The Role of Ate Complexes in Halogen(Metalloid)–Metal Exchange Reactions: A Theoretical Study

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Correlated electronic structure calculations predict that $[(CH_3)_{n+1}X]^-$ methyl ate anions, where X is an element of the main groups 14, 15, 16, or 17 up to Bi, possess widely varying stabilities that are governed by the electronegativities of their central atoms X. These stabilities correlate well with the propensities of the elements in question to undergo exchange with lithium and magnesium halide, except in the cases where steric hindrance in the transition states of the exchange reactions is important. These findings are nicely confirmed by calculations of the transition states $[(CH_3)_2XLi]^+$ (X = Cl, Br, I) and $[(CH_3)_3SeLi]^+$ of the corresponding degenerate exchange reactions CH_3X (X = Cl, Br, I) + CH_3Li and $(CH_3)_2Se$ + CH_3Li, respectively. The computed relative stabilities of the mixed $[R–I–CH_3]^-$ ate anions of iodine (where R = phenyl, ethynyl, vinyl, ethyl, or cyclopropyl) are in excellent agreement with the experimentally observed equilibria of the corresponding lithium–iodine exchange reactions. The recent experimental observation of a highly stable α-iodine-substituted iodine ate complex as an intermediate in an iodine–magnesium bromide exchange reaction is also corroborated by our studies. Thus, the present calculations provide strong evidence for ate complexes being key intermediates in halogen(metalloid)–lithium(magnesium halide) exchange reactions.

Introduction

The halogen−lithium exchange reaction (Scheme 1) has been known to organic chemists for over 60 years. Although Wittig[1] and Gilman[2] are usually credited with its discovery, this type of exchange was mentioned (but not recognized) in earlier chemical literature.[3] Most of the original research on this reaction has been carried out by Gilman et al., who demonstrated its reversibility that gives rise to equilibria favoring the thermodynamically more stable organolithium compounds.[2][4] These seminal investigations have also established the general order of halogen reactivity, with iodides reacting faster than bromides, and reactions with chlorides being very slow. There have been no credible accounts of fluorine−lithium exchange published in the chemical literature.[5][6]

Scheme 1

$$\text{R-X} + \text{R'-Li} \rightleftharpoons \text{R'-X} + \text{R-Li}\ ,\ \text{X} = \text{Cl, Br or I}$$

Halogen−lithium exchange, which has turned out to be one of the most useful methods of generating organolithium compounds not readily accessible by other means such as the direct metalation of C−H bonds by other organolithiums or the reaction of organic halides with lithium metal, has been the subject of numerous reviews.[4d][4e][7] In an effort to obtain organolithium compounds from an even wider range of precursors, metalloids such as Se[8], Te[9], Sn[10][11f] and Hg[11] have been successfully added to the palette of exchangeable elements. Exchange of lithium with P,[6] As,[6][12b][12c][12d] Sb,[6][12b][12c] Bi,[6][12a] and Pb[12b][12c][12d][13] has also been reported.

Several mechanisms have been proposed for the halogen-(metalloid)−lithium exchange. An initial single electron transfer (SET) from the organolithium molecule to a halide is consistent with the observation of coupling products.[14] This mechanism is supported by the detection of species with unpaired electrons under the reaction conditions by means of ESR[15][16] and ^{1}H-NMR CIDNP (chemically-induced dynamic nuclear polarization) spectroscopies.[17] Moreover, the results of experiments employing radical probes (molecules that undergo specific radical-induced rearrangements) confirm the involvement of radicals.[18] For example, the formation of the rearranged product **3** from

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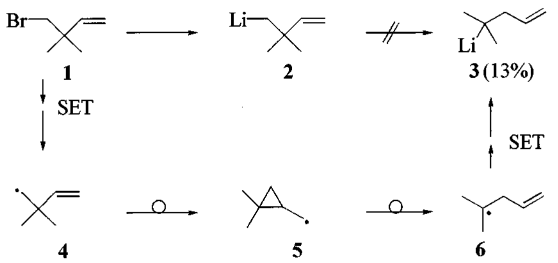
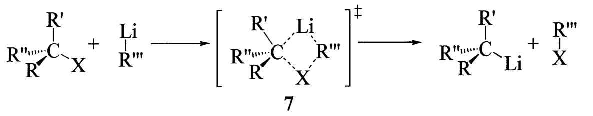
the bromide **1** has to proceed via the radical intermediates **4**, **5**, and **6** rather than via the lithium compound **2**, which does not rearrange to **3** (Scheme 2).[18c] However, it should be emphasized that the mere involvement of radicals does not establish the predominance of the SET mechanism. Indeed, such predominance could not be reconciled with the generally observed retention of configuration at the carbon center originally connected to the halogen atom.[19] This retention of configuration can, however, be explained by the exchange occurring via a four-center transition state **7** (Scheme 3), which constitutes a mechanistic alternative for this reaction.[7b]

Scheme 2

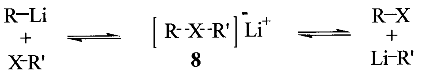


Scheme 3



In the late 1950s, Wittig and Schöllkopf[20a] postulated yet another mechanism, which invokes a nucleophilic displacement at the exchanged element (Scheme 4), and the term "ate complex" was coined by Wittig[20b] for the intermediate **8**.

