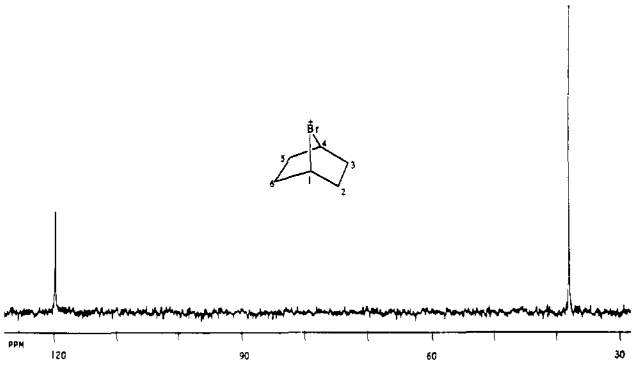
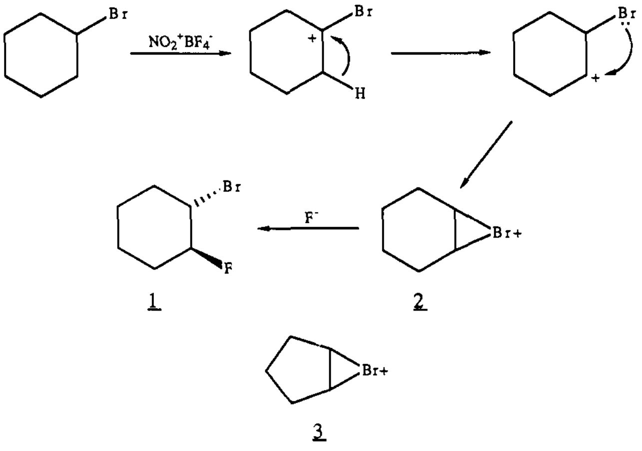


Figure 1. Proton-decoupled 50-MHz ^{13}C NMR spectrum of 7-bromoniabicyclo[2.2.1]heptane in SbF_5/SO_2ClF solution at −95 °C.

Scheme I



clohexene bromonium ion **2** had formed, it should have shown three distinct ^{13}C NMR absorptions instead of two. The observed spectrum, however, is still characteristic of a bromonium ion (based on the extent of ^{13}C deshielding of the α-carbon as well as an increase in the magnitude of the C–H coupling constant),[9] but with 4-fold symmetry. The only choice is the 4-fold-symmetrical ion 7-bromoniabicyclo[2.2.1]heptane (**4**). Formation of ion **4** can be best understood by successive 1,2-hydride shifts from the initially generated 2-bromocyclohexyl cation giving the 4-bromocyclohexyl cation, followed by transannular 1,4-bromine participation. The 200-MHz[8] ^1H NMR spectrum is also in agreement with the assigned structure with peaks at $\delta(^1H)$ 7.49 (br, 2 H, H_1 and H_4), 2.78 (d, $J_{H-H} = 9.0$ Hz, 4 H, endo, H_2, H_3, H_5, H_6), and 1.46 (d, $J_{H-H} = 9.0$ Hz, 4 H, exo, H_2, H_3, H_5, H_6). Interestingly, the same bicyclic bromonium ion **4** was formed by the ionization of 1,1-dibromocyclohexane (**5**),[10] which again involves successive 1,2-hydride shifts. Under no conditions attempted was the cyclohexene bromonium ion **2** formed, indicating that under long lived stable ion conditions **2** is not stable. To probe the suggested mechanism and assigned structure, we subsequently carried out ionization of *trans*-1,4-dibromocyclohexane (**6**)[11] in SbF_5/SO_2ClF at −95 °C, which very cleanly again yielded the same ion **4**, fully supporting the assigned structure and its formation path.

