Tuning Spin-States of Carbynes and Silylynes: A Long Jump with One Leg

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Ⓢ *Supporting Information*

ABSTRACT: The challenge motivating this paper is to induce, by chemical substitution, a silylyne, SiR, or a congeneric carbyne, CR, to adopt the high-spin quartet rather than the low-spin doublet as its ground state. The difficulty is seen in the preference for the doublet of the parent SiH (doublet−quartet energy difference ~39 kcal/mol, favoring the doublet) or CH (~17 kcal/mol). Strategies for having high-spin ground state parallel those for silylenes and carbenes: greater electropositivity (σ-donation) and π-acceptance of the single substituent favor the high-spin state. The electronegativity trend can be understood from an *ions in molecules* way of thinking already present in the literature in the works of Boldyrev and Simons, and of Mavridis and Harrison; i.e., the quartet ground state spin of some CR/SiR species is largely determined by the ground state spin of C^-/Si^-. In this study, we provide a diabatization analysis that solidly confirms the *ions in molecules* picture and explains the difference in the equilibrium internuclear distances for the two spin states. In general, electronegativity dominates the ordering of spin states. π-Acceptors also help to lower the quartet state energy of the many carbynes (silylynes) examined, whose range of doublet−quartet differences calculated is impressive, 120 (100) kcal/mol. The qualitative understanding gained leads to the prediction of some quartet-ground state carbynes (CMgH, CAlH$_2$, CZnH, CSiH$_3$, CSiF$_3$, etc.) and a smaller number of silylynes (SiMgH, SiMgF, SiBeH, etc.). A beginning is made on the energetics of approach geometries of the fragments in the highly exoergic dimerization of CH to acetylene; it should proceed for the ground state doublet CH through C_{2h}-like trajectories, with no activation energy.
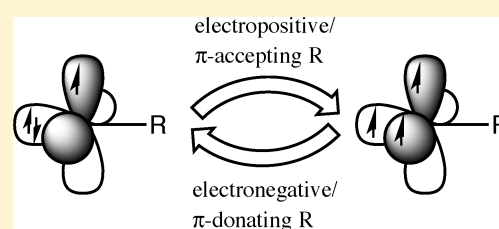
INTRODUCTION

The balance that certain Si and C-based molecular fragments strike between high and low spin ground states has been of interest to two of the coauthors of this paper for decades. One of us (H.F.S.) predicted that the triplet ground state of methylene has a strongly bent structure, at a time when the experimental facts were unclear,[1] and also suggested how one might obtain triplet silylenes through a combination of steric effects of bulky groups and electropositive substituents.[2] Another one of us (R.H.) earlier identified productive strategies for stabilizing singlet methylenes.[3−5]

In the parent EH$_2$ compounds, E = C, Si, CH$_2$ is a ground state triplet, 9 kcal/mol below the lowest singlet,[6,7] while SiH$_2$ is clearly a ground state singlet, with its lowest triplet being 21 kcal/mol higher.[8−10] The problem is the archetypical organic diradical one: a σ orbital and a p orbital, as shown in **1a**, and two electrons. The nature of the ground state is a function of the relevant Coulomb and exchange integrals, and extent of configuration interaction (multireference character). But the most decisive factor for whether one has a singlet or triplet ground state is the splitting in one-electron energy between the

σ and p orbitals. Note that as the bond angle α opens up to form a linear EH$_2$, the σ and the p orbitals evolve to the two degenerate p_x and p_y orbitals shown in **1b**, favoring a triplet ground state by the Hund's rule. It is this σ-p splitting and how it is influenced by σ/π donors/acceptors and any geometrical variables that provide handles for tuning the spin state energetics of carbenes and silylenes.[3−5,11,12]
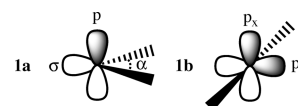
Before we jump to carbynes (CR) and silylynes (SiR), let us first look at their parent systems, CH and SiH, both with 5 valence electrons. As **2** shows, there are two low-lying σ orbitals (the EH bonding orbital (σ_{EH}) and the lone pair orbital (σ_{lp}) on E), two degenerate π orbitals (p_x and p_y), and the σ_{EH}^* antibonding orbital (not shown). The actual shape of all the

canonical valence orbitals of EH is shown in Figure 1 below; the representations in **2** are schematic.
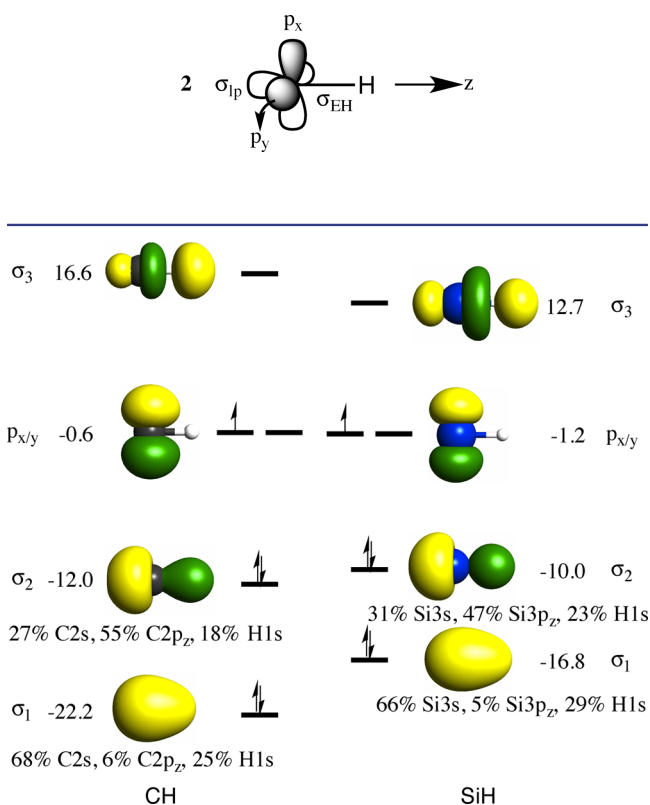

Figure 1. Valence molecular orbitals of CH and SiH from 5o5e complete active space self-consistent field calculations of the $^2\Pi$ states at their respective r_e values. Their orbital energies in eV are given beside them. Orbital occupation schemes of the $^2\Pi$ states are also given. Mulliken population decompositions in percentage are given for the occupied σ orbitals. Black, blue, and white spheres represent C, Si, and H atoms. Yellow and green represent orbital phases. Note the 2-fold degeneracy of the p orbitals.

While both σ_{EH} and σ_{lp} are variable linear combinations of ns and np_z on E and the H $1s$, it is not too much of an oversimplification to think of them as the σ_{EH} bond (often polar) and a directed, "out-pointing" hybrid on E. The competition for the ground state of the molecule is then between a doublet **3**, with four electrons paired in the two σ orbitals and one in the degenerate π (p) shell ($\sigma^2_{EH}\sigma^2_{lp}p_x^1$ or $\sigma^2_{EH}\sigma^2_{lp}p_y^1$), and a quartet **4**, with the configuration $\sigma^2_{EH}\sigma^1_{lp}p_x^1p_y^1$ (or $\sigma^2_{lp}\sigma^1_{EH}p_x^1p_y^1$, e.g., see CLi below).[13,14] Their connections to the electronic configurations of the lowest triplet and singlet states of ER_2 is apparent.
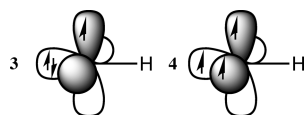
The magnitude of the problem facing the tuner of spin states is that the doublet ($^2\Pi$) state is below the quartet ($^4\Sigma^-$) by about 17 kcal/mol for CH,[15−18] and about 39 kcal/mol for SiH.[19,20] Experimental data for the quartet−doublet energy difference of SiH has been questioned, and here we quote results from high-level calculations. The difficulty is obvious: the quartet−doublet energy differences are much greater for EH than the triplet-singlet counterparts of EH_2. And we have

one less handle on the molecule. With only one ligand in carbynes and silylynes, we also lose the structural means (the angle α in **1a**) that can be used in tuning spin of ER_2. Overall, with the larger energy difference and only one ligand, reversing the energy order of the doublet and quartet states is a little like asking us to jump farther using one leg. That electronegativity of the ligand R provides a means of stabilizing the quartet has already been demonstrated for CLi, CNa, and SiLi, in the works of Boldyrev et al.[21,22] and in those of Mavridis et al.[11,23,24] How generally applicable is this strategy? We will expand below on their argument and show the wide range of the tuning possible.

