

Solvation and Structural Effects on the Stability of 10-X-2 Ate-Complexes: A Computational Study

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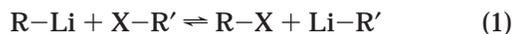
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The structures and energies of a variety of 10-X-2 ate-complexes derived from reaction of alkyllithiums and aryllithiums with the corresponding organohalides have been studied at the B3LYP/6-31++G** theoretical level. The results of the calculations, which are in good agreement with the available experimental data, indicate that diaryl ate-complexes are more stable than their dialkyl counterparts. Fluorine substitution was found to confer substantial stability to both diaryl and dialkyl ate-complexes, and the calculations suggest that perfluoro dialkyl 10-X-2 ate-complexes should be experimentally observable species. One of the most important factors contributing to stability of a 10-X-2 ate-complex is removal of the formally cationic lithium from the vicinity of the ate-anion via coordination with a Lewis basic solvent.

Introduction

The lithium–halogen exchange (eq 1), a reversible metathesis favoring the more stable organolithium and most readily accomplished with organobromides and iodides,¹ was discovered independently and virtually simultaneously by Wittig² and Gilman³ some 60 years ago. The mechanism of this intriguing reaction has been the subject of a number of studies,⁴ and it now appears that the detailed course of the exchange is dependent on the structure of the reactants and the reaction conditions.^{5,6}



Two general mechanistic scenarios have been proposed to account for the exchange:⁴ (i) a process involving

radical intermediates initiated by single-electron transfer (SET) from the organolithium to the organohalide⁷ and (ii) nucleophilic attack of the organolithium on the halogen atom of the organohalide to give a 10-X-2 ate-complex (eq 2)⁸ either as a transition state⁹ or as an intermediate.¹⁰ More recently, it has been suggested the latter mechanism may be the elementary step in all lithium–halogen exchange reactions, since homolytic fragmentation within a 10-X-2 ate-complex could account for the observation of radical intermediates.¹¹



The existence of 10-X-2 species having a formally anionic halogen bonded to two carbons is well established, but fully characterized structures are rather rare.^{12–15} A particularly simple example is the ICN–KCN adduct isolated as a stable complex (1) with the diethyl ester of

(1) (a) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974. (b) Wakefield, B. J. *Organolithium Methods*; Pergamon Press: New York, 1988. (c) Sapse, A. M.; Schleyer, P. v. R. *Lithium Chemistry: A Theoretical and Experimental Overview*; Wiley: New York, 1995. (d) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 1, p 43. (e) Schöllkopf, U. In *Methoden der Organischen Chemie*; Georg Thieme: Stuttgart, 1970; Vol. 13/1. (f) Jones, R. G.; Gilman, H. *Chem. Rev.* **1954**, *54*, 835. (g) Gilman, H.; Jones, R. G. *Org. React. N. Y.* **1951**, *6*, 339.

(2) Wittig, G.; Pockels, U.; Dröge, H. *Chem. Ber.* **1938**, *71*, 1903.

(3) (a) Gilman, H.; Jacoby, A. L. *J. Org. Chem.* **1938**, *3*, 108. (b) Gilman, H.; Langham, W.; Jacoby, A. L. *J. Am. Chem. Soc.* **1939**, *61*, 106.

(4) For a review of the literature dealing with the mechanism of the lithium–halogen exchange reaction, see: Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, *352*, 1.

(5) For a discussion of the mechanism of the exchange involving aliphatic substrates, see: (a) Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098. (b) Newcomb, M.; Williams, W. G.; Crumpacker, E. L. *Tetrahedron Lett.* **1985**, *26*, 1183 (c) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T.; Wang, W. *Tetrahedron Lett.* **1986**, *27*, 1861. (d) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T. *Tetrahedron Lett.* **1986**, *27*, 1865. (e) Ashby, E. C.; Pham, T. N. *J. Org. Chem.* **1987**, *52*, 1291. (f) Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404.

(6) For a discussion of the mechanism of organolithium–aryl halide exchange, see: (a) Winkler, H. J. S.; Winkler, H. J. *Am. Chem. Soc.* **1966**, *88*, 964. (b) Winkler, H. J. S.; Winkler, H. J. *Am. Chem. Soc.* **1966**, *88*, 969. (c) Rogers, H. R.; Houk, J. J. *Am. Chem. Soc.* **1982**, *104*, 522. (d) Beak, P.; Allen, D. J.; Lee, W. K. *J. Am. Chem. Soc.* **1990**, *112*, 1629. (e) Beak, P.; Allen, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 3420.

(7) (a) Fisher, H. *J. Phys. Chem.* **1969**, *73*, 3834. (b) Russell, G. A.; Lamson, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 3967. (c) Ward, H. R. *Acc. Chem. Res.* **1972**, *5*, 18 and references therein. (d) Lawler, R. G. *Acc. Chem. Res.* **1972**, *5*, 25. (e) Ward, H. R.; Lawler, R. G.; Cooper, R. A. In *Chemically Induced Magnetic Polarization*; Lepley, A. R., Closs, G. L., Eds.; Wiley: New York, 1973; Chapter 7.

(8) The 10-X-2 nomenclature follows a general classification of hypervalent N-X-L species, see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(9) Gilman's group appears to have been the first to suggest that lithium–halogen exchange may proceed via nucleophilic attack of an organolithium on the halogen atom of an organic halide. This early mechanistic formulation viewed the exchange as an S_N2-like process in which a hypervalent 10-X-2 species would be the transition state, see: Sunthakar, S. V.; Gilman, H. *J. Org. Chem.* **1951**, *16*, 123.

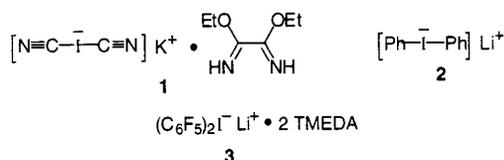
(10) Wittig and Schöllkopf appear to have been the first to suggest that nucleophilic attack by an organolithium on the halogen atom of a substrate may give a 10-X-2 species as an intermediate, see: Wittig, G.; Schöllkopf, U. *Tetrahedron Lett.* **1958**, *3*, 91. The putative 10-X-2 intermediate was termed an "ate-complex" by Wittig, see: Wittig, G. *Angew. Chem.* **1958**, *70*, 65.

