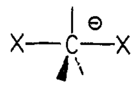
Stabilization of D_{3h} Pentacoordinate Carbonium Ions. Linear Three-Center-Two-Electron Bonds. Implications for Aliphatic Electrophilic Substitution Reactions

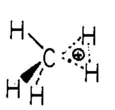
Eluvathingal D. Jemmis,[1] Jayaraman Chandrasekhar, and Paul v. R. Schleyer*

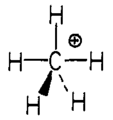
Contribution from the Institut für Organische Chemie der Universität Erlangen-Nürnberg, 8520 Erlangen, Federal Republic of Germany. *Received August 3, 1978*

Abstract: The structures of pentacoordinate carbon species, $CH_3M_2^+$ (M = Li, BeH, Na, and MgH), were probed by ab initio molecular orbital calculations. Two general types of structures were considered, those with C_s symmetry which model electrophilic substitutions occurring with retention of configuration, and those with D_{3h} symmetry modeling processes proceeding with inversion. All ions studied were indicated to be very stable toward dissociation; $CH_3Li_2^+$ is known experimentally in the gas phase. In contrast to CH_5^+, which prefers C_s structures to D_{3h}, some $CH_3M_2^+$ species favored D_{3h} geometries. At the RHF/6-31G* level the C_s–D_{3h} energy differences follow: $CH_3Li_2^+$, 2.5; $CH_3(BeH)_2^+$, 5.7 kcal/mol. Electron correlation does not appear to change these differences appreciably. These results indicate that systems with three-center-two-electron bonds may favor linear over cyclic arrangements, depending on the atoms involved. Likewise, electrophilic aliphatic substitutions of this type can be expected to proceed either with inversion or with retention depending on the conditions; there may be no strong inherent preference for either stereochemical pathway.

Thermodynamically stable trigonal bipyramidal (D_{3h}) pentacoordinate structures are unknown in carbon chemistry.[2] Nevertheless, such geometrical arrangements are familiar to organic chemists; one only has to be reminded of the S_N2 transition states (**1**) which account for the inversion of configuration characterizing bimolecular nucleophilic substitutions.[2,3] At least in a formal sense, the carbon atom in **1** can be assigned ten valence electrons; what is to be expected of pentacoordinate carbon with two fewer electrons? The simplest example is CH_5^+. Structures with C_s symmetry, e.g., **2**, involving cyclic three-center-two-electron bonds are favored, albeit not overwhelmingly (**3** is calculated to be 11 kcal/mol less stable).[4] This preference, and that of H_3^+ for a triangular arrangement,[4c] has contributed to the widespread belief that $CH_3X_2^-$ and $CH_3M_2^+$ structures involving ten and eight valence electrons on carbon, respectively, should be basically different. Likewise, textbooks, following earlier experimental leads,[5] often proclaim that S_E2 reactions proceed with retention of configuration. More recently, many cases of inversion during S_E2 reactions have been reported,[6] and frontier orbital treatments have shown that both inversion and retention are allowed mechanistically.[7] It would appear that the geometrical preferences of eight valence electron pentacoordinate carbon species are not great, but may depend on the reaction conditions or on the substituents. As a continuation of our exploration of unusual geometries of carbon,[8] we have considered the possibility of minimum energy D_{3h} pentacoordinate arrangements. To this end, we have examined the structures of $CH_3M_2^+$ species, where M is an electropositive substituent. To facilitate ab initio calculations, M was chosen to be Li, BeH, Na, and MgH. These results are also pertinent to the nature of three-center-two-electron bonding and to the stereochemistry of S_E2 reactions, where one metallic cation or electrophilic species displaces another.

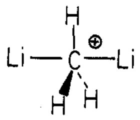

1

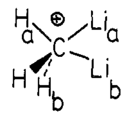

2

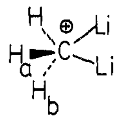

3

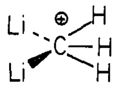
Computational Methods and Structures Considered

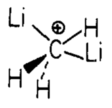
Standard single-determinant SCF-MO theory in the spin-restricted form (RHF) was used throughout.[9] Using the GAUSSIAN 70 series of programs,[10,11] all structures were fully optimized (i.e., changes in total energy less than 10^{-5} au, bond lengths less than 10^{-3} Å, and bond angles less than 0.1° after a further cycle of optimization) with the STO-3G minimal basis set.[12] In the case of Li and BeH derivatives found to be minima within the assumed symmetry, geometry optimizations were also carried out using the split-valence 4-31G basis set[13a,b] (5-21G on Li and Be).[13c] By analogy with the previous calculations on CH_5^+[4a,b] structures **4** (D_{3h}), **5** (C_s), **6** (C_s), **7** (C_{2v}), and **8** (C_s) were considered. When optimized within the given symmetry constraints, **7** gave **4** and **8** gave **9**. The latter represents **4** with the methyl slightly distorted along the C_3 axis to give overall C_{3v} symmetry. At STO-3G **9** is indicated to be only 0.02 kcal/mol more stable than **4**, and may be a computational artifact. $CH_3(BeH)_2^+$, unlike $CH_3Li_2^+$, showed no tendency to distort from D_{3h} toward C_{3v} symmetry. Since **4** is preferred at 4-31G, we did not consider **9** further. Structures **4** and **5** also were optimized at STO-3G by a program option omitting all p orbitals on Li in order to test the effect of these p orbitals on relative energies and geometries. The analogous Be compounds **10**, **11**, and **12** were calculated using STO-3G and 4-31G/5-21G basis sets while $CH_3Na_2^+$ (**13**, **14**) and $CH_3(MgH)_2^+$ (**15**, **16**) were considered only at the STO-3G