There are further reasons for studying these fragments. Because of the considerable cosmic abundance of silicon, molecules bearing Si have attracted much attention in the study of extraterrestrial environments,[25−27] as well as in the laboratory for the construction of new compounds with metal−silicon multiple bonds.[28−31] For instance, So et al. have synthesized and characterized different diaminochlorosilyl substituent from silylilylenes, in which Si−Si, Si−N, Si−S, and Si−Se chemical bonds are contained.[32] The carbyne, CR, fragment has a long history as a ligand in organometallic chemistry[33−36] and an active reactant in both organic and inorganic chemistry.[37−40] These diverse instances of the interest and utility of SiR and CR fragments add to our motivation to explore their ground state spins.

■ SiH AND CH, A STARTING POINT

A series of theoretical studies of SiH has been summarized by Kalemos and Mavridis in 2002.[19] To our best knowledge, the only experimental quartet−doublet energy difference ($\Delta E(Q - D) = E(^4\Sigma^-) - E(^2\Pi)$) for SiH was reported to be $\sim$5000 cm^{-1} (14.3 kcal/mol).[41] However, this 1979 experimental value was claimed to be "wrong" by Kalemos and Mavridis:[19] they calculated the value to be 38.9 kcal/mol. In 2013, Li et al. reported the theoretical $\Delta E(Q - D)$ as 38.7 kcal/mol at the CCSD(T)/cc-pwCV5Z level.[20] With our methodology (*vide infra*), the value is calculated to be 36.8 kcal/mol (Table 1), in decent agreement with the previous high-level calculations.

Table 1. Calculated Properties of ER with R = Li, H, F

E\R	Li	H	F
	$\Delta E(Q - D)^a$ in kcal/mol		
C	−35.3	13.1	78.4
Si	−17.0	36.8	81.6
	r_e of $^4\Sigma^-$ in Å		
C	1.89	1.09	1.33
Si	2.36	1.50	1.62
	r_e of $^2\Pi$ in Å		
C	2.09	1.13	1.28
Si	2.69	1.53	1.62

$^a\Delta E(Q - D) = E(^4\Sigma^-) - E(^2\Pi)$. $E(^4\Sigma^-)$ and $E(^2\Pi)$ are energies at the optimized structures of the respective states. Energies are calculated using GMCPT method (see Computational Methods section in the end of paper).

Our calculated $\Delta E(Q - D)$ for CH (13.1 kcal/mol, Table 1) deviates somewhat from the experimental value[15−17] (17.1 kcal/mol) and the result (17.2 kcal/mol) of a good theoretical study.[18] By expanding our basis set to approach the one in ref 18 and using their larger 10o5e (see Computational Methods section) active space, we improve our $\Delta E(Q - D)$ to 16.0 kcal/mol, suggesting that the error mainly comes from the imperfect

basis set and active space. Since we wish to study a wide range of substituents, we need to compromise between computational accuracy and efficiency. We are interested in the overall trend of the quartet−doublet energy ordering, and we believe a computational error on the order of 4 kcal/mol will not alter our main conclusions.

We show in Figure 1 the valence molecular orbitals (MOs, alternatively canonical MOs, CMOs) of the CH and SiH ground states side by side. The occupation schemes are described in 3: two doubly occupied σ and one singly occupied π (p) orbital in the doublet. For both molecules, Mulliken population analysis shows that the lowest σ_1 orbital is mainly the E ns ($2s/3s$ for C/Si) orbital, with some bonding mixing with the H $1s$. σ_2 is the E np_z, hybridized with ns, and interacting in a bonding way with the H $1s$. The H $1s$ makes greater contributions in the two bonding σ orbitals of SiH than in CH, consistent with the lower electronegativity of Si. The CMOs of the $^4\Sigma^-$ states of the two molecules differ in small ways and are not shown. The doublet-to-quartet transitions promote one electron from σ_2 to the unoccupied p orbital.

In the canonical orbitals, the EH bonding is distributed over the two lowest orbitals. More "concentrated" or localized orbitals, the σ_{lp} lone pair and the σ_{EH} bonding orbitals, can be recovered through a natural bonding orbital (NBO) analysis[42,43] (see Section S1 in the Supporting Information (SI)) The MOs shown in Figure 1 thus supports 2. With the orbitals and states of the parent CH and SiH systems in clear focus, we proceed with a systematic chemical strategy for tuning the doublet−quartet splitting.

■ ELECTRONEGATIVITY AS A FACTOR

There is both experimental and theoretical evidence that electronegative R substituents favor low-spin ground states of the two-coordinated fragments ER_2,[44−47] while electropositive ones favor high-spin.[12,48−52] Considering the aforementioned connection between the low and high spin electronic configurations of ER and ER_2, a natural thought is to tune the doublet and quartet energetics of ER through the electronegativity of R. We first look at three cases: the typical electronegative R = F, the electropositive R = Li, and the intermediate R = H. Li is also a π-acceptor and F a π-donor, but we think the σ effect will dominate. The calculated $\Delta E(Q - D)$ values are compared in Table 1. The GMCPT methodology used is described in the Computational Methods section at the end of this paper. Negative $\Delta E(Q - D)$ implies a quartet ground state. Our calculated bond lengths are reasonably reliable; for instance, the calculated doublet CF bond length compares favorably with the experimental[53,54] value (1.28 vs 1.27 Å). Our quartet CLi and SiLi bond lengths (1.89 and 2.36 Å) are similar to other theoretical[21,22] values (1.88 and 2.38 Å).

Clearly the electropositive Li favors the quartet (which is not a new finding[11,12,21−23]), the electronegative F favors the doublet, and the intermediate H lies in between. This trend can be qualitatively understood in the following way. In the limit of complete electron transfer, E^-Li^+, the entity E^- becomes isoelectronic to an N or P atom, which has a quartet ground state (the ^4S_u term), while Li^+ has the closed-shell term symbol ^1S_g. Coupling the spins of the two terms can only give a quartet state, and coupling their projections of orbital angular momenta of the two ions can only give a Σ state. The $^4\Sigma^-$ state then evolves naturally.

In this E^-Li^+ extreme, σ_{ER} is completely localized on E and becomes its np_z orbital; σ_{lp} remains doubly occupied and becomes its ns orbital. These features of localized orbitals are clearly seen in the CLi natural orbitals shown in Figure 2. Note that this *ions in molecules* picture for high-spin carbynes and silylynes with Li and Na ligands has been proposed by Mavridis et al.[11,23] and Boldyrev et al.[21,22]
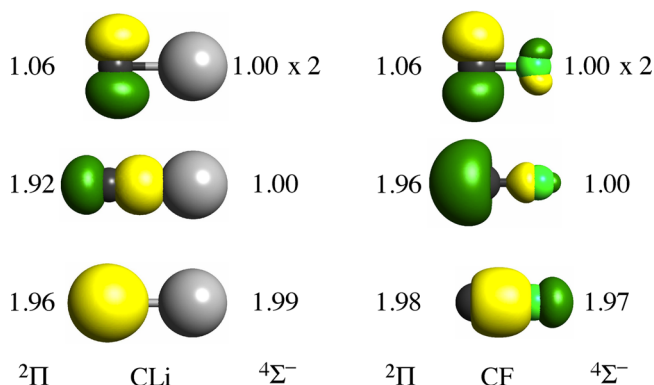

Figure 2. Substantially occupied natural orbitals of CLi and CF. The orbitals are obtained from the $^2\Pi$ states of the two molecules. They are visually indistinguishable from those from the $^4\Sigma^-$ states. The occupation numbers in the two states are given on the two sides of each orbital. The "1.00 × 2" means the degenerate π orbitals are occupied by one electron in each. The natural orbitals and occupation schemes are similar for SiLi and SiF. Black, gray, and lime spheres represent C, Li, and F atoms. Yellow and green represent orbital phases.

Conversely, in the opposing completely ionic limit of EF, i.e., E^+F^-, the entity E^+ is isoelectronic to B or Al, both in ^2P_u ground states. Spin-coupling of this term and the closed-shell ^1S_g term of F^- can only yield a doublet state. Coupling the projections of orbital angular momenta of the E^+ and F^- can give both Π and Σ states. The latter, however, has the singly occupied np_z orbital pointing from E^+ to F^- and the larger electrostatic repulsion of $^2\Sigma^-$ makes $^2\Pi$ the ground state. In this limit, σ_{ER} is polarized toward R and becomes the $2p_z$ orbital of F. σ_{lp} again becomes the ns of E. Both are doubly occupied. The CF natural orbitals in Figure 2 largely show these orbital features, but also that the ionized limit is not completely reached. σ_{CF}, mainly composed of F $2p_z$, still has some contribution from C; σ_{lp} is an s-rich hybrid but not as pure s (spherical) as the CLi counterpart.

