

# Mixed Aggregates of Alkali Metal Compounds: Structure and Stability of “Superbase” Models

Thomas Kremer, Sjoerd Harder, Michael Junge, and Paul von Ragué Schleyer\*

Institut für Organische Chemie der Friedrich Alexander Universität Erlangen-Nürnberg,  
Henkestrasse 42, D-91054 Erlangen, Germany

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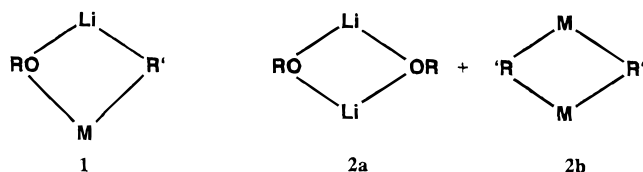
This *ab initio* study of the structure and stability of mixed alkali metal dimers models the transmetalation reactions which may lead to “superbasic reagents”. Such reagents are mixtures of RLi and MOR' (M = Na–Cs) and show strongly enhanced metalating power. The possible existence of mixed dimers RM/LiOR' (M = Li–Cs, R = H, CH<sub>3</sub>, NH<sub>2</sub>, OH, F, and R' = H) has been evaluated at reasonably high levels of *ab initio* theory by MP2 calculations, using the pseudopotential method for the heavier alkali metals (K–Cs) and the 6-31++G\*\* basis set for all other elements. Structures and energies of dimeric aggregates resulting from possible transmetalation reactions (metal exchange, anion exchange, anion and cation exchange and complete transmetalation) are calculated and compared. In almost every case, mixed aggregates are more stable than other possible combinations. The driving force favoring such mixed aggregates is the formation of stronger Li bonds and the reduction of electrostatic metal–metal repulsion. Additional BECKE3LYP calculations on the (MOH)<sub>2</sub>/(LiCH<sub>3</sub>)<sub>2</sub> (M = Na, K) equilibria using the 6-311+G\* basis sets for H, C, O, Li, and Na, as well as pseudopotentials for K were performed on the RHF optimized geometries. One O(CH<sub>3</sub>)<sub>2</sub> molecule on each of the metals decreases the differences in the relative stabilities of mixed aggregates and transmetalated compounds, relative to the unsolvated equilibria.

## Introduction

Organoalkali reagents are of fundamental importance in modern preparative organic chemistry,<sup>1,2</sup> but the complex mechanisms of their reactions are only poorly understood. Polar organometallics are “self-assembling” systems par excellence and solvate and self-associate into higher aggregates. The degree of complexity depends on the nature of the solvent as well as the metal and the counterion. Experimental mechanistic research is complicated not only by the complexity but also by the high reactivity and extreme moisture and oxygen sensitivity of these species.

Mixtures of organolithium compounds and alkali metal alkoxides ROM (M = Na, K, Rb, Cs) are known to be more reactive than the separate reagents.<sup>3</sup> Such “superbases”, “complex-bases”, or “LICKOR” reagents have been studied for more than 20 years, but the nature of the actual reactive species as well as the structure in solution remains controversial.<sup>4</sup> When *n*BuLi is mixed with KO*t*Bu in indifferent solvents (e.g. hexane) the heavier alkali-species (e.g. *n*BuK) precipitates, while the lithium alkoxide remains in solution.<sup>5</sup> As polar organometallics usually are associated, mixed aggregates **1** (i.e. species with different metals and anions) or separate aggregates **2a/2b** built from R'M and

ROLi oligomers may be involved. A recent article provides a good overview.<sup>6</sup>



A mixed *n*BuLi/LiO*t*Bu aggregate forms in heptane solution,<sup>7</sup> and the X-ray structure of a mixed *n*BuLi/LiO*t*Bu species was reported by Boche, Lochmann, *et al.*<sup>8</sup> A high field <sup>1</sup>H-NMR study of *n*BuLi together with LiO*n*Bu in THF, by McGarrity and Ogle, shows the existence of mixed tetramers *n*Bu<sub>x</sub>Li<sub>4</sub>(O*n*Bu)<sub>4-x</sub> (*x* =

