ORGANIC
LETTERS

2001
Vol. 3, No. 9
1249−1252

A Theoretical Prediction of Potentially Observable Lithium Compounds with Planar Tetracoordinate Carbons

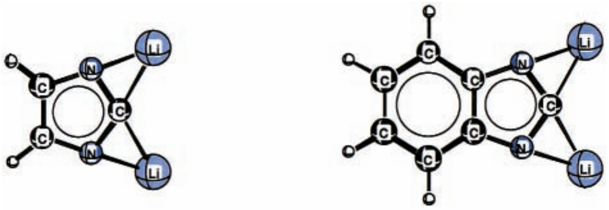
Zhi-Xiang Wang,[†] Thanathu Krishnan Manojkumar,[‡] Chaitanya Wannere,[†] and Paul von Ragué Schleyer*,[†]

*Computational Chemistry Annex, Department of Chemistry, University of Georgia,
Athens, Georgia 30602-2525, and Regional Sophisticated Instrumentation Center,
Indian Institute of Technology, Madras, Chennai, Tamil Nadu, India 600 036*

schleyer@chem.uga.edu

Received January 17, 2001

ABSTRACT



Several potentially experimentally accessible lithiated heterocyclic and heteroatom compounds with planar tetracoordinate carbons (ptC) have been predicted computationally. These utilize the strong electron-donating ability and the bridging proclivity of lithium to achieve the ptC preferences. As the p orbitals on the central carbons are only partially occupied, their electronic structures are similar to those of the related carbenes, eg. imidazole-2-ylidene, rather than to the other ptC compounds such as dilithiocyclopropane.

By comparing the computed energies of planar versus tetrahedral arrangements of an extensive set of molecules, Schleyer, Pople, and their co-workers[1] followed a hint of Hoffmann et al.[2] and found that lithium was particularly effective in stabilizing planar tetracoordinate carbon (ptC) arrangements. While the planar and "tetrahedral" structures of dilithiomethane (**1**) were close in energy, 1,1-dilithiocyclopropane (**2**) was the first molecule predicted to prefer a structure with a ptC arrangement[1] that has withstood subsequent scrutiny.[3a] This finding has stimulated experimentalists and theorists to achieve ptC arrangements in organolithium compounds,[3a] as well as in a wide variety of molecules.[3]

As a result of the ionic character of its bonding, lithium prefers bridging positions and in the structures of lithium compounds often does not follow classical considerations.[4] The lithium bridging in lithiomethylamine (**3**) and lithiomethanol (**4**)[5] are examples pertinent to this communication. We have now achieved new ptC arrangements computationally[6−8] by utilizing the strong lithium bridging tendency to heteroatoms as well as its strong electron-donating ability. Some of our predications involving readily available compounds invite experimental investigation.

The ptC arrangement in **2** is due to the combination of electronic and strain (bond angle) effects.[1,3a] The Li−C bond

---

[†] University of Georgia.

[‡] Indian Institute of Technology.

(1) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P.v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419.

(2) Hoffmann, R.; Alder, R. G.; Wilcox, C. F. *J. Am. Chem. Soc.* **1970**, *92*, 4992.

(3) Recent reviews: (a) Sorger, K.; Schleyer, P. v. R. *J. Mol. Struct. (Theochem)* **1995**, *338*, 317. (b) Rottger, D.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 812 (c) Radom, L.; Rasmussen, D. R. *Pure Appl. Chem.* **1998**, *70*, 1977. (d) Siebert, W.; Gunale, A. *Chem. Soc. Rev.* **1999**, *28*, 367.

(4) Review: Streitwieser, A.; Bachrach, S. M.; Dorigo, A.; Schleyer, P. v. R. *Lithium Chemistry, A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1994; p 1.