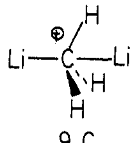

4 D_{3h}

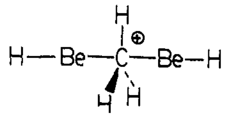

5 C_s

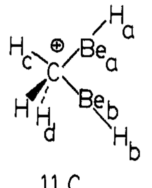

6 C_s

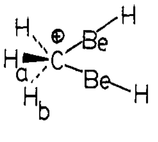

7 C_{2v}


8 C_s


9 C_{3v}


10 D_{3h}


11 C_s


12 C_s

0002-7863/79/1501-0527\$01.00/C

Table I. Calculated Geometries (Distances in Ångstroms and Angles in Degrees)

molecule	point group	parameter	optimization level	
			STO-3G	4-31G/5-21G
$CH_3Li_2^+$ (**4**)	D_{3h}	$r(\mathrm{C-Li})$	2.015	2.096
		$r(\mathrm{C-H})$	1.085	1.082
(without p orbitals on Li)		$r(\mathrm{C-Li})$	2.067	
		$r(\mathrm{C-H})$	1.073	
$CH_3Li_2^+$ (**5**)	C_s	$r(\mathrm{C-Li_a})$	2.043	2.064
		$r(\mathrm{C-Li_b})$	1.967	2.013
		$r(\mathrm{C-H_a})$	1.100	1.095
		$r(\mathrm{C-H_b})$	1.096	1.096
		$r(\mathrm{Li_a-Li_b})$	2.963	3.041
		$r(\mathrm{Li_a-H_a})$	2.104	2.060
		$r(\mathrm{Li_b-H_b})$	2.130	2.172
		$\angle\mathrm{LiCLi}$	95.2	96.5
		$\angle\mathrm{H_aCLi_a}$	77.7	74.4
		$\angle\mathrm{H_bCLi_b}$	82.9	83.0
		$\angle\mathrm{H_bCH_b}$	106.5	107.6
		$\angle\mathrm{H_aCH_b}$	101.2	102.2
$CH_3Li_2^+$ (**6**)	C_s	$r(\mathrm{C-Li})$	2.020	2.045
		$r(\mathrm{C-H_a})$	1.087	1.093
		$r(\mathrm{C-H_b})$	1.102	1.097
		$r(\mathrm{Li-Li})$	2.927	3.024
		$r(\mathrm{Li-H_a})$	2.541	2.544
		$r(\mathrm{Li-H_b})$	2.052	2.044
		$\angle\mathrm{LiCLi}$	92.9	95.3
		$\angle\mathrm{H_aCLi}$	105.8	104.2
		$\angle\mathrm{H_bCLi}$	76.0	74.4
		$\angle\mathrm{H_aCH_b}$	107.0	105.7
		$\angle\mathrm{H_bCH_b}$	99.0	100.2
$CH_3(BeH)_2^+$ (**10**)	D_{3h}	$r(\mathrm{C-Be})$	1.762	1.790
		$r(\mathrm{C-H})$	1.097	1.091
		$r(\mathrm{Be-H_b})$	1.295	1.307
$CH_3(BeH)_2^+$ (**11**)	$C_s{}^a$	$r(\mathrm{C-Be_a})$	1.794	1.793
		$r(\mathrm{C-Be_b})$	1.754	1.766
		$r(\mathrm{C-H_c})$	1.113	1.100
		$r(\mathrm{C-H_d})$	1.100	1.097
		$r(\mathrm{Be_a-H_a})$	1.295	1.305
		$r(\mathrm{Be_b-H_b})$	1.295	1.304
		$\angle\mathrm{BeCBe}$	85.9	88.2
		$\angle\mathrm{H_cCBe_a}$	77.5	76.9
		$\angle\mathrm{H_dCBe_b}$	89.4	89.3
		$\angle\mathrm{H_aBe_aC}$	178.6	180.0
		$\angle\mathrm{H_bBe_bC}$	175.3	178.6
		$\angle\mathrm{H_cCH_d}$	100.1	99.4
		$\angle\mathrm{H_dCH_d}$	109.4	108.5
		$\phi\mathrm{H_aBe_aCBe_b}$	0.0	
		$\phi\mathrm{H_bBe_bCBe_a}$	0.0	
$CH_3(BeH)_2^+$ (**12**)	C_s	$r(\mathrm{C-Be})$	1.776	1.781
		$r(\mathrm{C-H_a})$	1.090	1.090
		$r(\mathrm{C-H_b})$	1.112	1.102
		$r(\mathrm{Be-H})$	1.295	1.305
		$\angle\mathrm{BeCBe}$	85.7	88.2
		$\angle\mathrm{H_aCH_b}$	106.8	105.8
		$\angle\mathrm{H_aCBe}$	108.1	107.9
		$\angle\mathrm{H_bCBe}$	78.9	78.4
		$\angle\mathrm{H_bCH_b}$	95.8	95.5
		$\angle\mathrm{CBeH}$	177.2	179.1
		$\phi\mathrm{HBeCBe}$	0.0	
$CH_3(Na)_2^+$ (**13**)	D_{3h}	$r(\mathrm{C-Na})$	2.171	
		$r(\mathrm{C-H})$	1.067	
$CH_3(Na)_2^+$ (**14**)	C_s	$r(\mathrm{C-Na_a})$	2.165	
		$r(\mathrm{C-Na_b})$	2.147	
		$r(\mathrm{C-H_a})$	1.093	
		$r(\mathrm{C-H_b})$	1.089	
		$\angle\mathrm{NaCNa}$	89.1	
		$\angle\mathrm{H_aCNa_a}$	74.7	
		$\angle\mathrm{H_aCH_b}$	109.5	
		$\angle\mathrm{H_bCH_b}$	104.4	
$CH_3(MgH)_2^+$ (**15**)	D_{3h}	$r(\mathrm{C-Mg})$	2.072	
		$r(\mathrm{C-H})$	1.075	
		$r(\mathrm{Mg-H})$	1.516	
$CH_3(MgH)_2^+$ (**16**)	$C_s{}^a$	$r(\mathrm{C-Mg_a})$	2.078	
		$r(\mathrm{C-Mg_b})$	2.062	
		$r(\mathrm{C-H_c})$	1.095	

