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Carbenes with Reduced Heteroatom Stabilization: A Computational Approach

M. Z. Kassaee,* F. A. Shakib, M. R. Momeni, M. Ghambarian, and S. M. Musavi

Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

kassaeem@modares.ac.ir

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$\Delta E_{S\text{-}T}$: X = $OCH_3 > N(CH_3)_2 > SCH_3 > P(CH_3)_2 > C(CH_3)_3 > Si(CH_3)_3$

$\Delta E_{S\text{-}T}$: Y = $NCH_3 > O > S > PCH_3 > C(CH_3)_2 > Si(CH_3)_2$

High-level DFT calculations, coupled with appropriate isodesmic reactions, are employed to investigate the effects of monoheteroatom substitution, cyclization, and unsaturation on the stability, multiplicity, and reactivity of amino-, oxy-, silyl-, phosphino-, and thioalkylcarbenes. The results of these calculations are compared to those of di-*tert*-butylcarbene, 2,2,5,5-tetramethylcyclopentanylidene, and 2,2,5,5-tetramethylcyclopent-3-enylidene as the reference molecules. The calculated singlet−triplet energy gaps (ΔE_{S-T}) demonstrate the following trend: (amino ≈ oxy) > thio > phosphino > alkyl > silyl. In contrast to the previous reports, isodesmic reactions show that π-donor/σ-acceptor amino substituents stabilize not only the singlet but also the triplet states. The stabilization of the triplet states by amino substitution is much less than the singlet states. The ΔE_{S-T} values of all the carbenes are increased through cyclization, while the introduction of unsaturation causes small and rather random changes. These changes are carefully probed by means of isodesmic reactions for the singlet and triplet states, separately. The reactivity of the species is discussed in terms of nucleophilicity, electrophilicity, and proton affinity issues showing amino- and phosphinoalkylcarbenes to be more nucleophilic, more basic, and less electrophilic than oxy- and thioalkylcarbenes, respectively. This detailed study offers new insights into the chemistry of these novel carbenes.

Introduction

Carbenes are divalent carbon atoms that possess an empty p orbital and two nonbonding electrons that are capable of existing in the singlet or triplet state.[1] The two adjacent groups influence the electronic structure of carbenes through mesomeric or inductive effects.[2] π-Electron donors such as amino and phosphino groups stabilize singlet states[3] while σ-donors (groups possessing elements less electronegative than carbon) stabilize triplet states.[4] The mesomeric effect of amino substituents is the primary mode of stabilization in the

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first isolable singlet cyclic diaminocarbene, reported in 1991.[5] This initial account was followed by reports of a wide variety of stable cyclic diheteroatom carbenes, including aminothio- and aminoxycarbenes.[6] Indeed, in addition to nitrogen, sulfur and oxygen are also capable of stabilizing singlet carbenes, but with different steric protection.[7] Synthesis of the first stable acyclic carbene, phosphinosilylcarbene, by Bertrand et al. was achieved through the π-electron donation of a phosphino group as well as the π-electron acceptance of the silyl substituent.[8] It has now been noticed that the presence of one π-electron donor heteroatom is sufficient to stabilize singlet carbenes. After synthesis of the stable acyclic phosphinoalkylcarbenes and aminoalkylcarbenes,[9] Bertrand et al. introduced cyclic aminoalkylcarbenes (CAACs) with stabilities comparable to diaminocarbenes.[10] While their study was extended to carbenes without heteroatom stabilization,[11] the current study is focused on the wide variety of monoheteroatom-substituted carbenes. It seems this variety necessitates a comprehensive investigation of different stabilizing effects on these species. Hence, following our interest in novel stable singlet carbenes,[12] this study is intended to shed some light on the effects of three sets of substituents: π-donor/σ-acceptor ($N(CH_3)_2$ and OCH_3), π-donor/σ-donor ($P(CH_3)_2$ and SCH_3), and π-acceptor/σ-donor ($Si(CH_3)_2$) on the singlet−triplet energy gaps ($\Delta E_{S\text{-}T}$) of the acyclic di-*tert*-butylcarbene analogues (**1**$_X$, Figure 1). By applying the appropriate isodesmic reactions, we can show in detail how these substituents affect singlet (s) and/or triplet (t) states of carbenes, separately. Due to the importance of the carbene bond angle on the multiplicity of carbenes, the effect of cyclization is also probed using cyclic saturated five-membered dialkylcarbene- and its heteroatom-substituted counterparts (**2**$_Y$, Figure 1). In our previous study, we showed that unsaturation had a favorable effect on the enlargement of the ΔE_{S-T} of dimethylcarbene.[13] Here, the effect of unsaturation is also taken into account for all of the scrutinized carbenes (**3**$_Y$, Figure 1).

1$_C$: X = $C(CH_3)_3$	**2**$_C$: Y = $C(CH_3)_2$	**3**$_C$: Y = $C(CH_3)_2$
1$_{Si}$: X = $Si(CH_3)_3$	**2**$_{Si}$: Y = $Si(CH_3)_2$	**3**$_{Si}$: Y = $Si(CH_3)_2$
1$_N$: X = $N(CH_3)_2$	**2**$_N$: Y = NCH_3	**3**$_N$: Y = NCH_3
1$_P$: X = $P(CH_3)_2$	**2**$_P$: Y = PCH_3	**3**$_P$: Y = PCH_3
1$_O$: X = OCH_3	**2**$_O$: Y = O	**3**$_O$: Y = O
1$_S$: X = SCH_3	**2**$_S$: Y = S	**3**$_S$: Y = S

FIGURE 1. Three series of acyclic (**1**$_X$), cyclic (**2**$_Y$), and cyclic unsaturated (**3**$_Y$) carbenes studied in this work.

