Singlet-Triplet Gaps in Substituted Carbenes CXY (X, Y = H, F, Cl, Br, I, SiH_3)

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Abstract: Trends in the singlet-triplet state-splittings of substituted carbenes are found to be reproduced accurately with a very simple level of ab initio theory. The minimum balanced description, GVB(1/2), with a simple basis set yields singlet-triplet gaps that correlate linearly with available accurate values. This linear relationship is exploited to predict the state-splitting for the remaining members of the title series of carbenes. The magnitudes of the singlet-triplet splittings can be rationalized in terms of the charge on the carbenic carbon atom as well as π-donation from the substituents. The correlation with charge, in conjunction with electronegativity equalization, permits singlet-triplet gaps to be predicted for arbitrary simple carbenes using only a hand calculator. Since both charge and π-donation are important in determining the energy gaps, we conclude that σ-donation and π-backbonding act synergistically.

Introduction

The reactivity of substituted carbenes CXY is determined by their spin multiplicity.[1] Thus triplet carbenes react by two-step radical processes, whereas singlets can undergo single-step bond insertions. The relative stabilities of the lowest singlet and triplet states are in turn a sensitive function of the electronegativity of the substituents. For example, referring to eq 1, ΔE_{st} = 57 kcal/mol for CF_2, putting the triplet state far above the singlet

$$\Delta E_{st} \equiv E(\text{triplet}) - E(\text{singlet}) \quad (1)$$

ground state,[2] while for CH_2 ΔE_{st} = -9.2 kcal/mol, making the triplet the ground state.[3] Consequently, substantial efforts have been made to determine the singlet-triplet energy gaps in carbenes. On the theoretical front, increased accuracy from ab initio work has generally been obtained by using large basis sets and extensive configuration-interaction (CI).[4,5] In particular, reliable state-splittings have been calculated by the dissociation-consistent CI (DCCI) method.[6] When combined with available experimental results,[2,3,7] the DCCI calculations yield values for the five carbenes CH_2, CHF, CHCl, CF_2, and CCl_2 that are reliable to ~1 kcal/mol. In the present work, we find that a much simpler level of theory yields state-splittings that correlate linearly with the accurate values. This linear relationship is used to predict accurate values for other carbenes CXY (X, Y = H, F, Cl, Br, I, SiH_3).

The practice of scaling the results of ab initio calculations is well-established. Scaling of vibrational frequencies is probably the best-known example.[8,9] For the CH_2 molecule alone, numerous workers have calibrated their energy gap results using known values for CH, the carbon atom, or both.[10-14] Others have used the experimental gap in CH_2 to adjust state-splittings calculated for substituted carbenes.[15-17] Still others emphasize trends rather than absolute values.[18-20] We have chosen a simple combination of these approaches.

Calculational Details

A very large CI is needed to compensate unbalanced zero-order descriptions of singlet and triplet carbenes.[11,21] For a balanced description, the two nonbonding electrons must be permitted to occupy two distinct orbitals.[22] As indicated in Scheme I, this description of the singlet corresponds to the generalized valence bond (GVB) wave function with one correlated pair,[23] which is equivalent to a two-configuration CI. For the triplet this leads to the ordinary Hartree-Fock (single configuration) wave function.

It is well-known that basis d functions on the carbenic carbon are required to obtain accurate singlet-triplet energy separations.[22] Indeed, Bauschlicher et al. showed that very large basis sets (through *g* functions on carbon and *d* functions on hydrogen) and a large CI (over 700 000 configurations) are required to calculate $\Delta E_{st}(CH_2)$ to within 0.1 kcal/mol of the experimental value.[4] Unfortunately, such thorough calculations are impractical for most substituted carbenes. We have developed an alternative approach where the focus is on relative accuracy.