A more detailed examination of the electronegativity trend in a diabatization analysis is presented in Section S2 of the SI. It takes apart the contributions of pure ionic or neutral component fragment states (diabats) to the lowest doublet and quartet adiabatic states of SiLi and SiF, two representative species. The respective $Si^-(^4S_u)Li^+(^1S_g)$ and $Si^+(^2P_u)F^-(^1S_g)$ ionic contributions are shown to be dominant in the ground adiabatic states of the two spieces. We are able to explain there a curious feature in the calculated bond lengths of the doublet and quartet states for R = Li: the quartets consistently have a shorter distance, by 0.2−0.3 Å. This feature is not seen for R = F. The reader will note the large ranges of the calculated $\Delta E(Q - D)$ values, nearly 120 kcal/mol for the carbynes and 100 kcal/mol for the silylynes. We give an explanation for this large range in Section S2 of the SI.

Another simple way to see the effect of electronegativity is to consider the charge distribution in the doublet and quartet

Table 2. Calculated Properties of ER with R Being Alkali Metals, Halogens, and Group 12 Hydrides

E\R	Li	Na	K	Rb	F	Cl	Br	I	ZnH	CdH
$\Delta E(Q-D)^a$ in kcal/mol										
C	−35.3	−30.5	−37.5	−39.9	78.4	52.8	46.5	37.0	−19.3	−30.4
Si	−17.0	−13.8	−19.2	−20.8	81.6	69.4	65.3	56.8	1.5	−0.4
r_e of $^4\Sigma^-$ in Å										
C	1.89	2.21	2.54	2.64	1.33	1.66	1.82	2.01	1.91	2.10
Si	2.36	2.68	3.05	3.18	1.62	2.06	2.22	2.45	2.31	2.49
r_e of $^2\Pi$ in Å										
C	2.09	2.49	3.02	3.25	1.28	1.66	1.82	2.03	2.01	2.17
Si	2.69	2.87	3.28	3.42	1.62	2.07	2.23	2.46	2.39	2.62

$^a\Delta E(Q-D)$ is the quartet−doublet energy difference: $E(^4\Sigma^-) - E(^2\Pi)$. $E(^4\Sigma^-)$ and $E(^2\Pi)$ are energies at the optimized structures of the respective states. Energies are calculated using GMCPT method (see Computational Methods section in the end of paper).

states of CH and SiH. Since an electron is transferred from the slightly bonding σ_2 (Figure 1) to the nonbonding p_E orbital in the doublet-to-quartet transition, and σ_2 perforce has some density at H, the quartet will have a more positive charge on H. From first-order perturbation theory considerations, a substituent less electronegative than H (e.g., alkali metals) would favor the quartet, a more electronegative one (e.g., halogens) the doublet.

It should be noted that diatomic EH and E−X (E = Si, Ge, Sn, Pb; X = F, Cl, Br, I) species, in which the doublet state is the ground electronic state, have been theoretically studied previously.[20] Some of the E−X species, e.g., SiF, SiCl, SiBr, CF, CCl, and CBr, have also been experimentally investigated.[53−60] And there are calculations on CLi, CNa, SiLi and SiNa that confirm their quartet ground states.[21,22,24,61,62]

For a more complete comparison, we carried out additional calculations for a wider series of alkali metal ligands (AM) Na, K, Rb, as well as halogen ligands (X) Cl, Br, I (Table 2). The trend that an electropositive group R favors the quartet and an electronegative R favors the doublet ground state is maintained. Similarly, the E-AM molecules have longer r_e values in their doublet states while the E−X molecules have similar r_e values for both spin states. These trends hold for both E = C and Si. Evidently, the reasoning based on the SiLi and SiF ionicity and bonding is applicable to other cases.

As anticipated, the electronegativity argument applies when we examine congener effects. As X moves down the periodic table from F to I and becomes less electronegative, the energy difference between the $^4\Sigma^-$ and $^2\Pi$ states gets smaller. As the metal moves from Li to Rb and becomes more electropositive, the energy difference between the two states gets larger (we address the anomaly of the sodium compounds a little later). As element E moves down from C to Si (less electronegative), for the same R group, ER has a lower $^2\Pi$ energy relative to the $^4\Sigma^-$ state.

We also examine two ligands involving Group 12 elements, i.e., R = ZnH and CdH. The results are shown in Table 2. The two groups are electropositive enough to give substantially negative $\Delta E(Q - D)$ values (−19.3 and −30.4 kcal/mol) for the carbynes. But for silylynes, the two hydrides are not sufficiently electropositive and both $\Delta E(Q - D)$ values are close to zero, making it difficult to judge the ground state spins of SiZnH and SiCdH. We also have longer r_e in the $^2\Pi$ state than in the $^4\Sigma^-$ state for these substituents. All trends observed for the main group AM and X ligands hold for the two Group 12 ligands. We did not go down to Hg in order to avoid the possible complication from strong relativistic effects in this atom.

Finally, the electronegativity effect can actually be probed further, by making E even more electronegative than C. This may be accomplished by moving to N^+ in the place of C; as Harrison, Liedtke, and Liebman noted "NH_2^+ is more triplet than CH_2."[12] The $\Delta E(Q - D)$ value of NH^+ is calculated to be −2.3 kcal/mol. With such an electronegative E, even H gives a low lying quartet state. The limited accuracy of our methodology prohibits us from claiming that NH^+ has a quartet ground state.

■ DIMERIZATION

Because of their radical or triradical character, the E-AM and E−X species are unlikely to be bench-stable. Though their heats of formation are all very positive, these molecules have reasonable bond energies (shown by the adiabatic energy curves in Figure S2(a) and (d) in the SI for SiLi and SiF, for example), and should be spectroscopically observable in cryogenic matrix isolation, interstellar environment (like CH[63]), or molecular beams. As mentioned above, some of the E−X species, including SiF, SiCl, SiBr, CF, CCl, and CBr, have been observed as transient species.[53−60] The E-AM diatomics, some of our best candidates for quartet ground states, appear to be less studied, though there are calculations for some of them.[21,22,24,61,62]

Might there be an effect of the ground state spin on the kinetic persistence of these fleeting molecules? Let us think about the possible reactions of the archetype CH, as, say, a Ne matrix containing a reasonable number of such molecules is heated up from liquid He temperatures. Aside from potential reaction with the atoms constituting the matrix (which we have not yet studied), dimerization to acetylene is the first likely reaction. Note that the formation of alkynes has been considered as evidence of having carbynes as the products of decomposing complexes with metal−carbon triple bond in aqueous solution.[64] The process of CH dimerization to acetylene is exoergic by a whopping 249 kcal/mol for the doublet, 275 kcal/mol for the quartet CH (these are GMCPT calculated values). Using the NIST Chemistry Webbook[65] data of $\Delta_f H^\circ_{gas}$, the standard dimerization enthalpy is evaluated to be −230 kcal/mol).

There is more to this simple reaction. In the discussion that follows we were anticipated by two excellent studies, of Siegbahn[66] and of Danovich, Bino, and Shaik;[67] our analysis does not differ substantially from theirs. For two quartet CH fragments, the head-to-head orientation obviously favors the bonding between three pairs of unpaired electrons (Figure 3(a)) and a "least-motion", linear dimerization is expected.
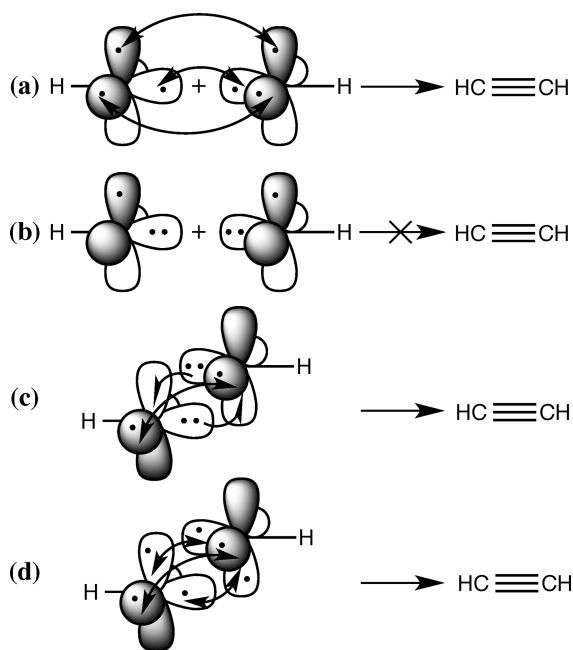
Figure 3. (a) Linear dimerization of two CH fragments in $^4\Sigma^-$ states; (b) failed linear dimerization of two CH fragments in $^2\Pi$ states; (c) sideway dimerizations of two CH fragments in $^2\Pi$ states and (d) in $^4\Sigma^-$ states. Double-headed curved arrows are used to indicate bonding between unpaired electrons; single-headed curved arrows are for dative bonding.