Table I (*Continued*)

molecule	point group	parameter	optimization level STO-3G	optimization level 4-31G/5-21G
		r(C-H$_d$)	1.088	
		r(Mg$_a$-H$_a$)	1.515	
		r(Mg$_b$-H$_b$)	1.514	
		∠MgCMg	88.0	
		∠H$_c$CMg$_a$	75.7	
		∠H$_c$CH$_d$	107.7	
		∠H$_d$CH$_d$	106.5	
		∠H$_a$Mg$_a$C	168.2	
		∠H$_b$Mg$_b$C	172.0	
		ϕH$_a$Mg$_a$CMg$_b$	0.0	
		ϕH$_b$Mg$_b$CMg$_a$	0.0	
CH_3BeH	C_{3v}	r(CH)	1.085	1.089
		r(CBe)	1.691	1.698
		r(BeH)	1.291	1.335
		∠HCBe	111.8	111.8
CH_3Li	C_{3v}	r(CH)	1.083	1.092
		r(CLi)	2.009	1.989
		∠HCLi	112.6	111.5
CH_3MgH	C_{3v}	r(CMg)	1.967	
		r(MgH)	1.539	
		r(CH)	1.089	
		∠HCMg	112.9	
CH_3Na	C_{3v}	r(CH)	1.092	
		r(CNa)	2.087	
		∠HCNa	114.3	
Li_2	$D_{\infty h}$	r(LiLi)	2.698	2.803
LiH	$C_{\infty v}$	r(LiH)	1.510	1.637
$(Li\cdots H\cdots Li)^+$	$D_{\infty h}$	r(Li-H)	1.646	1.692
		r(Li-Li)	3.292	3.384
CH_2Li^+	C_{2v}	r(C-H)	1.110	1.085
		r(C-Li)	2.085	2.139
		∠HCH	107.2	109.6
$CHLi_2^{+b}$	C_{2v}	r(C-Li)		2.084
		r(C-H)		1.098
		∠HCLi		112.9

[a] ϕ = dihedral angle. [b] SCF procedure gives different configurations at the STO-3G level.

level. The effect of larger basis sets on relative energies was examined by single calculations using the 6-31G* basis which contains d-type polarization functions on C, Li, and Be. Møller–Plesset second-order perturbation theory applied to the 4-31G wave function (MP2/4-31G)[13e,f] was used to estimate the contribution from electron correlation to the total energy of **4**, **5**, **10**, and **11**. Structural information is summarized in Table I, absolute energies in Table II, and relative energies in Table III.

For convenience, the following notations will be used to refer to the calculational methods employed: "4-31G" also implies 5-21G for Li and Be, RHF is understood unless otherwise indicated, and a double slash // indicates the level of geometry optimization, e.g., 6-31G*//4-31G designates a single 6-31G* calculation on a 4-31G/5-21G optimized geometry.

Results and Discussion

Structure and Energy of $CH_3Li_2^+$. The initial screen of structural possibilities gave two principal minimum-energy forms for $CH_3Li_2^+$, **4** (D_{3h}) and **5** (C_s) (Tables I and II). A second C_s geometry, **6**, like **5** obtained by imposing a plane of symmetry during optimization, probably would give slightly more stable **5** if this constraint were removed. As Table III shows, the relative energies of **4** and **5** vary with the calculational method employed, but **4** (D_{3h}) is always indicated to be the most stable form. At the highest single-determinant level investigated (6-31G*//4-31G), the difference is 2.5 kcal/mol. The effect of electron correlation, probed by comparing the RHF/4-31G with the MP2/4-31G results on **4** and **5**, is indicated to be negligible. Based on these calculations we conclude that **4** is 2–3 kcal/mol more stable than **5** or **6**. However, we did not ascertain whether **5** is a true local minimum, or, if so, the magnitude of its barrier to rearrangement to **4**.

The structures of **5** (and **6**) can be viewed as CH_3^+ interacting strongly with Li_2. The Li-Li distance (4-31G) increases from 2.80 Å in Li_2 to 3.04 Å in **5**. Corresponding Li-Li STO-3G overlap populations decrease from 0.714 in Li_2 to 0.166 in **5** (Table IV). As lithium does not attain coordinative saturation by taking part in a single three-center-two-electron bond, there is significant positive overlap between Li and nearby hydrogens both in **4** and **5**. The 4-31G C-Li distances are increased slightly by D_{3h} pentacoordination, from 1.989 Å in CH_3Li to 2.096 Å in **4**.

The possible decomposition pathways (reactions 1-4) are all highly endothermic (Table V), indicating that $CH_3Li_2^+$ is a very stable species in the gas phase, more stable in fact than CH_5^+. The least unfavorable reaction (eq 2) is endothermic by 52.4 kcal/mol (MP2/4-31G//4-31G); this value corresponds to the lithium cation affinity[14] of monomeric methyllithium. Reaction 1 is the methyl cation affinity of Li_2; the MP2/4-31G//4-31G value, 164.7 kcal/mol, is much larger than the methyl cation affinity of H_2 (to give CH_5^+), 38.2 kcal/mol, at the same level.[15a]

$$CH_3Li_2^+\ (\mathbf{4}) \rightarrow CH_3^+ + Li_2 \tag{1}$$

$$CH_3Li_2^+\ (\mathbf{4}) \rightarrow CH_3Li + Li^+ \tag{2}$$

$$CH_3Li_2^+\ (\mathbf{4}) \rightarrow CHLi_2^+ + H_2 \tag{3}$$

$$CH_3Li_2^+\ (\mathbf{4}) \rightarrow CH_2Li^+ + LiH \tag{4}$$

Table II. Calculated Total Energies (hartrees)

