

balt(II) product was oxidized to Co(III) with 10  $\mu\text{L}$  of  $\text{BrCCl}_3$ , and the  $^1\text{H}$  NMR spectrum was taken. No peaks assigned as  $\beta$ -hydroxypropionaldehyde or the expected dehydration product, acrolein, were obtained.

(ii) **Attempted Use of Cobalt Alkyls as Traps.** A solution of 5 mg of **3** and 5 mg of  $(\text{PHCH}_2)\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{I}$  in 1.0 mL of  $\text{CH}_3\text{OH}$  was treated with 1.0 equiv of standard methoxide solution. After 2 min the products included 100% Co(II) (based on **3**), 50%  $\text{CH}_3\text{OCO}_2\text{CH}_3$ , 50%  $\text{CH}_3\text{OCO}_2^-$ , and 60%  $\text{CH}_3\text{CHO}$ . Oxidation of the Co(II) with 10  $\mu\text{L}$  of  $\text{BrCCl}_3$  and  $^1\text{H}$  NMR analysis showed ca. 100% of the Co(III)-benzyl complex to be intact ( $\delta$  2.5 (s, 2 H,  $\text{PhCH}_2-\text{CO}$ ), 6.6-7.3 (m, 5 H,  $\text{PhCH}_2-\text{CO}$ )).

A solution of 5 mg of **3** and 5 mg of  $(\text{CH}_2=\text{CHCH}_2)\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Br}$  (ca. 90% pure) in 1.0 mL of  $\text{CH}_3\text{CHO}$  was treated with 1.0 equiv of standard methoxide solution. After 2 min the products included 100% Co(II), 60%  $\text{CH}_3\text{CHO}$ , 50%  $\text{CH}_3\text{OCO}_2\text{CH}_3$ , and 50%  $\text{CH}_3\text{OCO}_2^-$ . Upon  $\text{BrCCl}_3$  oxidation and workup, the allyl complex had decomposed (the  $\delta$  4.58, 5.00 peaks were absent).

(iii) **Use of  $\text{PhCH}_2\text{OH}$  as a Solvent. Attempted  $\text{PhCHOH}$  Trapping by  $\text{Co}-\text{CH}_2\text{CHO}$ .** With the hope of generating the more stable trapping product,  $\text{PhCH}=\text{CHCHO}$ , benzyl alcohol was used as the solvent. A solution of 5 mg of **3** and 10 mg of **6** in 1.0 mL of  $\text{PhCH}_2\text{OH}$  (purified by the described procedure<sup>1</sup>) was treated with 1.0 equiv of standard base. After 30 min, the observed products included 80% Co(II) and ca. 180% **6**; i.e., the formylmethyl complex did not react with the  $\text{PhCHOH}$  generated under the reaction conditions. This result is consistent with Espenson's observations<sup>23a</sup> that  $\cdot\text{C}(\text{CH}_3)_2\text{OH}$ , but not  $\text{PhCH}_2\cdot$ , show apparent  $\text{S}_{\text{H}}2$  reactions with  $\text{RCo}$  complexes ( $\text{R} = \text{PhCH}_2-$  in Espenson's case).

(I) **Search for  $\cdot\text{CH}_2\text{CHO}$ .** The intermediacy of the proposed  $\cdot\text{CH}_2\text{CHO}$  radical was probed by the attempted trapping by Co(II) and by the use of deuterated solvent.

(i) **Co(II) Trapping.** A solution of 5 mg of **3** and 20 mg (4.5 equiv, the limit of solubility) of  $\text{Co}^{\text{II}}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Br}$  in 1.0 mL of  $\text{CH}_3\text{OH}$  was treated with 1 equiv of standard methoxide solution, and the products were analyzed by GC, IR, and visible spectroscopy. Aside from the large amount of Co(II), the products were unaffected by the Co(II): 50%  $\text{CH}_3\text{OCO}_2\text{CH}_3$ , 50%  $\text{CH}_3\text{OCO}_2^-$ , and a normal,  $\sim 60\%$   $\text{CH}_3\text{CHO}$ .

(ii) **Solvent Isotope Effect.** Solutions of 5 mg of **3** in 1.0 mL  $\text{CH}_3\text{OH}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$  were all treated with 1.0 equiv of the appropriate solvent conjugate bases, and the products were analyzed by GC, IR, and visible spectroscopy. Identical product yields of 60%  $\text{CH}_3\text{CHO}$ , 50%  $\text{CH}_3\text{OCO}_2^-$ , 50%  $\text{CH}_3\text{OCO}_2\text{CH}_3$ , and 100% Co(II) were obtained (or their deuterated analogues).

(J) **Methanolysis of **3** in the Presence of Both Nitroxide and 1,5,6-Trimethylbenzimidazole.** In order to try to determine the relative order of the nitroxide and axial base effects on the methanolysis of **3**, i.e., whether they affect the same or different intermediates, the deprotection was run in the presence of both reagents.

A solution of 5 mg of **3**, 1 mg (1 equiv) of the nitroxide **9**, and 45 mg (25 equiv) of 1,5,6-trimethylbenzimidazole in 1.0 mL of  $\text{CH}_3\text{OH}$  was treated with 12  $\mu\text{L}$  (1 equiv) of the standard methoxide solution. The observed reaction products included 90% Co(II) ( $\lambda_{\text{max}}$  520 nm), ca. 100% *N*-hydroxy-2,2,6,6-tetramethylpiperidone ( $\nu_{\text{CO}} = 1709 \text{ cm}^{-1}$ ), 100%  $\text{CH}_3\text{OCO}_2\text{CH}_3$  ( $\nu_{\text{CO}} = 1755 \text{ cm}^{-1}$ ), and no ( $<5\%$ )  $\text{CH}_3\text{CHO}$ .

In a control experiment a solution of 5 mg of **3** and 45 mg of 1,5,6-trimethylbenzimidazole in 1.0 mL of  $\text{CH}_3\text{OH}$  was treated with 1.0 equiv of standard base. After 2 min the resultant blue Co(I) solution was treated with 1 mg of the nitroxide **9**, which gave rise to an immediate reaction producing 100% Co(II),  $\lambda_{\text{max}}$  520 nm. This control shows that it is impossible to tell whether Co(I) or Co(II) is first produced in this experiment, and therefore, whether or not the axial base effect precedes the nitroxide trapping effect in the methanolysis reaction.