(5) (a) Clark, T.; Schleyer, P.v. R.; Houk, K. N.; Rondan, N. *J. Chem. Soc., Chem. Commun.* **1981**, 579. (b) Vincent, M. A.; Schaefer, H. F., III. *J. Chem. Phys.* **1982**, *77*, 6103. (c) Schleyer, P.v. R. *Pure Appl. Chem.* **1984**, *56*, 151,

(6) All calculations were carried out using the GAUSSIAN 98 program.[7] Geometries were optimized initially and characterized by frequency calculations at B3LYP/6-31G* and were then refined and further characterized at B3LYP/6-311+G**. Wave function stability checks were carried out at B3LYP/6-311+G**. Nucleus independent chemical shift (NICS) criterion[8] was used to probe aromaticity. NICS values were computed using the gauge-individual atomic orbital (GIAO) method at B3LYP/6-311+G**.

10.1021/ol015573a CCC: $20.00

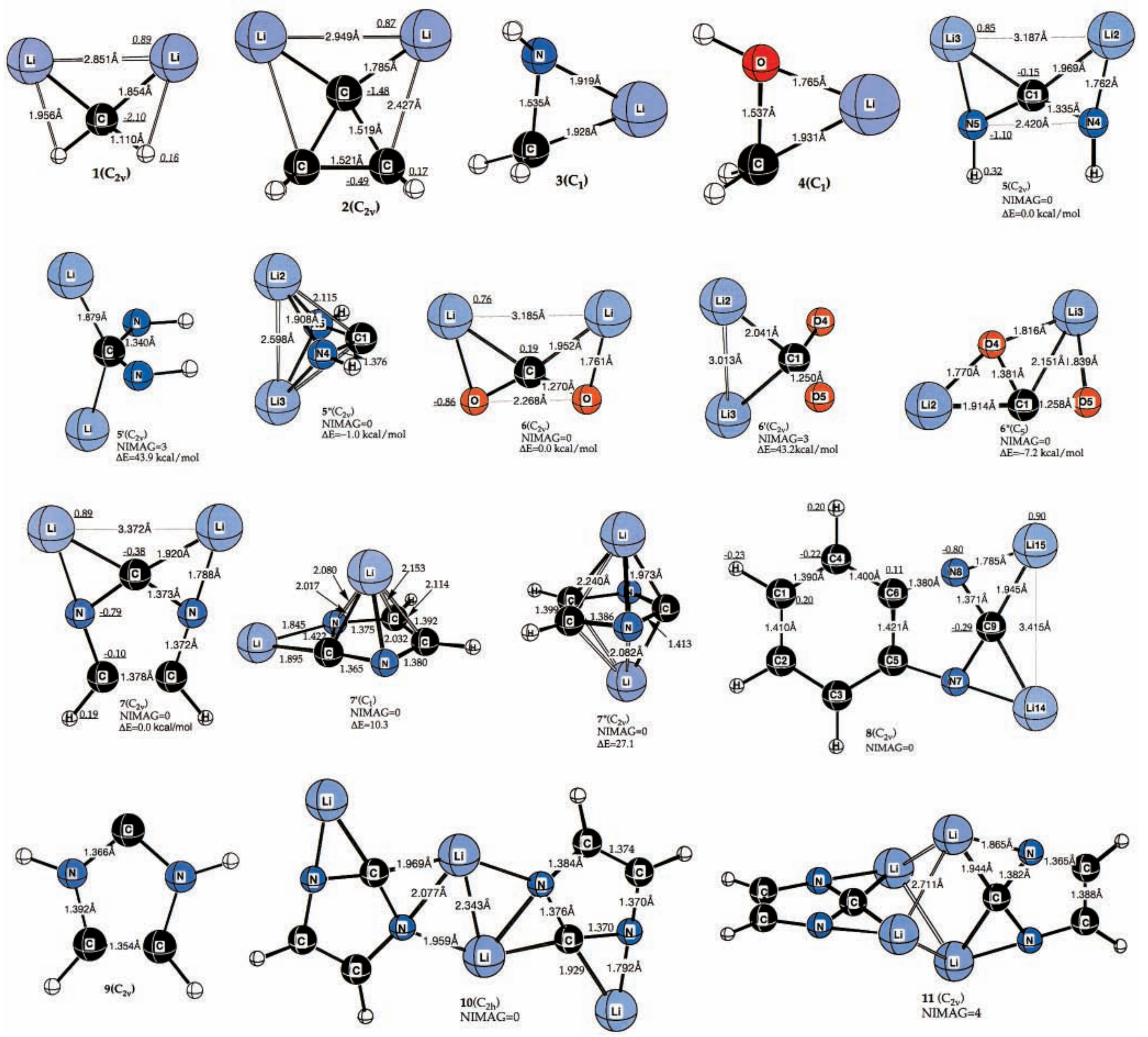


Figure 1. B3LYP/6-311+G** geometries of **1**−**11**. The underlined data are the NBO charges.