Scheme 4



$$\begin{matrix}\text{R–Li}\\+\\\text{X–R'}\end{matrix} \rightleftharpoons \underset{\mathbf{8}}{[\text{R–X–R'}]^{-}\text{Li}^{+}} \rightleftharpoons \begin{matrix}\text{R–X}\\+\\\text{Li–R'}\end{matrix}$$

Since the publication of this mechanism, various experimental findings have furnished support for its validity. For example, an excess of negative charge in the transition states of several halogen–lithium exchange reactions has been demonstrated.[21] In addition, Beak and co-workers[22] have shown by isotope labeling experiments that bromine–lithium exchange occurs via linear bromine ate complexes (or S_N2 transition states), ruling out both the SET and the four-center concerted mechanism. Furthermore, Reich et al.[23] and Ogawa et al.[24] succeeded in detecting aryl- and alkyl-substituted ate complexes of I,[23a][23d][23e][23f] Te,[23e][23f][24] Se,[23g] Sn,[23b][23c] and Hg[23e][23f] by NMR spectroscopy in THF solutions in both the presence and absence of HMPA. As observed by Reich,[23e] "the formation constant for $Ph_2I^-Li^+$ is strongly temperature-dependent, consistent with the powerful solvent-ordering capacity of a solvent-separated ion pair". Indeed, the crystal structure of the iodine ate complex $[(C_6F_5)_2I]^-[Li(TMEDA)_2]^+$ as determined by Farnham and Calabrese in 1986, confirms the separate ion pair character of such species.[25] Thus far, however, this compound is the only hypervalent ate complex relevant to the exchange reaction with a fully characterized structure. Its geometry exhibits a linear C–I–C unit with C–I bonds that are much longer (2.403 and 2.331 Å) than that in C_6F_5I (2.090 Å).[26] However, no information concerning the thermodynamic stability of this as well as other ate complexes and ate anions is presently available.[43]

The main objective of the research presented in this paper is to assess the role played by ate complexes as intermediates in halogen(metalloid)–lithium(magnesium halide) exchange reactions. In particular, we address the question of the consistency of the Wittig-Schöllkopf ate complex mechanism with the great variation in the experimentally determined rates of these exchange reactions with different elements X. In order to accomplish this goal, comprehensive ab initio electronic structure calculations on the methyl ate anions $[(CH_3)_{n+1}X]^-$ and the corresponding neutral species $(CH_3)_nX$, where X are the elements of the main groups 1, 2, and 13–17 (Scheme 5), have been carried out. Investigational calculations on four ate complexes with X = Cl, Br, I and Se involving the Li^+ cation, more precisely: on the transition states $[(CH_3)_{n+1}X]Li^+$ of the corresponding degenerate exchange reactions, reveal the validity of neglecting the solvent and counterion effects in the present study, in agreement with the experimentally observed anion–cation separation in the donating solvents used in the exchange reactions.[23] In addition, the results of quantum-chemical studies of phenyl, ethynyl, vinyl, ethyl, and cyclopropyl ate anions of iodine that eludicate the importance of the experimentally observed substituent effects in the exchange reactions are discussed. Finally, the recent experimental observation of a highly stable α-iodine-substituted iodine ate complex as an intermediate in an iodine–magnesium bromide exchange reaction is corroborated.

Scheme 5

$$(CH_3)_nX + CH_3^- \rightleftharpoons [(CH_3)_{n+1}X]^{-[a]}$$

X=	Li	Be	B	C	N	O	F
	Na	Mg	Al	Si	P	S	Cl
	K	Ca	Ga	Ge	As	Se	Br
	Rb	Sr	In	Sn	Sb	Te	I
	Cs	Ba	Tl	Pb	Bi		

[a] In the case of the underlined elements X also the reaction with CH_3Li was calculated.

Details of Calculations

In all the calculations reported in this paper, the MP2 treatment of electron correlation (including the core electrons where applicable) was employed. Geometries of the $(CH_3)_nX$ and RI (where R = phenyl, ethynyl, vinyl, ethyl, or cyclopropyl) neutral compounds, the CH_3^- and R^- carbanions, the $[(CH_3)_{n+1}X]^-$ and $[R-I-CH_3]^-$ ate anions, as well as the ate complexes $[(CH_3)_{n+1}X]Li$ (X = Se, Cl, Br and I) were fully optimized. The resulting stationary points

Table 1. The basis sets employed in the calculations[a]

	basis set I	basis set II
C, H	6-31+G*	6-31+G*
Li−F	6-31+G*	−
Na−Cl	6-31+G*	(211/211/1)/ECP
K−Bi	(211/211/1)/ECP	

[a] See the text for full description.

on the respective potential energy hypersurfaces were analyzed in subsequent vibrational frequency calculations. Properties of atoms in molecules (AIMs)[27] were computed for a representative set of ate anions, namely $[(CH_3)_5Si]^-$, $[(CH_3)_4P]^-$, $[(CH_3)_3S]^-$, $[(CH_3)_2Cl]^-$, $[(CH_3)_2Br]^-$, and $[(CH_3)_2I]^-$. The standard 6-31+G* basis sets of Pople[28] were used for the elements up to Cl, whereas the pseudopotentials (ECPs) of Hay and Wadt[29] were used in conjunction with the (211/211/1) valence basis sets for the heavier elements. The latter basis sets were obtained by augmenting the (21/21/1) sets of Frenking et al.[30] [which, in turn, were derived from the (3/3) basis sets of Hay and Wadt[29]] with diffuse s and p functions[31] (note that 5d rather than 6d functions were used for the sake of consistency). Geometries and electronic properties of neutrals and ate anions of Na, Mg, Al, Si, P, S, and Cl were also calculated with ECPs on the central atoms. The results of these calculations (denoted by "basis set II" in Table 1 and in the following) were found to be almost identical with their all-electron "basis set I" counterparts.

