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Electronic Stabilization of Ground State Triplet Carbenes

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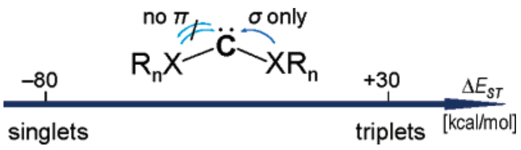

Based on systematic ab initio (CCSD(T)/cc-pVDZ) studies of substituent effects, we present a concept for the construction of electronically stabilized triplet ground state carbenes with singlet−triplet energy separations (ΔE_{ST}) exceeding that of methylene. Sterically demanding and conjugating substituents were excluded from the selection of model compounds under investigation, as these either destabilize both the singlet and the triplet states or delocalize unpaired spins away from the carbene carbon. Negative partial charges on the carbene center allow for the prediction of the electronic stabilization of substituted carbenes. To decrease carbene reactivity, we chose β-substituents with strong polar bonds. Among them, highly electronegative elements such as fluorine and oxygen enlarge the ΔE_{ST} value with respect to hydrogen, while chlorine does not due to p-orbital participation.

Introduction

Stabilizing triplet carbenes is not trivial[1] since the major part of the chemist's arsenal of electronic substituent effects, typically π-donation and -acceptance,[2,3] as well as hyperconjugation[4] and electronegative substituents[5] mainly stabilize the closed-shell singlet state; even electropositive substituents yield singlet carbenes, if at least one of them bears a lone pair.[6] A merely topological approach to enforce the degeneracy of the frontier orbitals through enlargement of the angle at the carbene center by demanding substituents[7−9] is equally unsuccessful to deliver stabilized triplet carbenes because both singlet and triplet states are destabilized with the effect being larger for the smaller angle singlets.[10] Because of these constraints, triplet ground state carbenes remained methodologically behind, and most of the known triplet carbenes possess singlet−triplet energy separations smaller[11] (Figure 1) than that of parent methylene[12] (**1**), resulting in characteristic reactivity[13] of the thermally populated closed-shell singlet state. The elucidation of structural features favoring triplet carbenes is the prime motivation for the present study.

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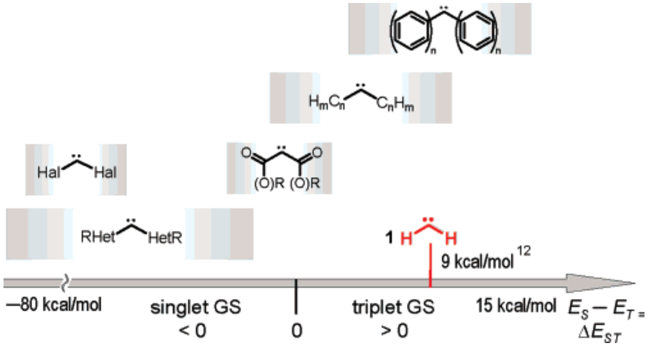
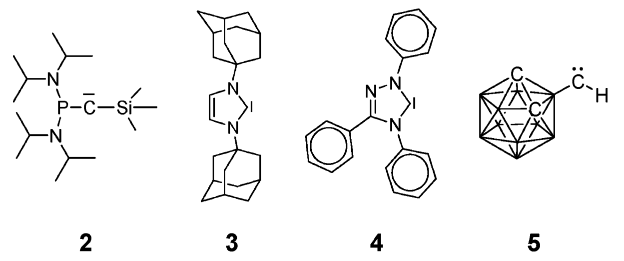


FIGURE 1. ΔE_{ST} ranges of carbene prototypes; according to the IUPAC convention, the values for the triplet ground state (GS) carbenes are positive.

SCHEME 1. Selected Carbene Structures



While powerful strategies have been developed to obtain[14] singlet[15] carbenes stable under normal conditions over months, only a few[16b] sterically congested bis-aryl carbenes survive maximally one day[17] at room temperature, and most other triplets can be observed only at cryogenic temperatures.[18] Whereas Arduengo et al. (e.g., **3**, Scheme 1)[19] and Enders et al. (e.g., **4**, Scheme 1)[20] managed to suppress reactions of the vacant out-of-plane orbital of Wanzlick's $+M/-I$ substituted singlet carbenes[21] through its incorporation into a formally aromatic cyclic six π-electron system, application of the aromaticity concept to triplet carbenes attempted in 1964 by Wasserman and Murray with 4-oxo-2,5-cyclohexadienylidene (**6**, Scheme 2) and its 2,6-dichloro-, 3,5-dichloro-, as well as 2,3-cyclobutadienyl derivatives[22] led to species that are better described as reactive σ/π-biradicals[23] with at least one highly delocalized electron.