molecule	energy					
	STO-3G opt geom			4-31G opt geom		
	STO-3G	4-31G	6-31G*	4-31G	6-31G*	UMP2/4-31G
Li^+ [a]	−7.135 45	−7.233 26	−7.235 54	−7.233 26	−7.235 54	−7.233 46
H_2[a]	−1.117 51	−1.126 58	−1.12658[f]	−1.126 83	−1.126 83	−1.144 10
LiH[a]	−7.863 38	−7.975 16	−7.978 74[f]	−7.977 35	−7.980 87	−7.990 19
Li_2[f]	−14.638 75	−14.860 35	−14.866 56[f]	−14.860 66	−14.866 93	−14.877 29
CH_3^+ [a]	−38.779 48	−39.171 29		−39.175 12	−39.230 63	−39.242 05
CH_2Li^+	−45.619 71	−46.117 93		−46.119 07	−46.175 35	−46.186 43
$CHLi_2^+$	−52.324 98[e]			−53.008 44	*e*	−53.078 37
CH_3Li	−46.421 59[c]	−46.959 62[c]	−47.015 33[f]	−46.960 00	−47.015 40	−47.064 90
CH_4[b]	−39.726 86	−40.139 76	−40.195 17[f]	−40.139 77	−40.195 15	−40.240 09
CH_5^+ (C_s)[d]	−39.918 87	−40.322 07		−40.327 15	−40.388 22	−40.432 28
CH_3BeH	−54.153 22[c]	−54.733 49[c]	−54.815 26[f]	−54.754 69	−54.815 98	−54.874 82
CH_3Na[c]	−198.940 68					
CH_3MgH[g]	−236.828 04					
$CH_3Li_2^+$ (**4**)	−53.665 87	−54.273 16	−54.328 87	−54.275 98	−54.330 41	−54.381 83
(**9**)	−53.665 89	−54.274 38				
(**5**)[h]	−53.640 70	−54.267 40	−54.325 91	−54.267 91	−54.326 36	−54.374 05
(**6**)	−53.640 00	−54.266 93		−54.267 41		
$CH_3(BeH)_2^+$ (**10**)	−68.936 77	−69.696 03	−69.766 09	−69.696 58		−69.837 15
(**11**)	−68.919 78	−69.683 37	−69.756 95	−69.683 87		−69.826 73
(**12**)	−68.919 99	−69.683 36		−69.683 87		
$CH_3Na_2^+$ (**13**)	−358.801 75[i]					
(**14**)	−358.799 26[i]					
$CH_3(MgH)_2^+$ (**15**)	−434.425 57[i]					
(**16**)	−434.409 94[i]					

[a] Reference 15a. [b] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93,** 808 (1971). [c] Reference 8b. [d] W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93,** 6377 (1971). [e] SCF procedure gives different configurations. [f] J. D. Dill, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **99,** 6159 (1977). [g] M. B. Krogh-Jespersen, unpublished. [h] Total energies of **4** and **5** using STO-3G basis deleting p orbitals on lithium are −53.579 69 and −53.560 13 au, respectively. [i] Total energies at STO-3G* are: **13,** −358.815 64; **14,** −358.829 66; **15,** −434.442 78; **16,** −434.447 44.

Table III. Calculated Relative Energies (kcal/mol)

molecule	STO-3G opt geom			4-31G opt geom		
	STO-3G	4-31G	6-31G*	4-31G	6-31G*	MP2/4-31G
$CH_3Li_2^+$ (**4**)	0.0 (0.0)[a]	0.0	0.0	0.0	0.0	0.0
(**9**)	0.0	0.8				
(**5**)	15.8 (12.3)[a]	3.6	1.9	5.1	2.5	4.9
(**6**)	16.3	3.9		5.4		
$CH_3(BeH)_2^+$ (**10**)	0.0	0.0	0.0	0.0		0.0
(**11**)	10.7	7.9	5.7	8.0		6.5
(**12**)	10.5	8.0		8.0		
$CH_3Na_2^+$ (**13**)	0.0					
(**14**)	1.6[d]					
$CH_3(MgH)_2^+$ (**15**)	0.0					
(**16**)	9.8[e]					
CH_5^+ (D_{3h})	0.0	0.0		0.0	0.0	0.0
CH_5^+ (C_s)	−6.3[b]	−4.4[b]		−7.2[b]	−12.9[b]	−6.2[c]

[a] Numbers in parentheses are relative energies calculated without p orbitals on lithium. [b] Reference 4b. [c] J. A. Pople, private communication. [d] At STO-3G*, this value is −8.8. [e] At STO-3G*, this value is −0.1.

The stability of $CH_3Li_2^+$ is reflected in the mass spectra of alkyllithium compounds; RLi_2^+ appears as the base peak in all reported spectra.[16] Owing to the low volatility of methyllithium (the $(CH_3Li)_4$ units are further associated in the solid), its mass spectrum has not been determined directly. However, thermal decomposition of $LiB(CH_3)_4$ in the mass spectrometer results in a spectrum corresponding to that of methyllithium tetramer at higher temperatures.[17] Both at 250 and 300 °C the most abundant ion is $CH_3Li_2^+$. Structures involving cyclic three-center-two-electron bonds have been proposed for RLi_2^+ species.[16d] However, the calculated stability of D_{3h} $CH_3Li_2^+$ (**4**) relative to the C_s structures (**5** and **6**) indicates that RLi_2^+ species may adopt geometries similar to **4**, with nearly linear LiCLi arrangements, instead.

Linear vs. Cyclic Three-Center Two-Electron (3c-2e) Bonding in Lithium Compounds. Qualitative molecular orbital arguments, first employed by Coulson to predict the structure of H_3^+,[18] suggest that three-center-two-electron systems should be bent (cyclic).[19] Exceptions are known. Gimarc has explained the preference of Li-H-Li$^+$ for a linear structure[20] by pointing out that the low Li-Li bond energy in Li_2 and its long internuclear distance (2.80 Å at 4-31G, almost twice as long as in LiH, 1.64 Å) enable a proton to slip in between the lithiums, to "form two LiH bonds and still maintain the Li-Li bond". However, the Li···Li distance in Li-H-Li$^+$, 3.38 Å at 4-31G, is significantly lengthened, and this argument cannot be applied to **4** with a Li···Li separation of 4.19 Å and antibonding character between lithiums indicated by the overlap population (Table IV). The simplest explanation for the preferred structure (**4**) of $CH_3Li_2^+$ is electrostatic. The positive charge, divided between the metal atoms, is better distributed in the D_{3h} form where these atoms are farther apart. At