All geometry optimizations and vibrational frequency calculations were carried out with the TURBOMOLE[32] and GAUSSIAN[33] suites of programs. The molecular structures were visualized with the program SCHAKAL92.[34] In many of the neutrals and methyl ate anions under study, the rotation of methyl groups is essentially barrierless. Accordingly, the optimized geometries of such species were occasionally found to possess one or two imaginary frequencies describing these rotations. Because of the low magnitude of these frequencies, no further geometry optimizations were attempted in such cases.

Results and Discussion

The calculated structural parameters of the neutral methyl compounds are in good agreement with both the values obtained in earlier calculations[35] and the available experimental gas-phase data[36] (Table 2). However, linear

Table 2. Calculated and experimental bond lengths [Å] and angles [°] of selected neutral methyl compounds

	X−C bond lengths			C−X−C angles		
Compound	MP2/I[α]	prev. calcd.[β]	exp.[γ]	MP2/I[α]	prev. calcd.[β]	exp.[γ]
CH_3Li	2.010	2.003[a]	n/a			
CH_3Na	2.346	2.334[a]	n/a			
CH_3K	2.796	2.743[b]	n/a			
CH_3Rb	3.033	2.897[b]	n/a			
CH_3Cs	3.180	3.073[c]	n/a			
$(CH_3)_2Be$	1.692	n/a	1.698(5)[a]	180.0	n/a	180.0[a]
$(CH_3)_2Mg$	2.109	2.111[δ]	2.126(6)[δ][b]	180.0	180.0[δ]	180.0[δ][b]
$(CH_3)_2Ca$	2.488	2.488[ε]	2.459(9)[ε][c]	180.0	180.0[e]	149.7(6)[ε][c]
$(CH_3)_2Sr$	2.663	2.621[e]	n/a	180.0	130.6[e]	n/a
$(CH_3)_2Ba$	2.688	2.757[e]	n/a	180.0	115.9[e]	n/a
$(CH_3)_3B$	1.576	1.588[f]	1.578(1)[d]	120.0	120.0[f]	119.4(3)[d]
$(CH_3)_3Al$	1.971	1.991[g]	1.957(3)[e]	120.0	120.0[g]	120.0[e]
$(CH_3)_3Ga$	1.988	1.992[g]	1.967(2)[f]	120.0	120.0[g]	120.0[f]
$(CH_3)_3In$	2.166	2.219[g]	2.161(3)[g]	120.0	120.0[g]	120.0[g]
$(CH_3)_3Tl$	2.170	2.152[h]	2.206(3)[g]	120.0	120.0[h]	120.0[g]
$(CH_3)_4C$	1.530	1.520[i]	1.534(3)[h]	109.5	109.5[i]	109.5[h]
$(CH_3)_4Si$	1.885	1.875[i]	1.875(2)[i]	109.5	109.5[i]	109.5[i]
$(CH_3)_4Ge$	1.969	1.968[j]	1.958(4)[j]	109.5	109.5[j]	109.5[j]
$(CH_3)_4Sn$	2.150	2.149[j]	2.144(3)[k]	109.5	109.5[j]	109.5[k]
$(CH_3)_4Pb$	2.203	2.248[k]	2.238(9)[l]	109.5	109.5[k]	109.5[l]
$(CH_3)_3N$	1.455	1.452[a]	1.458(2)[m]	110.8	110.4[a]	110.9[m]
$(CH_3)_3P$	1.848	1.854[g]	1.845(1)[n]	99.2	99.4[g]	98.8(2)[n]
$(CH_3)_3As$	1.974	1.966[g]	1.968(3)[o]	96.7	98.6[g]	96.1(5)[o]
$(CH_3)_3Sb$	2.170	n/a	2.163(3)[o]	94.4	n/a	94.1(5)[o]
$(CH_3)_3Bi$	2.244	2.392[l]	2.264(6)[p]	93.1	90.6[l]	96.7(10)[p]
$(CH_3)_2O$	1.419	1.420	1.415(1)[q]	111.5	111.4	111.8(2)[q]
$(CH_3)_2S$	1.805	1.807[m]	1.8023(15)[r]	98.4	98.4[m]	98.8(1)[r]
$(CH_3)_2Se$	1.954	1.954[n]	1.945(1)[s]	95.7	97.5[n]	96.1(1)[s]
$(CH_3)_2Te$	2.148	2.168[n]	2.142(5)[o]	93.4	95.4[n]	94(2)[o]
CH_3F	1.407	1.406[o]	1.390(1)[t]			
CH_3Cl	1.779	1.779[o]	1.7756(20)[uf]			
CH_3Br	1.947	1.949[p]	1.9340(03)[v]			
CH_3I	2.147	2.150[p]	2.1358(20)[w]			

[α] This work. − [β] Indices in brackets refer to ref.[35]. − [γ] Indices in brackets refer to ref.[36]; all structures have been determined in the gas phase; the values in parentheses are experimental errors that refer to the last digit(s) of the listed data. − [δ] Values given for bis(neopentyl)magnesium; the structure of $(CH_3)_2Mg$ has not been determined. − [ε] Values given for $[\{(CH_3)_3Si\}_3C]_2Ca$. The nonlinear C−Ca−C angle in the experimental structure is most likely due to crystal packing, consistent with the very low force constant computed for the angle distortion.