The unexpected 1,4-bridged bicyclic bromonium ion **4** is stable below −90 °C, above which it gives a mixture of 1-methylcyclopentenyl cation **7**[12] and cyclohexenyl cation **8**.[12] The observed unprecedented 1,4-transannular participation in the intermediate 4-bromocyclohexyl cation is rather interesting. No such participation in six-membered-ring systems is known. However, transannular participation in 7–11-membered rings is well recognized.[13] It appears that the bulky bromine atom is of the right size to effect such transannular participation in a six-membered ring through a boat type of transition state. Attempts to prepare the corresponding bicyclic chloronium ion by the ionization under a variety of conditions of both *trans*-1,2- and *trans*-1,4-dichlorocyclohexane were unsuccessful.[14] In these cases, the 1-methylcyclopentenyl cation was the only product. This shows that the smaller chlorine atom cannot readily induce similar transannular 1,4-participation in a six-membered ring.

To further rationalize the observed results, we also carried out semiempirical SCF-MO calculations. Using MNDO theory,[15] the C_{2v}-symmetrical **4** was found to be 2.6 kcal more stable than the C_s-symmetrical three-membered-ring bromonium ion **2**. Furthermore, the unbridged 4-bromocyclohexyl cations (both chair and boat forms) are also unstable compared to **4** by 2.9 and 3.8 kcal, respectively. On the other hand, the 1-bromocyclohexyl cation (chair form) is slightly more stable than **4** (by 1.1 kcal), although this ion was not observed under stable-ion conditions.

In conclusion, we have found under long lived stable ion conditions unprecedented 1,4-transannular participation in the 4-bromocyclohexyl cation leading to the unexpected persistent bicyclic bromonium ion **4**. Bromine appears to be of the proper size to effect such 1,4-participation in a six-membered ring. Smaller chlorine was found incapable of effecting such bridging. The observed experimental results are also in accord with semiempirical MNDO calculations.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

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[9] Olah, G. A. *Halonium Ions*; Wiley Interscience: New York, 1975.

[10] Prepared by using the published procedure: Naopolitano, E.; Fiaschi, R.; Mastrorilli, E. *Synthesis* **1986**, 122.

[11] Purchased from Aldrich Chemical Company and used as such.

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[13] March, J. *Advanced Organic Chemistry*, 3rd ed., Wiley Interscience: New York, 1985.

[14] Ionizations carried out at −120 °C (using pentane/liquid N_2 slush) gave similar results.

[15] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. Full results of these calculations along with ab initio results will be the subject of a forthcoming paper.

Thermally Generated Benzannelated Trimethylenemethane Biradicals of the 2-Methylenecyclohexene-1,3-diyl Series Escape Capture by a New Rearrangement to Benzannelated Bicyclo[3.2.0]hept-1-enes

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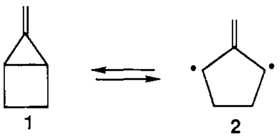
Because a finite energy barrier opposes intramolecular ring-closure of singlet 2-methylenecyclopentane-1,3-diyl biradicals (e.g., **2**) generated thermally from 5-methylenebicyclo[2.1.0]pentanes (e.g., **1**), it is possible to observe dimerization and intermolecular cycloaddition of these trimethylenemethane (TMM) species. These reactions are precluded in most TMM derivatives by fast intramolecular cyclization.[1,2] Thus, although a vinyl TMM



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[1] (a) Rule, M.; Mondo, J. A.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2209. (b) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2217.

[2] Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 151.

[3] (a) Pikulin, S.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 8276; (b) *J. Am. Chem. Soc.* **1988**, *110*, 8500.

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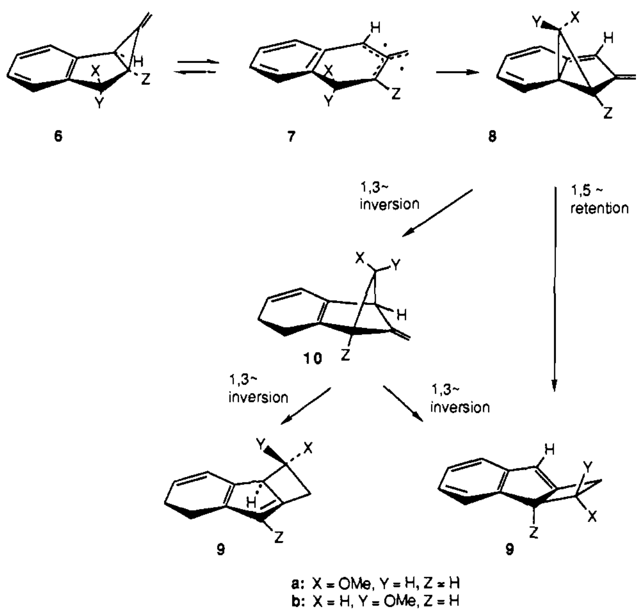
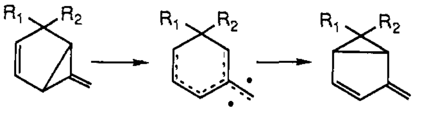
Scheme I



