## Structures and Stabilities of α-Hetero-Substituted Organolithium and Organosodium Compounds. Energetic Unimportance of Second-Row d-Orbital Effects

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Abstract: The structures and stabilities of organolithium and organosodium compounds, MCH_2X, where M = Li or Na and X = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, and Cl, are predicted by ab initio calculations. The 3-21G basis set was used for full geometry optimizations, and single point calculations with the 6-31G* basis set provide energies. Correlation corrections at the MP2 level and further optimizations with diffuse functions (3-21+G) were carried out in several cases on the lithium compounds. Comparisons were also made with the corresponding free anions (which were examined with diffuse orbital-augmented basis sets). The first-row $LiCH_2X$ species, X = NH_2, OH, and F, are better stabilized than the corresponding anions due to lithium bridging. Sodium displays a diminished tendency to bridge. Such extra stabilization is therefore not found in the corresponding sodium compounds. The second-row systems behave differently. The MCH_2Cl carbenoids are stabilized to the same extent as the free anions by Cl. The presence of the metals in MCH_2SH, MCH_2SiH_3, and especially MCH_2PH_2 cancel much of the α-substituent stabilizing effects in the corresponding anions. The favored conformations of the CH_2X fragments are substantially different for X = NH_2, OH, PH_2, and SH in the organometallics (syn generally best) than in the free anions (anti or gauche best). The relevance of these predictions on monomeric species to the chemical behavior of the aggregated and solvated organometallics present in solution is discussed. Carbanions are stabilized more by second-row than by first-row substituents. This is due to the more electropositive character of the second-row elements (Cl vs. F, S vs. O, etc.), to the more effective negative hyperconjugation, and to the greater polarizability of the second-row groups. d-Orbital effects do not contribute significantly to the stabilization energies of second-row-substituted carbanions, although the geometries are improved significantly.

Organometallic compounds with the general formula **1** and **2** are widely used in organic synthesis.[2] Common examples include alkyl or alkenyl lithium compounds with α substituents taken from the main groups 4–7. These substituents often have good car-

1   **2**
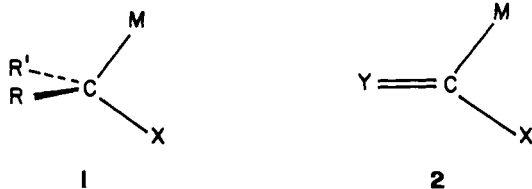
banion-stabilizing abilities, e.g., OR, SiR_3, PR_2, SR, Cl, AsR_2, SeR, Br, etc.[2–3] In spite of the practical importance of such

reagents, little is known experimentally about their energies, geometries or electronic structures.[4] A few computational studies have been reported.[5–7] The earliest systematic investigations of

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metalated species involved standard (or partially optimized) geometries[5] and were concerned with energetic relationships[5a] and the possible involvement of d orbitals in the bonding.[5b]

More recent theoretical developments make it possible to optimize geometries and to use more sophisticated basis sets and computational levels to provide reasonably accurate structures and energies both for the anions.[8,9] and for the corresponding organometallic species.[6,7] Such geometry optimization not only led to the discovery of rather remarkable non-tetrahedral bridged structures[6] but also revealed that the energies of standard geometry forms[5] were often not representative.[7]

Earlier studies of substituted carbanions with standard basis sets appropriate for neutral (or positively charged) species also were inadequate. The use of diffuse orbital-augmented basis sets[8] now permits definitive evaluations of the effects of first-row[8] and second-row[9] substituents on the stabilities of methyl anions. The influence of the more electronegative first-row substituents is mainly inductive;[8] substituents F and OH (which models experimentally realistic OR groups[10]) stabilize CH_2X^- modestly. CH_3 is destabilizing, and NH_2 (a model for NR_2)[10] has no appreciable influence. In accord with chemical experience, the second-row model substituents (SiH_3, PH_2, SH, and Cl) stabilize carbanions much more effectively than their first-row counterparts.[9] The possible role of d orbitals on second-row atoms in stabilizing carbanions was once a major concern, but the polarizability of such atoms and/or the availability of low-lying σ^* orbitals are now known to be more important (see below).

The "anions" used synthetically are seldom free. This paper is concerned with the effects of the commonly employed alkali metal counterions, M = Li and Na, in the prototype reagents, MCH_2X, where X = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, and Cl. Although only the monomeric species were investigated, this study provides insight into the tendency of metal cations to bridge to α heteroatoms and compares the abilities of the heteroatom substituents to stabilize anions as well as the corresponding organo alkali metal compounds.

Background

The comparative ease of formation of α-heteroatom-substituted organolithium compounds[2,3] has been attributed to various possible factors:

(1) Electronegative first-row heteroatoms or polarizable second-row heteroatoms may stabilize organolithiums in the same way that they stabilize the corresponding anions. Such models implicitly assume that there is not specific interaction between Li^+ and X, e.g., as in the ion-pair representation, 3.
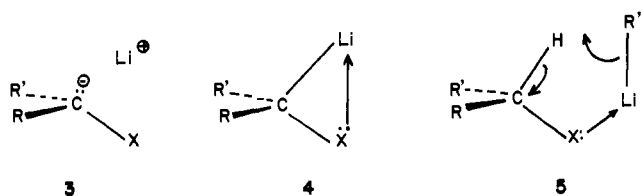

(2) Direct interaction of a lone pair of X with the metal cation, 4, may provide more stabilization in the organometallic compound than in the free anion. Such heteroatom–metal interactions are not limited to α-substituents.[2,3,10]

(3) The heteroatom may direct lithiations by kinetic assistance to deprotonation rather than by thermodynamically stabilizing

the product. As shown in 5, this could result from prior coordination of the organolithium base to the heteroatom and subsequent stabilization of the proton-transfer transition structure.

In a detailed discussion of "heteroatom-assisted metalations", Gschwend and Rodriquez[3] suggested that thermodynamic stability of products sometimes dominates (factors 1 and 2) but that some results can only be explained by kinetic assistance to deprotonation (factor 3), since the thermodynamically most stable species is not always formed. First-row substituents on carbon, such as amines and alkoxy groups, are believed to coordinate with organolithium compounds and kinetically direct deprotonation to α or β carbons. Second-row elements such as sulfur are strong acidifiers but poorer coordinators and direct metalations by stabilizing the organolithium products.[3]

Substituent effects on anion stabilities in solution are complicated by the unknown and condition-dependent nature of the species involved. Association and solvation are well recognized influences.[4,10] The most stable anions might exist as "solvent-separated ion pairs" (6) and exhibit equivalent, if attenuated, substituent effects to the free ions in the gas phase. However, the less stable "anions" in "contact ion pairs" may have more covalent character (7) and exhibit coordination of the metal to the lone pairs of the substituent, X (8). Such organometallic
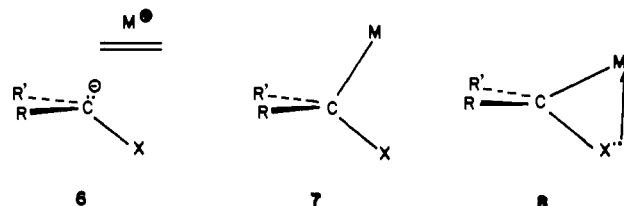
species may be influenced by substituents in quite different ways to the free carbanions.

