How to Make the $\sigma^0\pi^2$ Singlet the Ground State of Carbenes

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S Supporting Information

ABSTRACT: Successful strategies have previously been developed to stabilize the $\sigma^2\pi^0$ singlet states of carbenes, relative to $\sigma^1\pi^1$ triplet states. However, little or no attention has been paid to the stabilization of the $\sigma^0\pi^2$ singlet states. We present two simple strategies to stabilize the $\sigma^0\pi^2$ singlet states of carbenes, relative to both the $\sigma^2\pi^0$ singlet and $\sigma^1\pi^1$ triplet states. These strategies consist of destabilization of the carbene σ orbital by two, adjacent, sp^2 nitrogen lone pairs of electrons and stabilization of the carbene 2p$-\pi$ orbital by incorporating it into a five-membered ring, containing two double bonds, or into a six-membered ring, containing two double bonds and a sixth atom that has a low-lying empty π orbital. B3LYP, CASPT2, and CCSD(T) calculations have been performed in order to assess the success of these strategies in creating derivatives of cyclopenta-2,4-dienylidene and cyclohexa-2,5-dienylidene with $\sigma^0\pi^6$ singlet ground states. Differences between the calculated geometries and binding energies of the Xe complexes of the $\sigma^0\pi^6$ singlet ground state of 2,5-diazacyclopentadienylidene (**5**) and the $\sigma^2\pi^0$ singlet states of CH$_2$ and CF$_2$ are discussed.
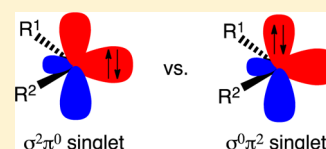
■ INTRODUCTION

The beginning of the enduring interest in the electronic structure of carbenes[1] can be traced back over 80 years to Mulliken's 1932 paper on methylene.[2] Mulliken recognized that CH$_2$ should have two, low-lying electronic states. One of these states is the triplet (^{3}B$_1$-$\sigma^1\pi^1$ in Figure 1). In the ^{3}B$_1$ state one
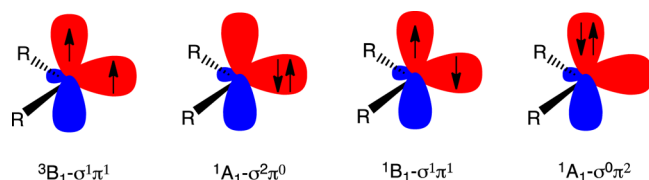

Figure 1. Schematic depiction of four electronic configurations of a carbene. Both ^{1}A$_1$-$\sigma^2\pi^0$ and ^{1}A$_1$-$\sigma^0\pi^2$ contribute to the wave function for the lowest ^{1}A$_1$ state, with the larger contribution coming from the configuration, most commonly ^{1}A$_1$-$\sigma^2\pi^0$, that is the lower in energy.

of the two nonbonding electrons occupies the hybridized σ orbital that is largely (but not completely) localized on the carbene carbon; the other nonbonding electron occupies the carbene 2p$-\pi$ atomic orbital (AO); and the spins of the two electrons are parallel.

The lowest-lying singlet state of CH$_2$ is ^{1}A$_1$. In the electronic configuration ($\sigma^2\pi^0$ in Figure 1) that dominates the ^{1}A$_1$ electronic state, both nonbonding electrons occupy the σ orbital. In methylene and in most carbenes the σ orbital is lower in energy than the 2p$-\pi$ orbital, because the σ orbital is a hybrid, containing a substantial contribution from the carbon 2s AO; whereas, the π orbital consists of a pure carbon 2p AO.

Herzberg's 1959 spectroscopic study of CH$_2$ identified the ground state as the triplet, with an H−C−H bond angle of

between 140° and 180°.[3] However, it was not until 1970 that the results of calculations and experiments led to the conclusion that the H−C−H bond angle in the triplet is at the lower end of this range; and another 15 years passed before calculations and experiments agreed on a value of ΔE_{ST} = 9.0 kcal/mol for the energy difference between the lowest singlet and triplet states of methylene.[4]

Although the lower Coulombic repulsion energy between the nonbonding electrons in the ^{3}B$_1$-$\sigma^1\pi^1$ configuration makes the triplet the ground state of CH$_2$, the ^{1}A$_1$-$\sigma^2\pi^0$ configuration can be selectively stabilized by substituents. In this singlet configuration, which dominates the ^{1}A$_1$ state of lowest energy, the σ orbital is doubly occupied and the 2p$-\pi$ AO is empty; whereas, in the triplet state both of these orbitals are singly occupied. Therefore, ^{1}A$_1$-$\sigma^2\pi^0$ can be selectively stabilized, relative to ^{3}B$_1$-$\sigma^1\pi^1$, by lowering the energy of the σ molecular orbital (MO) and/or raising the energy of the 2p$-\pi$ AO.[5]

Carbenes in which both of these factors contribute to making the singlet the ground state are, for example, difluorocarbene (**1**)[6] and cyclopropenylidene (**2**).[7,8] In **1** the σ MO of the carbene contains contributions from AOs on the fluorines; and the greater electronegativity of fluorine, compared to hydrogen, stabilizes the σ MO of CF$_2$, relative to the σ MO of CH$_2$. In **2** the small C−C−C bond angle at the carbene center, enforced by its incorporation into the three-membered ring, increases the 2s character of the σ MO, thus stabilizing it, relative to the σ MO in CH$_2$.

In both **1** and **2** the 2p$-\pi$ AO on the carbene carbon is destabilized by delocalization of a pair of electrons into it. In **1**

the pair of electrons that is delocalized into 2p−π comes from the in-phase combination of the 2p−π lone pair AOs on fluorine. In **2** it is the pair of electrons in the bonding π MO of the double bond that is delocalized into the 2p−π orbital on the carbene carbon. Equivalently, the singlet ground state of **2** can be rationalized by arguing that the $^1A_1$ state of **2** has 2π electrons and, hence, is aromatic; whereas the triplet has 3π electrons and, hence, is not aromatic.
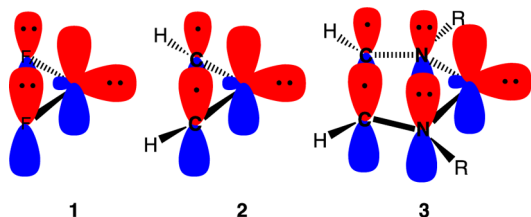
Destabilization of the carbene 2p−π AO by adjacent lone pair donor atoms can, by itself, be sufficient to render the singlet the ground state of a carbene. A good example is provided by the Arduengo carbenes (**3**), in which π donation by the two nitrogens not only makes the singlet the ground state but also provides so much thermodynamic and kinetic stabilization that the singlet carbenes can be isolated.[9] Many other relatively stable singlet carbenes, with π-donating groups adjacent to the carbene center, are now known;[10] so the aromatic, six-electron, π system in **3** is not a prerequisite for thermodynamic and kinetic carbene stability. Carbenes with adjacent lone pair π-donor atoms have proven to be sufficiently stable that they are now used as ligands for transition metals.[11]

The second lowest singlet state of CH_2 is the open-shell $^1B_1$ state, which has the same $\sigma^1\pi^1$ orbital occupancy as the $^3B_1$ state. The antiparallel spins of the two nonbonding electrons in the $^1B_1$ state make the Coulombic repulsion between them substantially larger than that between this pair of nonbonding electrons in the $^3B_1$ state, and the energy of $^1B_1$ is computed to be 33 kcal/mol higher than that of $^3B_1$.[12] A substituent, such as a phenyl group, which allows the electron in the carbene 2p−π AO to delocalize away from the electron of opposite spin in the carbene σ MO can lower the energy of the open-shell singlet, relative to the triplet.[13] However, Hund's rule predicts that $^3B_1$ will always be lower in energy than $^1B_1$,[14] so the open-shell, $^1B_1$-$\sigma^1\pi^1$, singlet state of a carbene cannot be its ground state.

Of the four low-lying electronic configurations of CH_2, the $^1A_1$-$\sigma^0\pi^2$ configuration in Figure 1 has the highest energy. The calculated energy of the excited $^1A_1$ state of CH_2, in which the $\sigma^0\pi^2$ configuration is dominant, is 50 kcal/mol higher than that of the lowest $^1A_1$ state, in which the $\sigma^2\pi^0$ configuration is dominant and 59 kcal/mol higher in energy than the $^3B_1$ ground state.[12] Therefore, it might seem highly unlikely that an excited $^1A_1$ state, in which the $\sigma^0\pi^2$ configuration is dominant, could ever become the lowest singlet state, much less the ground state, of any carbene.

