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Comparison of Computational Studies of Internal Stabilization of 1-Butadienyllithiums and Representative 1-Chloro-1-lithio-2-phenylalkenes

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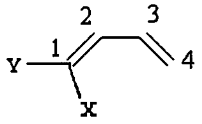
ABSTRACT: *Comparison of molecular orbital calculations of 1-butadienyllithiums and representative 1-chloro-1-lithio-2-phenylalkenes, carried out by using MNDO and AM1, reveals that the major stabilizing interaction with lithium in these systems is predicted to be agostic bonding between lithium and hydrogen. MNDO and AM1 calculations for 1-chloro-1-lithio-2-phenylethenes give evidence for agostic bonding between lithium and the ortho H, such as compressed pertinent bond angles and increased pertinent bond lengths.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:263–269, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10027

INTRODUCTION

Lithium coordination to heteroatoms [1] and agostic bonding with hydrogen [2] are examples of stabilizing effects which can be important to stereo- and regiochemistry. The significance of coordination by lithium to a π bond [3,4] has been demonstrated in the calculations of structures such as 7-lithionorbornadiene [3a], 1-penta-2,4-dienyllithiums [4a], and butadienyl compounds 1–6 [4b].



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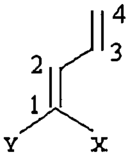
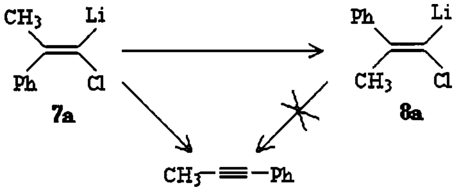


4 X = Li, Y = H
5 X = H, Y = Li
6 X, Y = H

In some systems, such as (*Z*)- and (*E*)-1-chloro-1-lithio-2-phenylpropene (**7a** and **8a** respectively), there is evidence of stabilization, but the type of stabilization has not been fully explored.



7a **8a**

Experimental data show that compound **8a** does not undergo cis–trans isomerization at temperatures at which the Z isomer **7a** will (see above) [5]. At low temperatures, the E isomer is unusually stable; under these conditions, neither isomer undergoes elimination to form the corresponding alkyne, and the E isomer does not isomerize to the Z isomer [5]. Compound **7a** is also more susceptible than is **8a** to

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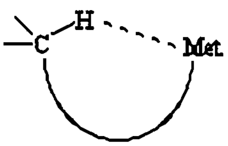
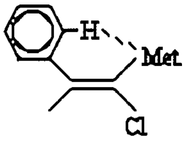
the Fritsch–Buttenburg–Wiechell (FBW) rearrangement [6], in which an aryl group migrates simultaneously with α-elimination of lithium chloride. Thus, an aryl substituent syn to the metal decreases reactivity toward either isomerization or the FBW rearrangement, and thereby greatly increases the synthetic utility of these intermediates.

Experimental and computational (MNDO) investigations of 1-lithio-1,2-diphenylhex-1-ene indicate [2a] a preference for Ph–Li interaction over heteroatom–Li complexation in these systems. However, this system has some steric effects and other interactions which are not present in compounds such as **7a** and **8a** because Li is α to one phenyl group and cis to another. The interaction of Li with the cis Ph group in the presence of the second Ph, is not guaranteed to be identical to the interaction of Li with the cis Ph group in compound **8a**.

Experimental evidence [2c] shows the greater stability of (*E*)-1-iodo-2-phenyl-2-isopropoxyethenyllithium over the Z isomer and indicates a preference for Ph–Li interaction over heteroatom–Li complexation. However, no data were presented [2c] which could determine whether agostic bonding or π complexation is the stabilizing Ph–Li interaction in that system.

By using BeH as a model for Li, MNDO calculations [2b] exploring a series of 1-chloro-1-lithio-2-phenylalkenes indicated that agostic bonding between the metal and an ortho hydrogen would be in agreement with calculated stabilities of and experimental observations in reactions of 1-chloro-1-metallo-2-methylstyrenes [5]. However, pertinent geometrical values were not compared in the context of agostic bonding versus π complexation.