Therefore, kinetic protection of the reactive triplet carbene center, which is needed to avoid barrierless[24] dimerization,[25] might be achieved by steric shielding. The reactivity of di-*t*-butyl carbene[8] implies further that bulky substituents with strong σ-bonds are required; bis-aryl triplet carbenes serve this purpose well. However, these kinetically stabilized species, addressed as early as 1911 by Staudinger and Kupfer[26] and systematically studied by Tomioka,[16] reveal reaction patterns[27,28] and EPR *D*-values[16,17,29] (which approximately evaluate the average distance between radical centers)[30] for unpaired spins effectively delocalized over the unsaturated moieties of, for example, **7** (Scheme 2). Hence, conjugation increases the thermodynamic stability but inevitably converts a genuine carbene into a biradical with distant radical centers.

Our strategy to stabilize triplet ground state carbenes electronically is to influence the degenerate orbitals of the carbon atom as little as possible, while simultaneously compensating for its electron deficiency by bonds to electropositive atoms (Scheme 3). This means a desirable combination of structural features such as (i) use of an element more electropositive than carbon in the α-position, lacking multiple bonds, empty or occupied p-orbitals, as well as strongly hyperconjugating groups to minimize preferential singlet state stabilization; (ii) identical substituents ideally with a high local symmetry to retain the degeneracy of the carbene frontier orbitals; and (iii) incorporation of strong polar bonds to the α-atom to avoid intramolecular rearrangements (to improve kinetic stability).

Conceptually, this approach appears highly promising since H−C-3-*o*-carborane (**5**, Scheme 1),[31] $H{-}C{-}SiH_3$,[32] $H{-}C{-}Si(CH_3)_3$,[33] $H{-}C{-}SiH(CH_3)_2$,[33] and $(CH_3)_3Si{-}C{-}Si(CH_3)_3$[33] possess triplet ground states, and $H{-}C{-}Si(OCH_3)_3$,[34] H−C−

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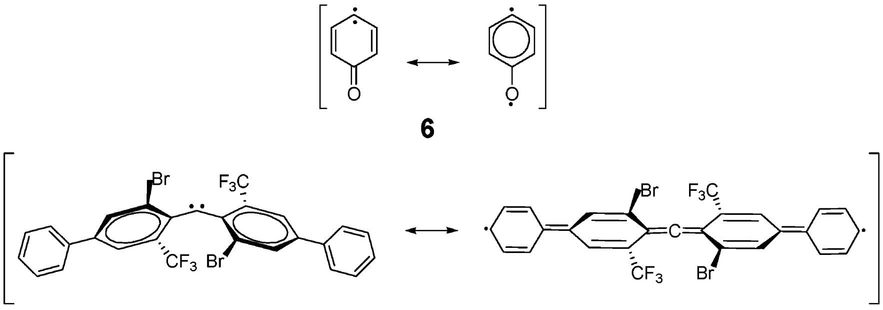
SCHEME 2. State of the Art: Strategies and Drawbacks of Stabilizing Triplet Carbenes



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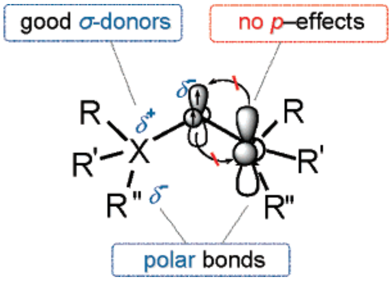
SCHEME 3. Effects toward the Stabilization of Triplet Carbenes



SiHCl$_2$,[35] as well as $C_6H_5-C-PO(OCH_3)_2$[36] have proven not to undergo intramolecular insertions into Si−O, Si−Cl, and P−O bonds. To increase their lifetime additionally, substituents of the model triplet carbenes can be modified by established methods[37] for the kinetic protection of the reactive carbene center (e.g., steric shielding).

Computational Methods

Model singlet and triplet carbenes were optimized at the coupled cluster level of theory truncated to single, double, and perturbatively included triple substitutions [CCSD(T)][38] combined with a correlation consistent polarized valence double-ζ basis set, cc-pVDZ.[39] Keeping in mind the comparably good performance of the density functional theory approach, utilizing the Becke, Lee, Yang, and Parr three-parameter hybrid functional B3LYP[40] to carbenes in general[3] and to the selected structures (cf. Supporting Information) in particular, we also applied it to compute formal reaction energies of isodesmic equations in combination with a Pople-type triple split valence contracted basis set, containing polarization and diffuse functions on all atoms, B3LYP/6-311++G(*d*,*p*). The same level of theory was chosen to carry out natural population analyses[41] to determine charges and spin densities. All stationary points were characterized based on analytical frequency computations. For the singlet carbenes we utilized restricted and for triplet carbenes unrestricted HF reference wave functions. Errors in the description of singlet closed-shell carbenes by single reference computational approaches[42] are neglected since the singlet−triplet energy separations reported here exceed them by one order of magnitude.