Table IV. Selected STO-3G Overlap Populations

molecule	pair of atoms	overlap
LiH	LiH	0.780
Li_2	LiLi	0.714
CH_4	CH	0.740
CH_3Li	CLi	0.640
$CH_3Li_2^+$ (**4**)	CLi	0.384
	CH	0.741
	LiH	0.022
without p orbitals on Li	CLi	0.200
	CH	0.781
	LiH	0.002
$CH_3Li_2^+$ (**5**)	CLi_a	0.406
	CLi_b	0.342
	CH_a	0.709
	CH_b	0.723
	LiLi	0.166
	Li_aH_a	0.049
	Li_bH_b	0.036
without p orbitals on Li	CLi_a	0.254
	CLi_b	0.194
	CH_a	0.736
	CH_b	0.752
	LiLi	0.110
	Li_aH_a	−0.009
	Li_bH_b	−0.019

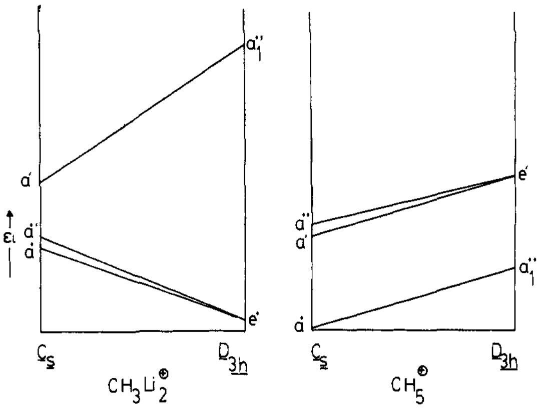
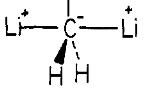
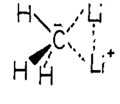


Figure 1. Walsh–Mulliken diagrams relating C_s and D_{3h} structures of $CH_3Li_2^+$ and of CH_5^+. Only the three highest occupied molecular orbitals, obtained using the STO-3G basis, are shown.

STO-3G the indicated Mulliken charges in **4** follow (4-31G values in parentheses): Li +0.530 (+0.712); H, +0.096 (+0.197); C, −0.346 (−1.01). Similar values are found for **5**. The indicated charge distribution is shown schematically below.



17



18

This explanation is not without its problems. Table III suggests that the D_{3h} preference over C_s may be greater for Be and Mg than for Li and Na, contrary to their electronegativity order and expected ionic character. Other factors contribute to these preferences.

The problem of cyclic vs. linear three-center-two-electron bonds can be regarded in another way. H_2 has a bond energy of 103 kcal/mol;[21] the proton affinity of H_2 is 101 kcal/mol.[15,22] Thus, in D_{3h} H_3^+ the average energy per H-H bond is (103 + 101)/3 = 68 kcal/mol. Since linear H_3^+ is calculated to be 40 kcal/mol less stable than the triangular form,[23] the energy for each of the two bonds in the linear arrangement is (204 − 40)/2 = 82 kcal/mol. Even though the individual bond strengths are higher in linear H_3^+, the greater number of bonds favors the triangular H_3^+ structure. In other words, bending linear H_3^+ gives one more moderately strong H-H bond, and this more than compensates for the weakening of the two initial bonds. The same argument rationalizes the preferred triangular structure for Li_3^+ despite the smaller Li-Li bond energy.[24] LiH_2^+ also favors a bent structure[15a,25] as the new H-H bond formed by bending linear H-Li-H$^+$ is strong relative to the Li-H bonds being weakened. (In fact, the LiH_2^+ structure resembles an H_2 molecule interacting weakly with Li^+).[15a] In contrast, linear $LiHLi^+$ would gain only a weak Li-Li bond in the triangular form; the energy of this new bond is insufficient to compensate for the weakening of the Li-H bonds upon bending. Consequently, Li_2H^+ prefers to be linear.[15a,25a,26] $CH_3Li_2^+$ behaves similarly; **4** is more stable than **5** or **6**. In contrast, CH_5^+ (like H_3^+) prefers the C_s structure with a cyclic three-center-two-electron bond.[4]

A comparison of Walsh-Mulliken diagrams[27] relating C_s and D_{3h} structures of CH_5^+ and of $CH_3Li_2^+$ provides another way of examining these contrasting geometrical preferences. These diagrams (Figure 1) are constructed using one-electron energies obtained from STO-3G calculations.[28] Only the three highest occupied MOs are shown. These are designated in both CH_5^+ and $CH_3Li_2^+$ simply as e′ and a₁″ in D_{3h} symmetry. The a₁″ orbitals (D_{3h}), roughly representing the three-center-two-electron bonds, are not responsible for the differences in behavior of $CH_3Li_2^+$; in agreement with qualitative expectations, *both* are stabilized in going to the corresponding C_s structures. The major difference occurs in the D_{3h} e′ orbitals, split into a′ and a″ in C_s symmetry. During transformation from C_s to D_{3h} these orbitals go *up in energy* in CH_5^+, but *down in energy* in $CH_3Li_2^+$, consistent with the greater stability of **4** over **5**. This decrease in the energy of the e′ orbitals in D_{3h} $CH_3Li_2^+$ is not due to the contribution of lithium p orbitals. The Walsh diagram does not change significantly when canonical orbital energies obtained from calculations without p orbitals on lithium are used. The relative energies with and without p orbitals on lithium at the STO-3G level (Table III) also are similar.