Scheme I

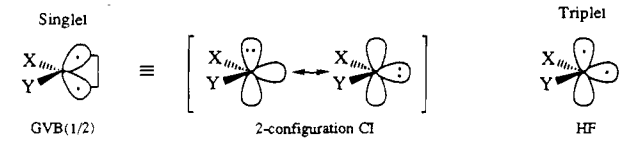

Table I. Optimized Bond Angles and Predicted Singlet-Triplet Gaps in Carbenes CXY[a]

X	Y	ΔE_{st}, kcal/mol			θ(X-C-Y), deg	
		uncorr	corr[b]	ref	singlet	triplet
F	F	33.56	56.43	56.7[c]	104.0	118.0
F	Cl	17.10	37.09		105.6	121.7
F	Br	12.67	31.89		106.3	122.8
F	I	7.20	25.46		107.2	124.1
Cl	Cl	2.59	20.04	20.5[d]	109.0	126.1
Cl	Br	-0.75	16.12		110.2	127.6
H	F	-1.00	15.83	14.7[e]	102.2	120.6
Br	Br	-3.85	12.48		111.5	129.2
Cl	I	-5.02	11.10		111.5	129.2
Br	I	-7.83	7.80		113.0	131.2
H	Cl	-9.03	6.39	6.4[e]	101.4	123.7
H	Br	-11.04	4.03		101.8	125.4
I	I	-11.25	3.78		114.6	133.4
H	I	-13.81	0.77		102.6	127.7
F	SiH_3	-15.58	-1.31		105.5	126.0
Cl	SiH_3	-21.66	-8.45		108.1	130.8
H	H	-22.73	-9.71	-9.215[f]	104.8	130.2
Br	SiH_3	-23.49	-10.60		110.4	133.8
I	SiH_3	-25.45	-12.90		113.1	137.3
H	SiH_3	-30.71	-19.08		110.4	141.0
SiH_3	SiH_3	-31.15	-19.60		180.0	180.0

[a] The uncorrected values are calculated directly from the simple wave functions. Corrected values are based upon eq 2, which is derived using the five reference cases listed here. [b] Estimated accurate to ±2 kcal/mol; see text. [c] Reference 2. [d] Reference 6b. [e] References 6 and 7. [f] Reference 3.

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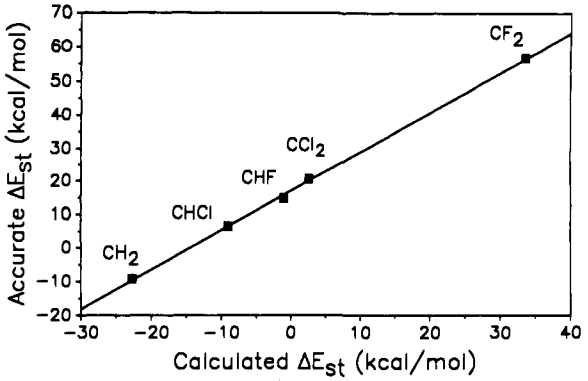

Figure 1. Singlet–triplet gaps calculated by our simple method plotted against all five available accurate values from refs 2, 3, 6, and 7. The least-squares line (eq 2) has slope 1.175 ± 0.036, intercept 17.02 ± 0.70 kcal/mol, and correlation coefficient 0.9996. Energy gaps predicted using this linear relation are estimated to be accurate to ±2 kcal/mol.

Although the addition of *d* functions tends to increase ΔE_{sl} substantially, it has little effect on *relative* ΔE_{sl} values among carbenes.[24] We have therefore omitted polarization functions in our calculations. In addition we use effective potentials[25] to replace the core electrons of Cl, Br, and I, which greatly reduces the cost with little effect (0.37 kcal/mol for CCl_2[26]) on the calculated ΔE_{sl} value. Basis sets for fluorine[27] and carbon[28] were contracted to (3s2p) and (5s3p), respectively, and the (4s/2s) basis for hydrogen[29] was scaled by 1.2. All geometries were fully optimized at the restricted Hartree–Fock level (triplets) or the GVB(1/2) level (singlets). The resulting bond angles θ(X–C–Y) agree well (1.5° root mean square) with those from ref 6 and are listed in Table I. Because of the lack of polarization functions, the bond lengths are consistently too large and are not listed.

Results

Figure 1 illustrates the linear relation between the five accepted carbene state-splittings and those from the present work. A least-squares fit leads to eq 2 (correlation coefficient of 0.9996). Error estimates are twice the estimated standard deviations.[30] We

$$\Delta E_{sl}^{exp} = A + B\Delta E_{sl}^{calc} \quad (2)$$

$$A = 17.02 \pm 0.70 \text{ kcal/mol}, B = 1.175 \pm 0.036$$

Table II. Orbital Ionization Energies in Carbon[a]

species	IE(2s) – IE(2p), eV
C^-	4.18
C	5.34
C^+	6.50

[a] Atomic energy levels from ref 43.