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**Registry No.** **3**, 75504-42-6; **6**, 87728-42-5; **9**, 2896-70-0; **10**, 3637-11-4;  $\text{ICo}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{PF}_6$ , 87728-35-6;  $\text{ICo}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{I}$ , 75962-04-8;  $(\text{CH}_2=\text{CHCH}_2^-)\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Br}$ , 87728-48-1;  $(\text{OC})\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Br}$ , 87728-49-2;  $\text{AgPF}_6$ , 26042-63-7; allyl bromide, 106-95-6; ethylene carbonate, 96-49-1; diol dehydratase, 9026-90-8.

## On the Structure and Stability of 1,3-Dilithiopropanes and Other $\alpha,\omega$ -Dilithioalkanes. The Importance of LiH Complexes as Structural Alternatives and Reaction Intermediates

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**Abstract:** A doubly lithium bridged structure (**3**) is found by ab initio theory (3-21G basis set) to be the lowest-energy geometry of 1,3-dilithio propane. This form exhibits considerable thermodynamic stability, e.g., opening to an extended conformation (**6**) is endothermic by 24.6 kcal/mol and disproportionation with propane into 2 mol of *n*-propyllithium is calculated to require 19.4 kcal/mol. Doubly bridged structures like **3** are the intramolecular equivalent of organolithium dimers, and the stabilization energy of **3** is about half that for methyl lithium dimerization. On the other hand, elimination of LiH from 1,3-dilithio propane (**3**) is more favorable than from primary alkylolithiums, in agreement with experimental observations. Conversion of **3** to an allyllithium-LiH complex, **8** (a possible elimination intermediate), is exothermic by 29.0 kcal/mol whereas the ethylene-LiH complex (**13**) is 7.2 kcal/mol less stable than ethyllithium. The corresponding vinyl lithium-LiH complex (**15**) is 29.8 kcal/mol more stable than the most favorable 1,2-dilithioethane geometry (**14**). While the second lithiations of ethane and of propane are favorable thermodynamically, both 1,2-dilithioethane and 1,3-dilithio propane are unstable toward conversion to LiH complexes. When such eliminations are blocked structurally or the carbanionic sites substituted by stabilizing groups, vicinal and 1,3-dilithio derivatives can be expected. Truncated basis sets were employed to investigate the role of lithium *p* and valence orbitals in bonding. While electrostatic interactions (ion triplets) are most important, some multicenter covalent character is also indicated. MNDO structures for the dimers of the  $\alpha,\omega$ -dilithioalkanes indicate opened tetrahedral arrangements. Unlike the lower homologues, the doubly bridged form (**20**) of 1,4-dilithio butane is indicated to be stable thermodynamically toward elimination to a 3-butenyllithium-LiH complex (**22**). This explains why the higher  $\alpha,\omega$ -dilithioalkanes are more readily accessible as synthetic reagents.

In their classical study of the lithiation of  $\alpha,\omega$ -dibromoalkanes, West and Rochow<sup>1</sup> were able to prepare 1,4-dilithio butane and

higher  $\alpha,\omega$ -dilithioalkanes but not 1,2-dilithioethane or 1,3-dilithio propane. While 1,2-dilithioethane is still unknown,<sup>2</sup> Seetz,



Table II. Effects of Removal of Lithium 2p and 2sp Functions on Absolute and Relative Energies of 1,3-Dilithiopropane Isomers; Comparisons with Point-Charge Models

species	total energies, au			relative energies, kcal/mol			
	3-21G(-Li <sub>2p</sub> )/ 3-21G(-Li <sub>2p</sub> )	3-21G(-Li <sub>2sp</sub> )/ 3-21G(-Li <sub>2sp</sub> )	point charge// 3-21G <sup>b</sup>	3-21G// 3-21G	3-21G(-Li <sub>2p</sub> )/ 3-21G(-Li <sub>2p</sub> )	3-21G(-Li <sub>2sp</sub> )/ 3-21G(-Li <sub>2sp</sub> )	point charge// 3-21G <sup>b</sup>
3, C <sub>2v</sub>	-131.14613 (24.0) <sup>a</sup>	-131.11342 (44.5) <sup>a</sup>	-116.83413	0.0	0.0	0.0	0.0
4, C <sub>s</sub>	-131.13225 (18.0) <sup>a</sup>	-131.09142 (43.6) <sup>a</sup>	-116.82881	14.7	8.7	13.8	3.3
5, C <sub>2v</sub>	-131.10723 (31.7) <sup>a</sup>	-131.07502 (51.9) <sup>a</sup>	-116.78370	16.7	24.4	24.1	31.6
6, C <sub>2v</sub>	-131.12267 (14.1) <sup>a</sup>	-131.06419 (50.8) <sup>a</sup>	-116.78263	24.6	14.7	30.9	32.3
CH <sub>3</sub> Li	-46.73991 (7.9) <sup>a</sup>	-46.71611 (22.8) <sup>a</sup>					

<sup>a</sup> Energy raisings (in kcal/mol) related to the full basis set 3-21G//3-21G values (Table I) for each species. See text. <sup>b</sup> The Li's in 3-6 (3-21G geometries) were replaced by point charges (H<sup>+</sup>s without any valence functions).

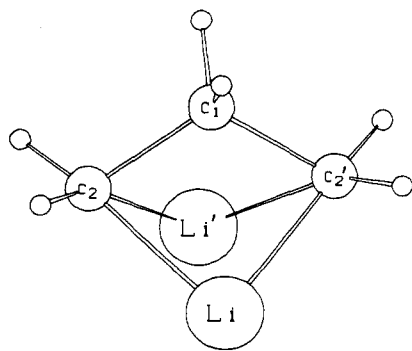


Figure 1. The 3-21G//3-21G structure of 1,3-dilithiopropane (3). Distances in angstroms and angles in degrees: C1-C2, 1.609; C2-Li, 2.059; C1-Li, 2.292; Li-Li', 2.298; C1-H, 1.088; C2-H, 1.093; C2-C1-C2', 111.3; C2-Li-C2', 80.3; H-C1-H, 105.6; H-C2-H, 104.4; (C2HH)-C2-C1, 124.8.

ab initio optimization (designated 3-21G//3-21G; the "//" means "at the geometry of") of 3-6 and additional C<sub>3</sub>H<sub>6</sub>Li<sub>2</sub> species, 7 and 8, complexes between allyllithium and LiH. Geometry optimizations were carried out by using analytically evaluated atomic forces in a Davidson-Fletcher-Powell multiparameter search routine.<sup>22</sup> Important bond lengths and angles (3-21G) are given in the structural formulas. With the exception of 7, the 3-21G and MNDO energy orderings agree well. Included in Table I are the energies of reference compounds needed for thermochemical evaluations and a number of LiH complexes discussed in the text and several dimers.