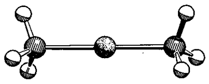
structures are predicted for the Me_2Sr and Me_2Ba molecules, which have previously been found to be bent at the HF level of theory.[35e] The computed equilibrium geometries exhibit a variety of symmetries, including C_{3v} [linear CH_3X with X = Li, Na, K, Rb, Cs, F, Cl, Br, and I; trigonal pyramidal $(CH_3)_3X$ with X = N, P, As, Sb, and Bi], $D_3/D_{3d}/D_{3h}$ [linear $(CH_3)_2X$ with X = Be, Mg, Ca, Sr, and Ba], C_{3h} [trigonal planar $(CH_3)_3X$ with X = B, Al, Ga, In, and Tl], T_d [tetrahedral $(CH_3)_4X$ with X = C, Si, Ge, Sn, and Pb], and C_{2v} [bent $(CH_3)_2X$ with X = O, S, Se, and Te].

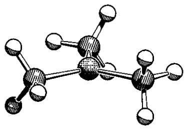
The corresponding ate anions fall into four distinct categories according to a classification based upon the energetics of formation and the distribution of charge among the central atom and the ligands.[37] The computed formation energies of these species, obtained from eq. 1, where E_K is the total energy of the chemical system K, are compiled in Table 3. The values of ΔE_X vary in a regular manner with the position of the central atom X in the periodic table.

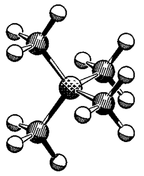
$$\Delta E_X = E_{[(CH_3)_{n+1}X]^-} - E_{(CH_3)_nX} - E_{CH_3^-} \qquad (1)$$

The ionic ate complexes of the first three main-group elements (Figure 1) are remarkably stable to dissociation into the respective neutral methyl compounds and CH_3^-.

Figure 1. The MP2/I-optimized geometries of the methyl ate anions of Li, Be, and B


$[(CH_3)_2Li]^-$ (D_3)


$[(CH_3)_3Be]^-$ (C_{3h})


$[(CH_3)_4B]^-$ (T_d)

Accordingly, many compounds containing these anions are stable enough to be amenable to the determination of their crystal structures by X-ray diffraction[38]. This stability has been previously shown to originate from the strongly ionic character of the X−C bonds in these species.[37] Due to the increased electronegativity difference between the CH_3 carbon and X, this ionicity becomes more pronounced for heavier central atoms. However, the increasingly longer X−C bonds in the latter result in less negative formation energies ΔE_X (Table 3). In all ate anions of this type, the X−C bonds are predicted to be slightly longer than those in the corresponding neutral compounds (Table 4).

Table 3. The MP2/I formation energies ΔE_X [kcal/mol] of the ate anions under study[a]

Li	Be	B	C[b]	N[c]	O[c]	F
−58.9	−62.7	−71.6	+58.3	+46.1	+85.2	+24.7
Na	Mg	Al	Si	P	S	Cl
−49.4	−65.0	−80.1	−22.0	−9.1	−0.1	−1.3
(−48.1)	(−64.6)	(−78.9)	(−20.7)	(−9.2)	(−0.3)	(+0.4)
K	Ca	Ga	Ge	As	Se	Br
−42.1	−63.0	−73.8	−23.7	−16.8	−13.1	−14.1
Rb	Sr	In	Sn	Sb	Te	I
−38.6	−60.2	−72.9	−38.7	−31.6	−29.9	−27.8
Cs	Ba	Tl	Pb	Bi		
−37.9	−58.8	−65.1	−33.3	−30.0		

[a] Eq.1; see Scheme 5 for the respective reaction. All energies at 0 K, inclusive of ZPEs. Where available, the MP2/II energies are given in parentheses. − [b] A higher-order transition state (see the text for explanation). − [c] "Double-Rydberg" anions that are unstable with regard to electron loss.

Table 4. The relative lengthening [%] of the X−C bonds in $(CH_3)_nX$ upon the attachment of CH_3^-[a]

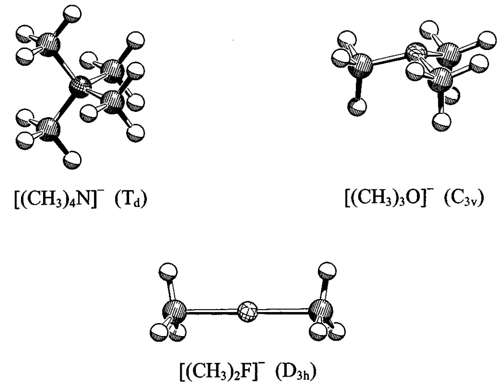
Li	Be	B	C[b]	N	O	F
6.2	6.3	4.4	41.3/−0.2	3.0	4.7	43.3
Na	Mg	Al	Si	P	S	Cl
6.3	4.3	3.4	8.2/3.4	12.2/1.4	18.7/0.7	26.0
(5.6)	(5.0)	(3.4)	(8.8/3.4)	(12.5/1.3)	(18.6/0.7)	(26.9)
K	Ca	Ga	Ge	As	Se	Br
5.8	4.7	3.5	8.8/3.2	11.8/1.1	15.1/0.6	19.3
Rb	Sr	In	Sn	Sb	Te	I
6.0	4.7	3.4	6.4/2.9	8.5/1.2	10.4/0.9	13.9
Cs	Ba	Tl	Pb	Bi		
6.2	2.2	3.3	7.1/2.9	10.1/0.8		

[a] MP2/I data with the corresponding MP2/II values (where available); the latter are listed in parentheses. For ate anions with two symmetry-inequivalent groups of ligands, the values for axial bonds are followed by those for their equatorial counterparts. − [b] A higher-order transition state (see the text for explanation).