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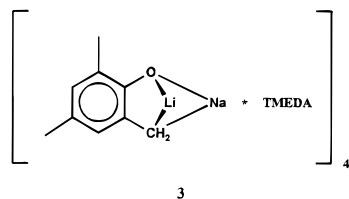
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1–4).<sup>9a</sup> Their rapid-injection NMR study revealed these mixed tetramers to be more reactive toward benzaldehyde than tetrameric *n*-buthyllithium alone.<sup>9b</sup> The involvement of mixed anion aggregates in aldol type reactions was established by Seebach's pioneering X-ray and NMR studies.<sup>10</sup> Williard and Collum demonstrated the existence of mixed aggregates of lithium amides/lithium halides and lithium amides/lithium enolates.<sup>11,12</sup> Williard also studied the structures of bis(trimethylsilyl)amide bases which contain two different alkali metals.<sup>13</sup> A phenyllithium/lithium bromide complex was isolated by Power.<sup>14</sup> Very recently Jackman et al. used solutions of methylithium with chiral lithium alkoxides for the enantioselective addition of alkyl-lithium compounds to aldehydes.<sup>15</sup>

Little information on mixed aggregates with different metals and different anions exists. Bauer and Lochmann studied trityllithium together with cesium 3-ethyl-3-heptoxide as a model "superbase" by <sup>6</sup>Li, <sup>1</sup>H, and <sup>133</sup>Cs, <sup>1</sup>H HOESY NMR spectroscopy.<sup>6</sup> A homogeneous THF solution of an equimolar combination of the two species results in metal exchange. Tritylcesium and lithium 3-ethyl-3-heptoxide are formed in stoichiometric amounts, and no mixed aggregate of type **1** could be detected within the NMR detection limits. Model MNDO calculations,<sup>6</sup> using monomeric tritylorganic compounds and tetrameric alkoxides, both solvated by dimethyl ether, predict transmetalation to be strongly exothermic, e.g. to give tritylpotassium/LiO*t*Bu. Formation of mixed aggregates of type **1** was calculated to be endothermic with respect to the transmetalated products, **2a** and **2b**, in agreement with the NMR observations.

Attempts to isolate crystals of superbasic mixtures for X-ray studies have failed.<sup>16</sup> When a heavier alkali alkoxide is added to an organolithium compound in an indifferent solvent like hexane, a microcrystalline precipitate of the pure organometallic compound of the heavier alkali metal forms; the lithium alkoxide resulting remains in solution.<sup>5</sup> However, the formation of mixed aggregates is not precluded, since the precipitate only represents the least soluble species. Very recently, the first X-ray structure of an lithium alkoxide/organosodium compound was published.<sup>17</sup> Although an intramolecular example, this lithium 4,6-dimethyl-2-(sodiummethyl)phenoxide (represented schematically by **3**) is a model for an intermolecular superbase and overcomes the problem of differing solubility of lithium alkoxides and the heavier alkali organometallic compound. In the solid state **3**·TMEDA is a tetrameric



aggregate. The central Li–O cube stresses the importance of Li–O bonding: Both, the Li and the Na atoms bridge between CH<sub>2</sub><sup>−</sup> and O<sup>−</sup>.

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*Ab initio* calculations provide a powerful alternative to study polar organometallic compounds.<sup>18,19</sup> They obviate many of the experimental difficulties and give instructive results. This paper describes a model *ab initio* study of the structure and the relative stabilities of mixed alkali metal systems. Alkali metal hydrides and methides serve as models for alkyl alkali metal derivatives, hydroxides for alkoxides, amines for dialkylamides, and fluorides for halogens. We computed the energies of interaggregate exchange, to find out if there is any evidence for mixed aggregates—and, if so, which combinations favor mixed aggregation. The effect of cation and of anion exchanges, considered separately, are compared with the exchange processes involving both anions and cations. Since a major interest is the nature of the activation of lithium compounds by heavier alkali metal alkoxides,<sup>3–5</sup> the exchanges with hydroxides are emphasized. As many other combinations of mixed species are possible in higher aggregates (e.g. tetramers), this study is limited to dimers as the first stage of a systematic investigation.

Since superbases are generated and used in THF or in the presence of TMEDA in hexane, we also modeled solvation effects, using one O(CH<sub>3</sub>)<sub>2</sub> molecule on each of the metals, on simplified superbasic systems (MOH)<sub>2</sub>/(LiCH<sub>3</sub>)<sub>2</sub> (M = Na, K).