The doublet is much more interesting. The head-to-head orientation of two doublet CH fragments point the two lone pairs toward each other (Figure 3(b)) and the least-motion

dimerization is unfavorable. With a doubly occupied lone pair and an empty p orbital (Figure 1 and Figure S1 (SI)), the most convenient dimerization path for two doublet CH fragments should involve the C_{2h} sideways (or *trans*-bent, from the acetylene perspective) configuration shown in Figure 3(c). With the two lone pairs pointing to the two empty p orbitals, a strong two-way acid–base acceptor–donor interaction evolves, along with covalent bonding between the two singly occupied p orbitals. To put it in another way, two doublet CH fragments should dimerize in a "non-least-motion" trajectory. This is reminiscent of a similar path for singlet methylene dimerization suggested by one of us (R.H.) 44 years ago.[68] Note that the C_{2h} reaction pathway is also viable for the two quartet fragments (Figure 3(d)). The only difference between the doublet and quartet species in the pathway is that the acid–base interaction in the former is replaced by the radical coupling in the latter.

These analyses are supported by GMCPT calculation for the potential energy surfaces (PESs) of two CH fragments, maintaining a C_{2h} symmetry of the whole dimer. The $^1\Sigma_g^+$ ground state of C_2H_2 correlates to a ^1A_g state in the C_{2h} subgroup, and there are two ^1A_g states stemming from the two $^2\Pi$ CH fragments, and one from the two $^4\Sigma^-$ fragments. Therefore, we include three ^1A_g states in our state-averaged GMCPT calculation. The CH bond length is fixed to 1.10 Å in this calculation, and the only two remaining degrees of freedom within the C_{2h} symmetry constraint, the intercarbon distance r_{CC} and the tilt angle θ, are defined in Figure 4(a). The 1-dimensional (1D) cuts of the PESs with $\theta = 0°$ are shown in Figure 4(b); those are the potential energy curves along the linear, least-motion dimerization pathway.

Figure 4(b) shows that as the two CH fragments approach each other in a head-to-head fashion, the two lower states ($^1\Sigma_g^+$
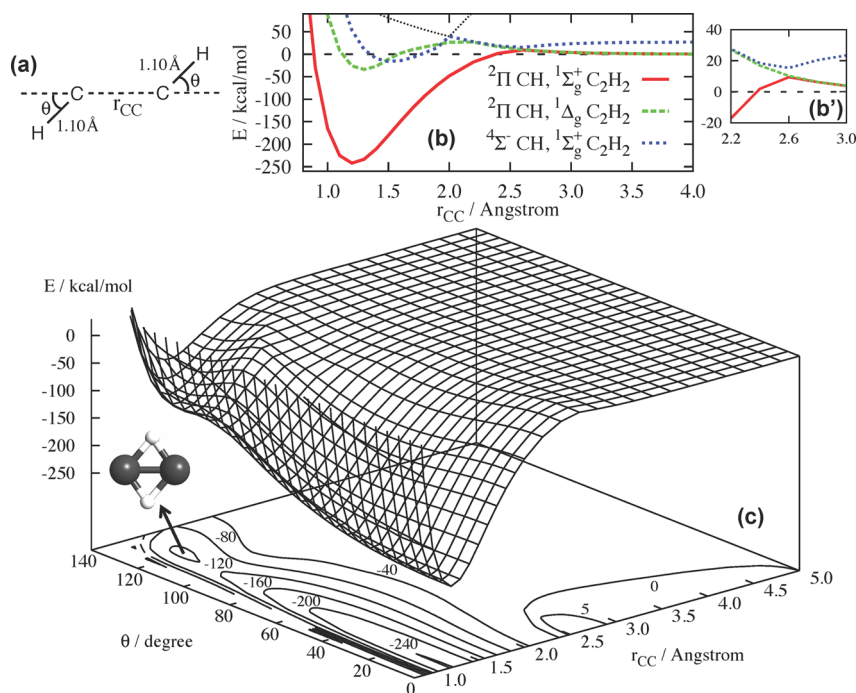

Figure 4. (a) Definitions of geometrical variables r_{CC} and θ for the C_{2h} CH dimer; (b) potential energy curves of the three lowest ^1A_g states of the C_{2h} CH dimer with tilt angle $\theta = 0°$. The three states are labeled by their term symbols in the $D_{\infty h}$ point group and their correlating CH fragment term symbols at the large r_{CC} limit. A blowup view for the avoided crossing at $r_{CC} \approx 2.6$ Å is shown in panel b'. The two black dashed curves follow quadratic extrapolations of the blue curve on the two sides of $r = 2.0$ Å; (c) the lowest ^1A_g state potential energy surface of the C_{2h} CH dimer as a function of r_{CC} and θ. In both (b) and (c), all C−H bond lengths are fixed at 1.10 Å.

and $^1\Delta_g$), stemming from the two doublet fragments climb up in energy, while that ($^1\Sigma_g^+$) from the two quartet fragments declines. The two $^1\Sigma_g^+$ adiabatic states have an avoided crossing (shown in Figure 4b′) at $r_{CC} \approx 2.6$ Å, where they exchange their diabatic configurations. An about 10 kcal/mol barrier (S. P. Walch reported a 12 kcal/mol barrier, as cited in ref 23, and Siegbahn reported a 13 kcal/mol one[66]) arises due to this avoided crossing. After the avoided crossing, the lower $^1\Sigma_g^+$ state (now with character of two quartet fragments) goes straight down to the minimum. The other (the blue curve) increases in energy until it is crossed by another higher-lying state which is not of $^1\Sigma_g^+$ symmetry but correlates to ^1A_g in the C_{2h} point group. This crossing is marked by the cusp at $r = 2.0$ Å and the two extended black curves.

But the least-motion approach is just a single trajectory among many. The 2D PES of the lowest ^1A_g state of the C_{2h} CH dimer is shown in Figure 4(c). A real dimerization will, of course, explore a variety of impact parameters, not necessarily constrained by the C_{2h} symmetry. Starting from the ground state doublet fragments at the large r_{CC}, one can see that any initial configuration outside of the zone surrounded by the 0 kcal/mol contour leads to a barrier-less dimerization. Starting from a linear far configuration at $r_{CC} = 5.0$ Å and $\theta = 0°$, the most direct non-least-motion dimerization pathway for the two doublet fragments would be roughly to follow the 0 kcal/mol contour to circumvent the aforementioned barrier in the 1D cut, which is surrounded by the 5 kcal/mol contour. The large area of barrier-less entrance (the area between the 0 and −40 kcal/mol contours) indicates that the doublet CH dimerization does not require activation energy. It is noteworthy that for those CR species with quartet ground states, like CLi,[23] there should be no barrier along both the least and non-least-motion dimerization pathways.

We note that there is a local minimum in the PES at $r \approx 1.4$ Å and $\theta \approx 125°$. This is unexpected, but similar to the dibridged structure of Si_2H_2.[69−71] With the large exoergicity (~124 kcal/mol) and the small barrier (~14 kcal/mol) to converting to the linear acetylene structure, this rhombic C_2H_2 should hardly be observed. Also, this structure may not survive as a minimum with respect to nuclear displacements that depart from C_{2h} symmetry, like the planar dibridged Si_2H_2 which distorts to a nonplanar, C_{2v} dibridged structure.[69,71] Clearly, the PES we show will be very different from the one for SiH dimerization: the acetylene-like minimum will be destabilized and the rhombic minimum (definitely not planar) will come down in energy.[69]

Still another reaction channel for CH dimer is hydrogen abstraction, a typical radical reaction. With another CH, this would lead to CH_2 and C. This process is spin allowed for all reactants and products in their ground states. The exoergicity of the reaction is evaluated to be 27 kcal/mol, very mild compared to that of dimerization to acetylene. A third reaction is "C-abstraction", to HC_2, the acetylyl radical and H. This channel is exoergic by 114 kcal/mol (GMCPT value), more promising than the H-abstraction. HC_2 and H can be byproducts in the acetylene dimerization if the released electronic energy is transferred to the vibrational energy of a CH bond. Note that the HC_2 radical itself can abstract H from H_2.[72] It may also abstract H from CH, i.e., $HC_2 + CH \rightarrow C_2H_2 + C$. We calculate the reaction energy of this process to be −57 kcal/mol, more than twice more exoergic than the H-abstraction between two CH fragments. We mention here that the relative reactivity of doublet and quartet carbynes has been studied experimentally

by Strausz[73,74] and Bayes,[38,39] as well as theoretically by Schaefer.[75,76]

Here we just scratch the surface of the EH dimerization. We restrict our discussion for the CH dimer with C_{2h} (and implicitly higher) symmetry, and only consider dimerization to the ground state acetylene. We reserve for a future analysis the effect of the doublet−quartet energy difference on the kinetic persistence of the metastable E-AM and E−X fragments, as well as the difference between C and Si and their congeners down Group 14 (remembering the story of how the geometries of ethylene analogues evolve for this group). It is also interesting to speculate if putting energy into a selected vibrational mode of acetylene could lead to differentiated fragmentation to two CH radicals. For instance, exciting a π_g mode involving H−C−C−H trans-bending and letting the molecule climb up the gradually increasing PES along θ may favor fragmentation to two CH doublets. Exciting the C−C stretching mode might favor instead fragmentation to two CH triradicals.

