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Allyllithium, Allylsodium, and Allylmagnesium Hydride: Geometries and Bonding. A Comparative ab Initio Study

Timothy Clark, Cornelia Rohde, and Paul von Ragué Schleyer*

Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen,
Federal Republic of Germany

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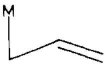
Allyllithium, allylsodium, and allylmagnesium hydride have been investigated by ab initio molecular orbital theory. The lithium and sodium compounds are predicted to have symmetrically bridged structures. Allylmagnesium hydride prefers an unsymmetrical geometry, but the barriers for 1,3 MgH shift and CH_2 group rotation (stereomutation) are quite low. The bonding of allyl organometallic compounds is analyzed by truncating the metal basis sets; the p and then the sp valence functions were removed. Point charge models also were employed. The bending of the allyl hydrogens out of the plane of the three carbon atoms (the middle hydrogen toward and the inner, terminal hydrogens away from the metal) is mainly due to electrostatic interactions, rather than the involvement of metal p functions. On the other hand, the Li_{2p} (and Li_{2sp} valence) functions contribute significantly to the quantitative aspects of the bonding and favor the symmetrically bridged structure preferentially. The rotation barrier in unsolvated monomeric allylsodium is predicted to be lower than that in the corresponding lithium compound, in contrast to experimental observations in solution.

Introduction

The possible structures of allylmetal complexes involve a gradation between two extremes: static σ bonding to a single carbon (1) and static symmetrical π bridging (2a)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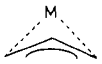
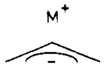
(or ion pairing (2b)). Fluxional systems are intermediate


2a


2b

and may involve oscillation between σ forms 3 or between unsymmetrical π structures (or ion pairs) 4.[1] The detailed nature of allyl alkali-metal and allylmagnesium compounds has long been of interest.[2-13] Initial infrared, UV, and ^1H NMR evidence suggested substantial differences between allyllithium and allylmagnesium derivatives.[2,3] The latter undergo rapid degenerate rearrangement (3) and possess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more covalent σ character. Allyllithium compounds are obviously more ionic, but experimental data have not been able to define the nature of the bonding unequivocally. For example, the barrier to CH_2 group rotation in allyllithium is the lowest among all alkali-metal derivatives (Li < Na < K < Rb < Cs)[9] and is only about half as large as that expected in a free allyl anion (22 kcal/mol).[14] This indicates lithium–allyl attachment in rotational transition states, like 1 (syn or anti), involving the metal. Although contact ion pair (2b) or multicenter covalent (2a) formulations are generally employed in discussion of allyllithium, the further complications due to dimerization (or higher aggregation) and solvation have been widely recognized.

Theoretical studies at various levels of sophistication[4-7] are unanimous in predicting the preferred structure for *monomeric, unsolvated* allyllithium to have C_s symmetry with lithium bridging symmetrically between C_1 and C_3 (2). Since earlier calculations had assumed a planar allyl moiety, our complete STO-3G optimization[7] revealed for the first time unusual out-of-plane deviations for the allyl hydrogens. The inner hydrogens on C_1 and C_3 were predicted to bend *away* from lithium, whereas the unique hydrogen on C_2 was found to bend *toward* the metal. These distortions from a planar allyl geometry were said to provide better bonding due to an increase in C–Li overlap.[7] The bonding in allyllithium was interpreted as being largely ionic with some multicenter covalent character involving a Li p orbital and the allyl anion HOMO. It is particularly gratifying that the X-ray structure of bis(π-allyl)nickel[8a] confirms the geometrical features of the allyl moiety predicted earlier.[7] Other predictions of the theory such as the relative heights of the syn and anti CH_2 rotation barriers[9] and the thermodynamic stability[10] of allyllithium were also in excellent agreement with experiment, despite the neglect of aggregation or solvation. This suggests that calculations on isolated monomers may

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provide information of use to experimentalists.

In contrast, Schlosser and Staehle,[11] in one of three independent applications[11–13] of Saunders' isotopic labeling technique[15] to allyllithium, chose to describe theoretical studies as "unrealistic". The small asymmetry of allyllithium claimed by these workers, based on tiny differences between expected and observed ^{13}C chemical shifts upon deuterium substitution, was interpreted in terms of a fluxional monomer, 4-Li. This assignment cannot be regarded as secure in view of the possibility of unsymmetrical aggregation,[16] the uncertainty of the estimated chemical shift changes,[17] the lack of temperature dependence studies, and the perturbation by deuterium substitution of the lowest vibration of allyllithium (a swinging motion of the metal toward C_1 or C_3). While the time-averaged structure of deuterated allyllithium when this vibrational level is populated must therefore be slightly unsymmetrical, motionless allyllithium is indicated to have C_s symmetry.[7,12,13]