Because of their high stability, the aforementioned ionic ate anions are of no importance to halogen(metalloid)−lithium(magnesium halide) exchange reactions. Another two categories of ate anions that are similarly unimportant (although for other reasons), include the $[(CH_3)_4N]^-$ and $[(CH_3)_3O]^-$ "double-Rydberg"[39] anions, and the $[(CH_3)_2F]^-$ system (Figure 2). In the nitrogen and oxygen compounds, the excess electron pairs are barely bound to the cationic cores that possess octets of electrons. Consequently, these anions are unstable with regard to electron loss. In contrast, $[(CH_3)_2F]^-$ is stable with respect to electron loss but readily dissociates into CH_3F and CH_3^-.[37]

The fourth category of ate anions has as its members the species formed by the elements of the main groups 14, 15, 16, and 17, other than N, O, or F. The extension of the electron octet in the neutral compounds of these elements to a decet in the corresponding ate anions affords hypervalent systems with trigonal-bipyramidal shapes. In accord with the VSEPR (valence shell electron pair repulsion) model of Gillespie and Nyholm,[40] lone pairs in these species preferentially occupy equatorial positions. Such an arrangement produces the following symmetries of the ate anions: C_{3h} for X = C, Si, Ge, Sn, and Pb; C_{2v} for X = P, As, Sb, and Bi; C_s for X = S, Se, and Te; and D_3/D_{3h} for

Figure 2. The MP2/I-optimized geometries of the methyl ate anions of N, O, and F

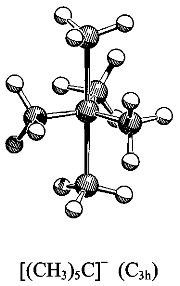


$[(CH_3)_4N]^-$ (T_d) $[(CH_3)_3O]^-$ (C_{3v})

$[(CH_3)_2F]^-$ (D_{3h})

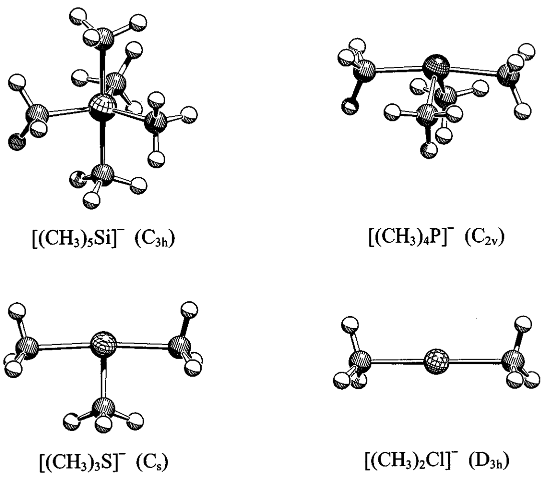
X = Cl, Br, and I. Where present, the equatorial X−C bonds are shorter than their axial counterparts (compare the relative bond lengthenings listed in Table 4). With the exception of $[(CH_3)_5C]^-$ (Figure 3), all methyl ate anions of this type are minima on their respective potential energy hypersurfaces (Figure 4). The only stationary point that can be located for the methyl ate anion of carbon is a fourth-order transition state, with one of its imaginary frequencies (672 cm^{-1}) corresponding to motion along the S_N2 reaction path.

Figure 3. The MP2/I-optimized geometry of the $[(CH_3)_5C]^-$ ate anion with C_{3h} symmetry



$[(CH_3)_5C]^-$ (C_{3h})

Figure 4. The MP2/I-optimized geometries of the methyl ate anions of Si, P, S, and Cl



$[(CH_3)_5Si]^-$ (C_{3h}) $[(CH_3)_4P]^-$ (C_{2v})

$[(CH_3)_3S]^-$ (C_s) $[(CH_3)_2Cl]^-$ (D_{3h})

The hypervalent ate anions exhibit varying degrees of stability with respect to the detachment of CH_3^- (Table 3). Within a given group of elements in the periodic table, this stability tends to increase with the atomic number of X. This effect is particularly well-pronounced in the ate anions of the halogens. An opposite trend is observed within individual rows of elements, where stabilities decrease as the atomic numbers increase from left to right. In both cases, higher thermodynamic stabilities correlate with lower electronegativities, which are associated with more positive charges at the central atoms (Table 5) and more polar X−C bonds.[41] This enhancement of bond ionicity is also responsible for a decrease in the relative X−C bond lengthening upon attachment of the methyl anion to the respective neutral species (Table 4). Analogous considerations readily rationalise the computed relative stabilities of the Sn/Pb and Sb/Bi pairs of methyl ate anions.