### Computational Methods

Compared to all-electron calculations,<sup>18</sup> the use of pseudopotentials to replace core electrons for compounds of the heavier elements K, Rb, and Cs diminishes the computational costs considerably.<sup>20,21</sup> Core polarizability is significant for the heavier alkali-metals K–Cs.<sup>22,191</sup> Thus we used quasirelativistic nine-valence electron (valence plus *n* – 1 shell) effective core potentials (9 VE-ECP) for K, Rb, and Cs,<sup>23a</sup> as the implicit frozen-core approximation leads to large errors in a one-valence electron, effective core potential treatment. General<sup>18</sup> basis sets 6-31+G\* (basis A) and 6-31++G\*\* (basis B)

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Table 1. Computational Results on Monomers<sup>a</sup>

species	PG	//RHF basis A	//RMP2(full) basis B	ZPE [kcal/mol] <sup>b</sup>	BDE (MX) [kcal/mol] <sup>c</sup>	MX bond distance [Å] <sup>d</sup>
M = Li						
LiH	C <sub>∞v</sub>	-7.98096	-8.00324	2.0	58.0	1.625
LiCH <sub>3</sub>	C <sub>3v</sub>	-47.017360	-47.19491	22.1	43.7	2.004
LiNH <sub>2</sub>	C <sub>2v</sub>	-63.04986	-63.25989	15.7	69.3	1.754
LiOH	C <sub>∞v</sub>	-82.91403	-83.13955	8.4	100.0	1.598
LiF	C <sub>∞v</sub>	-106.94523	-107.14785	1.3	135.8	1.587
M = Na						
NaH	C <sub>∞v</sub>	-162.37246	-162.39605	1.7	45.3	1.915
NaCH <sub>3</sub>	C <sub>3v</sub>	-201.40317	-201.58498	21.6	29.4	2.342
NaNH <sub>2</sub>	C <sub>2v</sub>	-217.42623	-217.63930	14.9	45.6	2.121
NaOH	C <sub>∞v</sub>	-237.28828	-237.51472	7.8	72.9	1.953
NaF	C <sub>∞v</sub>	-261.32047	-261.52490	0.8	109.8	1.947
M = K						
KH	C <sub>∞v</sub>	-28.56073	-28.77145	1.4	42.6	2.261
KCH <sub>3</sub>	C <sub>3v</sub>	-67.59119	-67.95876	20.9	26.0	2.694
KNH <sub>2</sub>	C <sub>2v</sub>	-83.62177	-84.02189	14.6	46.3	2.421
KOH	C <sub>∞v</sub>	-103.48735	-103.89926	7.8	76.4	2.242
KF	C <sub>∞v</sub>	-127.51889	-127.91070	0.6	113.9	2.225
M = Rb						
RbH	C <sub>∞v</sub>	-24.31455	-24.47083	1.3	40.1	2.417
RbCH <sub>3</sub>	C <sub>3v</sub>	-63.34571	-63.65758	20.8	23.4	2.855
RbNH <sub>2</sub>	C <sub>2v</sub>	-79.37670	-79.72035	14.5	42.8	2.577
RbOH	C <sub>∞v</sub>	-99.24270	-99.59776	7.7	73.0	2.394
RbF	C <sub>∞v</sub>	-123.27450	-123.60957	0.5	113.0	2.375
M = Cs						
CsH	C <sub>∞v</sub>	-20.36872	-20.52357	1.2	42.3	2.546
CsCH <sub>3</sub>	C <sub>3v</sub>	-59.40372	-59.71043	20.6	26.4	2.949
CsNH <sub>2</sub>	C <sub>2v</sub>	-75.43770	-75.77701	14.4	49.4	2.662
CsOH	C <sub>∞v</sub>	-95.30459	-95.65549	7.6	80.4	2.478
CsF	C <sub>∞v</sub>	-119.33708	-119.66783	0.5	119.1	2.440

<sup>a</sup> Total energy in atomic units (au) (1 au = 627.5095 kcal/mol). Basis A: Li, Na, H, C, N, O, F (6-31+G\*), K, Rb, Cs: 9VE-ECP MWB 6s6p1d/4s4p1d. Basis B: Li, Na, H, C, N, O, F (6-31++G\*\*), K, Rb, Cs: 9VE-ECP MWB 6s6p2d/5s5p2d. Basis C: Li, Na, H, C, N, O, F (6-311++G(2d,2p)) K, Rb, Cs: 9VE-ECP MWB 6s6p2d/5s5p2d. <sup>b</sup> ZPE: zero point energy at the RHF basis A level. <sup>c</sup> BDE: homolytic MX bond dissociation energies at UBECKE3LYP (basis C)//UMP2(full) basis B + ΔZPE (basis A) (ref 33b). <sup>d</sup> //MP2(full) basis B.