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The uncertainty as to the nature of allyllithium in solution[2a,10,16] complicates the interpretation of experimental studies. The degree of aggregation of allyllithium is known to vary with the solvent and with the concentration; the "structure" depends on the conditions. Indeed, a low-resolution X-ray structure of allyllithium, which became available as this paper was being written, shows an *endless polymer* with TMEDA-solvated lithium attached to *both* terminal allyl carbons.[18] Smaller aggregates joined in a similar manner would be unsymmetrical and might account for the NMR observation.[11]

The ^{13}C^{1}H coupling constants of alkali-metal and magnesium allyl and pentadienyl[3,19–21] derivatives have been determined several times, with good agreement. For the parent allyl system, the values vary remarkably little with changes in the alkali metal (Li, Na, K, Rb, and Cs)[3,12] and with changes in conditions. Thus, the ^{13}C^{1}H coupling constants of allyllithium increase by 4 Hz or less in going from a 2 M solution in tetrahydrofuran (where the association number is 1.4 or more)[16] to a 2 M solution in diethyl ether (where the association number is at least 12).[10] The C_2–H coupling constant (131–133 Hz in THF for all alkali metals)[12,19] is the most remarkable, being reduced by about 15 Hz from the normal sp^2 value found in propene (157.4 Hz). The average C–H coupling constant at the terminal carbons (145–149.5 Hz) deviates from the propene values (161–163 Hz)[22] to a smaller extent. However, stereomutation in allylrubidium[12] and in allylpotassium[11] is sufficiently slow that individual values for the inner (143 Hz) and outer (154–155 Hz) methylene hydrogens can be measured; the allyllithium coupling constants are 140.8 and 149.8 Hz, respectively.[21] What causes these lowerings?

In his comprehensive studies of the NMR spectra of a variety of lithium compounds, Van Dongen[3] was unable to differentiate between changes in hybridization and changes in the effective nuclear charge at carbon as the principle factor causing a decrease in C–H coupling constants. For example, the value of the α-carbon of vinyllithium, 88 Hz, seems impossible to explain on the basis of rehybridization alone. Bywater et al.[12] concluded that "other factors than hybridization are important in the determination of $J(^{13}C^1H)$". Schlosser and Staehle,[19] on the other hand, only considered hybridization in their audaciously detailed interpretation of the structural deformations to be expected in the allyl derivatives. The effects were attributed entirely to the bending of the hydrogens out of the CCC plane toward or away from the metal (assumed to be in a π-bridging position).

The detailed structural proposal of Schlosser and Staehle[19] agrees qualitatively with the features we predicted earlier by theoretical calculations[7] on symmetrically π-bridged allyllithium: the outer hydrogens remain more or less in the carbon plane, but the inner hydrogens bend away from and the middle hydrogen bends toward the metal. Nearly identical values are found in the X-ray structures of bis(π-allyl)nickel[8a] and an allylnickel phosphine derivative.[8b] In particular, the middle hydrogen is bent less out of the plane than the inner hydrogens. This is contrary to Schlosser's NMR interpretation, that the out-of-plane distortion of the middle hydrogen is the most extreme. We do not believe that the $J(^{13}C^1H)$ values are correctly interpreted on this basis. There are several reasons:

1. The more ionic and larger alkali metals in, e.g., allylrubidium and allylcaesium, are much further from the allyl fragments. Such metal–allyl interactions cannot produce as much distortion as in allyllithium. This is shown by comparing our calculated structures of allyllithium and allylsodium (described below); the trend should continue for K, Rb, and Cs. However, C–H coupling constants *do not change* in going from lithium to the larger alkali metals.[12,19] Although there may be compensating geometrical changes along these series (see below), allylcesium must have a more nearly planar allyl anion moiety. Reduction in the magnitude of the coupling constants must be due to effects other than those postulated by Schlosser and Staehle;[19] these effects must be present in allyllithium as well.

2. Bis(π-allyl)nickel[8a] and the allylnickel phosphine complex[8b] are known from their X-ray structures to have the kind of distorted geometries we have found calculationally for the allyllithium monomer (now being postulated by Schlosser for allylpotassium in solution). However, the ^{13}C–H coupling constants in these π allylnickels (middle H, 154, inner H, 151, and outer H, 161 Hz)[21] when compared with those of propene vinyl hydrogens (middle H, 157, inner H, 163, and outer H, 161 Hz)[22] do show modest decreases, but the magnitude is far less than expected on the basis of Schlosser's interpretation.[19]

3. Allyllithium in a 2 M solution in diethyl ether shows nearly the same C–H coupling constants as in tetrahydrofuran,[12,19,21] depsite the differences in aggregation

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Table I. C_3H_5Li: Geometries (3-21G),[a] Total Energies,[b] and Relative Energies[c]

