	−270.0	−110.1	267.1	260.9	244.4
	BP86/TZP/GIAO	−244.2	−261.1	−110.5	267.4	261.7	244.7
	PW91/TZP/GIAO	−245.3	−262.8	−112.2	267.7	262.0	245.7
	PBE/TZP/GIAO	−243.9	−261.5	−111.3	267.6	262.1	245.7
	B3LYP/6-31G*/GIAO	−227.1	−242.6	−97.0	265.0	260.2	240.2

largest electric field will be from the two electrons in the carbene C lone pair to the vacant orbital on that center. The largest effective electric field will create the largest effective magnetic field and the largest paramagnetic shift component. As the singlet becomes more stable, the first allowed transition energy increases so that the promotion of electrons from the lone pair on the carbene center to the empty out-of-plane p orbital becomes less likely energetically. This leads to a decrease in the paramagnetic in-plane component just as observed. The excitation energy for the $^1A_1 \rightarrow {}^1B_1$ transition in CF_2 is ~4.3 eV and the gas-phase UV spectrum for **2** shows a strong absorption at 236 nm and a weaker shoulder at ~270 nm. If the weak shoulder is assigned to the n → π* transition, the excitation energy would be ~4.6 eV. A second component to consider is how much electron density is in the out-of-plane p orbital in the ground state due to π donation from the R substituents. No π back-bonding is expected for R = H so the out of plane p orbital is vacant, which would generate the largest electric field and the largest value for $\sigma_{11,p}$. The significant amounts of π back-donation in CF_2 and **2** make the lone pair less accessible reducing the magnitude of $\sigma_{11,p}$. Thus there is a combination of the possibility of generation of an electric field (excitation energy) and the magnitude of the field (electron repulsion due to back-bonding to the empty p orbial on the carbene) that governs the size of $\sigma_{11,p}$.

The out-of plane σ_{33} (z) component is generated by rotation of the n lone pair on the carbene C into the occupied C(carbene)−R bonds. This is mixing of two doubly occupied electrons, which is repulsive, so one would expect the resulting electric field to be smaller yielding a smaller magnetic field. This mixing is in the xy plane resulting in a magnetic field along z. Thus the paramagnetic σ_{33} component is expected to be the smallest of the three components. The size of σ_{33} would be expected to correlate with the electronegativity of R. The larger the electronegativity difference between C and R for R more electronegative, the more the C−R bond is polarized toward R. There is less repulsion between C−R σ bonds and the lone pair on mixing leading to a larger electric field and a larger magnetic field in the z direction. When C is more electronegative than R, there is more density near C, so the electric field is lower and one gets a smaller magnetic field in the z direction. For the small sample size we have, this is exactly what is predicted. The largest value for $\sigma_{33,p}$ is found for R = F with the largest electronegativity difference and the smallest is for R = H where C is more electronegative than H.

The $\sigma_{22,p}$ component is expected to have an intermediate value. It results from rotating the C−R σ bond density into the empty p orbital. These electrons are more stable than the lone pair and hence less available to generate the effective magnetic field. However, there is less repulsion because the mixing is with an empty or partially occupied orbital so that the magnetic field in the y (22) direction should be larger than that in the z (33) direction. The size of the electric field should correlate with the electronegativity of R with a larger value expected for a less electronegative R because there are more electrons around the C in the C−R σ bond. It should also correlate with the amount of π back-donation to C from R. This is exactly what is predicted by the calculations. The largest value of $\sigma_{22,p}$ is for CH_2, which has the most density around C in the C−R bond and the least amount of π back-donation. The values for $\sigma_{22,p}$ for CF_2 and **2** are comparable.

Table 7. NICS(0,1) for Benzene, 1, 2, and the Parent Carbene (in ppm)[a]

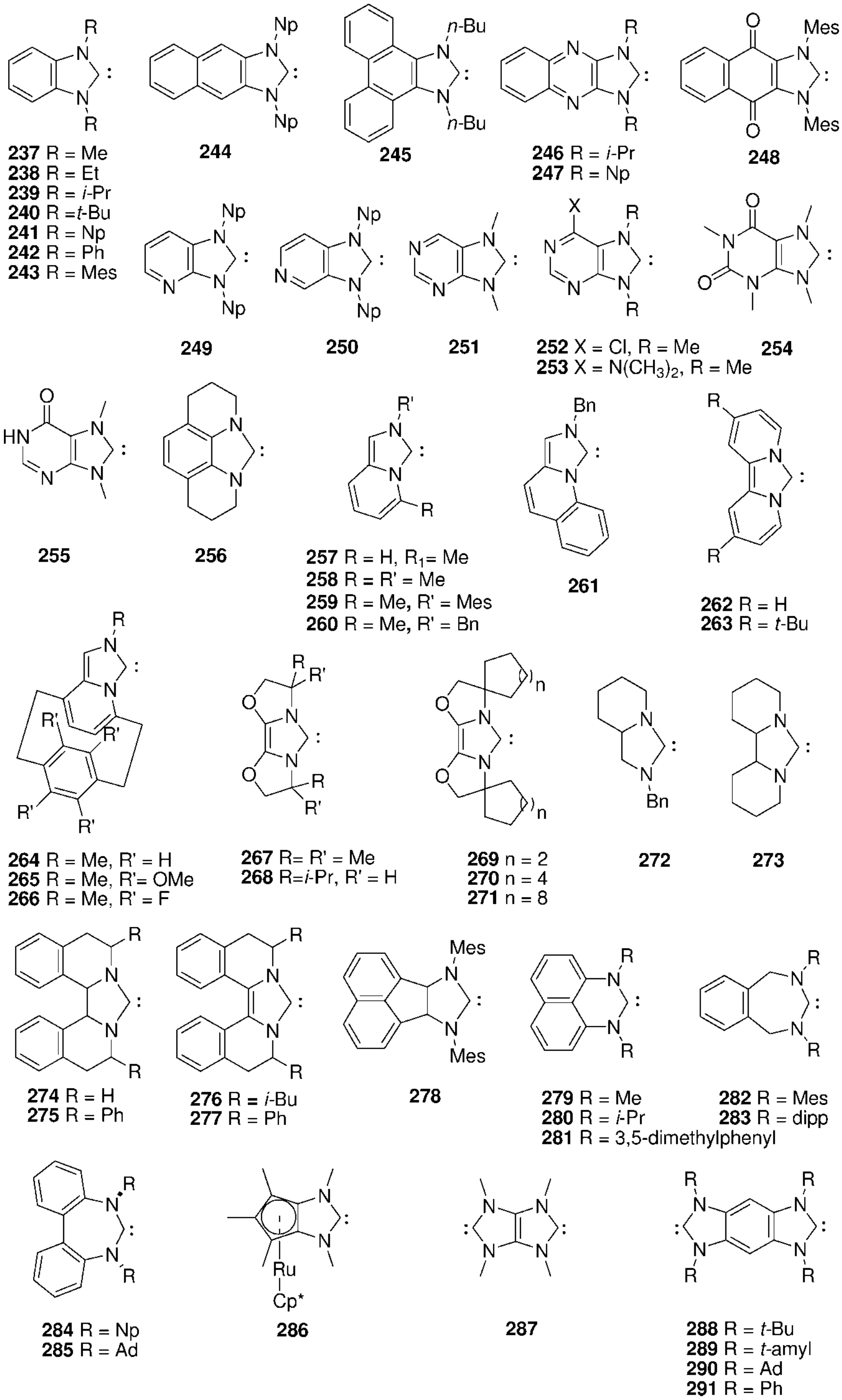
shift	benzene	**1**	**2**	parent
		NICS(0)		
σ_{iso}[b]	−8.8	−13.7	−12.8	−14.0
σ_{11}	5.8	26.2	26.2	21.3
σ_{22}	5.8	7.6	8.6	8.7
σ_{33}	14.8	7.1	3.7	12.0
$\sigma_{11,p}$	−17.1	−11.9	−14.1	−11.0
$\sigma_{22,p}$	−17.1	−20.2	−22.3	−17.3
$\sigma_{33,p}$	−19.9	−23.4	−36.3	−20.0
$\sigma_{11,d}$	22.9	38.1	40.4	32.3
$\sigma_{22,d}$	22.9	27.9	30.9	25.9
$\sigma_{33,d}$	34.7	30.5	40	32.1
		NICS(1)		
σ_{iso}	−10.4	−10.1	−9.8	−10.4
σ_{11}	1.2	5.2	5.3	1.5
σ_{22}	1.2	−0.3	0.6	0.8
σ_{33}	28.8	25.3	23.4	28.6
$\sigma_{11,p}$	−2.5	−0.4	−2.7	−0.9
$\sigma_{22,p}$	−2.5	−2.9	−4.6	−0.2
$\sigma_{33,p}$	1.1	−0.1	−5.0	4.0
$\sigma_{11,d}$	3.7	5.6	8.0	2.4
$\sigma_{22,d}$	3.7	2.6	5.2	1.0
$\sigma_{33,d}$	27.7	25.4	28.4	24.5

