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Computational Study of 10-X-2 Ate Complexes Derived from Vinyllithiums and Vinyl Halides

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The 10-X-2 ate complexes formed by reaction of vinyllithiums with the corresponding vinyl halides have been studied via B3LYP/6-31++G** geometry optimization. The effect of fluorine substitution on the structures and energies of the both the vinyllithiums and the ate complexes is examined. The results of the calculations indicate that trifluoroethene is 35 kcal/mol more acidic than ethene. The ate complexes generated by reaction of vinyllithium with vinyl bromide or iodide are calculated to be transition states, but the corresponding perfluorinated complexes are found to be minima on the potential energy surface.

The lithium−iodine and lithium−bromine exchange reactions are widely used in synthesis,[1] and 10-X-2 ate complexes $(R-X-R)^-Li^+$ have been implicated as intermediates in these processes.[2] We recently reported the results of a computational study of the structures and energies of a variety of 10-X-2 ate complexes derived from reaction of alkyllithiums or aryllithiums with the corresponding alkyl or aryl halides.[3] Diaryl 10-X-2 ate complexes were found to be more stable than their dialkyl counterparts, electron-withdrawing substituents were found to increase the stability of the both the aryl and alkyl complexes, and removal of the formally cationic lithium from the vicinity of the ate anion via coordination with a Lewis-basic solvent was found to be important in increasing stability.[3] Herein we report the results of a study of 10-X-2 ate complexes derived from vinyllithiums and the corresponding vinyl halides; as might be anticipated, such complexes have characteristics similar to those of the analogous diaryl species but, as disclosed below, there are significant differences.

Computational Methods

B3LYP hybrid density functional calculations[4] were carried out using the Gaussian 99 series of programs.[5] The standard polarized 6-31++G** basis set with added diffuse functions was used for all elements except iodine; for iodine, a standard all-electron TZ-quality basis set,[6] augmented by two D polarization functions (0.30 and 0.08 exponents) and one SP diffuse function (0.025 exponent) was employed. It should be noted that hybrid density functional calculations using this basis set have been shown to provide energies and structures for lithium diaryl 10-X-2 ate complexes that are in good accord with the available experimental data.[3] Equilibrium geometries and transition state (TS) structures were fully optimized, and vibrational frequencies were calculated for all species in order to characterize them as minima, TS, or higher order saddle points on the potential energy surface (PES) and for evaluating their zero-point vibrational energies (ZPE). Enthalpies of the various compounds at 0 K (represented as $\Delta H°$) were calculated as the sum of total energies and the ZPE. The calculated absolute energies and zero point energies are given in the Supporting Information (Table S-1).

Results and Discussion

Prior to an analysis of 10-X-2 ate complexes, it seems appropriate to first consider the structures of the vinyl anions and the vinyllithiums.[7] In this connection, it might be noted that an early computational study by

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(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) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 1, p 43. (d) Schölkopf, U. In *Methoden der Organischen Chemie*; Georg Thieme: Stuttgart, Germany, 1970; Vol. 13/1. (e) Jones, R. G.; Gilman, H. *Chem. Rev.* **1954**, *54*, 835. (f) Gilman, H.; Jones, R. G. *Org. React. (N.Y.)* **1951**, *6*, 339.

(2) (a) For a review of the literature dealing with the mechanism of the lithium-halogen exchange, see: Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, *352*, 1. (b) Farnham, W. B.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2449. (c) Reich, H. J.; Phillips, N. H.; Reich, I. L. *J. Am. Chem. Soc.* **1985**, *107*, 4101. (d) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444. (e) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414. (f) Reich, H. J.; Green, D. P.; Phillips, N. H.; Borst, J. P.; Reich, I. L. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 83.

(3) Wilberg, K. B.; Sklenak, S.; Bailey, W. F. *J. Org. Chem.* **2000**, *65*, 2014.

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

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortis, J. V.; Baboul, A. G.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.;. Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 99*, Development Version (Rev. B); Gaussian, Inc., Pittsburgh, PA, 1998.