	5-Li	7-Li	8-Li
geometries			
C_1C_2	1.393	1.322	1.320
C_2C_3		1.522	1.534
C_1Li	2.141		
C_2Li	2.093	2.891	3.043
C_3Li		2.013	2.020
CCC	125.9	126.3	125.7
C_2C_1Li	68.9		
C_2C_3Li		109.0	117.2
$LiC_2C_1C_1$	49.1		
$H_1C_1C_2C_1$	−28.1		
$H_2C_1C_2C_1$	1.0		
$H_3C_2C_1C_1$	168.7		
total and rel energies			
3-21G//3-21G	−123.228 23 (0.0)	−123.199 79 (17.8)	−123.194 15 (21.4)
6-31G*//3-21G	−123.917 21 (0.0)	−123.891 09 (16.4)	−123.884 87 (20.3)
6-21G*//3-21G	−123.794 15 (0.0)	−123.767 04 (17.0)	−123.761 60 (20.4)
MP2/6-21G*//3-21G	−124.069 51 (0.0)	−124.041 37 (17.7)	−124.036 17 (20.9)

[a] Bond lengths in angstroms and angles in degrees. [b] In hartrees (= 627.49 kcal/mol). [c] In parentheses (kcal/mol).

numbers in the two solvents.[10,16] The X-ray structure of allyllithium, determined recently,[18] shows endless polymeric units with lihtium attached to both C_1 and C_3 of each allyl unit. Similar structures are to be expected for the allyllithium aggregates in solution. Such aggregated structures, which do not have symmetrically π-briding lithiums, must also be capable of explaining the C–H coupling constants. Allyllithium is also known to be associated in THF, but to a diminished extent.[16]

4. In-plane angular distortions probably are more effective than out-of-plane distortions in causing rehybridization at carbon. The dependence of CH coupling constants on ring size has long been appreciated; e.g., Laszlo pointed out many years ago that the small C–H coupling constants in the cyclononatetraenyl anion (137 Hz) can be explained on this basis.[23] Because of the 1–3 antibonding character of the allyl anion HOMO, the C–C–C angle widens to 132°. This is shown quite consistently by ab initio calculations at various levels including basis sets augmented by diffuse functions.[14,24] This C–C–C angle widening alone, or in conjunction with out-of-plane hydrogen bending, accounts best for the low coupling constants of the central hydrogen. It should be possible to test this hypothesis by examining the NMR spectra of cyclic allyl anions involving smaller rings. (See note added in proof.)

Our alternative explanation can also be tested by examining pentadienyl anions in acyclic and cyclic systems.[19,20] In the W form of pentadienyllithium only the two outer angles are widened, but not the inner $C_2C_3C_4$ angle.[25] In the pentadienyl anion HOMO, nodes are present at C_2 and C_4, but antibonding π interactions between C_1, C_3, and C_5 lead to larger angles. The degree of angle widening found calculationally correlates with the C–H coupling constants reported experimentally.[20] In the cyclohexadienyl anion and the cycloheptadienyl anion, such angle widening is restricted by the cyclic structure, and smaller deviations from the normal sp^2 values result.[20g]

In view of the criticisms[11,19] of our work[7] and because we believe that molecular orbital calculations represent the only reliable method currently available to determine the structure of monomeric, unsolvated organoalkalimetal compounds, we have reexamined the structure of allyllithium at higher theoretical levels. Indicative of the progress in ab initio programs made since our first paper,[7] we have now optimized all structures with a split-valence basis set and have included allylsodium and allylmagnesium hydride (a model for Grignard reagents)[26] for comparison.

The comparison of these three compounds at a uniform level of theory should provide indications of trends to be expected in π-allyl compounds and provide a conceptual basis for further experimental studies.

Methods

All calculations used the GAUSSIAN 76 series of programs.[27] Geometry optimizations with the 3-21G[28] (33-21G for Na and Mg)[29] basis set were performed by using analytically evaluated atomic forces[30] in a Davidon–Fletcher–Powell search routine.[31] Single point calculations on the 3-21G optimized geometries were carried out by using the 6-21G*[28,29,32] and 6-31G*[33,34] basis sets. For 6-21G* calculations it was also possible to apply a second-order Møller–Plesset correction for electron correlation[35] (MP2). MP2 calculations did not include nonvalence orbitals.

Results and Discussion

The geometries and energies of allyllithium, -sodium, and -magensium hydride are summarized in Tables I, II,

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Table II. C_3H_5Na: Geometries (3-21G),[a] Total Energies,[b] and Relative Energies[c]

	5-Li	7-Na	8-Na
geometries			
C_1C_2	1.393	1.321	1.321
C_2C_3		1.518	1.530
C_1Na	2.475		
C_2Na	2.426	3.184	3.322
C_3Na		2.323	2.331
CCC	128.1	127.3	125.6
C_2C_1Na	71.6		
C_2C_3Na		110.2	117.2
$NaC_2C_1C_1$	54.9		
$H_1C_1C_2C_1$	−23.4		
$H_2C_1C_2C_1$	−4.2		
$H_3C_2C_1C_1$	172.6		
total and rel energies			
3-21G//3-21G	−276.670 14 (0.0)	−276.648 61 (13.5)	−276.642 75 (17.2)
6-31G*//3-21G	−278.294 70 (0.0)	−278.276 61 (11.4)	−278.270 13 (15.4)
6-21G*//3-21G	−278.175 21 (0.0)	−278.154 02 (13.3)	−278.148 35 (16.9)
MP2/6-21G*//3-21G	−278.453 59 (0.0)	−278.434 63 (11.9)	−278.429 35 (15.2)

[a] Bond lengths in angstroms and angles in degrees. [b] In hartrees (= 627.49 kcal/mol). [c] In parentheses (kcal/mol).