Computational Methods

Full geometry optimizations are accomplished without any symmetry constraints using hybrid functional B3LYP[14−16] and the 6-31+G* basis set, employing the Gaussian 98 code.[17] The applied basis set comprises Pople's well-known 6-31G* basis set[18,19] and an extra plus due to the importance of diffuse functions.[20,21] To obtain more accurate energetic data, single-point calculations are performed at the B3LYP/AUG-cc-pVTZ level.[22] Vibrational frequencies are calculated to establish the nature of stationary points as true minima.[23]

The nucleophilicity index, N, which was recently introduced by Domingo et al.,[24] is calculated as $N = E_{\mathrm{HOMO(Nu)}} - E_{\mathrm{HOMO(TCNE)}}$, where tetracyanoethylene (TCNE) is chosen as the reference. The global electrophilicity, ω,[25] is also calculated following the expression, $\omega = (\mu^2/2\eta)$, where μ is the chemical potential ($\mu \approx (E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}})/2$) and η is the chemical hardness ($\eta = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$).[26]

Results and Discussion

DFT calculations and isodesmic reactions are employed to compare the stability and multiplicity of three series of acyclic (**1**$_X$), cyclic saturated (**2**$_Y$), and cyclic unsaturated (**3**$_Y$) carbenes, demonstrating the effects of monoheteroatom

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TABLE 1. B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G*-Calculated Singlet−triplet Energy Gaps (ΔE_{S-T}, kcal/mol) along with Their Dipole Moments (D) and the Smallest Calculated Vibrational Frequencies (ν_{min}, cm^{-1}) for Ground States

structure	ΔE_{S-T}	D[a]	ν_{min}[a]	structure	ΔE_{S-T}	D[a]	ν_{min}[a]
$\mathbf{1_C}$[b]	−4.2	0.67	40.43	$\mathbf{1_{Si}}$[b]	−15.9	0.48	11.27
$\mathbf{2_C}$	5.5	2.03	76.05	$\mathbf{2_{Si}}$[b]	−7.0	0.99	58.32
$\mathbf{3_C}$	5.7	1.71	46.58	$\mathbf{3_{Si}}$[b]	−9.1	0.66	65.10
$\mathbf{1_N}$	27.8	3.18	37.00	$\mathbf{1_P}$	8.6	2.86	28.41
$\mathbf{2_N}$	51.8	3.11	90.77	$\mathbf{2_P}$	12.1	3.25	87.21
$\mathbf{3_N}$	47.1	2.78	102.58	$\mathbf{3_P}$	12.2	3.19	51.78
$\mathbf{1_O}$	29.0	1.49	27.49	$\mathbf{1_S}$	18.7	0.98	32.91
$\mathbf{2_O}$	37.3	3.79	96.34	$\mathbf{2_S}$	29.6	3.36	127.46
$\mathbf{3_O}$	35.1	3.61	125.67	$\mathbf{3_S}$	29.9	3.15	102.04

[a] At B3LYP/6-31+G*. [b] Triplet ground states.

(N, O, Si, P, and S) substitutions on di-*tert*-butylcarbene ($\mathbf{1_C}$), 2,2,5,5-tetramethylcyclopentanylidene ($\mathbf{2_C}$), and 2,2,5,5-tetramethylcyclopent-3-enylidene ($\mathbf{3_C}$), respectively (Figure 1).

Substituent effects on Singlet−Triplet Energy Separations ($\boldsymbol{\Delta E_{S-T}}$).

(i) Dialkylcarbenes. In 1982, ESR studies on di-*tert*-butylcarbene ($\mathbf{1_C}$) indicated that it had a triplet ground state with a wide carbene bond angle of 143° which had eased the promotion of an electron from σ to p-orbital in favor of the triplet state.[27] Quantitatively, Schleyer et al. showed that the energy of triplet methylene drops below that of singlet state if the carbene bond angle is enlarged over 104°.[28] Now, our calculated wide carbene bond angle of 141.53° (Table 2) puts triplet $\mathbf{1_C}$(t) 4.2 kcal/mol lower in energy than its singlet $\mathbf{1_C}$(s) (Table 1).

Going from acyclic $\mathbf{1_C}$ to cyclic $\mathbf{2_C}$, the smaller carbene bond angle of the latter (106.15°) justifies the alteration of the ground state from triplet to singlet ($\Delta E_{S-T} = +5.5$ kcal/mol). Maintaining the angle, unsaturation makes the structure planar and upgrades the C_2 symmetry in $\mathbf{2_C}$(s) to C_{2v} symmetry in $\mathbf{3_C}$(s), without a considerable difference in the ΔE_{S-T} (Tables 1 and 2).

(ii) Aminoalkylcarbenes. Different amino substituents which are well-known for the significant singlet-state stabilization through their π-donating/σ-accepting interactions are grouped in a series of aminoalkylcarbenes ($\mathbf{1_N}$−$\mathbf{3_N}$) following the species synthesized by Bertrand et al.[9,10] Evidently, the σ-acceptor substituents (Pauling electronegativities, EN: C = 2.5, N = 3.0) are anticipated to induce a large gap between σ and p orbitals in favor of the singlet state (Figure 2). Hence, the presence of a π-donor/σ-acceptor amino group enlarges the ΔE_{S-T} of $\mathbf{1_N}$ to 27.8 kcal/mol with the N−C$_{\mathrm{carbene}}$ bond length of 1.314 Å which falls between those of single C−N and double C═N bonds while being much closer to the latter (1.470 and 1.294 Å, respectively). The surprising observation is the N−C$_{\mathrm{carbene}}$ bond length of $\mathbf{1_N}$(t) which also appears between single C−N and double C═N bonds with the value of 1.376 Å. This may imply that the amino substituent stabilizes not only the singlet but also the triplet state, calling for further examination presented in the following discussion on isodesmic reactions.