(11) (a) Bailey, W. F.; Carson, M. W. *J. Org. Chem.* **1998**, *63*, 9960. (b) Bailey, W. F.; Carson, M. W. *Tetrahedron Lett.* **1999**, *40*, 5433.

(12) (a) Tebbe, K. F.; Fröhlich, R. *Z. Anorg. Allg. Chem.* **1983**, *505*, 19. (b) Arduengo, A. J.; Kline, M.; Calabrese, J. C.; Davidson, F. J. *Am. Chem. Soc.* **1991**, *113*, 9704.

(13) Tebbe, K. F.; Fröhlich, R. *Z. Anorg. Allg. Chem.* **1983**, *505*, 7.

(diimino)oxalic acid by Tebbe and Frölich.¹³ More to the point, 10-X-2 ate-complexes have been characterized as intermediates in the lithium–iodine exchange between aryl iodides and aryllithiums. Elegant kinetic and spectroscopic studies by Reich's group have demonstrated that lithium diphenyliodinanide (**2**) is an intermediate in the degenerate exchange between PhLi and iodobenzene,¹⁴ and the perfluoro analogue **3**, prepared by treatment of pentafluoriodobenzene with (pentafluorophenyl)lithium and crystallized as the TMEDA adduct, was found by Farnham and Calabrese to be stable at room temperature.¹⁵ Although 10-X-2 complexes have been postulated as intermediates in both lithium–iodine and lithium–bromine exchanges involving simple aliphatic reactants,^{4,5,10} such species have not been directly observed.¹⁶ In this connection, it should be noted that Hoffmann's group has recently presented convincing spectroscopic and kinetic evidence for the existence of long-lived 10-I-2 ate-complexes in both lithium–iodine and magnesium–iodine exchange reactions of aliphatic gem-diiodides.¹⁷



In light of the extensive literature concerning the role of 10-X-2 ate-complexes in the lithium–halogen exchange, it was of interest to explore the factors that might influence the ability of such species to exist as detectable intermediates. Herein we report the results of a computational investigation of the effect of structural changes and solvation¹⁸ on the stability of hypervalent 10-X-2 species. This work complements and extends the insightful theoretical studies by the groups of Boche and Cioslowski on the role of halogen ate-complexes in the lithium–halogen exchange reaction.¹⁹

Computational Methods

B3LYP hybrid density functional calculations²⁰ were carried out using the Gaussian 95 series of programs.²¹ The standard

(14) (a) Reich, H. J.; Phillips, N. H.; Reich, I. L. *J. Am. Chem. Soc.* **1985**, *107*, 4101. (b) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444. (c) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414. (d) Reich, H. J.; Green, D. P.; Phillips, N. H.; Borst, J. P.; Reich, I. L. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 83.

(15) Farnham, W. B.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2449.

(16) The only authentic 10-X-2 ate-complex having aliphatic carbon attached to a central halogen of which we are aware is tris(dimethylamino)sulfonium bis(perfluoro-*tert*-butyl)iodinanide, [(CF₃)₃C-I-C(CF₃)₃]⁺TAS[−]. This species, which was prepared by Farnham and Calabrese (ref 15), was fully characterized but structural data were not reported.

(17) (a) Müller, M.; Stiasny, H. C.; Brönstrup, M.; Burton, A.; Hoffmann, R. W. *J. Chem. Soc., Perkin Trans 2* **1999**, 731 and references therein. (b) Schulze, V.; Hoffmann, R. W. *Chem. Eur. J.* **1999**, *5*, 337. (c) Schulze, V.; Brönstrup, M.; Böhm, V. P. W.; Schwerdtfeger, P.; Schimeczek, M.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 824. (d) Stiasny, H. C.; Hoffmann, R. W. *Chem. Eur. J.* **1995**, *1*, 619.

(18) A recent theoretical investigation of the role of solvation on a model lithium–iodine exchange reaction between methyl iodide and vinyl lithium indicates that introduction of a single water molecule as a ligand for lithium lowers the activation energy, leading to a 10-I-2 complex transition state for the process, see: Jedlicka, B.; Crabtree, R. H.; Siegbahn, P. E. M. *Organometallics* **1997**, *16*, 6021.

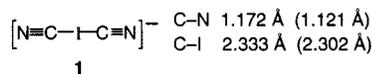
(19) (a) Cioslowski, J.; Piskorz, P.; Schimeczek, M.; Boche, G. *J. Am. Chem. Soc.* **1998**, *120*, 2612. (b) Boche, G.; Schimeczek, M.; Cioslowski, J.; Piskorz, P. *Eur. J. Org. Chem.* **1998**, 1851, 1.

polarized 6-31++G** basis set²² with added diffuse functions was used for all elements except iodine. A standard all-electron TZ quality basis set,²³ augmented by two D polarization (0.30 and 0.08 exponents) and one SP diffuse (0.025 exponent) functions, was employed for iodine. Equilibrium geometries and transition state (TS) structures were fully optimized, and vibrational frequencies were calculated for all species to characterize them as minima, TSs, or higher order saddle points on the potential energy surface and for evaluating their zero-point vibrational energies (ZPE). Enthalpies of the various compounds at 0 K (here represented as ΔH°) were then calculated as the sum of total energy and the ZPE. The calculated absolute energies and zero point energies are given in the Supporting Information.

Results and Discussion

At the inception of our investigation of factors that affect the stability of 10-X-2 ate-complexes having a central halogen bonded to carbon, it seemed prudent to first demonstrate that the computational methods employed serve to accurately describe those few ate-complexes (i.e., **1** and **3**) whose structures have been reported.

The structure of the linear ICN–KCN adduct (**1**) reported by Tebbe and Frölich¹³ was well reproduced if the counterion was ignored; the calculated bond lengths are shown below along with the experimental values¹³ in parentheses. Inclusion of a Li or K cation in the calculation led to imaginary frequencies characteristic of a transition state. Indeed, as noted by Tebbe and Frölich,¹³ the stability of **1** is undoubtedly related to the fact that the counterion is well removed from the ate-complex anion by strong coordination to the diethyl (diimino)oxalate ligand. This aspect of ate-complex stability will be addressed below.



