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Mechanism of Anionic [3 + 2] Cycloadditions. An ab Initio Computational Study on the Cycloaddition of Allyl-, 2-Borylallyl-, and 2-Azaallyllithium to Ethylene

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Abstract: The anionic [3 + 2] cycloaddition of allyl anions or allyllithium compounds to double or triple bonds is an elegant route both to carbocyclic and to heterocyclic five-membered rings. The mechanism of such reactions has not yet been established conclusively. In this computational study, the concerted $4\pi_s + 2\pi_s$ mechanism, expected on the basis of the Woodward−Hoffmann rules, is found to be less favorable than two-step pathways for the cycloadditions of ethylene to the allyl, 2-borylallyl, and 2-azaallyl anions and their lithiated counterparts at Becke3LYP/6-311+G** and MP2(fc)/6-31+G* levels of theory. Except for allyllithium, the $4\pi_s + 2\pi_s$ cycloadditions (in C_s symmetry) are not concerted, since only second-order saddle points, rather than true transition structures, are involved. The anisotropy of the reactant polarizabilities is responsible. Instead, two-step cycloaddition pathways are followed by all three model systems. In accord with experimental experience, 2-borylallyl and 2-azaallyl compounds are found to undergo this type of reaction more readily than the unsubstituted allyl anion or allyllithium. The second, ring-closing step is facilitated by the anion-stabilizing effect of nitrogen and the boryl substituent.

Introduction

The [3 + 2] cycloaddition of allyl anions and olefins, resulting in the formation of cyclopentyl anions, is one of the most straightforward routes to five-membered carbocyclic rings. An equally elegant access to pyrrolidine ring systems is provided by the cycloaddition of 2-azaallyl anions and olefins. Numerous examples of both reactions have been reported in the literature.[1−14] Frontier orbital considerations (the Woodward−Hoffmann rules)[15] predict that, for these reactions, a concerted $4\pi_s + 2\pi_s$ cycloaddition mechanism is symmetry-allowed (route A in Scheme 1). Alternatively, a two-step pathway may be followed, involving pentenyl or azapentenyl anion intermediates (route B).

Which of these two possible mechanisms is favored? The concerted pathway implies stereospecificity with respect to the olefin and the allyl anion configuration (provided they are stable under the experimental conditions). The two-step pathway is equally compatible with a stereospecific or nonstereospecific reaction course, as outlined in Scheme 1.

Secondary kinetic isotope effect measurements can distinguish concerted from stepwise cycloadditions.[16] However, such experiments often are rather lengthy and exacting,[16a−l] unless they can be carried out on a very large scale.[16k,l] A two-step mechanism can also be demonstrated experimentally if a cycloaddition is nonstereospecific, or by the isolation of products derived from open-chain intermediates.

More easily, both pathways can be examined in detail theoretically. The present study analyzes the basic factors that govern the course of these reactions.

Background

The first example of an allyl anion−olefin cycloaddition was reported by Kolobielski and Pines in 1957.[1a] Treatment of α-methylstyrene with sodium, benzylsodium, or potassium[1b] afforded, among other products, 1-methyl-1,3-diphenylcyclo-

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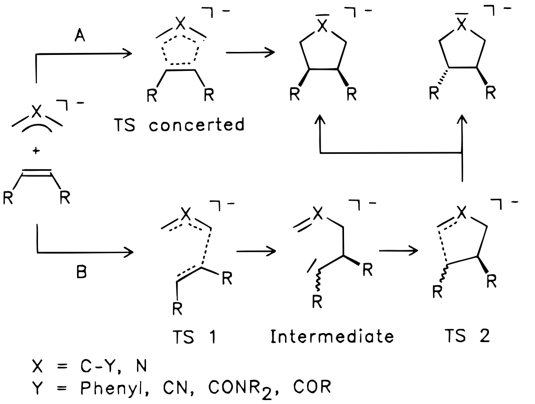
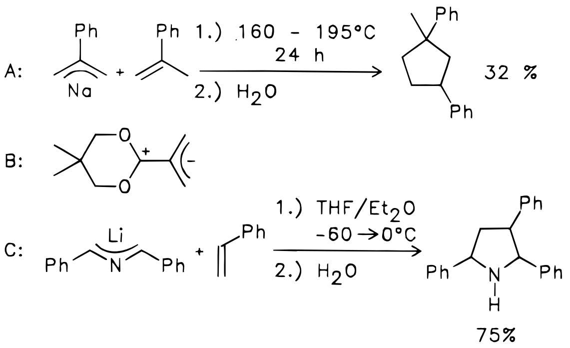
Scheme 1



Scheme 2



pentane by addition of 2-phenylallyl anion to an excess of α-methylstyrene (Scheme 2A). During the cycloaddition, the negative charge shifts toward the central carbon of the allyl anion. Hence, only allyl anions with appropriate substituents at the central carbon usually undergo such reactions. These substituents stabilize the developing cyclopentyl anion.[2] In addition to 2-phenylallyl anions,[1,3] cycloadditions of 2-cyano,[4] 2-carbamoyl-,[5] and 2-carbonylallyl anions[6] have been reported. A closely related zwitterionic system, for which calculations indicated some diradical character,[7b] has been described recently (Scheme 2B).[7] The scope of this type of reaction has been extended to the synthesis of cyclopentenes via an addition−elimination sequence by introduction of a phenylsulfonyl or phenylthio substituent at a terminal carbon of the allyl anion.[2a,5c,f] Since allyl anions are very electron-rich systems, only olefins with aromatic and/or electron-withdrawing substituents were found to be suitable reaction partners for this type of cycloaddition.[1−7] The only additions to nonolefinic multiple bonds have been reported for azobenzene[5a,b,d,e] and, more recently, for a number of electron-deficient alkynes.[7e]

Kauffmann et al.[8] pioneered the field of cycloaddition reactions of 2-azaallyl anions in 1970. Both 1,1- and 1,3-diphenyl-2-azaallyllithium were found to react with styrene, stilbene, and diphenylacetylene, affording the corresponding pyrrolidines in moderate to good yields (Scheme 2C). Since nitrogen is more electronegative than carbon, the increase of negative charge at the center atom of the 2-azaallyl moiety during the cycloaddition is more favorable than that in allyl anions. Therefore, 2-azaallyl anions undergo cycloadditions with a greater variety of multiple bonds. There are many examples involving olefins with aromatic and/or electron-

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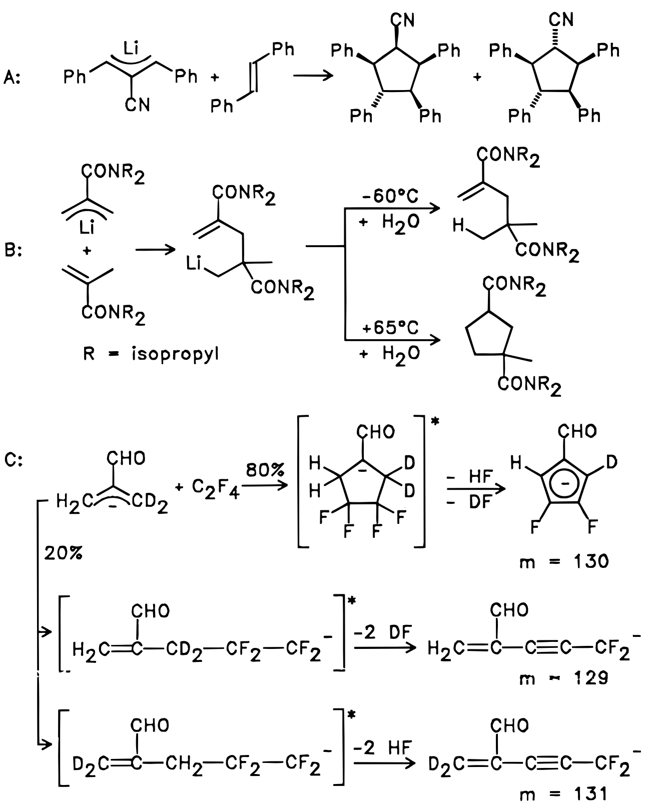
Scheme 3



withdrawing substituents.[8,9] Alkenes bearing organoelement groups containing Si, Ge, P, As, S, and Se have proved to be very useful extensions,[9bb,cc,10] since such substituents can easily be replaced by a large number of other functionalities. Cycloadditions with some dienes and alkynes,[8,9bb,11] aromatic nitriles,[12] and with C=N, C=S, and N=N double bonds[9r,13] also have been reported.

Considerable effort has been expended to elucidate the mechanisms of these reactions. Some allyl anions react stereospecifically without forming any open-chain side products, evidently favoring the concerted $4\pi_s + 2\pi_s$ cycloaddition mechanism.[4b,6,7a,c] For example, a very thorough study employing NMR and X-ray techniques revealed that the addition of 2-cyano-1,3-diphenylallyllithium to *trans*-stilbene results in the formation of only 2 out of 10 possible diastereomeric 1-cyano-2,3,4,5-tetraphenylcyclopentanes (Scheme 3A).[4b]

However, other mechanistic investigations gave clear evidence for two-step pathways.[5a,b,d] The products of the reaction of 2-carbamoylallyllithium with azobenzene and some acrylamides was strongly temperature dependent (Scheme 3B). Quenching of the reaction mixtures by addition of water at −78 to −60 °C afforded open-chain products exclusively, whereas warming to +25 to +65 °C prior to quenching resulted in the formation of cyclopentanes.

Nibbering et al. investigated the cycloaddition reactions of the parent allyl anion and of the 2-cyano- and 2-formylallyl anions with tetrafluoroethylene in the gas phase by Fourier transform ion cyclotron resonance mass spectroscopy.[14] The use of specifically deuterated allyl and 2-formylallyl anions allowed the pentenyl and cyclopentyl anion products to be detected separately (Scheme 3C): 65% of the reaction products from the allyl anion resulted from open-chain intermediates, 20% from a [2 + 2] cycloaddition, and only 15% from a [3 + 2] cycloaddition. In contrast, 80% of the products from the 2-formylallyl anion resulted from a [3 + 2] cycloaddition and 20% from open-chain intermediates. This change in product ratio due to the presence of a charge-stabilizing substituent at the central carbon of the allyl anion parallels the behavior of these species in solution.