Similar to dialkylcarbenes, cyclization has a favorable effect on the enlargement of ΔE_{S-T} of aminoalkylcarbenes. Evidently, $\mathbf{2_N}$ shows ΔE_{S-T} of 51.8 kcal/mol which is the largest value found among our studied carbenes. It seems that both stabilization of the singlet and destabilization of the triplet state due to the narrowing of the carbene bond angle may rationalize this observation. The calculated ΔE_{S-T} of $\mathbf{3_N}$ appears 4.7 kcal/mol lower than that of $\mathbf{2_N}$. Apparently, the conjugation of the nitrogen lone pair with the C═C double bond weakens the stabilizing interaction of the lone pair with the empty p orbital of the carbene. This is roughly confirmed through the lengthening of the N−C$_{\mathrm{carbene}}$ bond in $\mathbf{3_N}$ compared to that in $\mathbf{2_N}$ (1.326 vs 1.312 Å, Table 2).

(iii) Oxyalkylcarbenes. Besides group 15 elements, substituting those of group 16 may also stabilize singlet carbenes through π-donation and σ-acceptance. Evidently, trivalent nitrogen provides higher steric protection on the carbene center than divalent oxygen or sulfur. Based on Pauling electronegativities, oxygen is a weaker π-donor but a stronger σ-acceptor than nitrogen (EN: N = 3.0, O = 3.5). Generally, the stabilizing effect of oxygen on the carbene centers causes ~8.5% decrease in the O−C$_{\mathrm{carbene}}$ bond length compared to a typical O−C single bond, while such decrease for N−C$_{\mathrm{carbene}}$ bond in aminoalkylcarbenes is ~10.4%. The concurrency of π-donation and σ-acceptance induces a slightly higher ΔE_{S-T} in $\mathbf{1_O}$ compared to $\mathbf{1_N}$ (29.0 vs 27.3 kcal/mol). This is somewhat lower for $\mathbf{2_O}$ and $\mathbf{3_O}$, compared to $\mathbf{2_N}$ and $\mathbf{3_N}$, respectively (Table 1). Interestingly, cyclization does not alter the carbene bond angle of $\mathbf{1_O}$ (Table 2). Hence, both $\mathbf{1_O}$ and $\mathbf{2_O}$ show a similar carbene bond angle of ~109°, almost equal to the H−C−H angle of methane. Like aminoalkylcarbenes, the ΔE_{S-T} of the unsaturated cyclic $\mathbf{3_O}$ is smaller than that of the saturated cyclic $\mathbf{2_O}$.

(iv) Silylalkylcarbenes. On the basis of Pauling electronegativity (EN: Si = 1.8), electropositive Si is a σ-donor substituent which is anticipated to cause a small gap between σ and π orbitals leading to triplet ground-state carbenes (Figure 2). The calculated negative ΔE_{S-T} values for all silylalkylcarbenes ($\mathbf{1_{Si}}$, $\mathbf{2_{Si}}$, and $\mathbf{3_{Si}}$) fulfill this expectation with the highest gap obtained for the acyclic $\mathbf{1_{Si}}$ (ΔE_{S-T} = −15.9 vs −7.0, and −9.1 kcal/mol, respectively, Table 1). Evidently, the wider carbene bond angle of acyclic $\mathbf{1_{Si}}$(t) compared to the corresponding cyclic structures $\mathbf{2_{Si}}$ and $\mathbf{3_{Si}}$ (162.22° vs 117.29° and 116.37) is the main reason beyond this observation (Table 2). The Si−C$_{\mathrm{carbene}}$ bonds of the triplet states of all the silylalkylcarbenes emerge with an average length of 1.845 Å which is shorter than a typical Si−C bond length (1.940 Å) as well as the average bond length of the singlet states (1.905 Å). These indicate rather high stabilizing effects of σ-donor Si on the triplet carbenes (Table 2).

(v) Phosphinoalkylcarbenes. The electropositive phosphorus (EN: P = 2.1) is both a σ- and π-donor substituent. These two opposing effects result in singlet ground states with the smallest ΔE_{S-T} values found among the scrutinized carbenes. Hence, in contrast to the large values encountered for aminoalkylcarbenes, we face small ΔE_{S-T} values for phosphinoalkylcarbenes caused by lower π-donation of phosphorus compared to nitrogen, due to the higher energetic cost required by the former to achieve planar geometry (about 30−35 kcal/mol for phosphorus vs 5 kcal/mol for nitrogen).[30] Indeed, it was shown that in the presence of an

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TABLE 2. Bond Lengths (Å) and Angles (deg) for the Ground-State Carbenes at B3LYP/6-31+G* for X = C, N, O, Si, P, and S

species	symmetry	$X-C_{carbene}$	$C_{carbene}-C$	$X-C_{carbene}-C$	species	symmetry	$X-C_{carbene}$	$C_{carbene}-C$	$X-C_{carbene}-C$
$\mathbf{1_{C}}^{a}$	C_2	1.492	1.492	141.54	$\mathbf{1_{Si}}^{a}$	C_1	1.829	1.479	162.22
$\mathbf{2_{C}}$	C_2	1.497	1.497	106.15	$\mathbf{2_{Si}}^{a}$	C_1	1.858	1.497	117.29
$\mathbf{3_{C}}$	C_{2v}	1.508	1.508	106.07	$\mathbf{3_{Si}}^{a}$	C_s	1.861	1.499	116.37
$\mathbf{1_{N}}$	C_1	1.314	1.535	120.87	$\mathbf{1_{P}}$	C_s	1.623	1.505	132.80
$\mathbf{2_{N}}$	C_1	1.312	1.531	105.86	$\mathbf{2_{P}}$	C_1	1.704	1.523	104.88
$\mathbf{3_{N}}$	C_s	1.326	1.533	103.94	$\mathbf{3_{P}}$	C_1	1.685	1.536	102.04
$\mathbf{1_{O}}$	C_1	1.308	1.525	109.68	$\mathbf{1_{S}}$	C_s	1.669	1.517	115.87
$\mathbf{2_{O}}$	C_1	1.299	1.529	108.07	$\mathbf{2_{S}}$	C_1	1.657	1.518	109.92
$\mathbf{3_{O}}$	C_s	1.321	1.529	105.94	$\mathbf{3_{S}}$	C_s	1.670	1.518	108.09

[a] Triplet ground states.