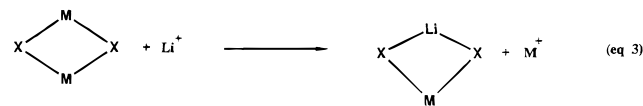
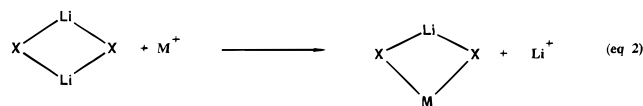
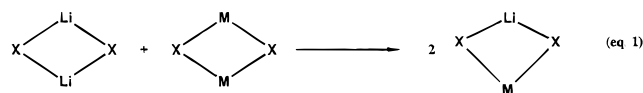
were used for Li, Na, H, C, N, O, and F. More flexible (3111/3111/1) (basis A) and (21111/21111/11) (basis B) valence basis sets, optimized with pseudopotentials,<sup>23a</sup> including a single or a double set of uncontracted d functions from Huzinaga *et al.*<sup>23b</sup> for the heavier alkali metals (K, Rb, Cs). All geometries were optimized with the symmetry given at Hartree-Fock (//RHF basis A) and second order correlated (//MP2(full) basis B) levels using the gradient optimization techniques implemented in the GAUSSIAN-92<sup>24a</sup> program package. All stationary points were characterized to be true minima by frequency analysis at the basis A level. Total energies and geometries are given in Tables 1–5. The energies in Tables 6, 9–11, and 14 at the highest level of theory employed in this study including zero point energy (scaled by 0.91)<sup>18</sup> (//MP2(full) (basis B) + ΔZPE (basis A)) are our final estimates and these are the energies discussed in the text.

The G92/DFT program<sup>24b</sup> was employed to study solvation effects. All molecules were optimized within the given symmetry at the RHF basis A level. Single-point calculations using BECKE3LYP density functional theory<sup>25</sup> (6-311+G\* for Li, Na, C, O, H, and (21111/21111/11) for K) on the RHF optimized geometries gave

the final energies (which include electron correlation effects). Total energies and selected bond distances for the dimethyl ether complexes are shown in Table 12; solvation energies are given in Table 13.

### Metal Exchange

We first consider the driving forces for the interaggregate exchange involving the metals in the (LiX)<sub>2</sub> and (MX)<sub>2</sub> dimers; eq 1 is an isodesmic reaction in which both the number and the types of bonds are conserved.<sup>18</sup>



The exothermicities of eq 1 vary from -0.5 to -3.5 kcal/mol (see Table 6, M = Na), and increase regularly on going down the group from sodium to cesium.

The exchange process (eq 1) can be separated into two independent reactions. A LiX dimer exchanges a lithium cation with a heavier alkali metal cation (eq 2). This is a nonisodesmic process in which two LiX bonds replace two MX bonds. Since LiX bonds are much stronger than analogous MX bonds (compare the homolytic bond dissociation energies, BDE in Table 1), such metal exchange is quite endothermic.

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**Table 2. Computational Results on Dimers<sup>a</sup>**