The first mechanistic studies of 2-azaallyl anions were undertaken by Kauffmann et al.[9a,13a] The cycloadditions of 1,1- and 1,3-diphenyl-2-azaallyllithium to *cis*- and *trans*-stilbene and to some azomethines and azoarenes were shown to proceed completely stereospecifically, thus favoring the concerted mechanism. Later, the same conclusion was reached by others for a variety of 2-azaallyl anions and alkenes.[9h,k,q,s,t,v,y,aa,bb] Indications of the two-step mechanism were given by the isolation of compounds resulting from the linear addition of 2-azaallyl anions to alkenes together with cycloaddition products in some systems.[9g,m,n,r,w,z] In addition, there is a single report of a nonstereospecific cycloaddition of a 2-azaallyl anion to *cis*-stilbene.[9cc]

During the preparation of this paper, Sauers published an ab initio computational study of the concerted $4\pi_s + 2\pi_s$ cycloaddition of allyl, 2-fluoroallyl, and 2-azaallyl anions and 2-azaallyllithium to ethylene.[17] He found that the only stationary points with C_s symmetry on the reaction coordinates of these systems were second-order saddle points with two imaginary vibrational frequencies. For the simplest reaction, allyl anion plus ethylene, a C_1 symmetry transition structure for the linear addition (**TS 1** in Scheme 1) also was located. Although narrower in scope than our study, Sauers's investigation gave results which, in general, are consistent with the findings discussed below.

Computational Details

Calculations were performed using the GAUSSIAN 92/DFT and GAUSSIAN 94 program packages,[18a,b] employing standard basis sets and theoretical methods as defined in these programs.[18c,d] Geometries were optimized initially at the HF/6-31+G* level.[19] All structures were characterized as minima (number of imaginary frequencies, NIMAG = 0), transition structures (NIMAG = 1), or second-order saddle points (NIMAG = 2) by analytic energy second-derivative calculations of harmonic vibrational frequencies.[20] These provided the zero-point vibrational energies (ZPEs), which were scaled for the calculation of relative energies by an empirical factor of 0.89.[20] Geometries were then reoptimized with inclusion of valence-electron correlation at MP2-(frozen core, fc)/6-31+G*.[19,20] For some transition structures and second-order saddle points, vibrational frequencies were calculated at this level as well. Finally, single-point energies were computed for the MP2(fc) geometries at Becke3LYP/6-311++G**.[18c,d,21,22] To

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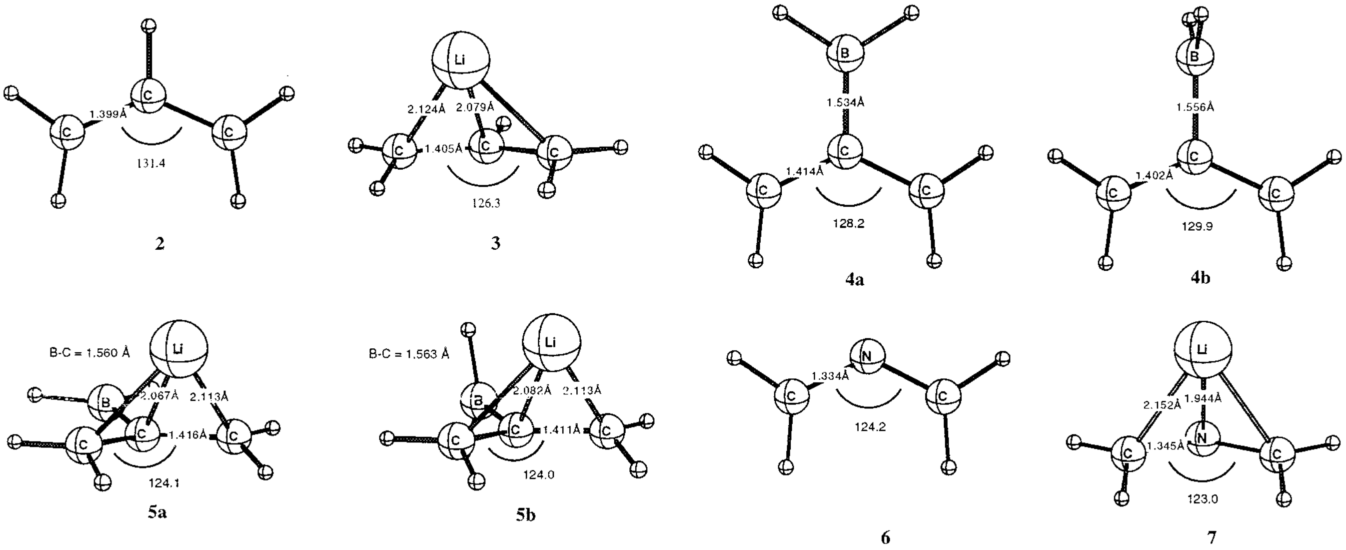

2 **3** **4a** **4b**

5a **5b** **6** **7**

Figure 1. Calculated geometries (MP2(fc)/6-31+G*) of allylic anions and allyllithium compounds.

confirm the characterization of some species as transition structures or second-order saddle points, geometry optimizations and vibrational frequency calculations were also carried out at Becke3LYP/6-311+G** and CID/ 6-31+G*.[18c,d,19−22]

Bond lengths are given in angstrøms, bond angles in degrees, and relative energies and ZPEs in kcal/mol. Absolute energies (in hartrees) and most of the ZPEs are provided as Supporting Information. Unless otherwise noted, the Becke3LYP/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*) relative energies are discussed in the text.

Results and Discussion

A. Reactants and Products. The allyl, 2-borylallyl, and 2-azaallyl anions, as well as their lithiated counterparts (Figure 1), were chosen as model systems to investigate the mechanism of anionic [3 + 2] cycloadditions. As prototypes of π-delocalized carbanions and organometallic compounds, the allyl anion **2** and its alkali metal derivatives (e.g., allyllithium, **3**) have been investigated extensively experimentally[23,24] and theoretically.[19b,25] Our calculations on these two systems agree with previous results and are not discussed in detail here. The 2-azaallyl analogons (**6** and **7**) have received much less attention.[26] To our knowledge, there are no reports on the 2-borylallyl system (**4** and **5**), which serves here as a simple model for allylic compounds with a strong anion-stabilizing substituent at the central carbon (vide supra).[27,28]

The 2-boryl substituent stabilizes the allylic system, as can be seen from isodesmic equations 1a (for the anion) and 1b (for the Li salt):[19a,29,30]

$$\mathbf{2} + \mathrm{H_3C{-}BH_2} \rightarrow \mathbf{4a} + \mathrm{CH_4} \quad \Delta E = -10.0\ \text{kcal/mol} \quad (1a)$$

$$\mathbf{3} + \mathrm{H_3C{-}BH_2} \rightarrow \mathbf{5a} + \mathrm{CH_4} \quad \Delta E = -2.8\ \text{kcal/mol} \quad (1b)$$

$$\mathrm{H_3C{-}BH_2} + \mathrm{CH_3}^- \rightarrow [\mathrm{CH_2{-}BH_2}]^- + \mathrm{CH_4} \quad \Delta E = -52.5\ \text{kcal/mol} \quad (1c)$$

$$\mathrm{H_3C{-}BH_2} + \mathrm{CH_3Li} \rightarrow [\mathrm{CH_2{-}BH_2}]\mathrm{Li} + \mathrm{CH_4} \quad \Delta E = -25\ \text{kcal/mol} \quad (1d)$$

Being less electronegative than carbon and hydrogen, boron can act as a weak σ-donor, but, due to its vacant p-orbital, more importantly it can act as a π-acceptor. The interaction of the allylic π-system with the vacant p-orbital on boron is "switched off" in transition structures **4b** and **5b**, due to the perpendicular conformations of the BH_2 groups. Compound **4a** is 8.0 kcal/mol lower in energy than **4b**; the difference between **5a** and **5b** is 2.4 kcal/mol (consistent with eqs 1a and 1b, respectively). In **4a** and **5a**, the boron p-orbital perpendicular to the CCC plane does interact with the allyl π-system, mainly in the HOMO-1 π-orbitals, while its coefficient is zero in the HOMO orbitals. Therefore, π-stabilization due to the BH_2 group is only small in **4a** and **5a**, compared to the 52.5 kcal/mol methyl anion stabilization (eq 1c)[30a,19a] and the 25 kcal/mol for H_2BCH_2Li (eq 1d).[30b] Consequently, the B−C distances of 1.534 Å in **4a** and of 1.560 Å in **5a** are close to $R_2B{-}C$ single bond values: 1.563 Å calculated for $H_3C{-}BH_2$[29] and 1.572−1.575 Å in triethylborane determined by X-ray crystallography.[31] In contrast, $R_2B{-}C$ bonds with strong π-contributions are significantly shorter: 1.458 Å computed for $H_2B{-}CH_2^-$ [19a] and 1.438−1.450 Å found in $[\mathrm{Li(12\text{-}crown\text{-}4)_2}][\mathrm{Mes_2BCH_2}]\cdot0.75\mathrm{THF}$ (Mes = mesityl) by X-ray crystallography.[28c] The C−C bonds in **4** and **5** are slightly elongated (+0.015 Å in **4a** vs **2**; +0.011 Å in **5a**

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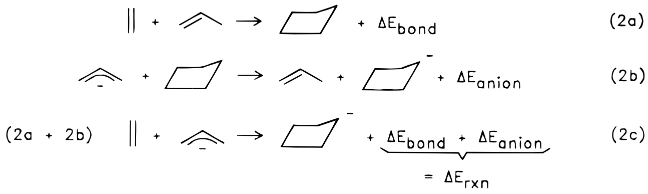
vs **3**), and the CCC angle is decreased by 3.2° (**2** → **4a**) and 2.2° (**3** → **5a**).

The cycloaddition of the allyl anion **2** and of allyllithium **3** to ethylene results in the formation of the cyclopentyl anions **8** and **9** and the cyclopentyllithium compounds **10** and **11**, respectively (Figure 2). While **8** is 0.5 kcal/mol more stable than **9**, **10** is 1.2 kcal/mol less stable than **11**. For the parent cyclopentane, both a twisted C_2 symmetry conformer and an envelope-like C_s form are isoenergetic minima.[32] For the cyclopentyl anion and for cyclopentyllithium, however, no C_2 minima could be located.

The cycloaddition of the 2-borylallyl anion (**4a**) and of 2-borylallyllithium (**5a**) to ethylene results in the formation of the cyclopentylboryl anion (**12**) and the cyclopentylboryllithium compounds, **15** and **18**, respectively. The anionic center in **12** is strongly stabilized by the π-interaction with the vacant p-orbital on boron: **13** and **14**, the envelope-like (C_s) transition structures for the rotation of the BH_2 groups, are 46.6 and 53.0 kcal/mol less stable than **12**. Consequently, B, C_1, C_2 and $C_{2'}$ are coplanar, and the C−B bond is quite short (1.467 Å). Since lithium can coordinate to the borylcyclopentyl anion from either side of the BCCC plane, borylcyclopentyllithium has two minima (**15** and **18**); **15** is 5.3 kcal/mol lower in energy than **18**. Transition structure **16**, 6.4 kcal/mol less stable than **15**, is involved in the automerization of the latter. In **15**, **16**, and **18**, the BH_2 group is only slightly bent out of the $C_1C_2C_{2'}$ plane (**15**, 4.8°; **16**, 5.6°; **18**, 1.6°), and the C−B distances are virtually identical to that found in **12**. However, the five-membered ring in **15** is twisted and has nearly C_2 symmetry, whereas in **16** and **18** it is envelope-like (C_s). In **17** and **19**, the π-stabilization of the anionic centers by boron is "switched off" due to the perpendicular conformations of the BH_2 groups. Transition structure **17** is 38.3 kcal/mol less stable than **15**, while the energy difference between **19** and **18** is 33.3 kcal/mol.