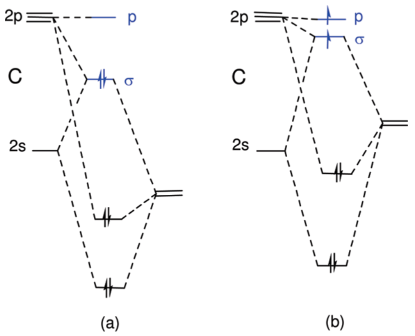

FIGURE 2. Perturbation orbital diagrams showing the influence of inductive effects: (a) σ-acceptor and (b) σ-donor substituents.[29]

amino group in aminophosphinocarbenes, the phosphino group acts as a spectator substituent incapable of π-donating to the carbene center.[31] The higher stability of the triplet acyclic carbenes than the corresponding cyclic ones gives smaller ΔE_{S-T} for $\mathbf{1_{P}}$ (8.6 kcal/mol) than $\mathbf{2_{P}}$ and $\mathbf{3_{P}}$ (∼12 kcal/mol).

(vi) Thioalkylcarbenes. The Pauling electronegativity of sulfur is the same as carbon (EN: 2.5) which ranks this π-donor element less electropositive than Si and P while less electronegative than N and O atoms. The average $S-C_{carbene}$ bond length of 1.665 Å is between those of typical S−C and S═C bonds (1.780 and 1.566 Å, respectively, Table 2). It is considerably shorter than that of silylalkylcarbenes (1.849 Å) but closer to phosphinoalkylcarbenes (1.671 Å). Rather high ΔE_{S-T} values of $\mathbf{1_{S}}$, $\mathbf{2_{S}}$, and $\mathbf{3_{S}}$ (18.7, 29.6, and 29.9 kcal/mol, respectively) show higher resemblance to the electronegative oxyalkylcarbenes than the electropositive phosphinoalkylcarbenes (Table 1).

Probing Substituent Effects by NBO Atomic Charges. The stabilization of the carbene center by substituents may result in negative or less positive partial atomic charges on the carbene centers. The lower positive atomic charge of 0.157 on the singlet carbene center of $\mathbf{1_{C}}$(s) compared to the 0.227 on its corresponding triplet $\mathbf{1_{C}}$(t) indicates the stabilization of the former caused by hyperconjugation (Table 3). Nevertheless, this rather weak hyperconjugation effect is overwhelmed by the pronounced steric effects exerted by *tert*-butyl groups, suggesting triplet as the ground state for $\mathbf{1_{C}}$. The increase of the carbene atomic charge from +0.157 in $\mathbf{1_{C}}$(s) to +0.162 in $\mathbf{2_{C}}$(s) shows such a stabilizing effect slightly decreases upon cyclization. This change is parallel to the lengthening of the $C_{carbene}-C$ bond from 1.491 Å in the former to 1.497 Å in the latter (Table 2).

TABLE 3. NBO Atomic Charges on the Scrutinized Singlet and Triplet Carbene Centers ($^{1}C_{carbene}$ and $^{3}C_{carbene}$, Respectively) at B3LYP/6-311++G**

species	$^{1}C_{carbene}$	$^{3}C_{carbene}$	species	$^{1}C_{carbene}$	$^{3}C_{carbene}$
$\mathbf{1_{C}}$	0.157	0.227	$\mathbf{1_{Si}}$	−0.261	−0.413
$\mathbf{2_{C}}$	0.162	0.226	$\mathbf{2_{Si}}$	−0.814	−0.394
$\mathbf{3_{C}}$	0.217	0.247	$\mathbf{3_{Si}}$	−0.511	−0.157
$\mathbf{1_{N}}$	0.106	0.236	$\mathbf{1_{P}}$	−0.590	−0.217
$\mathbf{2_{N}}$	0.102	0.273	$\mathbf{2_{P}}$	−0.402	−0.151
$\mathbf{3_{N}}$	0.101	0.299	$\mathbf{3_{P}}$	−0.474	−0.117
$\mathbf{1_{O}}$	0.268	0.358	$\mathbf{1_{S}}$	−0.266	−0.112
$\mathbf{2_{O}}$	0.311	0.377	$\mathbf{2_{S}}$	−0.238	−0.068
$\mathbf{3_{O}}$	0.309	0.415	$\mathbf{3_{S}}$	−0.245	−0.040

Due to the higher electronegativities of nitrogen and oxygen atoms than carbon, they are anticipated to place partial positive atomic charges on their adjacent carbene centers. Yet, stabilization by π-donor amino and oxy substituents places less positive partial atomic charge on the singlet carbene centers than their corresponding triplet states (∼+0.106 vs ∼+0.278 for aminoalkylcarbenes and ∼+0.296 vs ∼+0.383 for oxyalkylcarbenes, Table 3). Similar NBO atomic charges of $\mathbf{1_{N}}$, $\mathbf{2_{N}}$, and $\mathbf{3_{N}}$ is a justification for the comparable stabilizing effects of amino substituents in acyclic and cyclic carbenes. In contrast, acyclic $\mathbf{1_{O}}$(s) benefits from a higher stabilizing effect than cyclic $\mathbf{2_{O}}$(s) and $\mathbf{3_{O}}$(s) (+0.268 vs ∼+0.310, respectively).