Diaryl 10-X-2 Ate-Complexes. The lithium bis(pentafluorophenyl)iodinanide complex (**3**) and the analogous, albeit unknown, brominanide were investigated in more detail. At the outset it is perhaps good to note explicitly that, although many organolithium compounds are known to exist as aggregates,¹ it is not practical to model the reactions of interest in terms of higher aggregates and all computations involved monomeric species. In this connection, it is appropriate to recall that the monomer is often the reactive form of the organolithium.¹

Reaction of (pentafluorophenyl)lithium with pentafluoriodobenzene, which was used by Farnham and Calabrese to prepare **3**, is calculated to be exothermic by 3.8 kcal/mol, and the product (**3a**) is predicted to be a

(20) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 95, Development Version (Rev. D)*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(22) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

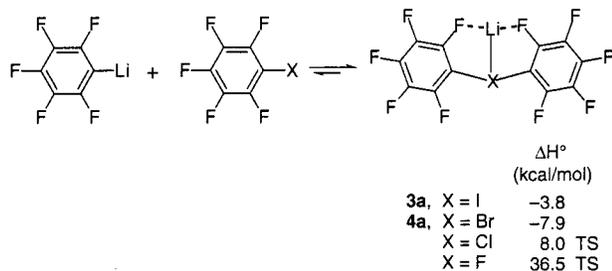
(23) Poirier, R.; Kari, R.; Csiszmadia, I. G. *Handbook of Gaussian Basis Sets*; Elsevier: Amsterdam, 1985.

Table 1. Comparison of Representative Bond Lengths and Bond Angles Computed for Lithium Bis(pentafluorophenyl)iodinanide (3a**) and Bis(pentafluorophenyl)iodinanide Anion (**3b**) with Experimental Data for $(C_6F_5)_2I^- Li^+ \cdot 2TMEDA$ (**3**)^a**

entry	bond length (Å) or angle (deg)	structure		
		3a (C_{2v})	3b (D_{2d})	$(C_6F_5)_2I^- Li^+ \cdot 2TMEDA$ (3)
1	C(1)–I	2.384	2.405	2.403, 2.331 ^b
2	C(1)–C(2)	1.376	1.386	1.375
3	C(2)–C(3)	1.389	1.395	1.371
4	C(3)–C(4)	1.395	1.392	1.368
5	C(2)–F	1.417	1.362	1.365
6	C(3)–F	1.344	1.355	1.348
7	Li–I	2.596		5.839 ^c
8	C(1)–I–C(7)	164.5	180	175.2
9	C(1)–I–Li	82.4		90.7
10	I–C(1)–C(2)	117.2	122.1	123.5
11	aryl–aryl ^d	0	90	69.6

^aData are taken from ref 15. ^bAs a result of the asymmetric environment in the crystal, there are two reported C–I bond lengths. ^cThis nonbonded Li–I distance is included for comparison. ^dDihedral angle between the planes defined by the two C_6F_5 aryl groups.

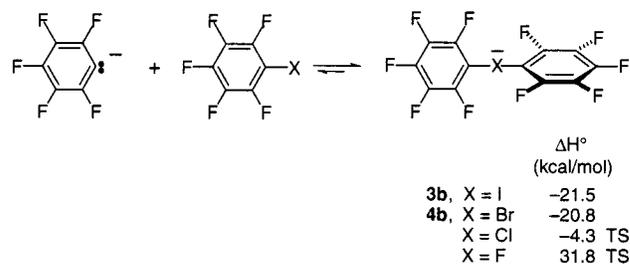
stable intermediate. As illustrated below, **3a** is computed to be a planar but nonlinear C_{2v} species with long C–I bonds (2.384 Å; by way of comparison, the corresponding bond length in C_6F_5I is calculated to be 2.100 Å). The planar, nonlinear structure of **3a** is a consequence of significant bonding interactions between the formally cationic lithium, at 2.596 Å from the central iodine, with the two ortho fluorine atoms 1.901 Å away; additional representative structural parameters computed for **3a** are summarized in Table 1. The corresponding lithium brominanide, **4a**, was also investigated, and the results were analogous. The reaction shown below ($X = Br$) is calculated to be exothermic by 7.9 kcal/mol for the bromine analogue, and the gross structural features²⁴ are similar to those found for **3a**. The fact that the brominanide (**4a**) is predicted to be more stable, relative to the reactants, than the iodinanide (**3a**) is likely a consequence of the stronger and shorter (2.390 Å) Li–Br bond in the bromine-containing ate-complex. Formation of the lithium 10-X-2 complexes having a central chlorine or fluorine are computed to be endothermic, and both species are transition states characterized by an imaginary frequency corresponding to the exchange.



Although it is encouraging that the B3LYP calculation predicts formation of a stable ate-complex when C_6F_5I is treated with C_6F_5Li , the computed structure is not in accord with that reported¹⁵ for the TMEDA adduct of lithium bis(pentafluorophenyl)iodinanide (**3**). A cursory comparison of the computed structure of **3a** with that of

3 (Table 1) reveals the origin of the discrepancy. In contrast to the computed structure of **3a**, the coordinated lithium atom in the TMEDA adduct (**3**) is well removed from the central iodine (the nonbonded distance is 5.839 Å),¹⁵ and there is no interaction between the cation and the fluorine atoms. In this connection, it should be noted that coordination of the lithium ion in **3** with TMEDA is most likely responsible for the observed stability of the complex at room temperature. In fact, Farnham and Calabrese report that a lithium bis(pentafluorophenyl)iodinanide may be isolated at $-78^\circ C$ in the absence of TMEDA, but the molecule decomposes violently at higher temperatures.¹⁵ It is tempting to speculate that the lithium iodinanide initially formed upon reaction of C_6F_5I with C_6F_5Li in ether–petroleum ether (1:1 by vol) has the structure of **3a**.