[a] Calculated at the center of the ring at the GIAO/B3LYP/TZVP level. For all molecules, the out of plane is σ_{33}. For the carbenes, see Figure 2 for axis orientations. [b] The sign of σ_{iso} has been switched for consistency with other reported NICS shifts. The signs of the components have not been switched. NICS(1) is obtained at 1 Å above the plane.

It is clear that further work is needed to make accurate predictions of the chemical shifts of these heterocarbenes. One will have to look at even larger basis sets as well as calculations at the correlated molecular orbital theory level[232] or with improved exchange−correlation functionals,[233] perhaps with a focus on improving the HOMO−LUMO gaps.[234,235] The role of the individual σ and π components could also be further investigated following the localized and canonical molecular orbital NICS approaches developed by Schleyer and co-workers[236] or the ring current approaches of Steiner and Fowler.[237,238]

Nucleus-independent chemical shifts (NICS)[236,239−242] calculated at the approximate center of a ring or above it have been used extensively in the analysis of aromaticity. For benzene at the B3LYP/6-31+G* level, the NICS value at the origin is −9.7 ppm, and for **1** it is −12.7 ppm.[243] Although it is tempting to argue that the NICS(0) value for **1** is larger than that of benzene so **1** is more aromatic, it must be remembered that one has to look at all of the shift tensor components to see which term is contributing the most to the NICS(0) value. It is clear that there is a substantial difference between benzene and the three carbenes, **1**, **2**, and the parent, even though the NICS(0) shifts of the carbenes are even more negative as shown in Table 7. The NICS value is reported as the negative of the actual value. In benzene, the NICS(0) shift is dominated by the out of plane σ_{33} due to the large diamagnetic component. The in-plane σ_{11} and σ_{22} are comparable and less than half the size of σ_{33}. The paramagnetic components are about equal for all three directions. Schleyer and co-workers have analyzed the total tensor components for the NICS π orbitals for benzene previously.[236] In the carbenes, the NICS(0) value is dominated by the in-plane σ_{11}, the component perpendicular to the axis passing through the carbene lone pair, just as found for the chemical shift tensor for the carbene carbon. The larger NICS value in the carbenes is due to a small

Chart 1



paramagnetic shift coupled with a large diamagnetic component for σ_{11}. This is exactly opposite to the carbene C chemical shift tensor because the paramagnetic shift in the carbenes is smallest for σ_{11} in contrast to being the largest at the carbene center. The results show that the NICS(0) value for the carbenes arises from a completely different mechanism from that in benzene and that NICS(0) values should not be used to compare aromaticity for two different types of molecules if they arise from different mechanisms, which is obviously the case here. The NICS(1) values are obtained at 1 Å above the plane on a line passing through the point where NICS(0) was evaluated. The NICS(1) values are all about equal for benzene and the three carbenes, and NICS(1) for the carbenes decreases with respect to NICS(0), whereas NICS(1) for benzene increases with respect to NICS(0). The NICS(1) values are all dominated by the out-of-plane σ_{33} diamagnetic component. Further work will be needed to evaluate the NICS values for the carbenes and the information they provide about the bonding in these novel compounds.

2.2. Fused Diaminocarbenes

It was recognized that expanding on the structural and electronic diversity of Arduengo-type carbenes had the potential to extend the ability to fine-tune their electronic properties, which is of prime importance for the design of tailored catalysts with enhanced activities. One of the strategies used to modify the electronic and steric proper-

Table 8. Chemical Shifts (in ppm) for Fused Cyclic Diaminoarbene and Their Corresponding Azolium Salts

carbene	δC2	azolium salt (X)	δC2
237[251]	224.9^{i,k}	(Cl)[273]	143.0^{e}
238[251]	225.3^{i,k}		
240[250]	224.7^{a}	(Cl)[250]	139.1^{e}
241[245]	231.5^{c}	(BF_4)[250]	143.6^{e}
244[256]	239.9^{a}	(Cl)[256]	148.1^{g}
245[257]	225.1^{b}	(BF_4)[257]	141.6^{e}
248[258]	232^{a}	(Cl)[258]	147.9^{d}
249[262]	235.23^{a}	(PF_6)[262]	148.4^{g}
250[262]	235.76^{a}	(PF_6)[262]	145.8^{g}
257[274]	209.7^{b}	(I)[274]	127.0^{f}
258[259]	206.9^{a}	(I)[259]	133.6^{d}
259[259]	206.9^{a}	(PF_6)[259]	*h,j*
260[259]	206.2^{a}	(Br)[259]	135.6^{d}
261[259]	208.7^{a}	(Cl)[259]	134.0^{g}
262[260]	197.8^{b}	(PF_6)[275]	116.1^{e}
263[260]	196.3^{b}	(Br)[274]	114.5^{e}
268[276]	195.8^{b}	(OTf)[276]	116.3^{d}
280[35,265]	241.7^{a}	(Cl)[265]	149.9^{b}
288[272]	228.3^{a}	(BF_4)[277]	142.9^{e}
289[272]	230.2^{a}	(Cl)[272]	144.3^{e}
290[272]	227.6^{a}	(BF_4)[277]	142.9^{a}