biradical (e.g., **4**) can be detected as a mechanistically discrete intermediate in the rearrangements of 6-methylenebicyclo[3.1.0]hex-2-enyl derivatives (e.g., **3**),[3] attempted intermolecular interception of these biradicals fails to compete with intramolecular cyclization to homofulvene rearrangement products (e.g., **5**).

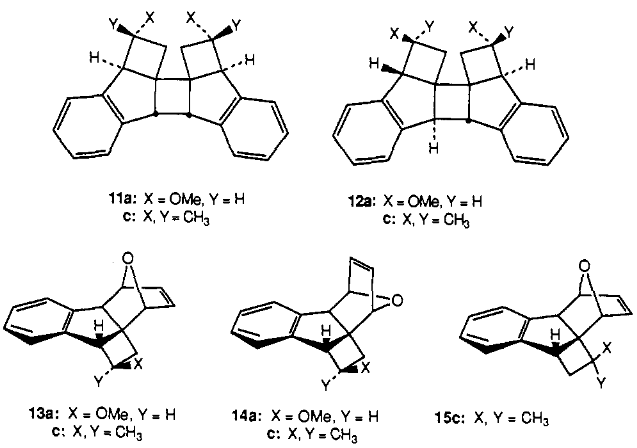


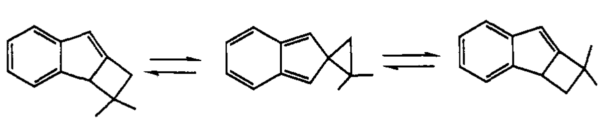
3 4 5

In the present study, we hoped to shut off this rearrangement channel and thereby improve the chances for capture of the biradical intermediate by fusing a benzo ring onto **3**, giving reactant **6** (Scheme I), whose hypothetical homofulvene product **8** should be destabilized. Bond additivity[4] and strain energy[5] calculations suggest that whereas **3** → **5** is exothermic by ~5 kcal/mol, **6** → **8** would be endothermic by ~16 kcal/mol. However, although dimers and cycloadducts were obtained in reactions of **6**, they proved to be derived not by interception of the TMM intermediate **7** but rather by reactions of a new type of rearrangement product, the 3,4-benzobicyclo[3.2.0]hept-1-ene **9**, apparently formed in a secondary isomerization of the unanticipated homofulvene **8** (Scheme I).

A compound of structure **9a** or **9b** could not be isolated as such from solution-phase pyrolysis (benzene, 80 °C) of **6a** or **6b** but was recognized as the corresponding [2 + 2] dimers **11a–12a** (70% yield) or, when furan was incorporated into the solution-phase reaction mixture, as the Diels–Alder adducts **13a–14a**[6] (50% yield) (Chart I). Structures and stereochemical configurations for the dimers and adducts of the entire series were established by NMR spectroscopy and by single-crystal X-ray analysis. Details are given in the supplementary material. Similar dimerization reactions were observed with the *gem*-dimethyl reactant **6c**. From **6c**, we obtained not only the **9c**–furan Diels–Alder adducts **13c** and **14c** but also a third adduct, **15c**, apparently derived from a well-precedented[7] spiroheptadiene rearrangement **9c** → **16** succeeded by capture of the latter.

Chart I





9c 17 16

Either of the epimeric methyl ethers **6a** or **6b** gave the same mixture of dimers **11a** and **12a**. Moreover, partial interconversion of the epimers **6a** and **6b** occurred in competition with dimerization and trapping reactions. These findings suggest the intervention of a common TMM intermediate **7** (Scheme I).