It is not practical at the present state of the art to attempt a calculation that includes two molecules of TMEDA as ligands for lithium. On the reasonable assumption, supported by the single-crystal X-ray analysis of **3**, that TMEDA serves to effectively remove the lithium cation from interaction with the anionic portion of the ate-complex, structures were simply modeled as anions. As illustrated below, the reaction of a pentafluorophenyl anion with C_6F_5I to give the bis(pentafluorophenyl)iodinanide anion (**3b**) is predicted to be exothermic by 21.5 kcal/mol. The corresponding reaction involving C_6F_5Br to give **4b** is also favorable, but as expected, it is less exothermic by ca. 1 kcal/mol. These results suggest that **4b** should also be an experimentally accessible species. The corresponding ate-anions having a central chlorine or fluorine are computed to be transition states.²⁴ Although formation of the chlorinanide anion is predicted, as shown below, to be mildly exothermic, intrinsic reaction coordinate (IRC) analysis revealed that the chlorinanide is a transition state characterized by an imaginary frequency (172i cm^{-1}) related to formation of a weakly bound association of chlorobenzene and the phenyl anion lying some 3.6 kcal/mol below the transition state. The fluorinanide anion is considerably less stable than the reactants and possesses a single imaginary frequency (465i cm^{-1}) characteristic of a transition state for the exchange.

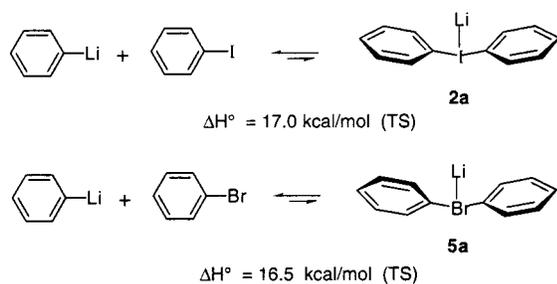


The lowest energy structures computed for both **3b** and **4b** have D_{2d} symmetry. Apparently, the anions adopt a conformation in which the aryl rings are perpendicular so as to avoid peri-like interaction between the ortho fluorine atoms. A comparison of the structural parameters calculated for **3b** with those reported for **3** (Table 1) leaves little doubt that the anion (**3b**) is an excellent model for the TMEDA adduct of lithium bis(pentafluorophenyl)iodinanide (**3**). The bond lengths and bond angles predicted for **3b** are virtually identical to those reported for **3**. The only significant differences between the structure calculated for **3b** and the actual adduct are

(24) Detailed structural data may be found in the Supporting Information.

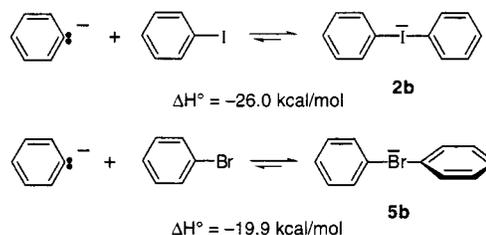
the C–I–C angle (180° in **3b** versus 175.2° in **3**) and the dihedral angle between the planes defined by the aryl groups (90° in **3b** versus 69.6° in **3**). Given the unsymmetrical environment of the ate-anion in the solid state of **3**,¹⁵ the agreement between the experimental structure and that predicted for the isolated anion (**3b**) is remarkable. These results serve to validate the computational approach to understanding factors affecting stability of 10-X-2 ate-complexes.

Diphenyl 10-X-2 ate-complexes (**2**), which have been detected as intermediates in the degenerate exchange reaction between PhLi and PhI,¹⁴ were next investigated. As shown below, both lithium diphenyliodinanide (**2a**) and the corresponding brominanide (**5a**) are calculated to be transition states; each displays one imaginary frequency ($193i\text{ cm}^{-1}$ for X = I and $223i\text{ cm}^{-1}$ for X = Br) corresponding to the exchange reaction. Thus, as might be anticipated, both **2a** and **5a** are considerably less stable, relative to the reactants, than **3a** and **4a**. As illustrated below, the lowest energy structure for **2a** displays C_s symmetry, whereas the brominanide structure (**5a**) has C_2 symmetry (the phenyl–phenyl dihedral angle is 84°); both structures are computed to have a C–X–C angle of $160\text{--}161^\circ$. These transition states have the expected long C–X bonds (2.385 \AA in **2a**, 2.236 \AA in **5a**) and Li–X bond lengths of 2.507 \AA (**2a**) and 2.270 \AA (**5a**). The considerably less stable chlorinanide ($\Delta H^P = 29.8\text{ kcal/mol}$) and fluorinanide ($\Delta H^P = 49.7\text{ kcal/mol}$) complexes, as well as the corresponding ate-anions (vide infra), were also investigated, but for the sake of continuity, discussion of the computed structural data for these species is deferred to the Supporting Information.²⁴

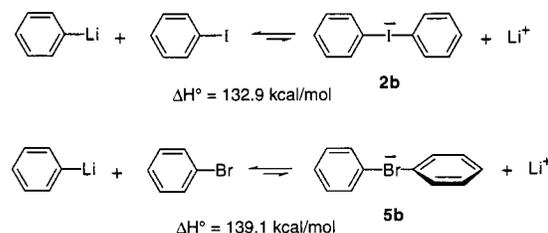
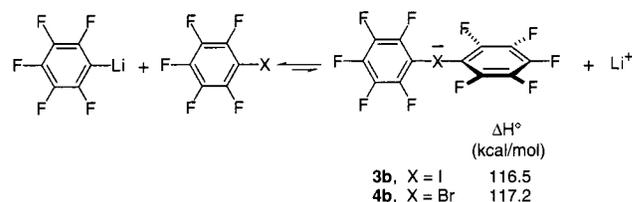