^{a} In d_6-benzene. ^{b} In d_8-THF. ^{c} In d_8-toluene. ^{d} In d_3-chloroform. ^{e} In d_6-DMSO. ^{f} In d_3-acetonitrile. ^{g} In d_4-methanol. ^{h} In d_6-acetone. ^{i} Solvent not reported. ^{j} Not assigned. ^{k} Low temp, −50 °C.

ties of these carbenes is annulation by aromatic or nonaromatic carbo- and heterocycles. Hahn et al. were the first to report the isolation of a stable benzimidazolin-2-ylidene (**241**).[245] This carbene exhibits the topology of an unsaturated imidazol-2-ylidene but has the electronics of the saturated imidazolin-2-ylidenes.[245] The ambivalent nature of this carbene is corroborated by a chemical shift of 231.5 ppm, a value that does not fall in the range normally observed for the unsaturated N-heterocyclic carbenes, but it is observed instead in the range typical for the saturated carbenes. Since Hahn's report, key advances have been made in the areas of benzannulated (e.g., **237**−**243**,[245−252] **256**,[253] and **282**−**285**[79,254,255]), extended annulated (e.g., **244**,[256] **245**,[257] **248**,[258] and **257**−**263**[39,259,260]), heterocycle annulated (e.g., **246**,[81] **247**,[81] **249**−**255**,[10,261,262] and **267**−**271**[263]), metallocene annulated (e.g., **286**),[264] and other carbocycle annulated diaminocarbenes (e.g., **272**−**281**[10,35,265−270]), as well as Janus-type biscarbenes (e.g., **287**−**291**[271,272]) (Chart 1). ^{13}C NMR spectroscopic data of the free carbenes and their corresponding protonated precursors, where available, are summarized in Table 8.

Annulation can have a significant impact on the stability[251,278,279] and the electronic nature of Arduengo-type carbenes.[10,280] While nonannulated imidazol-2-ylidenes are monomeric,[14,17,244] sterically less crowded benzimidazol-2-ylidenes dimerize easily, a characteristic reaction for nonbulky saturated N-heterocyclic carbenes.[251,278,281] Upon dimerization of the N-methylated derivative **237**, the resonance of the former carbene center shifts upfield to 121.0 ppm, an upfield shift of about 104 ppm compared to free carbenes.[282] Sterically demanding substituents on nitrogens have a stabilizing effect on fused diaminocarbenes. For example, while the benzannulated carbene **241** is stable and distillable[245,283,284] and the naphtho[2,3-*d*]imidazol-2-ylidene **244** is isolable,[256] the quinoxaline-annulated carbenes **246** and **247** are not detectable even at low temperatures (− 50 °C).[66] A decrease of the π-charge density of the C2 as a result of an increased transfer of π-density from the divalent carbon to the more extended annulated π-system seems to be the main reason for destabilization of the naphtho- and quinoxaline-annulated carbenes in comparison with their non- and benzannulated counterparts.[81,256,66] The decreasing stability in the non-, benzo-, and naphtho-annulated imidazol-2-ylidene series is accompanied by an increased deshielding of the carbene center (δ = 217, 231.8, and 239.9 ppm for **7**,[66] **241**,[245] and **244**,[256] respectively). Recently reported phenanthro[9,10-*d*]imidazol-2-ylidene **245** revealed a signal of the N*C*N carbon at 225.1 ppm, an indication that the π-charge density is comparable to that of benzimidazol-2-ylidenes **237**−**240**.[257]

The uniformity of the NMR data within a single series of fused carbenes (e.g., **237**−**243**) suggests that the electronic properties of the carbene are not significantly affected by variation of the steric bulk of the nitrogen substituents. In contrast, comparison of the chemical shifts of the carbenic carbon for the identically substituted carbenes **6**, **20**, **240**, and **288** reveals a decrease in the chemical shift as follows: imidazolin-2-ylidene **20** (238.2 ppm)[71] > bis(benzimidazol-2-ylidene) **288** (228.3 ppm)[272] > benzimidazol-2-ylidene **240** (224.7 ppm)[250] > imidazol-2-ylidene **6** (213.2 ppm), which correlates well with an increase of the aromatic stabilization of the imidazole moiety. Similar downfield shifts of the carbenic carbon were observed by annulation of six-membered diaminocarbenes (**280** vs **24**).[35,265] Small downfield shifts are observed going from benzimidazol-2-ylidene **241** (δ = 232 ppm)[245] to pyrido-annulated imidazol-2-ylidenes **249** and **250** (δ = 235.2 and 235.8 ppm).[262]