dimer	PG	//RHF basis A	//RMP2(full) basis B	ZPE [kcal/mol]	E DIM [kcal/mol] <sup>b</sup>	bond distances [Å]		
(LiX) <sub>2</sub>								
X = H	<i>D</i> <sub>2h</sub>	-16.03544	-16.08328	7.3	-48.2	Li	XX	LiLi
X = CH <sub>3</sub>	<i>C</i> <sub>2h</sub>	-94.10114	-94.46201	45.4	-45.3	2.131/2.099	3.640	2.153
X = NH <sub>2</sub> <sup>c</sup>	<i>D</i> <sub>2h</sub>	-126.20364	-126.62527	34.8	-66.2	1.924	3.115	2.260
X = OH	<i>D</i> <sub>2h</sub>	-165.93379	-166.37988	19.3	-63.3	1.775	2.781	2.206
X = F	<i>D</i> <sub>2h</sub>	-213.99315	-214.39720	4.6	-63.7	1.731	2.660	2.215
(NaX) <sub>2</sub>								
X = H	<i>D</i> <sub>2h</sub>	-324.80627	-324.85485	5.8	-39.4	NaX	XX	NaNa
X = CH <sub>3</sub>	<i>C</i> <sub>2h</sub>	-402.85863	-403.22201	43.3	-32.7	2.517/2.477	4.201	2.670
X = NH <sub>2</sub> <sup>c</sup>	<i>D</i> <sub>2h</sub>	-434.94581	-435.37277	32.3	-59.1	2.320	3.582	2.950
X = OH	<i>D</i> <sub>2h</sub>	-474.67427	-475.12374	17.2	-59.2	2.156	3.207	2.883
X = F	<i>D</i> <sub>2h</sub>	-522.73851	-523.14523	2.7	-61.0	2.093	3.039	2.879
(KX) <sub>2</sub>								
X = H	<i>D</i> <sub>2h</sub>	-57.18083	-57.60123	4.9	-36.6	KX	XX	KK
X = CH <sub>3</sub>	<i>C</i> <sub>2h</sub>	-135.23530	-135.96759	42.2	-31.4	2.473	3.380	3.610
X = NH <sub>2</sub> <sup>c</sup>	<i>D</i> <sub>2h</sub>	-167.31814	-168.11720	30.7	-46.1	2.848/2.810	4.470	3.468
X = OH	<i>D</i> <sub>2h</sub>	-207.05270	-207.87442	16.3	-47.6	2.658	3.922	3.588
X = F	<i>D</i> <sub>2h</sub>	-255.12137	-255.90273	2.0	-51.0	2.476	3.505	3.497
(RbX) <sub>2</sub>								
X = H	<i>D</i> <sub>2h</sub>	-48.68542	-48.99738	4.5	-35.0	RbX	XX	RbRb
X = CH <sub>3</sub>	<i>C</i> <sub>2h</sub>	-126.74198	-127.36302	41.9	-30.0	2.637	3.520	3.928
X = NH <sub>2</sub> <sup>c</sup>	<i>D</i> <sub>2h</sub>	-158.82131	-159.50820	30.1	-42.4	3.013/2.966	4.621	3.796
X = OH	<i>D</i> <sub>2h</sub>	-198.55639	-199.26606	15.8	-44.3	2.823	4.072	3.910
X = F	<i>D</i> <sub>2h</sub>	-246.62697	-247.29607	1.7	-48.3	2.636	3.653	3.801
(CsX) <sub>2</sub>								
X = H	<i>D</i> <sub>2h</sub>	-40.79173	-41.10222	4.3	-34.6	CsX	XX	CsCs
X = CH <sub>3</sub>	<i>C</i> <sub>2h</sub>	-118.85388	-119.46887	41.8	-30.1	2.782	3.562	4.274
X = NH <sub>2</sub> <sup>c</sup>	<i>D</i> <sub>2h</sub>	-150.93154	-151.61093	29.7	-35.7	3.144/3.082	4.643	4.148
X = OH	<i>D</i> <sub>2h</sub>	-190.66860	-191.37145	15.5	-38.0	2.950	4.080	4.262
X = F	<i>D</i> <sub>2h</sub>	-238.74127	-239.40292	1.5	-42.2	2.756	3.663	4.119

<sup>a</sup> See footnote a) in Table 1. <sup>b</sup> Dimerization energy at MP2(full) basis B/MP2(full) basis B level. (ref 33b). <sup>c</sup> NH<sub>2</sub> perpendicular to MNM plane.