The σ-donicity of electropositive silyl, phosphino, and thio substituents expectedly induces negative charges on the carbene centers. Nevertheless, the synergistic π-donating stabilizing effect of phosphino and thio groups is clearly shown in the more negative charges on the singlets relative to their triplet states (∼−0.489 vs ∼−0.162 for the phosphino and −0.250 vs −0.073 for the thio).

Probing Heteroatom Effects via Isodesmic Reactions. In a computational study on triplet carbenes, Nemirowski and Schreiner stated that a classical π-donor/σ-acceptor substituent such as the amino group simultaneously stabilizes the singlet and destabilizes the triplet state.[4e] The basis for their statement is the common isodesmic reaction employed for the comparison of carbenes of interest to the parent methylene showing 48.3 kcal/mol stabilization for the singlet state of diaminocarbene and 15.9 kcal/mol destabilization for the corresponding triplet state. In order to reach a clear overview of monoheteroatom effects on singlet and triplet states, three sets of isodesmic reactions are designed here (Table 4). The high structural similarities on two sides of these reactions, compared to those of Nemirowski and Schreiner, reduce possible contaminations and make them better norms for analyzing the effects of monoheteroatom substitutions. Interestingly, our isodesmic reaction 1

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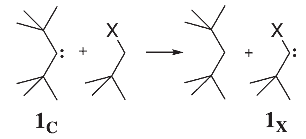
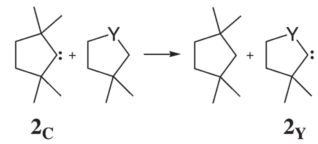
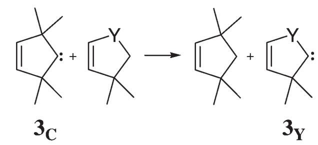
[31] (a) Merceron, N.; Miqueu, K.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **2002**, *124*, 6806. (b) Merceron-Saffon, N.; Baceiredo, A.; Gornitzka, H.; Bertrand, G. *Science* **2003**, *301*, 1223.

TABLE 4. Three Isodesmic Reactions Employed for Estimation of Energy Changes Anticipated for Monoheteroatom-Substituted Singlet (ΔE_S) and Triplet (ΔE_T) Acyclic (1), Cyclic (2), and Unsaturated Cyclic (3) Carbenes (in kcal/mol)

	Rxn	ΔE_S	ΔE_T
(1)  1_C 1_X	$1_C \rightarrow 1_N$	-39.1	-7.2
	$1_C \rightarrow 1_O$	-32.0	1.1
	$1_C \rightarrow 1_{Si}$	4.6	-7.1
	$1_C \rightarrow 1_P$	-20.9	-8.1
	$1_C \rightarrow 1_S$	-29.0	-6.2
(2)  2_C 2_Y	$2_C \rightarrow 2_N$	-50.5	-4.2
	$2_C \rightarrow 2_O$	-30.8	1.0
	$2_C \rightarrow 2_{Si}$	10.4	-2.1
	$2_C \rightarrow 2_P$	-10.2	-3.7
	$2_C \rightarrow 2_S$	-25.8	-1.7
(3)  3_C 3_Y	$3_C \rightarrow 3_N$	-44.8	-3.4
	$3_C \rightarrow 3_O$	-28.7	0.6
	$3_C \rightarrow 3_{Si}$	10.2	-4.6
	$3_C \rightarrow 3_P$	-13.7	-7.2
	$3_C \rightarrow 3_S$	-28.4	-4.2

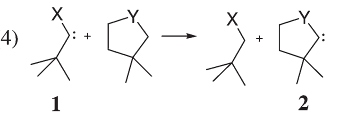
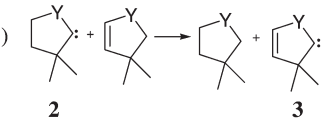
(Table 4) indicates both singlet and triplet states of acyclic aminoalkylcarbene are stabilized by the π-donor/σ-acceptor amino group.

This group has a 39.1 kcal/mol stabilizing effect on $\mathbf{1_N}$(s) and 7.2 kcal/mol on its triplet state $\mathbf{1_N}$(t). Applying isodesmic reactions 2 and 3 gives the same trend for the saturated and unsaturated cyclic aminoalkylcarbenes $\mathbf{2_N}$ and $\mathbf{3_N}$ (Table 4). Specifically, the presence of the amino substituent has a stabilizing value of 50.5 kcal/mol on the singlet cyclic carbene which reduces to 44.8 kcal/mol for the unsaturated cyclic counterpart. Both isodesmic reactions indicate about 3−4 kcal/mol stabilization of the corresponding triplet states.

The π-donor/σ-acceptor oxy groups do not stabilize triplet states (ΔE_T = 1.1, 1.0, 0.6 kcal/mol, isodesmic reactions 1−3, Table 4). This is related to the higher electronegativity of oxygen atom which makes it a stronger σ-acceptor and hence prefers the singlet over the triplet state (Figure 2). However, such small energy differences are not enough to prove the idea of Nemirowski and Schreiner concerning the destabilizing effects of π-donor/σ-acceptor substituents on the triplet states of carbenes.[4e] On the basis of isodesmic reactions, the stabilizing effect of oxy group on the singlet cyclic carbene is lower than that of the amino group and for acyclic carbene appears close to that of the amino group.