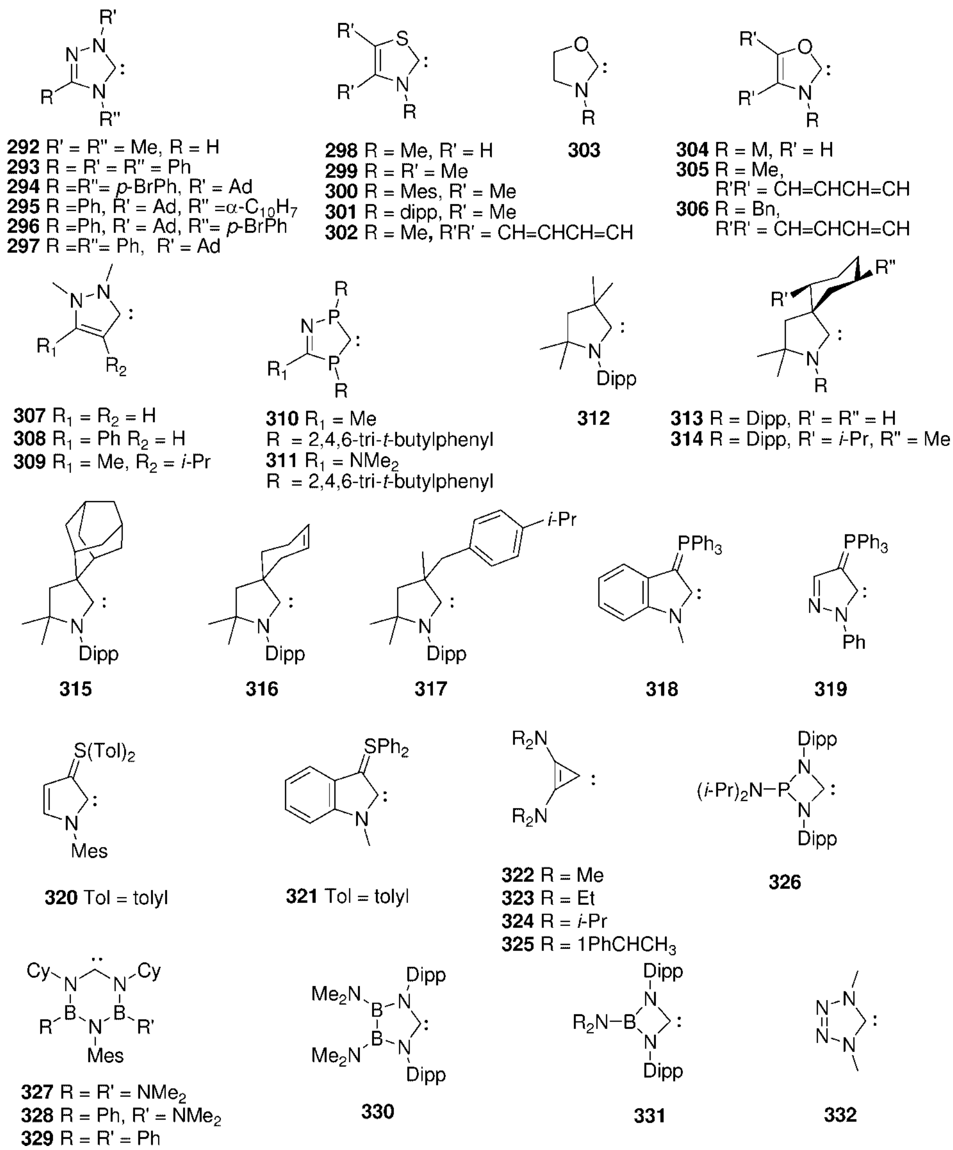
High-field shifts of the carbenic resonance are observed for the bipyridocarbenes **262** (δ = 197 ppm) and **263** (δ = 196 ppm), presumably due to an increased electron density at the carbene center due to conjugation of the empty p_π orbital with the conjugated 14-electron π-system.[260,285,286] A position between bipyridocarbenes and the 6π-electron imidazol-2-ylidenes is taken by 10π-electron monopyridocarbenes **257**−**260** and the related imidazo-[1,5-*a*]quinoline-3-ylidene **261** (206−209 ppm).[259,274] The upfield shift of the oxazolidine-annulated carbene **268** (δ = 195.8 ppm) as compared with nonannulated imidazol-2-ylidenes reflects the influence of the π-donating substituents in the 4 and 5 positions of the imidazole moiety on the divalent carbon and makes this compound, like pyridocarbenes, electron-rich.[276] Upon complexation of the annulated carbenes to different Lewis acids, the essential trends remain the same as in the free carbenes. For example, the chemical shifts of the carbenoid center in complexes of type [(carbene)$Cr(CO)_5$] decrease in the following order: imidazolin-2-ylidenes (217−225 ppm),[108,112] benzimidazol-2-ylidenes (200−210 ppm),[252,287] imidazol-2-ylidenes (186−200 ppm),[113,114,287] and bipyridocarbenes **262** and **273** (168−171 ppm).[260]

2.3. Other Cyclic Carbenes

The introduction of donor atoms other than nitrogen, the modification of the number of heteroatoms in the ring, or the adjustement of the ring size are other strategies used to achieve variation of the steric or electronic properties of heterocyclic carbenes. The isolation of a considerably large number of stable nucleophilic carbenes with novel architectures has proven that the carbene backbone can be considerably modified without significant loss of stability (Chart 2).

Enders and co-workers introduced for the first time an extra heteroatom into the backbone of an unsaturated diaminocarbene. They obtained the first crystalline triazole-derived carbene, **293**, by endothermic elimination of methanol from the corresponding 5-methoxytriazole in the solid

Chart 2



state.[288] The alteration of the carbene backbone does not have a significant effect on the chemical shift of the carbene center (δ = 214.6 ppm; Table 9), a value that is only 5 ppm downfield of that for 1,3,4,5-tetraphenylimidazol-2-ylidene (**10**).

Attempts to replace the nitrogen atoms in Arduengo-type carbenes with other heteroatoms were carried out shortly after the first report on stable nucleophilic carbenes appeared. In 1997, Arduengo et al. described the first stable thiazol-2-ylidene, **301**.[289] This carbene was synthesized through deprotonation of the corresponding thiazolium chloride and is considerably more reactive than its diaminocarbene counterparts.[289] The chemical shift of the NCS carbon in **301** is 254.3 ppm, over 34 ppm downfield from the same carbon of imidazol-2-ylidenes. In the presence of a protic acid catalyst, **301** exists in equilibrium with its dimer. Upon dimerization, the resonance for the former carbene center is shifted upfied by 146.5 ppm. Even though free ylidenes derived from the oxazoline, oxazole, benzoxazole, or pyrazole frameworks are not stable, several examples of metal complexes incorporating carbenes **303**−**309** were reported.[10,114,290−301] The chemical shifts for the carbenic carbons in these metal complexes range between 169 and 225 ppm, with benzoxazole carbene **306** at the higher end of the range.

A stable phosphorus heterocyclic carbene **310** has been reported recently by Bertrand and co-workers.[302] Carbene **310** is a phosphorus analogue of Ender's carbene **293**. The carbene center is stabilized by sterically demanding phosphorus substituents. The ^{13}C NMR signal for the PCP carbon of **310** (δ = 184 ppm, pseudotriplet, J_{PC} = 147 Hz) is strongly deshielded compared with the same carbon in the corresponding phosphonium salt (δ = 119 ppm), and it is observed at slightly higher field than the analogous signals of N-heterocyclic carbenes.[302] The ^{13}C NMR signal for the related carbene **311** resonates at 187.3 ppm as a doublet of doublets (J_{PC} = 127, 153 Hz).[303]

Another interesting modification of the carbene skeleton is the replacement of one of the electronegative amino groups in cyclic five-membered diaminocarbenes by an alkyl group, thus giving rise to nucleophilic (alkyl)(amino)carbenes. The first stable cyclic alkylaminocarbene ligands, **312**−**314**, were reported by Bertrand's group in 2005.[304] Several other stable alkylaminocarbenes with different architectures (**315**−**317**) were reported soon after.[305,306] The range of chemical shifts for the carbenic carbon in **312**−**317** extends from 304.2 to