The cycloaddition of the 2-azaallyl anion (**6**) and of 2-azaallyllithium (**7**) to ethylene results in the formation of the pyrrolidyl anion (**20**) and of pyrrolidyllithium (**21**), respectively. In **21**, lithium is coordinated to nitrogen in the middle between an axial and an equatorial position. A combined gas-phase electron diffraction and ab initio computational study revealed that an envelope-like conformation with nitrogen out-of-plane is preferred not only by **20** and **21** but also by the parent pyrrolidine.[32g,33a] The structures of two oligomers of pyrrolidyllithium, $[(C_4H_8NLi)_3{\cdot}PMDETA]_2$ and $[(C_4H_8NLi)_2{\cdot}TMEDA]_2$, have been determined by X-ray crystallography.[33b,c] In these compounds, the pyrrolidine rings also adopt envelope-like conformations, but each lithium is coordinated to more than one nitrogen (and each nitrogen to more than one lithium). Hence, a direct comparison of these structures with **21** is not possible.

The reaction energies ΔE_{rxn} (Table 1) show the cycloadditions of allyl anion (**2**) and allyllithium (**3**) to ethylene to be nearly thermoneutral; however, the reactions of the 2-borylallyl compounds **4a** and **5a** are strongly exothermic, and the cycloadditions of the 2-azaallyl species **6** and **7** are moderately so. The reaction energies ΔE_{rxn} (eqs **2a−c**) can formally be regarded as a sum of two components: ΔE_{bond} is the energy that results from the transformation of the π-bonds of ethylene and the allylic system into two σ-bonds of the five-membered ring, and ΔE_{anion} is the energy that results from the change in the location and environment of the negative charge.



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(27) An ab initio computational study on cyclopropylboryl and 2-methyleneboratirane systems, which are isomers of the 2-borylallyl compounds considered here, will be published shortly.

(28) For a review on boron-stabilized carbanions, see: (a) Pelter, A.; Smith, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S. L., Eds.; Pergamon Press: Oxford, 1991; Vol. 1, p 487. For X-ray structures of such species, see: (b) Bartlett, R. A.; Power, P. P. *Organometallics* **1986**, *5*, 1916. (c) Olmstead, M. M.; Power, P. P.; Weese, K. J.; Doedens, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2541.

(29) At Becke3LYP/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*).

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(32) At Becke3LYP/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*). Some earlier computational studies, using small basis sets, also found the C_2 and C_s comformers to be isoenergetic (a, b); some other studies found the C_2 form to be slightly more stable than the C_s form (c, d): (a) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1358. (b) Saebø, S.; Cordell, F.; Boggs, J. E. *J. Mol. Struct. (THEOCHEM)* **1983**, *104*, 221. (c) Hoyland, J. R. *J. Chem. Phys.* **1969**, *50*, 2775. (d) Ferguson, D. M.; Gould, I. R.; Glauser, W. A.; Schroeder, S.; Kollman, P. A. *J. Comput. Chem.* **1992**, *13*, 525. Experimental studies (thermodynamic, infrared spectroscopy, and electron diffraction) revealed that the cyclopentane ring is puckered. The puckering displacement was shown to move freely around the ring (pseudorotation). See: (e) Adams, W. J.; Geise, H. J.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 5013 and references therein. (f) Fuchs, B. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Wiley & Sons: New York, 1978; p 1. (g) Legon, A. C. *Chem. Rev.* **1980**, *80*, 231.

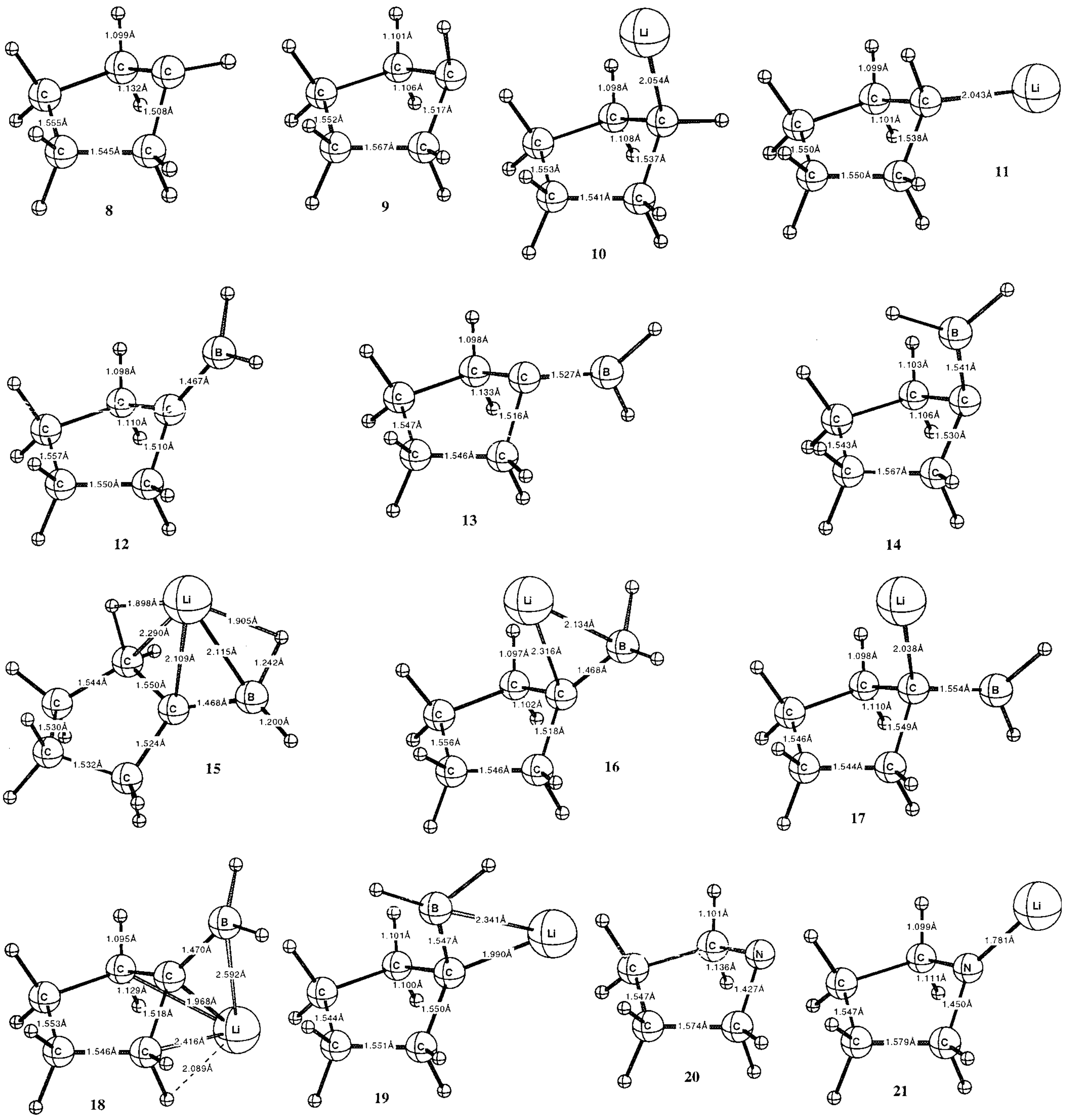

Figure 2. Calculated geometries (MP2(fc)/6-31+G*) of cyclopentyl and pyrrolidyl compounds.

The proton-transfer and transmetalation energies $\Delta E_{\mathrm{anion}}$ for the formation of the most stable product isomers are given in Scheme 4 and are summarized in Table 1. All the calculated ΔE_{bond} values are negative and vary only slightly from reaction to reaction. The large differences in $\Delta E_{\mathrm{anion}}$, however, account for the considerable differences in reaction energies ΔE_{rxn}. The allyl anion (**2**) is stabilized by 25.3 kcal/mol due to π-delocalization;[25g] the allyllithium (**3**) value is 18.5 kcal/mol.[25f] This π-stabilization is lost in the cyclopentyl anion (**8**) and in cyclopentyllithium (**10**). Therefore, the $\Delta E_{\mathrm{anion}}$ values for these systems are positive and nearly balance the ΔE_{bond} components. The additional anion-stabilizing effect of the boryl group in the 2-borylallyl anion (**4a**) and in 2-borylallyllithium (**5a**) is rather small (as discussed above). In the cyclopentylboryl anion (**12**) and cyclopentylboryllithium (**15**), however, the stabilization of the negative charge by the BH_2 group is so effective that the loss of the allylic resonance stabilization is more than compensated. Therefore, the $\Delta E_{\mathrm{anion}}$ values for these systems are negative, and the cycloaddition reactions are strongly exothermic. Although the proton affinity and the resonance stabilization of the allyl anion (**2**) and the 2-azaallyl anion (**6**) are virtually identical,[25e,26a] the $\Delta E_{\mathrm{anion}}$ values for the cycloadditions of **6**

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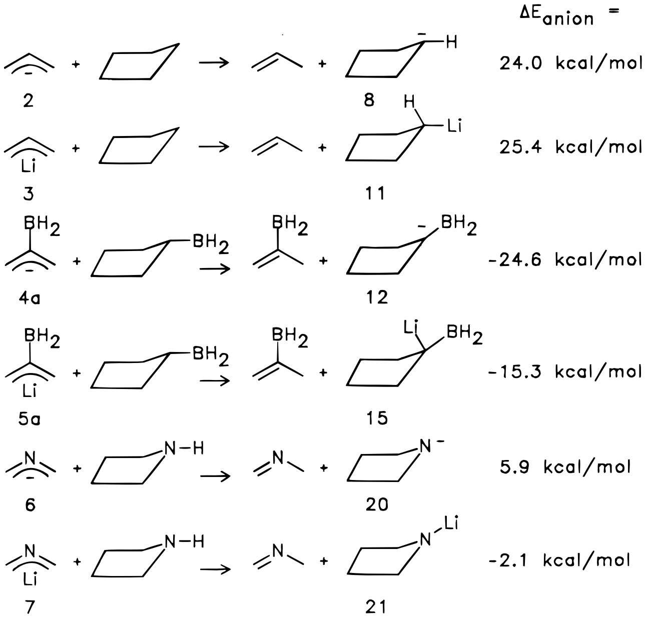
(33) However, similar to cyclopentane, the barrier for pseudorotation of the pyrrolidine ring has been found to be very small: (a) Pfafferott, G.; Oberhammer, H.; Boggs, J. E.; Caminati, W. *J. Am. Chem. Soc.* **1985**, *107*, 2305. (b) Armstrong, D. R.; Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 869. (c) Armstrong, D. R.; Barr, D.; Clegg, W.; Hodgson, S. M.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wright, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 4719.