In both sets of derivatives, the dimers **11a** and **12a** and the furan adducts **13a** and **14a**, the methoxy group is cis to the adjacent bridgehead hydrogen, which implies a substantial stereoselectivity in the sequence of rearrangement steps leading to product **9**. We suggest that this originates in stereoselective cyclization of biradical **7** to the *endo*-methoxy derivative **8a**, a reaction with close precedent[3] in the case **4** → **5** (R_1 = H, R_2 = OMe). Subsequent sigmatropic rearrangement of **8a**, either a [1,5] reaction with retention or two successive [1,3] reactions with inversion, would give **9a** with the correct stereochemistry (see Scheme I). Because the sequential [1,3] reactions pass through a (not isolated) symmetrical intermediate **10**, an equal distribution of the deuterium label between the bridgehead and vinyl positions of the bicyclo[3.2.0]hept-1-ene product would be expected. The predicted scrambling was in fact observed by NMR analysis of the furan adduct **13c**-*d* of product **9d** from the labeled dimethyl reactant **6d**. However, the likely possibility that the reaction **9c** → **17** may be reversible precludes the use of this fact to make a choice in favor of the sequential [1,3] pathway.

The difference in behavior between the **3** → **5** system[3] and that of **6** and, in particular, how the TMM biradical **7** escapes capture over the barrier **8**, which we naively had hoped would be insurmountable, can be understood as a perturbation by the benzo unit. Energy calculations from literature analogies[4,5] show that in effect the **3** → **5** reaction stops because the bicyclo[3.2.0]hept-1-ene product from hypothetical further rearrangement of **5** would be enthalpically 13 kcal/mol less stable than **5**. The **8** → **9** rearrangement, however, leads downhill by 12 kcal/mol, largely because it reestablishes the benzo unit, thereby providing the driving force of this rearrangement.

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[5] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

[6] Several examples of dimerization and of Diels–Alder trapping of bicyclo[3.2.0]hept-1-enes with electron-rich dienes have been reported: (a) Breslow, R.; Washburn, W.; Bergman, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 196. (b) Cava, M. P.; Narasimhan, K.; Zeiger, W.; Radonovich, L. J.; Glick, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 2378. (c) Bauld, N. L.; Dahl, C. E.; Rim, Y. S. *J. Am. Chem. Soc.* **1969**, *91*, 2787. (d) Miller, R. D.; Kaufmann, D.; Mayerle, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8511.

[7] Oda, M.; Breslow, R. *Tetrahedron Lett.* **1973**, 2537.

Supplementary Material Available: Summaries of single-crystal X-ray analyses, ORTEP drawings, and tables of positional parameters and B(eq), intramolecular distances and bond angles involving the non-hydrogen atoms, torsion or conformation angles, and U values for five structures (59 pages). Ordering information is given on any current masthead page.

Spectroscopic and Reactivity Studies of Lithium Reagent–HMPA Complexes[1]

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The dipolar aprotic solvent hexamethylphosphoramide (HMPA) has superior ability to form cation–ligand complexes and effectively solvates a variety of lithium salts. It is used to activate and modify the chemical behavior of lithium salts and organolithium reagents.[2,3] We report here on the coordination chemistry of lithium using reactivity studies and direct NMR observation. Under suitable conditions, it is possible to detect $^2J_{\mathrm{LiP}}$ coupling for $\mathrm{Li^+{\cdot}HMPA}$ complexes in both ^{7}Li and ^{31}P NMR spectra.[1c,4a] This promises to be a powerful tool to study the complexation of lithium by HMPA, to determine how various lithium species compete (as Lewis acids) for HMPA in solution, and to determine the effect of HMPA on ion-pair composition of organolithium species.

During our studies of "ate" complex intermediates in the metal halogen and other lithium-metalloid exchange reactions,[1] we examined the reactivity of solutions in which PhLi and species such as $\mathrm{Ph_2I^-Li^+}$ were present.[1b] Figure 1 presents the results of a model study on the metallation reactivity of PhLi as a function of [HMPA]. Both $\mathrm{Et_3PhB^-Li^+}$ and LiBr inhibit the effect of added HMPA. With 1 equiv of $\mathrm{Et_3PhB^-Li^+}$ present, the rate did not increase significantly up to 2.0 equiv of HMPA.