However, as discussed above, substituents that stabilize the σ orbital of a carbene and/or destabilize the carbene 2p−π orbital can lead to a $^1A_1$ ground state, in which the $\sigma^2\pi^0$ configuration is dominant.[5] In this paper we report the results of a computational investigation of whether in-plane, lone pair donors, which destabilize the carbene σ MO, and π acceptors, which stabilize the carbene 2p−π orbital, can lead to a carbene with a singlet ground state, in which the $^1A_1$-$\sigma^0\pi^2$ configuration is dominant. Our calculations have identified several carbenes in which this is likely to be the case. Two of these carbenes have

already been prepared, and others seem likely to succumb to efforts to synthesize them, thus providing opportunities to test our computational predictions experimentally.

■ COMPUTATIONAL METHODOLOGY

The geometries of the carbenes were optimized with both (U)B3LYP[15] and CASSCF calculations, using the 6-31G(d) basis set.[16] In the CASSCF calculations, the active space consisted of the σ and 2p−π carbene orbitals and the two electrons in them, the σ lone pair electrons on the nitrogens, adjacent to the carbene center, and all of the low-lying filled and empty π orbitals and the electrons in the filled π MOs. Vibrational analyses were performed on both the (U)B3LYP and CASSCF optimized structures to confirm that the optimized geometries were, in fact, energy minima and also to obtain the zero-point vibrational energy (ZPVE) corrections. CASPT2[17] and (U)CCSD(T)[18] single-point energies were computed at, respectively, the CASSCF and the (U)B3LYP optimized geometries, with the cc-pVTZ[19] basis set.

In order to calibrate the computational methods, described in the previous paragraph, we performed calculations of the singlet−triplet enegy difference in CH_2. After correction for zero-point energy (ZPE) differences, the B3LYP, (U)CCSD-(T), and CASPT2 levels of theory that we used provided values of the singlet−triplet energy difference in methylene of, respectively, ΔE_{ST} = 13.1, 9.9, and 11.2 kcal/mol. These values are higher by 4.1 kcal/mol (B3LYP), 0.9 kcal/mol [CCSD(T)], and, 2.2 kcal/mol (CASPT2) than the experimental value, ΔE_{ST} = 9.0 kcal/mol.[4]

We also carried out calculations on the Xe complexes of some carbenes. The geometries of the complexes and of the isolated carbenes were optimized by performing CCSD(T) calculations, using the aug-cc-pVTZ[19] basis set for H and first-row atoms and the aug-cc-pVTZ-PP[20] basis set, with a relativistic pseudopotential,[21] for the Xe atoms.

The Xe binding energies of the carbenes were computed by extrapolating the CCSD(T) binding energies at the optimized geometries to the complete basis set (CBS) limit.[22] The CCSD(T)/CBS//CCSD(T)/aug-cc-pVTZ energies were obtained by adding the MP2-based, CBS corrections to the CCSD(T)/aug-cc-pVQZ[19] (plus aug-cc-pVQZ-PP[20,21] for Xe) energies, using the formula
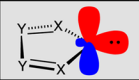
$$E[CCSD(T)/CBS]$$
$$= E[CCSD(T)/apVQZ] + E(MP2/CBS)$$
$$- E(MP2/apVQZ) \qquad (1)$$

where, for the sake of conciseness, "ap" is used in eq 1, instead of "aug-cc-p". The MP2/CBS energies, needed for use in eq 1, were calculated by extrapolation of the MP2/aug-cc-pVQZ and MP2/aug-cc-pV5Z energies to the MP2/CBS limit, using the formula:[22]

$$E(MP2/CBS) = E(MP2/apV5Z) + [E(MP2/apV5Z)$$
$$- E(MP2/apVQZ)]/[(5/4)^\alpha - 1] \qquad (2)$$

where α = 5 for SCF and MP2 triplet-pair energies and α = 3 for MP2 singlet-pair energies. The ZPE corrections to the CCSD(T)/CBS binding energies were calculated by performing frequency analyses at the CCSD(T)/aug-cc-pVTZ level of theory, using finite energy differences.

Table 1. (U)B3LYP/6-31G(d), CASPT2/cc-pVTZ//CASSCF/6-31G(d), and (U)CCSD(T)/cc-pVTZ//(U)B3LYP/6-31G(d) Energies (with zero-point corrected values in parentheses) of Different Electronic States of Cyclopentadienylidene (4) and Some Derivatives[a]

	computational method	$^3B_1$-$\sigma^1\pi^5$	$^3A_2$-$\sigma^1\pi^5$	$^1B_1$-$\sigma^1\pi^5$	$^1A_2$-$\sigma^1\pi^5$	$^1A_1$-$\sigma^2\pi^4$	$^1A_1$-$\sigma^0\pi^6$	$^1A'$-nonplanar
X = Y = CH (4)	B3LYP	**0 (0)**	6.6 (5.2)[b]	14.3 (12.7)[b]	**3.9 (3.1)**	26.5 (25.9)[c]	24.4 (22.3)[c,d]	10.4 (9.8)[e,f]
	CASPT2	**0 (0)**	6.7 (5.0)[b]	17.4 (20.9)[c]	**4.5 (3.9)**	22.3 (21.7)[c]	24.0 (22.0)[c,g]	**12.0 (10.9)**
	CCSD(T)	**0 (0)**	6.7 (5.4)[b]	18.9 (17.3)[b]	**4.9 (4.1)**	20.1 (19.5)[c]	23.7 (21.6)[c,d]	8.5 (7.8)[e]
X = N, Y = CH (5)	B3LYP	**0 (0)**	26.4 (28.4)[c]	13.2 (10.8)[c]	25.4 (21.9)[b,c,d]	32.8 (31.2)[c]	**3.4 (2.8)**	
	CASPT2	**0 (0)**	26.5 (24.2)[b]	15.3 (12.8)[b,c]	26.8 (24.1)[b]	28.5 (27.6)[c]	**-1.3 (-2.1)**	
	CCSD(T)	**0 (0)**	25.6 (27.5)[c]	15.9 (14.7)[c]	26.0 (22.5)[b,c,d]	25.0 (23.4)[c]	**0.3 (-0.4)**	
X = CH, Y = C-CN (6)	B3LYP	**0 (0)**	6.1 (4.9)[b]	12.6 (11.3)[b]	**3.6 (2.9)**	30.3 (29.8)[c]	22.8 (21.2)[c,d]	**12.3 (11.9)**
	CASPT2	**0 (0)**	6.4 (4.8)[b]	15.1 (17.5)[c]	**4.3 (3.7)**	25.9 (25.4)[c]	22.5 (21.3)[c,d,g]	11.3 (9.8)[e]
	CCSD(T)	**0 (0)**	4.9 (3.7)[b]	[b,h]	**3.1 (2.3)**	22.0 (21.4)[c]	20.2 (18.6)[c,d]	**8.2 (7.9)**
X = N, Y = C-CN (7)	B3LYP	**0 (0)**	25.0 (25.8)[c]	11.2 (10.1)[c]	24.0 (26.2)[c,d]	36.8 (35.4)[c]	**2.6 (2.5)**	
	CASPT2	**0 (0)**	**25.5 (30.9)**	12.8 (10.6)[b,c]	25.6 (23.2)[b]	32.2 (31.3)[c]	**-2.4 (-2.7)**	
	CCSD(T)	**0 (0)**	23.4 (24.1)[c]	[c,h]	24.4 (26.6)[c,d]	27.0 (25.5)[c]	**-2.0 (-2.1)**	
X = CH, Y = C-CHO (8)	B3LYP	**0 (0)**		**4.8 (4.2)**		32.9 (32.2)[c]	13.1 (11.7)[c]	**9.0 (8.6)[f]**
	CASPT2	**0 (0)**		**4.3 (3.8)**		27.1 (26.6)[c]	14.9 (13.7)[c,g]	
	CCSD(T)	**0 (0)**		[i]		23.6 (22.9)[c]	12.4 (11.0)[c]	**5.9 (5.5)**
X = N, Y = C-CHO (9)	B3LYP	**0 (0)**		11.4 (10.2)[c]		38.7 (37.1)[c]	**-4.7 (-4.7)**	
	CASPT2	**0 (0)**		14.7 (13.9)[c]		33.2 (32.4)[c]	**-7.9 (-8.1)**	
	CCSD(T)	**0 (0)**		[c,i]		28.3 (26.7)[c]	**-7.8 (-7.8)**	