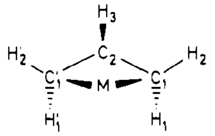
Table III. C_3H_5MgH: Geometries (3-21G),[a] Total Energies,[b] and Relative Energies[c]

	5-MgH	6-MgH	7-MgH	8-MgH
geometries				
C_1C_2	1.400	1.334	1.319	1.318
C_2C_3		1.499	1.520	1.533
C_1Mg	2.310			
C_2Mg	2.309	2.571	3.030	3.100
C_3Mg		2.111	2.117	2.117
CCC	124.8	125.9	126.3	124.6
C_2C_1Mg	72.3			
C_2C_3Mg		89.2	111.2	115.3
$MgC_2C_1C_1$	49.1			
$H_1C_1C_2C_1$	−33.3			
$H_2C_1C_2C_1$	2.4			
$H_3C_2C_1C_1$	166.8			
total and rel energies				
3-21G//3-21G	−314.861 24 (2.8)	−314.865 65 (0.0)	−314.858 89 (4.2)	−314.853 12 (7.9)

[a] Bond lengths in angstroms and angles in degrees. [b] In hartrees (= 627.49 kcal/mol). [c] In parentheses (kcal/mol).

and III, respectively. The full 3-21G geometries are available as supplementary material.

Allyllithium. The 3-21G optimized geometry of allyllithium, **5**-Li, confirms the features found in our STO-3G study.[7] In particular, the deviations of the hydrogen atoms from the $C_1C_2C_3$ plane are similar in both studies. The two "classical" structures **7**-Li and **8**-Li lie higher in energy. The estimated MP2/6-31G* rotation barrier for monomeric allyllithium (via **7**-Li) is 17.1 kcal/mol, compared with 10.7 kcal/mol observed[9] in solution for, presumably,[10,16] an aggregate. The best available rotation barrier for the allyl anion (MP2/4-31+G//4-31+G) is 22.2 kcal/mol.[14,24] Interestingly, the best allyl anion rotation transition state is the perpendicular form in which the lone pair is anti to the olefinic methylene group,[14] whereas the better of the two allyllithium rotation transition states is the perpendicular structure in which the metal is syn to the double bond.



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Allylsodium. The three allylsodium isomers **5**-Na, **7**-Na, and **8**-Na exhibit similar geometries to their lithium counterparts. However, symmetrically bridged **5**-Na, calculated to be the most stable form, reveals structural details that are closer to the unperturbed allyl anion than in **5**-Li, although thermodynamic considerations[36] indicate that sodium and lithium compounds are equally ionic. The unique hydrogen in allylsodium, for instance, lies only 7.4° above the C–C–C plane, compared with 11.3° in **5**-Li. Similarly, the out-of-plane angle of the C_1H_1 bond in **5**-Na (−23.4°) is lower than that in **5**-Li (−28.1°). The C–C bond lengths are similar for M = Li or Na, but the C–C–C angle is smaller (125.9°) in **5**-Li than in **5**-Na (128.1°). The 4-31+G value for the free allyl anion[14] is 131.6°, again indicating the larger deformation of the C_3H_5 fragment in the lithium compound. The rotation barrier for allylsodium (via **7**-Na) is 11.9 kcal/mol, compared with 17.7 kcal/mol for allyllithium (MP2/6-21G*). This is somewhat unexpected, as the rotation barrier in the allyl anion is higher than that in allyllithium; allylsodium should be expected to lie between the two. Experimentally[9] the rotation barriers of allylpotassium and allylcesium in solution are higher than that of allyllithium although there are clear experimental indications[37] that more than one form exists for such compounds and that rotation barriers are lower in the metastable form. The situation may also be similar to that for the planar inversion of RCH_2Li compounds, in which aggregation lowers the barrier.[38] The lithium compound would then be expected to show the

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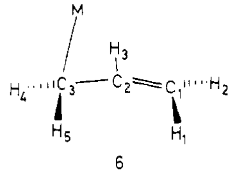
[36] (a) Clark, T.; Rohde, C.; Schleyer, P. v. R., manuscript in preparation. (b) See also: Schleyer, P. v. R.; Chandrasekhar, J.; Kos, A. J.; Clark, T.; Spitznagel, G. W. *J. Chem. Soc., Chem. Commun.* **1981**, 882.