Table 9. Chemical Shifts (in ppm) and Coupling Constants (in Hz) of the Carbenic Carbon for Other Cyclic Carbenes and Their Corresponding Protonated Precursors

carbene	δC2 (J)	salt (X)	δC2 (J)
293[288]	214.6[a]		
294[328]	210.1[a]		
295[328]	212.7[a]		
296I[328]	210.6[a]		
297[328]	210.7[a]		
301[289]	254.3[b]	(Cl)[289]	157.6[e]
310[302]	184.4[b] (J_{PC} = 147)	(OTf)[302]	119.3[d] (J_{PC} = 51, 44)
311[303]	187.3[a] (J_{PC} = 127, 153)	(OTf)[303]	115.4 (J_{PC} = 65, 7)
312[304]	304.2[b]	(OTf)[304]	192.2[f]
313[304]	309.4[b]	(OTf)[304]	191.3[f]
314[304]	319.0[b]	(OTf)[304]	192.6[d]
315[305]	322.7[a]		
316[306]	313.0[a]	(HCl_2)[306]	192.5[f]
317[306]	313[a]	(HCl_2)[306]	192.8[f]
319[309]	218.8[b] (J_{PC} = 51.2)	(BF_4)[309]	*d*
324[311]	185.5[a]	(BPh_4)[311]	133.2[d]
325[312]	188.2[a]	(BF_4)[312]	102.8[d]
326[322]	285.0[c] ($^2J_{CP}$ = 13)	(OTf)[322]	163.0[g] ($^2J_{CP}$ = 17)
327[325]	282.9[b]	(Br)[325]	165.0[d]
328[325]	281.5[b]	(Br)[325]	165.0[d]
329[325]	281.6[a]	(Br)[325]	163.6[d]
330[324]	303.6[b]	(OTf)[324]	173.5[a]
331[323]	312.6[a]	($B(C_6F_5)_4$)[323]	182.7[d]

[a] In d_6-benzene, [b] In d_8-THF, [c] In d_8-toluene, [d] In d_3-chloroform, [e] In d_6-DMSO, [f] In d_3-acetonitrile, [g] In d_2-methylene chloride, [i] Solvent not reported.

322.7 ppm, a significant downfield shift in comparison with the saturated cyclic diaminocarbenes **17**−**22** ($\Delta\delta$ = 60−80 ppm). A similar trend was noted by the replacement of one of the nitrogen atoms of the acyclic diaminocarbenes with other elements such as sulfur, oxygen, carbon, or silicon (see section 3). Upfield shifts of 36.8−129 ppm were observed by coordination of **312**−**317** to a metal center.[304−307] Another interesting alkylaminocarbene, **318**, was reported recently by Kawashima's group.[308] This carbene features a phosphorus ylide moiety as a carbene-stabilizing substituent, and it has the highest electron-donating ability among the Arduengo-type carbenes known to date. Even though the free carbene was too unstable to be characterized, a series of metal complexes of **318** were reported. The ^{13}C NMR chemical shift for the carbene center ranges between 187 and 201 ppm by coordination to rhodium. The related carbene **319**, reported by Fürstner et al., displays a characteristic carbenic signal at 218.8 ppm.[309] The amino(sulfur-ylide)carbenes **320** and **321** were characterized only as metal complexes.[309,310]

Among the most striking examples of backbone modification of the Arduengo-type carbenes are the two π-electron cyclopropenylidenes **322**−**325**. Although metal complexes of these carbenes have been known for many years, the first stable cyclopropenylidene (**324**) was isolated as a "bottlable" species only recently by Bertrand's group starting from the corresponding cyclopropenium salt.[311] The carbene carbon has a chemical shift, as predicted theoretically, at 185.5 ppm, 52 ppm downfield of the shift of the same carbon center in the starting material (δ = 133.16 ppm). The other two carbons in the ring have a chemical shift at 159 ppm vs 99 ppm in the starting cyclopropenium salt.[311] The chiral carbene **325**, reported by Tamm et al., shows characteristic signals at 160.8 ppm (*C*N) and 188.2 ppm for the carbenic center.[312] Both **324** and **325** display dynamic ^{1}H NMR and ^{13}C NMR

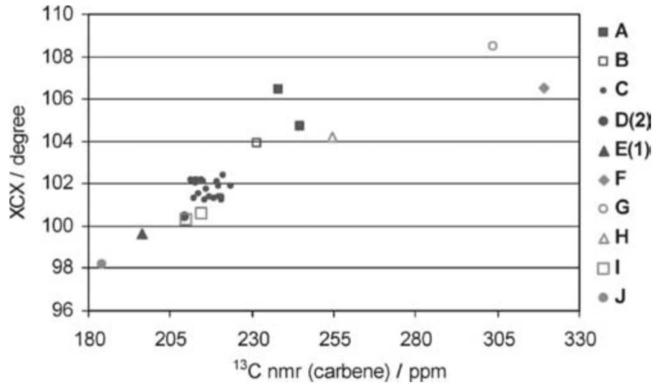


Figure 3. Plot of the X−C$_{carbene}$−X angles of five-membered ring carbenes against the chemical shift of the carbene ^{13}C NMR signal (X = C, N, P, S), where A = **20**, **21**; B = **251**; C = **3**, **6**, **8**, **10**, **11**, **12**, **14**, **15**, and **16**; D = **257**; E = **263**; F = **314**; G = **330**; H = **301**; I = **294**; and J = **310**. Reprinted from ref 274 by permission of The Royal Society of Chemistry.

behavior, due to the hindered rotation about the N−C$_{ring}$ bonds as a result of the weak π-donation from the amino groups to the electron-deficient ring. The estimated barriers of rotation around C−N bonds are between 52 and 53 kJ/mol.[311,312] Upfield shifts of up to 79 ppm were observed by complexation of **324**.[313−321] By complexation of **325** to silver, the ^{13}C NMR resonance of the former carbene center is shifted upfield by about 42 ppm (δ = 146.2 ppm).[312]

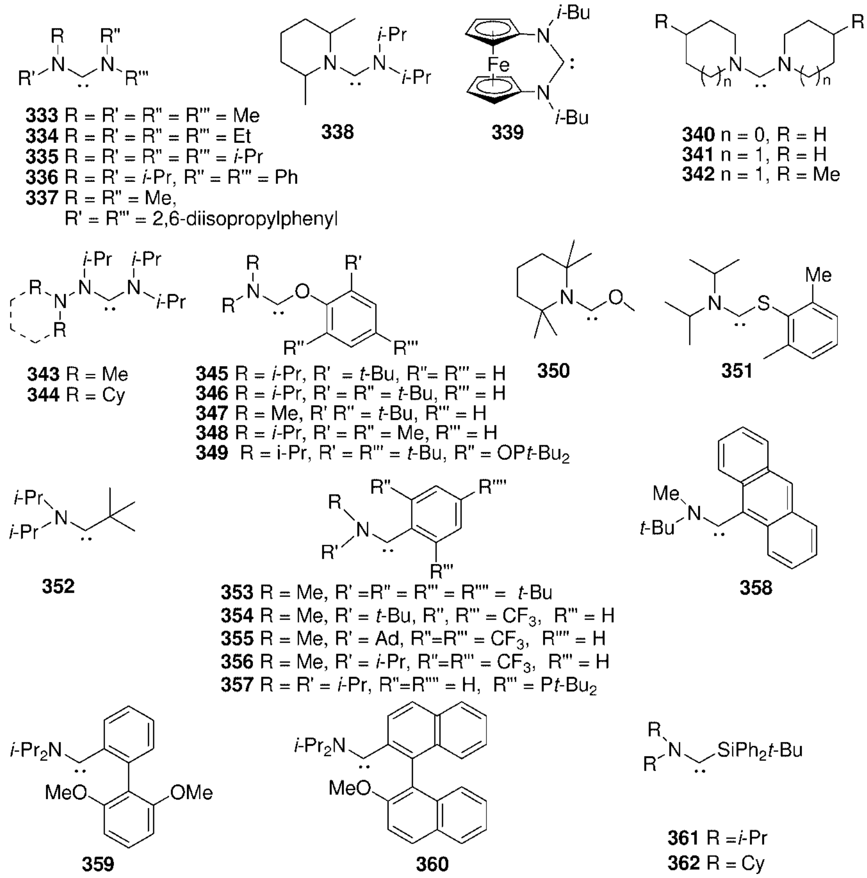
Recently, a number of cyclic diaminocarbenes with fully inorganic backbones (**326**−**332**) were reported.[10,298,322−327] Experimental evidence shows that these modified carbenes display typical nucleophilic behavior.[298,324,325] The nonplanar four-membered carbene **326** has a pyramidal phosphorus backbone, and it is stable at room temperature.[322] The ^{13}C signal for the carbene center appears at 285 ppm as a doublet ($^2J_{CP}$ = 13 Hz). Similar chemical shifts were observed for the six π-electron six-membered N-heterocyclic carbenes **327**−**329** (δ = 282.9, 282.5, and 281.6 ppm for **327**, **328**, and **329**, respectively).[325] These carbenes are perfectly stable at room temperature in solution and solid state, and they form stable transition metal complexes.[325] Upfield shifts of 40−60 ppm were observed for the carbenic atoms by coordination to a rhodium center. Significantly higher chemical shifts were observed for the carbenic centers of the five-membered ring carbene **330** (δ = 303.6 ppm)[324] and the four π-electron four-membered heterocyclic carbene **331** (δ = 312.6 ppm).[323] Free tetrazolinylidene **332** is not stable, but it forms stable complexes with iron, chromium, and rhodium in which the chemical shifts of the carbenic center atoms range between 178.8 and 186.9 ppm.[10,326,327]