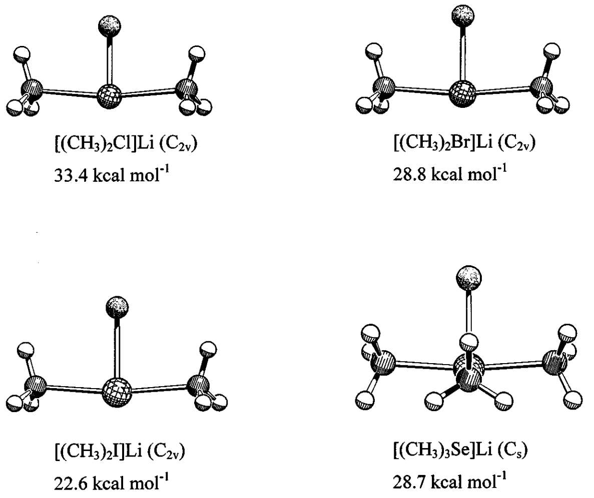
Table 5. The MP2/I charges on the central atoms of selected hypervalent ate anions

X	Si	P	S	Cl	Br	I
Q_X	2.957	1.431	0.041	−0.344	−0.232	−0.035

Within main groups of the periodic table, the trends in the formation energies ΔE_X of the ate anions exhibit conspicuous correlations with the experimentally determined rates of the respective halogen(metalloid)−lithium exchanges. Thus, both the computed thermodynamic stabilities of methyl ate anions and the empirical propensities of the elements to undergo exchange reactions decrease within the sequences I > Br >> Cl, Te >> Se >> S, Bi ≈ Sb > As, and Sn ≥ Pb > Ge > Si. In contrast, the trends in the computed stabilities ΔE_X within rows of elements seem to be inconsistent at first glance with the experimental observation that the disubstituted methanes of the type $I-CH_2-SnR_3$ (R = Ph, *n*-Bu, or Me) preferentially exchange their iodine atoms.[12b] Furthermore, the order of the recently measured[42] relative rates of the exchange reactions of Ph−Y with BuLi in THF ($PhSnBu_3$ << PhTeBu < PhI) is exactly opposite to that of the calculated formation energies of the ate anions, $[SnMe_5]^-$ > $[TeMe_3]^-$ > $[IMe_2]^-$ (Table 3). However, $PhSn\mathit{Bu}_3$ has been found to react much more slowly than $PhSn\mathit{Me}_3$, the latter undergoing exchange at a rate comparable to that of PhTeBu. These experimental facts underscore the dominant effect of steric hindrance in the transition states on the rates of these exchange reactions. This effect, the magnitude of which increases in the sequence PhI < PhTeR < $PhSnR_3$ and with the size of R, is more important than the relative stability of the respective ate complexes. Analogous reasoning pertains to the elements of other rows of the periodic table.

In order to confirm the validity of neglecting the Li^+ counterion and correlating the thermodynamic ate anion stabilities $[(CH_3)_{n+1}X]^-$ with the propensities of the elements X to undergo exchange reactions with lithium and magnesium halide, also four lithiated complexes $[(CH_3)_{n+1}X]Li$, where X = Se, Cl, Br, and I, were selected for an investigation. In all cases, the complexes are found to consist of only slightly perturbed ate anions with the additional Li^+ cation coordinated to the central atom X (Figure 5 and Table 6). Vibrational frequency calculations reveal that these structures, which are similar to the ate complex $[H_2C{=}C{-}I{-}CH_3]Li$ studied recently by Crabtree et al.,[43] constitute transition states pertaining to the X−Li exchange between $(CH_3)_nX$ and CH_3Li. The respective reaction barriers as compared to $(CH_3)_nX$ and CH_3Li are predicted to equal to 28.7 kcal mol^{-1} for X = Se, 33.4 kcal mol^{-1} for X = Cl, 28.8 kcal mol^{-1} for X = Br, and 22.6 kcal mol^{-1} for X = I. The energetic upshifts relative to the corresponding ate anions (Table 3) stem mainly from avoiding the uncoordinated methyl anion. Most significantly with respect to the propensity of an element X to undergo lithium (magnesium halide) exchange, the calculations involving the counterion yield an overall picture which is consistent with the results obtained for the ate anions. Thus the formation energies of the methyl ate anions as reported in Table 3 follow the same order as the energetic barriers of the X−Li(MgX) exchange reactions.

Figure 5. The MP2/I-optimized geometries and energies of the ate complex transition states $[(CH_3)_{n+1}X]Li$, X = Se, Cl, Br, I



$[(CH_3)_2Cl]Li$ (C_{2v})
33.4 kcal mol^{-1}

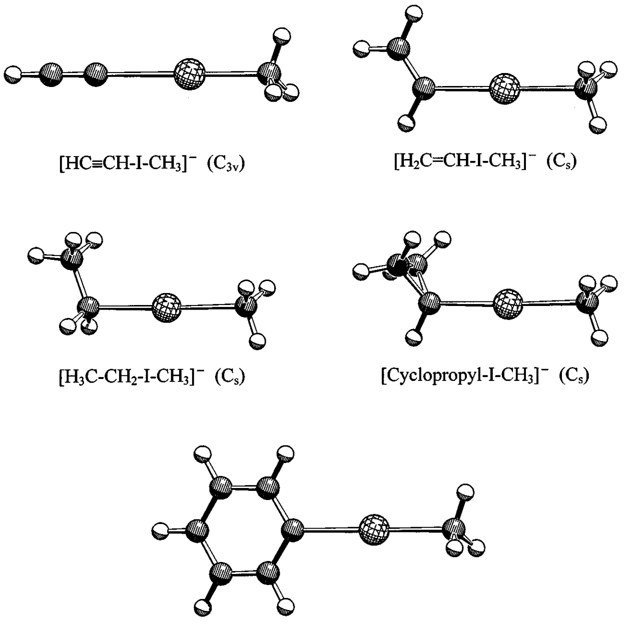
$[(CH_3)_2Br]Li$ (C_{2v})
28.8 kcal mol^{-1}

$[(CH_3)_2I]Li$ (C_{2v})
22.6 kcal mol^{-1}

$[(CH_3)_3Se]Li$ (C_s)
28.7 kcal mol^{-1}

Iodine ate anions of the type $[R{-}I{-}CH_3]^-$, where R = phenyl, ethynyl, vinyl, ethyl, or cyclopropyl, all possess a nearly linear C−I−C moiety with elongated I−C bonds (Figure 6).