Table 1. Reaction Energies of Cycloadditions

	B3LYP//MP2[a]			MP2//MP2[d]		
reaction	$\Delta E_{rxn}{}^{a,b}$	$\Delta E_{anion}{}^{a,b}$	$\Delta E_{bond}{}^{a,b} = (\Delta E_{rxn} - \Delta E_{anion})$	$\Delta E_{rxn}{}^{b,d}$	$\Delta E_{anion}{}^{b,d}$	$\Delta E_{bond}{}^{b,d} = (\Delta E_{rxn} - \Delta E_{anion})$
2 + **1** → **8**	−2.0	24.0[c]	−26.0	−15.0	22.8[c]	−37.8
2 + **1** → **9**	−1.5			−14.7		
3 + **1** → **10**	0.6			−14.8		
3 + **1** → **11**	−0.6	25.4	−26.9	−16.0	21.8	−37.8
4a + **1** → **12**	−45.4	−24.6	−20.8	−62.5	−28.5	−34.0
5a + **1** → **15**	−36.1	−15.3	−20.8	−51.8	−17.4	−34.4
5a + **1** → **18**	−30.8			−46.6		
6 + **1** → **20**	−17.5	5.9	−23.4	−31.5	0.5	−32.0
7 + **1** → **21**	−25.5	−2.1	−23.4	−40.6	−8.6	−32.0

[a] Becke3LYP/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*). [b] See eqs 2a−c and Scheme 4. [c] Experimental value: 25.3 kcal/mol, calculated from the gas-phase deprotonation enthalpies of propene and cylopentane.[34] [d] MP2(fc)/6-31+G*//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*).

Scheme 4. Proton Transfer and Transmetalation Energies at Becke3LYP/6-311++G**//MP2(fc)/6-31+G*



and 2-azaallyllithium (**7**) are more favorable than those for **2** and **3**. ΔE_{anion} is small and positive for the 2-azaallyl anion (**6**); it is slightly negative for the 2-azaallyllithium (**7**). Since nitrogen is more electronegative than carbon, the concentration of the negative charge on nitrogen in the pyrrolidyl anion (**20**) and in pyrrolidyllithium (**21**) is more favorable than that on carbon in the cyclopentyl species **8** and **10**. Therefore, the cycloadditions of **6** and **7** are moderately exothermic.

B. The Concerted Cycloaddition Mechanism. According to the Woodward−Hoffmann rules,[15] a concerted and, due to the symmetry of the reactants, synchronous $4\pi_s + 2\pi_s$ cycloaddition mechanism is allowed for the reactions of the allyl anions **2**, **4a**, and **6** and their lithiated counterparts **3**, **5a**, and **7** with ethylene **1** (Scheme 1). Consequently, all geometries of the stationary points on the reaction coordinates were optimized initially in C_s symmetry.

The stationary points for the concerted cycloadditions of the free anions **2**, **4a**, and **6** to ethylene are **22**−**24**, respectively (Figure 3). In **22**, which is 20.1 kcal/mol higher in energy than the reactants, the critical C−C distance of the developing σ-bonds is 2.169 Å (Tables 2 and 3). Such distances are considerably larger in **23** (2.555 Å) and in **24** (2.413 Å), which are 5.1 and 6.7 kcal/mol higher in energy than the reactants.

Two different reaction coordinates were considered for the corresponding allyllithium compounds **3**, **5a**, and **7**, since ethylene can approach either from the lithium or from the opposite side. The complexes **25**−**27** are formed first when ethylene approaches from the lithium side. The complexation energies are all very similar (−9.1 to −9.6 kcal/mol), as are the C═C bond lengths in the complexed ethylene molecules (1.349−1.350 Å) and the $\mathrm{Li}\cdots\mathrm{C}_{ethylene}$ distances (2.335−2.354 Å). The geometrical changes in the allylic parts of the complexes, relative to the reactants, are negligible. Stationary points **28**−**30** are farther along the reaction coordinates; **28** is 33.1 kcal/mol higher in energy than the reactants (42.2 kcal/mol higher than **25**), and the critical C−C distance is 1.999 Å. As with the free anions, considerably less energy is required to reach the stationary points on the reaction coordinates of the 2-borylallyl and 2-azaallyllithium compounds: **29** is 13.6 kcal/mol higher in energy than the reactants (22.8 kcal/mol higher than **26**); the corresponding values for **30** are 8.6 kcal/mol relative to the reactants and 18.2 kcal/mol relative to **27**. The critical C−C distances are 2.349 Å in **29** and 2.171 Å in **30**; both are larger than those in **28**.

When ethylene approaches the allyllithium compounds from the side opposite to the metal, no pre-reaction complexes form, and the only stationary points on the reaction coordinates are **31**−**33**. While **31** is 37.7 kcal/mol higher in energy than the reactants, the values for **32** and **33** are lower, 23.9 and 21.5 kcal/mol, respectively. Compared to the energies required to reach the stationary points **28**−**30** from the complexes **25**−**27**, the path from the reactants to **31** is more favorable by 4.5 kcal/mol; to **32** and **33**, it is less favorable by 1.1 and 3.3 kcal/mol, respectively. The critical C−C distance in **31** (2.186 Å) is 0.187 Å longer than that in **28**; in **32** it is 2.337 Å (−0.012 Å relative to **29**), and in **33** it is 2.372 Å (+0.201 Å relative to **30**).

Harmonic vibrational frequency calculations at HF/6-31+G* on **22**−**33** showed complexes **25**−**27** to be minima and species **31** and **32** to be transition structures, as expected (Table 3). *However, **22**−**24**, **28**−**30**, and **33** are second-order saddle points with two relatively large imaginary frequencies, rather than true transition structures!* Very recently, Sauers reported the same results for **22**, **24**, and **33** and for the corresponding stationary point for the reaction of the 2-fluoroallyl anion with ethylene.[17,35] To verify these surprising findings, frequency calculations for **22**−**24** and **28**−**33** also were carried out at MP2-

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(34) Experimental gas-phase deprotonation enthalpies ΔH^0_{acid} are as follow. Propene, 390.8 kcal/mol: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas-Phase Ion and Neutral Thermochemistry*; American Institute of Physics: Williston, VT, 1988. Cyclopropane, 416.1 kcal/mol: DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968.

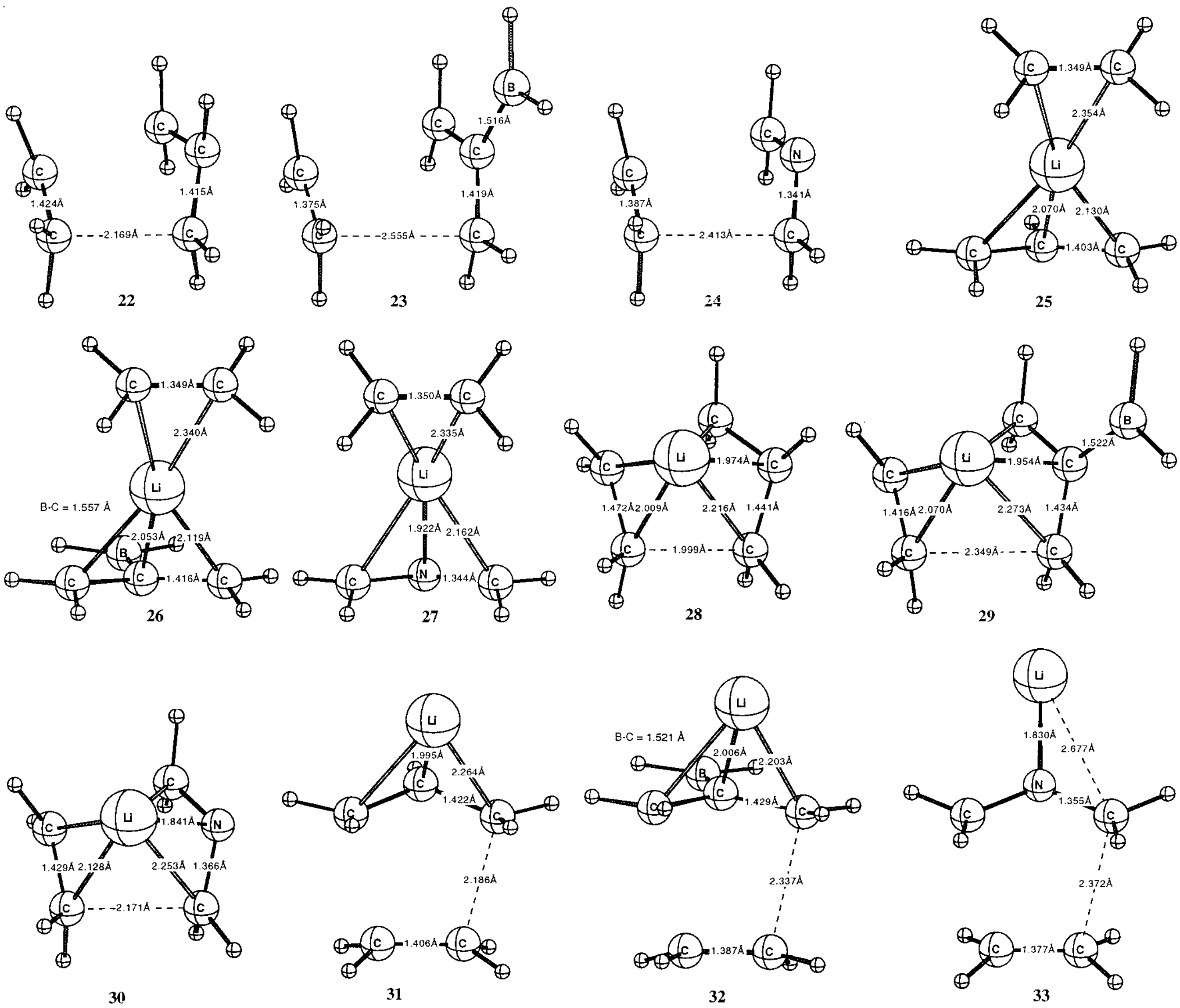

Figure 3. Calculated geometries (MP2(fc)/6-31+G*) of stationary points on the reaction coordinates of the concerted cycloaddition pathways.