On the basis of the XCX angles of different structurally characterized five-membered ring carbenes, Nonnenmacher et al. observed a good correlation between this angle and the ^{13}C NMR chemical shift of the carbene (Figure 3).[274] No other structural parameter was found to exhibit an approximate linear correlation at low shifts that flattens out at higher chemical shifts.

3. Acyclic Carbenes

Bis(diisopropylamino)carbene **335** (Chart 3) is the first stable acyclic diaminocarbene ever isolated.[329] The isolation of this carbene by Alder et al. demonstrated for the first time that neither the geometric constraints nor the ring aromatic stabilization are necessary to obtain stable diaminocarbenes.

Chart 3



The NCN angle of **335** (121.0°) is much larger than that of any cyclic imidazol(in)-2-ylidene. The ^{13}C NMR chemical shift of the carbene center at $\delta = 255.5$ ppm is 45 ppm downfield of the carbene carbon chemical shift of the unsaturated imidazol-2-ylidene **4**[62] and 18.7 ppm downfield of that for imidazolin-2-ylidene **19**.[71] This shift for **335** was correlated with the increased NCN angle.[329] Recently, Bertrand reported the generation and characterization in solution at low temperature (−80 °C) of the unhindered bis(dimethylamino)carbene **333**. Generated from 2-chloro-1,1,3,3-tetramethylformamidinium chloride and $Hg(SiMe_3)_2$, this carbene has a half-life of a few hours at 0 °C. The carbene carbon of **333** resonates at 259.7 ppm, a value that is substantially higher than the chemical shifts observed experimentally by Alder for its corresponding lithium complexes (238.4−244.0 ppm),[64] and very close to the theoretically calculated chemical shifts (246.9−265.1 ppm).[64,231] Similarly, by treatment of a lithium complex of **334** with 1 equiv of [2.1.1]cryptand, a downfield shift of the carbene carbon from 244 to 252 ppm was observed due to the formation of the free carbene. Once formed, this carbene is stable for at least a week in solution at room temperature.[330] Similar chemical shifts were reported for the carbenes **337** and **338** and for the diaminocarbene[3]ferrocenophanes **339** ($\delta = 249$, 259, and 260 ppm, respectively).[331] Significant upfield shifts of the carbene carbon in comparison with carbenes **333**−**339** were reported for bis(*N*-pyrrolidinyl) and bis(*N*-piperidinyl) carbenes **340**−**342** ($\delta = 237$−241 ppm).[10,125,332] Even greater upfield shifts were reported for aminohydrazinocarbenes **343** and **344** ($\delta = 228.9$ and 228 ppm, respectively).[333]

The replacement of one of the nitrogen atoms of the acyclic diaminocarbenes with other elements such as sulfur, oxygen, carbon, or silicon results in large downfield shifts of the carbenic carbon. The chemical shifts of the acyclic NE-aminocarbenes (E = O, S, C, Si; **345**−**362**) are summarized in Table 10 and follow an increasing downfield shift going from oxy- to thio- to alkyl/aryl- and, finally, to silyl-amino carbenes. The carbene chemical shifts of the acyclic aminooxycarbenes **345**−**350** are in the range 263−278 ppm,[334,335] while that of the aminothiocarbene **351** is $\delta = 297$ ppm.[334] The range of chemical shifts for alkyl-amino carbene **352** and aryl-amino carbenes **353**−**360** extends from 299 to 326 ppm.[38,336−339] The signals observed at 377.3 and 380.7 ppm for amino-silyl carbenes **361** and **362** are the most deshielded signals reported so far for a carbenic center.[340] *Ab initio* calculations at the B3LYP/6-31g* level on **361** and **362** suggest a negligible interaction between the carbene lone-pair and the vacant σ^*-orbital of silicon. The stabilizing effect of the amino group toward the carbene center is very efficient, such that there is no need for a second electron-active group.[340]

Following on the original discussion of Arduengo et al.,[46] Alder et al. calculated that the paramagnetic contribution to the shielding tensor at the carbene nucleus plays an important role in the chemical shift changes upon substitution in NE-aminocarbenes (E = N, O, S, Se).[231] They attributed the origin of the large paramagnetic contribution to a smaller singlet−triplet gap brought about by relatively poorer $C2(p_\pi)-E(\pi)$ interaction in carbenes with an oxygen, sulfur, or selenium substituent vs nitrogen. A weaker $C2(p_\pi)-E(\pi)$ interaction would result in a reduced donation of electron density from $E(\pi)$ into the carbene p_π orbital.[231]

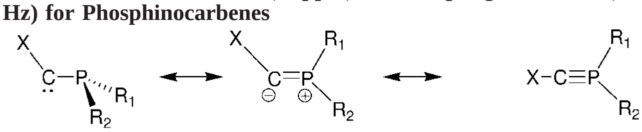
Bertrand was the first to observe that flash thermolysis of α-diazophosphines under vacuum affords compounds that, depending on the nature of the reagents, can behave as either