Coordination of the formally cationic lithium in **2a** and **5a** would be expected to stabilize the ate-complex and alter its geometry. In light of the success of modeling **3** as an anion, the reaction of a phenyl anion with iodo- and bromobenzene to give the ate-anions **2b** and **5b** was investigated. As illustrated below, generation of the ate-anions in this way is predicted to be exothermic. The iodinanide anion is more stable than the brominanide, relative to the reactants, by some 6 kcal/mol, but both **2b** and **5b** display no imaginary frequencies and are intermediates. The more stable conformer of the iodinanide anion (**2b**) has D_{2h} symmetry, as shown, but the D_{2d} isomer, in which the phenyl rings are perpendicular, is calculated to lie only 0.2 kcal/mol higher in energy. Presumably, there is little conformational preference as a result of the long (2.407 \AA) C–I bonds in **2b**. The brominanide anion **5b** by contrast is found to preferentially adopt the D_{2d} conformation (the D_{2h} isomer is less stable by 0.6 kcal/mol). Apparently the shorter C–X bonds in this species (2.233 \AA) engender repulsive periklike interaction between the ortho hydrogens when the phenyl rings are parallel in the rotamer having D_{2h}

symmetry. It is significant that lithium diphenyliodinanide (**2**) has been detected spectroscopically only in solutions containing lithiophilic ligands that coordinate the lithium cation and presumably remove it from the vicinity of the ate-anion;¹⁴ the computational results suggest that such solvation plays an important role in stabilizing 10-X-2 species.

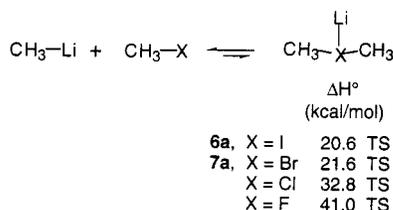


The ability of fluorine substituents to stabilize diaryliodinanide ate-complex anions is apparent from the fact that the perfluoro iodinanide adduct, **3**, exists at room temperature as a stable crystalline species,¹⁵ whereas the lithium-solvated parent diphenyliodinanide, **2**, has only been observed at low temperature in solution.¹⁴ While this seems intuitively reasonable, given the inductive effect of fluorine, it would be useful to have a quantitative gauge of the magnitude of such stabilization. Clearly, it is not sufficient to simply compare reactions involving generation of the ate-complexes from an anion precursor to make an assessment of the effect of fluorine substitution on the stability of such complexes; such a comparison (viz., formation of **3b** from a pentafluorophenyl anion and C_6F_5I versus formation of **2b** from a phenyl anion and C_6H_5I) will necessarily include as an artifact stabilization of the anion precursor by the fluorines. The problem was approached computationally by calculating the enthalpy change for each of the hypothetical reactions, shown below, involving generation of the ate-anion and an unsolvated lithium cation from an aryllithium and an halobenzene. All four reactions are endothermic as a consequence of the relatively high energy content of a naked Li^+ cation in the gas phase. Nevertheless, a comparison of the reaction energetics is instructive. Relative to the neutral reactants, the bis(pentafluorophenyl)iodinanide ate-anion (**3b**) is approximately 16.5 kcal/mol more stable than is the parent **2b**. The results suggest that fluorine substitution has an even larger effect on the stability of the brominanide; **4b** is predicted to be more stable than **5b** by some 22 kcal/mol . Thus,



the stabilization afforded by fluorine substitution is considerable.

Dialkyl 10-X-2 Ate-Complexes. Aliphatic 10-X-2 ate-complexes, which are often invoked as transition states for the lithium–halogen exchange between an alkyl-lithium and an alkyl iodide or bromide,^{1,4,5} were investigated by exploring the reaction of methyllithium (MeLi) with each of the methyl halides. As illustrated below, the resulting 10-X-2 species are calculated to be transition states. Calculations revealed that each structure possessed a single imaginary frequency (i.e., 186i, 256i, 315i, and 410i cm⁻¹ for X = I, Br, Cl, and F, respectively) corresponding to the exchange reaction. It might be noted that the calculated activation energies, summarized below, are in very good agreement with those reported by Boche and Cioslowski from an MP2/6-31+G* treatment of these systems.²⁵ Not surprisingly, lithium dimethyliodinane (**6a**) and the corresponding brominane (**7a**) lie considerably lower in energy, relative to the reactants, than do the chlorinane or fluorinane. These transition states, all of which are computed to have C_{2v} symmetry with C–X–C angles of 169° to 175°, have C–X bonds that are significantly longer (2.456, 2.349, 2.287, and 2.116 Å for X = I, Br, Cl, and F, respectively) than those of the methyl halides.²⁶ However, the Li–X bond lengths in these lithium ate-complexes (2.475, 2.213, 2.061, and 1.618 Å for X = I, Br, Cl, and F, respectively) are quite similar to those computed at this level of theory for the lithium halides,²⁶ suggesting a strong interaction between the formally anionic ate-anion and the associated lithium cation. This conclusion mirrors that drawn by Boche and Cioslowski from their MP2/6-31+G* analysis of these systems.^{19b}



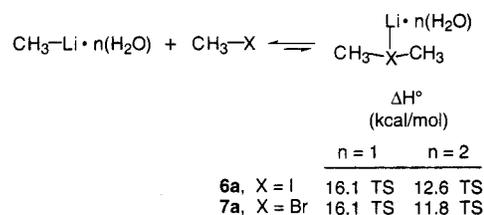
It might be anticipated that solvation of the lithium cation would lead to lengthening of the Li–X contact and stabilization of the ate-complex. Indeed, the lithium–halogen exchange reaction is typically conducted in an ethereal medium capable of solvating the lithium cation in an ate-complex transition state.^{1,18} Of course, such solvents may also serve to stabilize the MeLi reactant via coordination with its Lewis acidic lithium site, and this would tend to raise the activation energy leading to the ate-complex transition state. In an effort to probe the effect of solvation on the activation energies for lithium–iodine and lithium–bromine exchange, solvent was modeled computationally by using water as a surrogate for a generic Lewis base.