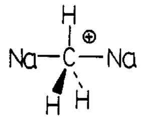
The contrasting behavior of the e′ vs. a′, a″ orbitals (Figure 1) is the consequence of significant structural differences in

Table V. Calculated Heats of Reactions 1-8 (kcal/mol)

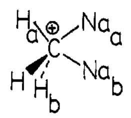
reaction	STO-3G opt geom			4-31G opt geom		
	STO-3G	4-31G	6-31G*	4-31G	6-31G*	MP2/4-31G
1	155.4	151.6		150.7	146.1	164.7
2	68.3	50.4	49.0	51.9	49.9	52.4
3				88.3		100.0
4	114.7	113.0		112.7	109.3	128.8
5	−224.4	−195.4		−193.5	−189.3	−188.2
6	−103.7	−117.0		−87.6		−85.0
7	−285.7					
8	−191.0					

CH_5^+ vs. $CH_3Li_2^+$. These orbitals are largely associated with the methyl moieties in both ions. In the D_{3h} forms, the methyl groups necessarily are flat, but the C–H bonds in CH_5^+ are significantly lengthened (to 1.110 Å (4-31G); compare the 1.076 Å value in CH_3^+ and average value of 1.079 Å for the methyl hydrogens in the C_s forms of CH_5^+).[4] In CH_5^+, the eight valence electrons are involved in bonding all five hydrogens to carbon; consequently, on average each C–H bond is weakened relative to those in $CH_3Li_2^+$ where the charge is borne far more by the lithiums than the hydrogens. Consequently, C–H overlap is reduced in going from C_s to D_{3h} CH_5^+ and the energy of the e′ orbitals rises above those of the a′–a″ set. In contrast, the CH bonds are *shortened* in going from C_s to D_{3h} $CH_3Li_2^+$ (1.082 Å in **4** (4-31G) vs. average values of 1.096 Å in **5** and **6**). A second factor is also involved. Pyramidal distortion of the methyl in C_s $CH_3Li_2^+$ (the average ∠HCH in **5** and **6** is 103°) is much greater than in C_s CH_5^+ (the average ∠HCH value is 112° for the two C_s forms). As is well known, the e′ orbitals in planar CH_3 are lower in energy than the corresponding e orbitals of pyramidal methyl (assuming the CH bond lengths to be the same).[27] Thus, the greater pyramidal distortion in $CH_3Li_2^+$ should also contribute to the behavior indicated in Figure 1.

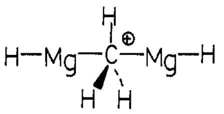
Structure and Energy of $CH_3(BeH)_2^+$, $CH_3Na_2^+$, and $CH_3(MgH)_2^+$. The greater stability of the D_{3h} structure of $CH_3Li_2^+$ prompted us to examine the analogous ions, $CH_3(BeH)_2^+$, $CH_3Na_2^+$, and $CH_3(MgH)_2^+$. D_{3h} structures **10, 13,** and **15** are found to be more stable than the corresponding C_s structures at all levels of theory considered (Table III). Correlation is indicated to be of minor importance by a comparison of RHF/4-31G//4-31G with MP2/4-31G//4-31G differences, 8.0 and 6.5 kcal/mol, respectively. At 6-31G*//STO-3G **10** is found to be more stable than **11** by 5.7 kcal/mol. Only STO-3G calculations were carried out for $CH_3Na_2^+$ and $CH_3(MgH)_2^+$. D_{3h} structures **13** ($CH_3Na_2^+$) and **15** ($CH_3(MgH)_2^+$) are more stable than the corresponding C_s alternatives by 1.6 and 9.8 kcal/mol, respectively.



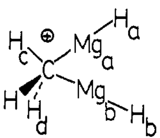
13 D_{3h}



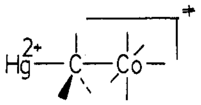
14 C_s



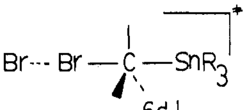
15 D_{3h}



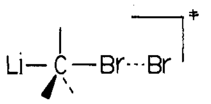
16 C_s



19[6f]



20[6d,l]



21[6a]

Stabilization of Carbonium Ions by Electropositive Substituents. The following isodesmic reactions[31] demonstrate the stabilization of CH_5^+ by substitution by metals or electropositive groups. For uniformity, STO-3G values are given; data at higher levels are summarized in Table V.

$$CH_5^+ + 2CH_3Li \rightarrow CH_3Li_2^+\ (\mathbf{5}) + 2CH_4 \quad -224.4\ \text{kcal/mole} \quad (5)$$

$$CH_5^+ + 2CH_3BeH \rightarrow CH_3(BeH)_2^+\ (\mathbf{10}) + 2CH_4 \quad -103.7\ \text{kcal/mole} \quad (6)$$

$$CH_5^+ + 2CH_3Na \rightarrow CH_3Na_2^+\ (\mathbf{13}) + 2CH_4 \quad -285.7\ \text{kcal/mole} \quad (7)$$

$$CH_5^+ + 2CH_3MgH \rightarrow CH_3(MgH)_2^+\ (\mathbf{15}) + 2CH_4 \quad -191.0\ \text{kcal/mole} \quad (8)$$

The high exothermicity of all these reactions shows that electropositive elements are able to stabilize carbonium ions as well as carbenium ions.[30] These large stabilizations seem largely to be electrostatic or inductive in origin: the more electropositive atoms or groups delocalize the positive charge more effectively. The energies of reactions 5–8 follow the Pauling electronegativity order.[32]

Model for S_E2 Reaction with Inversion. Two general stereochemical pathways for bimolecular aliphatic electrophilic substitution reactions lead to inversion or retention of configuration in the product.[33] As the leaving group L is displaced without the C–L bonding pair of electrons, L must be more electropositive than carbon. Consequently, most of the electrophilic substitutions studied involve metallic leaving groups.[4-6] Many of these reactions have been shown to proceed with retention.[5] The lower energy obtained for **2** (C_s), the "intermediate" in the displacement of H^+ from CH_4 by H^+, supports this mechanism.[4] The present results indicate that this stereochemical course is not general. $CH_3Li_2^+$, the "intermediate" in the substitution of Li^+ on CH_3Li by Li^+, prefers the D_{3h} structure **4**. $CH_3Li_2^+$ may be a better general model for S_E2 reactions than CH_5^+ when the substituents in experimental systems are highly electropositive compared to carbon. Therefore, suggestions that S_E2 reactions should proceed with retention of configuration based on the preferred structure of CH_5^+ are misleading.[5b,33] Depending on the relative stabilities of the linear and bent three-center arrangements, a gradation from one mechanism to the other, from retention to inversion, can be expected. Recently several examples of inversion have been observed.[6] Transition states **19–21**[6a,d,f] are illustrative. While inversion might be due to steric reasons in some cases,[5f] the available experimental results indicate that both retention and inversion are possible in S_E2 reactions.[6f]

Primary alkyllithium aggregates $(RCH_2Li)_{4\text{ or }6}$ with a prochiral CH_2 group are known to undergo inversion.[34] A mechanism has been proposed involving RCH_2Li_2 fragments in which the two lithiums are bound on opposite sides of a planar RCH_2 group.[34] D_{3h} $CH_3Li_2^+$ can be taken to model this behavior.