The π-acceptor/σ-donor silyl substituents are anticipated to stabilize triplet and destabilize singlet carbenes. The isodesmic reactions 1−3 for the singlet and triplet states of $\mathbf{1_{Si}}$, $\mathbf{2_{Si}}$, and $\mathbf{3_{Si}}$ quantify this expectation. The stabilizing effect of silyl is more significant for acyclic $\mathbf{1_{Si}}$ than cyclic $\mathbf{2_{Si}}$ and $\mathbf{3_{Si}}$ (ΔE_T = −7.1 vs −2.1 and −4.6 kcal/mol). Interestingly, the silyl substituent stabilizes the triplet state of unsaturated cyclic carbene $\mathbf{3_{Si}}$ more than the saturated cyclic $\mathbf{2_{Si}}$ which rationalizes the larger absolute ΔE_{S-T} of the former (9.1 vs 7.0 kcal/mol). It also destabilizes singlet cyclic carbenes considerably more than the acyclic counterpart (ΔE_S = 10.4 and 10.2 vs 4.6 kcal/mol). In contrast to the π-acceptor/σ-donor silyl substituent, π-donor/σ-donor phosphino and thio substituents stabilize both singlet and triplet states of carbenes. Interestingly, phosphino groups stabilize singlet states about twice higher than their corresponding triplets (Table 4). The lower electronegativity of phosphorus than nitrogen leads to the higher triplet-state stabilization by the former. This can be recognized as another factor contributing to smaller ΔE_{S-T} in phosphinoalkylcarbenes compared to aminoalkylcarbenes.

TABLE 5. Two Isodesmic Reactions for Estimation of Energy Changes for Singlet (ΔE_S) and Triplet (ΔE_T) Carbenes upon Cyclization (4) and Unsaturation (5) (in kcal/mol)

	Rxn	ΔE_S	ΔE_T
(4)  1 2	$1_C \rightarrow 2_C$	-4.7	5.0
	$1_N \rightarrow 2_N$	-16.1	7.9
	$1_O \rightarrow 2_O$	-3.5	4.9
	$1_{Si} \rightarrow 2_{Si}$	1.1	9.9
	$1_P \rightarrow 2_P$	6.0	9.4
	$1_S \rightarrow 2_S$	-1.5	9.4
(5)  2 3	$2_C \rightarrow 3_C$	2.8	3.0
	$2_N \rightarrow 3_N$	8.6	3.9
	$2_O \rightarrow 3_O$	4.9	2.7
	$2_{Si} \rightarrow 3_{Si}$	3.7	10.5
	$2_P \rightarrow 3_P$	-0.7	-0.6
	$2_S \rightarrow 3_S$	0.3	0.5

Probing Cyclization and Unsaturation Effects via Isodesmic Reactions. The isodesmic reactions 4 and 5 help the understanding of cyclization and unsaturation effects on the stability of the singlet and triplet carbenes (Table 5). Isodesmic reaction 4 clearly shows the 9.7 kcal/mol enhancement in ΔE_{S-T} for going from $\mathbf{1_C}$ to $\mathbf{2_C}$ is related to 4.7 kcal/mol stabilization of the singlet and 5.0 kcal/mol destabilization of the triplet state. The isodesmic reaction 5 reveals that there is a concealed similar destabilization of the singlet and triplet states of $\mathbf{2_C}$ upon unsaturation to $\mathbf{3_C}$ which is not detectable in comparison of their ΔE_{S-T} values.

Considering aminoalkylcarbenes, isodesmic reaction 4 shows 16.1 kcal/mol stabilization of the singlet and 7.9 kcal/mol destabilization of the triplet state, constituting 24 kcal/mol difference in ΔE_{S-T} values between $\mathbf{1_N}$ and $\mathbf{2_N}$. The stabilizing effect of cyclization on singlet oxyalkylcarbene is rather low (3.5 kcal/mol). This is attributed to the almost unchanged carbene bond angle upon cyclization (Table 2). As mentioned previously, the presence of a double bond slightly prevents the interaction of the lone pair with the empty p orbital of the singlet carbene center. This is indicated by the positive energy differences of isodesmic reaction 5 for both amino- and oxyalkylcarbenes with the values of 8.6 and 4.9 kcal/mol energies, respectively (Table 5). Surprisingly, the same observation is encountered for the triplet states (ΔE_T = 3.9 and 2.7 kcal/mol), which emphasizes the lower stabilizing effects of the amino and oxy lone pairs on the singly occupied p orbitals of the triplet states.

Based on the isodesmic reaction 4, cyclization shows the greatest destabilizing effect on the triplet states of silyl-, phosphino-, and thioalkylcarbenes by 9.9, 9.4, and 9.4 kcal/mol, respectively. Unsaturation also is not favorable in electropositive substituted carbenes except for phosphinoalkylcarbene (Table 5). Two unprecedented distinct results are observed for phosphinoalkylcarbenes through isodesmic reactions 4 and 5 (Table 5). Cyclization destabilizes both singlet and triplet states while unsaturation does not show a considerable effect on both of them. The effect of cyclization on the thioalkylcarbene $\mathbf{1_S}$ is similar to that of oxyalkylcarbene congener (stabilization of the singlet/destabilization of the triplet).