lengths, 2.427 Å, are somewhat too long for optimal bridging (Figure 1). However, this is improved if the CH_2 groups in **2** are replaced by the more electronegative but isoelectronic groups, e.g., NH (**5**) and O (**6**). As expected, the lithiums bridge the central carbon and the nitrogens (in **5**) or the oxygens (in **6**) effectively**.** The ptC minima are confirmed by B3LYP/6-311+G** frequency calculations.[9] The planar geometries of **5** and **6** are 43.9 and 43.2 kcal/mol more stable than their respective C_{2v} "tetrahedral" **5′** [NIMAG (numbers of imaginary requency) = 3] and **6′** (NIMAG = 3) forms. In contrast, **2** is only 8.0 kcal/mol[2a] lower in energy than its C_{2v} singlet tetrahedral isomer (NIMAG = 2). The triplets of **5** and **6** are less favorable than their singlets.

Other isomers are higher in energy than **5**. The exception, **5″**, is 1.0 kcal/mol more stable than **5.** Both **5** and **5″** are about 58.0 kcal/mol lower in energy than HN=C=NH + Li_2. Carbodiimide (HN=C=NH), the tautomer of cyanamide, has been the subject of several experimental and theoretical studies.[10] Its derivatives ($R_1N{=}C{=}NR_2$) are common reagents.[11] It may be possible to prepare derivatives of **5** by reacting carbodiimides with lithium.

---

(7) Frisch, M. J.; et al. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(8) Schleyer, P.v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N.v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(9) At B3LYP/6-311+G**, the smallest frequencies of **1**, **2**, **5**, **6**, **7**, and **8** are 220.9, 101.7, 168.6, 183.0, 160.7, and 128.9 cm^{-1}, respectively.

(10) (a) Koupt, J.; Jabs, W.; Winnewisser, M. *Chem. Phys. Lett.* **1998**, *295*, 462. (b) Jabs, W.; Winnewisser, M.; Belov, S. P.; Klaus, Th.; Winnewisser, G.; Birk, M. *Chem. Phys.* **1997**, *225*, 77. (c) Wagener, V.; Winnewisser, M.; Belini, J. *J. Mol. Spectrosc.* **1995**, *170*, *323*. (d) Pracna, P.; Winnewisser, M.; Winnewisser, B. P. *J. Mol. Spectrosc.* **1993**, *162*, 127. (e) Winnewisser, M.; Birk, M. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1341. (f) Birk, M.; Winnewisser, M. *Chem. Phys. Lett.* **1986**, *123*, 386.

Another ptC compound, **6″**, is 7.2 kcal/mol more stable than **6**. Both have the minimum number of atoms (five) for planar tetracoordinate carbon. Compounds **6** and **6″** are 45.9 and 53.1 kcal/mol lower in energy than $CO_2 + Li_2$, which implies that they may be prepared by reacting CO_2 with lithium. Manceron and Andrews[12] have performed matrix studies on the reaction of lithium with, e.g., carbon monoxide but not with carbon dioxide. Recently, several pentaatomic ptC compounds isoelectronic with those predicted theoretically[13] were characterized experimentally by Wang's group.[14]

However, experimental investigation of species related to **5** might be best achieved in heterocyclic systems. Thus, **7** takes further advantage of the aromaticity of imidazole. The C═C double bond in **7** contributes two additional p electrons to **5** and completes the six p electron system (see below). As in **3**, **5**, and **6**, the lithiums in **7** also favor bridging positions, 1.920 and 1.788 Å from the central carbon and the nitrogens, respectively. Isomeric minima with alternative lithium placements, **7′** and **7″**, are 10.3 and 27.1 kcal/mol higher in energy than **7**.