[37] See ref 12. If allylsodium, allylpotassium, allylrubidium, or allylcesium are prepared and kept below −20 °C, a metastable, freely rotating form is observed.

[38] Clark, T.; Schleyer, P. v. R.; Pople, J. A. *J. Chem. Soc., Chem. Commun.* **1978**, 137.

lowest barrier as the covalent stabilization of the transition state[38] in the aggregate must be more effective for lithium than for sodium. Our calculations, however, clearly predict a *lower* barrier for *unsolvated monomeric* allylsodium than for the lithium counterpart.

Allylmagnesium Hydride. The lowest energy structure for allylmagnesium hydride is found to be the C_1 geometry **6-MgH**. NMR studies[19] also suggest allyl Grignard reagents to be unsymmetrical. The C–C bond lengths are unequal, but not as much as in the syn and anti isomers **7** and **8**. The C_2C_3Mg angle is 89.2° and represents a compromise between the bridged structure **5** and a "classical" geometry. The allyl moiety in **6-MgH** shows small deviations from planarity at C_1 and C_2 in the same directions as expected from **5-Li** and **5-Na**.



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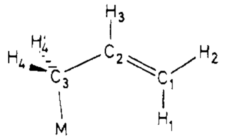

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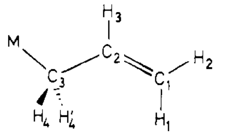

8

The C_s-bridged structure **5-MgH** illustrates the effects of covalent interactions on the geometry of the C_3H_5 fragment. The deviations from planarity are larger, but in the same direction as for **5-Li**. Similarly, the C–C–C angle is smaller than in **5-Li**. There deviations can be attributed to covalent overlap in **5-MgH**, although electrostatic factors can also cause similar distortions (see below). The barrier for a 1,3 MgH shift is calculated to be 2.8 kcal/mol and for a rotation about the C_2C_3 bond 4.2 kcal/mol, again via **7-MgH** (3-21G).

Discussion

The nature of the C–Li bond and of the bonding in allyllithium has been the subject of a number of papers.[39,40] In an attempt to identify the effects responsible for the structural preferences of allylmetal compounds we have carried out a number of model calculations intended to emphasize or eliminate certain properties of the metal atom.

Table IV. C_3H_5M (M = Li, Na): Geometries (3-21G-p),[a,b] Total Energies,[c] and Relative Energies[d]

	5-Li	7-Li	8-Li	5-Na	7-Na	8-Na
geometries						
C_1C_2	1.396	1.321	1.321	1.393	1.321	1.321
C_2C_3		1.519	1.533		1.517	1.529
C_1M	2.100			2.367		
C_2M	2.106	2.951	3.038	2.388	3.111	3.289
C_3M		2.012	2.015		2.264	2.268
CCC	125.9	126.7	125.8	127.8	126.5	125.7
C_2C_1M	70.8			78.3		
C_2C_3M		112.6	117.2		109.2	118.8
$MC_2C_1C_1$	42.5			45.8		
$H_1C_1C_2C_1$	166.5			169.8		
$H_2C_1C_2C_1$	−33.2			−28.6		
$H_3C_2C_1C_1$	1.8			−2.5		
total and rel energies	−123.197 17 (0.0)	−123.188 78 (5.3)	−123.182 79 (9.0)	−276.638 18 (0.0)	−276.628 29 (6.2)	−276.622 11 (10.1)

[a] Normal 3-21G basis set, but lithium without 2p orbitals and sodium without 3p orbitals. [b] Bond lengths in angstroms and angles in degrees. [c] In hartrees (= 627.49 kcal/mol). [d] In parentheses (kcal/mol).

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(39) Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1980**, 672. Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Organomet. Chem.* **1972**, *44*, 59. Cowley, A. H.; White, W. D. *J. Am. Chem. Soc.* **1969**, *91*, 34. Baird, N. C.; Barr, R. F.; Datta, P. K. *J. Organomet. Chem.* **1973**, *59*, 65. Fitzpatrick, *J. Inorg. Nucl. Chem. Lett.* **1974**, *10*, 263. Hinchliffe, A.; Saunders, E. *J. Mol. Struct.* **1976**, *31*, 283. Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1978**, 137. Graham, G.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 5759. Graham, G. D.; Marynick, D. S.; Lipscomb, W. *Ibid.* **1980**, *102*, 4572. Herzig, L.; Howell, J. M.; Sapse, A. M.; Singman, E.; Snyder, G. *J. Chem. Phys.* **1982**, *77*, 429.

(40) Streitwieser, A., Jr.; Williams, J. E.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980**, *1*, 81. Streitwieser, A., Jr. *J. Organomet. Chem.* **1978**, *156*, 1.