Dimerization. Dimerization has been considered as one of the fundamental aspects of carbenes. In the classic dimerization mechanism of singlet carbenes, the filled σ orbital of each carbene was anticipated to interact with the empty p orbital of the other.[32] Recently, Alder et al. showed that most dimers are formed by proton-catalyzed or possibly metal-ion-catalyzed routes.[33] Hence, they stated that in the absence of appropriate catalyst several diaminocarbenes including acyclic as well as saturated and unsaturated cyclics do not dimerize, within a reasonable frame of time, at ambient temperature (in THF). Following these studies, we wonder about the effects of reduced heteroatom stabilizations on dimerization of carbenes. To reach an overview as complete as possible, we designed two sets of doubly bonded and cyclic bridged dimers for our carbenes and calculate the energy differences of these two modes of dimerization (ΔE_{dim1} and ΔE_{dim2}, respectively), at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G*.

From a theoretical viewpoint, the CGMT model[34] states that doubly bonded dimers are to be formed only when the sum of the $\Delta E_{\mathrm{S-T}}$ values of two interacting carbenes ($\sum\Delta E_{\mathrm{S-T}}$) is smaller than the corresponding double bond energy (expressed based on ΔE_{dim1} values in Table 6). Accordingly, $\sum\Delta E_{\mathrm{S-T}}$ values for our aminoalkylcarbenes are greater than the related double bond energies (55.6 vs 52.8 kcal/mol, for $\mathbf{1_N}$; 103.6 vs 49.1 kcal/mol, for $\mathbf{2_N}$; and 94.2 vs 55.6 kcal/mol, for $\mathbf{3_N}$) which strongly rebuff the probability of dimerization. This is completely in accord with the experimental results obtained for diaminocarbenes.[33]

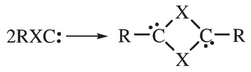
The cyclic bridged dimerization necessitates a formal negative charge on the carbene center and a formal positive charge on the heteroatom. All efforts for optimization of $\mathbf{1_O}$−$\mathbf{3_O}$ cyclic bridged dimers led to the cleavage of C−O bonds, possibly due to the high electronegativity of oxygen. Hence, dimerization of oxyalkylcarbenes proceeds only through the doubly bonded path. For amino- and thioalkylcarbenes both dimerization routes are possible but the cyclic bridged path is less probable for being endothermic (see ΔE_{dim2} values in Table 6). The small $\sum\Delta E_{\mathrm{S-T}}$ values of phosphinoalkylcarbenes compared to the corresponding double bond energies suggest favorable dimerization to doubly bounded dimer. Yet, dimerization of phosphinoalkylcarbenes to cyclic bridged dimers is highly exothermic and in the case of $\mathbf{1_P}$ the cyclic bridged dimer is 8.7 kcal/mol more favorable than the doubly bonded. The former dimer has a C_{2h} planar structure with P−$\mathrm{C_{carbene}}$ bonds of 1.753 Å (Figure 3) which is longer than that of $\mathbf{1_P}$ (1.623 Å, Table 2).

Nucleophilicity, Electrophilicity, and Proton Affinity. The excellent σ-donating properties of NHCs make them ligands of choice for transition metals leading to the preparation of a variety of organometallic catalysts.[35] The potential of similar applications for the monoheteroatom-substituted carbenes, shown experimentally for aminoalkylcarbenes,[10] encourages an investigation on their nuleophilicity and electrophilicity. On the other hand, the basicity of NHCs and the acidity of the corresponding imidazolium salts have already been studied by several groups.[36−39] The gas-phase proton affinities of carbenes (PA, the negative of the enthalpies of their protonation reactions) is an accepted criterion for discussing the basicity of carbenes.[40] Hence, the nuleophilicity (N) and the global electrophilicity (ω) indices as well as the PAs for the singlet-ground-state divalent species are calculated and compared to some synthesized NHCs at B3LYP/6-311++G**//B3LYP/6-31+G* (Table 7).

TABLE 6. B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G*-Calculated Dimerization Energies Leading to Doubly Bonded (ΔE_{dim1}) and Cyclic Bridged (ΔE_{dim2}) Dimers for Singlet Ground States (kcal/mol)

structure	ΔE_{dim1}[a]	ΔE_{dim2}[b]	structure	ΔE_{dim1}[a]	ΔE_{dim2}[b]
$\mathbf{1_N}$	−52.8	43.5	$\mathbf{1_O}$	−76.5	
$\mathbf{2_N}$	−49.1	53.2	$\mathbf{2_O}$	−97.0	
$\mathbf{3_N}$	−55.6	58.2	$\mathbf{3_O}$	−103.8	
$\mathbf{1_P}$	−68.5	−77.2	$\mathbf{1_S}$	−72.7	7.8
$\mathbf{2_P}$	−117.3	−71.7	$\mathbf{2_S}$	−96.0	8.4
$\mathbf{3_P}$	−124.9	−72.4	$\mathbf{3_S}$	−98.6	16.6

[a] Based on the equation: 2RXC: → RXC=CXR. [b] Based on the equation:



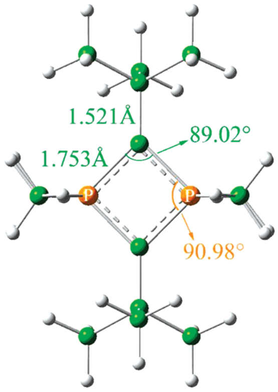


FIGURE 3. Cyclic bridged dimer of $\mathbf{1_P}$ with C_{2h} symmetry.

Aminoalkylcarbenes followed by phosphinoalkylcarbenes rank with the highest nucleophilicities among our carbenes.

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(34) This model was suggested independently by Carter and Goddard and by Trinquier and Malrieu: (a) Carter, A. E.; Goddard, W. A., III. *J. Phys. Chem.* **1986**, *90*, 998. (b) Trinquier, G.; Malrieu, J. -P. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (c) Malrieu, J. -P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916. (d) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 1039.

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(39) Chen, H.; Justes, D. R.; Cooks, R. G. *Org. Lett.* **2005**, *7*, 3949.