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

(7) For a review of theoretical studies of organolithiums and vinyl anions, see: Sapse, A. M.; Schleyer, P. v. R. *Lithium Chemistry: a Theoretical and Experimental Overview*; Wiley: New York, 1995.

10.1021/om000820k CCC: $20.00

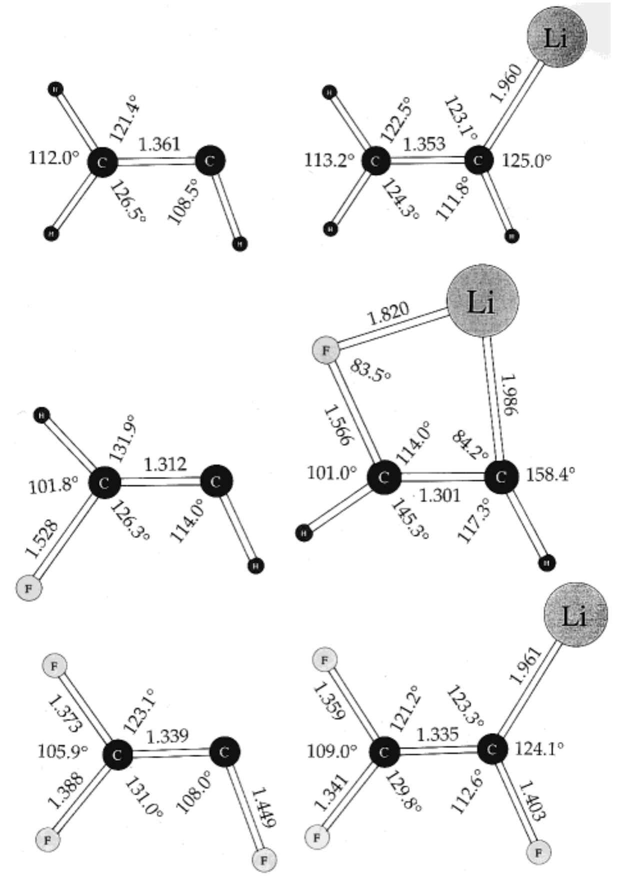

Figure 1. Optimized B3LYP/6-31++G** structures of vinyl anions and vinyllithiums.

Schleyer and Kos of the effect of fluorine substitution on the structure and energies of vinyl anions attributed the stabilization of vinyl anions by fluorine substitution to negative hyperconjugation.[8] The calculated lowest energy structures of these species are summarized in Figure 1.

Vinyl anion and the perfluorovinyl anion have similar structures; in accord with Bent's rule,[9] which suggests fluorine prefers to be bonded to a carbon orbital with high p character, the F−C−F angle in the latter is smaller than the H−C−H angle in the former. The (*Z*)-2-fluorovinyl anion has a relatively short C═C bond and a long C−F bond, suggesting, not unexpectedly, that it is on its way toward loss of fluoride ion to give acetylene. The (*E*)-2-fluorovinyl anion, which is not depicted in Figure 1, was found to lie some 2.3 kcal/mol higher in energy than its *Z* isomer.

A similar pattern is found for the corresponding vinyllithiums. As illustrated in Figure 1, both vinyllithium and (trifluorovinyl)lithium have comparable structures. However, (*Z*)-(2-fluorovinyl)lithium,[10] with a short C═C bond and lengthened C−F and C−Li bonds, displays a tendency to dissociate to give acetylene and LiF. In this connection, it is significant that perfluoro substitution appears to stabilize both $F_2C{=}CF^-$ and $F_2C{=}CFLi$ to such an extent that incipient loss of lithium fluoride is not apparent in the calculated structures of these species (Figure 1). Indeed, Seyferth,[11] Tarrant,[12] and others[13] have shown that (perfluorovinyl)lithiums may be prepared and used at low temperatures.[14]