Table 10. Chemical Shifts (in ppm) and Coupling Constants (in Hz) of the Carbenic Carbon for Selected Acyclic Carbenes and Their Corresponding Salts

carbene	δC2	salt (X)	δC2	carbene	δC2 (*J*)	salt (X)	δC2
333[76]	259.7[b]			**348**[334]	262.8[a]		
334[330]	252[b]			**349**[335]	268.1[b]		
335[329]	255.5[a]	(PF6)[77]	152.2[h]	**350**[334]	277.8[a]		
336[341]	258.2[b]			**351**[334]	296.6[a]		
337[342]	248.9[a]	(I)[342]	*e*	**352**[38]	326.3[b]	(OTf)[38]	186.7[d]
338[343]	258.9[a]	$(POCl_2)$[343]	154.4[d]	**353**[336]	314.2[b]		
339[331]	260[a]	(BF_4)[331]	162.8[e]	**354**[336]	302.2[b] (J_{FC} = 5.7)		
340[125]	241.9[a]	(PF_6)[77]	152.4[h]	**355**[336]	303.3[b]		
341[332]	236.8[c]	(BF_4)[77]	153.7[d]	**356**[336]	299.2[b] (J_{FC} = 60)		
342[10]	237.4[a]	(PF_6)[10]	154.4[d]	**357**[338]	314.9[b] (J_{CP} = 15.6)		
343[333]	228.9[b]	(Cl)[333]	149.0[f]	**358**[337]	315.0[b]	(OTf)[337]	175.4[f]
344[333]	228.0[b]	(Cl)[333]	149.4[f]	**359**[339]	304.6[b]	(OTf)[339]	173.9[f]
345[344]	262.4[b]			**360**[339]	307.1[b]	(OTf)[339]	172.8[f]
346[334]	267.3[a]			**361**[340]	377.3[b]		
347[334]	263.8[b]			**362**[340]	380.8[b]		

[a] In d_6-benzene. [b] In d_8-THF. [c] In d_8-toluene. [d] In d_3-chloroform. [e] In d_6-DMSO. [f] In d_3-acetonitrile. [g] In d_2-methylene chloride. [h] In d_6-acetone. [i] Solvent not reported.

Table 11. Chemical Shifts (in ppm) and Coupling Constants (in Hz) for Phosphinocarbenes



λ^3-phosphinocarbene λ^4-phosphavinylylide λ^5-phosphaacetylene

	X	R_1[f]	R_2	$\delta^{13}C$ (J_{PC})
363[348,349]	$SiMe_3$	*i*-Pr_2N	*i*-Pr_2N	142.7 (159)
364[347]	$SiMe_3$	Tmp	*i*Pr_2N	145.5 (203)
365[347]	Si(*i*-Pr)$_3$	Tmp	Me_2N	120.7 (181)
366[347]	$SiMe_3$	Tmp	Me_2N	133.5 (147)
367[347]	$SiMe_3$	Tmp	Ph	136.9 (147)
368[347]	$SiMe_3$	*c*-Hex_2N	*c*-Hex_2N	139.3 (160)
369[354]	$SiMe_3$	N(*t*Bu)$SiMe_2$N*t*Bu		77.6[a] (153)
370[355,356]	P(N*i*$Pr_2)_2H^+$	*i*-Pr_2N	*i*-Pr_2N	98.9 (157)
371[360]	P(N*i*$Pr_2)_2Cl^+$	*i*-Pr_2N	*i*-Pr_2N	103.9 (154)
372[361]	*o,p*-$(CF_3)_2$Ph	*i*-Pr_2N	*i*-Pr_2N	149.2[c] (193)
373[361]	*o*-(CF_3)Ph	*i*-Pr_2N	*i*-Pr_2N	148.6[c] (124)
374[362]	*o,o′*-$(CF_3)_2$Ph	*i*-Pr_2N	*i*-Pr_2N	146.1[a] (271)
375[362]	CF_3	*c*-Hex_2N	*c*-Hex_2N	135[c] (23.8) (J_{FC} = 55.2)
376[361]	*p*-(CF_3)Ph	*i*-Pr_2N	*i*-Pr_2N	159.7[c] (66)
377[361]	C_6F_5	*i*-Pr_2N	*i*-Pr_2N	133.3[c] (55)
378[361]	C_6F_5	*c*-Hex_2N	*c*-Hex_2N	
379[361]	*o*-Me-*p*-(NMe_2)Ph	*i*-Pr_2N	*i*-Pr_2N	
380[361]	*o*-MePh	*i*-Pr_2N	*i*Pr_2N	156.1[c] (46)
381[363]	Mes	*i*-Pr_2N	*i*-Pr_2N	151.1[d] (65)
382[363]	*t*-Bu	*i*-Pr_2N	*i*-Pr_2N	186.3[e] (32)
383[363]	Me	*i*-Pr_2N	*i*-Pr_2N	164.8[e] (44)
384[364]	*i*-Pr_2N	*c*-Hex_2N	*c*-Hex_2N	329.7[b] (23.1)
385[364]	*i*-Pr_2N	*i*-Pr_2N	*i*-Pr_2N	329.2[b] (22.1)
386[364]	*i*-Pr_2N	Ph	Ph	320.4[b] (101.6)
387[364]	*i*-Pr_2N	*t*-Bu	*t*-Bu	346.6[b] (57.3)

[a] In d_6-benzene, [b] In d_8-THF, [c] In d_8-toluene, [d] In d_4-methanol, [e] Solvent not reported. [f] Abbreviations: Tmp = 2,2,6,6-tetramethylpiperidino.

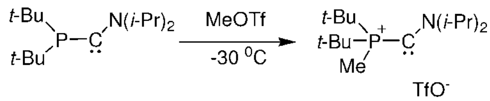
"usual" carbenes or polarized λ^5-phosphaacetylenes.[345−350] Table 11 summarizes the typical ^{13}C chemical shifts of the X*C*P carbon and the first-order coupling constants ($^1J_{PC}$) for all phosphinocarbenes reported to date.[347−349,351−354] In addition to high-field chemical shifts for silicon ($\delta = -3$ to -21 ppm) and phosphorus ($\delta = -24$ to -50 ppm), these carbenes are also characterized by high-field chemical shifts for carbon ($\delta = 78-145.5$ ppm) and large coupling constants of the carbene carbon to phosphorus ($J = 147-203$ Hz). The spectroscopic data indicate multiple bond character of P−C bonds in **363**−**369**. The multiple bond formulation is also supported by the bond lengths and angles from X-ray diffraction studies[354−356] and *ab initio* calculations.[47,354,357−359] Replacement of the trialkylsilyl group by isoelectronic phosphonio-substituents (**370** and **371**) does not produce a significant change of the NMR spectroscopy characteristics.[355,356,360]

Compounds **372**−**383** feature a phosphanyl group and an alkyl/aryl substituent. The phosphino group behaves as a weak π- and σ-donor substituent, whereas the role of the alkyl/aryl substituents strongly depends on their electronic and steric properties.[361−363,365] The chemical shifts are in general slightly higher than those observed for neutral push−pull phosphanyl carbenes **363**−**371**. A noticeable difference is the magnitude of the coupling constant J_{PC}, which is significantly smaller for **375**−**383** ($^1J_{PC}$ = 24−66 Hz) than for **363**−**373** ($^1J_{PC}$ = 124−203 Hz) and **374** ($^1J_{PC}$ = 271 Hz).[361−363]