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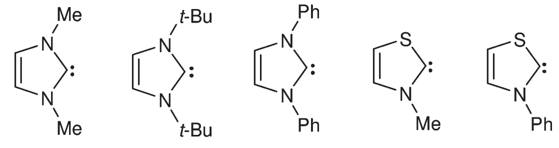
TABLE 7. Nucleophilicity (N), Global Electrophilicity (ω), and Proton Affinity (PA) for the Singlet States of All the Scrutinized Carbenes Compared to the Synthesized NHCs (**4**–**8**)



4 **5** **6** **7** **8**

structure	HOMO (au)	LUMO (au)	$\Delta E_{\text{HOMO-LUMO}}$	N (eV)	ω (eV)	PA
$\mathbf{1_N}$	−0.18151	−0.0163	103.7	4.52	0.81	277.32
$\mathbf{2_N}$	−0.19945	−0.01517	115.6	4.03	0.85	271.55
$\mathbf{3_N}$	−0.20691	−0.03442	108.2	3.83	1.15	269.69
$\mathbf{1_O}$	−0.20746	−0.03919	105.6	3.81	1.23	258.80
$\mathbf{2_O}$	−0.21249	−0.03852	109.2	3.68	1.23	256.48
$\mathbf{3_O}$	−0.22498	−0.05977	103.7	3.34	1.67	252.87
$\mathbf{1_P}$	−0.19066	−0.02556	103.6	4.27	0.96	272.17
$\mathbf{2_P}$	−0.20553	−0.0708	84.5	3.87	1.93	274.40
$\mathbf{3_P}$	−0.20872	−0.06362	91.1	3.78	1.74	275.85
$\mathbf{1_S}$	−0.20734	−0.06262	90.8	3.82	1.71	260.28
$\mathbf{2_S}$	−0.22347	−0.06596	98.8	3.38	1.81	257.87
$\mathbf{3_S}$	−0.23014	−0.07455	97.6	3.20	2.03	256.90
4	−0.21693	−0.00817	131.00	3.56	0.83	267.98
5	−0.20902	−0.01098	124.27	3.77	0.83	276.33
6	−0.22738	−0.03619	119.97	3.27	1.24	270.59
7	−0.23188	−0.02357	130.71	3.15	1.07	256.74
8	−0.23474	−0.04272	120.49	3.07	1.36	259.99

Generally, group 16 substituents (oxy and thio) are less nucleophilic and more electrophilic carbenes than their group 15 congeners (amino and phosphino). Cyclization decreases the nucleophilicity of $\mathbf{1_N}$ (by 0.49 eV), with a small effect on its electrophilicity (0.04 eV). Unsaturation decreases the nucleophilicity to 3.83 eV but increases the electrophilicity to 1.15 eV for $\mathbf{3_N}$. The decreasing trend of nucleophilicity from acyclic to unsaturated cyclic carbenes is followed in oxy-, thio-, and phosphinoalkylcarbenes. Like aminoalkylcarbenes, the nucleophilicity of all other carbenes is more influenced by cyclization than unsaturation. Subsequently, it is found that aminoalkyl- and phosphinoalkylcarbenes are more basic than oxy- and thioalkylcarbenes. Except for phosphinoalkylcarbenes, the remaining species show a slight decrease in PAs through cyclization and unsaturation.

Compared to NHCs **4**–**8**, our aminoalkylcarbenes show higher nucleophilicities but similar electrophilities. Specifically, $\mathbf{1_N}$ is the most nucleophilic species studied in this work with $N = 4.52$ (compare to the 3.07–3.77 range obtained for NHCs **4**–**8**). Even phosphinoalkylcarbenes with $N = \sim 3.97$ are more nucleophilic than NHCs. However, the nucleophilicities of oxy- and thioalkylcarbenes fall within or near the range obtained for NHCs. The calculated PAs for amino- and phosphinoalkylcarbene resemble those of diaminocarbenes **4**–**6**, while PAs for oxy- and thioalkylcarbenes appear similar to those of the aminothiocarbenes **7** and **8**.

Conclusion

High-level DFT calculations coupled with appropriate isodesmic reactions are employed for investigation of the effects of heteroatom substitution, cyclization, and unsaturation on the stability, multiplicity, and reactivity of the parent di-*tert*-butylcarbene. Amino and oxy substituents induce the largest ΔE_{S-T} due to the stabilization of the singlet state through both π-donating and σ-accepting characteristics. While σ-donor silyl substituents engender triplet ground states, phosphino and thio prefer singlet states due to the π-donating character but with smaller ΔE_{S-T} values than the σ-acceptor substituents. In contrast to the previous reports, it is found that π-donor/σ-acceptor amino substituents stabilize not only the singlet but also the triplet states while oxy substituents do not show a considerable effect on the triplet states. Cyclization increases the ΔE_{S-T} values of the singlet ground-state carbenes due to the stabilization of the singlet and destabilization of the triplet states with the exception of phosphinoalkylcarbene which experiences destabilization of both. The overall effect of unsaturation is the destabilization of both singlet and triplet states for all our carbenes except phosphinoalkylcarbene. Amino- and phosphinoalkylcarbenes appear more nucleophilic and less electrophilic than oxy- and thioalkylcarbenes, respectively. The proton affinities of aminoalkylcarbenes are slightly higher than those of phosphino counterparts. Indeed, amino- and phosphinoalkylcarbenes seem more nucleophilic than some of the synthesized NHCs. The acyclic aminoalkylcarbene with the proton affinity of 278.26 kcal/mol appears as the most basic species among our studied carbenes.

Supporting Information Available: Full reference for Gaussian 98 (ref 17), $\langle S^2 \rangle$ parameter for the open shell structures, and Cartesian coordinates for all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.