**Table 3. Computational Results on Mixed-Metal Dimers<sup>a</sup>**

dimer	PG	//RHF basis A	//RMP2(full) basis B	ZPE	bond distances [Å]			
(LiX/NaX)								
X = H	<i>C</i> <sub>2v</sub>	-170.42259	-170.47042	6.6	LiX	NaX	LiNa	XX
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-248.48233	-248.84392	44.5	1.773	2.140	2.561	2.928
X = NH <sub>2</sub>	<i>C</i> <sub>2v</sub>	-280.57570	-280.99983	33.5	2.114	2.484	2.394	3.878
X = OH	<i>C</i> <sub>2v</sub>	-320.30459	-320.75322	18.1	1.914	2.328	2.616	3.298
X = F	<i>C</i> <sub>2v</sub>	-368.36831	-368.77422	3.8	1.752	2.179	2.531	2.965
(LiX/KX)								
X = H	<i>C</i> <sub>2v</sub>	-36.61516	-36.84865	6.2	LiX	KX	LiK	XX
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-114.67840	-115.22332	44.4	1.748	2.525	2.922	3.006
X = NH <sub>2</sub>	<i>C</i> <sub>2v</sub>	-146.76581	-147.37671	32.7	2.133	2.820	2.835	3.910
X = OH	<i>C</i> <sub>2v</sub>	-186.49615	-187.13227	17.6	1.903	2.668	2.946	3.376
X = F	<i>C</i> <sub>2v</sub>	-234.56728	-235.15744	3.5	1.743	2.513	2.850	3.044
(LiX/RbX)								
X = H	<i>C</i> <sub>2v</sub>	-32.37010	-32.54827	6.0	LiX	RbX	LiRb	XX
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-110.43428	-110.92344	44.4	1.746	2.697	3.074	3.050
X = NH <sub>2</sub>	<i>C</i> <sub>2v</sub>	-142.51897	-143.07370	32.5	2.110	2.893	2.997	3.940
X = OH	<i>C</i> <sub>2v</sub>	-182.24916	-182.82957	17.4	1.901	2.836	3.092	3.421
X = F	<i>C</i> <sub>2v</sub>	-230.32163	-230.85577	3.3	1.738	2.679	2.998	3.080
(LiX/CsX)								
X = H	<i>C</i> <sub>2v</sub>	-28.42641	-28.60199	5.9	LiX	CsX	LiCs	XX
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-106.49248	-106.97847	44.4	1.743	2.853	3.236	3.066
X = NH <sub>2</sub>	<i>C</i> <sub>2v</sub>	-138.57551	-139.12608	32.3	2.108	3.124	3.146	3.956
X = OH	<i>C</i> <sub>2v</sub>	-178.30626	-178.88298	17.2	1.900	2.977	3.238	3.440
X = F	<i>C</i> <sub>2v</sub>	-226.37901	-226.90946	3.2	1.737	2.807	3.142	3.086

<sup>a</sup> See footnotes in Tables 1 and 2.

In the other reaction (eq 3), a heavier alkali metal dimer exchanges M<sup>+</sup> for Li<sup>+</sup>, replacing two MX bonds for LiX bonds. As expected from the bond dissociation energies, this process is exothermic.

The metal exchange in eq 1 is exothermic because of

the changes in the structure and bonding energy in the mixed dimer. Replacing Li in an LiX dimer by a heavier alkali metal M (eq 2) results in shorter (and stronger) LiX bonds (see Table 6) in the remaining LiX<sub>2</sub><sup>-</sup> moiety. Replacing M in a MX dimer by Li (eq 3), results in an