To assess basis set effects with respect to lithium we carried out model calculations by truncation of the original 3-21G set. First, all lithium p orbitals were omitted (designated 3-21G(-Li<sub>2p</sub>)) and then all valence functions (3-21G(-Li<sub>2sp</sub>)). Single-point calculations using the 3-21G geometries were followed by complete geometry reoptimizations of 3-6

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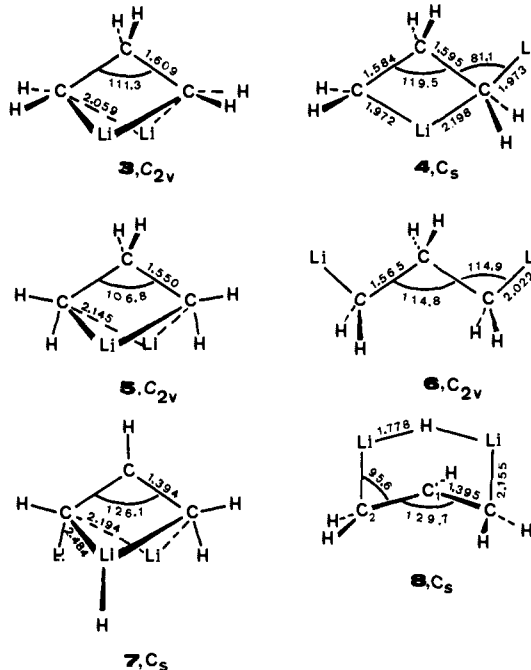
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(22) Davidson, W. C. *Comput. J.* **1968**, *10*, 406. Fletcher, R.; Powell, M. J. D. *Ibid.* **1963**, *6*, 163. Schlegel, H. B.; Wolfe, S.; Bernardi, F. *J. Chem. Phys.* **1975**, *63*, 3632.

at both truncated levels. Since these structural redeterminations produced only relatively small changes in geometries and energies, only the 3-21G(-Li<sub>2p</sub>)/3-21G(-Li<sub>2p</sub>) and 3-21G(-Li<sub>2sp</sub>)/3-21G(-Li<sub>2sp</sub>) absolute and relative energies of 3-6 are compared in Table II. When the Li<sub>2p</sub> and Li<sub>2sp</sub> functions are omitted, the absolute energies are raised. The magnitudes are of interest, and this information is included in Table II along with similar data for CH<sub>3</sub>Li for comparison. The final set of data refers to point-charge models in which the Li's have been replaced by H's without any valence functions.<sup>23</sup> The 3-21G geometries were employed for this purpose.



## Results and Discussion

The least stable, classical, W-shaped form of 1,3-dilithiopropane (6) does not exhibit any "through-bond" stabilization. This is shown by the negative energy of eq 1, a hypothetical disproportionation reaction. Carbon-lithium bonds are highly polar, and the presence of the two carbanionic centers in 6 is destabilizing electrostatically.

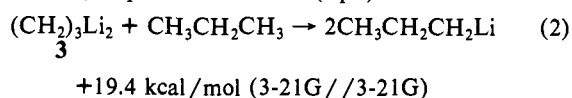
$$6 \rightarrow 2 \text{CH}_3\text{CH}_2\text{CH}_2\text{Li} \quad (-5.2 \text{ kcal/mol (3-21G//3-21G)})$$

tionation reaction. Carbon-lithium bonds are highly polar, and the presence of the two carbanionic centers in 6 is destabilizing electrostatically.

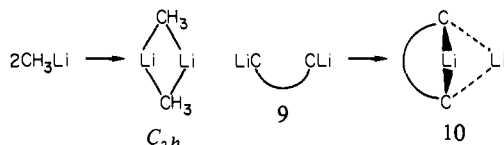
Symmetrical double lithium bridging, which we have also found to be very favorable in many other contexts,<sup>2,6,10,15,16,18</sup> is responsible

(23) Streitwieser, A., Jr., James Flack Norris Award Address, 183rd National Meeting of the American Chemical Society, Las Vegas, Nevada, March 1982, and private communications. Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502. See ref 5b.

for the stability of 1,3-dilithiopropanes like **2**, which cannot eliminate. Structure **3** (full geometrical details are given in the figure caption) is the minimum energy isomer. Unlike eq 1, the analogous disproportionation reaction, with the much more stable **3** in place of **6**, is quite endothermic (eq 2).

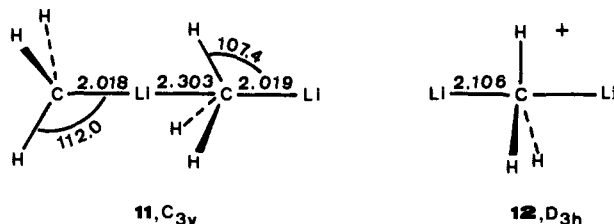


The dimerization of methyl lithium releases 46.3 kcal/mol (3-21G//3-21G) due to a large extent to the gain in Coulombic attraction.<sup>11,23</sup> Similarly, the cyclization of  $\alpha,\omega$ -dilithium compounds, symbolized by **9**  $\rightarrow$  **10**, can be regarded as an "intramolecular dimerization".<sup>18</sup> Thus, the "ring closure" process converting open **6** to doubly bridged **3** is exothermic by 24.6 kcal/mol. Larger systems, e.g., 1,4-dilithiobutane,<sup>24</sup> have even more favorable cyclization energies.

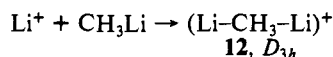
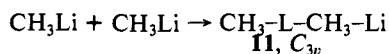


Streitwieser<sup>23</sup> has stressed the electrostatic advantages of such "ion triplet" arrangements (e.g., **3** and **10**, regarded as dianions associated with two  $\text{Li}^+$  cations). On this basis, another doubly bridged isomer, **5**, bears consideration. The staggered conformations of the methylene groups in **5** should favor this form over **3**, where the  $\text{CH}_2$ 's are eclipsed. The relatively long C-C bonds in **3** also suggest unfavorable negative hyperconjugative interactions. Nevertheless, **5** proves to be 16.7 kcal/mol (3-21G//3-21G) less stable than **3**. We consider reasons for this below.