In the preliminary accounts of this work, we have already presented such examples. The stabilization energies, relative to CH_3Li, of 15 small lithiohydrocarbons were calculated as hypothetical gas-phase monomers[11] and shown to correlate with the methyl stabilization energies of the corresponding carbanions.[12] The attenuation factor, RLi vs. R$^-$, was 0.71. However, $LiCH_2NH_2$, $LiCH_2OH$, and $LiCH_2F$ were much more stable than expected on this basis.[5,7] In all three cases, the "extra" stabilization was attributed to bridging between the Li and the heteroatom. This bridging, represented in 8, may arise either from Coulombic attraction of $M^{\delta+}$ and $X^{\delta-}$ or from a covalent interaction of the high-lying HOMO of the carbanion and a low-lying vacant p orbital of the metal, as shown in 9.[7,13]
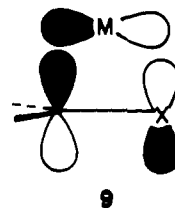
Bridged structures are also commonly observed in transition-metal complexes of α-phosphino, amino, and mercapto carbanions. X-ray crystal structures show that the metal atom bridges more or less symmetrically between the formal carbanionic center and the α heteroatom. Nevertheless, some unbridged complexes are also observed.[14]

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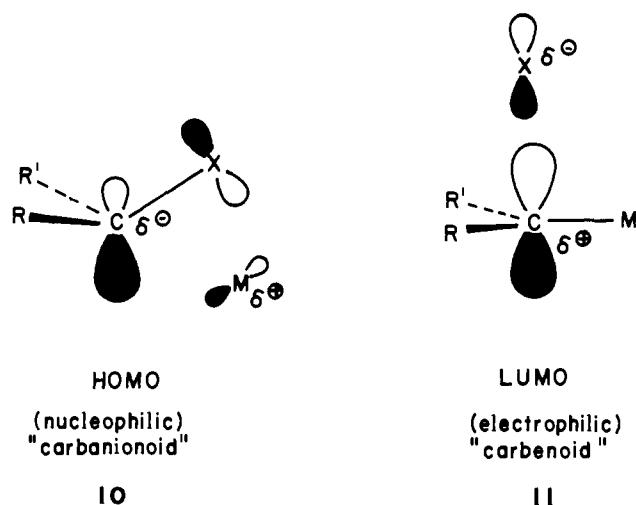
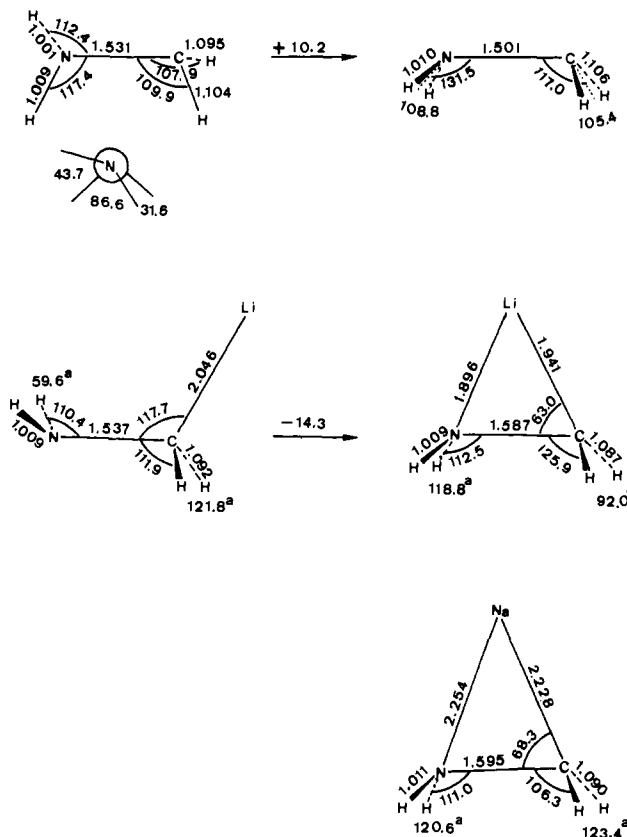(14) Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153.

Organolithium and Organosodium Compounds

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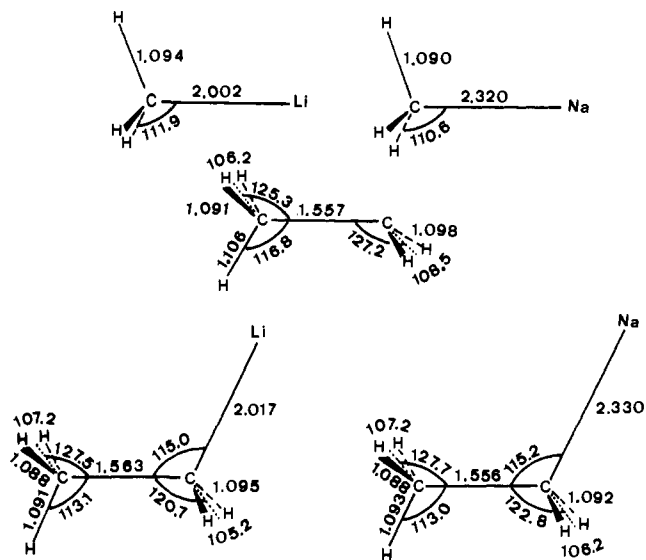
Figure 1. Geometries of α-hetero-substituted organolithium and organosodium compounds. Basis sets are 3-21G for neutral molecules and 3-21+G and 3-21+G$^{(*)}$ (values in parentheses) for anions. Bond distances in Å, angles in degrees. Superscript a indicates the dihedral angle HCYX.

If there are specific M–X interactions, the nature of the metal in MCH$_2$X should influence the nature of these species. For example, the quite different synthetic behavior of organolithiums and organocuprates is well-known, but even a change from Li$^+$ to K$^+$ may cause the chemistry to vary significantly.[2] A detailed comparison of sodium and lithium species, NaCH$_2$X and LiCH$_2$X, was a primary goal of the present study.
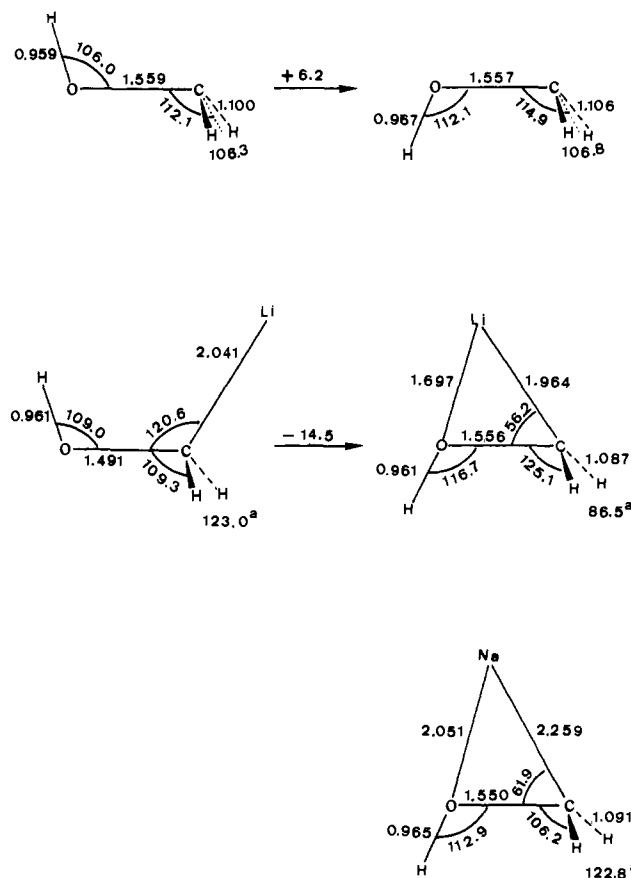
Our final objective was to explain why some organometallics, like MCH$_2$Cl and MCH$_2$F, exhibit carbenoid character rather than behaving as carbanions. Such carbenoids, which have already been studied in detail,[5,6,15] resemble MCH$_2^+$X$^-$ (**10**), with long M–X and C–X bonds, relatively positive carbon atoms, and low-lying LUMO's. We wished to see if the carbanion-like compounds would prefer structures more like XCH$_2^-$M$^+$ (**11**).