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There could be an argument for a preference for agostic bonding over complexation, in systems with an aryl group cis to Li, due to geometrical requirements. This is because the π cloud of the phenyl ring in these molecules is directed somewhat away from lithium, destabilizing the geometry required for π complexation. Such constraints would not operate in simple alkenyl systems which have not been explored for evidence of agostic bonding. Also, structural characteristics of compounds such as **7a** and **8a** have not been examined thoroughly in the context of agostic bonding. Moreover, since the previous calculations were reported, parameters for lithium have become available [7] (also, M. J. S. Dewar, private communication). Therefore, it seemed of interest to investigate lithium complexation with a π bond versus agostic bonding with hydrogen in simple alkenyl and aryl systems without geometrical bias and using computational methods. Accordingly, we report the results of such calculations using MNDO and AM1 molecular orbital programs.

THEORETICAL PROCEDURES

Calculations were carried out by using the AMPAC package [7] available from QCPE. Some AM1 parameters were obtained from M. J. S. Dewar (private communication). The MNDO parameters have been extensively tested in treating structures such as these [8]. MNDO has been shown to give results consistent with *ab initio* calculations [8c,e] and the general geometrical features of organolithium compounds shown by X-ray structures [8f–i]. The method is reported [2a,8d,e] to be remarkably successful in predicting the preferred mode of lithium complexation. MNDO has been shown to give satisfactory results for agostic bonding and complexation in other systems [9]. Geometries of stable species were found by minimizing the total energy, and all geometrical variables were allowed to optimize unless noted otherwise.

RESULTS AND DISCUSSION

1-Butadienyllithiums

Minimum energy geometries for four isomers of 1-butadienyllithium (**1, 2, 4**, and **5**) and their two parent compounds (**3** and **6**) were obtained using AM1 and MNDO for comparison with results [4b] from calculations run at the 4-31G level. The calculated compounds are *cis*-*S*-*cis*-1-butadienyllithium (**1**), *trans*-*S*-*cis*-1-butadienyllithium (**2**), *S*-*cis*-butadiene (**3**), *cis*-*S*-*trans*-1-butadienyllithium (**4**), *trans*-*S*-*trans*-1-butadienyllithium (**5**), and *S*-*trans*-butadiene (**6**). The results agree remarkably well for most of the characteristics compared; AM1 results are more similar to those of the 4-31G calculations than are those of MNDO. Absolute and relative heats of formation for the compounds are given in Table 1. MNDO predicts the energy differences between compound **1** and each of compounds **2, 4**, and **5** to be 15.11, 10.52, and 14.65 kcal/mol respectively. Similar differences were found by using AM1: 5.16, 4.07, and 3.97 kcal/mol respectively. Compound **1** was previously calculated at the 4-31G level to be more stable than compounds **2** by 7.45 kcal/mol, **4** by

TABLE 1 Heats of Formation (kcal/mole) of Isomers of Butadienyllithium and their Parent Compounds Calculated by Different Methods (Relative Energies for **1** vs **2** and for **4** vs **5** are in Parentheses)

	Compound					
Method	***1***	***2***	***3***	***4***	***5***	***6***
MNDO	13.70 (0)	28.82 (15.11)	29.25	24.22 (10.52)	28.35 (14.65)	28.96
AM1	44.02 (0)	49.18 (5.16)	30.78	48.09 (4.07)	47.99 (3.97)	29.92
4–31G^a	(0)	(7.45)		(4.16)	(4.10)	

^{a}Ref [4b].

4.16 kcal/mol, and **5** by 4.10 kcal/mol. Compound **3** is calculated to be marginally higher in energy than compound **6**: 0.86 kcal/mol (AM1) and 0.29 kcal/mol (MNDO), as expected.

In these data, there is a general trend that an S-cis isomer is higher in energy than the corresponding S-trans isomer. The sole exception is compound **1**, which is calculated to be the most stable isomer by several kcal/mol, regardless of the computational method used. This indicates a possible internal stabilization involving lithium. Precedents suggest that this internal stabilization could either be complexation with the C3—C4 π bond or agostic bonding to hydrogen at C4. Characteristics of the molecules can be compared to explore this and to identify the type of interaction.

Pertinent bond lengths for the isomers are given in Table 2. Although differences are small in some cases, there are some trends, which are independent of the computational method used: (1) the C—Li bond is longer in the cis isomers **1** and **4** than in the trans ones **2** and **5**, (2) the C4—H bond in compound **1** is longer than that in **2**, (3) the C3—H bond in compound **4** is longer than that in **5**, and (4) the C3—C4 bond length in compound **1** is longer than in the other compounds. The first three trends all support agostic bonding in these compounds, because the bonds involved in agostic bonding would be expected to be lengthened. In addition, the longer C3—C4 bond in compound **1** also supports agostic Li—H bonding because π complexation with that bond would be expected to shorten it [3e].