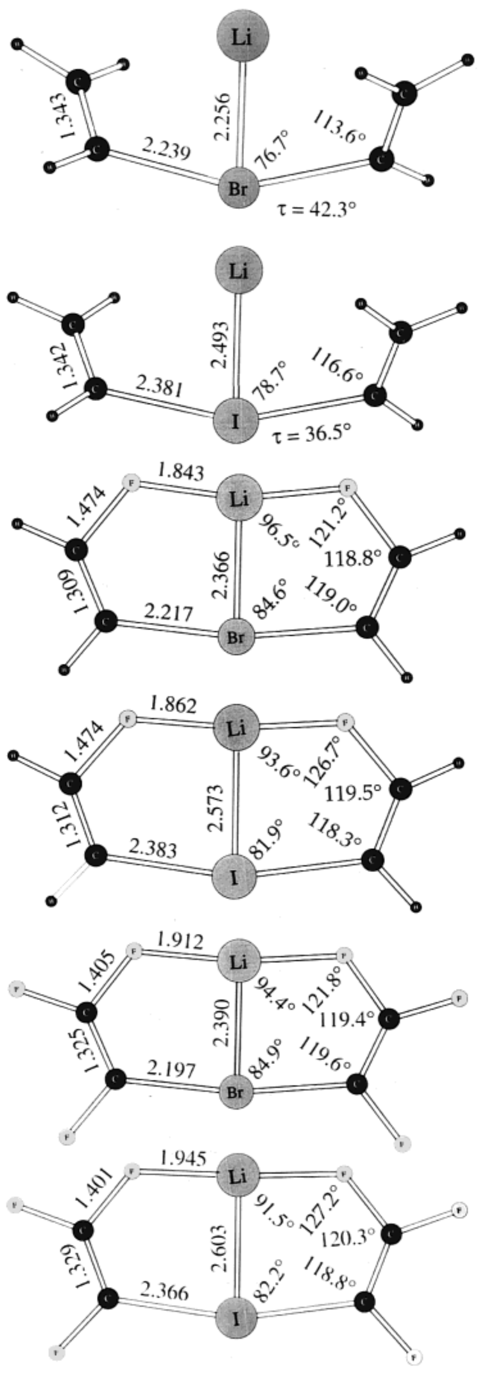

Figure 2. Optimized geometries for the lithium 10-X-2 ate complexes derived from reaction of vinyllithiums with vinyl iodides or bromides.

The stabilization of perfluorovinyl anion may be examined using the isodesmic reaction $F_2C{=}CF^- +$

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[8] Schleyer, P. V. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141.

[9] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

[10] It is perhaps worth noting explicitly that, despite sharing the same sterochemical descriptor, the (*Z*)-2-fluorovinyl anion and (*Z*)-(2-fluorovinyl)lithium do not have the same geometry (Figure 1). Thus, H(1) and H(2) are trans in the *Z* anion but they are cis in (*Z*)-(2-fluorovinyl)lithium.

[11] Seyferth, D.; Welch, D. E.; Raad, G. *J. Am. Chem. Soc.* **1962**, *84*, 4266.

[12] Tarrant, P.; Johncock, P.; Savory, J. *J. Org. Chem.* **1963**, *28*, 839.

[13] An account of the historical development of fluorovinyl organometallics has recently appeared. See: Brisdon, A. K.; Banger, K. K. *J. Fluorine Chem.* **1999**, *100*, 35.

[14] For a recent review of chemistry of (polyfluorovinyl)lithium compounds, see: Coe, P. L. *J. Fluorine Chem.* **1999**, *100*, 45.