Figure 2. Geometries of nitrogen compounds; for details see Figure 1.

HOMO

(nucleophilic)
"carbanionoid"

10

LUMO

(electrophilic)
"carbenoid"

11

Methanes substituted by a metal and an electronegative atom or group typically have three isomeric non-tetrahedral structures.[6,7,15] However, the bridged geometries are more stable than the other two. Hence, the present paper only deals with the most stable bridged forms of each MCH$_2$X species, except where alternative conformations are computed in order to assess the importance of bridging.

Figure 3. Geometries of oxygen compounds; for details see Figure 1.

Computational Methods

Analytical gradient optimizations employed the GAUSSIAN 76 and GAUSSIAN 80 series of programs[16] and the 3-21G and 3-21+G basis sets[17]

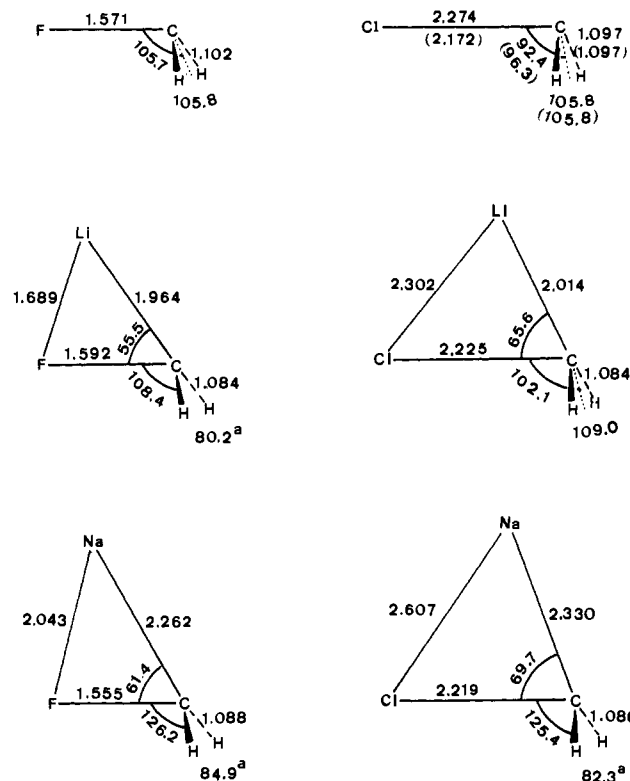(15) Rohde, C. Diplomarbeit, Erlangen, 1982.

Figure 4. Geometries of fluorine and chlorine compounds; for details see Figure 1.

for the neutral species. Single point calculations were carried out on the 3-21G geometries at the 6-31G* level[18] (6-31G*//3-21G). In a few cases, second-order Møller-Plesset (MP2)[19] correlation energy corrections were computed with use of the frozen core approximation (MP2/6-31G*//3-21G). The energies are given in Table I and the geometries are summarized in Figures 1-6.

The anion calculations included for comparison were carried out with basis set augmented by diffuse s and p functions on the heavy (nonhydrogen) atoms.[8,12] Such extra functions are necessary since carbanions generally have diffuse HOMO's. These basis sets (3-21+G, 4-31+G, and 6-31+G*[8,12]) improve the description of weakly bound anions dramatically. Stabilized anions, however, are more strongly bound so that diffuse functions are less important. As a result, the calculations summarized in Table II (second and third columns) show a more compressed (and realistic) range of anion stabilities than obtained by using normal split valence basis sets.

Such diffuse functions have little effect on the relative energies of the neutral organometallic species so that standard basis sets can generally be employed successfully. However, heteroatom lone pairs present problems especially when these are involved in bonding or partially bonding interactions. Polarization functions, which tend to describe the heteroatoms more satisfactorily, may be necessary for more refined quantitative comparisons. In extreme cases, notably for molecules containing N, O, F, and diffuse functions are also needed for neutral organometallics. Therefore, we have also optimized some geometries with 3-21+G, although 6-31G* energies are used in the following discussion. We have recognized more recently that diffuse functions may be even more effective than polarization functions in augmenting the basis sets of neutral species with lone pair electrons.[8]

Lithium and sodium compounds are generally well represented at the 3-21G level, because there are many more basis orbitals than electrons.
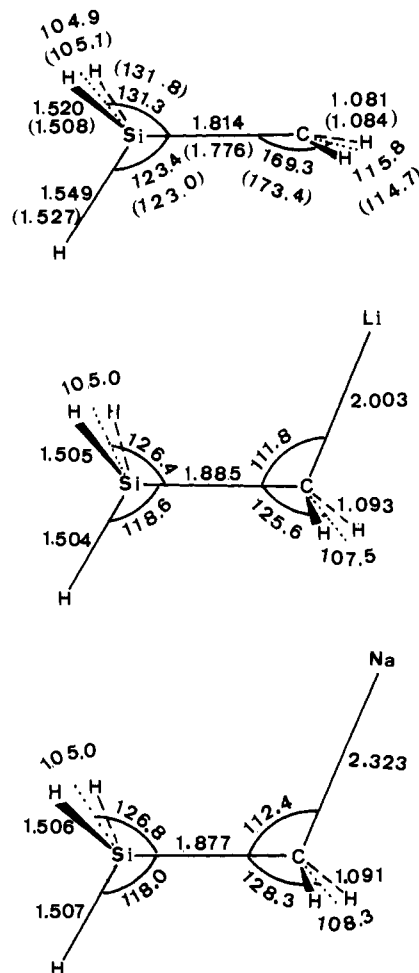
Figure 5. Geometries of silicon compounds; for details see Figure 1.
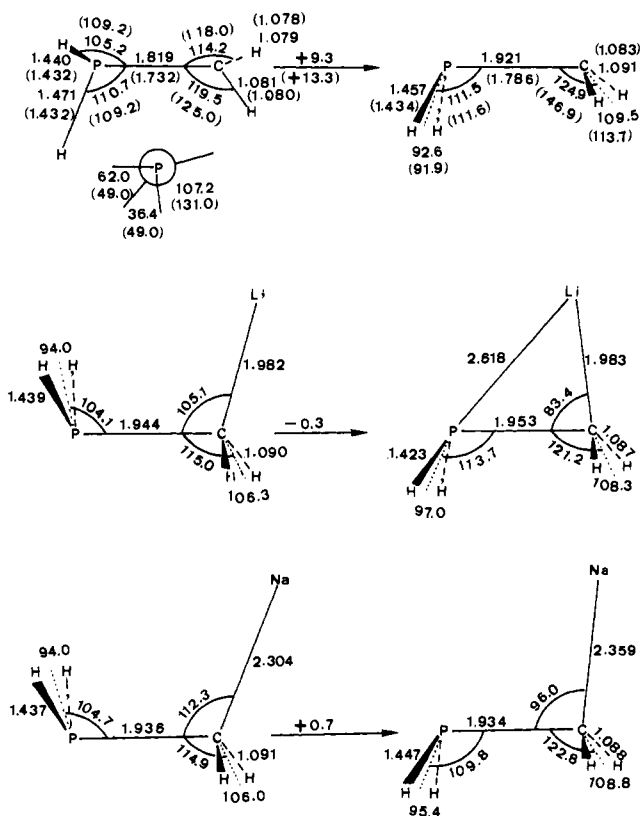
Figure 6. Geometries of phosphorus compounds; for details see Figure 1.