Results and Discussion

Singlet−Triplet Energy Separations. To probe the proposed concept, we focused on symmetrically substituted carbenes with electropositive atoms Si (EN = 1.8),[43] B (EN = 2.0),[43] P (EN = 2.1),[43] and S (EN = 2.5)[43] in the α-position, possessing highly polar, strong bonds such as SO, PO, SiO, SiF, and BF. A selection of alkyl carbenes was considered for comparison. Since the singlet−triplet energy splittings are a function of multiple variables including p- as well as σ-contributions, T_e values (purely electronic ΔE_{ST} without consideration of the zero-point vibrational energy), summarized in Figure 2, do not strictly follow the electronegativities of the α-atom. $C(BH_2)_2$, for example, exhibits a T_e value, which does not lie between that of methylene (**1**, 12.1 kcal/mol, CCSD(T)/cc-pVDZ) and disilyl carbene $C(SiH_3)_2$, as expected merely on the grounds of inductive effects. As the occupancy of the empty p-orbital on boron increases from BH_2 over BF_2 to BF_3^- due to the lone pair electron donation from adjacent F atoms, the energetic preference of the closed shell singlet vanishes, and the respective boryl carbene adopts a T_e value consistent with its electronegativity. That is, the smaller the p-acceptor ability of the substituent, the weaker its interaction with the occupied p-orbital on the carbene carbon is, as displayed by the rotational barriers for triplet carbenes (Figure 3a), and the larger the T_e value is. Similarly, in singlet silyl carbenes, both negative and positive hyperconjugative interactions are diminished with respect to alkyl carbenes,[45] and in the triplets, these are almost absent [the D_{3d} and D_{3h} structures of $^3C(SiH_3)_2$ and $^3C(SiF_3)$ are quasi-isoenergetic, with rotational barriers smaller than 0.1 kcal/mol at CCSD(T)/cc-pVDZ (Figure 3b)]. Hence, in accord with Si's

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[44] For each of the singlets **13** and **12**, there is one imaginary frequency of ^{a}74 and ^{b}153 cm^{-1}, indicating attractive interactions between the carbene carbon and the oxygen perpendicular to the carbene plane (parallel to the out-of-plane unoccupied orbital) were found; for structures ^{3}**10**, ^{3}**12**, ^{3}**13**, and ^{1,3}**14**, vibrational frequencies could not be computed; an examination of the respective Hessian matrices revealed no negative eigenvalues.

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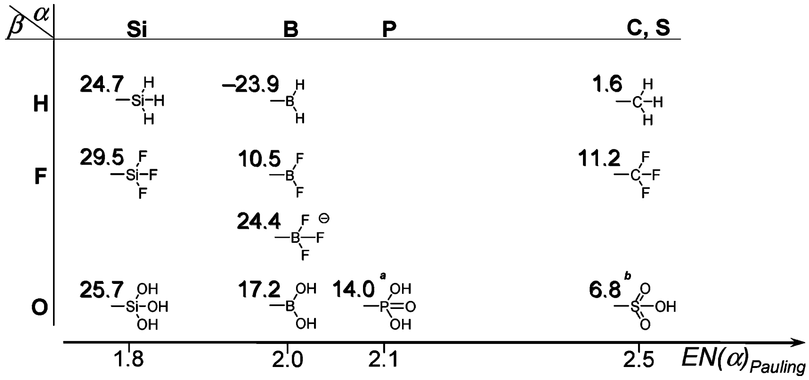


FIGURE 2. Electronic singlet−triplet energy separations (T_e) for carbenes of the general structure CR_2 (CCSD(T)/cc-pVDZ) as a function of Pauling electronegativity, EN, of the α-atoms for the rows of varying β-substituents.[44]