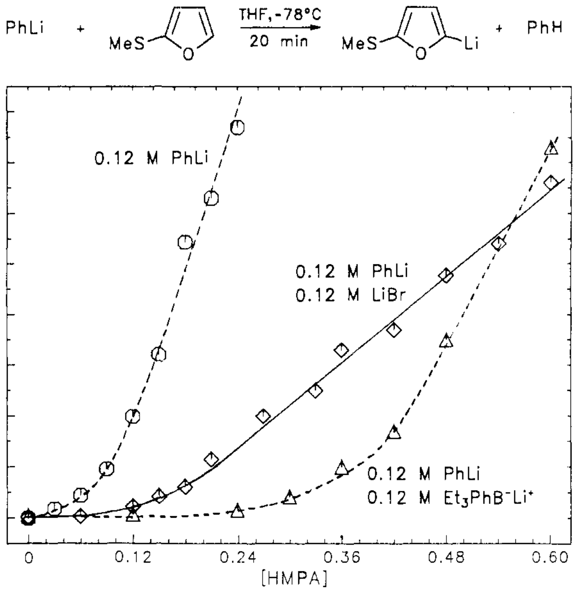

Figure 1. Effect of HMPA on the metalation of 2-methylthiofuran with PhLi in THF at −78 °C in the absence and presence of added lithium salts. The extent of metalation was monitored by trapping with dimethyl disulfide and analyzing the methyl sulfides by GLC. The lines have no mathematical significance.

Table I. Li and P NMR Parameters for PhLi and $\mathrm{PhEt_3BLi}$ Complexes with HMPA[a]

	$\mathrm{PhEt_3B^-Li^+{\cdot}(HMPA)}_n$					$\mathrm{(PhLi)_1{\cdot}(HMPA)}_n$	
	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 0$	$n = 1$
δ(Li)[b]	−0.66	−0.61	−0.59	−0.55	−0.49	−0.95	0.84
δ(P)[c]		27.5	27.2	27.1	27.2		27.7
$J_{^7\mathrm{LiP}}$ (Hz)[d]		11.2	10.3	9.2	7.5		7.4[d]

[a] Measured at −110 °C in THF on a Brucker AM-360 spectrometer. [b] Referenced to external 0.3 M LiCl in methanol at −100 to −105 °C; ^{6}Li and ^{7}Li data were used. [c] Referenced to internal $\mathrm{PPh_3}$ at −6.0 ppm. Free HMPA at 26.4 ppm. [d] Reported for ^{7}Li, the measured $^6\mathrm{Li}$–$^{31}\mathrm{P}$ coupling was 2.8 Hz.

The reactivity of PhLi can be understood in terms of the NMR spectra (−110 °C) presented in Figures 2 and 3. In pure THF (Figure 2A), the lithium is tetrahedrally solvated, as shown by the chemical shift[5] and narrow line width (2 Hz)[6] of the ^{7}Li signals of $\mathrm{Et_3PhB^-Li^+}$.[7] As HMPA was added, the ^{7}Li and ^{31}P NMR spectra clearly showed the presence of a series of coordination complexes having one to four HMPA molecules attached to lithium. Addition of 0.5 equiv of HMPA converted half of the lithium cations to $\mathrm{Li^+(HMPA)_1}$, giving rise to a 1:1:1:1 quartet in the ^{31}P NMR spectrum and a doublet superimposed on the remaining $\mathrm{Li^+S_4}$ (S = THF) singlet in the ^{7}Li NMR spectrum (Figure 2B).[8a] With 1 equiv (Figure 2C), a mixture of cations was observed, approximately 70% of which is $\mathrm{Li^+(HMPA)_1}$, with 15% each of $\mathrm{Li^+S_4}$ and $\mathrm{Li^+(HMPA)_2}$. This is most clear from the ^{31}P NMR spectrum since ≈70% of HMPA is present as $\mathrm{Li^+(HMPA)_1}$ and 30% is $\mathrm{Li^+(HMPA)_2}$. The association constants for the first two HMPAs are thus quite similar.[8b] The ^{7}Li signals with 2 (Figure 2E) and 3 (Figure 2G) equiv of HMPA resemble a triplet and quartet, showing that HMPA sequentially replaces THF as ligand to form $\mathrm{Li^+(HMPA)_2}$ and $\mathrm{Li^+(HMPA)_3}$. The fourth equivalent of HMPA was complexed weakly, ≈40% of the lithium was converted to $\mathrm{Li^+(HMPA)_4}$, and free HMPA could be seen in the ^{31}P NMR spectra. Complete conversion to $\mathrm{Li^+(HMPA)_4}$ required up to 10 equiv of HMPA.[8c] The $^2J_{\mathrm{LiP}}$ coupling