Figure 6. The MP2/I-optimized geometries of the mixed iodine ate anions



$[HC{\equiv}CH{-}I{-}CH_3]^-$ (C_{3v})

$[H_2C{=}CH{-}I{-}CH_3]^-$ (C_s)

$[H_3C{-}CH_2{-}I{-}CH_3]^-$ (C_s)

[Cyclopropyl-I-$CH_3]^-$ (C_s)

[Phenyl-I-$CH_3]^-$ (C_s)

In agreement with the experimental results reported earlier,[23][24] these species are very stable with respect to the detachment of one of their carbanion ligands. The values of the negative bond dissociation energies ΔE_1 and ΔE_2 (Scheme 6 and Table 7) correlate with the relative bond lengthenings (Table 8). As expected, the less elongated I−C bonds are stronger, i.e. their dissociations are associated with more negative values of ΔE. The experimental finding that the equilibria of the halogen−lithium exchange reactions favor the lithium compounds according to the ethynyl > vinyl > cyclopropyl > *n*-alkyl[44] sequence of stabilities are reflected in the calculated values of ΔE_1 and ΔE_2, with the phenyl anion being the sole exception.[45]

Calculated stabilities of methyl and other ate anions are also relevant for ate complexes being intermediates in the halogen−magnesium halide exchange reaction. Thus, the α-iodine-substituted iodine ate complex **11** has recently been shown to be the intermediate in the iodine−magnesium

Table 6. Selected bond lengths [Å] and angles [°] in the ate complex transition states $[(CH_3)_{n+1}X]Li$, X = Se, Cl, Br, I

X	Li−X	C_{ax}−X	C_{eq}−X	Li−X−C_{ax}	Li−X−C_{eq}	C_{ax}−X−C_{eq}
Se	2.374	2.218	1.967	87.0	109.9	86.7
Cl(I)[a]	2.063	2.346	–	85.3	–	–
Cl(II)[b]	2.061	2.393	–	84.9	–	–
Br	2.240	2.360	–	85.8	–	–
I	2.475	2.433	–	85.9	–	–

[a] Basis I. – [b] Basis II.

Scheme 6

$$\text{R–I} + \text{CH}_3^- \underset{}{\overset{\Delta E_1}{\rightleftharpoons}} [\text{R–I–CH}_3]^- \overset{\Delta E_2}{\rightleftharpoons} \text{R}^- + \text{I–CH}_3$$

Table 7. The MP2/I formation energies [kcal/mol] of selected ate anions of iodine[a]

R	ΔE_1[b]	ΔE_1[c]	ΔE_2[b]	ΔE_2[c]
HC≡C	−57.0	−53.8	−11.9	−11.5
Phenyl	−39.4	n/a	−23.8	n/a
$H_2C{=}CH$	−32.5	−30.9	−25.1	−25.1
Cyclopropyl	−31.9	−30.5	−32.0	−31.6
Ethyl	−26.8	−25.9	−33.8	−33.2

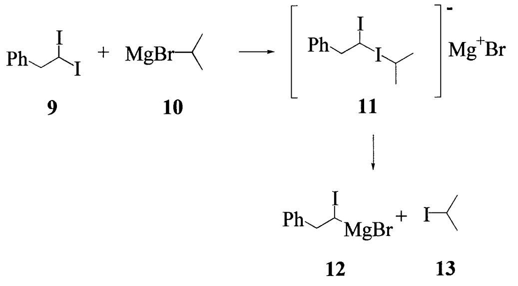
[a] All energies at 0 K; see Scheme 6 for the definition of ΔE_1 and ΔE_2. – [b] Exclusive of zero-point energies. – [c] With zero-point energies included.

Table 8. Bond lengthening [%] of the I−C bonds in the $[R{-}I{-}CH_3]^-$ ate anions relative to the respective I−C bond lengths in the neutral compounds

	R				
Bond	Ethynyl	Phenyl	Ethenyl	Cyclopropyl	Ethyl
I−R	32.3	15.7	15.0	13.1	12.0
$I{-}CH_3$	4.5	11.0	12.3	12.7	14.9

bromide exchange reaction of the diiodo compound **9** with isopropylmagnesium bromide **10**, which yields the carbenoid **12** and isopropyl iodide **13** (Scheme 7).[46]

Scheme 7



The ate complex **11**, which is formed within 2 min at −78 °C, transforms only slowly into **12** and **13**. **11** is characterized by its yellow color and its reactivity, which is different from that of **12**. The present quantum-chemical calculations account for the extraordinary stability of the α-iodine-substituted **11**. Table 9 summarizes the MP2/I formation energies of the $Y{-}CH_2{-}X{-}CH_3^-$ ate anions with Y = H, Br, I, and X = Br, I. The $YCH_2{-}X$ and $X{-}CH_3$ bond lengths are also given in Table 9.