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Table I. Energies of Substituted Methanes, Methyl Anions, Methyllithium, and Methylsodium Derivatives

			CH$_3$X		
X	3-21G//3-21G^a	6-31G*//3-21G^b	3-21+G$^{(*)}$//3-21+G$^{(*)}$	6-31+G*//3-21+G$^{(*)}$	MP2/6-31+-G*//3-21+G$^{(*)}$
H	−39.97688	−40.19517	−39.97871	−40.19567	−40.33394
CH$_3$	−78.79395	−79.22861	−78.79678	−79.22935	−79.49718
NH$_2$	−94.68166	−95.20843	−94.69921	−95.21153	−95.51287
OH	−114.39802	−115.03378	−114.42608	−115.03850	−115.35658
F	−138.28189	−139.03339	−138.32116	−139.04178	−139.35259
SiH$_3$	−328.52612	−330.27240	−328.62815	−330.27396	−330.48887
PH$_2$	−379.53374	−381.48623	−379.64599	−381.48741	−381.72425
SH	−435.52629	−437.70030	−435.64223	−437.70128	−437.95539
Cl	−496.68949	−499.09297	−496.80118	−499.09399	−499.35690

		−CH$_2$X		
X	3-21G//3-21G^b	3-21+G$^{(*)}$//3-21+G$^{(*)}$	6-31+G*//3-21+G$^{(*)}$	MP2/6-31+G*//3-21+G$^{(*)}$
H	−39.23940^a	−39.29075	−39.50352	−39.65411
CH$_3$	−78.06125	−78.10041	−78.53070	−78.82140
NH$_2$	−93.95307	−94.01078	−94.51652	−94.83310
OH	−113.68144	−113.75386	−114.35190	−114.68514
F	−137.57673	−137.66057	−138.36485	−138.68762
SiH$_3$	−327.85073	−327.98356	−329.62238	−329.84865
PH$_2$	−378.84985	−378.99903	−380.83239	−381.08109
SH	−434.85247	−434.98906	−437.04319	−437.30883
Cl	−496.03877	−496.15671	−498.44210	−498.69906

	LiCH$_2$X			NaCH$_2$X	
X	3-21G//3-21G	3-21+G//3-21+G	6-31G*//3-21G	3-21G/3-21G	6-31G*//3-21G
H	−46.75248^a		−47.01549	−200.20030	−201.39970^c
CH$_3$	−85.56288^a		−86.04123	−239.01111	−240.42647
NH$_2$	−101.48281^c	−101.49619	−102.03778^c	−254.91461	−256.41028
OH	−121.21151^c	−121.23701	−121.86697^c	−274.64522	−276.24466
F	−145.09508^a		−145.87380	−298.52881	−300.25134
SiH$_3$	−335.31710		−337.10753	−448.76648	−491.49412
PH$_2$	−386.31949	−386.32770	−388.31065	−539.76677	−542.69359
SH	−442.32779	−442.33286	−444.53247	−595.77268	−598.91596
Cl	−503.50995		−505.93897	−656.95616	−660.32210

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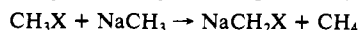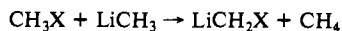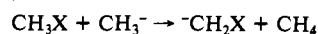
Table II. Substituent Stabilization Energies (kcal/mol) of Methyl Anions, Methyllithium, and Methylsodium Derivatives (MCH$_2$X)^a

	M = −(anions)					M = Li			M = Na	
X	3-21G//3-21G	3-21+G//3-21+G	3-21+G$^{(*)}$//3-21+G$^{(*)}$	6-31+G*//3-21G$^{(*)}$	best^b	3-21G	3-21+G	6-31G*//3-21G	3-21G	6-31G*//3-21G
H	0	0		0	0	0	0	0	0	0
CH$_3$	−3.0	+5.2		+4.1	+3.1	+4.2		+4.5	+3.9	+4.2
NH$_2$	−5.6	+0.3		+1.8	0.0	−16.0	−11.0	−6.0 (8.2)^c	−6.0	+1.2
OH	−13.1	−9.9		−3.5	−5.3	−23.8	−19.7	−8.5 (−9.4)^c	−14.9	−4.0
F	−20.3	−17.2		−9.6	−9.3	−23.6		−13.0	−14.8	−8.4
SiH$_3$	−39.0	−22.7	−27.2	−25.5	−24.9	−9.7		−9.3	−10.6	−10.8
PH$_2$	−33.6	+15.9	−25.7	−23.3	−23.0	−6.4	−5.5	−2.6	−5.6	−1.8
SH	−39.9	−23.8	−21.3	−21.3	−20.9	−16.3	−12.9	−7.4	−14.4	−7.0
Cl	−47.9	−35.1	−27.3	−25.3	−13.8	−28.2		−16.5	−27.2	−15.4

^{a} Calculated by isodesmic reaction, MCH$_3$ + CH$_3$X → MCH$_2$X + CH$_4$. ^{b} MP2/6-31+G*//3-21+G for first row;[8] MP2/6-31+G*//3-21+G$^{(*)}$ for second row.[9] Other theoretical levels give the following ranges of methyl anion stabilization energies:[8,9] NH$_2$, 0 to +2; OH, −9 to −10; F, −9 to −15; PH$_2$, −19 to −29; SH, −14 to −24; Cl, −16 to −35 kcal/mol. ^{c} MP2/6-31G*//3-21G values.[7]

On the other hand, this basis set becomes less adequate in the elements like N, O, and especially F to the right in the periodic table, since the ratio of occupied orbitals to basis orbitals steadily increases. As will be shown later, the 3-21G level overemphasis bridging, since the extra functions of the metals tend to compensate for the basis set inadequacies of the electronegative elements. This is corrected at the 6-31G* level (diffuse functions perform similarly).

The substituent stabilizations relative to the methyl carbanion, methyllithium, and methylsodium are compared in Table II, according to the following reactions:

$$CH_3X + CH_3^- \rightarrow {}^-CH_2X + CH_4$$

$$CH_3X + LiCH_3 \rightarrow LiCH_2X + CH_4$$

$$CH_3X + NaCH_3 \rightarrow NaCH_2X + CH_4$$

The addition of diffuse functions to the 3-21G basis set (3-21+G) gives results intermediate between 3-21G and 6-31G*. Table III gives the

relative proton, lithium cation, and sodium cation affinities of the various anions calculated by comparing the following reaction:

$$^-CH_2X + M^+ \rightarrow MCH_2X$$
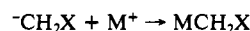
where M$^+$ = H$^+$, Li$^+$, and Na$^+$, with those for CH$_3^-$ (i.e., X = H). Table IV lists data for comparison purposes: the Li$^+$ and Na$^+$ cation affinities of the XH$_n$ first- and second-row bases and the M−X distances in the resulting MXH$_n^+$ complexes, in MXH$_{n-1}$ compounds, and in the most stable (bridged) conformations of the MCH$_2$X compounds.

Discussion

There is an interplay between the energetic effect of the substituents, X and the geometries of MCH$_2$X species. Noteworthy M−C and C−X bond length changes from the parent M−CH$_3$ and CH$_3$−X compounds are found when energetic effects are large. If the X groups have lone pairs, bridged structures, reflecting M−X

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Table III. Relative Proton, Lithium Cation, and Sodium Cation Affinities of α-Substituted Methyl Anions[a]

X	M = H best[b]	M = Li 3-21G	M = Li 6-31G*//3-21G	M = Na 3-21G	M = Na 6-31G*//3-21G
H	0	0	0	0	0
CH₃	-3.1	+1.2	+1.5	+0.9	+1.2
NH₂	-0.0	-16.6	-6.6 (-8.8)[c]	-6.6	+0.6
OH	+5.3	-18.2	-2.9 (-3.8)[c]	-9.3	+1.6
F	+9.3	-14.6	-4.0	-5.8	+0.6
SiH₃	+24.9	+15.6	+16.0	+14.7	+14.5
PH₂	+23.0	+15.9	+19.7	+16.7	+20.5
SH	+20.9	-1.8	+7.1	+0.1	+7.5
Cl	+13.8	-12.0	-0.3	-11.0	+0.8

[a] Evaluated by using the isodesmic reaction, $CH_2X^- + CH_3M \rightarrow CH_3^- + XCH_2M$. [b] See Table II, footnote *a*. [c] MP2/6-31G*//3-21G.

interactions, often result, and M–X distances are instructive. The metal cation affinities of the free bases, i.e., energies for the reaction $M^+ + XH_n \rightarrow M^+XH_n$ (Table IV), and the M–X distances in the resulting M^+XH_n complexes serve as references.