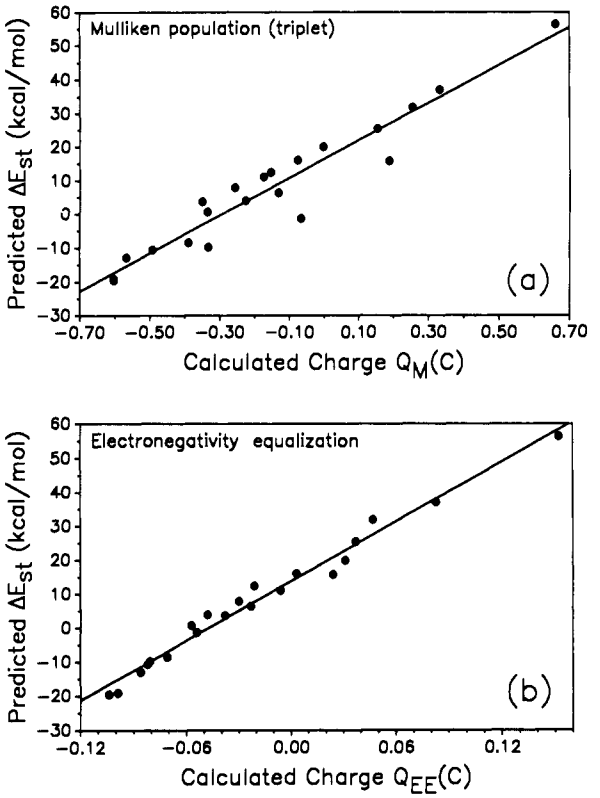

Figure 2. Predicted energy gaps plotted against the charge on the carbenic carbon. (a) Charges from Mulliken population analysis of the triplet wave functions. The least-squares line (eq 3) has slope 55.8, intercept 16.4, and correlation coefficient 0.96. (b) Charges calculated using the sp^2 parameter set and electronegativity equalization procedure of ref 45. The least-squares line (eq 4) has slope 293 ± 20, intercept 13.9 ± 1.4, and correlation coefficient 0.990. Energy gaps predicted using this line are estimated to be accurate to ±4 kcal/mol.

use this relation to correct our calculated state-splittings. The resulting values, which we estimate to be accurate to ±2 kcal/mol, are listed in Table I in order of decreasing energy gap.

The predicted values are consistent with available experimental and theoretical results. For CFCl, a thermochemical estimate of ΔE_{sl} = 39.4 ± 4 kcal/mol[31] is in agreement with 37.1 from Table I. For CBr_2 we predict a singlet ground state with ΔE_{sl} = 12.5 kcal/mol, consistent with its observed reactivity.[32] For CHBr, our value ΔE_{sl} = 4.0 kcal/mol is in agreement with the experimental[7] upper bound of 9 ± 2 kcal/mol and with the most recent theoretical value of 4.1 kcal/mol.[33] For CI_2 we predict ΔE_{sl} = 3.8 kcal/mol, which is consistent with the observed stereospecific addition of CI_2 to butenes.[34] Pressure and quenching studies have determined a singlet ground state for CHI as well,[35] consistent with our predicted ΔE_{sl} = 0.8 kcal/mol. For $CH(SiH_3)$, our predicted value of −19.1 is consistent with recent ab initio values of −20.3,[36] −25.8,[37] and −18.4[38] kcal/mol.

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Table III. Charges on Carbon and Degree of π-Donation in CXY

X	Y	Mulliken charge[a]	electronegativity charge[b]	π-donation,[c] %
H	H	−0.332	−0.081	0.0
H	F	0.188	0.024	12.8
H	Cl	−0.131	−0.023	9.2
H	Br	−0.226	−0.048	8.5
H	I	−0.336	−0.057	7.5
H	SiH_3	−0.603	−0.099	1.4
F	F	0.661	0.152	22.0
F	Cl	0.332	0.083	18.8
F	Br	0.255	0.047	17.2
F	I	0.155	0.037	16.5
F	SiH_3	−0.065	−0.054	10.7
Cl	Cl	−0.001	0.031	15.6
Cl	Br	−0.076	0.003	14.7
Cl	I	−0.175	−0.006	13.5
Cl	SiH_3	−0.389	−0.071	9.9
Br	Br	−0.154	−0.021	13.8
Br	I	−0.257	−0.030	12.6
Br	SiH_3	−0.492	−0.082	9.3
I	I	−0.350	−0.038	11.4
I	SiH_3	−0.568	−0.086	8.2
SiH_3	SiH_3	−0.603	−0.104	3.3