Although intermediate in energy (14.7 kcal/mol less stable than **3**), the singly-bridged isomer **4** is intriguing. This structure can also be interpreted electrostatically in terms of an approximately linear  $\text{Li}^+\text{C}^-\text{Li}^+\text{C}^-$  arrangement. A simple model is the linear,  $C_{3v}$ -constrained methyl lithium dimer, **11**, with an association



energy of 22.3 kcal/mol (3-21G//3-21G)). That this is only about half of the dimerization energy of  $(\text{CH}_3\text{Li})_2$  ( $C_{2h}$ ) emphasizes the superiority of cyclic over linear arrangements. Another example is the  $\text{LiH}$  dimer, which is 19.5 kcal/mol (3-21G//3-21G) more stable in cyclic ( $D_{2h}$ ) than linear ( $C_{\infty v}$ ) geometries.<sup>21</sup> The  $D_{3h}$   $\text{CH}_3\text{Li}_2^+$  structure, **12**, is similar to **11**, but the larger  $\text{Li}^+ + \text{CH}_3\text{Li}$  interaction energy (52.7 kcal/mol with zero-point corrections) induces planarity of the  $\text{CH}_3$  group.<sup>14</sup>



How well, in a quantitative sense, do electrostatic models or truncated basis sets reproduce the results of the full 3-21G basis calculations? To learn more about the bonding details in these species, we first investigated the effects of deleting *all* p orbitals from the basis set (3-21G(- $\text{Li}_{2p}$ )/3-21g(- $\text{Li}_{2p}$ )). Not only are the "vacant" lithium p orbitals (e.g., those perpendicular to a Li-R axis) removed but also the coaxial p orbital which contributes to  $\sigma$  bonding. This raises the absolute energy of  $\text{CH}_3\text{Li}$  by 7.9 kcal/mol and that of the "classical" isomer **6** by about twice this

amount, 14.1 kcal/mol (Table II). The effect on **4** is similar. Significantly, the energy of **5** is raised to the greater extent, 31.7 kcal/mol, and this isomer becomes the least stable at this level.

Electron transfer from the  $\text{sp}^2$ -hybridized terminal methylene carbons to the vacant lithium p orbitals is necessary to stabilize structure **5** differentially. The  $\text{Li}_{2p}$  effect on **3**, 24.0 kcal/mol, is also abnormally large.

Streitwieser has suggested another interpretation.<sup>23</sup> When smaller basis sets are used,  $\text{Li}_{2p}$  functions may operate by providing a better description of the rest of the molecule ("basis set superposition error" (BSSE))<sup>25</sup> rather than lithium itself. To some extent this is certainly true. However, in more detailed studies on smaller systems to be published subsequently, we have found the  $\text{Li}_{2p}$  orbital effects to be about the same at 6-31G\* as at 3-21G but smaller when diffuse basis functions are present on the carbon atoms. However, this may be a reverse BSSE: the carbon orbitals help to describe lithium. We believe  $\text{Li}_{2p}$  orbital contributions to be significant and have emphasized their importance in other contexts.<sup>2,12,15,16,19</sup>

We next investigated three ionic models. The first two of these retained the full  $\text{C}_3\text{H}_6^{2-}$  3-21G wave function to describe the anion centers. In the first model, all electron transfer to lithium was precluded by omitting the valence functions from the Li basis set (3-21G(- $\text{Li}_{2sp}$ )). This forces each lithium to be a cation,  $\text{Li}^+$ , with unit charge. At this level, the original (3-21G) stability order is restored, but the relative energy of **5** vs. **3** is not improved. In the second model, the lithium atoms in the 3-21G geometries of **3-6** are replaced by point charges ( $\text{H}^+$  without valence functions). Rather similar results are obtained, except that **4** becomes relatively more stable.

The intramolecular Coulombic repulsion between the two negative charges in a dianion leads to considerable destabilization, but as Streitwieser has pointed out, this may be reduced or even overcome by the proper placement of the two positive counter-ions, i.e., between the negative centers.<sup>23</sup>

Taking twice the 3-21G(- $\text{Li}_{2sp}$ ) energy raising (Table II) of ionic  $\text{CH}_3\text{Li}^+$  as a standard, the extra electrostatic interactions in the 1,3-dilithiopropane isomers can be evaluated. These are over 5 kcal/mol destabilizing *both* for "classical" **6** (which has poor  $\text{Li}^+$  placements) and for doubly-bridged **5** (expected to be much better electrostatically). The values for **3** (also doubly bridged) and for **4** (singly bridged) are normal. Why are these ionic models inadequate? Many factors determine the structures even of pure ion triplets, e.g., ionic radii and steric effects, and prevent the attainment of Streitwieser's ideal Coulombic geometries.<sup>23</sup> This was explored by means of the third ionic model which involved simple electrostatic calculations using the 3-21G geometries of **3** and **5** and assuming positive point charges at the Li positions and negative point charges at the terminal carbons. The results suggest **5** (incorrectly) to be 14.7 kcal/mol more stable than **3**. However, in **3** the negative charges in lone-pair lobes probably are modeled poorly by location at the carbon nucleus; they should extend somewhat forward. Indeed, the opposite conclusion was reached (Table II) when only point-positive charges or  $\text{Li}^+$  cations were employed along with the full 3-21G wave functions for the  $\text{C}_3\text{H}_6^{2-}$  dianion moieties. The orientation and distribution of the negative charges are obviously crucial. In **3** the  $\text{sp}^3$ -hybridized carbanion lone pairs point more favorably toward the lithiums. While the contribution of partial ionic bonding certainly is important, ion triplet models<sup>23</sup> do not reproduce the energy differences found at the full 3-21G basis set levels satisfactorily.

Multicenter covalent bonding also contributes especially in the doubly bridged structures, **3** and **5**. In both cases, two four-center MO's are occupied. The symmetries of the higher-energy MO's require Li p-orbital involvement. This is particularly so in **5**, since both terminal carbanion lone-pair orbitals are pure p in character. Hence, the energy raising of this isomer is largest when the  $\text{Li}_{2p}$

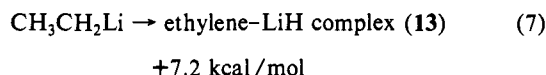
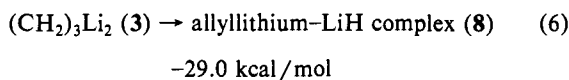
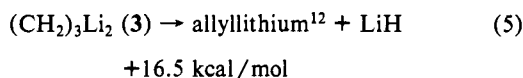
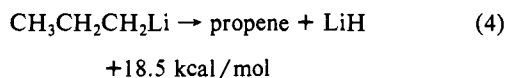
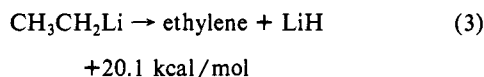
(24) Andrade, J.; Kaufmann, E.; Kos, A.; Unpublished calculations.