To this end, the reactions of methyl iodide and methyl bromide with water-solvated MeLi to give solvated ate-complexes, **6a** and **7a**, were investigated. As depicted

Table 2. Effect of Solvation on the Li–X Distance in (CH₃)₂X⁻ Li⁺·nH₂O

entry	no. H ₂ O molecules	Li–X distance (Å)	
		6a , X = I	7a , X = Br
1	0	2.475	2.213
2	1	2.501	2.230
3	2	2.644	2.421
4	3	3.953	3.640
5	4	4.108	3.717

below, introduction of a single water molecule lowers the activation energy leading to the transition states for both the iodide (**6a**) and the bromide (**7a**) exchange by approximately 5 kcal/mol, in good agreement with a recent calculation of the effect of water solvation on the barrier height for a related exchange reaction.¹⁸ A second water molecule reduces the activation energy leading to **6a** or **7a** by a further 4 kcal/mol. Thus, solvent stabilization of the transition state for the exchange more than compensates for the effect of solvation on the ground-state energy of the MeLi reactant. Although it would be useful to have an estimate of the effect of three and four water molecules on the energetics of the exchange reactions, these calculations posed an intractable problem: solvation of the MeLi reactant with more than two water molecules leads computationally to the formation of methane and LiOH regardless of any symmetry constraints imposed on the system. It was, however, possible to explore the effect of additional water molecules on the structure of the ate-complex transition states, and these results provide additional insight into the etiology of ate-complex stabilization by solvent.



Solvation of the lithium cation in **6a** and **7a** by water has only a minor effect on the CH₃–X–CH₃ portion of the ate-complex. The formally anionic moiety retains the C_{2v} symmetry of the unsolvated ate-complex, and the C–X bond lengths are little changed.²⁴ The major effect of solvation is to remove the lithium cation from the vicinity of the central halogen of the complex. Indeed, the effect of increased solvation of lithium on the Li–X distance in **6a** and **7a** may be quite dramatic, as evidenced by the computed structural data summarized in Table 2. Whereas inclusion of one or two water molecules results in a slight lengthening of the Li–X distance in both complexes (Table 2, entries 1–3), the addition of a third or fourth water ligand leads to a dramatic increase in the Li–X separation to a distance well in excess of a typical bonding interaction (Table 2, entries 4–5). Moreover, the tri- and tetrasolvated complexes of **6a** and **7a** approach the status of true intermediates as these species are characterized by very small imaginary frequencies (~35i cm⁻¹). The implication of these results seems clear: strong solvation of the lithium cation in a 10-X-2 ate-complex confers considerable stability. In the extreme, such solvation results in formation of an ate-anion and a ligated lithium cation.

Dimethyl 10-X-2 ate-anions were generated computationally by reaction of a methyl anion with each of the

(25) The MP2/6-31+G* activation energies for reaction of CH₃Li with CH₃X to give a 10-X-2 ate-complex transition state of C_{2v} symmetry are reported by Boche, Cioslowski, and co-workers (ref 19b) to be 22.6, 28.2, and 33.4 kcal/mol for X = I, Br, and Cl, respectively.

(26) The calculated C–X bond lengths for the methyl halides are 2.178 Å for CH₃I, 1.970 Å for CH₃Br, 1.805 Å for CH₃Cl, and 1.399 Å for CH₃F. The calculated bond lengths for the lithium halides are 2.435 Å for LiI, 2.195 Å for LiBr, 2.055 Å for LiCl, and 1.584 Å for LiF.

Table 3. Calculated Energies (kcal/mol) for Reaction of a Methyl Anion with the Methyl Halides

$$\text{CH}_3^- + \text{CH}_3\text{-X} \rightleftharpoons \text{CH}_3\text{-X}^-\text{-CH}_3$$

entry	X	basis set		
		B3LYP/ 6-31++G* ^a	MP2/ 6-31+G* ^b	MP2/ 6-311++G(2d,2p) ^c
1	I (6b)	-30.2	-27.8	
2	Br (7b)	-19.8	-14.1	
3	Cl	-6.9	-1.3	-6.6
4	F	28.3 TS	24.7 TS	26.3 TS

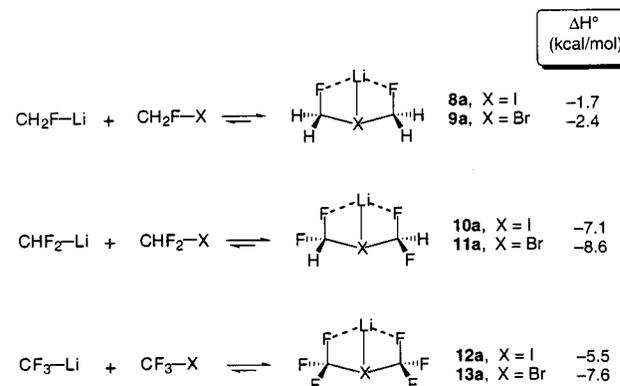
^a This work. ^b Reference 19b. ^c Reference 19a.

methyl halides: $\text{CH}_3^- + \text{CH}_3\text{-X} \rightleftharpoons (\text{CH}_3)_2\text{X}^-$. The calculated energies (ΔH°) are summarized in Table 3. Also included in Table 3 are the MP2 energies calculated by Boche and Cioslowski for these reactions.¹⁹ It is significant that the hybrid density functional calculations give relative energies that are in very good agreement with the available larger basis set MP2/6-311++G(2d,2p) results^{19a} (Table 3, entries 3 and 4) and in satisfactory agreement with the MP2/6-31+G* calculations^{19b} (Table 3, entries 1–4). Moreover, the B3LYP structural parameters²⁴ are essentially identical to those reported by Boche and Cioslowski.¹⁹

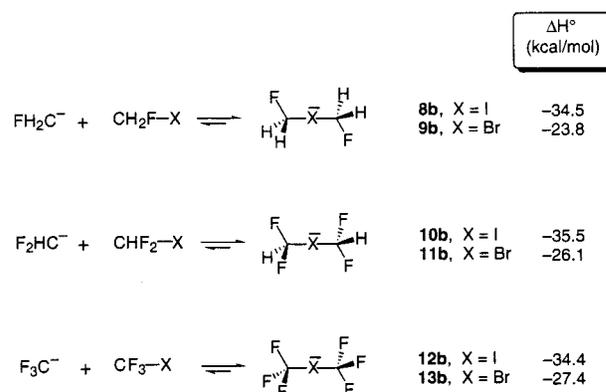
Formation of the iodinanide anion (**6b**), the brominanide anion (**7b**), and the chlorinanide anion are predicted to be exothermic, and all three species are computed to be intermediates having no imaginary frequencies. The corresponding fluorine-containing ate-anion is clearly a transition state as it has a large imaginary frequency ($326i \text{ cm}^{-1}$) corresponding to cleavage of the C–F bond. Not surprisingly, given the long C–X bonds in the ate-anions, both the D_{3h} and the D_{3d} conformations of each anion were found to have essentially the same energy.²⁴ As expected, the order of stability of the dimethyl ate-anions increases as one proceeds from F to I. In this connection, it is worth noting that although the iodinanide ate-anion (**6b**) is calculated to be some 10 kcal/mol more stable than the corresponding brominanide anion (**7b**), the lithium dimethyl-iodinanide transition state (**6a**) is found by computation to be only 1 kcal/mol more stable than the analogous lithium dimethylbrominanide transition state (**7a**). The difference in relative stabilities is clearly a consequence of the effect of differing Li–X bond strengths in the lithium-containing ate-complexes. Insofar as solvation removes the lithium cation from close proximity to the central halogen of the ate-complex, the relative stabilities of the ate-anions, rather than the neutral complexes, is likely a better reflection of the actual situation to be found in solution.