Table 2. Relative Energies of Stationary Points on the Reaction Coordinates of the Concerted Cycloaddition Mechanism

	relative energy[b]				relative energy[b]		
compd[a]	MP2//MP2[c]	B3L//MP2[d]	B3L//B3L[e]	compd[a]	MP2//MP2[c]	B3L//MP2[d]	B3L//B3L[e]
22	9.3	20.1	20.3	**28**	24.9	33.1	33.2
23	−1.3	5.1	6.3	**29**	5.2	13.6	13.8
24	−1.5	6.7	8.7	**30**	−1.4	8.6	8.8
25	−12.2	−9.1		**31**	27.7	37.7	37.6
26	−12.9	−9.2		**32**	15.0	23.9	24.4
27	−13.1	−9.6		**33**	12.3	21.5	21.4

[a] Compound numbers as in Figure 3. [b] Reference energy (0.0) is for allylic compound + ethylene. [c] MP2(fc)/6-31+G*//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*). [d] Becke3LYP/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*). [e] Becke3LYP/6-311+G**//Becke3LYP/6-311+G** + 0.89 ZPE (HF/6-31+G*).

(fc)/6-31+G*, at Becke3LYP/6-311+G**,[36] and, for the parent systems **22** and **28**, at CID/6-31+G* (Table 3). The HF, MP2, Becke3LYP, and CID results agree, except for **23** and **24**, which are transition structures (NIMAG = 1) only at MP2, and for **32**, which is a second-order saddle point (NIMAG = 2) only at Becke3LYP. For **23** and **24**, the critical C−C distances calculated at MP2 are considerably larger ($\Delta r_{\text{C-C crit}}$ = 0.161−0.241 Å) than those found at HF and Becke3LYP. For all other species, the differences of the critical C−C distances are much smaller (average MP2 vs HF, 0.051 Å; MP2 vs Becke3LYP, 0.021 Å). In addition, the relative energies of **22**, **28**−**31**, and **33** calculated at Becke3LYP/6-311+G**//Becke3LYP/6-311+G** are only 0.1−0.2 kcal/mol (Table 2) larger than those found at Becke3LYP/6-311++G**//MP2(fc)/6-31+G*, whereas, for **23** and **24**, the corresponding energy differences are 1.2 and 2.0 kcal/mol, respectively. We are therefore convinced that

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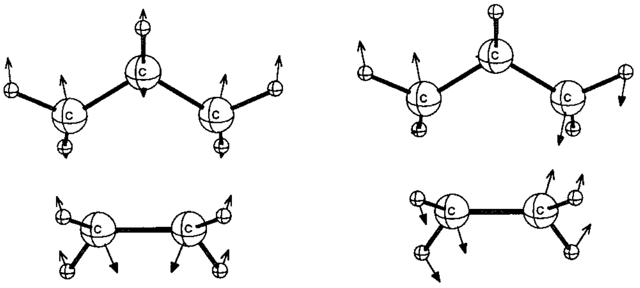
(35) The geometry reported for **33** by Sauers (ref 17) at MP2/6-31+G* differs slightly from ours: the critical C−C distance of 2.279 Å is 0.093 Å shorter, and three imaginary frequencies were calculated for this structure at MP2/6-31+G*.

(36) Relative energies of products at Becke3LYP/6-311+G**//Becke3LYP/6-311+G**: **8**, −0.6; **9**, −0.5; **10**, 0.7; **11**, −0.6; **12**, −45.3; **15**, −36.4; **18**, −31.1; **20**, −16.3; **21**, −25.6.

Table 3. Critical C−C Distances (Å), Numbers, and Wavenumbers ($\tilde{\nu}$, icm^{-1}) of the Imaginary Frequencies of the Transition Structures and Second-Order Saddle Points on the Reaction Coordinates of the Concerted Cycloadditions[a]

	HF/6-31+G*		MP2(fc)/6-31+G*		Becke3LYP/6-311+G**	
compd[b]	C−C	NIMAG, $\tilde{\nu}$	C−C	NIMAG, $\tilde{\nu}$	C−C	NIMAG, $\tilde{\nu}$
22[c]	2.162	2, −658.2; −334.3	2.169	2, −336.4; −166.5	2.138	2, −469.9; −245.2
23	2.314	2, −617.8; −177.8	2.555	1, −202.2	2.394	2, −354.6; −80.5
24	2.233	2, −553.7; −271.5	2.413	1, −172.2	2.225	2, −391.1; −173.5
28[c]	2.103	2, −531.9; −370.2	1.999	2, −441.5; −284.8	2.005	2, −405.1; −303.9
29	2.307	2, −549.9; −217.1	2.349	2, −306.6; −102.5	2.321	2, −362.9; −151.0
30	2.240	2, −472.3; −245.0	2.171	2, −318.4; −166.7	2.168	2, −358.2; −204.2
31	2.173	1, −870.3	2.186	1, −490.1	2.176	1, −600.5
32	2.243	1, −832.2	2.337	1, −472.7	2.289	2, −497.2; −176.9
33	2.317	2, −572.9; −68.0	2.372	2, −332.8; −114.3	2.349	2, −386.3; −114.0

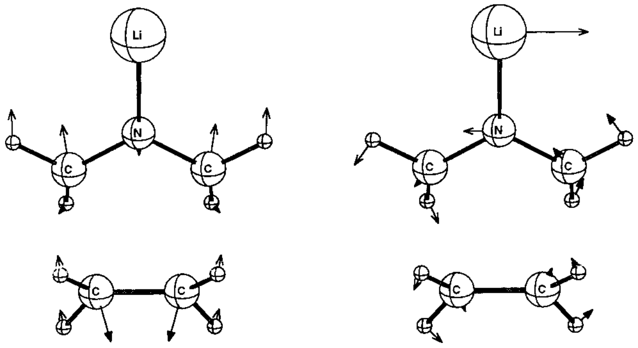
[a] Complexes **25**−**27** are minima (NIMAG = 0) and, therefore, are omitted from this table. [b] Compound numbers as in Figure 3. [c] CID/6-31+G*: **22**, C−C = 2.166 (Å), NIMAG = 2, $\tilde{\nu}$ = −552.0, −273.5; **28**, C−C = 2.080 (Å), NIMAG = 2, $\tilde{\nu}$ = −487.5, −328.6.



Normal modes associated with the

larger smaller

imaginary vibration of **22**



Normal modes associated with the

larger smaller

imaginary vibration of **33**

Figure 4.

MP2 does not describe the critical regions of the potential energy surfaces correctly for **23** and **24**, whereas the Becke3LYP results are reliable.[21e,f]

While **32** is a transition structure at both HF and MP2, it has two imaginary frequencies at Becke3LYP. The critical C−C distance calculated at Becke3LYP/6-311+G** is 0.048 Å smaller than that found at MP2, and the Becke3LYP relative energy is 0.5 kcal/mol larger than that at Becke3LYP//MP2. Hence, we consider the Becke3LYP/6-311+G** results to be more reliable and, consequently, **32** to be a second-order saddle point rather than a transition structure.

The normal modes associated with the two imaginary vibrational frequencies are very similar for **22**−**24**, **28**−**30**, and **32**; an example (for **22**) is shown in Figure 4. The normal mode associated with the larger imaginary frequency corresponds to a concerted, synchronous ring closure. Following the smaller imaginary frequency vector reduces the symmetry to C_1 and corresponds to the formation of only one new σ-bond. Therefore, **22**−**24**, **28**−**30**, and **32** are second-order saddle points linking two identical **TS 1** transition structures (Scheme 1) of the stepwise addition mechanism. The normal mode associated with the larger imaginary frequency of **33** also corresponds to the synchronous ring closure, as shown in Figure 4. However, the normal mode associated with the smaller imaginary frequency corresponds mainly to a sideward movement of lithium, rather than to the formation of a single σ-bond. Nevertheless, reoptimization of **33** without symmetry (C_1) failed to locate a concerted but nonsynchronous transition structure. Transition structure **57**, **TS 1** of the stepwise addition mechanism, was reached instead.

The fact that **22**−**24**, **28**−**30**, **32**, and **33** are second-order saddle points rather than the true transition structures expected on the basis of the Woodward−Hoffmann rules can be rationalized in terms of the anisotropy of the molecular polarizabilities of ethylene and the allylic compounds. The diagonal elements of the polarizability tensors (α_{xx}, α_{yy}, and α_{zz}) define the molecular polarizabilities along the *x*, *y*, and *z* axes and measure the ease and direction in which the electrons in a molecule are shifted by an external electric field. The polarizabilities of the reactants, calculated at Becke3LYP/6-311++G(3df,3pd)//MP2-(fc)/6-31+G*,[37] are summarized in Table 4, together with the orientations of the *x*, *y*, and *z* axes. The only experimental data available for this set of molecules are those for ethylene,[38] which are reproduced excellently.

The following information from Table 4 is the most significant. First, the polarizability of ethylene along the C═C bond (*z* axis) is about 50% larger than that perpendicular to it (*x* and *y* axes). Second, the polarizabilities of the allylic compounds along the *z* axis (i.e., along the "CXC backbone" of the molecules) are also significantly larger than those along the *x* and *y* axes, although the differences are not as large as in ethylene. As a consequence of the charge-localizing effect of the counterion,[25h] the polarizabilities of the allyllithium compounds are generally smaller than those of the corresponding free anions. Furthermore, the electrons of the allyllithium compounds are attracted by the positively charged counterion. Therefore, in these systems, the center of negative charge is not located in the CXC plane, as in the free anions, but somewhere between the anions and lithium.

When approaching an allylic anion on the reaction coordinate of the concerted cycloaddition pathway, ethylene is polarized

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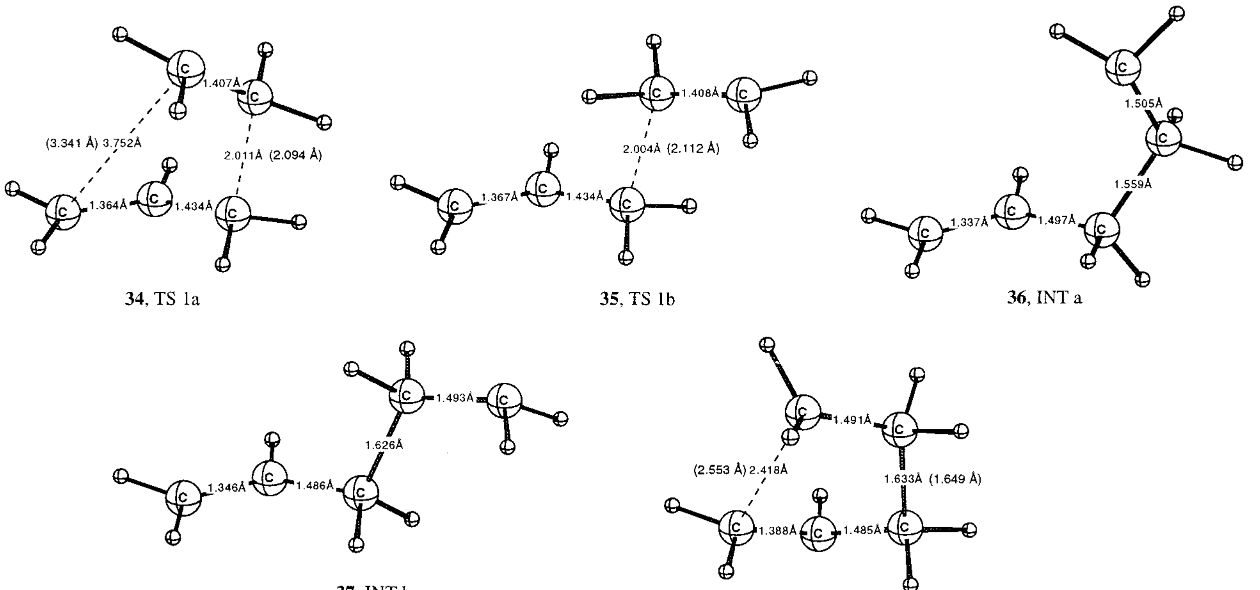
[37] For the influence of basis sets and electron correlation on the calculation of molecular polarizabilities, see: (a) Gough, K. M. *J. Chem. Phys.* **1989**, *91*, 2424. (b) Spackman, M. A. *J. Phys. Chem.* **1989**, *93*, 7594. (c) Craw, J. S.; Hinchliffe, A.; Perez, J. J. In *Self-Consistent Field: Theory and Applications*; Carbó, R., Klobukowski, M., Eds.; Elsevier: Amsterdam, 1990; p 866 and references therein.