Table V. C_3H_5+:[a] Geometries (3-21G),[b] Total Energies,[c] and Relative Energies[d]

	5-+	7-+	8-+
geometries			
C_1C_2	1.415	1.317	1.316
C_2C_3		1.484	1.492
C_1+	1.541		
C_2+	1.598	2.192	2.212
C_3+		1.112	1.110
CCC	115.4	125.2	126.1
C_2C_1+	65.3		
C_2C_3+		114.4	115.7
$+C_2C_1C_1$	25.6		
$H_1C_1C_2C_1$	−47.5		
$H_2C_1C_2C_1$	9.1		
$H_3C_2C_1C_1$	166.5		
total and rel energies	−116.105 75 (85.9)	−116.242 57 (0.0)	−116.237 40 (3.2)

[a] + means a point positive charge, i.e., a proton without orbitals. [b] Bond lengths in angstroms and angles in degrees. [c] In hartrees (= 627.49 kcal/mol). [d] In parentheses (kcal/mol).

The simplest of these calculations used the normal 3-21G basis set without 2p orbitals on lithium. Compounds **5**-Li, **7**-Li, and **8**-Li were fully optimized. The results are shown in Table IV. The structure of **5**-Li without p orbitals on lithium shows larger deviations from planarity for the allyl fragment than with the full lithium basis set, but the C–C–C angle is unchanged. The lithium atom without p orbitals is closer to the C–C–C plane than that with p orbitals. These changes can be attributed to electrostatic factors (see below) and indicate that the lithium without p orbitals is behaving more like a point charge than that with the full basis set. The structure of **7**-Li is practically unchanged on removal of the lithium p orbitals, and for **8**-Li the C–C–C angle is slightly widened and the C–C–Li angle is increased by 3.6°. The energy lowering attributable to the lithium p orbitals is small for **7**-Li and **8**-Li (7.1 and 6.9 kcal/mol, respectively) but significantly larger (19.5 kcal/mol) for **5**-Li. We attribute the extra 12–13 kcal/mol stabilization of **5**–Li to the involvement of lithium in the 5a″ orbital (HOMO) of **5**-Li (see below). Streitwieser[40] has proposed that the lithium p orbitals in such compounds act as extra diffuse functions for carbon, rather than as true valence orbitals. Our calculations do not support this interpretation. The lithium p orbitals at 3-21G in **5**-Li are highly contracted (the coefficient of the inner part in the HOMO is 6 times larger than that of the outer part), suggesting a true valence role. Counterpoise calculations (see below) on the allyl anion with 3-21G show the *outer* lithium p orbitals improving the carbon basis set, but the inner part is not involved. Addition of diffuse functions to the basis set (3-21+G)[41] decreases the total population of the lithium p orbital that is antisymmetric with respect to the symmetry plane by approximately 20%. Thus, the valence role of this orbital remains important even with an "anion" basis set. With the diffuse-augmented basis set the "extra" stabilization in **5**-Li amounts to 4 kcal/mol, probably the lower limit which can be attributed to CLi multicenter covalent bonding. The corresponding calculations for allylsodium give an extra stabilization for **5**-Na of 7 kcal/mol at 3-21G, significantly less than for **5**-Li (see Table IV).

Streitwieser[42] has used point charges to model ionic behavior. We have used this technique to optimize the allyl anion associated with a point positive charge (actually a proton without basis functions) in structures corresponding to **5**, **7**, and **8**. The results are shown in Table V.

The geometry of **5**-+ exhibits many of the features (small C–C–C angle, and large out-of-plane deviations) found for **5**-Li and previously attributed to covalent C–Li overlap.[7] An examination of the geometry and MO's of **5**-+ leads to the conclusion that the positive charge induces a localization and redirection of the allyl anion orbitals. This effect is most evident for the HOMO. This conclusion approaches Streitwieser's view of C–Li bonding,[40,42] but we are uncertain as to how this type of stabilization should be classified. There is a large conceptual difference between this type of electrostatic orbital localization and covalent bonding, but the net effect is to direct electron density toward the metal in each case.

A better model for purely ionic bonding is to omit the valence orbitals from the metal basis set, thus leaving a naked core. The results of such calculations for **5**, **7**, and **8**-Li and -Na are shown in Table VI. The structures thus calculated for **5**-Li and **5**-Na show the characteristic out-of-plane deviations given in both the point charge and full basis set calculations. The extent of these distortions decreases in the order: point charge > core only > s only > full basis set, thus clearly establishing the electrostatic nature of the deformation. The importance of the ionic radius of the metal is shown by the fact that the out of plane distortions in the calculations without counterion valence orbitals are largest for **5**-+ and smallest for **5**-Na. We previously attributed the out-of-plane distortions to covalent overlap with the metal.[7] However, this now appears *not* to be responsible. Counterpoise calculations in which the allyl anion was optimized in the presence of lithium basis functions fixed at the C_2Li distance found in **5**-Li (3-21G) confirm this interpretation; the allyl hydrogens bend slightly in the opposite directions to those found in **5**-Li.