[a] Calculations on 4−7 were performed at C_{2v} geometries, except for the calculations on the nonplanar singlets. In the lowest energy geometries of 8 and 9, there appears to be a weak C−H···O=C hydrogen bond between the two formyl groups. Consequently, the formyl groups in this conformation are not transformed into each other by any symmetry element, so the calculations on these two molecules were performed at the planar C_s geometries, except for the calculations on the nonplanar singlets. In C_s symmetry $\sigma^2\pi^4$ and $\sigma^0\pi^6$ configurations both have A′ symmetry, and $\sigma^1\pi^5$ has A″ symmetry. The energies of the two possible C_{2v} conformers of 8 and 9 are given in the Supporting Information. The (U)B3LYP and (U)CCSD(T) energies of the open-shell singlets were corrected using the formula of Houk and Yamaguchi.[31] An energy in boldface denotes that the optimized geometry (B3LYP or CASSCF) is an energy minimum, while an energy in plain text denotes that the optimized geometry has imaginary frequencies, which are given in the footnotes. [b] B_2 imaginary frequency corresponding to in-plane antisymmetric C−C bond stretch. [c] B_1 imaginary frequency (or A″ imaginary frequency in planar C_s structure) corresponding to out-of-plane bending. [d] A_2 imaginary frequency corresponding to out-of-plane antisymmetric bending. [e] A″ imaginary frequency corresponding to antisymmetric bending of the nonplanar C_s structure, to a C_1 structure. [f] (R)B3LYP wave function not stable. [g] Empty hybrid AO on the carbene carbon could not be forced to remain in the active space in the CASSCF calculation on the $\sigma^0\pi^6$ singlet state from which this CASPT2 energy was derived. [h] Large amount of spin contamination in the open-shell "singlet" UHF wave function ($<S^2> > 1.3$) resulted in the Houk−Yamaguchi formula giving much higher (U)CCSD(T) energies for the pure singlet states than either the (U)B3LYP or the CASPT2 calculations. [i] A calculation at the optimized geometry of the open-shell singlet gave a triplet with a different orbital occupancy. Therefore, the energy of the triplet could not be used to correct the energy of the open-shell singlet for spin contamination.

DFT calculations were also carried out on the Xe complexes, using the ωB97XD[23] functional, the def2-QZVP[24] basis set, and a relativistic pseudopotential[21] for Xe. The ωB97XD/def2-QZVP binding energies were computed with counterpoise correction for basis set superposition errors.[25] The ZPE corrections to these binding energies were calculated by performing frequency analyses at the ωB97XD/def2-QZVP level of theory.

The (U)B3LYP and (U)CCSD(T) calculations for the electronic states of the carbenes and the ωB97XD calculations on the Xe complexes were carried out with Gaussian 09.[26] The CASSCF and CASPT2 calculations were performed with MOLCAS 7.4.[27] The CCSD(T) optimizations of the geometries and the frequency analyses of the carbene-Xe complexes and the MP2 extrapolations were done with Molpro 2010.[28]

■ RESULTS AND DISCUSSION

Cyclopentadienylidene (4). We began our computational investigation of whether a $^1A_1$ state, with a dominant $\sigma^0\pi^2$ configuration, can be made the ground state of a carbene by investigating the effects of σ-donating and π-accepting substituents on the relative energies of the low-lying electronic states of cyclopenta-2,4-dienylidene (4). This carbene seemed like a good starting point, because the $\sigma^2\pi^0$ configuration of the carbene center in 4 leaves the five-membered ring with only 4π electrons. With only 4π electrons, a bonding π MO of the five-membered ring is left empty, and the availability of this empty MO would be expected to selectively stabilize both the $\sigma^1\pi^5$ and $\sigma^0\pi^6$ electronic configurations of 4, relative to the $\sigma^2\pi^4$ configuration.

The electronic structures of cyclopentadienylidene (4) and its derivatives (5−9) in Table 1 are complicated by the fact that the five-membered ring of these carbenes contains two bonding π MOs that have nearly the same energies. This pair of π MOs, ($1a_2$ and $2b_1$ in C_{2v} symmetry), is shown schematically in Figure 2. The presence of these two, nearly degenerate π MOs means that, as is also shown in Figure 2, there are actually four, potentially low-lying, states with two electrons in the carbene σ MO and four more with one electron in the σ MO.

However, when two electrons occupy the σ MO, by far the lowest-lying electronic state is the $^1A_1$ state that places two π electrons in the $1a_2$ MO and leaves the $2b_1$ MO empty. Since the $1a_2$ MO has a node at the carbenic carbon atom, whereas the $2b_1$ MO does not, placing two electrons in $1a_2$ minimizes the Coulombic repulsion between this pair of π electrons and the pair of electrons in the carbene σ MO.

The results of our calculations on the relative energies of the six lowest low-lying electronic states of 4 are given in Table 1.[29,30] The good agreement between the relative energies obtained by our (U)B3LYP, CASPT2, and (U)CCSD(T) calculations gives us confidence that the relative energies of the
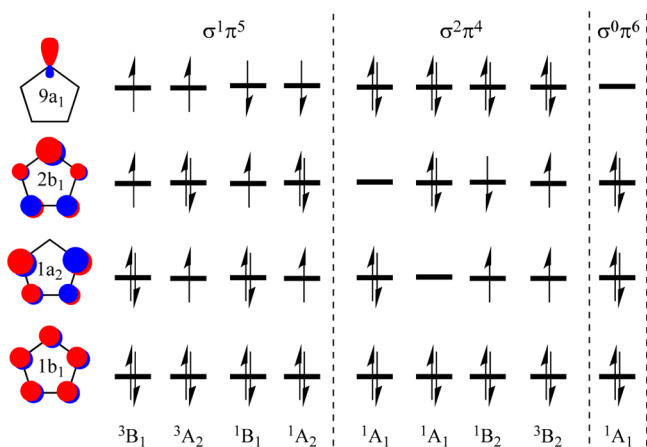
Figure 2. Low-lying electronic configurations of C_{2v} cyclopentadienylidene (**4**). The three bonding π MOs and the hybridized σ MO at the carbene carbon are depicted schematically at the left side of the figure, and the symmetry of each electronic configuration is given under it.

states in Table 1 are qualitatively, if not quantitatively, accurate. Our results are also in good agreement with the results of previous CI calculations on **4**, published by Olivella and Vilarrasa.[30b]

As indicated by the footnotes to Table 1, most of the electronic states on which we performed calculations were found not to be energy minima. On reducing the molecular symmetry from C_{2v}, MOs of different symmetry can mix, and this mixing can lead to energy lowering.[32] In other cases an electron in a higher energy C_{2v} MO of one symmetry can fall into a lower energy C_{2v} MO of different symmetry, when the symmetry is reduced from C_{2v}, so that the two orbitals can no longer be distinguished by their different C_{2v} symmetries.

We have chosen to simplify the discussion of the results in Table 1 by focusing on those electronic states that are found to be energy minima at the B3LYP and/or CASSCF levels of theory and whose energies are given in boldface in Table 1. We begin with the triplet ground state of **4**.

As already noted, minimization of Coulombic repulsion results in the $1a_2$ π MO being doubly occupied and the $2b_1$ π MO being empty in the lowest energy $\sigma^2\pi^4$ state of **4**. For the same reason, in the lowest energy $\sigma^1\pi^5$ triplet state of **4**, the $1a_2$ π MO is doubly occupied, and the $2b_1$ π MO is occupied by the unpaired π electron.

Although the unpaired σ and π electrons both appear at the carbene carbon in the $^3B_1$ state, in this state these two electrons have the same spin. Consequently, through antisymmetrization of the wave function, the Pauli exclusion principle correlates the motions of these two electrons, so they never appear simultaneously in the same region of space. Therefore, the Coulombic repulsion energy between these two electrons is much lower than it would be if electrons of opposite spin occupied the σ and the $2b_1$ π MOs.

Of course, in the $\sigma^1\pi^5$ open-shell singlet the unpaired σ and π electrons do have opposite spins. However, in the lower of the two open-shell singlet states, the unpaired π electron occupies the $1a_2$ MO. Since this MO has a node at the carbene carbon, the unpaired σ and π electrons in the $^1A_2$ state of **4** occupy MOs that are disjoint (i.e., have no atoms in common).[33] Therefore, although these two electrons have opposite spins, the disjoint nature of the MOs that they occupy ensures that

they do not appear in the same region of space in the $^1A_2$-$\sigma^1\pi^5$ open-shell singlet state.

This is the reason why the $^1A_2$ state is calculated to have an energy that is only 4−5 kcal/mol higher than that of the $^3B_1$ ground state of **4**. This is also the reason why **4** is predicted to be a rare example of a carbene in which the electronic configuration of the lowest singlet state has an open-shell structure, where one electron occupies the carbene σ orbital and the other unpaired electron occupies a π orbital.

The results in Table 1 show that the low energy of the bonding, $2b_1$, π MO in **4** makes the energy separations between the $^3B_1$-$\sigma^1\pi^5$ ground state and the $^1A_1$-$\sigma^2\pi^4$ and $^1A_1$-$\sigma^0\pi^6$ excited states in **4** very different than the energy separations between the $\sigma^1\pi^1$ triplet ground state and the $^1A_1$-$\sigma^2\pi^0$ and $\sigma^0\pi^2$ excited states in CH_2.[4,12] The energy difference between the σ MO and the $2b_1$ bonding π MO in **4** is considerably less than the energy difference between the σ and 2p−π MO in CH_2. Consequently, transfer of an electron from the singly occupied π orbital in the triplet to the σ MO is more unfavorable in **4** than in CH_2, but transfer of an electron from the singly occupied σ orbital in the triplet to the π MO is more favorable in **4** than in CH_2.