Note Added in Proof: Single point calculations including d functions on the heavy atoms (STO-3G*)[35] have now been carried out on $CH_3Na_2^+$ and on $CH_3(MgH)_2^+$ using the STO-3G geometries. Significant changes in relative energies of about 10 kcal/mol favoring the C_s forms resulted. At STO-3G*, C_s $CH_3Na_2^+$ (**14**) is indicated to be favored over the D_{3h} form (**13**) by 8.8 kcal/mol, while the two geometries of $CH_3(MgH)_2^+$ are nearly equal in energy (**16** is 0.1 kcal/mol more stable than **15**). Clearly, still higher level calculations are needed before final conclusions can be drawn concerning the preferred structures of $CH_3Na_2^+$ and of $CH_3(MgH)_2^+$.

Acknowledgments. This work was supported at Erlangen by the Fonds der Chemischen Industrie, and was facilitated by a NATO Grant. We thank Professor John A. Pople for his interest, suggestions, hospitality, and, in particular, for the development of the GAUSSIAN 70 series of programs. Professor G. A. Stucky, Professor T. L. Brown, and Dr. Peter Hofmann provided information and helpful comments.

References and Notes

(1) Taken in part from the Ph.D. Thesis of E. D. Jemmis, Princeton University, 1978.

(2) See (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1969; (b) S. R. Hartshorn, "Aliphatic Nucleophilic Substitution", Cambridge University Press, New York, N.Y., 1973; (c) C. A. Lieder and J. I. Brauman, *J. Am. Chem. Soc.*, **96**, 4028 (1974); (d) J. I. Brauman, C. A. Lieder, and W. N. Olmstead, *ibid.*, **96**, 4030 (1974); (e) D. Groves, W. Rhine, and G. D. Stucky, *ibid.*, **93**, 1553