These conclusions can, however, not be applied to **5**-MgH, which shows the largest deviations from planarity of the C_3H_5 fragment of the π-metal species investigated but which clearly favors a more covalent structure **6**-MgH. This illustrates one of the major difficulties with such structures: that electrostatic and multicenter covalent arguments lead to the same, or similar, preferred geometries. We therefore agree with Streitwieser[40,42] that additional calculations, such as those without metal p orbitals, with only core orbitals on the metal and so on, are necessary in order to characterize the bonding in such organometallic species. Arguments based on geometries can clearly support both extreme viewpoints.[39,40] This work suggests that for **5**-Li the major geometrical effects are electrostatic in nature (electrostatic orbital localization) but that the inclusion of lithium p orbitals gives an extra stabilization between 4 and 12 kcal mol^{-1} that can be at-

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(41) (a) See ref 14. (b) Spitznagel, G. W.; Clark, T.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(42) Kost, D.; Klein, J.; Streitwieser, A., Jr; Schriver, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922.

Table VI. C_3H_5M (M = Li, Na): Geometries (3-21G-sp),[a,b] Total Energies,[c] and Relative Energies[d]

	5-Li	7-Li	8-Li	5-Na	7-Na	8-Na
geometries						
C_1C_2	1.394	1.324	1.322	1.390	1.328	1.323
C_2C_3		1.525	1.534		1.531	1.535
C_1M	2.058			2.356		
C_2M	2.083	2.827	2.966	2.390	2.879	3.229
C_3M		1.913	1.907		2.212	2.208
CCC	125.4	124.7	127.4	127.9	124.4	128.1
C_2C_1M	71.3			74.3		
C_2C_3M		110.2	118.7		98.9	118.1
$MC_2C_1C_1$	39.8			44.2		
$H_1C_1C_2C_1$	−34.1			−28.6		
$H_2C_1C_2C_1$	1.8			−2.6		
$H_3C_2C_1C_1$	165.2			168.8		
total and rel energies	−123.186 02 (0.0)	−123.168 55 (11.0)	−123.161 77 (15.2)	−276.625 65 (0.0)	−276.601 18 (15.4)	−276.592 08 (21.1)

[a] Normal 3-21G basis set, but lithium and sodium with core orbitals only. [b] Bond lengths in angstroms and angles in degrees. [c] In hartrees (= 627.49 kcal/mol). [d] In parentheses (kcal/mol).

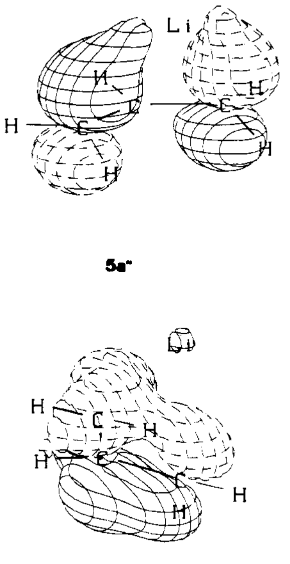

Figure 1. The 5a'' and 8a' orbitals of allyllithium. The apparently antibonding contribution from Li in the 8a' is due to the 1s orbital.

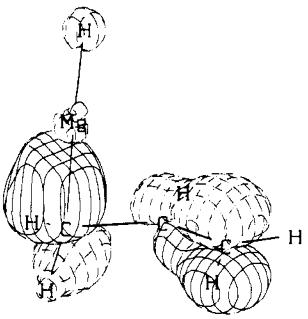

Figure 2. The HOMO of allylmagnesium hydride.

tributed to multicenter covalent overlap. This overlap does not, however, increase the deformation of the allyl fragment from the anion geometry, rather the reverse.

The Nature of the π-MO's in Allylmetal Compounds. The two orbitals of 5-Li, 5a'' and 8a', which correspond to the two π orbitals of the allyl anion, are shown in Figure 1. The inclination of the carbon p-orbitals towards the metal can be clearly seen, as can the contribution from the lithium p orbital in 5a''. The 2p/2s ratio in the 5a'' orbital is 4.2 at C_1 and C_3, compared with 58 at these two carbons (and 13 at C_2) in the 8a'. The p orbitals at C_1 and C_3 in the 8a' orbital are, however, inclined at an angle of 60° to the C–C–C plane, compared with an angle of 69° between the C_1C_2 bond and the C_1Li bond. The direction of this orbital toward lithium is therefore achieved without increasing the s character at C_2 and C_3. Only the 5a'' HOMO shows a high degree of s character. The 11° deviation of the unique hydrogen from the plane is reflected in the p contribution at C_2 in the 8a' orbital, which is inclined 10° toward Li.

The total population of the lithium p orbital that is antisymmetric with respect to the molecular plane is 0.30 electron, showing some multicenter covalent bonding,[7,43] as exemplified by the 5a'' orbital of allyllithium.