Indeed, the calculated energy difference of 20−27 kcal/mol between the $^3B_1$-$\sigma^1\pi^5$ ground state and the $^1A_1$-$\sigma^2\pi^4$ excited state in **4** is much larger than that of 9.0 kcal/mol between the $^3B_1$-$\sigma^1\pi^1$ ground state and the $^1A_1$-$\sigma^2\pi^0$ state in CH_2.[4,12] Similarly, the calculated energy difference between the $^3B_1$-$\sigma^1\pi^5$ ground state and the $^1A_1$-$\sigma^0\pi^6$ excited state in **4** of ~24 kcal/mol is much smaller than that of 59 kcal/mol between the $^3B_1$-$\sigma^1\pi^1$ ground state and the $^1A_1$-$\sigma^0\pi^2$ state in CH_2.[12]

In **4** the large stabilization of the $\sigma^0\pi^6$ configuration, relative to the $\sigma^2\pi^4$ configuration, makes the energy difference between these two $^1A_1$ states much smaller than that of 50 kcal/mol between the $\sigma^2\pi^0$ and $\sigma^0\pi^2$ $^1A_1$ states of CH_2. In fact, these two $^1A_1$ states are calculated to be nearly equienergetic in **4**. Unlike the case in CH_2, where the 2p−π and σ orbitals have very different energies, in **4** the $2b_1$ and the σ MOs apparently have very similar energies.

Destroying the molecular plane of symmetry, which differentiates σ from π MOs, allows the $9a_1$ σ and $2b_1$ π MOs of **4** to mix, giving a hybrid orbital that interacts in a bonding way with the π AOs at the two adjacent carbons.[32] In terms of the electronic states in Table 1, this mixing involves the $^1A_1$-$\sigma^2\pi^4$, $^1A_1$-$\sigma^0\pi^6$, and $^1B_1$-$\sigma^1\pi^5$ states. Table 1 shows that at the CASSCF/6-31G(d) level, the optimized, nonplanar geometry of the $^1A'$ state is a minimum, and the corresponding CASPT2 energy is, after vibrational corrections, >10 kcal/mol lower in energy than the optimized planar geometries of the $^1A_1$-$\sigma^2\pi^4$, $^1A_1$-$\sigma^0\pi^6$, and $^1B_1$-$\sigma^1\pi^5$ states of **4**.

Summarizing the results for **4**, our calculations find that incorporating a carbene center into a cyclopentadiene ring has the expected effect of stabilizing the 2p−π AO at the carbene carbon, by allowing it to interact in a bonding fashion with the empty $2b_1$ π MO of the diene. The low energy of the $2b_1$ MO that results from this orbital mixing in **4** stabilizes the $^1A_1$-$\sigma^0\pi^6$ state, relative to both the $^1A_1$-$\sigma^2\pi^4$ and the $^3B_1$-$\sigma^1\pi^5$ states. However, the planar $^1A_1$-$\sigma^0\pi^6$ state is not even a local minimum, and it is not close to being the ground state of **4**. In the next section we discuss one way that substituents can be used to lower the energy of the $^1A_1$-$\sigma^0\pi^6$ state of a cyclopentadienylidene, relative to the energies of both the $^1A_1$-$\sigma^2\pi^4$ and the $^3B_1$-$\sigma^1\pi^5$ states.

2,5-Diazacyclopentadienylidene (5). One strategy to accomplish this change in relative energies is to destabilize the $^1A_1\text{-}\sigma^2\pi^4$ and $^3B_1\text{-}\sigma^1\pi^5$ states by destabilizing the σ MO at the carbene center. Destabilization of this MO can be accomplished by replacing the C–H bonds at C2 and C5 of **4** with the nitrogen lone pairs in **5**. The enhanced donor ability of the in-plane, nitrogen, lone pairs in **5**, relative to the C–H bonds in **4**, serves to raise the energy of the carbene σ orbital, thus lowering the excitation energy of the electrons from it into the $2b_1$ π MO.

The results summarized in Table 1 show that this strategy is successful in stabilizing the $^1A_1\text{-}\sigma^0\pi^6$ state in **5**, relative to both the $^1A_1\text{-}\sigma^2\pi^4$ and $^3B_1\text{-}\sigma^1\pi^5$ states. The energy difference between the $2b_1$ π and the $9a_1$ σ MO in **5** is large enough that the $^1A_1\text{-}\sigma^0\pi^6$ state is calculated to lie well below $^1A_1\text{-}\sigma^2\pi^4$ state in energy. In addition, the out-of-plane distortion in **4** that mixes the σ and π MOs in these two states is no longer favorable in **5**, so that the planar $^1A_1\text{-}\sigma^0\pi^6$ state of **5** is an energy minimum. In fact, as shown in Table 1, this state is calculated to be the only singlet energy minimum in **5**.

Table 1 also shows that the $^1A_1\text{-}\sigma^0\pi^6$ state of **5** is computed to have nearly the same energy as the $^3B_1\text{-}\sigma^1\pi^5$ state. Indeed, after correction for ZPE differences, $^1A_1\text{-}\sigma^0\pi^6$ is actually computed to be the ground state of **5** at both the CASPT2 and CCSD(T) levels of theory. Moreover, as already noted, calculations at these two levels of theory overestimate the stability of the $^3B_1\text{-}\sigma^1\pi^1$ state of CH$_2$, relative to the $^1A_1\text{-}\sigma^2\pi^0$ state by, respectively, 2.2 and 0.9 kcal/mol, when compared to the experimental value of ΔE_{ST} = 9.0 kcal/mol.[4] Assuming that these two methods are similarly biased toward the triplet state in **5**, based on the results in Table 1, it seems likely that **5** really does have a $^1A_1\text{-}\sigma^0\pi^6$ ground state.

Previous calculations on **5**, at lower levels of theory, have made conflicting predictions about the ground state of **5**, predictions that were highly dependent on the computational methodology used.[34] However, Maier and Endres were successful in generating this carbene in matrix isolation, and their experiments found that **5** apparently does have a singlet ground state, with unusually high electrophilic reactivity.[34d,35] For example, matrix-isolated carbene **5** reacts with CO, to give the corresponding ketene, with N$_2$, to reform the diazo compound from which **5** was generated, and with Xe, to form an adduct that could be characterized spectroscopically.[34d] The Xe complex of **5** is discussed in the next section.[36]

Before moving on to discuss the Xe complex of **5**, there is an additional observation worth making about the computational results for uncomplexed carbene **5** in Table 1. The nitrogen lone pairs in **5** are calculated to have a much larger effect on reducing the energy difference between the $^1A_1\text{-}\sigma^0\pi^6$ and $^3B_1\text{-}\sigma^1\pi^5$ states of **4**, than on reducing the energy difference between the $^3B_1\text{-}\sigma^1\pi^5$ and $^1A_1\text{-}\sigma^2\pi^4$ states of **4**. The reason is that, in the $^1A_1\text{-}\sigma^0\pi^6$ state of **5**, the empty σ MO is a much better acceptor for the nitrogen lone pairs in **5** than the singly occupied σ MO is in the $^3B_1\text{-}\sigma^1\pi^5$ state of **5**. Consequently, going from the $^1A_1\text{-}\sigma^0\pi^6$ state to the $^3B_1\text{-}\sigma^1\pi^5$ state, by moving one electron from the $2b_1$ π MO into the σ MO, is more destabilizing than going from the $^3B_1\text{-}\sigma^1\pi^5$ state to the $^1A_1\text{-}\sigma^2\pi^4$ state, by moving a second electron from the $2b_1$ π MO into the σ MO.

A Digression: Differences between the Bonding in the Xe complexes of 5, CH$_2$, and CF$_2$. The most obvious explanation of the apparently strong electrophilicity of **5**[34d,35] is that the lowest singlet state of this carbene is $^1A_1\text{-}\sigma^0\pi^6$, in which the carbene σ MO is empty.[37] The nature of the LUMO of **5**

accounts for the geometry of its Xe complex, in which the Xe atom lies in the plane of the five-membered ring of **5**,[34d,38] and the large amount of carbon 2s character in the empty σ orbital of the carbene could then account for the apparently strong electrophilicity of **5**.

In contrast, since the lowest singlet state of CH$_2$ is $^1A_1\text{-}\sigma^2\pi^0$, the empty orbital that is available to act as a Lewis acid in CH$_2$ is a pure 2p AO. This difference between the nature of the LUMO in the lowest singlet states of **5** and CH$_2$ predicts that, instead of the planar equilibrium geometry favored by the Xe complex of **5**, the equilibrium geometry of the Xe complex of the $\sigma^2\pi^0$ singlet state of CH$_2$ should have an angle (α in Scheme 1) between the Xe and the H–C–H plane of $\alpha \approx 90°$.