(1971); (f) W. N. Olmstead and J. I. Brauman, *ibid.*, **99**, 4219 (1977).
(3) (a) T. Clark, Y. Apeloig, and P. v. R. Schleyer, unpublished results; (b) H. B. Schlegel and K. Mislow, *Theor. Chim. Acta*, **44**, 245 (1977); A. Dedieu and A. Veillard, *J. Am. Chem. Soc.*, **94**, 6730 (1972).
(4) (a) V. Dyczmons and W. Kutzelnigg, *Theor. Chim. Acta*, **33**, 239 (1974); (b) L. Radom, D. Poppinger, and R. C. Haddon, "Carbonium Ions", Vol. V, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1976, Chapter 38; (c) G. A. Olah, G. Klopman, and R. H. Schlosberg, *J. Am. Chem. Soc.*, **91**, 3261 (1969), and references cited therein; (d) M. D. Sefcik, J. M. S. Harris, and P. P. Gaspar, *J. Chem. Phys.*, **61**, 4321 (1974); (e) R. D. Smith and J. H. Futrell, *Chem. Phys. Lett.*, **36**, 545 (1975).
(5) (a) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials", McGraw-Hill, New York, N.Y., 1968; (b) G. A. Reutov, "Fundamentals of Theoretical Organic Chemistry", North-Holland Publishing Co., New York, N.Y., 1967; (c) H. B. Charman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2530 (1959); (d) F. R. Jensen, *J. Am. Chem. Soc.*, **82**, 2469 (1960); (e) D. H. R. Barton, R. H. Hesse, R. E. Markwell, M. M. Pechet, and H. T. Toh, *ibid.*, **98**, 3034 (1976); (f) A. Rahm and M. Pereyre, *ibid.*, **99**, 1672 (1977); also see ref 2 and 4.
(6) (a) D. E. Applequist and G. N. Chmurny, *J. Am. Chem. Soc.*, **89**, 875 (1967); (b) W. H. Glaze, C. M. Selman, A. L. Ball, Jr., and L. E. Bray, *J. Org. Chem.*, **34**, 641 (1969); (c) G. M. Whitesides and D. J. Boschetts, *J. Am. Chem. Soc.*, **93**, 1529 (1971); (d) F. R. Jensen and D. D. Davis, *ibid.*, **93**, 4048 (1971); (e) F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **93**, 5283 (1971); (f) H. L. Fritz, J. H. Espenson, D. A. Williams, and G. A. Molander, *ibid.*, **96**, 2378 (1974); (g) P. L. Bock, D. J. Boschetts, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *ibid.*, **96**, 2814 (1974); (h) J. H. Espenson and D. A. Williams, *ibid.*, **96**, 1008 (1974); (i) J. P. Leslie, II, and J. H. Epsenson, *ibid.*, **98**, 4839 (1976); (j) K. Stanley and M. C. Baird, *ibid.*, **99**, 1808 (1977); (k) D. E. Bergbreiter and D. P. Rainville, *J. Organomet. Chem.*, **121**, 19 (1976); (l) N. S. Isaacs and K. Javaid, *Tetrahedron Lett.*, 3073 (1977).
(7) (a) T. L. Gilchrist and R. C. Storr, "Organic Reactions and Orbital Symmetry", Cambridge University Press, New York, N.Y., 1972. (b) G. Klopman, "Chemical Reactivity and Reaction Paths", Wiley-Interscience, New York, N.Y., 1974. (c) Interestingly, while our work was in progress a book was published with a cover illustrating Li$^+$ as a leaving group in an S$_E$2 reaction proceeding with inversion: I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley-Interscience, New York, N.Y., 1976.
(8) (a) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 4332 (1976); (b) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *ibid.*, **98**, 5419 (1976); (c) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and W. L. Jorgensen, *Tetrahedron Lett.*, 3923 (1976); (d) E. D. Jemmis, D. Poppinger, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 5796 (1977); (e) G. Rauscher, T. Clark, D. Poppinger, and P. v. R. Schleyer, *Angew. Chem.*, **90**, 306 (1978).
(9) C. C. J. Roothan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(10) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
(11) A single precision version of GAUSSIAN 70 program was used for some of the calculations on a Telefunken TR 440 computer; the 48-bit word length of this machine ensures the necessary accuracy. We thank Dr. H.-U. Wagner for making this program available to us.
(12) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.*, **52**, 2769 (1970).
(13) (a) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); (b) W. J. Hehre and J. A. Pople, *ibid.*, **56**, 4233 (1972); (c) J. D. Dill and J. A. Pople, *ibid.*, **62**, 2921 (1975); (d) J. S. Binkley and J. A. Pople, *ibid.*, **66**, 879 (1977); (e) *Int. J. Quantum Chem.*, **S9**, 229 (1975); (f) J. A. Pople, J. S. Binkley, and R. Seeger, *ibid.*, **S10**, 1 (1976).
(14) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 5920 (1975); R. L. Woodin and J. L. Beauchamp, *ibid.*, **100**, 501 (1978).
(15) (a) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and L. Radom, *J. Am. Chem. Soc.*, **98**, 3436 (1976); (b) C. Hoheisel and W. Kutzelnigg, *ibid.*, **97**, 6970 (1975).
(16) (a) J. Berkowitz, D. A. Bafus, and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961); (b) M. Y. Darensbourg, B. Y. Kimura, G. E. Hartwell, and T. L. Brown, *J. Am. Chem. Soc.*, **92**, 1236 (1970); (c) G. E. Hartwell and T. L. Brown, *Inorg. Chem.*, **5**, 1257 (1966); (d) T. L. Brown, *Ann. N.Y. Acad. Sci.*, **136**, 98 (1966).
(17) (a) W. E. Rhine, G. Stucky, and S. W. Petersen, *J. Am. Chem. Soc.*, **97**, 6401 (1975); (b) G. Stucky, private communication. We thank Professor Stucky for providing the mass spectra of LiB(CH$_3$)$_4$ at higher temperatures.
(18) C. A. Coulson, *Proc. Cambridge Philos. Soc.*, **31**, 244 (1935).
(19) B. M. Gimarc, *J. Am. Chem. Soc.*, **93**, 593 (1971).
(20) B. M. Gimarc, *J. Am. Chem. Soc.*, **93**, 815 (1971).
(21) E. A. G. Armour, *Mol. Phys.*, **24**, 181 (1972).
(22) P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977).
(23) (a) W. Kutzelnigg, R. Ahlrichs, I. Labib-Iskovder, and W. A. Bingel, *Chem. Phys. Lett.*, **1**, 447 (1967); (b) W. A. Lester, Jr., and M. Krauss, *J. Chem. Phys.*, **44**, 207 (1966).
(24) (a) R. Janoschek, *J. Mol. Struct.*, **6**, 283 (1970); (b) N. K. Ray, *J. Chem. Phys.*, **52**, 463 (1970); (c) R. C. Raffenetti and K. Ruedenberg, *ibid.*, **59**, 5978 (1973).
(25) (a) N. K. Ray, *J. Chem. Phys.*, **52**, 463 (1970); (b) W. A. Lester, *ibid.*, **53**, 1511 (1970).
(26) G. Dierksen and H. Preuss, *Int. J. Quantum Chem.*, **1**, 637 (1967).
(27) (a) A. D. Walsh, *J. Chem. Soc.*, 2260–2301 (1953); (b) R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 204 (1942); (c) R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, 74, 127 (1974).
(28) Electron wave functions for CH$_5^+$ were recalculated using published geometries.[29]
(29) W. A. Lathan, W. J. Hehre, and J. A. Pople, *Tetrahedron Lett.*, 2699 (1970).
(30) Y. Apeloig, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 1291 (1977).
(31) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).
(32) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960.
(33) T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, N.Y., 1976. In the present discussion we do not include reactions that proceed through four-center intermediates.
(34) T. Clark, P. v. R. Schleyer, and J. A. Pople, *J. Chem. Soc., Chem. Commun.*, 137 (1978), and references cited therein.
(35) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

Effect of Carbon Atom Pyramidalization on the Bonding in Ethylene

Walter V. Volland, Ernest R. Davidson, and Weston Thatcher Borden*

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98115. *Received July 18, 1978.*

Abstract: The changes in the bonding that occur on syn and anti carbon atom pyramidalization in ethylene are analyzed from the perspective of the second-order Jahn-Teller effect. Situations in which a pyramidalized geometry might actually be favored over a planar one are discussed, and a preference for anti over syn pyramidalization is predicted. The results of ab initio SCF calculations on planar and pyramidalized geometries are reported. It is found that the energy difference between the lowest singlet and triplet state decreases monotonically with increasing pyramidalization. The C-C bond lengthens and the HCH angle opens on pyramidalization; and, as expected, the anti mode is found to be less energetically costly than the syn. The changes in the bonding that occur on pyramidalization are elucidated by population analyses, which show that orbital following of the motions of the hydrogens is far from complete.

Although bridgehead olefins with torsionally strained double bonds have been studied extensively in recent years,[1] olefins in which the carbon atoms forming the double bonds are pyramidalized have received much less attention. Greene and co-workers have prepared two molecules (**1a** and **1b**) belonging to the latter class of compounds,[2] and recently one of

0002-7863/79/1501-0533$01.00/0