The fusion of a benzene ring to **7**, giving the benzoimidazole **8**, results in no significant changes in either the geometrical or electronic features of the ptC unit. However, the presence of the additional benzene ring in **8** may result in a more crystalline compound amenable for experimental X-ray determination. Note that somewhat related benzo-fused, crystalline, and thermally stable silylenes, $Si[N(CH_2Bu^t)]_2C_6H_4{-}1{,}2\text{-}R\text{-}$**4** (R = H or Me), have been reported.[15]

The extended Hückel calculations of Hoffmann and coworkers[2] indicated that the planar methane HOMO is a nonbonding lone pair in a perpendicular carbon p-orbital. Analogous electronic structures also can be found in most ptC compounds, e.g., **1** and **2**, Radom's alkaplanes,[16] and in molecules such as CAl_2Si_2, CAl_3Ge^- and CAl_3Si[1−3,14] However, we recently reported a new class of ptC compounds, the "boraplanes", which benefit from a different principle.[17] In boraplanes, the central carbon p-orbital is formally vacant and is the LUMO, rather than the HOMO. The two "missing" electrons are accommodated in an energetically more favorable orbital, the 4c-2e BBBB perimeter HOMO.

The electronic structures of the new lithiated ptC compounds discussed in the present paper are similar to those of the latter situation. Compound **7** can be derived conceptually by lithiation of imidazole-2-ylidene (**9**). This "stable carbene" has been studied intensively[18,19] since Arduengo and co-workers[20] synthesized the first persistent 1,3-diadamantyl derivative. Compound **7** is derived conceptually from the formal lithiation of imidazole-2-ylidene (**9**) and therefore retains, to some extent, the s lone pair character of the carbene. Figure 2 compares the s carbon lone pair HOMO of **9** with the HOMO-1 of **7**. In both cases, the central carbon p(p) occupancy is only part of the usual aromatic 6 π electron delocalization. The central carbon p(p) occupancy in **7**, 0.97*e*, is larger than 0.64*e* in **9** (Table 1) but still much less than the occupancies 1.87*e* of **1** and 1.72*e* of **2**. Despite the dianionic character, the central carbon in **7** has a negative charge of only −0.38*e*, much less than the carbon charges in **1** (−2.1*e*) and **2** (−1.5*e*). Both **7** and **9** are aromatic and have three occupied p orbitals. Indeed, at GIAO-B3LYP/6-311+G**//B3LYP/6-311+G**, the NICS(1) values (i.e., 1 Å above the ring centers)[21] of the five-membered rings of **7** and **9** are −11.0 and −10.1, respectively, compared with

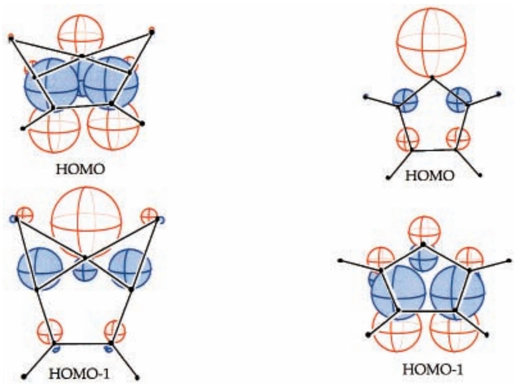


Figure 2. HOMO and HOMO-1 of **8** and **9**.

Table 1. Central (ptC) Carbon p Orbitals and Natural Charges at B3LYP/6-311+G**

	p(π)[a]	q(C)[b]	q(X)[c]	q(Y)[d]
1	1.87	−2.1	0.15	0.89
2	1.72	−1.5	−0.49	0.89
5	0.80	−0.15	−1.1	0.85
6	0.70	0.19	−0.85	0.76
7	0.97	−0.38	−0.79	0.89
8	0.90	−0.28	−0.78	0.86
9	0.64	0.10	−0.59	0.40

[a] The p(π) values are natural atomic orbital occupancies of the central carbon p orbitals perpendicular to the molecular plane. [b] Natural charges on the central carbon. [c] Charges on the atoms adjacent to the central carbon: X = H in **1**, C in **2**, O in **6**, and N in **5** and **7**−**9**. [d] Charges on Y, the lithiums in **1**−**8** and the hydrogen in **9**.