Scheme 1

$\sigma^2\pi^0$ carbene Xe complex   vs. $\sigma^0\pi^2$ carbene Xe complex
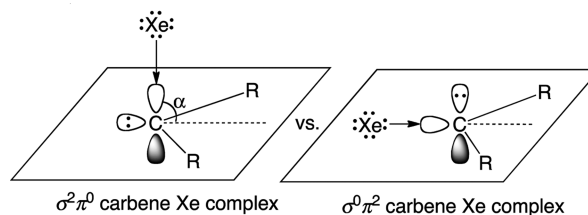
In addition, from the difference between the amounts of 2s character in the LUMO of the lowest singlets of **5** and of CH$_2$, one might conjecture that the Xe binding energy in the Xe complex of **5** should be much larger than that in the Xe complex of CH$_2$.

In order to test these qualitative predictions about the differences between the geometries and Xe binding energies of the Xe complexes of the $\sigma^0\pi^6$ singlet state of **5** and the $\sigma^2\pi^0$ singlet state of CH$_2$, we performed CCSD(T)/aug-cc-pVTZ calculations to optimize the geometries of both complexes. We also computed the Xe binding energies of both complexes, with extrapolations of the CCSD(T) energies to the complete basis set limit.[22]

DFT calculations with the ωB97XD functional[23] were also carried out on the carbene–Xe complexes. Noncovalent interactions are presumably important in the carbene-Xe complexes of **5** and CH$_2$, and the ωB97XD functional includes long-range and empirical dispersion corrections.

We also performed both CCSD(T) and ωB97XD calculations on the Xe complex of CF$_2$, a carbene with a $^1A_1\text{-}\sigma^2\pi^0$ ground state.[6] We conjectured that the geometry of the Xe complexes of the lowest singlet states of CH$_2$ and CF$_2$ would be similar but that donation of the fluorine lone pairs into the empty 2p–π orbital on the carbene center would raise the energy of the LUMO of the $\sigma^2\pi^0$ singlet state of CF$_2$, resulting in the Xe complex of CF$_2$ having a much longer C–Xe bond and a much lower Xe binding energy than the Xe complex of CH$_2$.

Table 2 shows good agreement between the results of our CCSD(T) and ωB97XD calculations. Our expectations about the difference between the value of α in the Xe complex of the $\sigma^0\pi^6$ singlet state of **5**, and the values of α in the Xe complexes of the $\sigma^2\pi^0$ states of CH$_2$ and CF$_2$ are confirmed. Also as expected, the C–Xe distance is more than 1.2 Å longer in the Xe complex of CF$_2$ than in the Xe complex of CH$_2$, and the Xe binding energy in the Xe–CF$_2$ complex is much weaker than that in the Xe–CH$_2$ complex.

However, it is somewhat surprising that the Xe–C distance in the Xe complex of **5** is actually calculated to be ∼0.2 Å

Table 2. Calculated Xe Binding Energies, ΔE_{bind} (with ZPE corrected values in parentheses) of the Lowest Closed-Shell Singlet States of CH_2, CF_2, and 5, Computed at the CCSD(T)/CBS//CCSD(T)/aug-cc-pVTZ, and ωB97XD/def2-QZVP Levels of Theory[a]

Xe complex Formed with	computational method	ΔE_{bind} (kcal/mol)	d_{Xe-C} (Å)	α (°)
$\sigma^0\pi^6$ singlet state of 5	CCSD(T)	2.5 (2.1)	2.860	180.0
	ωB97XD	2.1 (1.7)	2.834	180.0
$\sigma^2\pi^0$ singlet state of CH_2	CCSD(T)	3.7 (1.4)	2.647	89.1
	ωB97XD	4.1 (1.7)	2.637	90.7
$\sigma^2\pi^0$ singlet state of CF_2	CCSD(T)	0.6 (0.5)	3.887	87.4
	ωB97XD	0.5 (0.3)	3.969	99.9

[a]The ωB97XD/def2-QZVP binding energies include counterpoise corrections for basis set superposition errors.[25] Also shown are the Xe−C distances, d_{Xe-C}, and the angles, α, between the Xe−C bond and carbene plane (see Scheme 1) in the CCSD(T)/aug-cc-pVTZ and ωB97XD/def2-QZVP optimized geometries. The CCSD(T)/CBS binding energies are very close to the CCSD(T) binding energies, computed with the aug-cc-pVQZ basis set, after counterpoise corrections.[25] A comparison is given in Table S3 of the Supporting Information.

longer than that in the Xe complex of CH_2 and that, before ZPE corrections, the Xe binding energy in the Xe complex of the $\sigma^0\pi^6$ singlet state of 5 is actually 1.2−2.0 kcal/mol less than that in the Xe complex of the $\sigma^2\pi^0$ singlet state of CH_2. From these Xe complexation energies, it seems that the $\sigma^0\pi^6$ singlet state of 5 is less electrophilic than Maier and Endres assumed, based on the formation of an Xe complex of the carbene.[34d,39]

Apparently, donation of the nitrogen lone pairs into the empty carbene σ orbital in the $\sigma^0\pi^6$ singlet state of 5 has the same type of effect as donation of the fluorine lone pairs into the empty 2p−π orbital of the $\sigma^2\pi^0$ singlet state of CF_2. In both of these carbenes the energy of the LUMO is raised by lone pair donation, so that, before correction for ZPVE differences, $\sigma^2\pi^0$ singlet CH_2 is calculated to bond Xe significantly more strongly than either $\sigma^2\pi^0$ singlet CF_2 or $\sigma^0\pi^6$ singlet 5.

Perhaps the most surprising result in Table 2 is that, after addition of the corrections for ZPE differences, the Xe binding energy of the $\sigma^2\pi^0$ singlet state of CH_2 drops by ∼2.3 kcal/mol; whereas, the Xe binding energy the $\sigma^0\pi^6$ singlet state of 5 is calculated to decrease by only 0.4 kcal/mol. Why is the Xe complex of the $\sigma^2\pi^0$ singlet state of CH_2 computed to have a ZPE correction that is apparently ∼6 times greater than that of the Xe complex of the $\sigma^0\pi^6$ singlet state of 5?

One might guess that the difference in ZPEs resides in a difference between the C−Xe stretching frequencies in the two complexes, but this is not the case. The Xe−C stretching frequency in the Xe complex of the $\sigma^2\pi^0$ singlet state of CH_2 is computed to be 142.3 cm^{-1}, which is only 97.2 cm^{-1} higher than the Xe−C stretching frequency in the Xe complex of the $\sigma^0\pi^6$ singlet state of 5. The difference in ZPEs that is associated with this difference in stretching frequencies is only 1/2 × 97.2 cm^{-1}/(350 cm^{-1}/kcal·mol^{-1}) = 0.14 kcal/mol.

The 2.0 kcal/mol difference between the ZPEs in the two complexes largely resides in the differences between the frequencies for Xe bending. These frequencies are 816.9 and 679.1 cm^{-1} in the Xe complex of the $\sigma^2\pi^0$ singlet state of CH_2 and 107.7 and 86.3 cm^{-1} in the Xe complex of the $\sigma^0\pi^6$ singlet state of 5. The differences between these two sets of frequencies correspond to a difference between ZPEs of 1/2 [(816.9 −107.7) + (679.1 − 86.3)]/350 = 1.86 kcal/mol.

The reason for the large differences in Xe bending frequencies reflects a fundamental difference between the bonds to Xe in the two complexes. In the complex with the $\sigma^2\pi^0$ singlet state of CH_2, the bond to Xe is formed by the carbene 2p−π AO; whereas, in the complex with the $\sigma^0\pi^6$ singlet state of 5, the bond to Xe is formed by the carbene σ orbital. 2p AOs are highly directional, whereas, the 2s component of the sp^n hybridized σ AO is spherically symmetrical. Consequently, the bond to Xe has a much higher force constant for resisting angle deformation in the complex with the $\sigma^2\pi^0$ singlet state of CH_2 than in the complex with the $\sigma^0\pi^6$ singlet state of 5, and this difference is responsible for the much higher frequencies of the vibrational modes for Xe angle deformations in the complex with singlet CH_2 than in the complex with the $\sigma^0\pi^6$ singlet states of 5.[40,41]

The 1.4−1.7 kcal/mol Xe binding energy of the $\sigma^2\pi^0$ singlet state of CH_2 does not necessarily mean that the CH_2−Xe complex should exist, because the $\sigma^2\pi^0$ singlet state is not the ground state of CH_2. Moreover, the 9 kcal/mol singlet−triplet gap in CH_2 is much larger than the 1.4−1.7 kcal/mol Xe binding energy of the $\sigma^2\pi^0$ singlet state of CH_2, so the $^3B_1$ ground state of CH_2 should not complex Xe.