Important bond angles for the compounds are given in Table 3. The Li—C1—C2 bond angle is significantly smaller in compound **1** than that in any other isomer and also smaller than the H—C1—C2 angles in the parent compounds by all methods. The compressed Li—C1—C2 angles in compound **1** relative to **2** is part of the geometrical distortion necessary for the Li–H interaction. The H—C4—C3 angles in compounds **1, 2**, and **3** are essentially equal, as are the H—C3—C2 angles in compounds **4, 5**, and **6**. The lithium substituent itself is known to stabilize molecules having a high degree of C—C—Li angle strain [10], and the stabilization facilitates the Li–H interaction in this molecule.

1-Chloro-1-lithio-2-phenylalkene Models

Although energies of compounds such as **7b, 8b, 10b**, and **11b** had been compared earlier [2b], bond lengths and angles pertinent to the question of an

TABLE 2 Selected Bond Lengths (Å) of Butadienyllithium Isomers and their Parent Compounds

		Compound					
Method	*Bond*	***1***	***2***	***3***	***4***	***5***	***6***
MNDO	C1—Li	1.840	1.793		1.796	1.792	
	C3—H				1.123	1.097	1.096
	C4—H	1.111	1.088	1.089			
	C3—C4	1.372	1.345	1.343	1.349	1.345	1.344
AM1	C1—Li	1.931	1.880		1.891	1.878	
	C3—H				1.120	1.105	1.104
	C4—H	1.116	1.097	1.098			
	C3—C4	1.350	1.335	1.335	1.337	1.335	1.335
4–31G^a	C1—Li	1.969	1.966		1.975	1.966	
	C3—H				1.081	1.078	
	C4—H	1.077	1.073				
	C3—C4	1.340	1.323		1.324	1.324	

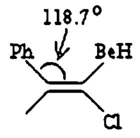
^{a}Ref [4b].

TABLE 3 Selected Bond Angles (°) of Butadienyllithium Isomers and their Parent Compounds

		Compound					
Method	*Angle*	*1*	*2*	*3*	*4*	*5*	*6*
MNDO	Li—C1—C2	93.6	97.9	124.5[a]	96.4	98.7	124.4[a]
	H—C3—C2				119.5	115.3	115.7
	H—C4—C3	125.1	124.8	124.9			
AM1	Li—C1—C2	103.6	119.8	122.9[a]	110.5	120.7	122.9[a]
	H—C3—C2				117.2	115.5	116.0
	H—C4—C3	123.4	122.7	122.7			
4–31G[b]	Li—C1—C2	97.5	122.4		125.6	122.9	
	H—C3—C2				115.6	115.4	
	H—C4—C3	121.7	121.7				

[a] Bond angle for H—C1—C2.
[b] Ref [4b].

agostic interaction versus π complexation had not been addressed. Such data from MNDO calculations, enabling comparison of the chloromethylstyrene system with a BeH substituent (compound **8b**) versus that without it (compound **9**), are given below. These show a slight Ph—C=C angle compression from 121.1° to 118.7° upon introduction of the substituent; this supports a Ph–Li agostic interaction. Data [2b] for compounds **8b** and **7b** can also be compared to assess the possible influence of agostic bonding upon the geometry of the E isomer **8b** relative to that of the Z isomer **7b**. Compression of C=C—Be and Ph—C=C bond angles in compounds with Ph syn to Be supports agostic bonding.



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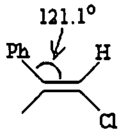

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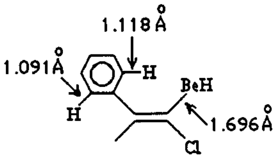
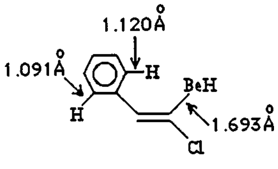
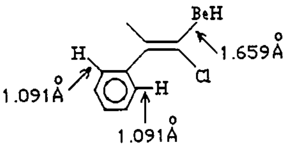
Additional data which support agostic bonding are shown in the scheme below: an increased ortho C—H bond length for the C—H bond syn to Be in the E isomers **8b** and **11b** (1.118 Å and 1.120 Å), relative to (1) that of the ortho C—H bond length anti to Be in the E isomers **8b** and **11b** (1.091 Å) or (2) either ortho C—H bond length in the Z isomers **7b** and **10b** (1.091 Å). Also in agreement with agostic bonding, the C—Be bond lengths in the E isomers (**8b** and **11b**) shows analogous increases: 1.696 Å (**8b**) and 1.693 Å (**11b**) versus 1.659 Å (**7b**) and 1.654 Å (**10b**).