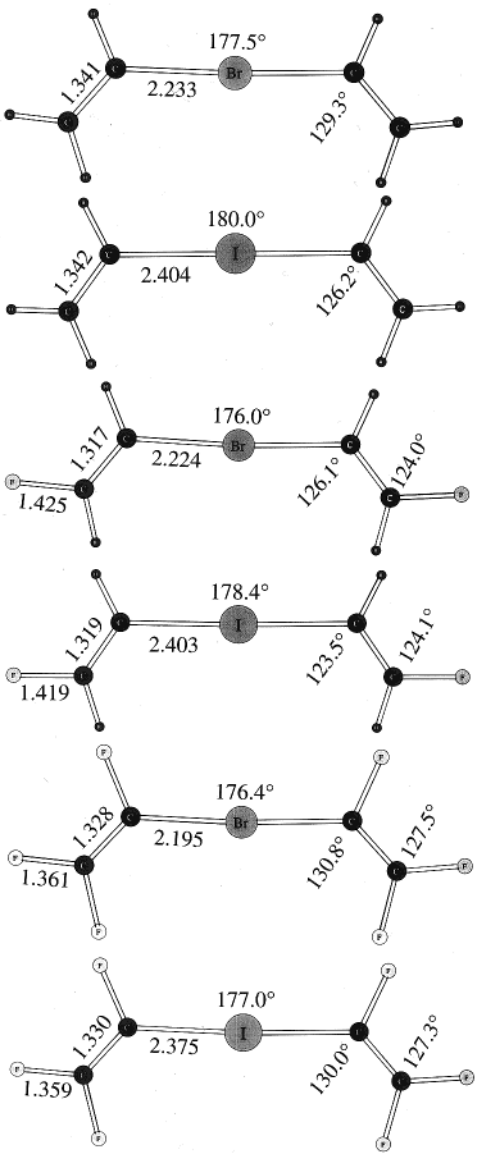


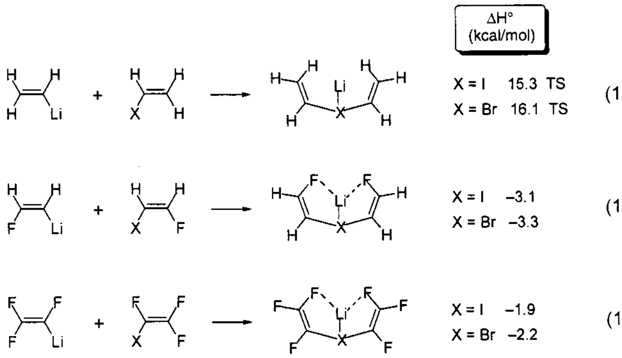
Figure 3. Optimized geometries for the 10-X-2 ate anions derived from reaction of vinyl anions with vinyl iodides or bromides.

$H_2C{=}CH_2 \rightarrow F_2C{=}CHF + H_2C{=}CH^-$. The reaction enthalpy for this process, which is calculated to be 34.6 kcal/mol, indicates that trifluoroethene is much more acidic than is ethene. An estimate of the acidity of trifluoroethene may be obtained from this calculated value and the experimentally measured ΔH_{acid} value of ethene (409.4 ± 0.6 kcal/mol).[15] The ΔH_{acid} value of trifluoroethene obtained in this way, 374 kcal/mol, is in reasonable accord with a value of 390 ± 9 kcal/mol obtained by an indirect method.[16] Thus, the acidity of trifluoroethene approaches that of acetic acid (i.e., ΔH_{acid} = 366 kcal/mol).[16]

Divinyl 10-X-2 Ate Complexes. Optimized geometries for the 10-X-2 ate complexes derived from reaction of vinyllithiums with vinyl iodides or bromides are shown in Figure 2. Cursory inspection of the structures reveals that the Br- and I-containing complexes have essentially the same structure, except for a slightly shorter bond from Li to Br in the brominanide. Both $(H_2C{=}CH{-}X{-}CH{=}CH_2)Li$ complexes (X = Br, I) possess C_2 symmetry, presumably to allow the vinyl hydrogens to move away from the lithium, and the species are substantially bent with C−X−C bond angles of 157.4 and 153.4° for X = I, Br, respectively. The $(F_2C{=}CF{-}X{-}CF{=}CF_2)Li$ and (*Z*)-$(FHC{=}CH{-}X{-}CH{=}CHF)Li$ ate complexes (X = Br, I) are calculated to have C_{2v} symmetry, and as illustrated in Figure 2, there are significant bonding interactions between the formally cationic lithium and the two proximal fluorine atoms of the vinyl groups. Just such stabilizing Li−F interactions were observed in the structures of $(C_6F_6{-}X{-}C_6F_6)Li$.[3] Indeed, the structures of the divinyl 10-X-2 ate complexes are quite similar to those calculated for the analogous diaryl complexes.[3]

The corresponding brominanide and iodinanide anions, $(H_2C{=}CH{-}X{-}CH{=}CH_2)^-$, $(F_2C{=}CF{-}X{-}CF{=}CF_2)^-$, and (*E*)-$(FHC{=}CH{-}X{-}CH{=}CHF)^-$, which are depicted in Figure 3, have C_{2v} symmetry, and the C−X−C moiety is almost linear. The C−X bond lengths in these anions are close to those of the corresponding ate complexes and, as expected,[9] the X−C−C angles are increased when substituted by fluorine. Not surprisingly, the fluorines prefer to be distant from the central halogen in (*E*)-$(FHC{=}CH{-}X{-}CH{=}CHF)^-$.