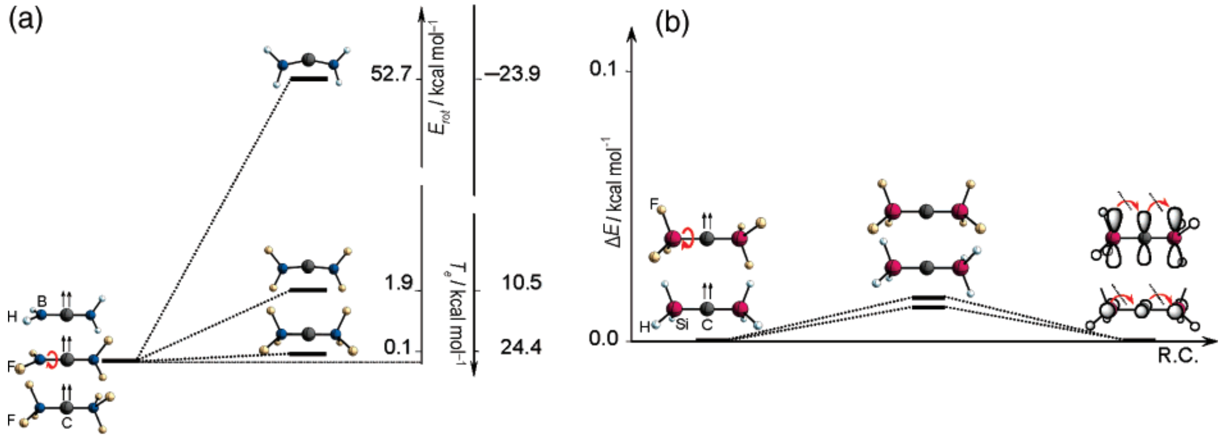


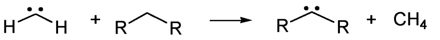
FIGURE 3. (a) Influence of the interaction of substituent's p-orbitals with carbene SOMOs (Singly Occupied Molecular Orbitals) on the ΔE_{ST} (CCSD(T)/cc-pVDZ) value. (b) Rotation energy and p-effects in Si carbenes (CCSD(T)/cc-pVDZ).

TABLE 1. Charges, q_C, on the Central Carbon Atom Obtained from NBO Analyses at B3LYP/6-311++G(*d*,*p*) for Carbenes with the General Structure CR_2

R	no.	$q_C(^1CR_2)$	$q_C(^3CR_2)$
NH_2	**8**	0.173	0.249
CH_3	**9**	0.121	0.179
CF_3	**10**	0.138	0.165
H	**1**	−0.109	−0.229
BF_3^-	**11**	−0.476	−0.457
SO_2OH	**12**	−0.397	−0.327
$PO(OH)_2$	**13**	−0.768	−0.588
$Si(OH)_3$	**14**	−0.926	−0.801
SiH_3	**15**	−0.735	−0.685
$SiCl_3$	**16**	−2.314	−0.759
SiF_3	**17**	−0.771	−0.820

electronegativity, these carbenes exhibit the largest T_e values among the model carbenes under consideration and any other carbenes discussed before. For the same reason, the dependence of T_e on the choice of β-substituents is the least pronounced in the series of silyl carbenes ($\Delta T_e(C(SiH_3)_2/C(SiF_3)_2)_{CCSD(T)/cc-pVDZ} = 4.7$ kcal/mol, $\Delta T_e(C(CH_3)_2/C(CF_3)_2)_{CCSD(T)/cc-pVDZ} = 9.6$ kcal/mol, and $\Delta T_e(C(BH_2)_2/C(BF_2)_2)_{CCSD(T)/cc-pVDZ} = 34.4$ kcal/mol).

Stabilization by Charge. The charges on the carbene carbon (Table 1) indicate that all chosen α-substituents less electronegative than C stabilize carbenes by σ-donation. They are proportional to the EN of the α-substituent (cf. the series PO, SO, and SiO), and the overall stabilization by Si, the strongest σ-donor, is the largest, as confirmed by the homodesmotic eq 1 (Table 2). The polarization of adjacent bonds to atoms in the β-position, determined by their EN and readily understood on the grounds of hybridization, dominates the charge on the triplet carbene carbon. In singlet carbenes, it is additionally affected by the hyperconjugation of the empty carbene out-of-plane orbital. Therefore, for all singlet carbenes, charges are less positive or more negative than for triplet pendants. The large value for the C_1 carbene $^1C(SiCl_3)_2$, **^{1}16**, with one bridging Cl atom can be rationalized in terms of attractive interactions of the carbene carbon with the p-orbitals on Cl, as depicted for the model compound $^1CH(SiClH_2)$ in Scheme 4.



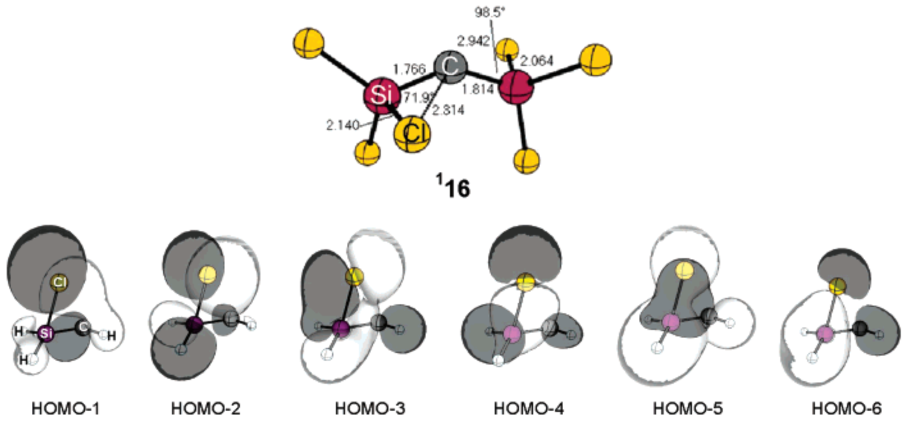
(1)

TABLE 2. Reaction Energies (ΔE_S for Overall Singlet, ΔE_T Triplet Multiplicity) of Isodesmic Eq 1 at B3LYP/6-311++G**