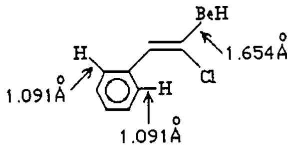
8b



11b



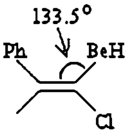
7b



10b

1-Chloro-1-lithio-2-phenylalkenes

Because the Li parameters for MNDO and AM1 have become available, it seemed of interest to include calculations on these and similar systems using Li instead of its model in order to (1) explore further the concept of agostic bonding to lithium, (2) assess the suitability of the model, and (3) do a more thorough analysis of agostic bonding.



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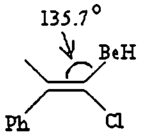


7b

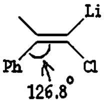
Studies of compound **7a** and its E isomer **8a** gave similar results by using both MNDO and AM1 (Table 4). Schemes comparing pertinent AM1 bond lengths and angles of compounds **7a** and **8a** follow. The Ph—C=C (115.5°, MNDO; 118.4°, AM1) and C=C—Li (99.6°, MNDO; 112.1°, AM1) angles are both compressed in the E isomer **8a** relative to those of the Z isomer **7a** Ph—C=C (130.7°, MNDO; 126.8°, AM1) and C=C—Li (104.5°, MNDO; 117.3°, AM1). The C—Li bond length for the E isomer **8a** (1.858 Å, MNDO; 1.957 Å, AM1) is longer than that for the Z isomer **7a** (1.849 Å, MNDO; 1.939 Å, AM1). A similar lengthening is observed in the ortho C—H bond of the phenyl group which is syn to Li; this bond

TABLE 4 Data for 1-Chloro-1-lithio-2-phenylalkenes Calculated by Using MNDO[a]

		Angles (°)		*Bond Length (Å)*		
Compound	ΔH_f	*Ph—C=C*	*C=C—Li (or H)*	*ortho C—H*	*C—Li*	*Dihedral H—C=C—C2 (°)*
Methylstyrene system						
7a (Z)	22.22 (18.78)	130.7	104.5	1.091	1.849	
8a (E)	3.44 (0)	115.5	99.6	1.118	1.858	57.4
9 (E)	28.8	121.0	126.5	1.086		
Styrene system						
10a (Z)	24.38 (15.67)	136.0	123.3	1.089	1.835	
11a (E)	8.71 (0)	121.1	96.9	1.114	1.849	44.5
12 (E)	28.9	127.2	127.5	1.090		
13 (trans)	38.74 (12.29)	129.7	100.4	1.092	1.798	
14 (cis)	26.45 (0)	123.0	95.1	1.115	1.831	42.6

[a] Relative values for **7a** vs. **8a**, for **10a** vs. **11a**, and for **13** vs. **14** are given in parentheses.

length in compound **7a** (1.091 Å, MNDO; 1.102 Å, AM1) is shorter than that for compound **8a** (1.118 Å, MNDO; 1.118 Å, AM1). The compressed bond angles and longer bonds in the E isomer **8a** are consistent with agostic bonding between H and Li.



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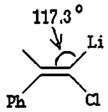
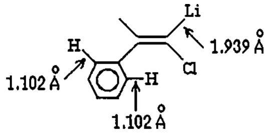
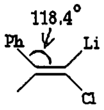


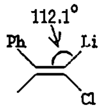
7a



7a



8a



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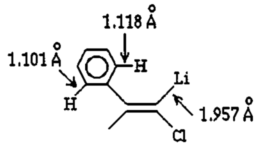
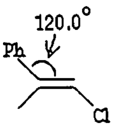


8a

The corresponding AM1 angles in compound **9** (see below) are also larger than those in compound **8a** (above), and the corresponding AM1 ortho C—H bond length in phenyl is also shorter in **9** than in **8a**. Therefore, this also supports agostic bonding in **8a**. Similar results are obtained by using MNDO.