■ π-ACCEPTANCE AS ANOTHER FACTOR

If the R of ER_2 (carbenes and silylenes) is a π-acceptor, its orbitals can interact with and stabilize the single p_π orbital in **1a**. With sufficient stabilization, the p_π can even move to lower energy than the σ orbital and lead to a singlet state with the $\sigma^0 p_\pi^2$ configuration.[5] This is an extreme case, but the logic of manipulating the p orbital through π-acceptance (or donation) can be transferred to ER. If we have a π-acceptor that stabilizes the two degenerate p_π orbitals enough to have an energy similar to σ_{lp} (see **2** for sketch of the orbitals), we can alter the electron configuration to a quartet ground state. A π-donor works in the opposite direction.

Let us start with R = CN, a familiar π-acceptor. The C atom of CN is "neutral" in electronegativity when compared to the terminal C, so the electronegativity effect is likely to be small. For CCN, we compute the quartet−doublet energy difference ($\Delta E(Q - D)$) to be 20.2 kcal/mol. CN thus does not stabilize the p_π orbitals sufficiently to achieve a quartet ground state, and CCN was found to have a $^2\Pi$ state in transient absorption spectroscopic experiment.[77] We then go one step further by replacing CN by the isoelectronic BO (for the moment not worrying about the effect of substitution on likely chemical stability). With the larger p_π lobes on B, we expect BO to be a stronger π-acceptor. The improvement is obvious: $\Delta E(Q - D)$ of CBO is calculated to be −3.9 kcal/mol. This lowering of the quartet state energy is consistent with the lower π orbital energy of CBO than that of CCN (−4.9 vs −4.6 eV). Adjusting the π-accepting ability of R is therefore another way to tune the ground state spin of ER. Considering the limited accuracy of our methodology (about 4 kcal/mol underestimation of the CH quartet−doublet energy difference, as discussed above), we cannot say for certain that CBO has a quartet ground state. But the trend toward a lower quartet state energy is evident.

We realize, however, that the π effect is secondary to the electronegativity effect. First, there are not many π acceptors stronger than CN. Second, the π effect is more relevant to E = C than E = Si, as SiR has a larger Si-R separation and weaker π overlap (see, e.g., the double bond rule[78]).

This π effect helps us understand the aforementioned anomaly in the variation of $\Delta E(Q - D)$ as we move R from Li to Rb. In the general trend that $\Delta E(Q - D)$ becomes more negative as R becomes more electropositive (Table 2); E-Na has a less negative $\Delta E(Q - D)$ than E-Li, −30.5 vs −35.3 kcal/mol for E = C and −13.8 vs −17.0 kcal/mol for

E = Si. This suggests that there is another factor in determining $\Delta E(Q - D)$, one that works against the electronegativity effect. This is likely to be the π effect. From Li to Rb, along with the elongation of the ER bond, the overlap between the p_π of E and the empty p_π of AM decreases, resulting in a weaker π effect in lowering the $^4\Sigma^-$ state energy. From Li to Na, the weakening of the π effect defeats the increase of the electronegativity effect, leading to a reduced $\Delta E(Q - D)$.

We have not mentioned in detail the effects of π-donation, because by and large they should move these systems away from our goal, which is to stabilize the quartet state. That they behave as expected, however, is a confirmation of our qualitative analysis. Halogen substituents are typically π-donors, and as Table 2 shows, they strongly favor the doublet states. The anomaly in the alkali metal series is not observed for the halogens. This is because the two factors of π donation and electronegativity go in the same direction for these substituents: from F to Br, E–X bonds are elongated, there is less p_π destabilization, and the $^4\Sigma^-$ state becomes less favorable.

■ A WIDER RANGE OF SUBSTITUENTS

The main factors influencing the relative energy of the doublet and quartet states of CR and SiR have been described, based on the study of a small group of molecules with distinguishing characteristics. Extending the range of potential substituents, we examine a representative and larger set of substituents for CR, using the same GMCPT method as in the above sections. The calculated quartet–doublet energy differences are reported in Table 3. All investigated carbynes (and silylynes below) have $\sigma_1^2\sigma_2^2\pi_1^1\pi_2^0$ and $\sigma_1^2\sigma_2^2\pi_1^1\pi_2^1$ configurations in their respective doublet and quartet states, as sketched in **3** and **4**.

Table 3. Quartet–Doublet Energy Differences $(\Delta E(Q - D)^a$ in kcal/mol) of 23 Carbyne Molecules Computed with the GMCPT Method[b]

$\Delta E(Q - D)$		$\Delta E(Q - D)$		$\Delta E(Q - D)$	
CMgH	−29.2	CSiH₃	−10.8	CCH₂F	23.2
CBeH	−27.0	CBH₂	6.2	CPH₂	23.4
CMgF	−25.5	CH	13.1	CCH₃	23.6[c]
CAlH₂	−21.5	CCAs	14.4	CSeH	36.6
CGaH₂	−14.8	CCF₃	14.8	CSH	43.8
CSiHF₂	−14.2	CAsH₂	16.2	COH	76.8
CSiF₃	−12.6	CCP	17.8	CNH₂	77.9
CSiH₂F	−12.1	CCN	20.2		

$^a\Delta E(Q - D) = E(Q) - E(D)$. $E(Q)$ and $E(D)$ are energies of the lowest states in the quartet and doublet spin manifolds at their optimized structures. [b]The values are listed from the smallest (CMgH) to the largest (CNH₂) from top to bottom and left to right. [c]Other theoretical $\Delta E(Q - D)$ values, 29 and 27 kcal/mol, have been reported for this species in refs 79 and 80, respectively.

The electronegativity of the atom directly attached to C is once again observed to have a strong influence on $\Delta E(Q - D)$. For congeners, we have CMgH < CBeH; CAlH₂ < CGaH₂ < CBH₂; CAsH₂ < CPH₂ < CNH₂; CSeH < CSH < COH. Note that although Ga is below Al in the periodic table, it has a higher electronegativity (1.81 vs 1.61, Pauling scale). For the attached atoms in the same period, we have CBeH < CBH₂ < CCH₃ < CNH₂ ∼ COH. The adjacent atom also exerts its electronegative influence given the same directly attached atom: CMgH < CMgF; CCAs < CCP < CCN. All orders are for the

calculated $\Delta E(Q - D)$ values and this statement applies in below.

The π-effects also manifest themselves for this set of molecules. For instance, CCF₃ has a $\Delta E(Q - D)$ about 9 kcal/mol lower than that of CCH₃, violating the common thought that the more electronegative F makes the CF₃ more electron-withdrawing and gives a larger $\Delta E(Q - D)$. The electronegativity difference between H and F[81] makes the CF antibonding orbitals lower-lying than the CH counterparts and more localized on the C. The CF antibonding orbitals are thus better π-acceptors and through hyperconjugation,[82] the quartet state is stabilized.

Another demonstration of the larger π-effect is the substantial decrease (55 kcal/mol) of $\Delta E(Q - D)$ from CNH₂ to CPH₂. N is a stronger π-donor for C (due the short N–C bond) and disfavors the quartet state more. Forfeiting this π-effect on moving from CNH₂ to CPH₂ thus leads to a substantial decrease of $\Delta E(Q - D)$. This strong π-donation also gives CNH₂ a slightly larger $\Delta E(Q - D)$ than COH against the electronegativity order of N and O.

The $\Delta E(Q - D)$ order of CSiHF₂ < CSiF₃ < CSiH₂F < CSiH₃ is nonmonotonic with respect to the number of F atoms. As the number of F atoms increases, the fluorinated silyl group becomes more electronegative, favoring the doublet state, but also more π-accepting, favoring the quartet state. It seems that the competition between the two opposite effects brings about the nonmonotonicity. However, the range of energy difference variation is not large (∼4 kcal/mol), and we cannot exclude that the nonmonotonicity stems from subtle structural difference between the ligands, e.g., the different F–C–H bond angles in CSiHF₂ and CSiH₂F. The series CCF₃, CCH₂F, and CCH₃ does not show such a nonmonotonic $\Delta E(Q - D)$ change. Given the shorter C–C bond than the C–Si bond, the π-acceptance effect is more influential and the greater the number of fluorines, the smaller the $\Delta E(Q - D)$. When we optimize the structure for the doublet CCHF₂, the H migrates and CHCF₂ results. This molecule, not a carbyne, is thus excluded in our discussion.