(25) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553-566. Kolos, W. *Theor. Chim. Acta* **1979**, *51*, 219-240. Čársky, P.; Urban, M. "Ab Initio Calculations, Methods and Applications in Chemistry"; Springer Verlag: Berlin, 1980; pp 176 and 177.

functions are removed from the basis set. In **3**, the carbanion lone-pair orbitals are hybridized and have some s character. The specific involvement of  $Li_{2p}$  orbitals is somewhat less important. Because of the nature of the four-center MO's involved, the Li's in **5** are strongly antibonding (Mulliken overlap population -0.70) while in **3** they are nonbonding (0.00). (The  $C_1C_3$  carbon overlap populations are nearly equal in **3** and **5** and are somewhat antibonding.)

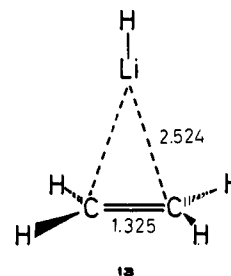
These are saturated systems. When conjugated  $\pi$  systems are involved, **5**-like conformations are preferred, e.g., in **7**, in 1,4-dilithio-*cis*-2-butene,<sup>26</sup> and, to a small extent, in 1,3-dilithiopropene.<sup>5</sup> We believe that *both* multicenter covalent and electrostatic interactions are important in determining the bonding and energetic features of lithium compounds. Although we have stressed the "Hückel-Möbius aromatic character" of compounds like *cis,cis*-1,4-dilithiobutadiene<sup>16</sup> and *o,o'*-dilithiobiphenyl,<sup>18</sup> ionic contributions are likely to be at least of comparable importance.

**LiH Complexes.** Why does 1,3-dilithiopropene eliminate LiH so readily experimentally? There may be an underlying thermodynamic reason. Although the chemistry of lithium compounds in solution is complicated by the effects of solvation and association,<sup>27</sup> calculations on unsolvated monomers often mirror experimental behavior surprisingly well.<sup>17</sup> We have already pointed out that the loss of LiH from ethyllithium is quite endothermic<sup>2</sup> (20.1 kcal/mol at 3-21G//3-21G, eq 3, the MP2/6-31G\*\*//3-3-21G value is 23.9 kcal/mol<sup>2</sup>). The energy required to eliminate HLi from *n*-propyllithium (eq 4) is similar.<sup>28</sup> Due to the greater stability of allyllithium,<sup>12</sup> LiH elimination from **3** into separated products (eq 5) is somewhat less endothermic.

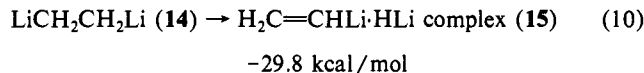
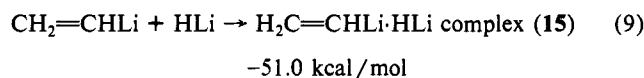
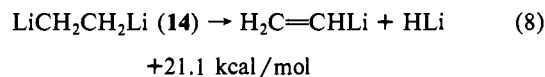


However, akin to **11**, allyllithium and HLi form a complex, **7**, 21.8 kcal/mol more stable than the separated species. Complex **7** has both Li's on opposite sides of the carbon plane; complex **8**, with the Li's on the same side, is even better (by 45.4 kcal/mol relative to HLi + allyllithium).<sup>29</sup> The conversion of **3** to **8**, which

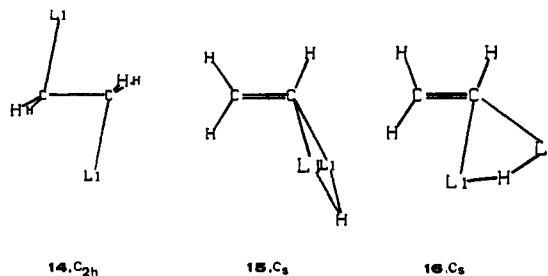
may well be the initial elimination product, is exothermic by 29.0 kcal/mol (eq 6). The analogous complexes between LiH and olefins are much less favorable; e.g., the ethylene-LiH and complexation energy (to give **13**) is 12.9 kcal/mol.<sup>30</sup> Hence, the conversion of primary allyllithiums to LiH-olefin complexes is endothermic and will occur less readily (compare eq 7 with eq 6). This is consistent with the experimental observations of Bickelhaupt et al.<sup>3</sup>



These findings prompted a reconsideration of the nature of 1,2-dilithioethane. Our extensive search of the potential energy surface has indicated the unsymmetrically bridged structure, **14**, to be the lowest-energy form.<sup>2</sup> Although 1,2-dilithioethane is a possible reaction intermediate,<sup>31</sup> it evidently is not a stable species.<sup>1</sup> Could ready HLi elimination be responsible? We already had evaluated eq 8 which indicates dissociation of **14** into separated vinylithium and HLi fragments to be very unfavorable (the 3-21G value is given; this increases to 29.3 kcal/mol at MP2/6-31G\*\*//3-21G).<sup>2</sup>



However, the vinylithium-HLi complex (**15**) is now found to be 51.0 kcal/mol (3-21G//3-21G) more stable than the separated fragments (eq 9). This complex, the global  $C_2H_4Li_2$  energy minimum, is 29.8 kcal/mol (3-21G//3-21G) more stable than **14**, the lowest-energy form found previously (eq 10).<sup>2</sup> The perpendicular geometry, **15**, is 4.1 kcal/mol more stable than the planar form, **16**.



(30) See: Clark, T., unpublished calculations, 1977. (Also see: Szcześniak, M. M.; Ratajczak, H. *Chem. Phys. Lett.* **1980**, *74*, 243.) A similar complex may be involved in the hydroboration reaction, but the  $BH_3$ -ethylene association energy is much less: Clark, T.; Schleyer, P. v. R. *J. Organomet. Chem.* **1978**, *156*, 191-202. Nagase, S.; Ray, N. K.; Morokuma, K. *J. Am. Chem. Soc.* **1980**, *102*, 4536-4537. Graham, G. D.; Freilich, S. C.; Lipscomb, W. N. *Ibid.* **1981**, *103*, 2546-2552. As expected, the ethylene-Li<sup>+</sup> association energy is greater (23.2 kcal/mol).<sup>20</sup>

(31) (a) Skinner, D. L.; Peterson, D. J.; Lagon, T. J. *J. Org. Chem.* **1967**, *32*, 105-108. (b) Kuus, H. *Uch. Zap. Tartu Gos. Univ.* **1966**, *193*, 130-134; *Chem. Abstr.* **1968**, *69*, 67443. Also see: Kuus, H. *Uch. Zap. Tartu Gos. Univ.* **1968**, *219*, 245-250; *Chem. Abstr.* **1969**, *71*, 19155. (c) Rautenstrauch, V. *Angew. Chem.* **1975**, *87*, 254-255; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 259-260. (d) Bogdanovič, B.; Wermeeckes, B. *Angew. Chem.* **1981**, *93*, 691-693; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 684-686.