---

(11) For examples, see: (a) Venenziani, G.; Reau, R.; Dahan, F. *J. Org. Chem.* **1994**, *59*, 5927 (b) Koketsu, M.; Suzuki N.; Ishihara H. *J. Org. Chem.* **1999**, *64*, 6473 (c) Sai, H.; Ohmizu, H. *Tetrahedron Lett.* **1999**, *40*, 5019 (d) Lewis M, Glaser R *J. Am. Chem. Soc.* **1998**, *120*, 8541.

(12) Manceron, L.; Andrews, L. *Lithium Chemistry, A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1994; p 89

(13) (a) Schleyer, P. v. R.; Boldrev, A. I. *J. Chem. Soc. Chem., Commun.* **1991**, 1536. (b) Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1998**, *120*, 7967.

(14) (a) Li, X.; Wang, L.-S.; Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1999**, *121*, 6033. (b) Li, X.; Zhang, H.-F.; Wang, L.-S.; Geske, G. D. Boldyrev, A. I. *Angew. Chem., Int. Ed*. **2000**, *39*, 3630.

(15) Haff, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704. (b) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaser, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1931.

(16) (a) McGrath, M. P.; Radom. L. *J. Am. Chem. Soc.* **1993**, *115*, 332 (b) Rasmussen, D. R.; Radom, L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2876. (c) (d) Radom. L.; Rasmussen, D. R. *Pure Appl. Chem.* **1998**, *70*, 1977.

(17) Wang, Z.-X.; Schleyer, P.v. R. *J. Am. Chem. Soc.* **2001**, *123*, 994.

(18) (a) Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1980**, 124 (b) Pauling, L. *J. Chem. Soc. Chem., Commun.* **1980**, 688

(19) Bourissou, D.; Guerret, O.; Gabbai, P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

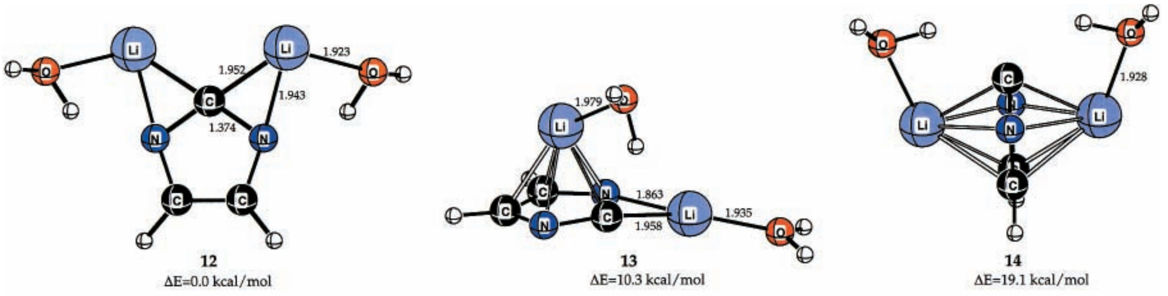


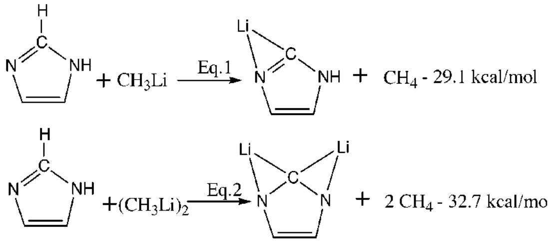
Figure 3. B3LYP/6-311+G** geometries of **12**−**14**.