LiCH₂CH₃ and NaCH₂CH₃. The geometries of LiCH₃, LiCH₂CH₃, NaCH₃, NaCH₂CH₃ (3-21G), and the ethyl anion (3-21+G) are shown in Figure 1. There are no large differences in the geometries of the ethyl groups in C_2H_5Li and C_2H_5Na, but the CLi and CNa bond lengths are somewhat longer than the corresponding values in CH₃Li and CH₃Na. The widened CCM angles (115°) are noteworthy and exceed the widening of the HCM angles in the CH₃M derivatives. The C–H bond anti to the ethyl carbanion lone pair is 0.015 Å longer than the other two C–H bonds, and the corresponding HCC angle is widened to 116.8°; these geometrical effects, while diminished in C_2H_5Li and C_2H_5Na, are typical for carbanionic systems. The methyl group destabilizes the ethyl anions (Table II) C_2H_5Li and C_2H_5Na to slightly larger extents. As shown in Table III, the ethyl anion has a greater proton affinity than the methyl anion, but the Li^+ and Na^+ affinities of the ethyl anion are slightly less than those of the methyl anion.

LiCH₂NH₂ and NaCH₂NH₂. The geometries of $CH_2NH_2^-$ (3-21+G) and the lithium and sodium derivatives (3-21G and 3-21+G) are compared in Figure 2. The most stable organometallic structures are bridged; the alternative geometries with anti CH₂ and NH₂ groups are 14.3 kcal/mol less stable (6-31G*//3-21G). About 10 kcal/mol is required to rotate the aminomethyl anion into the analogous syn conformation; the energetic advantage of Li–N coordination obviously is very large. This is also shown in the bridged species by the shortening of both the Li–C distance (by 0.06 Å vs the value for CH₃Li) and the Li–N distance (by 0.08 Å vs. the value in the Li^+NH_3 complex[20]) (Table IV). The C–N distances in the bridged and unbridged complexes are essentially identical with those in the corresponding anions and in the syn forms are 0.11 Å longer than in CH₃NH₂ (1.472 Å, 3-21G). In NaCH₂NH₂, the Na–C and Na–N distances are also contracted relative to their values in C_2H_5Na and in $Na(NH_3)^+$. As expected, the M–N distances in LiNH₂ and in NaNH₂, also listed in Table IV for reference purposes, are considerably shorter.

The energetic consequences of bridging are large. Thus, the stabilization energy of syn LiCH₂NH₂ due to the amino group is 6.0 kcal/mol (6-31G*//3-21G), or 8.2 kcal/mol at MP2/6-31G*, whereas the NH₂ group destabilizes a methyl anion by 0.6 kcal/mol. An amino group is predicted to *destabilize* aminomethyllithium by 8.3 kcal/mol in the anti conformation, presumably due in large part to dipolar repulsions.

The amino group influence in NaCH₂NH₂ is more like the effect on the free anion. In spite of the bridged structure, the amino substituent destabilizes methylsodium. In fact, higher level optimizations are expected to eliminate most of the bridging tendencies found at the 3-21G level. With this relatively small

basis, bridging serves artificially to expand the inadequate basis set of the amino group by means of vacant orbitals on Na. Indeed, this tendency is paralleled by the general improvement in the description of molecules with lone pairs when diffuse orbitals or polarization functions are added to the basis.[8,9,21]

LiCH₂OH and NaCH₂OH. The structures of MCH₂OH species (Figure 3) are similar to those of amino compounds. Due to the occupation of π*-like orbitals, the C–O bond lengths, especially in the syn isomers, are up to 0.12 Å longer than that (1.440 Å, 3-21G) found in methanol. The Li–C and Li–O distances in bridged LiCH₂OH are 0.05 Å and 0.2 Å shorter than the corresponding values in CH₃Li and $LiOH_2^+$.[20] Bridged LiCH₂OH is ~14 kcal/mol lower in energy than the unbridged anti isomer; in contrast, the anti hydroxymethyl anion is about 6 kcal/mol more stable than the syn conformation.

The hydroxy group stabilizes the lowest energy bridged syn conformation of HOCH₂Li by about 9 kcal/mol, 3–4 kcal/mol more than it stabilizes the lowest energy anti conformation of $HOCH_2^-$. However, in the anti geometry of HOCH₂Li, the hydroxy group is actually destabilizing by about 8 kcal/mol. This effect must arise from dipolar repulsion between the partially charged $Li^{\delta+}$ and $H^{\delta+}$ (O) atoms in the anti conformation. Whereas hydroxymethyllithium is staggered, the free anion prefers a geometry corresponding to a eclipsed conformation of methanol.

NaCH₂OH prefers a bridged geometry similar to that of LiCH₂OH. The Na–C distance is between those in CH₃Na and C_2H_5Na. The Na–O distance is 0.07 Å shorter than in $NaOH_2^+$ but 0.17 Å longer than in NaOH. The thermodynamic consequences of bridging are negligible, however, and the hydroxy group actually stabilizes NaCH₂OH slightly less than it stabilizes ⁻CH₂OH. Once again, optimizations with larger basis sets would be expected to diminish the bridging tendency indicated at the 3-21G level.

LiCH₂F and NaCH₂F. As described in more detail elsewhere,[6,7] the preferred structure of LiCH₂F (Figure 4) generally resembles the NH₂ and OH species described above. The C–F length is now much longer (0.19 Å) than that in CH₃F (1.404 Å, 3-21G). The C–Li distance again is between those in C_2H_5Li and CH₃Li, but the Li–F distance is essentially the same as in $LiFH^+$. Fluorine stabilization in LiCH₂F is 4 kcal/mol greater than in CH_2F^-; much of this can be attributed to favorable FLi interactions in the bridged form. In contrast, the fluorine stabilization in NaCH₂F is essentially the same as in CH_2F^-. In the former, Na^+ is simply an ionic spectator; F exerts its normal stabilizing inductive effect in the ion pair as in the anion.

LiCH₂SiH₃ and NaCH₂SiH₃. SiH₃ is indicated to be the strongest anion stabilizer of the second-row substituents studied here. Indeed, α-silyl anions and organometallics are common synthetic intermediates.[22] This stabilization can be attributed to the high polarizability of Si and to the presence of low-lying σ* SiH orbitals.[23] Clearly d orbitals are unnecessary for stabilization, since the 3-21G basis (which has no d functions) grossly overemphasizes the stabilizing effect. Addition of diffuse orbitals or d functions reduces the stabilization energy to more reasonable values.[9] The negative SiH hyperconjugation is clearly shown by lengths of the anti (1.549 Å) and the syn SiH bonds (1.520 Å) (Figure 5). For comparison, the SiH lengths in CH₃SiH₃ are 1.490 Å (3-21+G//3-21+G). The CLi bond in methyllithium is 1.915 Å, but increases to 2.003 Å in H₃SiCH₂Li. The Si–C bond length is 1.885 Å in the lithium compound but contracts by 0.1 Å in the anion, another indication of increased C–Si bonding in the anion.