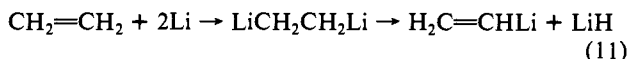
(26) (a) Kos, A., unpublished calculations. See: Bates, R. B.; Hess, B. A., Jr.; Ogle, C. A.; Schrad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052-5058. (b) For an X-ray structure of an aromatic analogue, *o*- $C_6H_4(CH_2SiMe_2)_2Li_2$ , see: Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 14-15.

(27) Wakefield, B. J. "The Chemistry of Organolithium Compounds", Pergamon Press: New York, 1974.

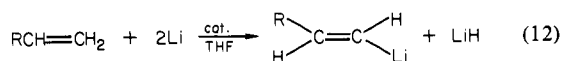
(28) For studies of aspects of the LiH elimination mechanism, see: Reetz, M. T.; Stephan, W. *Tetrahedron Lett.* **1977**, 2693-2696; *J. Chem. Res. Synop.* **1981**, *44*, 583-584. Also: Houk, K.; Rondan, N.; Clark, T.; Kaufmann, E.; Schleyer, P. v. R., to be published.

(29) Although the  $C_s$  form of complex **7** is the local minimum, the potential energy surface is very flat. If the lithiums are moved to opposite ends, a geometry results that models the X-ray structure of allyllithium, an endless chain of monomeric units associated end-to-end (Köster, H.; Weiss, E. *Chem. Ber.* **1982**, *115*, 3422-3426). Isomer **8**, with both Li's on the same side, is even better than **7**. The 3-21G//3-21G structure of **8**, distances in angstroms and angles in degrees:  $C_1-C_2$ , 1.395;  $C_2-Li$ , 2.155;  $C_1-Li$ , 2.678;  $Li-Li$ , 2.675;  $Li-H_b$  (bridged), 1.778;  $C_1-H$ , 1.082;  $C_2-H$  (pointed inside), 1.082;  $C_2-H_o$  (pointed outside), 1.078;  $C_1-H_b$ , 3.474;  $C_2-C_1-C_2'$ , 129.7;  $C_1-C_2-Li$ , 95.6;  $C_1-C_2-H$ , 118.3;  $C_1-C_2-H_o$ , 117.8;  $H_b-C_1-O$  (bisector  $C_2-C_1-C_2'$ ), 70.7;  $O-C_1-H$ , 176.1;  $PhLi-C_2-C_1-C_2'$ , 82.8;  $PhH-C_2-C_1-C_2'$ , 20.1;  $PhH_o-C_2-C_1-C_2'$ , 166.1.

Since the driving force for the formation of the HLi complex **15** is so large (compare eq 10 with eq 6), "elimination" of HLi from **14** is expected to be quite rapid.<sup>28</sup> Of course, the products of subsequent reactions of **15**, which can be regarded as a "mixed dimer", will be those expected from vinyl lithium itself. There are several experimental precedents.<sup>31</sup> Rautenstrauch<sup>31c</sup> examined the reaction of lithium metal (with biphenyl as "carrier" and naphthalene as catalyst) with ethylene; vinyl lithium was the major product. The reaction was postulated to proceed by HLi elimination from 1,2-dilithioethane, produced by addition of lithium to ethylene (eq 11). Bogdanović and Wermeckes<sup>31d</sup> extended these

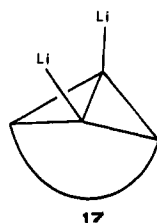


observations. By use of hypermetallated<sup>32</sup> lithium metal complexes and Lewis acid catalysts, ethylene was converted into vinyl lithium in 70–75% yield; the LiH byproduct precipitated under the experimental conditions (tetrahydrofuran (THF) solution, 0 °C).<sup>31d</sup> Propene (and other terminal olefins) reacted similarly to give (*E*)-propenyl lithium (and (*E*)-1-lithio-1-olefins) with high regio- and stereoselectivity (eq 12).

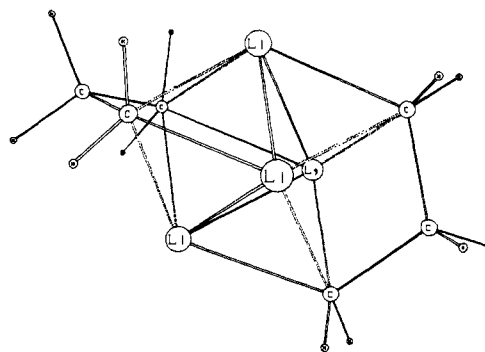


We suggest that these reactions proceed by the initial conversion of vicinal dilithium intermediates to HLi–vinyl lithium complexes (like **15**, but these may be involved in higher aggregates). Disproportionation of such aggregated complexes may lead to the observed precipitation of the insoluble lithium hydride. The potential importance of such LiH complexes as reaction intermediates has not been appreciated before and will be explored in greater detail in a future paper in this series.