R	ΔE_S[kcal/mol]	ΔE_T[kcal/mol]
NH_2	−48.3	15.9
CH_3	−27.8	−15.3
CF_3	−1.4	−0.5
SO_2OH	−3.2	3.1
$PO(OH)_2$	−10.8	−7.6
$Si(OH)_3$	−10.5	−21.9
SiH_3	−12.6	−23.8
SiF_3	1.9	−15.7

While σ-donation predominantly stabilizes the triplet and σ-acceptance the singlet carbenes, p-effects generally favor

SCHEME 4. Interaction of Orbitals of Carbene Carbon with Lone Pairs of Cl in the *β*-Position[a]



[a] $^1C(SiCl_3)_2$ parameters in Ångstroms, optimized at B3LYP/6-311++G**; for $^1CH(SiClH_2)$, NBOs (Natural Bond Orbitals) at CCSD(T)/cc-pVDZ.

singlet carbenes. That is, contrary to a previous suggestion,[46] T_e is generally not expected to correlate with the total charge on the carbene carbon, which would be further inconsistent with $q(C_{atom}) = 0$ possessing the largest ΔE_{ST} value. Rather, T_e correlates with each of these contributions individually, which are difficult to be differentiated because of the strong sp-admixture of the in-plane frontier ($3a_1$-type) orbital.

Whereas for the classical p-donor/σ-acceptor substituted singlet ground state diamino carbenes the homodesmotic equation indicates singlet stabilization/triplet destabilization and strongly hyperconjugating alkyl-substituents favor singlet multiplicity, σ-donor substituents lacking p-interactions with the carbene center preferentially stabilize triplet carbenes. The effect of the β-substituent is smaller for Si than for C carbenes: stabilization on going from H to F changes for Si less than for C in the α-position.

Structural Features. The geometries (cf. point groups (PGs), Figure 4) of symmetrically substituted singlet carbenes **9**−**17** may be interpreted as a compromise between hyperconjugation from bonds almost perpendicular to the carbene molecular plane (parallel to the out-of-plane b_1-type orbital) and the donation of the lone pair on the carbene center to the antibonding orbitals of antiperiplanar σ-bonds. The first structural characteristic is reminiscent of the intramolecular stabilization operating in symmetrically substituted C_2 carbenium ions.[47] In the preferred conformers of triplet carbenes, the interactions of the singly occupied orbitals with substituents leave their orientations relative to each other and to the carbene plane unchanged with respect to the corresponding CH_2R_2 compounds (cf. Supporting Information). To determine the individual effects of the substituents, structures of some monosubstituted carbenes were optimized (Figure 4) as well. The strongest hyperconjugation is observed with the methyl, sulfonyl, and phosphoryl groups, as the bond (C-α-atom) and angle (C-α-atom−β-atom$_{\perp\text{carbene−plane}}$) contraction in the singlet carbenes reveal. In the bis-sulfonyl and bis-phosphoryl carbenes, the bonds with higher p-character act as donors since the energy difference to the low lying b_1-type acceptor orbital is smaller than that of the nominal single bonds. Chlorine in the β-position preferentially stabilizes the singlet carbene via interaction with p-orbitals, leading to a smaller T_e value. As was already stated on the basis of the stabilization energies, carbon mediates this effect considerably better than Si, which manifests in a 10° larger angle contraction and three times larger bond lengthening. In triplet carbenes, all angles are almost equal and are only slightly smaller than those to the β-substituent anti to the CH bond of the singlet carbenes, in line with the weaker hyperconjugative interaction with the singly than doubly occupied and unoccupied orbitals on the carbene carbon. Hence, as further confirmed by singlet planarization with decreasing p-orbital occupancy from $-BF_3^-$ (120°, C_2) over $-BF_2$ (147°, C_{2v}) to $-BH_2$ (180°, D_{2h}) unlike the overall triplet boryl carbenes (D_{3d}, D_{2d}, and D_{2d}, respectively), the geometries of singlet carbenes are more sensitive to p-effects than those of the triplets. On the contrary, σ-effects have a predominant influence on the geometries of triplet carbenes: the angles on the carbene centers vary over 23° for triplets and only 8° for singlets.

The chosen disubstituted structures challenge[48] the commonly accepted view[4,49] based on Bent's rule[50] that there is a proportionality between the singlet−triplet energy splitting and the angle at the divalent carbon of a carbene. This rule holds only if inductive effects operate and all other through-space and through-bond contributions are negligible. The case of $C(BH_2)_2$ demonstrates that the 180° angle guaranteeing the degeneracy of the frontier orbitals in a triplet carbene is not a sufficient condition for $\Delta E_{ST} > 0$ since the stabilization of singlet carbene can surpass the exchange energy.