In contrast, our CASPT2 and CCSD(T) calculations predict that the $\sigma^0\pi^6$ singlet state is either the ground state of 5 or very close to it. Therefore, the 1.7−2.1 kcal/mol Xe binding energy of the $\sigma^0\pi^6$ singlet state of 5 means the Xe complex of 5 should certainly exist at low temperatures, and this computational result is in agreement with the experimental finding of Maier and Endres.[34d]
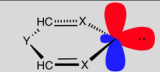
Although CF_2 has a singlet ground state,[6] to the best of our knowledge, the Xe complex of CF_2 has not been observed. The calculated C−Xe distance in this complex is just about the size of sum of the van de Waals radius of C and Xe atoms (1.70 + 2.16 = 3.86 Å),[42] and the very small binding energy of 0.3−0.5 kcal/mol that we calculate for the CF_2−Xe complex is probably just due to a weak van de Waals interaction between CF_2 and Xe.

Cyclopentadienylidene and 2,5-Diazacyclopentadienylidenes with π-Acceptors at C3 and C4. Our CASPT2 and CCSD(T) calculations find that, after corrections for ZPE differences, $^1A_1$-$\sigma^0\pi^6$ is computed to be the ground state of 5. However, without calibration against the CASPT2 and CCSD(T) values for ΔE_{ST} in CH_2, the calculated energy differences between the $^1A_1$-$\sigma^0\pi^6$ and $^3B_1$-$\sigma^1\pi^5$ states of 5 in Table 1 are, by themselves, too small to predict unequivocally that $^1A_1$-$\sigma^0\pi^6$ is the ground state of 5.

Therefore, we investigated the effects of the addition of π-electron acceptors to carbenes 4 and 5. Such substituents should selectively stabilize the $^1A_1$-$\sigma^0\pi^6$ state of each of these carbenes, by lowering the energy of the 2b$_1$ π MO while leaving the energy of the 9a$_1$ σ MO largely unaffected. We performed calculations in order to determine whether the cyano groups attached to C3 and C4 in 6 and 7 or the aldehyde groups attached to these two carbons in 8 and 9 are sufficiently strong π-electron acceptors for us to be able to predict unequivocally that $^1A_1$-$\sigma^0\pi^6$ is the ground state of one or more of these four carbenes.

As shown in Table 1, on going from 4 to 6, the pair of cyano groups at C3 and C4 decrease the energy difference between the $\sigma^0\pi^6$ singlet state and the $\sigma^1\pi^5$ triplet state by only 1−3 kcal/mol. Adding cyano groups at C3 and C4 of diazacarbene 5, has an even smaller predicted effect on the energy differences between the $^1A_1$-$\sigma^0\pi^6$ and the $^3B_1$-$\sigma^1\pi^5$ states. On going from 5

Table 3. (U)B3LYP/6-31G(d), CASPT2/cc-pVTZ//CASSCF/6-31G(d), and (U)CCSD(T)/cc-pVTZ//(U)B3LYP/6-31G(d) Relative Energies (with zero-point corrected values in parentheses) of Different Electronic States of Some Derivatives of Cyclohexa-2,5-dienylidenes[a]

	computational method	$^3B_1$-$\sigma^1\pi^5$	$^1B_1$-$\sigma^1\pi^5$	$^1A_1$-$\sigma^2\pi^4$	$^1A_1$-$\sigma^0\pi^6$
X = CH, Y = C=O (10)	B3LYP	**0 (0)**	**8.8 (8.5)**	31.8 (31.1)[b]	**38.6 (36.8)**[c,d]
	CASPT2	**0 (0)**	9.7 (8.4)	26.5 (26.1)[b]	**35.9 (37.1)**[e]
	CCSD(T)	**0 (0)**	[j]	23.0 (22.3)[b]	35.5 (33.7)[c]
X = N, Y = C=O (11)	B3LYP	**0 (0)**	7.6 (6.8)[b,g]	48.5 (51.3)[h]	9.2 (8.1)[b,g]
	CASPT2	**0 (0)**	8.4 (7.2)[b]	41.1 (40.5)[b]	1.6 (0.5)[b]
	CCSD(T)	**0 (0)**	[b,j]	36.6 (39.4)[h]	4.0 (2.9)[b,i]
X = CH, Y = C=NH$_2^+$ (12)	B3LYP	**0 (0)**	**9.1 (8.5)**	49.1 (49.6)	14.4 (11.4)[b]
	CASPT2	**0 (0)**	9.0 (7.3)[b]	42.4 (41.5)[b]	11.6 (8.2)[b,j]
	CCSD(T)	**0 (0)**	[j]	**39.9 (40.4)**	10.9 (7.9)[b]
X = N, Y = C=NH$_2^+$ (13)	B3LYP	**0 (0)**	**7.4 (8.4)**	65.6 (64.1)[h]	**-15.6 (-15.8)**[b]
	CASPT2	**0 (0)**	7.0 (5.4)[b]	57.2 (55.9)[b]	-22.0 (-24.1)[b]
	CCSD(T)	**0 (0)**	[j]	53.2 (51.7)[h]	-21.0 (-21.2)
X = CH, Y = C=OH$^+$ (14)	B3LYP	**0 (0)**	9.7 (8.7)[b]	**54.6 (54.5)**	2.8 (0.5)[b]
	CASPT2	**0 (0)**	12.0 (10.6)[b]	48.0 (46.7)[c]	-2.3 (-5.2)[b,j]
	CCSD(T)	**0 (0)**	12.9 (11.9)[b]	**46.0 (46.0)**	-1.6 (-3.9)[b]
X = N, Y = C=OH$^+$ (15)	B3LYP	**0 (0)**	**7.9 (8.4)**	72.3 (72.4)	**-29.6 (-28.7)**
	CASPT2	**0 (0)**	**7.9 (8.7)**	64.0 (62.2)[c]	**-36.8 (-37.7)**
	CCSD(T)	**0 (0)**	**9.2 (9.7)**	60.5 (60.6)	**-35.7 (-34.8)**
X = CH, Y = CH$^+$ (16)	B3LYP	**0 (0)**	**3.7 (4.5)**[k]	66.8 (66.3)	**-18.1 (-18.8)**
	CASPT2	**0 (0)**	4.7 (3.3)[h,k]	62.4 (62.0)	**-20.2 (-21.8)**[j]
	CCSD(T)	**0 (0)**	5.0 (5.8)[k]	59.7 (59.3)	**-22.2 (-22.8)**
X = N, Y = CH$^+$ (17)	B3LYP	**0 (0)**	**7.5 (7.9)**	90.3 (87.6)[b,c]	**-55.4 (-55.3)**
	CASPT2	**0 (0)**	**8.7 (8.7)**	[l]	**-60.9 (-61.2)**
	CCSD(T)	**0 (0)**	**8.3 (8.7)**	80.5 (77.8)[b,c]	**-60.5 (-59.4)**
X = CH, Y = BH (18)	B3LYP	**0 (0)**	**10.5 (9.8)**	38.2 (39.2)[b]	16.4 (13.8)[b]
	CASPT2	**0 (0)**	11.7 (9.4)[b]	33.9 (32.9)[b]	15.5 (13.3)[b,j]
	CCSD(T)	**0 (0)**	[j]	31.1 (32.1)[b]	13.3 (10.7)[b]
X = N, Y = BH (19)	B3LYP	**0 (0)**	**8.7 (9.6)**	56.9 (60.2)[b]	**-19.4 (-18.8)**
	CASPT2	**0 (0)**	9.4 (7.5)[b]	50.2 (48.6)[b]	**-25.7 (-26.5)**
	CCSD(T)	**0 (0)**	[j]	46.8 (50.1)[b]	**-25.0 (-24.3)**