[a] Charge on carbenic carbon calculated from Mulliken populations in the triplet state. [b] Charge calculated using the electronegativity equalization procedure from ref 45. [c] Percentage of nominal carbon p orbital, in the GVB(1/2) singlet state, from substituent-centered basis functions.

Discussion

As often observed, ΔE_{st} generally increases as the electronegativity of the substituents is increased. There appear to be two alternative explanations in the literature.[39] The most popular seems to be[4,5] that π-donor substituents favor the singlet state by bonding with the p-orbital on the carbenic carbon, which is vacant in the singlet state and singly-occupied in the triplet.[19,24,40,41] Some authors with this view maintain that inductive effects are negligible, or even that electronegativity is irrelevant.

Another popular explanation for the trend is that electron-withdrawing substituents inductively stabilize the σ nonbonding orbital by increasing its s-character.[18] This change in hybridization leads to a larger energy gap between the σ^2p^0 (singlet) and σ^1p^1 (triplet) states. A variation on this interpretation is that electronegative groups withdraw charge from the carbenic carbon, leading to an increased positive charge.[42] Increased positive charge on carbon stabilizes the 2s orbital relative to the 2p, favoring the singlet state relative to the triplet. This effect is evident even in the free atom, for which each unit of charge increases the s–p energy gap by 26.8 kcal/mol.[43]

Another related view[44] is to note that it is easier to ionize carbon from a 2p orbital than from the 2s orbital (Table II). Singlet carbenes have smaller bond angles than triplets, and therefore have more carbon p-character in the bonds to the substituents. The greater p-character leads to stronger ionic bonding and stabilization of the singlet. This stabilization is naturally more important for more electronegative substituents, resulting in an increase in ΔE_{st} with substituent electronegativity.

To test the validity of the simple charge model, we examined the relationship between the predicted ΔE_{st} and the charge on the carbenic carbon. Using Mulliken populations to calculate charges leads to the results presented in Table III and Figure 2a. The

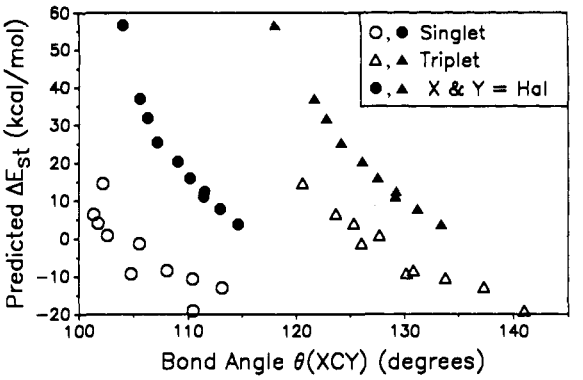

Figure 3. Predicted energy gaps (eq 2) plotted against calculated bond angles for both singlet and triplet states. Dihalogen carbenes are indicated by solid symbols. $C(SiH_3)_2$ is omitted (bond angle = 180°).

energy gap does indeed depend linearly upon the charge on carbon (eq 3). In order for the linear relation to be most useful, it is

$$\Delta E_{st} = A_M + B_M Q_M(C) \quad (3)$$

$$A_M = 16.4 \text{ kcal/mol}, \; B_M = 55.8$$

(correlation coefficient= 0.96)

necessary to predict the charge *before* doing the ab initio calculations. With this in mind, we investigated electronegativity equalization[45] as a simple way to determine the partial charge on the central carbon. In this method the electronegativity of each atom is assumed to depend linearly upon its charge. Charge is further assumed to be distributed thoughout the molecule in such a way as to result in equal electronegativities for all atoms. The resulting charges calculated for the carbenic carbon are listed in Table III and plotted in Figure 2b. The magnitudes of charges calculated in this way are only about 20% of the charges from Mulliken populations, but the trends with substituents are similar. Again there is a linear relation (eq 4), and we estimate that energy gaps predicted using this relation are accurate to within 4