**Table 4. Computational Results on Mixed-Anion Dimers<sup>a</sup>**

dimer	PG	//RHF basis A	//RMP2(full) basis B	ZPE	bond distances [Å]					
(LiOH/LiX)										
X = H	<i>C</i> <sub>2v</sub>	-90.98727	-91.23405	13.6	LiX	LiO	LiLi	XO		
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-130.01900	-130.42375	32.4	2.108/2.130	1.753/1.750	2.170	3.196		
X = NH <sub>2</sub>	<i>C</i> <sub>2v</sub>	-146.06962	-146.50441	27.2	1.926	1.765	2.228	2.940		
X = F	<i>C</i> <sub>2v</sub>	-189.96413	-190.38926	12.0	1.728	1.777	2.214	2.716		
(NaOH/NaX)										
X = H	<i>C</i> <sub>2v</sub>	-399.74190	-399.99077	11.6	NaX	NaO	NaNa	XO		
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-438.76727	-439.17378	30.3	2.478/2.519	2.149/2.137	2.780	3.694		
X = NH <sub>2</sub>	<i>C</i> <sub>2v</sub>	-454.81042	-455.24881	24.8	2.315	2.157	2.923	3.381		
X = F	<i>C</i> <sub>2v</sub>	-498.70668	-499.13487	10.0	2.089	2.157	2.885	3.116		
(KOH/KX)										
X = H	<i>C</i> <sub>2v</sub>	-132.11879	-132.73960	10.6	KX	KO	KK	XO		
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-171.14489	-171.92172	29.2	2.473	2.471	3.560	3.431		
X = NH <sub>2</sub>	<i>C</i> <sub>2v</sub>	-187.18557	-187.99614	23.5	2.817/2.872	2.459/2.472	3.846	3.991		
X = F	<i>C</i> <sub>2v</sub>	-231.08717	-231.88880	9.2	2.655	2.477	3.522	3.699		
(RbOH/RbX)										
X = H	<i>C</i> <sub>2v</sub>	-123.62305	-124.13317	10.2	RbX	RbO	RbRb	XO		
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-162.65001	-163.31515	28.8	2.635	2.633	3.870	3.574		
X = NH <sub>2</sub>	<i>C</i> <sub>2v</sub>	-178.68899	-179.38739	23.0	2.973/3.038	2.621/2.632	3.806	4.136		
X = F	<i>C</i> <sub>2v</sub>	-222.59179	-223.28124	8.8	2.819	2.637	3.864	3.848		
(CsOH/CsX)										
X = H	<i>C</i> <sub>2v</sub>	-115.73208	-116.23755	9.8	CsX	CsO	CsCs	XO		
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-154.76201	-155.42059	28.6	2.788	2.753	4.204	3.609		
X = NH <sub>2</sub>	<i>C</i> <sub>2v</sub>	-170.80024	-171.49145	22.6	3.088/31.70	2.740/2.752	4.142	4.148		
X = F	<i>C</i> <sub>2v</sub>	-214.70503	-215.38737	8.5	2.948	2.756	4.196	3.858		
					2.665	2.760	4.144	3.499		

<sup>a</sup> See footnotes in Tables 1 and 2.**Table 5. Computational Results on Mixed Aggregates<sup>a</sup>**

dimer	PG	//RHF basis A	//RMP2(full) basis B	ZPE	bond distances [Å]					
(LiOH/NaX)										
X = H	<i>C</i> <sub>s</sub>	-245.36598	-245.61347	12.6	LiX	NaX	LiNa	LiO	NaO	XO
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-284.39496	-284.80023	31.4	1.778	2.112	2.549	1.742	2.169	2.920
X = NH <sub>2</sub>	<i>C</i> <sub>s</sub>	-300.44135	-300.87795	26.0	2.121	2.482	2.459	1.731	2.157	3.408
X = F	<i>C</i> <sub>s</sub>	-344.33748	-344.76546	11.1	1.915	2.319	2.572	1.747	2.174	3.119
					1.703	2.109	2.533	1.761	2.165	2.886
(LiOH/KX)										
X = H	<i>C</i> <sub>s</sub>	-111.55944	-111.99219	12.2	LiX	KX	LiK	LiO	KO	XO
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-150.59025	-151.17980	31.2	1.744	2.521	2.899	1.742	2.494	2.999
X = NH <sub>2</sub>	<i>C</i> <sub>s</sub>	-166.63308	-167.25617	25.4	2.096	2.853	2.844	1.736	2.478	3.455
X = F	<i>C</i> <sub>s</sub>	-210.53226	-211.14592	10.7	1.904	2.662	2.891	1.736	2.509	3.203
					1.697	2.434	2.852	1.752	2.503	2.967
(LiOH/RbX)										
X = H	<i>C</i> <sub>s</sub>	-107.31375	-107.69048	12.0	LiX	RbX	LiRb	LiO	RbO	XO
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-146.34496	-146.87842	31.1	1.741	2.694	3.046	1.738	2.657	3.041
X = NH <sub>2</sub>	<i>C</i> <sub>s</sub>	-162.38637	-162.95330	25.2	2.095	3.017	2.997	1.735	2.642	3.492
X = F	<i>C</i> <sub>s</sub>	-206.28625	-206.84379	10.6	1.902	2.828	3.036	1.732	2.675	3.245
					1.695	2.597	3.001	1.749	2.670	3.007
(LiOH/CsX)										
X = H	<i>C</i> <sub>s</sub>	-103.37068	-103.74379	11.8	LiX	CsX	LiCs	LiO	CsO	XO
X = CH <sub>3</sub>	<i>C</i> <sub>s</sub>	-142.40274	-142.93261	31.0	1.734	2.863	3.196	1.737	2.779	3.054
X = NH <sub>2</sub>	<i>C</i> <sub>s</sub>	-158.44315	-159.00603	25.0	2.089	3.158	3.145	1.732	2.766	3.497
X = F	<i>C</i> <sub>s</sub>	-202.34367	-202.89726	10.4	1.900	2.968	3.182	1.728	2.806	3.255
					1.693	2.719	3.142	1.745	2.803	3.013