[a]All calculations were performed at C_{2v} geometries, except for those on **14** and **15**, since these molecules have only C_s symmetry. Where possible, the (U)B3LYP and (U)CCSD(T) energies of the open-shell singlets were corrected, using the formula of Houk and Yamaguchi.[31] An energy in boldface denotes that an optimized geometry (B3LYP or CASSCF) is an energy minimum, while an energy in plain text denotes that an optimized geometry has imaginary frequencies, which are given in the footnotes. [b]B_1 imaginary frequency (or A'' imaginary frequency in planar C_s structure) corresponding to out-of-plane symmetric bending. [c]B_2 imaginary frequency corresponding to in-plane antisymmetric C−C bond stretch. [d](R)B3LYP wave function not stable. [e]CASPT2/6-31G(d) optimized geometry. [f]The large amount of spin contamination in the open-shell "singlet" UHF wave function ($<S^2> > 1.3$) resulted in the Houk−Yamaguchi formula giving much higher CCSD(T) energies for the pure singlet states than either the B3LYP or the CASPT2 calculations. [g]A singlet A nonplanar geometry is a minimum with an energy of 4.3 (4.2) kcal/mol. [h]A_2 imaginary frequency corresponding to out-of-plane antisymmetric bending. [i]A singlet A nonplanar geometry is a minimum with an energy of 0.0 (−0.2) kcal/mol. [j]Empty hybrid AO on the carbene carbon could not be forced to remain in the active space for the CASSCF calculation on the $\sigma^0\pi^6$ singlet state from which this CASPT2 energy was derived. [k]$^1A_2$ state. [l]In the CAS calculation, the $\sigma^2\pi^4$ configuration is not the dominant configuration at the B3LYP-optimized geometry of the $\sigma^2\pi^4$ singlet state, but is the dominant configuration in the second excited state (root 3). Unfortunately, the CASSCF calculation on this excited state did not converge. [m]A'' imaginary frequency corresponding to antisymmetric bending of the nonplanar C_s structure, to a C_1 structure.

to **7**, the $\sigma^0\pi^6$ singlet state is stabilized, relative to the $\sigma^1\pi^5$ triplet state, by only 1−2 kcal/mol. Nevertheless, both our CASPT2 and CCSD(T) calculations predict that in **7** the $^1A_1$-$\sigma^0\pi^6$ state is lower in energy than the $^3B_1$-$\sigma^1\pi^5$ state, although only by 2−3 kcal/mol.

Our computational prediction that **7** has a $^1A_1$-$\sigma^0\pi^6$ ground state should be relatively easy to test, because the diazo precursor to **7** has already been prepared by Sheppard and Webster and found to liberate **7** on pyrolysis.[43] However, these authors did not report the photolysis of the diazo precursor in matrix isolation, where IR and EPR spectra could have been obtained, in order to probe the spin of the ground state of **7**. We hope that further experiments on **7** will be performed in order to test our CASPT2 and CCSD(T) predictions that the ground state of this carbene is the $^1A_1$-$\sigma^0\pi^6$ state.

Table 1 shows that adding aldehyde groups to C3 and C4 of **4** and **5** is calculated to have a much larger effect on the relative energies of the $\sigma^0\pi^6$ singlet and $\sigma^1\pi^5$ triplet states than adding cyano groups to these two carbons. Addition of aldehyde substituents to C3 and C4 of **4**, to form **8**, is calculated to decrease the energy difference between the $\sigma^0\pi^6$ singlet and the $\sigma^1\pi^5$ triplet states by 9−11 kcal/mol. On addition of aldehyde substituents to C3 and C4 of **5** to form **9**, the decrease in the energy of the $\sigma^0\pi^6$ singlet, relative to the $\sigma^1\pi^5$ triplet is a little less, 7−8 kcal/mol. Nevertheless, the size of this decrease in the energy of the $\sigma^0\pi^6$ singlet, relative to the $\sigma^1\pi^5$ triplet, is sufficiently large to allow us to predict unequivocally that carbene **9** should have a $\sigma^0\pi^6$ singlet ground state, with the $\sigma^1\pi^5$ triplet state calculated to be higher in energy by between 5 kcal/mol (B3LYP) and 8 kcal/mol [CASPT2 and CCSD(T)].

Derivatives of Cyclohexa-2,5-dienylidene. A simple-minded way to understand why cyclopentadienylidenes, such as **4**−**9**, are promising candidates for having $\sigma^0\pi^6$ ground states is that electronic states of cyclopentadienylidenes, containing 6π

electrons, are aromatic. However, conjugated, six-membered rings that contain 6π electrons are, of course, also aromatic. Therefore, cyclohexa-2,5-dienylidenes derivatives, such as **10**−**19** in Table 3, which have a low-lying empty π orbital at C4, are also promising candidates for having $\sigma^0\pi^6$, singlet ground states.

This is particularly true, if the C−H bonds at C2 and C6 in **10**, **12**, **14**, **16**, and **18** are replaced by the nitrogen lone pairs in 2,6-diazacyclohexa-2,5-dienylidenes **11**, **13**, **15**, **17**, and **19**. As in 2,5-diazacyclopenta-2,4-dienylidenes **5**, **7**, and **9**, the nitrogen lone pairs in **11**, **13**, **15**, **17**, and **19** should favor excitation of a pair of electrons from the carbene σ MO into the conjugated π system, thus stabilizing the aromatic $\sigma^0\pi^6$ electronic configuration.

Shown in Table 3 are the results of our calculations on derivatives of cyclohexa-2,5-dienylidenes and 2,6-diazacyclohexa-2,5-dienylidenes. The π-electron acceptors at C4 range from the π^* MO of a carbonyl group in **10** and **11** to the empty 2p AO of a carbocation in **16** and **17**. We have also performed calculations on **18** and **19**, in which a neutral boron atom replaces the cationic carbon at C4 in **16** and **17**.

Table 3 shows that, as expected, an increasingly good electron acceptor orbital at C4 lowers the energy of both the $\sigma^1\pi^5$ singlet and triplet and the $\sigma^0\pi^6$ singlet, relative to the $\sigma^2\pi^4$ singlet. Interestingly, although the π^* MO of the carbonyl group at C4 of **10** is not computed to be a sufficiently good π acceptor to make the $^1A_1$-$\sigma^0\pi^6$ state lower in energy than the $^1A_1$-$\sigma^2\pi^4$ state, the C4 carbonyl group is calculated to drop the energy of the open-shell $^1B_1$-$\sigma^1\pi^5$ state below that of the $^1A_1$-$\sigma^2\pi^4$ state.[44] Therefore, cyclohexa-2,5-dienylidene-4-one (**10**) joins **4**, **6**, and **8** as rare examples of carbenes in which the lowest singlet state is predicted to have an open-shell electronic structure, with one unpaired electron in the σ orbital and an electron of opposite spin in a π orbital.

Protonation of the carbonyl group in **10**, to form **14**,[45] makes the π^* orbital of the carbonyl group a sufficiently powerful two-electron acceptor that $\sigma^0\pi^6$ singlet state is computed at the CASPT2 and CCSD(T) levels to be slightly lower than the $\sigma^1\pi^5$ triplet state in **14**. However, in carbocation **16**, the $^1A_1$-$\sigma^0\pi^6$ state is computed to be much lower in energy than the $^3B_1$-$\sigma^1\pi^5$ state. This result is consistent with previous calculations that have found phenyl cation (**16**) to have a $\sigma^0\pi^6$ singlet ground state.[46]

As would be expected, the absence of a sixth proton in the nucleus of the boron atom in **18** makes it a weaker π acceptor than the isoelectronic, positively charged, carbon at C4 of **16**. The results in Table 3 indicate that the π electron-accepting ability of the empty 2p AO on the boron atom in **18** is roughly comparable to that of the π^* orbital of the protonated imino group at C4 in **12**[45] but considerably higher than that of the π^* orbital of the unprotonated carbonyl group at C4 in **10**.

Table 3 shows that the two nitrogen lone pairs in 2,6-diazacyclohexadienylidenes **11**, **13**, **15**, **17**, and **19** destabilize the $\sigma^1\pi^5$ triplet, relative to the $\sigma^0\pi^6$ singlet, by 32−42 kcal/mol and the $\sigma^2\pi^4$ singlet, relative to the $\sigma^1\pi^5$ triplet, by 13−23 kcal/mol. The reason for this difference in destabilization energies is the same as that in 2,5-diazacyclopentadienylidenes **5**, **7**, and **9**. In the $^1A_1$-$\sigma^0\pi^6$ state, the empty σ MO is a much better acceptor for the nitrogen lone pairs than the singly occupied σ MO is in the $^3B_1$-$\sigma^1\pi^5$ state of **5**. Consequently, going from the $^1A_1$-$\sigma^0\pi^6$ state to the $^3B_1$-$\sigma^1\pi^5$ state by transferring one electron from the 2b_1 π MO into the σ MO is more destabilizing than

going from the $^3B_1$-$\sigma^1\pi^5$ state to the $^1A_1$-$\sigma^2\pi^4$ state by transferring a second π electron into the σ MO.

The lone pairs on nitrogen are calculated to have the largest destabilizing effects on the $\sigma^2\pi^4$ singlet and the $\sigma^1\pi^5$ triplet states of **17** and **19** where, respectively, Y = CH$^+$ and BH are the electron acceptors. This result is not due to differences between the amount of destabilization of the σ MO by the nitrogen lone pairs in **11**, **13**, and **15** on one hand and **17** and **19** on the other. Instead, the larger effect of the nitrogen lone pairs in **17** and **19** is due to the larger effect in these two carbenes of the increased electronegativity of nitrogen, compared to carbon, on lowering the energy of the π MO into which the electrons are placed, when they are removed from the σ MO.[47]

The results in Table 3 show that the electron-accepting ability of the π^* MO of an unprotonated carbonyl group is insufficient to make the $\sigma^0\pi^6$ singlet the ground state of **11**, despite the presence of the lone pairs on the two nitrogens that are adjacent to the carbene carbon. However, all of the other 2,6-diazacarbenes in Table 3 are predicted to have $\sigma^0\pi^6$ singlet ground states, including **19**, in which the electron acceptor is the empty 2p AO on the boron atom.