A few of the carbynes calculated here have been experimentally observed. We have mentioned earlier CCN. CCP ($^2\Pi$ ground state) has been detected in interstellar space.[83] The rotational spectrum of CCAs ($^2\Pi$ ground state) has been measured.[84] The ethylidyne CCH₃ is known.[85]

Silylynes with the same set of substituents are also investigated and their quartet–doublet energy differences are reported in Table 4. An immediate impression of these results is that there are very few negative values, and the magnitudes of the negative values are small, in comparison with those in Table 3. This is the most straightforward manifestation of the electronegativity effect in determining quartet–doublet energy differences: the more electropositive Si makes all substituents comparatively more electronegative, giving larger $\Delta E(Q - D)$ values. All energy difference orders for the above carbynes based on electronegativity sequences are followed by the silylynes and are not discussed again.

Another factor operative for the silylynes is the weaker π nature of all effects. For instance, SiMgF < SiBeH. The weak π overlap between Si and Be makes the order follow the electronegativity of the atoms direct attached to Si, different from the order of CBeH < CMgF. Also, the orders SiSiH₃ < SiSiF₃, SiCH₃ < SiCF₃, and SiNH₂ < SiOH are all "electronegatively normal", in contrast to the reversed orders of the carbyne counterparts. The SiSiH₃₋ₙFₙ and SiCH₃₋ₙFₙ series

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dx.doi.org/10.1021/ja5073993 | J. Am. Chem. Soc. 2014, 136, 13388–13398

Table 4. Quartet−Doublet Energy Differences ($\Delta E(Q − D)^a$ in kcal/mol) of 24 Silylyne Molecules Computed with the GMCPT Method^b

$\Delta E(Q − D)$		$\Delta E(Q − D)$		$\Delta E(Q − D)$	
SiMgH	−8.3	SiSiF$_3$	20.5	SiCF$_3$	43.2
SiMgF	−4.1	SiBH$_2$	23.6	SiCAs	45.2
SiBeH	−2.1	SiAsH$_2$	31.6	SiCP	48.1
SiAlH$_2$	3.0	SiPH$_2$	36.1	SiCN	52.5
SiGaH$_2$	8.2	SiH	36.8	SiSeH	52.9
SiSiHF$_2$	15.9	SiCHF$_2$	37.5	SiSH	58.1
SiSiH$_2$F	16.1	SiCH$_2$F	39.3	SiNH$_2$	69.7
SiSiH$_3$	17.1	SiCH$_3$	40.2	SiOH	75.9

$^a\Delta E(Q − D) = E(Q) − E(D)$. $E(Q)$ and $E(D)$ are energies of the lowest states in the quartet and doublet spin manifolds at their optimized structures. ^{b}The values are listed from the smallest (SiMgH) to the largest (SiOH) from top to bottom and left to right.

have nonmonotonic quartet−doublet energy difference variation with n, similar to the CSiH$_{3−n}$F$_n$ series, and the ranges of variation are similar too: all are within 5 kcal/mol. Because of the weak π effect (hardly surprising for Si, whose π-bonding capability, for well-known reasons, is not worth much), it is more reasonable to ascribe the nonmonotonicity to the aforementioned subtle structural differences of the SiH$_{3−n}$F$_n$ (CH$_{3−n}$F$_n$ too) substituents.

Some of the investigated silylynes have also been observed and experimentally studied. The infrared spectrum of the $^2A''$ ground state SiCH$_3$ has been reported.[25] SiCN has been detected in an astronomical source and determined to have a $^2\Pi$ ground state.[86] The rotational spectrum of the $^2A'$ ground state SiOH has been measured.[87] For SiCH$_3$ and SiOH, we obtain the same ground state term symbols in our calculations.

The large series of numerical experiments for CR and SiR we have presented, effectively a "spin-state chemistry" of ER, supports the general conclusion that the effect of electronegativity is more significant than π-acceptance/donation. This is especially true for SiR, consistent with the general and well-known inability of Si to π-bond very effectively. In the SI, we also show the quartet−doublet energy differences calculated with DFT methods for the same set of CR (Table S2) and an even wider range of SiR (Table S3 and S4) molecules; they do not differ materially from the GMCPT results discussed here.

We repeat the obvious here: these fascinating molecules, playing out a dance between doublet and quartet states, are most unlikely to be bench-stable. But they certainly should be amenable to generation and characterization in matrix isolation or spectroscopic observation in the interstellar medium. Line splitting due to coupling with electronic spin should be a signature in their rotational spectra.

CONCLUSIONS

In this paper, we explore the possibility of tuning the ground state electronic spin for silylynes, SiR, and carbynes, CR. The parent hydrides have doublet ground states, their quartet excited states lying 39 and 17 kcal/mol higher, respectively. Although there is only one degree of freedom in choosing the ligand for C and Si, we find it still possible to systematically tune the spin, and, not without difficulty, to have species with quartet ground states. Overall, electronegative ligands favor a doublet ground state, while electropositive ones favor a quartet state. This is consistent with the high/low spin preference for carbenes and silylenes. A simple ionization picture helps to

understand this overall trend, and this picture is justified by a detailed diabatization analysis of the composition of the doublet and quartet states. The *ions in molecules* idea that emerges, that the spin state proclivity of ER is set by that of E^+ or $E^−$, depending on the relative electronegativity of R, is not original to us; it is already in the literature in the works of Boldyrev, Simons, and Schleyer and in the works of Mavridis, Harrison, and Liebman. For ER, the ligand π-accepting ability is found to be a noteworthy but secondary effect in tuning the spin.

The obvious, highly exoergic dimerization channel for the doublet CH should proceed preferentially through non-least-motion C_{2h}-like barrier-less trajectories. On the other hand, the quartet CH triradicals dimerize in both the non-least-motion and linear least-motion fashions.

We examine a wide range of substituents in their preference for the ground state spin of SiR and CR. Several substituent series support primary electronegative and the secondary π-acceptance/donation effects. In particular, ground state quartet molecules should be found in the C-AM, C-AE-R, C-IC-R$_2$, C-ZH, and C-SiR$_3$ molecules (AM = alkali metal, AE = alkaline earth element, IC = icosagens, ZH = hydride of zinc group element). Fewer quartet ground state silylynes are predicted, only Si-AM and Si-AE-R. If we compare the carbyne/silylyne quartet stabilizations relative to their R = H "parents", it becomes clear that it is much harder to make a quartet ground state silylyne by substitution than a corresponding carbyne. But it can be done!

COMPUTATIONAL METHODS

To accurately describe electronic excited states of molecules, one needs to include both nondynamical and dynamical electron correlations in quantum chemistry calculations. We employ the state-specific (except for the diabatization analysis, *vide infra*) general multi-configurational perturbation theory (GMCPT) developed by Nakano et al.[88−90] to treat the two correlations. We use the cc-pVTZ basis set[91−93] to treat most of the elements under consideration. For molecules containing elements K, Rb, I, Zn, and Cd, the Sapporo-TZP basis set[94] is used. This methodology gives a 42.8 kcal/mol dissociation energy for the $^4\Sigma^−$ state of SiLi, close to the recently reported value (43.3 kcal/mol) from a CCSD(T)/complete-basis-set calculation.[95] All calculations are performed using the program package GAMESS-US[96,97] unless further specified. All orbital graphical presentations are prepared using MacMolPlt.[98]

For EH and E-AM, we employ a five electrons in five orbitals (5o5e) active space that comprises four valence orbitals of E, one valence orbital of H or AM, and all five valence electrons. A 7o9e active space is used for E−X. In addition to 4o4e from E, the three valence p orbitals of X and the associated five electrons are included. For CCN and CBO, a 12o13e active space is used, including all valence orbitals and electrons of the three elements. A 7o7e active space is used for E-ZnH and E-CdH. Compared to the 5o5e of E-AM, the ZnH (CdH) bonding and antibonding orbitals and the two electrons are included. In the more accurate calculation of the $\Delta E(Q − D)$ of CH, we employ the cc-pV6Z and cc-pV4Z basis sets[91] for C and H respectively. We also enlarge the active space (10o5e) by including the $3d$ orbitals of C. In most of our computations of the wide range of CR and SiR molecules, 5o5e active spaces similar to those of EH and EAM are used. Exceptions include 7o7e for CBeH and CMgF, 12o12e for CCN, CCP, CCAs, SiCN, SiCP, SiCAs, and 6o6e for CNH$_2$, CPH$_2$, CAsH$_2$, SiNH$_2$, SiPH$_2$, and SiAsH$_2$. Larger active spaces are needed to have consistent orbitals in the two spin states for those molecules. In the CH dimerization calculations, a 6o6e active space that includes electrons and orbitals shown in each panel of Figure 3 is employed.