In view of the ability of fluorine substituents to stabilize diaryl 10-X-2 ate-complexes, it seemed worthwhile to assess the effect of fluorine substitution on the stability of aliphatic iodinanide and brominanide complexes. Thus, the reactions of $\text{CF}_n\text{H}_{3-n}\text{Li}$ with the corresponding fluoromethyl iodides and bromides were investigated. The results, summarized below, show the computed lowest-energy structures of the resulting lithium ate-complexes (**8a**–**13a**).²⁴ In each instance, generation of the fluorine-containing ate-complex is calculated to be an exothermic process, and all species were found to be minima on the potential energy surface. As indicated in the structures depicted below, there is a significant bonding interaction between the formally cationic lithium

and the two coplanar fluorine substituents located approximately 2 Å from the lithium in each of the complexes. As a result of this Li–F interaction, the calculated C–X–C bond angles in **8a**–**13a** (viz., $\sim 145^\circ$ in the iodinanides and $\sim 150^\circ$ in the brominanides) are substantially smaller than those of lithium dimethyl-iodinanide (**6a**) and lithium dimethylbrominanide (**6b**).

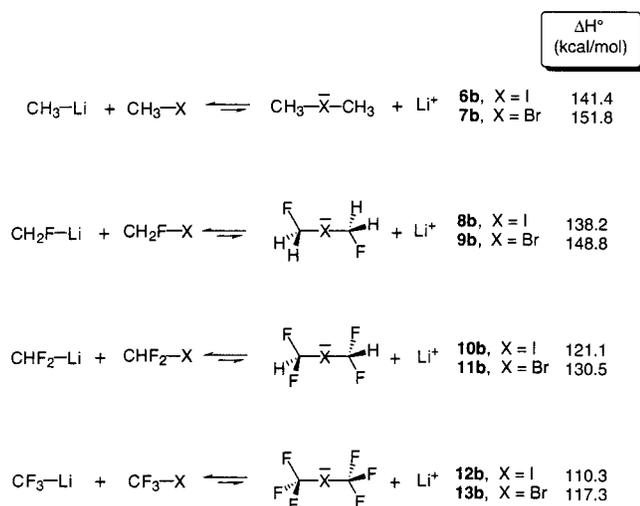


It is of some interest to note that the fluorine-containing 10-X-2 brominanide complexes (**9a**, **11a**, and **13a**) are computed to be more stable, relative to the reactants, than the corresponding iodinanides (**8a**, **10a**, and **12a**). To the extent that the Li–Br bond in the brominanides is shorter and presumably stronger than the Li–I bond in the iodinanides, the relative stabilities of the complexes reflect these differing bond strengths. Of course, the effect of Li–X bond strength is of no consequence provided that the formally cationic lithium is strongly solvated. This situation was modeled in the usual way by computing the energy changes attending generation of the ate-anions (**8b**–**13b**) by reaction of each of the $\text{CF}_n\text{H}_{3-n}$ anions with the appropriate fluoromethyl halide. The results, summarized below, indicate that, although formation of both the iodinanide and brominanide ate-anions is highly exothermic, the iodinanides (**8b**, **10b**, and **12b**) are considerably more stable (by some 7–11 kcal/mol relative to the reactants) than are the corresponding brominanides (**9b**, **11b**, and **13b**). All of the linear anions depicted below are predicted to be intermediates as none has an imaginary frequency, and the most stable conformation of each is found, as illustrated, to have a preferentially anti arrangement of C–F bonds.²⁴ Although a staggered arrangement of bonds is portrayed, the eclipsed conformations have essentially the same energy.



To assess the extent to which fluorine substitution stabilizes dimethyl 10-X-2 ate-anions, it is necessary to

take into account the effect of fluorine substitution on the stability of the reactants. Following the approach discussed above in connection with fluorine stabilization of diaryl 10-X-2 ate-ions, the enthalpy change accompanying reaction of methyllithium and each $\text{CF}_n\text{H}_{3-n}\text{Li}$ with the appropriate methyl or fluoromethyl iodide and bromide to give the corresponding ate-anion and a lithium cation was evaluated. Because of the high energy of the unsolvated Li^+ , all of these hypothetical reactions are calculated to be endothermic. Be that as it may, comparison of the computed ΔH° values reveals some unexpected trends.



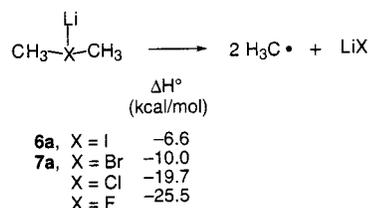
The effect of a single fluorine substituent attached to each carbon of the dimethyliodinane (**6b**) or brominane (**7b**) anion is small; **8b** and **9b** are computed to be only some 3 kcal/mol more stable than are the parent ions. A second fluorine substituent has a much more pronounced effect; both iodinane ion **10b** and brominane ion **11b** are predicted to be more stable than the parent anions (**6b** and **7b**) by ~ 20 kcal/mol. The fully fluorinated ate anions, **12b** and **13b**, are computed to be significantly more stable, by > 30 kcal/mol relative to the neutral reactants, than the corresponding $(\text{CH}_3)_2\text{X}^-$ species. Clearly, as was the case for diaryl 10-X-2 ate-anions, the ability of multiple fluorine substituents to stabilize aliphatic ate-complexes is substantial.