(20) Smith, S. F.; Chandrasekhar, J.; Jorgensen, W. F. *J. Phys. Chem.* **1982**, *86*, 3308. Also see: Del Bene, J. E.; Frisch, M. J.; Raghavachari, K.; Pople, J. A.; Schleyer, P.v.R. *J. Phys. Chem.* **1983**, *97*, 73.

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(22) For some leading references, see: (a) Peterson, D. J. *Organomet. Chem. Rev., Sect A* **1972**, *7*, 295. (b) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. (c) Burford, C.; Cooke, F.; Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1977**, *99*, 4537. (d) Seyferth, D.; Mammarella, R. E. *J. Organomet. Chem.* **1978**, *156*, 279. (e) Paquette, L. A. *Science (Washington, DC)* **1982**, *217*, 793. (f) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827. (g) Ager, D. J. *J. Org. Chem.* **1984**, *49*, 168.

(23) (a) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998. (b) Larson, J. R.; Epiotis, N. D. *J. Am. Chem. Soc.* **1981**, *103*, 410. (c) Durmaz, S. *J. Organomet. Chem.* **1975**, *96*, 331.

Table IV. Li^+ and Na^+ Binding Energies,[a] M–X Distances (Å) in M^+XH_n Complexes, Bridged (syn) MCH_2XH_{n-1} Conformations, and MXH_{n-1} Compounds

complex	3-21G//3-21G[b]		6-31G*//3-21G*[b] r_{M-X}			3-21G//3-21G r_{M-X} in MCH_2XH_{n-1}	3-21G//3-21G r_{M-X} in XMH_{n-1}
	ΔE (binding)	r_{M-X}	ΔE (binding)	6-31G*[b]	ΔH (exptl)[c]		
Li^+NH_3	−56.2	1.945	−44.9	2.002	−39.1 ± 2	1.869 ($LiCH_2NH_2$)	1.714 ($LiNH_2$)
Li^+OH_2	−57.0	1.769	−39.0	1.858	−34.0 ± 2	1.696 ($LiCH_2OH$)	1.537 (LiOH)
Li^+FH	−43.8	1.682	−27.9	1.793		1.689 ($LiCH_2F$)	1.520 (LiF)
Li^+PH_3	−28.5	2.575	−26.0			2.619 ($LiCH_2PH_2$)	
Li^+SH_2	−23.4	2.442	−17.9			2.438 ($LiCH_2SH$)	
Li^+ClH	−16.3	2.451	−13.7			2.295 ($LiCH_2Cl$)	2.112 (LiCl)
Na^+NH_3	−41.1	2.300	−32.5			2.228 ($NaCH_2NH_2$)	
Na^+OH_2	−41.3	2.118	−28.2		−24[d]	2.050 ($NaCH_2OH$)	1.869 (NaOH)
Na^+FH	−31.3	2.028	−20.7			2.043 ($NaCH_2F$)	1.863 (NaF)
Na^+PH_3	−20.6	2.936	−17.8			3.203 ($NaCH_2PH_2$)	
Na^+SH_2	−17.7	2.775	−12.5			2.847 ($NaCH_2SH$)	
Na^+ClH	−12.1	2.791	−8.8			2.607 ($NaCH_2Cl$)	2.422 (NaCl)

[a] Energies of the reactions, $M^+ + XH_n \rightarrow M^+XH_n$, in kcal/mol. [b] Reference 20. [c] Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501. For comparison with the calculated values, zero-point corrections to the 0 K motion-free state (3.2, 2.8, and 1.8 kcal/mol for the reactions of NH_3, OH_2, and FH, respectively)[20] are needed. This improves agreement, as does the use of larger basis sets and electron correlation corrections. [d] Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

The preferred geometries of both $LiCH_2SiH_3$ $LiCH_2SiH_3$ $NaCH_2SiH_3$ are staggered; the eclipsed conformations are 1.6 kcal/mol higher in energy. In these molecules, the C–M bond lengths are only 0.01 Å longer than the corresponding bond lengths in MC_2H_5. The Si–H bonds all contract from 1.52–1.55 Å in the anion to 1.504–1.507 Å in the organometallic species, and at the same time the C–M bonds lengthen. These geometrical changes indicate that most of the stabilizing effect of SiH_3 on the free anions is lost in the organometallic species. Indeed, the SiH_3 group stabilizes the organometallics to the extent of only 9–11 kcal/mol. The effect is unprecedented in the first-row substituents but has analogy in previous calculations on $LiCH_2BH_2$.[5] When lithium or sodium cannot bridge, the carbanionic character at the attached carbon is localized, and polarization by the SiH_3 group (or the BH_2 group)[5] diminishes. The SiH_3 substituent is less than half as effective in stabilizing either $LiCH_2SiH_3$ or $NaCH_2SiH_3$ than it is in stabilizing $^-CH_2SiH_3$. Although some additional stabilization is expected from inclusion of correlation, as is found for $LiCH_2BH_2$,[5] the generalization should hold.

The Li^+ and Na^+ affinities of $^-CH_2SiH_3$ (Table III) are quite low, reflecting the relatively low stability of the organometallics and the high stability of the anion.

$LiCH_2PH_2$ and $NaCH_2PH_2$. Like SiH_3, PH_2 stabilizes anions[22a,24] by polarization and by hyperconjugation.[9] The bond which is best arranged for hyperconjugation is stretched by 0.05 Å in the anions compared to the P–H bond of CH_3PH_2 (Figure 6). The P–C bond is 0.09 Å shorter in the anion. The lithium compound has a syn CH_2PH_2 geometry, but there is now only a 0.3 kcal/mol difference between the bridged and unbridged anti conformation. As observed for the OH and NH_2 species, the preferred conformation of the CH_2PH_2 unit is different in the free anion and in $LiCH_2PH_2$. While conversion of the gauche minimum of the phosphinomethyl anion to the syn conformation requires 9.3 kcal/mol (3-21+G, or 9.3–13.4 kcal/mol at higher levels), this higher energy conformation is the minimum for $LiCH_2PH_2$. This is due to dipolar effects and the attractive Coulombic and covalent interactions between Li and the phosphorus lone pair.

As observed for the SiH_3 derivative, the presence of a Li^+ counterion "shuts off" much of the stabilizing effect of the PH_2 group. The P–H and C–P bond lengths in $LiCH_2PH_2$ are essentially the same as the values found for CH_3PH_2. The large stabilizing effect of PH_2 on the anion is nearly eliminated in $LiCH_2PH_2$, due to electrostatic stabilization of the anion lone pair by the counterion.