$$\Delta E_{st} = A + BQ_{EE}(C) \quad (4)$$

$$A = 13.9 \pm 1.4 \text{ kcal/mol}, \qquad B = 293 \pm 20$$

(correlation coefficient = 0.990)

kcal/mol. The use of electronegativity equalization is appealing because it allows a good estimate to be made easily for the singlet–triplet gap in any simple carbene. For large carbenes, partial equalization of electronegativity may be preferable to the total equalization procedure used here.[46]

To illustrate the use of eq 4, consider hydroxycarbene, CH(OH). The parameters from ref 45 are used to obtain eq 5, which has the solution $Q_{EE}(H) = 0.144$, $Q_{EE}(O) = -0.304$, and $Q_{EE}(C) = 0.017$. Equation 4 then leads to $\Delta E_{st} = 19$ kcal/mol, which is in excellent agreement with the most recent literature value of 19.7 kcal/mol.[47]

$$\begin{aligned} 7.17 + 12.85Q_{EE}(H) &= 8.79 + 13.67Q_{EE}(C) \\ 7.17 + 12.85Q_{EE}(H) &= 14.39 + 17.65Q_{EE}(O) \\ 2Q_{EE}(H) + Q_{EE}(C) + Q_{EE}(O) &= 0 \end{aligned} \quad (5)$$

The correlation of Figure 2 supports the view that electron-withdrawing substituents increase ΔE_{st}. The strength of the dependence upon charge, however, is too large to be explained

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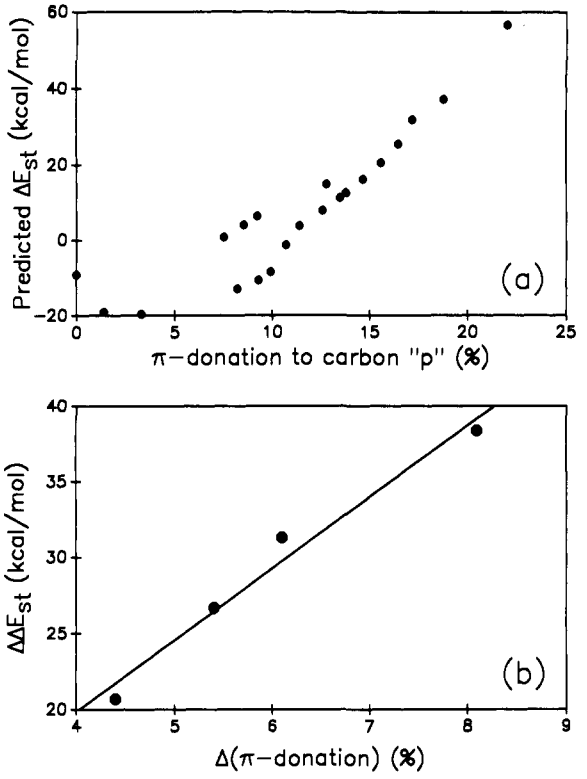

Figure 4. (a) Predicted energy gaps plotted against the amount of π-donation from the substituents to the central carbon p-orbital. (b) Differences in ΔE_{sl} and percentage of π-donation (in the singlet state) between di- and monohalogenated carbenes with the same central angle. The least-squares line has slope 4.7, intercept 0.97, and correlation coefficient 0.988.

simply by charge on the carbon atom. The GVB calculations indicate that ΔE_{sl} for carbenes increases by 56 kcal/mol per unit of charge on the carbon (Figure 2a), while the s–p gap on a bare carbon atom increases by only 26.8 kcal/mol per unit of charge (Table II). This amplification of the influence of charge may be due to a synergistic effect such as π-donation. Additional evidence for π-donation comes from the dependence of ΔE_{sl} upon the bond angle θ(X–C–Y). Opening the bond angle changes the hybridization of the central carbon. The resulting increase in p-character in the nonbonding σ orbital in turn leads to a generally lower ΔE_{sl}, as shown in Figure 3. When both substituents are halogens, however, ΔE_{sl} is substantially larger for any given angle. This may reflect the substantially greater π-bonding expected for the dihalogen carbenes. We can estimate the degree of π-bonding from the calculated wave functions. This is taken as the fraction of the nominal carbon p-orbital in the GVB(1/2) singlet that derives from substituent-centered basis functions. Although the relationship is not monotonic, a strong correlation between ΔE_{sl} and the amount of π-donation is apparent (Figure 4a). One may also define the "excess ΔE_{sl}" for a given carbon hybridization as the difference in ΔE_{sl} between dihalogenated and monohalogenated carbenes with the same central angle in the singlet. The excess ΔE_{sl} correlates well with the difference in π-donation between the corresponding carbenes (Figure 4b).