1,2-Dilithium derivatives are known in stabilized systems; e.g., the X-ray structures of related dilithium derivatives of 9,9-bifluorenyl,<sup>33a</sup> stilbene,<sup>33b</sup> and acenaphthylene<sup>33c</sup> are available. When LiH elimination is precluded, 1,2-dilithio derivatives are also possible in unconjugated systems. A number of double bridgehead-lithiated bicyclobutanes, summarized by **17**, are good examples.<sup>34</sup> Model calculations involving bicyclobutane and CH<sub>3</sub>Li show that both the first and the second metallation steps (e.g., to give **17**) are exothermic by 8.6 and 6.4 kcal/mol, respectively.<sup>35</sup>



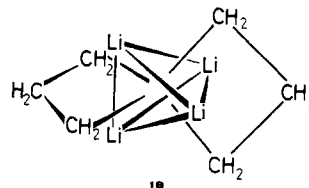
**Association of Dilithio Derivatives.** We wish to speculate about the possible nature of **1** and **2** in solution and in the solid, although the degree of association and solvation is not yet known experimentally. The two 1,4 doubly lithium bridged species for which X-ray structures are available, *o,o'*-dilithiobiphenyl<sup>18</sup> and a derivative of  $\alpha,\alpha'$ -dilithio-*o*-xylene,<sup>26b</sup> are both monomeric, with each lithium solvated by a tetramethylethylenediamine (TMEDA) ligand. Such  $\pi$ -stabilized systems may not be good models for **1** and **2**, which may prefer to dimerize instead. We have already



**Figure 2.** The MNDO-optimized structure (no symmetry imposed) corresponding to **18**, the dimer of **3**. The flattened Li<sub>4</sub> tetrahedron and the interlocking octahedral arrangements are notable. The two Li–Li distances are 2.28 and 2.83 Å; the C–Li distances (generally underestimated at the MNDO level) are 2.17 and 2.21 Å. The C–C–C angles (114.0°) are widened somewhat, and the CH<sub>2</sub> groups remain eclipsed (as in **3**).

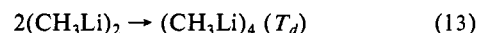
considered structural candidates for the dimers of dilithiomethane<sup>13</sup> and for 1,2-dilithioethane.<sup>2</sup> The former favors a head-to-head arrangement. The latter, even more reminiscent of the tetrameric structures of alkyllithiums,<sup>24</sup> suggests **18** (schematically represented), with terminal methylene groups bound to faces of a Li<sub>4</sub> tetrahedron, as a possibility for the dimers of **1** and **2**.

MNDO calculations on **18** gave the structure shown in Figure 2. While eclipsed rather than staggered CH<sub>2</sub> groups again are favored (cf. **3** and **5**), the most remarkable feature is the *opened* nature of the central Li<sub>4</sub> "tetrahedron". While each terminal CH<sub>2</sub>



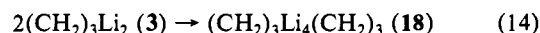
group is bound to three lithium atoms (as in RLi tetramers), only four of the six Li–Li distances are equal and short.

The dimerization of **3** and other doubly bridged dilithium compounds is akin to the conversion of two alkyllithium dimers into a tetramer; eq 13 gives ab initio and MNDO data for methyl lithium. While MNDO overestimates this energy, we are only able to evaluate the dimerization of 1,3-dilithio propane (eq 14) at that level. The exothermicity of eq 14 is larger than that of eq 13 and the dimerization of dilithiomethane (eq 16), and even greater than the dimerization energy of 1,2-dilithioethane (eq 15). It appears that dimers of 1,2- and 1,3-dilithium compounds, like **18**, may be particularly favorable. We will report other examples subsequently.

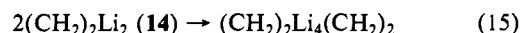


$$-63.2 \text{ kcal/mol (MNDO);}$$

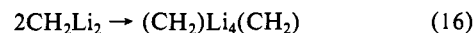
$$-46.2 \text{ kcal/mol (STO-3G // STO-3G)}$$



$$-119.5 \text{ kcal/mol (MNDO)}$$



$$-101.4 \text{ kcal/mol (MNDO)}$$



$$-37.0 \text{ kcal/mol (4-31G // STO-3G)}$$

Why is the energy of eq 14 so much larger than that of eq 13? Actually, the total association energy of methyl lithium in going from the monomer to the tetramer (–208 kcal/mol at MNDO) is somewhat larger than the comparable energy of 1,3-dilithio propane (–194 kcal/mol, leading from **6** to **18**), but the two stages

(32) Cf.: Schleyer, P. v. R.; Würthwein, E.-U.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5839–5841. Schleyer, P. v. R. In "New Horizons of Quantum Chemistry"; Löwdin, P.-O.; Pullman, B., Eds.; Reidel: Dordrecht, 1983; p 95–109. Schleyer, P. v. R.; Würthwein, E.-U.; Pople, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5930–5932.

(33) (a) Walczak, M.; Stucky, G. D. *J. Organomet. Chem.* **1975**, *99*, 313–323. (b) Walczak, M.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 5531–5539. (c) Rhine, W. E.; Davis, J. H.; Stucky, G. D. *J. Organomet. Chem.* **1977**, *134*, 139–149.

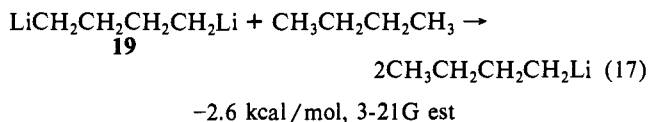
(34) Szeimies, G., private communication. We thank Professor Szeimies for this information.

(35) Kos, A. J., unpublished calculations.

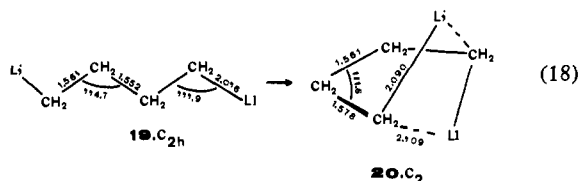
of the association processes are partitioned differently. The dimerization of methyl lithium ( $-72$  kcal/mol, MNDO, Table I) is more favorable than the cyclization of 1,3-dilithiopropene ( $6 \rightarrow 3$ :  $-37$  kcal/mol, MNDO). The structure of **6** is constrained, whereas methyl lithium dimer  $C_{2h}$  can adopt the best possible geometry. The second state of the association is more favorable for 1,3-dilithiopropene (eq 14 vs. eq 13). This results from a partial compensation for the non-ideal structural constraints in **3**; methyl lithium dimer,  $C_{2h}$ , benefits less from tetramer formation.

**1,4-Dilithiobutane.** West and Rochow had no difficulties in preparing 1,4-dilithiobutane by reaction of 1,4-dibromobutane with lithium metal.<sup>1</sup> Like higher  $\alpha,\omega$ -dilithioalkanes, 1,4-dilithiobutane was reported to be stable in ether solution and to give a respectable yield of bis(trimethylsilyl) quenching products. This behavior is quite different from that of 1,3-dilithiopropene and 1,2-dilithioethane under such conditions.