The energetics attending formation of the ate complexes was next examined. The simplest case, reaction of $H_2C{=}CHLi$ with $H_2C{=}CHX$ (X = I, Br) to give the corresponding lithium iodinanide and brominanide complexes, is illustrated in eq 1a. The influence of fluorine substitution on the energetics of divinyl ate complex formation was also explored in a similar fashion (eqs 1b,c).



Both the iodinanide and brominanide divinyl 10-X-2 ate complexes (eq 1a) are found to be transition states with one imaginary frequency (227*i* and 241*i* cm^{-1} for I and Br, respectively) corresponding to the exchange reaction, and both complexes are calculated to be less stable than the corresponding reactants. These results are similar to those previously reported for lithium diphenyliodinanide and lithium diphenylbrominanide: the $(Ph_2X)Li$ complexes are transition states lying 17.0 and 16.5 kcal/mol above the reactants for X = I, Br, respectively.[3]

In accord with our observations for dialkyl and diaryl ate complexes,[3] fluoro substitution significantly stabilizes divinyl 10-X-2 ate complexes. As indicated in eqs 1b,c, the fluoro-substituted divinyl 10-X-2 ate complexes

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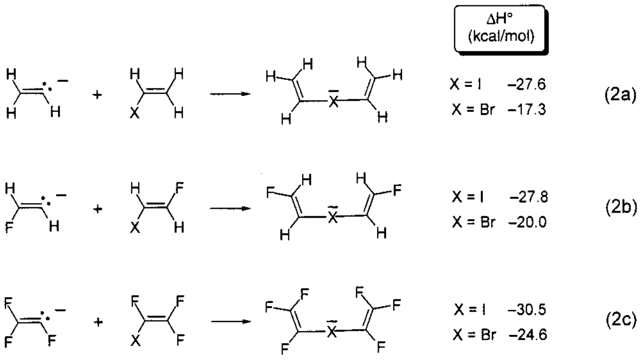
(15) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, K. K.; Harrison, A. G.; Bierbaum, V.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

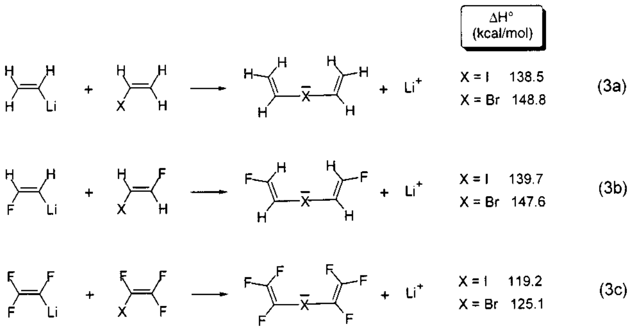
(16) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

are more stable than their reactants, and all are minima on the potential energy surface. Although the highest stabilization with respect to the corresponding reactants is reached for partly fluorinated bis(fluorovinyl) 10-X-2 ate complexes, this is of little practical significance since, as noted above, (*Z*)-(2-fluorovinyl)lithium is probably unstable in solution.[14] Moreover, while the fluorine-substituted brominanide complexes are calculated to be more stable, relative to the reactants, than are the corresponding iodinanide complexes (eqs 1b,c), this result is most likely influenced, as noted previously in connection with diaryl complexes,[3] by the shorter and stronger Li–Br bond in the brominanides.