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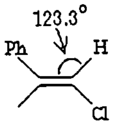

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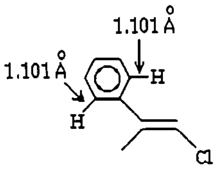

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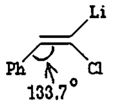
Comparisons of AM1 bond lengths and angles in the 1-chloro-1-lithio-2-phenylethenes, **10a, 11a**, and **12** give similar results. Smaller bond angles and longer C—H and C—Li bond lengths in compound **11a** relative to those for compounds **10a** or for **12** again give evidence for agostic bonding to Li.



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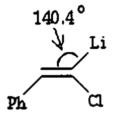

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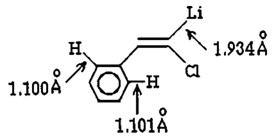

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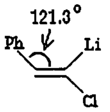
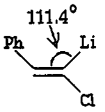
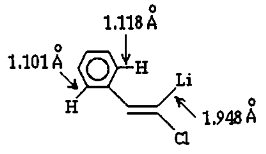


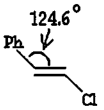
11a



11a



11a



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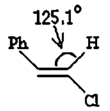

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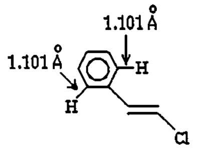

12

Similar results giving evidence for agostic bonding in the styryllithium system are also found by comparing the trans **13** and cis **14** isomers. By using MNDO or AM1, compound **14** is calculated to have a smaller Ph—C=C angle, a smaller C=C—Li angle, a longer ortho C—H bond length, and a longer C—Li bond length than the trans isomer **13**.

Ortho-H—C=C—C2 dihedral angles are given for the molecules in Tables 4 and 5, in each case in which the magnitude indicates a significant twist of the phenyl ring out of the molecular plane. The geometrical position of the ring relative to lithium in each, suggests interaction of Li with both C and H at the ortho position and support agostic bonding.

TABLE 5 Data for 1-Chloro-1-lithio-2-phenylalkenes Calculated by Using AM1[a]

		Angles (°)		*Bond Length (Å)*		
Compound	ΔH_f	*Ph—C=C*	*C=C—Li (or H)*	*Ortho C—H*	*C—Li*	*Dihedral H—C=C—C2 (°)*
Methylstyrene system						
7a (Z)	39.26 (5.52)	126.8	117.3	1.102	1.939	
8a (E)	33.74 (0)	118.4	112.1	1.118	1.957	41.1
9 (E)	22.7	120.0	123.3	1.101		
Styrene system						
10a (Z)	41.61 (2.35)	133.7	140.4	1.100	1.934	
11a (E)	39.74 (0)	121.3	111.4	1.118	1.948	
12 (E)	28.4	124.6	125.1	1.101		
13 (trans)	56.83 (1.04)	127.1	120.0	1.100	1.886	
14 (cis)	55.79 (0)	126.7	123.7	1.112	1.898	

[a]Relative values for **7a** vs. **8a**, for **10a** vs. **11a**, and for **13** vs. **14** are given in parentheses.
[b]Values given when significantly different from **0**.

Because the calculations using lithium give virtually the same results and conclusions as those using BeH as its model, it appears that BeH was a suitable model in those calculations. However, because the lithium parameters are now available, the use of a model for lithium in such calculations seems unnecessary.

CONCLUSION

An internal stabilizing interaction in the cis-S-cis isomer of butadienyllithium is predicted by bond lengths and angles calculated by AM1 and by MNDO. In the metalated styrenes (Met = BeH or Li), compressed Ph—C=C angles, compressed C=C—Met bond angles, and increased ortho C—H and C—Met bond lengths all support agostic bonding. Li—H agostic bonding, rather than π complexation with Li, explains phenomena observed experimentally, such as the reduced susceptibility of (*E*)-1-chloro-1-lithio-2-phenylpropene to undergo (1) cis–trans isomerization at temperatures at which the Z isomer will or (2) the FBW rearrangement, in which an aryl group migrates simultaneously with α-elimination of LiCl.