Spin Densities: True Carbenes. As evident from the spin densities on the carbene carbon (Figure 5), all chosen compounds possess fairly localized electronic structures as compared to diphenylcarbene at the same level of theory, legitimating their description as carbenes. The most delocalized of them are those bearing substituents with double bond participation (spin density on the out-of-plane oxygen amounts to 0.1 in $^3C(SO_2OH)_2$, **^{3}12**, and $^3C(PO(OH)_2)_2$, **^{3}13**). The delocalization of silyl carbenes is generally marginal and parallels the ΔE_{ST} values, with the leader $^3C(SiF_3)_2$, **^{3}17**, followed by $^3C(Si(OH)_3)_2$, **^{3}14**.

Bonding in Silyl Carbenes. An ideal triplet carbene with perfectly localized p-electrons and an ΔE_{ST} value approaching

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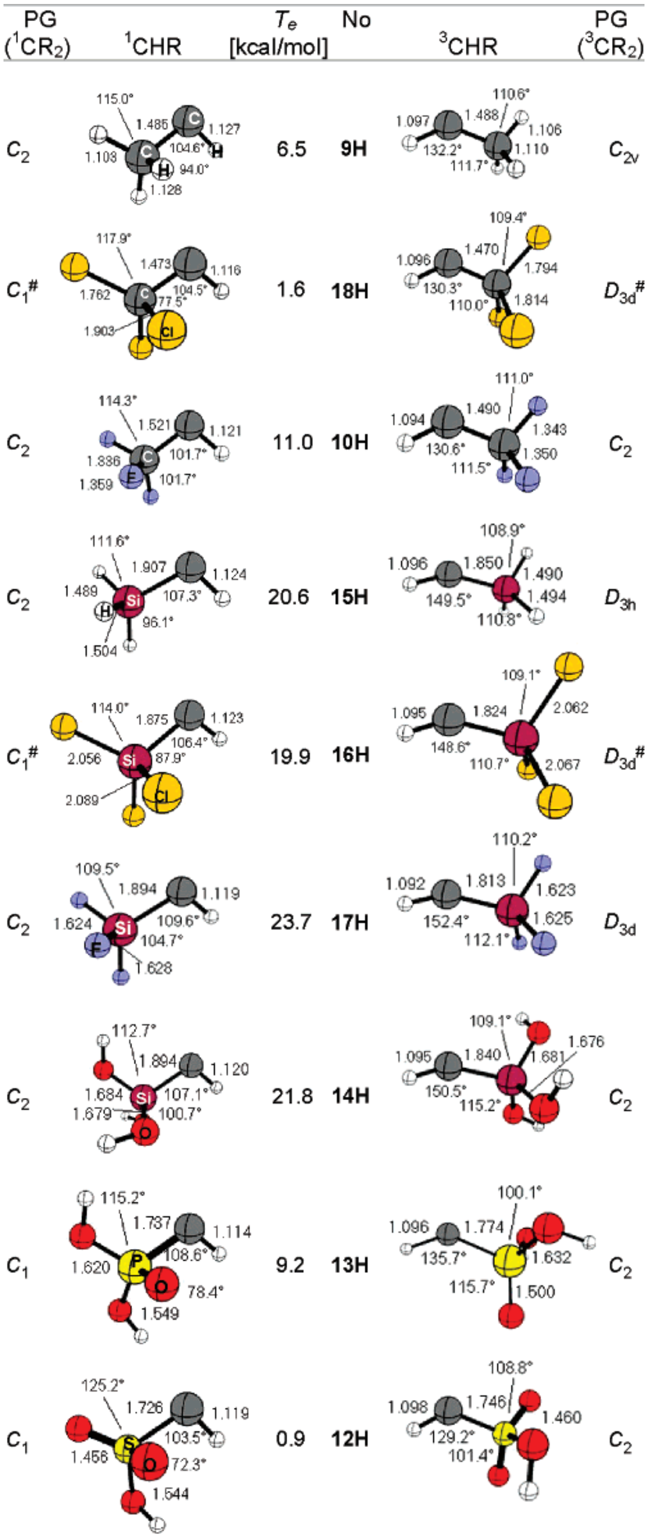

FIGURE 4. Optimized geometries and T_e values of selected monosubstituted carbenes, HCR, and PGs of respective disubstituted carbenes, CR_2, (CCSD(T)/cc-pVDZ); bond lengths in Ångstroms. All H^1CR carbenes, $H^3C(Si(OH)_3)$, $H^3C(SO_2OH)$, and $H^3C(PO(OH)_2)$ are asymmetric; the remaining triplet carbenes possess C_s symmetry. #: PGs of CR_2 structures optimized at B3LYP/6-311++G**.

that of a carbon atom due to purely through-bond electronic effects should acquire as much electron density as possible via σ-donation but should not interact with any (group) p-orbitals. This requirement is fulfilled by bis-trifluorboryl and bis-silyl carbenes.