−9.5 for $C_5H_5^-$, the prototype 6π aromatic cyclopentadienyl anion. In **1** and **2**, there are strong ionic interactions between the lithiums and the central carbons; these decrease significantly in **5**, **6**, **7**, and **8** as a result of the smaller charge of the central carbons. However, the decrease is compensated by the interaction between lithiums and the adjacent nitrogens (in **5**, **7** and **8**) or oxygens (in **6**) (see the charges and geometries in Figure 1).

The electronic structures of the present ptC compounds also result in different dimerization preferences described below.[23] For example, the side-to-side approach (**10**) is favored for **7** as a result of the electrostatic attraction between two monomers. This approach is preferred to the head-to-head arrangement favored for **1** **(**Figure 1**)**.[23] The side-to-side dimerization energy of **7** is 54.7 kcal/mol. The head-to-head approach results in a fourth-order saddle point (**11**) and a dimerization energy of only 7.2 kcal/mol. Note that the side-to-side dimer retains both ptC arrangements (**10**). Although the smallest frequency is only 12.0 cm^{-1}, this corresponds to an out-of-plane "flapping" mode rather than "tetrahedralization" of the ptC's.

Does solvation have a significant influence on the stabilization of planar versus "tetrahedral" arrangements?[3,25] Compound **7**, as an example, was taken to examine solvent effects by using the simple model [25] in which a water molecule is attached to each lithium. Figure 3 gives the relative energetic and structural results for **12**, **13**, and **14** (i.e., **7**, **7′**, and **7″** solvated by two water molecules). This solvation only bends the tetracoordinate carbon in **7** slightly from the exact plane (the ∠LiNCN dihedral angle is 175.8°), and does not change the large relative stabilization of **7** over **7′** and **7″**. Further solvation should not alter the planar preferences.

Recently, Boche and co-workers[24] have prepared 4-*tert*-butyl-1-methyl-2-lithium by deprotonation of an N(1)-substituted imidazole. Our model reaction (eq 1) for this deprotonation is exothermic by 29.1 kcal/mol, supporting the experimental process. The dilithiation of imidazole by methyllithium dimer (eq 2), giving **7**, also is exothermic by 32.7 kcal/mol. However, we have not found any compound similar to **7** in the literature. We suggest that the lithiation of imidazole or benzoimidazole derivatives be carried out to see if both NH and five-membered ring CH groups can be replaced.



7

In summary, we have designed computationally several lithium-containing ptC compounds (**5**−**8** and **10**) by utilizing the strong electron-donating ability and the bridging proclivity of lithium. To some extent, the electronic structures of **5**−**8** are similar to that of the related carbenes, e.g., **9**, rather than the usual ptC compounds, e.g., **1** and **2**. They have no p lone pair located on the central carbon: the p(p) occupancies of the central carbons are less than 1.0*e*. In **1** and **2**, there are strong ionic interactions between lithiums and the central carbons. Those interactions in **5**−**8** decrease significantly as a result of the smaller charge on the quaternary carbons but are compensated by the ionic interactions between the lithiums and the nitrogens (in **5**, **7**, and **8**) or the oxygens (in **6**). Our predications encourage the experimental characterization of these potential ptC compounds.

Acknowledgment. We thank the University of Georgia for support and Prof. W. Siebert and G. Boche for information and their interest.

OL015573A

---

(20) (a) Heinemann, C.; Muller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023 and references therein. (b) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039 and references therein.

(21) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(22) Schleyer, P. v. R., Jiao, H.; Hommes, N. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(23) Jemmis, E. D.; Schleyer, P. v. R. *J. Organomet. Chem.* **1978**, *154*, 327.

(24) (a) Boche, G.; Hilf, C.; Harms, K.; Marsch, M.; Lohrenz, J. C. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 4. (b) Hilf, C.; Bosold, F.; Harms, K.; Lohrenz, J. C. W.; Marsch, M.; Schimeczek, M.; Boche, G. *Chem. Ber.* **1997**, *130*, 1201. (c) Hilf, C.; Bosold, F.; Harms, K.; Marsch, M.; Schimeczek, M.; Boche, G. *Chem. Ber.* **1997**, *130*, 1213.

(25) Chandrasekhar, J.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1981**, 260.