The computational results discussed above suggest that fully fluorinated aliphatic 10-I-2 (and perhaps 10-Br-2) ate-complexes might, under appropriate circumstances, be experimentally observable intermediates. Indeed, such species may well have been observed but not recognized as such in a prescient 1969 study by Johncock describing the reaction of perfluoro-*n*-heptyl iodide with *n*-butyllithium (BuLi).²⁷ Johncock reported that the lithium-iodine exchange between equimolar quantities of *n*- $\text{C}_7\text{F}_{15}\text{I}$ and *n*-BuLi in diethyl ether solution at -95°C proceeds only to 50% completion to give a "stable heterogeneous system" that "reacts only slowly with acetaldehyde below -90°C ".²⁷ Although Johncock did not propose a structure for the precipitate detected in his experiments, he attributed its formation to the association of *n*- $\text{C}_7\text{F}_{15}\text{Li}$ with an equivalent quantity of *n*- $\text{C}_7\text{F}_{15}\text{I}$.²⁷ It seems quite reasonable in retrospect to formulate the species observed by Johncock as an ether-

solvated 10-I-2 ate-complex, $(n\text{-C}_7\text{F}_{15})_2\text{I}^- \text{Li}^+$, as initially suggested by Farnham and Calabrese.¹⁵

Homolytic Cleavage of Ate-Complexes. As noted in the Introduction, it has recently been suggested¹¹ that homolytic cleavage of a C-X bond within an ate-complex might account for reports implicating radical intermediates in reactions of organolithiums with organohalides.⁷ This proposal, if confirmed, would obviate the need to postulate SET as the initiating event for subsequent radical-mediated chemistry often observed in reactions of organolithiums and organic halides.^{1,7,11} In view of the data available from the studies discussed above, it seemed worthwhile to investigate whether there are circumstances under which homolysis of a C-X bond in a 10-X-2 complex would be an energetically favorable process. It was clear from the outset that there is a major difficulty in approaching this question: the systems most likely to display homolytic chemistry are those least likely to provide stable ate-complexes, and these latter species are, as noted above, computed to be transition states for the exchange reaction. In short, while it is possible to computationally investigate the energetics of homolytic cleavage within an ate-complex transition state, the results of such a study are relevant only if one makes the assumption that strong solvation of the lithium cation in such an ate-complex might stabilize the species to such an extent that it becomes an intermediate in the exchange process. Be that as it may, the results of this analysis suggest that homolytic cleavage within a dialkyl ate-complex may be an energetically accessible pathway.

As shown below, homolysis of a lithium dimethyl 10-X-2 ate-complex to give two methyl radicals and LiX is computed to be exothermic for all halogens. The formation of LiX provides the driving force for these hypothetical reactions, and not surprisingly, homolysis of the least stable complex (X = F) is predicted to be the most exothermic process. A limited study of the effect of solvation by a single water molecule on the energetics of the homolytic cleavage of the iodinane (**6a**) and the brominane (**7a**), to give two methyl radicals and a water-solvated LiX , revealed that such solvation reduces the exothermicity of each reaction by only $\sim 1-2$ kcal/mol. The extent to which these limited results might apply to other dialkyl 10-X-2 ate-complexes remains to be seen. In this connection, it might be noted that homolytic cleavage of dialkyl 10-X-2 complexes having a secondary or tertiary carbon bonded to the central halogen would be expected to be energetically more favorable than the dimethyl examples illustrated below because such homolyses would generate more stable secondary or tertiary radicals.



Homolytic cleavage within the fluorinated lithium 10-X-2 ate-complexes (**8a-13a**) was also investigated, and homolysis of the C-X bonds in each of these intermediates is computed to be a highly unfavorable process. Indeed, cleavage of the fully fluorinated complexes, **12a**

(27) Johncock, P. *J. Organomet. Chem.* **1969**, *19*, 257.

and **13a**, to give LiX and two CF₃ radicals is energetically uphill by more than 30 kcal/mol.

Conclusions

The results presented above demonstrate that modern computational methods are capable of providing detailed information about the structures and energetics of fairly complex systems. B3LYP hybrid density functional calculations, which reproduce the observed structure¹⁵ of (C₆F₅)₂I⁻ Li⁺·2TMEDA (**3**) to a high degree of accuracy (Table 1), suggest that solvation of the formally cationic lithium plays an important role in stabilizing lithium 10-X-2 ate-complexes. The major effect of solvation, modeled computationally by using water as a surrogate for a lithiophilic solvent, appears to be sequestration of the lithium cation, which effectively removes the lithium from the vicinity of the ate-anion (Table 2) with little change in the geometry of the core structure. As a result, substituent effects on the stability of solvated 10-X-2 ate-complexes may be modeled by considering the result of substitution on the computed energies of the ate-anions.

The effect of fluorine substitution on the stability of both diaryl and dialkyl 10-X-2 ate-complexes is considerable. Thus, the bis(pentafluorophenyl)iodinanide ate-anion (**3b**) was found to be some 16.5 kcal/mol more stable than the parent diphenyliodinanide anion (**2b**),

whereas the corresponding bis(pentafluorophenyl)brominanide (**4b**) is stabilized by more than 20 kcal/mol relative to the parent (**5b**). The ability of fluorine to stabilize dimethyliodinanide (**6b**) and dimethylbrominanide (**7b**) ate-anions was found to be most pronounced when multiple fluorine substituents were present. A single fluorine attached to each carbon in the C-X-C framework of **6a** or **7a** results in a stabilization of only 3 kcal/mol relative to the parent structures, whereas each of the fully fluorinated ate-anions, **12b** and **13b**, is computed to be more stable than the parent by >30 kcal/mol. These results suggest that perfluordialkyl 10-I-2 and 10-Br-2 ate-complexes may well be experimentally observable intermediates.²⁷

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Supporting Information Available: A summary of the calculations, including calculated absolute energies, zero point energies, as well as detailed structural data, are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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