All data presented above underline the superiority of bis-trifluorboryl and bis-silyl carbenes in every aspect: they possess the largest T_e values, the highest negative charges on the carbene carbon and thus the strongest stabilization, the least spin delocalizations, and triplet's angles around 180° due to purely electronic effects (at least for SiH_3 groups, steric repulsion can be excluded). The particularity of these substituents originates not only from strong σ-donation: the crucial property of the C_{3v} symmetrical SiX_3 groups, creating a cylindrical symmetry electronic environment for C, may be seen in their poor hyperconjugative ability. This is well-known from the diminished conformational preference of $H_3SiOSiH_3$^{51} and the rotational barrier of H_3SiSiH_3^{52} with respect to their alkyl^{53} pendants (cf. also Figure 4). Covalent bonding as well as antibonding interactions of Si to a given atom are known to be weaker than those of C, and the smaller^{55} overlap integrals lift the energetic advantage on bending of the a_1 frontier orbital in favor of the SOMOs degeneracy (Scheme 5).

Isogyric eqs 3 and 4 show that the energy (CCSD(T)/cc-pVDZ) of the bond between the silyl-substituents and the carbene carbon is of the same order of magnitude as in saturated covalently bonded compounds (eq 2).

$$H_3C{-}SiF_3 \longrightarrow H_3C\cdot + \cdot SiF_3 \qquad \Delta E_R = 101.4 \text{ kcal/mol} \qquad (2)$$

$$F_3Si{-}\ddot{C}{-}SiF_3 \longrightarrow F_3Si\dot{\underset{\cdot}{C}}\cdot + \cdot SiF_3 \qquad \Delta E_R = 105.3 \text{ kcal/mol} \qquad (3)$$

$$F_3Si{-}\ddot{C}{-}SiF_3 \longrightarrow |\dot{\underset{\cdot}{C}} + 2\cdot SiF_3 \qquad \Delta E_R = 175.6 \text{ kcal/mol} \qquad (4)$$

In contrast to an earlier proposal,^{33} the participation of Si d-orbitals is of minor importance for the description of the electronic configuration of the carbenes. There is no differential stabilization of the triplet state since the inclusion of d-functions on α-atoms does not change T_e significantly, irrespective of their belonging to the second or third row of elements (Figure 6).^{56} A much larger contribution stems from d-orbitals on the carbene center itself.^{57}

Conclusion

To obtain triplet ground state carbenes, substituents less electronegative than carbon should be utilized. However, the success of this approach depends largely on p-effects such as (hyper)conjugation, as demonstrated in a series of boryl carbenes and by the comparison of alkyl versus silyl carbenes. Moreover, p-donors as well as p-acceptors affect the charges and angles at the carbene carbon significantly, and no correlation with ΔE_{ST} can be generalized. While the hybridization concept helps rationalize trends in ΔE_{ST} values due to the electronegativity

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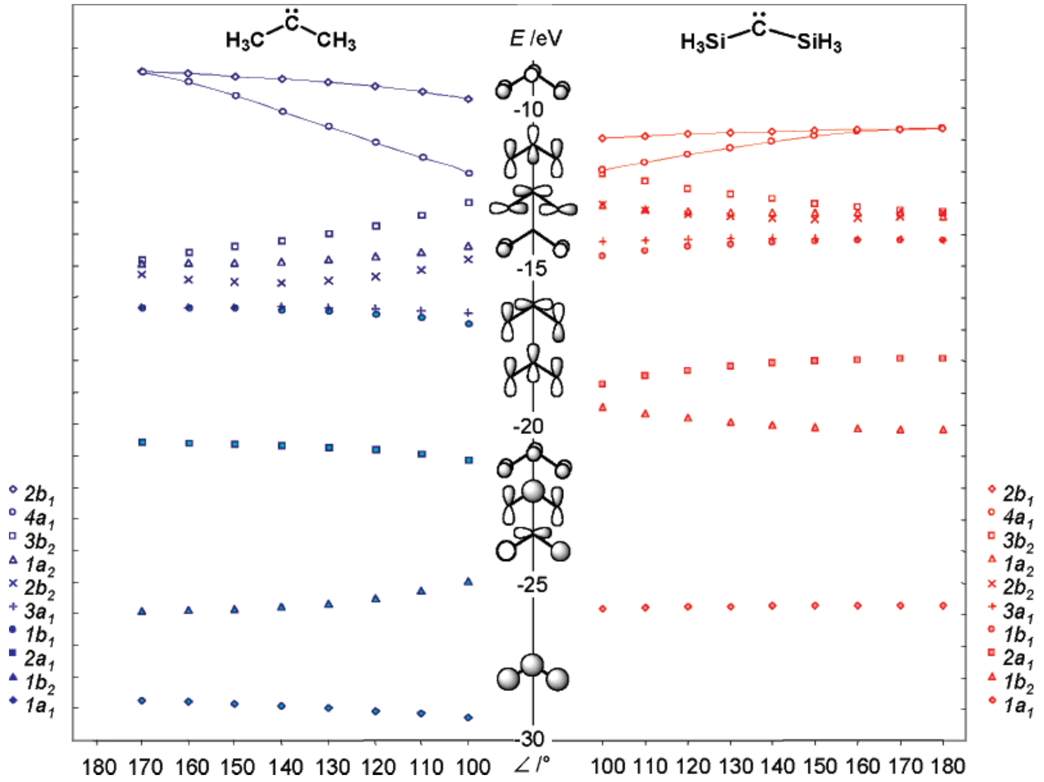
SCHEME 5. Comparison of Correlation Diagrams[54] of Orbital Energies (CCSD(T)/cc-pVDZ) with Angles at the Carbene Carbon for Carbenes $^3C(CH_3)_2$ and $^3C(SiH_3)_2$[a]