[38] Hills, G. W.; Jones, W. J. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 812.



34, TS 1a

35, TS 1b

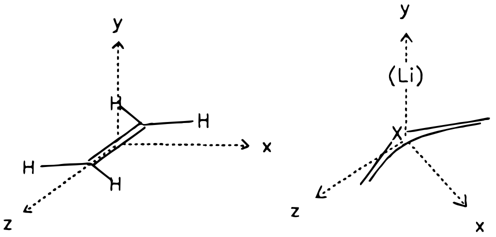
36, INT a

37, INT b

38, TS 2

Figure 5. Calculated geometries (Becke3LYP/6-311+G**) of transition structures (TS) and minima (INT) for the stepwise cycloaddition of allyl anion **2** to ethylene. Critical C−C distances at MP2(fc)/6-31+G* are given in parentheses.

Table 4. Diagonal Elements of the Polarizability Tensors of Ethylene and the Allylic Compounds[a]



X = CH, C−BH$_2$, N

compd[b]	α_{xx}[c]	α_{yy}	α_{zz}
ethylene, **1**[d]	24.91	22.68	36.22
2	48.65	89.51	111.42
3	50.73	50.31	81.56
4a	80.26	86.12	134.73
5a	71.44	59.22	95.69
6	51.35	75.06	113.26
7	42.53	49.77	83.34

[a] Becke3LYP/6-311++G(3df,3pd)//MP2(fc)/6-31+G*. [b] Compound numbers as in Figure 1. [c] In (atomic units)^3. [d] Experimental data (ref 38): $\alpha_{xx} = 26.05$; $\alpha_{yy} = 22.94$; $\alpha_{zz} = 36.44$.

by the negative charge of the anion in a direction perpendicular to the C=C bond. This induces an electric dipole moment in ethylene, which, in turn, polarizes the allylic anion along the *x* and *y* axes. Thus, the mutual polarization of the reactants occurs along the axes where the polarizabilities are small, which is quite unfavorable. Alternatively, ethylene can approach the allylic anion on the less symmetric reaction coordinate of the two-step cycloaddition pathway (vide infra), one end of the ethylene molecule always being much closer to the anion than the other. In this case, both ethylene and the allylic anion are polarized largely along the *z* axes. This polarization is more favorable than in the case of the concerted cycloaddition pathway, since the polarizabilities of the reactants are significantly larger along the *z* axes than along the *x* and *y* axes.

The electrostatic interaction between ethylene and an allyllithium derivative is similar in most respects to that between ethylene and an allylic anion, since the anisotropies of the polarizabilities are comparable in both cases. However, the center of negative charge in the allyllithium compounds is located between the allylic systems and lithium, rather than in the CXC planes. When ethylene approaches an allyllithium along the reaction coordinate of the concerted cycloaddition from the lithium side, ethylene is, therefore, polarized more strongly than in the case of an approach from the side opposite to lithium. This can explain the fact that **28** is a second-order saddle point, whereas **31** is a transition structure.

Similar arguments may hold for the cationic [4 + 3] cycloaddition of the allyl cation to butadiene. A recent ab initio computational study of this reaction by de Pascual-Teresa and Houk[39] revealed that only a two-step pathway and not the symmetry-allowed concerted cycloaddition mechanism is followed. Like the reactions discussed here, the stationary point on the reaction coordinate for the concerted cycloaddition was a second-order saddle point rather than a transition structure. In analogy to the anisotropy of the polarizabilities of the allylic anions, the polarizabilities of the allyl cation and of butadiene along the carbon chains can be expected to be larger than those perpendicular to it. Therefore, the electrostatic interaction between the allyl cation and butadiene should be more favorable on the stepwise than on the concerted cycloaddition pathway.

C. The Stepwise Pathway. The two-step pathways for the cycloadditions of the allyl anions **2**, **4a**, and **6**, and the allyllithium compounds **3**, **5a**, and **7** to ethylene are outlined in Scheme 1. At least three stationary points on the reaction coordinate were considered for every system. Transition structure **TS 1** separates the reactants from an open-chain pentenyl anion/lithium intermediate, **INT**. The latter is connected to the cyclic product(s) by the second transition structure, **TS 2**.

The geometries of the stationary points for the two-step cycloaddition of allyl anion (**2**) to ethylene (**34**−**38**) were optimized both at MP2(fc)/6-31+G* and at Becke3LYP/6-311+G** (Figure 5, Table 5). Both methods gave very similar geometries and nearly identical relative energies for **34**−**38**. Transition structures and intermediates for the corresponding

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(39) de Pascual-Teresa, B.; Houk, K. N. *Tetrahedron Lett.* **1996**, *37*, 1759.

Table 5. Relative Energies of Transition Structures and Minima for the Stepwise Cycloaddition of Allyl Anion **2** to Ethylene

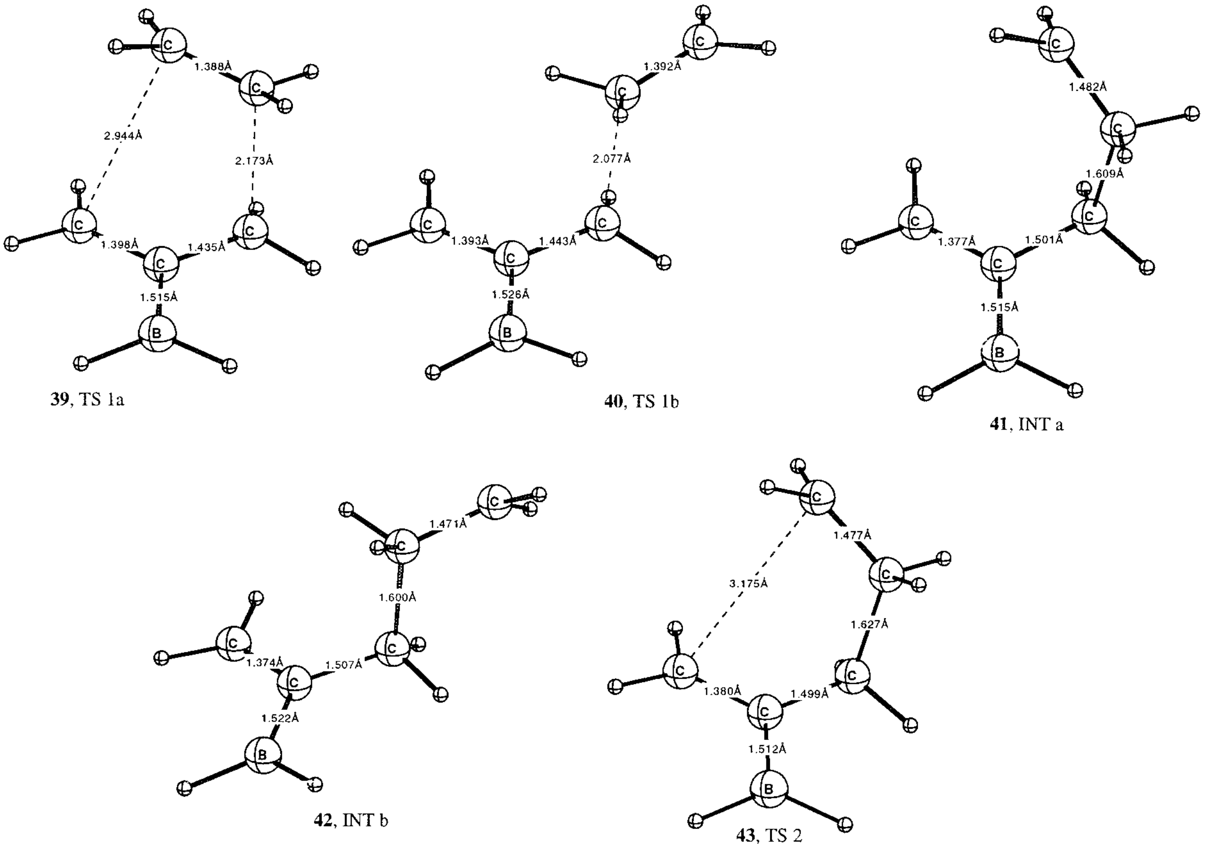
	relative energy[b]		
compd[a]	MP2//MP2[c]	B3L//MP2[d]	B3L//B3L[e]
34	4.6	8.9	8.6
35	4.5	6.8	7.2
36	−0.2	7.8	8.3
37	−1.3	5.8	5.9
38	6.7	16.2	16.6

[a] Compound numbers as in Figure 5. [b] Reference energy (0.0) is for allyl anion **2** + ethylene. [c] MP2(fc)/6-31+G*//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*). [d] Becke3LYP/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*). [e] Becke3LYP/6-311+G**//Becke3LYP/6-311+G** + 0.89 ZPE (HF/6-31+G*).

reactions of the 2-borylallyl anion **4a** (**39**−**43**, Figure 6) and the 2-azaallyl anion **6** (**44**−**48**, Figure 7), however, could be located only at Becke3LYP/6-311+G** (Table 6). Upon optimization at MP2(fc)/6-31+G*, **39**−**48** either separated into the reactants, collapsed to the reaction products, or gave the C_s-symmetric species **23** or **24**. This confirms that MP2 does not describe the critical regions of the potential energy surfaces for the additions of **4a** and **6** to ethylene correctly (vide supra). Consequently, only the Becke3LYP/6-311+G** results for the stepwise cycloadditions of the free anions will be discussed.