Strong solvation of the formally cationic lithium will serve to remove it from the vicinity of the central halogen in an ate complex, and in the limit, this results in formation of an ate anion. Indeed, as we have noted elsewhere, removal of the lithium cation from the vicinity of the ate anion by coordination with a lithiophilic ligand contributes to the stability of such complexes.[3] Thus, for example, in the two 10-X-2 ate complexes which have been isolated and whose structures have been determined, the cation is well removed from the ate anion moiety by strong coordination to a Lewis-basic ligand.[17] This situation was explored computationally by examining formation of ate anions via reaction of vinyl anions with vinyl halides as illustrated in eqs 2a–c. Insofar as strong solvation will tend to remove the lithium from the immediate vicinity of the central halogen of the ate complexes (eqs 1a–c), the relative stabilities of the ate anions (eqs 2a–c) are likely a better measure of the situation found in solution.[3]



The calculations reveal that all iodinanide and brominanide 10-X-2 ate anions are more stable than their reactants and all anions are minima on the potential energy surface. However, the stabilization is clearly stronger for an iodinanide species than for a brominanide anion by some 6–10 kcal/mol. The perfluorovinyl 10-X-2 ate anions are the most stable species (eq 2c), relative to the anion and vinyl halide reactants, but the effect of multiple fluorine substitution appears modest for the iodinanide anions and amounts to ~7 kcal/mol for the brominanides (cf. eqs 2a,c). Clearly, these calculations include as an artifact the stabilization of the anion precursors by the fluorine substituents and, as noted above, such stabilization is substantial. A better measure of the effect of fluorine substitution on the stability of the ate anions is provided by calculation of the enthalpy change for the hypothetical reactions shown in eqs 3a–c involving generation of the ate anion and a naked lithium cation from a vinyllithium and a vinyl halide.



It should be noted that, although each of the reactions depicted in eqs 3a–c is highly endothermic as a consequence of the high energy content of an unsolvated Li^+, the quantity of interest is the enthalpy changes attending replacement of hydrogens in the parent ate anion (eq 3a) with fluorine substituents (eqs 3b,c). A single fluorine on each of the vinyl groups has little effect on the overall stability of the ate anion (cf. eqs 3a,b). Thus, formation of (*E*)-$(FHC{=}CH{-}X{-}CH{=}CHF)^-$ from (*Z*)-(2-fluorovinyl)lithium and (*E*)-1-fluoro-2-haloethene (eq 3b) is calculated to be 1 kcal/mol more endothermic for the iodinanide and 1 kcal/mol more exothermic for the brominanide relative to formation of the parent ate anion (eq 3a). Multiple fluorine substitution, however, has a more pronounced effect on the stability of the ate anions (cf. eqs 3a,c). Indeed, the results of this analysis suggest that the perfluorinated ate anions are markedly stabilized relative to the parent anion: the stabilization afforded by multiple fluorine substitution is predicted to be some 19 kcal/mol for the iodinanide and 24 kcal/mol for the brominanide.

In summary, the reaction of vinyl iodides with vinyllithiums leads to 10-X-2 ate complexes with stabilities intermediate between those of their dialkyl and diaryl counterparts. The sp^2 hybridization of the vinyl carbons is probably in large measure responsible for the greater stability of the vinyl vs alkyl ate complexes, and fluorine substitution generally leads to significantly increased stability of these ate complexes.

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Supporting Information Available: A table of the B3LYP/6-31++G** calculated total energies and zero point energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Although most organolithium compounds are known to exist as contact ion pairs,[7] this is not the case for the 10-I-2 ate complexes, $(R{-}I{-}R)^-Li^+$, whose structures have been determined. The ICN–KCN adduct, which has been isolated as a stable 10-I-2 ate complex with the diethyl ester of (diimino)oxalic acid, owes its stability to the fact that the potassium cation is strongly coordinated to the diethyl (diimino)oxalate ligand (Tebbe, K. F.; Fröhlich, R. *Z. Anorg. Allg. Chem.* **1983**, *505*, 7). Similarly, lithium bis(pentafluorophenyl)iodinanide, which has been crystallized as the bis-TMEDA adduct and is stable at room temperature, displays a very long Li–I distance of 5.839 Å.[2b] Further discussion of the role of solvation in determining the stability of lithium 10-X-2 complexes may be found in ref 3.