Unlike, **13**, **15**, and **17**, which are ions, **19** is a neutral compound. With a bulky substituent attached to boron, it might be possible to isolate **19** as well as **18**, which lacks the nitrogen atoms that are adjacent to the carbene center in **19**.[48] Generation and isolation of both carbenes would allow experimental tests of our predictions that **18** has a $\sigma^1\pi^5$ triplet ground state, but that **19** has a $\sigma^0\pi^6$ singlet ground state.

■ CONCLUSIONS

In this paper we have reported the results of a computational investigation of which combinations of in-plane, lone pair donor, and π acceptor substituents can result in carbenes in which the ground state is a singlet, with the σ orbital on the carbene carbon empty and the 2p−π orbital doubly occupied ($\sigma^0\pi^2$). We have found that the in-plane lone pairs on two doubly bonded nitrogens that are both α to the carbene center are effective at destabilizing the carbene σ orbital.

Incorporation of two C=N groups and the carbene carbon into a five-membered ring (as in **5**, **7**, and **9**) gives an aromatic π system, containing six π electrons, provided that the electronic configuration of the carbene center is ($\sigma^0\pi^2$). Our CCSD(T) and CASPT2 calculations do, in fact, predict a $^1A_1$-$\sigma^0\pi^6$ ground state for each of these three carbenes. The experiments of Maier and Endres indicate that **5** does, in fact, have a singlet ground state, which forms a complex with Xe.[34d]

The π electron-accepting CN and CHO substituents in, respectively, **7** and **9** are predicted to further lower the energy of the $^1A_1$-$\sigma^0\pi^6$ ground state, relative to the $^3B_1$-$\sigma^1\pi^5$ state. Sheppard and Webster have reported the generation of **7**,[43] but they did not investigate whether this carbene has a singlet or triplet ground state. Spectroscopic studies of this carbene in matrix isolation should allow a test of our computational prediction that **7** has a $\sigma^0\pi^6$ singlet ground state.[49]

Expanding the five-membered ring in **5**, by joining the carbons of the C=N groups to a common atom that has a low-lying, empty, π MO (as in **11**, **13**, **15**, **17**, and **19**) also gives an aromatic 6π system, provided that the electronic configuration of the carbene center is ($\sigma^0\pi^2$). Our calculations predict that, of these five derivatives of 2,6-diazacyclohexadienylidene, **13**, **15**, **17**, and **19** should each have a $^1A_1$-$\sigma^0\pi^6$ ground state.

We hope that these predictions of a $^1A_1$-$\sigma^0\pi^6$ ground state for seven of the carbenes discussed in this paper will serve to stimulate experiments that will establish the ground state for some or all of these carbenes.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Geometries and absolute energies of other conformers of **8** and **9**, the electronic states of **4−19** and the carbene Xe complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Xe has also been found experimentally to form a complex with difluorovinylidene (F_2C_2) and with C_2. For the F_2C_2−Xe complex, see: (a) Kotting, C.; Sander, W.; Breidung, J.; Thiel, W.; Senzlober; Burger, H. *J. Am. Chem. Soc.* **1998**, *120*, 219. (b) Sander, W.; Kotting, C. *Chem.—Eur. J.* **1999**, *5*, 24. For the C_2−Xe complex, see: (c) Maier, G.; Lautz, C. *Eur, J. Org. Chem.* **1998**, 769. (d) Frankowski, M.; Smith-Gicklhorn, A. M.; Bondybey, V. E. *Can. J. Chem.* **2004**, *82*, 837.

(37) Maier and Endres did not propose this explanation, perhaps because they do not seem to have realized that the lowest singlet state of **5** is $^1A_1$-$\sigma^0\pi^6$, in which the σ orbital at the carbene center is left empty. Instead, they considered **5** to be a highly strained, planar carbodiimide.[34d] We explored a C_2, twisted, carbodiimide structure for **5** and found that a C_2 geometry is not a stationary point on the energy surface for the lowest singlet state. Attempted optimization of a C_2 structure leads the C_{2v}, $\sigma^0\pi^6$, singlet minimum.

(38) The donor−acceptor-type bond in rare gas complexes has been discussed, see: Zou, W.; Nori-Shargh, D.; Boggs, J. E. *J. Phys. Chem. A* **2013**, *117*, 207.

(39) It should be noted that the B3LYP/LANL2DZ calculations by Maier and Andres found a shorter Xe−C bond length (2.61 Å) and a stronger Xe complexation energy (3.3 kcal/mol, which we calculate is reduced to 2.6 kcal/mol, when counterpoise corrections for basis set superposition errors are included) than our CCSD(T)/CBS//CCSD(T)/aug-cc-pVTZ and ωB97XD/def2-QZVP calculations did.

(40) Decreases in force constants for C−H bending with increased 2s character in C−H bonds is responsible for the secondary, kinetic isotope effects that are observed in many organic reactions in which the hybridization of C−H bonds changes. See, for example: (a) Shiner, V. J., Jr.; Rapp, M. W.; Pinnick, H. R., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 232. (b) Do Amaral, L.; Bull, H. G.; Cordes, E. H. *J. Am. Chem. Soc.* **1972**, *94*, 7579. (c) Stevenson, C. D.; Brown, E.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 8864−8867.

(41) We are currently investigating the differences between the reactivities of $\sigma^2\pi^0$ and $\sigma^0\pi^2$ carbenes, and the results of these calculations will be reported in due course.

(42) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(43) Sheppard, W. A.; Webster, O. W. *J. Am. Chem. Soc.* **1973**, *95*, 2695.

(44) Previous calculations of the electronic states of **10** have also found the open-shell, $^1B_1$-$\sigma^1\pi^5$ state to be the singlet state of lowest energy. (a) Sole, A.; Olivella, S.; Bofill, J. M.; Anglada, J. M. *J. Phys. Chem.* **1995**, *99*, 5934. (b) Sander, W.; Hubert, R.; Kraka, E.; Grafenstein, J.; Cremer, D. *Chem.—Eur. J.* **2000**, *6*, 4567. (c) Perfluorination of **10** stabilizes the σ MO and destabilizes the π MO that is singly occupied in the $^1B_1$ state, so that the lowest singlet state of **10**-F_4 is calculated to be a nonplanar closed-shell singlet state, rather than the open-shell, $^1B_1$-$\sigma^1\pi^5$ state that is predicted to be the lowest singlet state in **10**.[44b]

(45) In experiments, alkyl groups, rather than protons could be used, in **12**−**15**.

(46) Phenyl cation calculations: (a) Jaffe, H.; Koser, G. F. *J. Org. Chem.* **1975**, *40*, 3082. (b) Dill, J. D.; Schleyer, P. v. R.; Binkley, J. S.; Seeger, R.; Pople, J. A.; Haselbach, E. *J. Am. Soc. Chem.* **1976**, *98*, 5428. (c) Bernardi, F.; Grandinetti, F.; Guarino, A.; Robb, M. A. *Chem. Phys. Lett.* **1988**, *153*, 309. (d) Hrusak, J.; Schroder, D.; Iwata, S. *J. Chem. Phys.* **1997**, *106*, 7541. (e) Nicolaides, A.; Smith, D. M.; Jensen, F.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 8083.

(47) In **11**, **13**, and **15** the π MO that becomes occupied in both the $^3B_1$-$\sigma^1\pi^5$ and $^1A_1$-$\sigma^0\pi^6$ states contains a contribution from a π-antibonding orbital between C4 and the exocyclic heteroatom that is attached to it. In contrast, in **17** and **19** the π MO that becomes occupied contains a contribution from a nonbonding AO that is localized at atom 4 of the ring. Consequently, the π MO that becomes occupied is more localized to the six-membered ring in **17** and **19** than in **11**, **13**, and **15**. Hence, the nitrogen AOs at ring atoms 2 and 5 make a larger contribution to this π MO in **17** and **19** than in **11**, **13**, and **15**.

(48) A mesityl-protected, dibenzo derivative of **18**, has, in fact, been generated, and as predicted for **18**, this mesitylboraanthrylidene has

13963

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been found to have a triplet ground state. Lapin, S. C.; Brauer, B.-E.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 2092.

(49) For example, by comparing the observed IR spectrum of the matrix-isolated carbene with the IR spectra computed for the two lowest singlet states and for the triplet, it should be easy to tell which state is responsible for the observed IR spectrum.[34d]