As expected from the results reported earlier, the iodine ate anions (X = I) are more stable than their bromine ate counterparts (X = Br). Most importantly with respect to the results shown in Scheme 7, the α-iodine-substituted iodine ate anion (X = I, Y = I) is highly stabilized: it is 20.1 kcal mol^{-1} more stable than the anion $CH_3{-}I{-}CH_3^-$, and 33.8 kcal mol^{-1} more stable than $CH_3{-}Br{-}CH_3^-$. The α-bromo-substituted iodine ate anion (X = I, Y = Br) is 3.1 kcal mol^{-1} less stable than the α-iodine-substituted species (X = I, Y = I). Indeed, the α-bromo analogue of **11** is not observed under the conditions that produce the α-iodine-substituted iodine ate complex **11**.[47]

Table 9. The MP2/I formation energies [kcal/mol] of $Y{-}CH_2{-}XCH_3^-$ ate anions, along with $YCH_2{-}X$ and $X{-}CH_3$ bond lengths [pm][a]

$$\text{Y-CH}_2\text{-X} + \text{CH}_3^- \overset{\Delta E}{\rightleftharpoons} [\text{Y-CH}_2\text{-X-CH}_3]^-$$

Y	X	ΔE	$\Delta E_{\text{rel.}}$	$YCH_2{-}X$	$X{-}CH_3$
H	Br	−14.1	0	232.2	232.2
Br	Br	−31.3	−17.2	239.0	216.7
I	Br	−35.2	−21.1	249.1	209.1
H	I	−27.8	−13.7	244.5	244.5
Br	I	−44.8	−30.7	247.6	235.2
I	I	−47.9	−33.8	249.5	233.1

[a] All energies at 0 K with zero-point energies.

The bond lengths $YCH_2{-}X$ and $X{-}CH_3$ in the ate anions listed in Table 9 are consistent with the finding that ate complex **11** is converted to the carbenoid **12** and isopropyl iodide **13** (Scheme 7), as the $YCH_2{-}X$ bonds (Y = Br, I) are much longer than the $X{-}CH_3$ bonds. Thus, the more stable MgBr species is preformed in the ate anion, as is also indicated by the bond lengths in Table 8.

Conclusions

The recently completed correlated electronic structure calculations on the methyl ate anions $[(CH_3)_{n+1}X]^-$ of the main-group elements Li − Cl have revealed the existence of four different types of ate anions.[37] The results reported in this paper convincingly establish the validity of this classification for analogous anions of all other main-group elements (other than the noble gases) up to Bi. Anions of the elements of the main groups 1, 2, and 13 with ionic X−C bonds are found to be very stable with respect to the detachment of a methyl anion, their stabilities being determined primarily by the X−C bond lengths. Together with the "double-Rydberg" anions of N and O, the unusual $[(CH_3)_2F]^-$ compound, and the higher-order transition state $[(CH_3)_5C]^-$, these species are not expected to play a role in halogen(metalloid)−lithium(magnesium halide) exchange reactions.

All the other elements of the main groups 14, 15, 16, and 17 are predicted to form hypervalent methyl ate anions with geometries that conform to the VSEPR model. These anions are (sometimes marginally) stable with respect to the loss of CH_3^-. The thermodynamic stability of a given ate anion can be directly inferred from the electronegativity of the central atom X, decrease of which enhances the ionicity, and thus also the strength, of the X−C bond. This enhancement is reflected in the reduced X−C bond lengthening upon the attachment of the CH_3^- anion to the neutral compound from which the ate anion in question is derived. The computed thermodynamic stabilities of the ate anions $[(CH_3)_{n+1}X]^-$ correlate well with the experimentally determined rates of the exchanges of the element X with lithium, except for the cases where steric hindrance in the pertinent transition states is important. Since, as indicated by our calculations of the ate complexes $[(CH_3)_{n+1}X]Li$, X = Se, Cl, Br, I, the energies of dissociation of these complexes into the constituting ions $[(CH_3)_{n+1}X]^-$ and Li^+ vary only little with X, this correlation is not unexpected. The results of our calculations on the mixed iodine ate anions $[R{-}I{-}CH_3]^-$ (where R = phenyl, ethynyl, vinyl, ethyl, or cyclopropyl) agree with the experimentally observed equilibria of the respective lithium−iodine exchange reactions. The recent experimental finding of the α-iodine-substituted iodine ate complex **11** being a detectable intermediate in the iodine−magnesium bromide exchange reaction of **9** and **10** that yields **12** and **13** (Scheme 7) is also in accord with our calculations. Thus, in the series $Y{-}CH_2{-}X{-}CH_3^-$ (X = Br, I, and Y = H, Br, I), the α-iodine-substituted iodine ate anion $I{-}CH_2{-}I{-}CH_3^-$ is clearly the most stable species.

In summary, in agreement with our calculations of the ate complexes $[(CH_3)_{n+1}X]Li$, X = Se, Cl, Br, I, our predictions for the relative thermodynamic stabilities of ate anions $[(CH_3)_{n+1}X]^-$ provide strong evidence for ate complexes being the key intermediates (or transition states) in halogen-(metalloid)−lithium (magnesium halide) exchange reactions.[48] This theoretical evidence will surely assist chemists in further studies of these versatile reactions as well as of the ate complex intermediates.

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Supporting Information Available

MP2 total energies of all neutral and anionic systems under study and MP2-optimized structural parameters of the $[(CH_3)_{n+1}X]^-$ ate anions (4 pages). This material is available on the WWW or from the author.

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