The results discussed above support both the electron-withdrawal and π-donation interpretations, suggesting that both are correct. Further indication that both are important comes from experimental electron affinities (EAs).[7] For X = Cl, Br, and I, and EAs increase in the series $CH_2 < CHX < CX_2$, indicating that electron-withdrawal is the major effect. For X = F, however, the EAs *decrease* sharply in the series, indicating that π-donation dominates. The switch for X = F is thought to be due to the shortness of the C-F bond, which crowds the fluorine lone pair into the carbon's π-orbital.[7]

The "alternative" explanations of electron-withdrawal and π-donation are readily compatible. Electronegative substituents withdraw electron density from the carbenic carbon, making it more positively charged. The increased charge, in turn, makes the carbon a better π-acceptor. As a result, π-donation from substituents is enhanced. Such "π-backbonding" is commonplace in transition metal chemistry, although the ligands are usually the σ-donors and π-acceptors in that context.

There is experimental support for a synergistic bonding model. Nuclear quadrupole coupling constants in CCl_2 indicate σ-transfer of 0.26 electron from C to Cl and π-transfer of 0.32 electron from Cl back to C.[48] In the series XCl, XCl_2, and H_2XCl_2 (X = C, Si), the amount of σ-transfer depends upon the electronegativity difference between X and Cl while the π-transfer depends upon the acceptor ability of X.[48] These observations are exactly what is expected from the bonding description presented above. More indirect evidence comes from studies of the reactivity of substituted carbenes. It is well-established that π-donor and electron-withdrawing substituents both increase selectivity in the reaction with olefins.[49] Both types of substituent are expected to yield the same general reactivity patterns if σ-withdrawal and π-donation are strongly interdependent, as in the synergistic bonding model described here.

Conclusions

An empirical correction to a very simple level of ab initio theory has been used to predict singlet–triplet energy gaps (ΔE_{sl}) for a series of substituted carbenes. Energy gaps are found to correlate linearly with the charge on the carbenic carbon. Electronegativity equalization procedures permit the charge on carbon, and hence the state-splitting, to be calculated easily for any simple carbene. Although correlation with charge supports the electron-withdrawal explanation for trends in ΔE_{sl} values, the strength of the charge-dependence suggests an additional mechanism. This is shown to be π-donation from the substituents to the empty carbon p-orbital in the singlet state. A synergistic model for bonding in carbenes, in which σ-donation and π-backbonding cooperate, is therefore consistent with experimental and theoretical observations.

Acknowledgment. We are grateful to the National Science Foundation for support under Grants CHE-83-18041 (W.A.G.) and CHE-87-11567 (J.L.B.). K.K.I. appreciates fellowship support from the Department of Education and thanks J. F. Liebman for helpful comments.

Registry No. Difluoromethylene, 2154-59-8; chlorofluoromethylene, 1691-88-9; bromofluoromethylene, 4539-11-1; fluoroiodomethylene, 65352-89-8; dichloromethylene, 1605-72-7; bromochloromethylene, 13590-47-1; fluoromethylene, 13453-52-6; dibromomethylene, 4371-77-1; chloroiodomethylene, 137059-13-3; bromoiodomethylene, 137059-14-4; chloromethylene, 2108-20-5; bromomethylene, 17141-28-5; diiodomethylene, 4371-79-3; iodomethylene, 36249-46-4; fluorosilylmethylene, 81875-09-4; chlorosilylmethylene, 137059-15-5; methylene, 2465-56-7; bromosilylmethylene, 137059-16-6; iodosilylmethylene, 137059-17-7; silylmethylene, 51067-84-6; disilylmethylene, 81639-37-4.

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