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(1) For earlier papers in this area, see: (a) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102. (b) Reich, H. J.; Reich, I. L.; Phillips, N. H. *J. Am. Chem. Soc.* **1985**, *107*, 4101. (c) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444.

(2) Normant, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1046.

(3) (a) Changes in ratio of 1,2- to 1,4-addition of RLi to enones: Cohen, T.; Abraham, W. D.; Myers, M. *J. Am. Chem. Soc.* **1987**, *109*, 7923. (b) Enolate reactivity: House, H. O.; Prabhu, A. V.; Phillips, W. V. *J. Org. Chem.* **1976**, *41*, 1209. Jackman, L. M.; Lange, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 4494. Liotta, C. L.; Caruso, T. C. *Tetrahedron Lett.* **1985**, *26*, 1599. Seebach, D.; Amstutz, R.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2622. Fataftah, Z. A.; Kopka, I. E.; Rathke, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3959. (c) Increased reactvity: Dolak, T. M.; Bryson, T. A. *Tetrahedron Lett.* **1977**, 1961. Fraser, R. R.; Mansour, T. S. *Tetrahedron Lett.* **1986**, *27*, 331. DePue, J. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 5524. (d) Unusual ion structures:[1] Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5657. Jackman, L. M.; Scarmoutzos, L. M.; Porter, W. *J. Am. Chem. Soc.* **1987**, *109*, 6524. (e) Solubilization of lithium salts: Snaith, R.; Barr, D.; Wright, D. S. *J. Am. Chem. Soc.* **1987**, *109*, 7891.

(4) (a) ^2J $^7\mathrm{Li}$–$^{31}\mathrm{P}$ coupling in ^{7}Li NMR for the lithium halide complex $\mathrm{(LiBr)_2{\cdot}3HMPA{\cdot}toluene}$: Barr, D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Berd, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1989**, 318. One-bond $^{31}\mathrm{P}$–$^7\mathrm{Li}$ couplings have been observed: Lappert, M. F.; Hitchcock, P. B.; Power, P. P.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1669. (b) Two separate HMPA signals in the ^{1}H NMR spectrum of a dihydroanthracenyllithium have been reported: Panek, E. J.; Rodgers, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 6921.

(5) Fraenkel assigns the region δ 0.55 to −1.3 in ^{7}Li NMR (relative to 0.3 M LiCl in methanol) to solvated lithium cation.[3d]

(6) Lithium-7 has spin $^3/_2$ and usually gives fairly broad resonances because of relaxation caused by interaction of the nuclear quadrupole moment with electric field gradients in the molecule. Sharp lines indicate a symmetrical (usually tetrahedral) environment.

(7) Lithium tetraphenylborate is monomeric in THF (Wong, M. K.; Popov, A. I. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3615) and is largely ion-paired (Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Swarc, M. *J. Chem. Phys.* **1965**, *69*, 608).

(8) (a) The coalescence temperature for the P–Li couplings in $\mathrm{LiBR_4{\cdot}(HMPA)}_n$ is approximately −100 °C for both the first and last coordinated HMPA. For $\mathrm{PhLi{\cdot}(HMPA)_1}$ with a deficiency of HMPA the coalescence is near −110 °C. (b) A variety of samples of $\mathrm{Et_3PhB^-Li^+}$ with varying concentrations of HMPA near 1 equiv have been analyzed and are consistent with this interpretation. (c) In the gas phase, the enthalpy of association for $\mathrm{Li^+(H_2O)}_n$ decreases steadily for n = 1–4 (Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466).

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