In the diabatization analysis for SiLi and SiF, we use the well-developed 4-fold way scheme of Truhlar et al.[99,100] to diabatize the

adiabatic states. To compare diabatic states of SiLi and SiF, we employ a reduced 5o5e active space for SiF; i.e., only the $2p_z$ and the associated one electron of F are included in the active space. All our diabatic orbitals are obtained by rotating the active orbitals to satisfy the maximum overlap reference molecular orbitals criterion.[99,100] With the diabatic orbitals so generated, our diabatization scheme is essentially that of Ruedenberg and Atchity.[101] The reference orbitals are atomic orbitals of the constituent atoms at dissociated limits. The multi-configurational quasi-degenerate perturbation theory (MCQDPT)[102,103] developed by Nakano is used as the electron correlation method in our diabatization calculations. In both GMCPT and MCQDPT, we use Granovsky's scheme[104] to prepare the zeroth order multielectron states. The intruder state avoidance shifting parameter is set to the conventional value 0.02 E_H for both types of perturbation theory calculations.[105,106]

We mainly employ Zhao and Truhlar's M06-2X functional[107] and the cc-pVDZ basis sets[91−93] in our DFT calculations for the large set of carbynes and silylynes. For the results in Table S4 in the SI, we also employ three other functionals (B3LYP,[108,109] BP86,[110,111] and ωB97X-D[112]) to compare with the M06-2X results. They all produce similar results. The results in Table S4 are obtained using the Q-Chem program,[113] with the default grid SG-1 for the B3LYP and BP86 functionals, and a finer grid (99, 590) for the M06-2X and ωB97X-D functionals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Discussion of the connection between the canonical molecular orbitals and natural bond orbitals for CH and SiH; diabatization analysis for the lowest quartet and doublet states of SiLi and SiF; all DFT $\Delta E(Q − D)$ values for the wide range of CR and SiR molecules; coordinates and absolute energies for all molecules using GMCPT calculations. This material is available free of charge via the Internet at http://pubs.acs.org/.

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■ REFERENCES

(1) Bender, C. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1970**, *92*, 4984−4985.

(2) Grev, R. S.; Schaefer, H. F.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 5638−5643.

(3) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485−1499.

(4) Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457−5460.

(5) Chen, B.; Rogachev, A. Y.; Hrovat, D. A.; Hoffmann, R. *J. Am. Chem. Soc.* **2013**, *135*, 13954−13964.

(6) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251−5264.

(7) Comeau, D. C.; Shavitt, I.; Jensen, P.; Bunker, P. R. *J. Chem. Phys.* **1989**, *90*, 6491−6500.

(8) Berkowitz, J.; Greene, J. P.; Cho, H.; Ruščić, B. *J. Chem. Phys.* **1987**, *86*, 1235−1248.

(9) Balasubramanian, K.; McLean, A. D. *J. Chem. Phys.* **1986**, *85*, 5117−5119.

(10) Allen, W. D.; Schaefer, H. F. *Chem. Phys.* **1986**, *108*, 243−274.

(11) Mavridis, A.; Harrison, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 3827−3833.

(12) Harrison, J. F.; Liedtke, R. C.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 7162−7168.

(13) Hay, P. J.; Hunt, W. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1972**, *94*, 8293−8301.

(14) Goddard, W. A.; Dunning, T. H.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368−376.

(15) Kasdan, A.; Herbst, E.; Lineberger, W. C. *Chem. Phys. Lett.* **1975**, *31*, 78−82.

(16) Nelis, T.; Brown, J. M.; Evenson, K. M. *J. Chem. Phys.* **1988**, *88*, 2087−2088.

(17) Nelis, T.; Brown, J. M.; Evenson, K. M. *J. Chem. Phys.* **1990**, *92*, 4067−4076.

(18) Kalemos, A.; Mavridis, A.; Metropoulos, A. *J. Chem. Phys.* **1999**, *111*, 9536−9548.

(19) Kalemos, A.; Mavridis, A.; Metropoulos, A. *J. Chem. Phys.* **2002**, *116*, 6529−6540.

(20) Li, H.; Feng, H.; Sun, W.; Xie, Y.; Schaefer, H. F. *Inorg. Chem.* **2013**, *52*, 6849−6859.

(21) Boldyrev, A. I.; Simons, J. *J. Phys. Chem.* **1993**, *97*, 1526−1532.

(22) Boldyrev, A. I.; Simons, J.; Schleyer, P. *J. Chem. Phys.* **1993**, *99*, 8793−8804.

(23) Mavridis, A.; Harrison, J. F. *J. Phys. Chem.* **1982**, *86*, 1979−1985.

(24) Mavridis, A.; Harrison, J. F.; Liebman, J. F. *J. Phys. Chem.* **1984**, *88*, 4973−4978.

(25) Bennett, C. J.; Sillars, D.; Osamura, Y.; Kaiser, R. I. *Chem. Phys. Lett.* **2005**, *404*, 327−335.

(26) McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P. *Mol. Phys.* **2003**, *101*, 697−704.

(27) Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 719−736.

(28) Watanabe, C.; Iwamoto, T.; Kabuto, C.; Kira, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5386−5389.

(29) Evans, W. J.; Perotti, J. M.; Ziller, J. W.; Moser, D. F.; West, R. *Organometallics* **2003**, *22*, 1160−1163.

(30) Amoroso, D.; Haaf, M.; Yap, G. P. A.; West, R.; Fogg, D. E. *Organometallics* **2002**, *21*, 534−540.

(31) Filippou, A. C.; Chernov, O.; Schnakenburg, G. *Chem.—Eur. J.* **2011**, *17*, 13574−13583.

(32) Zhang, S.-H.; Yeong, H.-X.; So, C.-W. *Chem.—Eur. J.* **2011**, *17*, 3490−3499.

(33) Cornor, J. A. In *Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Eds.; The Chemical Society: London, 1976; Vol. 5, Chapter 11, pp 245−258.

(34) Shi, C.; Jia, G. *Coord. Chem. Rev.* **2013**, *257*, 666−701.

(35) Sorokin, P. B.; Lee, H.; Antipina, L. Y.; Singh, A. K.; Yakobson, B. I. *Nano Lett.* **2011**, *11*, 2660−2665.

13396

dx.doi.org/10.1021/ja5073993 | *J. Am. Chem. Soc.* 2014, 136, 13388−13398

(36) Ning, Y.; Froese, R. D. J.; Margl, P.; Lee, E. L.; Nguyen, S. T.; Peterson, T. H.; Wagner, N.; Stern, C. L.; Sarjeant, A. A. *Organometallics* **2014**, *33*, 1120−1125.

(37) Loison, J.-C.; Bergeat, A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 655−664.

(38) Hou, Z.; Bayes, K. D. *J. Phys. Chem.* **1993**, *97*, 1896−1900.

(39) Bayes, K. D. *Chem. Phys. Lett.* **1988**, *152*, 424−426.

(40) Kellogg, C. B.; Valeev, E.; Galbraith, J. M.; Fowler, J. E.; Schaefer, H. F. *Mol. Phys.* **1996**, *89*, 1695−1705.

(41) Park, C. *J. Quant. Spectrosc. Radiat. Transfer* **1979**, *21*, 373−385.

(42) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211−7218.

(43) Read, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(44) Murray, K. K.; Leopold, D. G.; Miller, T. M.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *89*, 5442−5453.

(45) Gutsev, G. L.; Ziegler, T. *J. Phys. Chem.* **1991**, *95*, 7220−7228.

(46) Cameron, M. R.; Kable, S. H.; Bacskay, G. B. *J. Chem. Phys.* **1995**, *103*, 4476−4483.

(47) Sendt, K.; Bacskay, G. B. *J. Chem. Phys.* **2000**, *112*, 2227−2238.

(48) Gordon, M. S.; Schmidt, M. W. *Chem. Phys. Lett.* **1986**, *132*, 294−298.

(49) Colvin, M. E.; Breulet, J.; Schaefer, H. F. *Tetrahedron* **1985**, *41*, 1429−1434.

(50) Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 537−543.

(51) Colvin, M. E.; Schaefer, H. F.; Bicerano, J. *J. Chem. Phys.* **1985**, *83*, 4581−4584.

(52) Holthausen, M. C.; Koch, W.; Apeloig, Y. *J. Am. Chem. Soc.* **1999**, *121*, 2623−2624.

(53) Kawaguchi, K.; Yamada, C.; Hamada, Y.; Hirota, E. *J. Mol. Spectrosc.* **1981**, *86*, 136−142.

(54) Porter, T. L.; Mann, D. E.; Acquista, E. *J. Mol. Spectrosc.* **1965**, *16*, 228−263.

(55) Tanaka, T.; Tamura, M.; Tanaka, K. *J. Mol. Struct.* **1997**, *413−414*, 153−166.

(56) Jackson, N. A.; Randall, C. J.; McKendrick, K. G. *J. Phys. Chem. A* **1998**, *102*, 51−59.

(57) James, F. C.; Choi, H. K. J.; Ruzsicska, B.; Strausz, O. P.; Bell, T. N. In *Frontiers of Free Radical Chemistry*; Pyror, W., Ed.; Academic Press, Inc.: New York, 1980; Chapter 8.