Since stationary points **22**−**24** on the reaction coordinates of the concerted cycloadditions of the allylic anions **2**, **4a**, and **6** to ethylene are second-order saddle points, these structures were reoptimized without symmetry restrictions (C_1): **34**, **39**, and **44** resulted. These are the first transition structures (**TS 1a**) on the reaction coordinates of the two-step cycloaddition pathways of the free anions. Their geometries are quite similar. The critical C−C distances (i.e., the length of the incipient σ-bonds) range from 2.011 Å in **34** to 2.173 Å in **39**, in contrast to the separations of the remote ends of ethylene and the anions (2.94−3.75 Å). The pentenyl anion intermediates (**INT a**) **36**, **41**, and **46**, found farther along the reaction coordinates, may be characterized as "endo" conformers, since their terminal carbons are in relative proximity. Further reduction in the distances between these terminal carbons results in transition structures **38**, **43**, and **48** (**TS 2**), which separate the open-chain intermediates from the cyclic products **8**/**9**, **12**, and **20**, respectively. The critical C−C distances in the **TS 2** species increase from 2.418 Å in **38** to 2.773 Å in **48** and, finally, to 3.175 Å in **43**. The pentenyl anion intermediates are quite flexible. The "exo" intermediates **37**, **42**, and **47** (**INT b**) are quite similar in energy to the corresponding endo conformers **36**, **41**, and **46**. Compounds **37**, **42**, and **47** are separated from the reactants by the exo transition structures **35**, **40**, and **45** (**TS 1b**). The critical C−C distances (2.004 Å in **35** and **45**; 2.077 Å in **40**) are very similar to those found in the endo transition structures **34**, **39**, and **44**.

The energetic relationships of **34**−**48** (Tables 5 and 6) are summarized in Scheme 5.[36] The activation energies for the first steps on the reaction paths for all three anions are in the 5.4−8.6 kcal/mol range. The energy differences of only 0.4−1.3 kcal/mol between the endo (**TS 1a**) and exo (**TS 1b**) transition structures are especially small. Therefore, the regio- and stereochemical course of the first step of these reactions can be expected to be very sensitive to the steric and electronic properties of substituents. The pentenyl anion intermediates (**INT**) are 0.3−8.3 kcal/mol higher in energy than the reactants. The exo intermediate **37** is 2.4 kcal/mol more stable than the corresponding endo form **36**, whereas the exo intermediates **42** and **47** are 2.0 and 0.5 kcal/mol less stable than the endo



39, TS 1a

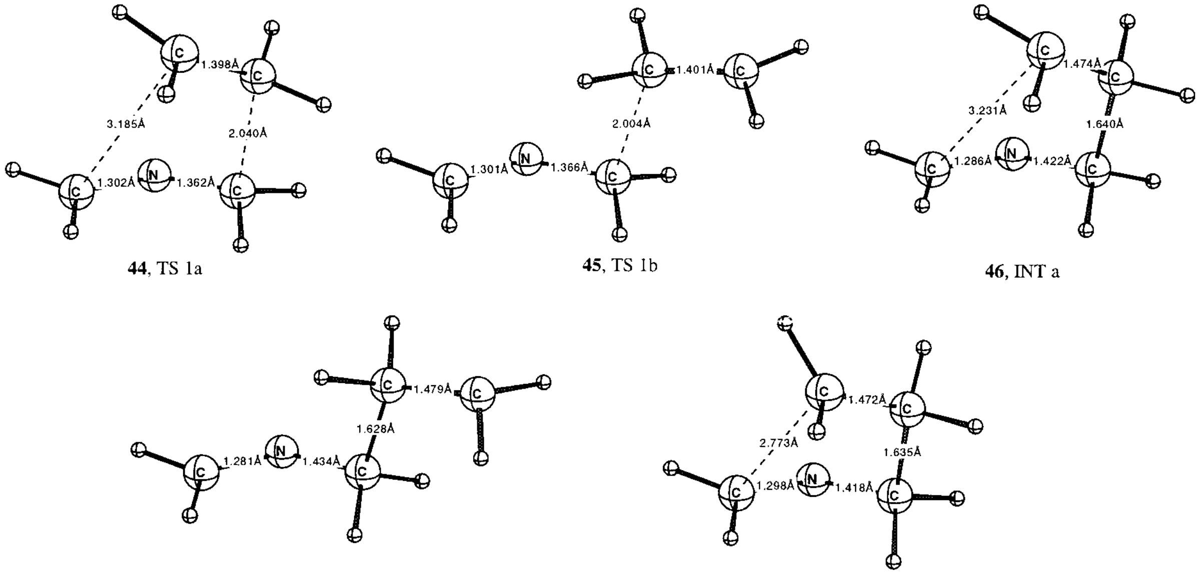
40, TS 1b

41, INT a

42, INT b

43, TS 2

Figure 6. Calculated geometries (Becke3LYP/6-311+G**) of transition structures (**TS**) and minima (**INT**) for the stepwise cycloaddition of 2-borylallyl anion **4a** to ethylene.



44, TS 1a **45**, TS 1b **46**, INT a

47, INT b **48**, TS 2

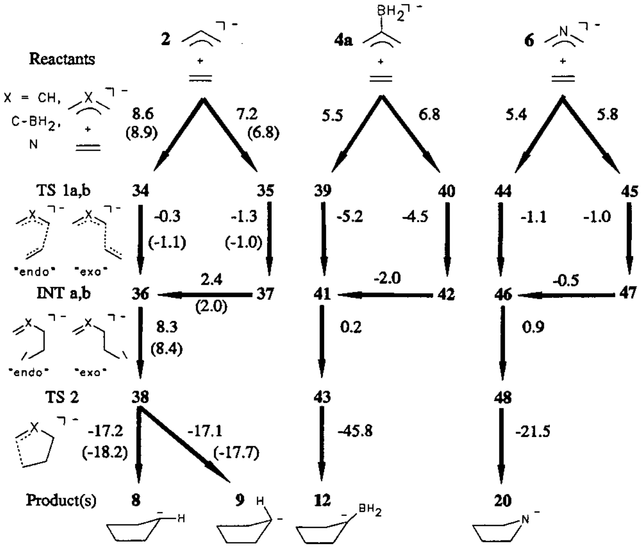
Figure 7. Calculated geometries (Becke3LYP/6-311+G**) of transition structures (**TS**) and minima (**INT**) for the stepwise cycloaddition of 2-azaallyl anion **6** to ethylene.

Table 6. Relative Energies of Transition Structures and Minima for the Stepwise Cycloadditions of 2-Borylallyl Anion **4a** and 2-Azaallyl Anion **6** to Ethylene

compd[a]	rel energy,[b] B3L//B3L[c]	compd[a]	rel energy,[b] B3L//B3L[c]
39	5.5	**44**	5.4
40	6.8	**45**	5.8
41	0.3	**46**	4.3
42	2.3	**47**	4.8
43	0.5	**48**	5.2

[a] Compound numbers as in Figures 6 and 7. [b] Reference energy (0.0) is for allylic anion + ethylene. [c] Becke3LYP/6-311+G**//Becke3LYP/6-311+G** + 0.89 ZPE (HF/6-31+G*).

Scheme 5. Energy Profiles for the Two-Step Cycloadditions of the Allylic Anions **2**, **4a**, and **6** to Ethylene[a]

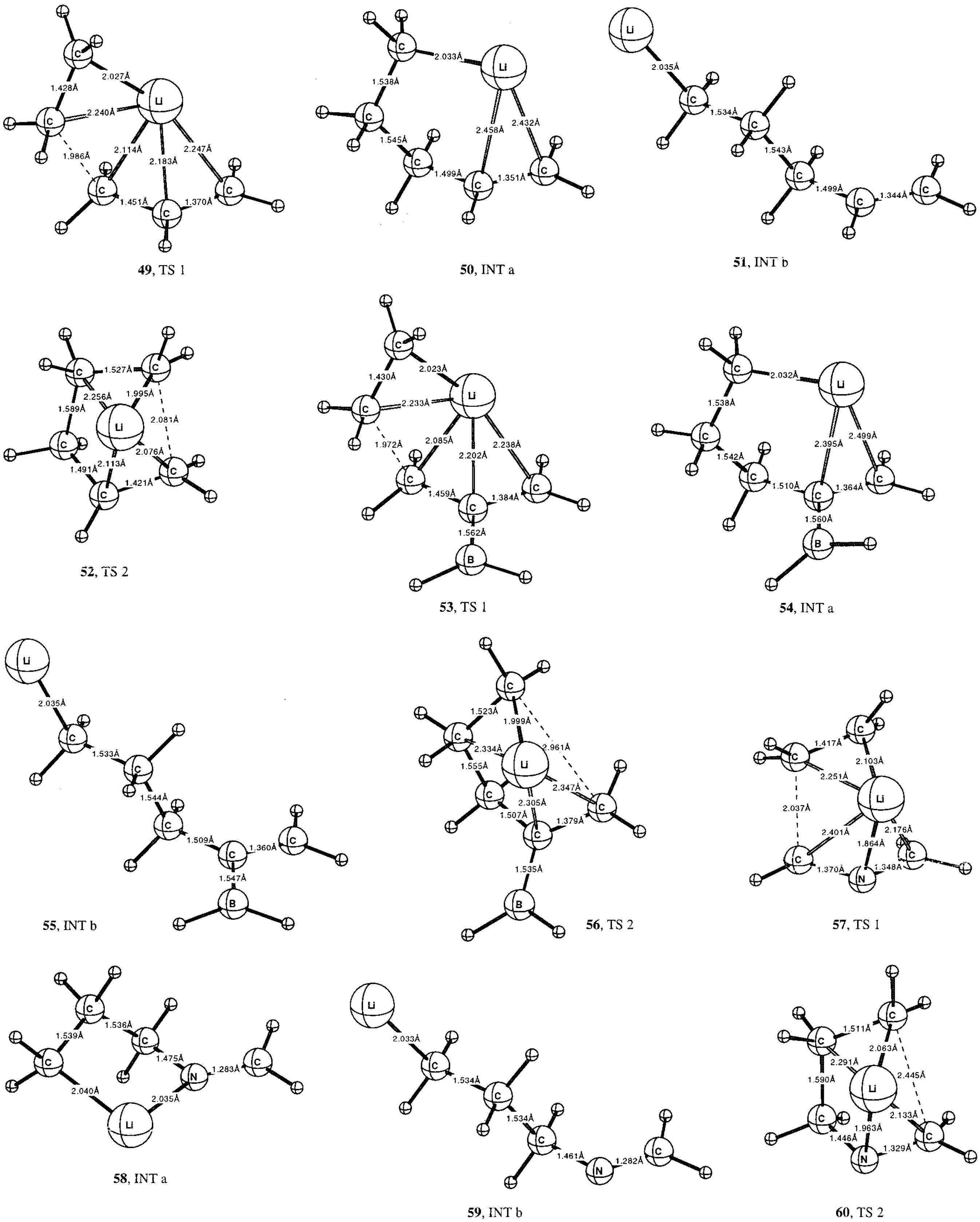


[a] Energy differences at Becke3LYP/6-311+G**//Becke3LYP/6-311+G**; values in parentheses at Becke3LYP/6-311++G**//MP2(fc)/6-31+G*.

conformers **41** and **46**. Since these energy differences are rather small, the steric and electronic properties of substituents in experimental systems may be decisive in determining whether the intermediates prefer the endo or exo form. However, the exo conformers must rotate to the endo forms before the rings can close. This conformational change may be hindered when the exo intermediate is much lower in energy than the endo conformer. Indeed, open-chain byproducts have been isolated in some experimental systems, together with the desired cyclic products.[5a,b,d,9g,m,n,r,w,z,cc;14]

In contrast to the first steps, the activation energies (E_a) for the exothermic second, ring-closing steps are very different for the three anions. The largest E_a is 8.3 kcal/mol for the unsubstituted allyl system (**38** vs **36**); for the 2-azaallyl (**48** vs **46**) and 2-borylallyl (**43** vs **41**) systems, the activation energies are only 0.9 and 0.2 kcal/mol, respectively. This is consistent with the experimental finding (see Introduction) that 2-azaallyl compounds and allylic compounds with anion stabilizing substituents at the central carbon undergo this type of cycloaddition much more easily than allylic compounds without such substituents.