REFERENCES

[1] (a) Clegg, W.; Lamb, E.; Liddle, S.; Snaith, R.; Wheatley, A. J Organomet Chem 1999, 573, 305–312; (b) Sekiguchi, A. Angew Chem Int Ed Engl 1997, 36, 1533–1534; (c) Kaiser, E. J Organomet Chem 1980, 203, 1; (d) Kaneti, J.; Schleyer, P. v. R.; Clark, T.; Kos, A.; Moffat, J.; Spitznagel, G.; Andrade, J. J Am Chem Soc 1986, 108, 1481; (e) Jastrzebski, J.; van Koten, G.; Konijn, M.; Stam, C. J Am Chem Soc 1982, 104, 5490; (f) Clark, T.; Schleyer, P. v. R. J Am Chem Soc 1979, 101, 7747.

[2] (a) Bauer, W.; Feigel, M.; Muller, G.; Schleyer, P. v. R. J Am Chem Soc 1988, 110, 6033, and references therein; (b) Nelson, D. J.; Mercer, B. Tetrahedron 1988, 44, 6287; (c) Barluenga, J.; Rodriguez, M.; Campos, P. J Am Chem Soc 1988, 110, 5567; (d) Brookhart, M.; Green, M. J Organomet Chem 1983, 250, 395.

[3] (a) Nagase, S.; Houk, K. N. Tetrahedron Lett 1982, 19; (b) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Courtneidge, J. L.; Davies, A. G. J Am Chem Soc 1984, 106, 361; (c) Condran, P. Jr.; Hammond, M. L.; Mourino, A.; Okamura, W. H. J Am Chem Soc 1980, 102, 6259; (d) Kos, A. J.; Schleyer, P. v. R. J Am Chem Soc 1980, 102, 7928; (e) Hess, B. A. Jr.; Ewig, C. S.; Schaad, L. J. J Org Chem 1985, 50, 5869.

[4] (a) Dewar, M. J. S.; Fox, M. A.; Nelson, D. J. J Organomet Chem 1980, 185, 157; (b) Nelson, Donna J.; Brammer, C. N. In 221st ACS National Meeting, San Diego, CA, ORGN 357, April 3, 2001.

[5] Köbrich, G. Angew Chem Int Ed Engl 1967, 6, 41–52.

[6] (a) Fritsch, P. Liebigs Ann Chem 1894, 279, 319–323; (b) Buttenburg, W. P. Liebigs Ann Chem 1894, 279, 324–337; (c) Wiechell, H. Liebigs Ann Chem 1894, 279, 337–344.

[7] Quantum Chemistry Program Exchange (QCPE), Program No. 455; Indiana University: Bloomington, IN.

[8] (a) Schleyer, P. v. R.; Kos, A. J.; Kaufmann, E. J Am Chem Soc 1983, 105, 7617; (b) Schleyer, P. v. R. Pure Appl Chem 1985, 55, 355; (c) McKee, M. L. J Am Chem Soc 1985, 107, 859; (d) McKee, M. L. J Am Chem Soc 1987, 109, 559, 7284; (e) Kaneti, J.; Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Andrade, J. G.; Moffat, J. B. J Am Chem Soc 1988, 108, 1481; (f) Hacker, R.; Schleyer, P. v. R.; Reber, G.; Muller, G.; Brandsma, L. J Organomet Chem 1986, 316, C4; (g) Neugebauer, W.; Geiger, G. A. P.; Kos, A. J.; Stezowski, J. J.; Schleyer, P. v. R. Chem Ber 1985, 118, 1504; (h) Kos, A. J.; Clark, T.; Schleyer, P. v. R. Angew Chem Int Ed Engl 1984, 23, 620; (i) Dietrich, H.; Mahdi, W.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. Angew Chem Int Ed Engl 1984, 23, 621.

[9] (a) Saá, J. M.; Morey, J.; Frontera, A.; Deyá, P. J Am Chem Soc 1995, 117, 1105–1116; (b) Saá, J. M.; Deyá, P.; Suñer, G.; Frontera, A. J Am Chem Soc 1992, 114, 9093–9100; (c) Nelson, D. J. J Org Chem 1986, 51, 3185–3186; (d) Suñer, G. A.; Deyá, P.; Saá, J. J Am Chem Soc 1990, 112, 1467–1471; (e) Bauer, W.; Schleyer, P. J Am Chem Soc 1989, 111, 7191–7198; (f) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. J Am Chem Soc 1988, 110, 6033–6046.

[10] Dill, J. D.; Greenburg, A.; Liebman, J. F. J Am Chem Soc 1979, 101, 6514.