(58) Ruzsicska, B. R.; Jodhan, A.; Choi, H. K. J.; Strausz, O. P.; Bell, T. N. *J. Am. Chem. Soc.* **1983**, *105*, 2489−2490.

(59) Hildenbrand, D. L.; Lau, K. H.; Sanjurjo, A. *J. Phys. Chem. A* **2003**, *107*, 5448−5451.

(60) Bazalgette Courreges-Lacoste, G.; Sprengers, J. P.; Ubachs, W.; Stolte, S.; Linnartz, H. *J. Mol. Spectrosc.* **2001**, *205*, 341−343.

(61) Kishi, R.; Nakajima, A.; Iwata, S.; Kaya, K. *Chem. Phys. Lett.* **1994**, *224*, 200−206.

(62) Sporea, C.; Rabilloud, F.; Cosson, X.; Allouche, A. R.; Aubert-Frécon, M. *J. Phys. Chem. A* **2006**, *110*, 6032−6038.

(63) Keenan, P. C.; Morgan, W. W. *Astrophys. J.* **1941**, *94*, 501−510.

(64) Bogoslavsky, B.; Levy, O.; Kotlyar, A.; Salem, M.; Gelman, F.; Bino, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 90−94.

(65) Burgess, D. R. Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J.; Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD; 20899, http://webbook.nist.gov (retrieved July 10, 2014).

(66) Siegbahn, P. E. M. *J. Chem. Phys.* **1981**, *75*, 2314−2320.

(67) Danovich, D.; Bino, A.; Shaik, S. *J. Phys. Chem. Lett.* **2013**, *4*, 58−64.

(68) Hoffmann, R.; Gleiter, R.; Mallory, F. B. *J. Am. Chem. Soc.* **1970**, *92*, 1460−1466.

(69) Lischka, H.; Köhler, H.-J. *J. Am. Chem. Soc.* **1983**, *105*, 6646−6649.

(70) Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J. L. *Phys. Rev. Lett.* **1991**, *66*, 413−416.

(71) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1992**, *97*, 7990−7998.

(72) Peeters, J.; Ceursters, B.; Nguyen, H. M. T.; Nguyen, M. T. *J. Chem. Phys.* **2002**, *116*, 3700−3709.

(73) Strausz, O. P.; DoMinh, T.; Font, J. *J. Am. Chem. Soc.* **1968**, *90*, 1930−1931.

(74) Strausz, O. P.; Kennepohl, G. J. A.; Garneau, F. X.; DoMinh, T.; Kim, B.; Valenty, S.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5723−5732.

(75) Brooks, B. R.; Schaefer, H. F. *J. Chem. Phys.* **1977**, *67*, 5146−5151.

(76) Kim, K. S.; So, S. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1982**, *104*, 1457−1461.

(77) Merer, A. J.; Travis, D. N. *Can. J. Phys.* **1965**, *43*, 1795−1830.

(78) Jutzi, P. *Angew. Chem., Int. Ed.* **1975**, *14*, 232−245.

(79) Lee, E. P. F.; Wright, T. G. *J. Phys. Chem. A* **1999**, *103*, 721−726.

(80) Nielsen, I. M. B.; Janssen, C. L.; Burton, N. A.; Schaefer, H. F. *J. Phys. Chem.* **1992**, *96*, 2490−2494.

(81) Heilbronner, E.; Bock, H. *Das HMO Modell und Seine Anwendung*; Verlag Chemie: Weinheim, Germany, 1968; p 168.

(82) Hoffmann, R.; Radom, L.; Pople, J. A.; v, R.; Schleyer, P.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221−6223.

(83) Halfen, D. T.; Clouthier, D. J.; Ziurys, L. M. *Astrophys. J.* **2008**, *677*, L101.

(84) Sun, M.; Clouthier, D. J.; Ziurys, L. M. *J. Chem. Phys.* **2009**, *131*, 224317.

(85) Hou, Z.; Bayes, K. D. *J. Phys. Chem.* **1994**, *98*, 6324−6326.

(86) Guélin, M.; Muller, S.; Cernicharo, J.; Apponi, A. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P. *Astron. Astrophys.* **2000**, *363*, L9−L12.

(87) McCarthy, M. C.; Tamassia, F.; Woon, D. E.; Thaddeus, P. *J. Chem. Phys.* **2008**, *129*, 184301.

(88) Nakano, H.; Uchiyama, R.; Hirao, K. *J. Comput. Chem.* **2002**, *23*, 1166−1175.

(89) Miyajima, M.; Watanabe, Y.; Nakano, H. *J. Chem. Phys.* **2006**, *124*, 044101.

(90) Ebisuzaki, R.; Watanabe, Y.; Nakano, H. *Chem. Phys. Lett.* **2007**, *442*, 164−169.

(91) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(92) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358−1371.

(93) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H. *J. Chem. Phys.* **1999**, *110*, 7667−7676.

(94) Noro, T.; Sekiya, M.; Koga, T. *Theor. Chem. Acc.* **2012**, *131*, 1124.

(95) Tai, T. B.; Nguyen, M. T. *J. Comput. Chem.* **2012**, *33*, 800−809.

(96) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(97) Gordon, M. S.; Schmidt, M. W. In *Theory and Applications of Computational Chemistry: The First Forty Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, 2005.

(98) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics Modell.* **1998**, *16*, 133−138.

(99) Nakamura, H.; Truhlar, D. G. *J. Chem. Phys.* **2011**, *115*, 10353−10372.

(100) Nakahara, H.; Truhlar, D. G. *J. Chem. Phys.* **2002**, *117*, 5576−5593.

(101) Ruedenberg, K.; Atchity, G. J. *J. Chem. Phys.* **1993**, *99*, 3799−3803.

(102) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983−7992.

(103) Nakano, H. *Chem. Phys. Lett.* **1993**, *207*, 372−378.

(104) Granovsky, A. A. *J. Chem. Phys.* **2011**, *134*, 214113.

(105) Choe, Y.-K.; Witek, H. A.; Finley, J. P.; Hirao, K. *J. Chem. Phys.* **2001**, *114*, 3913−3918.

(106) Witek, H. A.; Choe, Y.-K.; Finley, J. P.; Hirao, K. *J. Comput. Chem.* **2002**, *23*, 957−965.

(107) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(108) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(109) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

(110) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098–3100.

(111) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822–8824.

(112) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

(113) Shao, Y.; Fusti-Molnar, L.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'Neill, D. P.; Distasio, R. A.; Lochan, R. C.; Wang, T.; Beran, G. J. O.; Besley, N. A.; Herbert, J. M.; Lin, C. Y.; Van Voorhis, T.; Chien, S. H.; Sodt, A.; Steele, R. P.; Rassolov, V. A.; Maslen, P. E.; Korambath, P. P.; Adamson, D. A.; Austin, B.; Baker, J.; Byrd, E. F. C.; Dachsel, H.; Doerksen, R. J.; Dreuw, A.; Dunietz, B. D.; Dutoi, A. D.; Furlani, T. R.; Gwaltney, S. R.; Heyden, A.; Hirata, S.; Hsu, C. P.; Kedziora, G.; Khaliulin, R. Z.; Klunzinger, P.; Lee, A. M.; Lee, M. S.; Liang, W.; Lotan, I.; Nair, N.; Peters, B.; Proynov, E. I.; Pieniazek, P. A.; Rhee, Y. M.; Ritchie, J.; Rosta, E.; Sherrill, C. D.; Simmonett, A. C.; Subotnik, J. E.; Woodcock, H. L.; Zhang, W.; Bell, A. T.; Chakraborty, A. K.; Chipman, D. M.; Keil, F. J.; Warshel, A.; Hehre, W. J.; Schaefer, H. F.; Kong, J.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M.; Aspuru-Guzik, A.; Chang, C.; Edgar, R. G.; Sundstrom, E.; Parkhill, J.; Lawler, K.; Gordon, M. S.; Schmidt, M. W.; Shenvi, N.; Lambrecht, D.; Goldey, M.; Olivares-Amaya, R.; Bernard, Y.; Vogt, L.; Watson, M.; Liu, J.; Yeganeh, S.; Kaduk, B.; Vydrov, O.; Xu, X.; Kaliman, I.; Khistyaev, K.; Russ, N.; Zhang, I. Y.; Goddard, W. A.; Liu, F.; King, R.; Landau, A.; Wormit, M.; Dreuw, A.; Diedenhofen, M.; Klamt, A.; Lange, A. W.; Gosh, D.; Kosenkov, D.; Kus, T.; Landau, A.; Zuev, D.; Deng, J.; Mao, S. P.; Su, Y. C.; Small, D.; Jacobson, L. D. *Q-Chem*, Version 4.2; Q-Chem, Inc.: Pleasanton, CA, 2014.