The sodium compound is essentially unbridged. The staggered classical structure is now 0.7 kcal/mol lower in energy than the eclipsed, and the latter shows only 16° decrease in the CCNa
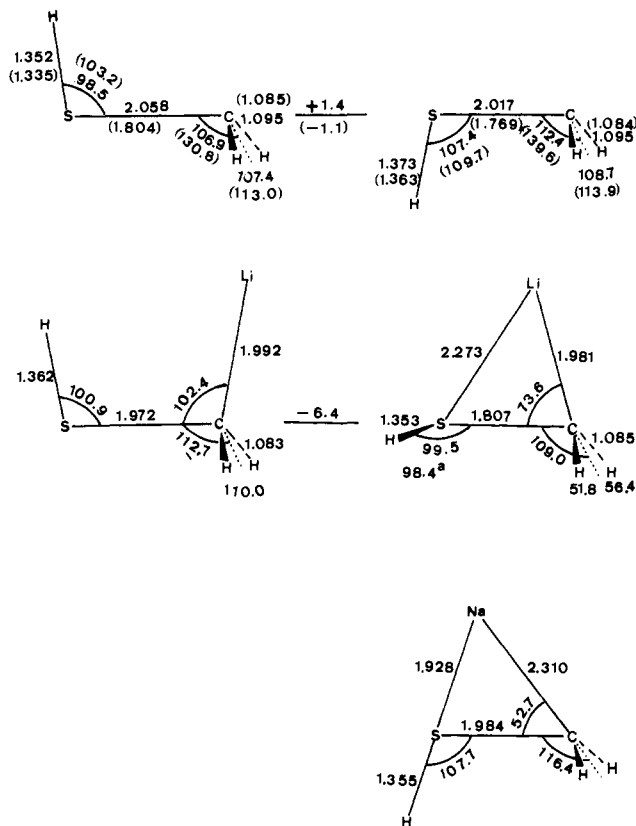
Figure 7. Geometries of sulfur compounds; for details see Figure 1.

angle. There is a 0.06-Å increase in the C–Na length in the eclipsed syn structure as compared to the staggered anti structure. Na is just as effective as Li in eliminating most of the stabilizing effect of the PH_2 group.

The failure of PH_2 to entice significant Li or Na bridging reflects the relatively small binding energy of Li^+ or Na^+ to PH_3 (Table IV). The Li–P and Na–P distances in the eclipsed structures are 0.05 and 0.27 Å longer than in the metal cation–PH_3 complexes. Like $^-CH_2SiH_3$, the phosphinomethyl anion has very low Li^+ and Na^+ affinities (Table III).

$LiCH_2SH$ and $NaCH_2SH$. The HS group stabilizes anions[23] mainly by a polarizability effect.[25] As discussed in detail elsewhere,[5b,9,24] d orbitals are not responsible, and their inclusion in the basis set actually diminishes the stabilization energy of $HSCH_2^-$. The geometry of the anti conformation (3-21+G) shows

(24) Peterson, D. J. *J. Organomet. Chem.* **1967**, *8*, 199. Corey, R. J.; Tiws, M. A. *Tetrahedron Lett.* **1980**, *21*, 3535, ref 5d. See ref 4 f for an X-ray structure. Karsch, H. H. *Chem. Ber.* **1982**, *115*, 818, 823.

(25) See ref 23b for an extensive list of references and interpretation of enhanced ability of second-row substituents to stabilize adjacent carbanions. Also see review: Kwart, H.; King, K. G. "d-Orbitals in the Chemistry of Silicon Phosphorus and Sulfur"; Springer-Verlag: Heidelberg, 1977; p 80 ff.

no evidence for SH hyperconjugation (Figure 7). However, the syn structure has a lengthened S–H bond and shortened C–S bond compared to the anti conformation and the corresponding values, 1.353 and 1.894 Å, in CH_3SH. The free anion has a very small conformational preference. The syn-mercaptomethyl anion is only 1.4 kcal/mol less stable than the anti form at the 3-21+G level, but the syn anion is 0.3 kcal/mol more stable at MP2/6-31G*//3-21+G. The lowest energy structure of $LiCH_2SH$ has nearly perpendicular HSC and LiCS planes (Figure 7, 3-21G). The high-lying 3p lone-pair orbital of S is thus aligned with Li vacant orbitals. This interaction geometry has been found to be favored generally in crystal structures of Lewis acid complexes of sulfides.[26] The energy is only modestly sensitive to rotation about the C–S bond, however. Relative to the C_1 bridged minimum, the C_s syn bridged structure is only 2.7 kcal/mol and the unbridged C_s anti conformation 6.4 kcal/mol higher in energy (3-21G). The Li–C distance is shorter than in C_2H_5Li, while the Li–S distance is nearly identical with that in $LiSH_2^+$.

The same generalizations hold for the Na compound, except that the C_s structure is the global minimum. The unbridged anti geometry of $NaCH_2SH$ is 4.2 kcal/mol less stable than the bridged minimum. Energetically, bridging provides only a small stabilization of the lithium and the sodium compounds. The coordination of Li^+ or Na^+ to the anion shuts off most of the stabilization by SH, but the bridging compensates for this, so that SH still provides 7 kcal/mol stabilization of $LiCH_2SH$ and $NaCH_2SH$.

Recent X-ray crystal structures of several $LiCH_2SR$ and $LiCR(SR')_2$ derivatives show no evidence of Li–S bridging in the sense being discussed here.[4a,e] This is expected since the carbanions are highly stabilized.

$LiCH_2Cl$ and $NaCH_2Cl$. While both of these carbenoid structures are bridged, the influence of chlorine on the stabilization energy of the free anion[25] is not enhanced. The large chlorine stabilization in the free anion (–16.2 kcal/mol) is nearly identical with the values for the Li and Na compounds (–16.5 and –15.4 kcal/mol, respectively). The Li–C and Na–C distances are essentially the same as the C_2H_5M values, while the C–Cl distances contract by 0.07 and 0.06 Å, in the Li and Na compounds, respectively, as compared to the anion (Figure 4). In these compounds, bridging must compensate for the decrease in stabilization of the anion by chlorine inductive electron withdrawal.[25] Since negative hyperconjugation is not possible in $ClCH_2^-$, chlorine polarization is the chief stabilizing effect. No $(p–d)_\pi$ conjugation is indicated by the results in Table II; the addition of d orbitals to chlorine actually *reduces* the stabilization energies.

Are Second-Row Substituent d Orbitals Important for Carbanion Stabilization? In agreement with earlier, but less extensive studies on the nature of carbanion stabilization by sulfur substituents,[5b,27] we have concluded that $(d–p)_\pi$ bonding is not significant. In a recent paper, Wolfe, LaJohn, Bernardi, Mangini, and Tonachini (WLBMT)[28] challenge these conclusions and claim that d-orbital effects are important after all. WLBMT do not analyze the stabilization energies but point out correctly that the geometries of sulfur compounds are improved significantly when d functions are added to the basis set. This is known to be general behavior for compounds of second-row elements.[29] WLBMT imply, but do not demonstrate that d-orbital effects are important energetically provided geometries optimized with such functions are employed.

Our results (Table II) disagree. Consider the $HSCH_2^-$ anion. With the 3-21G basis set, the stabilization energy (–39 kcal/mol
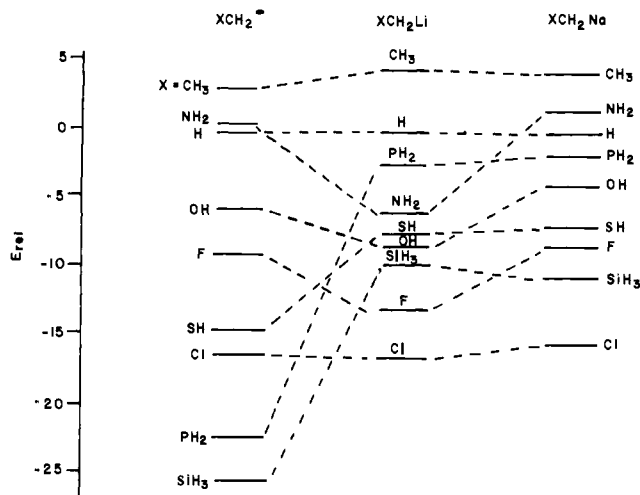
Figure 8. Comparison of stabilization energies of substituted methyl anions and their corresponding organosodium and organolithium compounds.

vs. CH_3^-) is too large. As pointed out by WLBMT, the 3-21G geometry is not very satisfactory at this level. Reoptimization at 3-21+G does not improve the geometry appreciably, but the diffuse functions reduce the stabilization energy to –22.7 kcal/mol, the near final value. Adding d functions to sulfur (3-21+G(*) basis set)[31b] and optimizing leads (Figure 7) to the change in preferred conformation and the shortening of the C–S bond noted by WLBMT, but the stabilization energy (–21.3 kcal/mol) actually becomes *smaller*. This is because the S d functions lower the energy of CH_3SH, the reference species, more than the energy of CH_2SH^-. Higher level single point calculations using the 3-21+G(*) geometries both without (–21.3 kcal/mol, 6-31+G*) and with electron correlation corrections (–20.9 kcal/mol, MP2/6-31+G*) do not change the stabilization energy.