The introduction of a C-amino substituent in phosphinocarbenes has a substantial effect on the appearance of the ^{13}C NMR spectra. The most striking feature of the NMR spectra of (amino)(phosphino) carbenes **384**−**387** is the very low field values of the carbene carbons (δ 320−348 ppm) with coupling constants of 22−101 Hz.[364] These signals are downfield in comparison to those of the diaminocarbenes (210−300 ppm) and in a totally different region than those of the phosphinocarbenes **363**−**383**. X-ray diffraction studies on **384** show a pyramidal geometry at phosphorus with a perpendicular orientation of the phosphorus lone pair to the p orbital of the carbenic center. The nitrogen atom is in a planar environment with a short N−C bond length. These data suggest that only the amino substituent interacts with the carbene center.[363,364] By η^1-coordination of **374** to rhodium, an upfield shift of 26−32 ppm was observed,[362] while a η^2-coordination mode produces a relatively large downfield shift of 66.3 ppm.[366] Carbene **387** coordinates to palladium and nickel in η^2-fashion with upfield shifts of the carbene carbon of 145 and 157 ppm, respectively.[367]

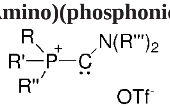
Bertrand's group showed that an (amino)(phosphino)carbene can be transformed into an (amino)(phosphonio)carbene (Scheme 3).[344] The carbenic carbon of **388** appears in the ^{13}C spectrum at 302 ppm with $^1J_{P-C}$ = 11.4 Hz, an indication of at most a slight interaction of the phosphonio group with the carbene center. As summarized in Table 12, the carbenic carbon of the related carbenes **389**−**394** resonate between

Scheme 3

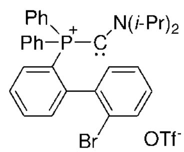


387 388

Table 12. Chemical Shifts (in ppm) and Coupling Constants (in Hz) of the Carbenic Carbon for Selected (Amino)(phosphonio)carbenes and Their Protonated Precursors



388 R = R' = *t*-Bu, R'' = Me, R''' = *i*-Pr
389 R = R' = R'' = Cy, R''' = *i*-Pr
390 R = R' = R'' = Ph, R''' = *i*-Pr
391 R = R' = Ph, R'' = *t*-Bu, R''' = *i*-Pr
392 R = R' = Ph, R'' = *t*-Bu, R''' = ^{c}Hex
393 R = R' = Ph, R'' = *o*-*i*-PrPh



394

carbene	δNCP (J)	salt	δPCHN (J)
388[344]	302 (J_{CP} = 11.4)		
389[341]	304.5^{a} (J_{CP} = 109)	(OTf)[341]	172.3^{b} (J_{CP} = 37.3)
390[341]	292.4^{a} (J_{CP} = 110.5)	(OTf)[341]	169.9^{b} (J_{CP} = 64.1)
391[340]	309.4^{a} (J_{CP} = 120.7)	(OTf)[340]	167.6^{b} (J_{CP} = 39.4)
392[340]	310.2^{a} (J_{CP} = 124.3)	(OTf)[340]	167.9^{b} (J_{CP} = 39.4)
393[338]	292.0^{a} (J_{CP} = 113.9)	(OTf)[338]	171.1^{b} (J_{CP} = 62.9)
394[368]	291.4^{a} (J_{CP} = 112.2)	(OTf)[368]	169.5^{b} (J_{CP} = 63.5)

^{a} In d_8-THF. ^{b} In d_3-acetonitrile.

291−310 ppm, considerably downfield relative to the resonances observed for their protonated precursors.[341]

4. Conclusion

We provide an overview of the extensive use of ^{13}C NMR spectroscopy as a technique for the analysis of the structure and bonding of nucleophilic carbenes. The measurement of the NMR chemical shift anisotropy at the carbene center coupled with electronic structure calculations confirms the highly anisotropic nature of the electron distribution around the carbene center. The most characteristic component of the chemical shielding tensor in singlet carbenes is the highly deshielded σ_{11} component. This arises from a large paramagnetic shift component due to the mixing of the lone pair on the carbene C with the vacant p orbital on this center. The electric field so generated leads to a magnetic field component perpendicular to the plane containing the lone pair and the vacant p orbital. The size of the component qualitatively correlates with the n → π* transition and with the amount of π-back-bonding into the vacant p orbital. The smallest paramagnetic shift component arises from the mixing of the lone pair on the carbene C and the in-plane σ orbitals, which contributes the out-of-plane component. The size of this component arises from the polarity of the C−R bond (relative electronegativities). The intermediate paramagnetic component arises from mixing of the σ C−R orbitals with the vacant p orbital. This component is lower than the largest one because these orbitals are more stable. It is affected as well by the polarity of the C−R bonds.

The experimental determination of the ^{13}C chemical shift of a carbene constitutes a highly reliable method for the characterization of a carbene. Imidazol-2-ylidenes exhibit ^{13}C resonances for the carbene center from about δ 210 to 220 ppm, whereas saturated imidazolin-2-ylidenes and acyclic diaminocarbenes display further downfield-shifted resonances between 236 and 260 ppm. This difference in the ^{13}C chemical shifts of the C2 center of saturated vs unsaturated diaminocarbenes is consistent with a higher anisotropy at the carbene center of saturated carbenes due to a lower population of the carbene p_π-orbital. Variation of the ring size and annulation of cyclic diaminocarbenes also has an effect on the chemical shift of the carbenic carbon. A large number of Arduengo-type carbene analogues have been reported, and the chemical shifts of the carbenic carbons are distinctly different from those of the diaminocarbenes. The replacement of both nitrogen atoms with other elements such as carbon, phosphorus, or silicon leads to a decrease in chemical shift of the carbenic center (e.g., **310**, **311**, **324**, and **325** with δ 184−188 ppm). The substitution of only one nitrogen atom with sulfur, oxygen, carbon, silicon, or phosphorus results in significantly downfield-shifted resonances in comparison with those displayed by the diaminocarbenes (e.g., **312**−**317**, **345**−**362**, **384**−**387**, and **388**−**394** with δ 262−380 ppm). Some nucleophilic diaminocarbenes with fully inorganic backbones (**326**−**331**) display the chemical shift of the carbenic carbon between δ 281 and 313 ppm. By complexation of the nucleophilic carbenes with main-group elements or transition metals, the ^{13}C shift of the former carbenic center is substantially shielded, so it provides a sensitive probe for adduct formation.

Carbenes are among the most investigated reactive species in the field of organic chemistry. A wide array of experimental and theoretical techniques has been employed to better understand their unique features. ^{13}C NMR spectroscopy has served and will continue to serve as one of the most convenient, fast, and reliable methods for the characterization of this very versatile class of ligands.

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