[a] Ordering (middle) and symmetry designations (margins) of schematic atomic orbital combinations with increasing energy. For generality, relative coefficients, exact orientation deviations from principal axis of contributing atomic orbitals on centers in the α-position, as well as atomic orbitals of β-substituents, comprising respective group orbitals, are omitted. Data for SOMOs, discussed in text, are connected for eye guidance.

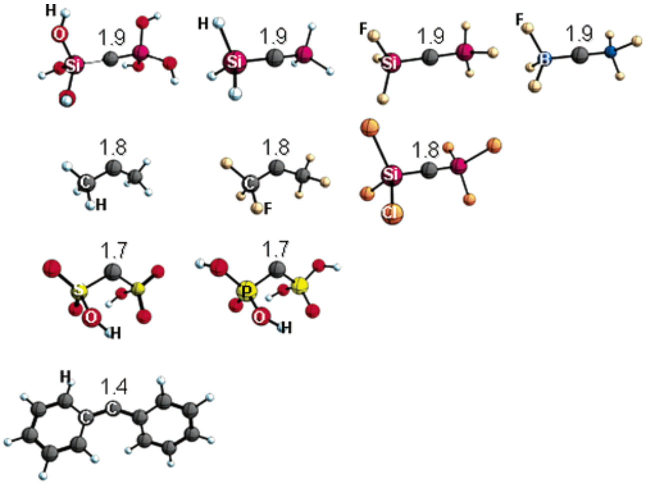


FIGURE 5. Spin densities on the central carbon atom obtained from NBO analyses at B3LYP/6-311++G(*d*,*p*) for carbenes with the general structure CR_2; the value for CH_2 equals 2.0. The expectation values of the spin operator amount to 2.00 at CCSD(T)/cc-pVDZ for all carbenes and 2.01 at B3LYP/6-311++G** with the exception of 2.09 for $^3C(C_6H_5)_2$ and 2.06 for $^3C(SO_2OH)_2$.

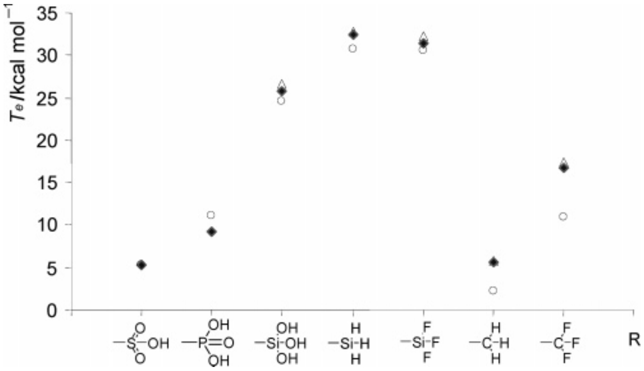


FIGURE 6. Dependence of the T_e values on the inclusion of d-functions. Δ: B3LYP/6-31G for all atoms. ♦: B3LYP/6-31G for all atoms except those in the α-position of the carbene carbon; B3LYP/6-31G(*d*) for the α-atoms. o: B3LYP/6-31G(*d*) for all atoms. At B3LYP/6-31G, structures ^{1}**12** and ^{1}**13** possess one imaginary frequency toward a stronger interaction of the out-of-plane oxygen with carbene carbon (−371 and −48 cm^{-1}, respectively) each; lifting symmetry constraints does not lead to chemically meaningful structures.

of the β-substituents, p-orbital contributions may be important, as exemplified for chlorine.

Partial charges (most negative for Si carbenes) show that electropositive substituents stabilize the carbene carbon thermodynamically, reducing its electron deficiency. The unpaired spins of all studied triplet carbenes are highly localized on the central carbon atom, in marked contrast to many so-called stable triplet carbenes. The highest spin densities are predicted for effectively linear triplet ground state silyl carbenes; their ΔE_{ST} values exceed the others by far.

In searching for electronically stabilized triplet ground state carbenes, one should thus focus on silyl carbenes. Furthermore, SiF, SiO, and SiCl substitution provides exceptional kinetic stability toward homolysis and rearrangement. While $^3C(SiF_3)_2$

should be the global minimum on the PES of respective stoichiometry, sterically demanding siloxy-substituents appear to be the most promising to facilitate kinetic stability toward inter- and intramolecular reactions.

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Supporting Information Available: Cartesian coordinates, electronic energies, ZPVEs, and expectation values of the spin operator of optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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