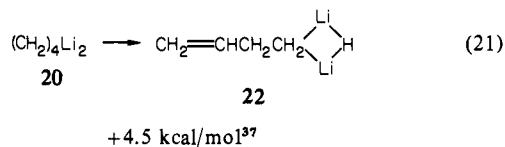
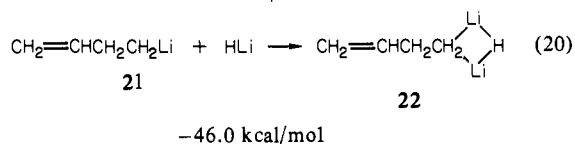
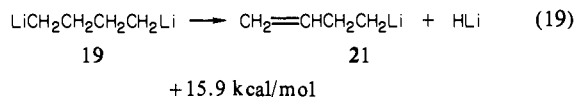
Like **6** (see eq 1), the extended form of 1,4-dilithiobutane (**19**) exhibits a modest destabilization according to the hypothetical disproportionation reaction (eq 17).



However, cyclization of **19** (eq 18) to give a doubly bridged, twisted  $C_2$  structure, **20** (this is 7.4 kcal/mol more stable than an eclipsed,  $C_{2v}$ , doubly bridged alternative), is 10 kcal/mol more exothermic than cyclization of 1,3-dilithiopropene (compare **19**  $\rightarrow$  **20** with **6**  $\rightarrow$  **3**).



Because of the greater flexibility afforded by the longer carbon chain, the cyclization energy (eq 18) approaches the dimerization energy of methyl lithium,  $-46.3$  kcal/mol at 3-21G//3-21G, more closely. Obviously, **20** is much more stable than **19** toward possible disproportionation processes (cf. eq 1 and 2). Is **20** also stable toward elimination? We have estimated the thermochemistry of this process in the following way.



The energy of the elimination of HLi from **19** (eq 19) to form 3-butenyllithium (**21**) is assumed to be the energy of eq 4 (splitting off of HLi from propyllithium) less the destabilization energy of **19** (eq 17). The association of **21** and HLi to give complex **22** (eq 20) is assumed to have the same energy as the association of

$\text{CH}_3\text{Li}$  and HLi. Since **20** is 34.6 kcal/mol more stable than **19** (eq 18), the conversion of **20** into **22** should be *endothermic* by 4.5 kcal/mol (eq 21).<sup>37</sup> This contrasts sharply with the corresponding elimination complex forming rearrangement reactions of 1,2-dilithioethane (eq 10) and of 1,3-dilithiopropene (eq 6), both of which are *exothermic* by nearly 30 kcal/mol. We believe the cyclization energy and the sharply reduced thermodynamic driving force for LiH elimination complex formation of 1,4-dilithiobutane rationalize the observed stability of the higher  $\alpha,\omega$ -dilithioalkanes in solution. The mechanisms and activation barriers of representative HLi elimination reactions are being studied computationally and will be reported subsequently.<sup>28</sup>

## Conclusions

Double bridging by metallic counterions like lithium (1,2-, 1,3-, 1,4-, etc.) should be a ubiquitous structural feature of "polyanion" systems.<sup>6,23</sup> 1,3 bridging provides an explanation for the stability of 1,3-dilithiopropanes (which cannot undergo elimination)<sup>3</sup> and has also been found in our published calculational studies on  $\text{C}_3\text{Li}_4$ ,  $\text{C}_3\text{H}_3\text{Li}_3$ ,  $\text{C}_3\text{H}_2\text{Li}_2$ ,<sup>10</sup> and  $\text{C}_3\text{H}_4\text{Li}_2$ .<sup>5</sup> Possible examples involving heteroatoms abound, e.g.,  $\text{HCONLi}_2$ ,  $\text{RCOCHLi}_2$ ,  $\text{LiCH}_2\text{COC-H}_2\text{Li}$  (written conventionally), etc.<sup>6</sup>

1,4 bridging in 1,4-dilithiobutane is even more favorable energetically. Earlier examples we have considered include 1,4-dilithiobutadiene<sup>16</sup> and *o,o'*-dilithiobiphenyl for which an X-ray structure is available.<sup>18</sup> Many additional systems should exhibit 1,4 and higher double bridging.<sup>6,23,26</sup>

The facile elimination observed for **3** may involve a thermodynamically-favorable allyllithium-LiH complex (**8**). A similar vinyl lithium-LiH complex (**15**), more favorable than any 1,2-dilithioethane geometry, is a likely reaction intermediate in reactions of lithium with ethylene and with terminal olefins. These lead to vinyl lithium derivatives and LiH. 1,4-Dilithiobutane<sup>36</sup> and higher  $\alpha,\omega$ -dilithioalkanes are expected to be stable in cyclic geometries since LiH elimination complex formations should be endothermic. These compounds are easily produced by conventional lithiation procedures.

When LiH elimination is precluded by structural considerations, unactivated  $\alpha,\omega$ -dilithioalkane derivatives may derive additional stabilization through dimerization. These dimers may involve flattened  $\text{Li}_4$  tetrahedra akin to **18** and Figure 2.

**Note Added in Proof.** Additional examples of double lithium bridging have now been found in the X-ray structures of 1,4-dilithio-1,4-diphenyl-*cis*-2-butene<sup>37a</sup> and 2,2'-dilithiobiphenyl ether.<sup>37b</sup>

**Acknowledgment.** We thank F. Bickelhaupt for suggesting the problem and providing information prior to publication, A. Streitwieser for stimulating discussions on the nature of lithium bonding, W. Thiel and T. Clark for the MNDO lithium parameterization, and J. Andrade for background calculations. We appreciate discussions with K. Houk and J. A. Pople, who have collaborated with us on related studies. The work was supported by the Fonds der Chemischen Industrie and was facilitated by the cooperation of the Regionales Rechenzentrum Erlangen.

(36) Reaction 21 may be more favorable than estimated since intramolecular lithium- $\pi$  interactions, for which there is experimental evidence (Oliver, J. P.; Smart, J. P.; Emerson, M. T. *J. Am. Chem. Soc.* **1966**, *88*, 4101. Also see: Nagase, S.; Houk, K. N. *Tetrahedron Lett.* **1982**, *23*, 19) were not taken into account. These intramolecular interactions are expected to be considerably less stabilizing than the intermolecular LiH-ethylene association energy (12.9 kcal/mol), however (Andrade, J. G., unpublished calculations).

(37) (a) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Dietrich, H.; Mandi, W. *J. Chem. Soc., Chem. Commun.*, submitted. (b) Dietrich, H.; Mandi, W.; Baumgärtner, W.; Neugebauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.*, submitted. Also see ref 6c.