Figure 2 shows the HOMO (18a) of 6-MgH. The preference for a localized C—Mg bond and a C=C double

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[43] (a) Patterman, S. P.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150. (b) Brooks, J. J.; Rhine, W.; Stucky, G. D. *Ibid.* **1975**, 737. (c) Arora, S. K.; Bates, R. B.; Beavers, W. A.; Cutler, R. S. *Ibid.* **1975**, *97*, 6271.

bond can clearly be seen, although the interaction between the two is still strong. The large backside lobe on C_1 and the strong resemblance to an unsymmetrical π system are indicative of polar bonding, but the extension of electron density to the metal (the antibonding lobe at Mg is due to core orbitals) is clearly more significant than in **5**-Li.

Conclusions

Allyllithium and allylsodium monomers prefer symmetrically bridged C_s structures. Allylmagnesium hydride monomer has a C_1 structure that represents a compromise between the bridged and "classical" geometries.

The barrier of rotation in *monomeric* allylsodium should be lower than that in *monomeric* allyllithium. The 1,3 MgH shift barrier in allylmagnesium hydride is calculated to be lower than the barrier to rotation. Both are rather small.

The geometry of the C_3H_5 fragment in C_3H_5M shows increasingly large deviations in the order M = Na < Li < MgH from the allyl anion geometry. We attribute the observation of the same, reduced C_2–H coupling constants to the compensating effects of CCC angle widening (greatest in the allyl anion and with the heavier metal counterions) and C_2–H out-of-plane bending (greatest for lithium). These effects should also be present in the π-allyl complexes of transition metals.[8,21]

The direction of electron density toward the metal is achieved largely by twisting pure p orbitals on carbon, although the HOMO of allyllithium shows about 25% s character on C_1 and C_3. Carbon–metal bonds are largely electrostatic in nature, but multicenter covalent bonding nonetheless contributes between 4 and 12 kcal/mol to the stability of allyllithiums. The role of the metal can be represented as a point charge with an ionic radius due to the core orbitals. Many of the differences observed between lithium and sodium are therefore simple distance effects.

Acknowledgment. We are particularly grateful to Prof. A. Streitwieser, Jr., for stimulating discussions on the nature of C–Li bonding and for preprints of relevant work. Thanks are due to Prof. E. Weiss and Dr. C. Krueger for making unpublished X-ray structures available to us and to Prof. W. J. Hehre for allowing us to use basis sets before publication. This work was supported by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. The cooperation of the Regionales Rechenzentrum Erlangen is gratefully acknowledged.

Note Added in Proof. Decher and Boche's[43] MNDO examination of allyllithium and solvated models (with two and three attached water molecules) has led to the same conclusions regarding the out-of-plane bending of the hydrogens. They also attribute the abnormal C_2–H coupling constants[19] primarily to CCC angle bending and call attention to the related X-ray structure of dilithiohexatriene–bis(tetramethylethylenediamine)[44] in which the "inner" hydrogens, as in allyllithium, are bent most strongly out of the plane of the carbon atoms.

Registry No. C_3H_5Li, 3052-45-7; C_3H_5Na, 2521-40-6; C_3H_5MgH, 86584-37-4.

Supplementary Material Available: Listings of 3-21G optimized geometries for allyllithium, -sodium, and -magnesium hydride isomers (4 pages). Ordering information is given on any current masterhead page.

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(44) Decher, G.; Boche, G. submitted for publication in *J. Organomet. Chem.*

(45) Arora, S. A.; Bates, R. B.; Beavers, W. A.; Cutler, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 6271.

Interaction of Alkali Metals with Unsaturated Heterocyclic Compounds. The Reductive Metalation of 3-Phenylcinnoline

Seniz Kaban*[†] and James G. Smith*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

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The reductive metalation of the cinnoline ring system was explored by using 3-phenylcinnoline, **1**. A dianion, **2**, formed with sodium and tetrahydrofuran, showed preferential reactivity at the 1,4-positions with various reagents. After initial reaction at the 4-position, the residual-delocalized 1-anion was a weak nucleophile and reacted only under favorable conditions.

The reductive metalation of conjugated unsaturated systems containing nitrogen has been studied for some time.[1,2] Several such conjugated systems are more readily available in heterocyclic compounds than in open-chain analogues. In addition, the reductive metalation of heterocyclic systems can provide synthetically useful dihydro dianionic derivatives. In this report, the reductive metalation of the cinnoline ring is described, using 3-phenylcinnoline as the example. Here, the reduction of conjugated alkene and azo functionalities is examined for the first time.

Reduction of 3-phenylcinnoline, **1**, with sodium in tetrahydrofuran (THF) occurred rapidly to form dianion **2**. The chemical behavior of **2** toward several reagents was

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[†] Visiting professor from the University of Istanbul, Istanbul, Turkey.

(1) Kalyanaraman, V.; George, M. V. *J. Organomet. Chem.* **1973**, *47*, 225.

(2) (a) Smith, J. G.; Sheepy, J. M. *J. Org. Chem.* **1977**, *42*, 78. (b) Smith, J. G.; Levi, E. M. *J. Organomet. Chem.* **1972**, *36*, 215 and references cited therein.