Stationary points **28**−**30** on the reaction coordinates of the concerted cycloadditions of the allyllithium compounds **3**, **5a**, and **7** to ethylene are second-order saddle points. When these structures are reoptimized at MP2(fc)/6-31+G* without symmetry restrictions, **49**, **53**, and **57** result (Figure 8, Table 7). These are the initial transition structures (**TS 1**) on the two-step cycloaddition pathways of the allyllithium compounds. Obviously, these species are preceded by the complexes **25**−**27** rather than the separate reactants. All attempts to locate other **TS 1** structures, in which the approaching ethylene is not coordinated to lithium, failed. As with the free anions, the geometries of the **TS 1** structures are very similar: the critical C−C distances range from 1.972 Å in **53** to 2.037 Å in **57**. The endo pentenyllithium intermediates (**INT a**) **50**, **54**, and **58** are farther along the reaction coordinates. Lithium is coordinated not only to the primary anionic center in **50** and **54** but also to the C=C double bond. The Li···(C=C) distances (2.4−2.5 Å) in these species are slightly longer than the Li···$C_{ethylene}$ distances in **25** and **26** (ca. 2.35 Å). Nevertheless, the intramolecular complexation of lithium in **50** and **54** results in considerable stabilization: the corresponding exo intermediates (**INT b**) **51** and **55** are 6.9 and 4.5 kcal/mol higher in energy than the endo conformers **50** and **54**, respectively. Rather than bridging the C=N double bond, the lithium in **58** is coordinated



49, TS 1
50, INT a
51, INT b
52, TS 2
53, TS 1
54, INT a
55, INT b
56, TS 2
57, TS 1
58, INT a
59, INT b
60, TS 2

Figure 8. Calculated geometries (MP2(fc)/6-31+G*) of transition structures (**TS**) and minima (**INT**) for the stepwise cycloadditions of allyllithium compounds **3**, **5a**, and **7** to ethylene.

to the anionic center and to the nitrogen lone pair. The stabilizing effect of this Li−N contact is even larger than that of the Li···(C=C) contacts in **50** and **54**: the exo intermediate **59** is 15.0 kcal/mol higher in energy than the endo conformer **58**.

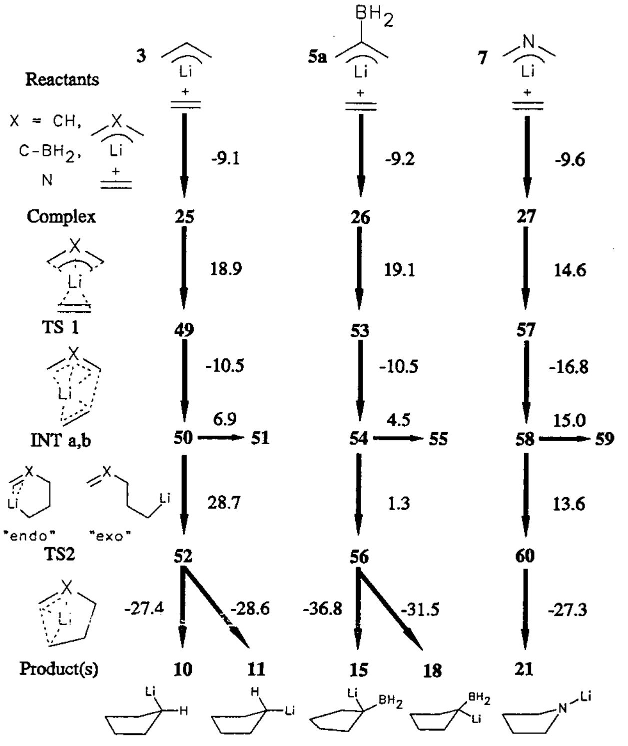
The critical C−C distances in the **TS 2** compounds **52**, **56**, and **60**, which separate the endo pentenyllithium intermediates **50**, **54**, and **58** from the cyclic products **10**/**11**, **15**/**18**, and **21**, are very different. The smallest distance (2.081 Å) is found in **52**, the **TS 2** structure of the unsubstituted allyl system. The

Table 7. ZPEs, Absolute and Relative Energies of Transition Structures, and Minima for the Stepwise Cycloadditions of the Allyllithium Compounds **3**, **5a**, and **7** to Ethylene

	relative energy[b]			relative energy[b]	
compd[a]	MP2//MP2[c]	B3L//MP2[d]	compd[a]	MP2//MP2[c]	B3L//MP2[d]
49	6.4	9.8	**55**	−5.8	3.9
50	−10.2	−0.7	**56**	−5.0	0.7
51	−3.0	6.2	**57**	−3.9	5.0
52	19.1	28.0	**58**	−22.7	−11.8
53	6.0	9.9	**59**	−7.6	3.2
54	−10.4	−0.6	**60**	−7.6	1.8

[a] Compound numbers as in Figure 8. [b] Reference energy (0.0) is for allyllithium compound + ethylene. [c] MP2(fc)/6-31+G*//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*). [d] Becke3LYP/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE (HF/6-31+G*).

Scheme 6. Energy Profiles for the Two-Step Cycloadditions of the Allyllithium Compounds **3**, **5a**, and **7** to Ethylene[a]



[a] Energy differences at Becke3LYP/6-311++G**//MP2(fc)/6-31+G*.

distances in the **TS 2** structures of the 2-azaallyl and 2-borylallyl systems are 2.445 Å in **60** and 2.961 Å in **56**. These data parallel the results for the free anions (Figures 5−7).

The energetic relationships of **49**−**60** (Table 7) are summarized in Scheme 6. The energy differences between the separate reactants and the complexes **25**−**27** are nearly identical (9.1−9.6 kcal/mol) for all these systems. The same is true for the activation energies of the first addition steps of the allyl and the 2-borylallyllithium compounds (18.9 and 19.1 kcal/mol); the activation energy (14.6 kcal/mol) for 2-azaallyllithium is somewhat smaller. Due to the intramolecular complexation of lithium, both the **TS 1** transition structures (**49**, **53**, **57**) and the endo intermediates **INT a** (**50**, **54**, **58**) are less flexible conformationally than the corresponding free anion structures. Therefore, the steric and electronic substituent effects on the geometries of experimental systems may be smaller than those for the free anions.

The activation energies for the ring-closing step are very different for the allyllithium model systems considered here. The largest value, 28.7 kcal/mol, is found for the unsubstituted allyllithium system (**52** vs **50**); for the 2-azaallyl and 2-borylallyllithium systems, the activation energies are 13.6 (**60** vs **58**) and only 1.3 kcal/mol (**56** vs **54**), respectively. Obviously, the beneficial effect of the anion-stabilizing substituents on the final, ring-closing step of the cycloadditions is very strong and is nearly independent of the presence of a counterion.

Conclusions

Contrary to the predictions of the Woodward−Hoffmann rules, the anionic [3 + 2] cycloadditions studied here are stepwise rather than concerted.[40] Concerted $4\pi_s + 2\pi_s$ cycloadditions in C_s symmetry are not viable reaction paths for the free allyl anions **2**, **4a**, and **6** and for 2-borylallyllithium (**5a**) and 2-azaallyllithium (**7**), since they involve second-order saddle points (**22**−**24**, **29**, **30**, **32**, and **33**) instead of transition structures (Table 3). The same is true for allyllithium (**3**) when ethylene approaches from the lithium side (second-order saddle point **28**). If ethylene approaches **3** from the side opposite to lithium, a concerted cycloaddition is possible via transition structure **31**. However, this is not favorable energetically, since the activation energy for this process is 37.7 kcal/mol (Table 2), whereas, for the stepwise cycloaddition (Scheme 6), activation energies of only 18.9 kcal/mol for the first and 28.7 kcal/mol for the second addition steps are required. The preference of the stepwise cycloaddition pathway does not compromise the validity of the Woodward−Hoffmann rules. These rules are useful to distinguish between favorable (allowed) and unfavorable (forbidden) *one-step* processes in terms of molecular orbital symmetry considerations, but they do not exclude the possibility that a two-step pathway may be even more favorable than a formally allowed one-step mechanism. As shown here, it is possible that a true transition structure (with one imaginary frequency) may not lie on the symmetry-allowed pathway.

The unfavorableness of the concerted cycloaddition mechanism can be rationalized in terms of the molecular polarizabilitiy anisotropy of the reactants (Table 4). The electrostatic interaction of ethylene and the allylic compounds is more favorable energetically for the stepwise than for the concerted cycloaddition mechanism.

The two-step cycloaddition pathway is preferred by all model systems. The activation energies for the first steps (5.4−8.6 kcal/mol for the free anions, 14.4−18.9 kcal/mol for the lithium compounds, Schemes 5 and 6) are very similar for all systems. The experimental finding that 2-azaallyl compounds and allylic compounds with an anion-stabilizing substituent at the central carbon undergo this type of cycloaddition much more easily than the unsubstituted allyl anion/allyllithium results from the facilitation of the second, ring-closing step by such substituents. The activation energies for the second cycloaddition steps are 8.3 and 28.7 kcal/mol for the allyl anion/allyllithium **2**/**3** but only 0.2 and 1.3 kcal/mol for the 2-borylallyl anion/2-borylallyllithium **4a**/**5a**, and 0.9 and 13.6 kcal/mol for the 2-azaallyl anion/2-azaallyllithium **6**/**7** (Schemes 5 and 6).

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Supporting Information Available: Absolute energies, ZPEs, and NIMAGs (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(40) For a recent report on the competition of concerted and stepwise mechanisms of various pericyclic reactions, see ref 21f.