We will go into more detail in a future publication,[9] but the data in Table II for the other second-row-substituted carbanions show variable effects. d-Orbitals only appear to contribute, modestly if at all, to the stabilization of $H_3SiCH_2^-$ and $H_2PCH_2^-$, but *destabilize* $ClCH_2^-$ (i.e., stabilize the neutral CH_3Cl more). The conclusion is clear: the stabilization of carbanions by second-row substituents is due chiefly to polarization and to negative hyperconjugation,[30] but not to d-orbital effects. d-Functions are important for the geometries of these species, but have little effect on the stabilization energies.

Summary

The organolithium and organosodium compounds differ from the corresponding anions in significant ways. Our computations lead to several generalizations.

(1) The tendency for bridging interaction between the metal and the α heteroatom follows the order of stabilities of the corresponding M^+XH_n complexes. Li^+ bridges more effectively than Na^+; presumably this trend will continue down the periodic table with K^+, Rb^+, and Cs^+, larger and more ionic cations.

(2) The second-row heteroatoms show little tendency to bridge with either Li or Na. α-NR_2, OR, and F-substituted organolithiums are strongly stabilized by bridging. These compounds are 5–10 kcal/mol more stable than the anions and as much as 20-kcal/mol more stable than the unbridged conformations. Dipolar interactions also favor the syn conformations.

(3) Hyperconjugative and polarization stabilization by SiH_3, PH_2, and SH are effectively eliminated in the corresponding organolithium and organosodium compounds. Only a small residual stabilization of the organometallic remains.

Figure 8 summarizes the energetic results pictorially. The extra stabilization of bridged organolithium compounds (X = NH_2, OH, F) and the greatly diminished stabilization of $LiCH_2X$ and

(26) See, for instance: Schmidt, M.; Hoffmann, G. G. *Z. Naturforsch G* **1978**, *33G*, 1334. *Inorg. Chim. Acta* **1979**, *32*, L19.

(27) (a) Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1975**, *97*, 2209. (b) Streitwieser, A, Jr.; Williams, J. E., Jr. *Ibid.* **1975**, *97*, 2209.

(28) Wolfe, S.; LaJohn, L. A.; Bernardi, F.; Mangini, A.; Tonachini, G. *Tetrahedron Lett.* **1983**, *24*, 3789. Also see: Wolfe, S.; Stolow, A.; LaJohn, L. A. *Ibid.* **1983**, *24*, 4071. Wolfe, S. *Can. J. Chem.* **1984**, in press.

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NaCH$_2$X when X = SiH$_3$, PH$_2$, and SH are quite obvious. The predicted stabilities of free anions decreases in the order X = SiH$_3$ > PH$_2$ > Cl > SH > F > OH > H > NH$_2$ > CH$_3$, while the order in the organolithium compounds, LiCH$_2$X, is X = Cl > F > SiH$_3$ > OH > SH > NH$_2$ > PH$_2$ > H > CH$_3$. The NaCH$_2$X species have the same relative energies as the free anions for first-row X substituents; for the second-row groups, the order of stabilities is the same as that for LiCH$_2$X.

In solution, either the organometallics are aggregated or the metal is solvated. Nevertheless, both solution and X-ray crystallographic studies indicate that the metal is closely associated to the formal anionic center.[4] The stabilities of anionic species in solution should follow an order intermediate between those calculated for the free anions and for the organometallics, since the anion is never really free. The calculations on monomers overestimate the tightness of association of the metal cation to the anion.

Finally, we note the close parallel between the tendency of lithium to bridge in the α-first-row heteroatom-substituted carbanions and the bridged structures found by Del Bene et al.[20] when Li$^+$ cations associate with the isoelectronic neutral analogues, NH$_2$NH$_2$, NH$_2$OH, NH$_2$F, etc. For example, the conformation of hydrazine alters so that both lone pairs can interact simultaneously with Li in the N$_2$H$_4$Li$^+$ complex.

Tricarbon Monoxide—A Theoretical Study

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Abstract: On the basis of molecular orbital calculations at the HF level with 6-31G* basis and MP3 correlation correction, C$_3$O is predicted to be a stable linear molecule with a singlet ground state. The lowest triplet state lies 168 kJ mol^{-1} above this. The fully optimized geometry leads to a predicted rotational constant within 0.2% of that determined experimentally from the microwave spectrum. C$_3$O is predicted to be stable with respect to dissociation into C$_2$ + CO by 433 kJ mol^{-1} and to have $\Delta H_f°$ of 282 kJ mol^{-1}. The dipole moment is predicted to be 1.85 D compared with the experimental value of 2.391 D. Various possible dimers were studied at the HF/STO-3G level. We conclude that gas-phase dimerization of C$_3$O is not likely to be rapid. A preliminary study of the reaction pathway for C$_3$O + C$_2$H$_4$ implies that reaction will not be rapid. Both the predicted internuclear distances and the Mulliken population analysis imply that the CC bonds are double and the CO bond is of somewhat higher order. The description in terms of Pauling resonance structures seems to represent the structure quite well.

Theoretical studies of the oxides of carbon have been almost exclusively devoted to CO and CO$_2$ although there has been some consideration of the well-known higher homologue of CO$_2$—tricarbon dioxide (carbon suboxide, C$_3$O$_2$). For example, Pauling,[1a] in a discussion of CO$_2$ and related molecules, discussed the geometry of C$_3$O$_2$ and wrote down resonance structures that include $^-$O—C≡C—C≡O$^+$. His analogous discussion[1b] of CO did not, however, include speculation about possible higher homologues for which analogous resonance forms could be written, the simplest being tricarbon monoxide, C$_3$O, for which a polar resonance form $^-$C≡C—O≡O$^+$ can be written, analogous to $^-$C≡O$^+$ for carbon monoxide.

Quantum chemical calculations on the oxides of carbon have been focused on CO, CO$_2$, and the oxycumulenes, C$_n$O$_2$, especially C$_3$O$_2$. We have been unable to find any previous theoretical study of C$_3$O.

Since simple valency arguments suggest that C$_3$O might bear the same relation to CO as does C$_3$O$_2$ to CO$_2$, we have speculated

Table I. Structure and Geometrical Parameters for C$_3$O

C$_3$–C$_2$–C$_1$–O

| level of calc/basis | optimum bond lengths (pm) in C$_3$O | | |
	C$_3$C$_2$	C$_2$C$_1$	CO
HF/STO-3G	125.6	129.2	116.9
HF/3-21G	125.7	127.9	114.7
HF/4-31G	126.0	128.1	114.7
HF/6-31G*	125.6	129.5	112.9
MP3/6-31G*	127.2	130.3	115.1

on the possibility of it intervening in the galactochemistry of interstellar molecular clouds. An extension of our theoretical model of such clouds[2] indicated that C$_3$O might be detectable in some molecular clouds. Preliminary investigations predict an abundance of C$_3$O similar to that of HC$_3$N, a widely observed interstellar species. It also seemed possible that a laboratory detection might be feasible.[3] As a basis for planning the gen-

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(2) Brown, R. D.; Rice, E. *Philos. Trans. R. Soc. London, Ser. A,* **1981**, *303*, 523–533.