<sup>a</sup> See footnotes in Tables 1 and 2.

increase in M–X bond distance and weakening of MX bonds in the remaining MX<sub>2</sub><sup>-</sup> moiety (see Table 6). The largest geometrical changes, however, are observed for the nonbonding XX and MLi distances (compare Tables 2 and 3).

Although a purely electrostatic model may not be adequate to describe alkalimetal organic aggregates the qualitative influence of geometrical changes on the overall mixing energies can be evaluated. Such electrostatic models, pioneered by Streitwieser,<sup>26a</sup> by Bushby<sup>26b-d</sup> and by Schleyer,<sup>26e</sup> reproduce the *ab initio* dimerization energies of organolithium compounds at

lower levels of theory (e.g. MP2/6-31G\*\*/3-21G) well,<sup>26a</sup> but fail in other cases (e.g. for tetramers).<sup>19m</sup> Anions and cations are replaced by negative and positive unit point charges, respectively, a model which is justified by the highly ionic nature of alkali metal compounds.<sup>27,28</sup> Polarization is neglected although it certainly is significant, especially with the heavier alkali metals K–Cs.<sup>26f</sup> Coulomb energies for attractive interactions (cation–anion) and repulsive interactions (cation–cation and anion–anion) are based on *ab initio* geometries (Tables 1–3) and summarized in Table 7. Mixing energies for the metal hydrides and fluorides are

**Table 6. Reaction Energies [kcal/mol] and Changes in LiX and MX Distances for Eqs 1–3 at MP2(full) (+ $\Delta ZPE$ )<sup>a</sup>**

	eq 1 <sup>b</sup>	eq 2 <sup>c</sup>	eq 3 <sup>d</sup>	$\Delta LiX$ [Å]	$\Delta MX$ [Å]
M = Na					
X = H	-1.6	23.2	-24.8	-0.018	+0.009
X = CH <sub>3</sub>	-0.5	27.2	-27.7	-0.015/+0.017	-0.033/+0.007
X = NH <sub>2</sub>	-1.1	30.6	-31.7	-0.010	+0.008
X = OH	-2.0	31.5	-33.5	-0.023	+0.023
X = F	-3.5	29.5	-33.0	-0.025	+0.019
M = K					
X = H	-7.8	44.3	-52.1	-0.043	+0.052
X = CH <sub>3</sub>	-9.6	46.9	-56.5	+0.002/+0.034	-0.028/+0.010
X = NH <sub>2</sub>	-7.0	52.1	-59.1	-0.021	+0.010
X = OH	-6.8	51.9	-58.7	-0.032	+0.037
X = F	-9.0	47.5	-56.5	-0.033	+0.040
M = Rb					
X = H	-9.8	49.9	-59.7	-0.045	+0.060
X = CH <sub>3</sub>	-12.4	52.4	-64.8	-0.021/+0.011	-0.020/-0.073
X = NH <sub>2</sub>	-8.7	59.4	-68.1	-0.023	+0.013
X = OH	-8.6	58.9	-67.5	-0.037	+0.043
X = F	-11.2	53.9	-65.1	-0.035	+0.047
M = Cs					
X = H	-11.4	54.1	-65.5	-0.048	+0.071
X = CH <sub>3</sub>	-14.9	55.8	-70.7	-0.023/+0.009	-0.020/+0.042
X = NH <sub>2</sub>	-9.9	64.3	-74.2	-0.024	+0.027
X = OH	-9.5	63.2	-72.7	-0.038	+0.051
X = F	-11.5	58.1	-69.6	-0.037	+0.062

<sup>a</sup> See footnotes in Tables 1 and 2. <sup>b</sup> (LiX)<sub>2</sub> + (MX)<sub>2</sub> → 2(LiMX<sub>2</sub>) (eq 1). <sup>c</sup> (LiX)<sub>2</sub> + M<sup>+</sup> → (LiMX<sub>2</sub>) + Li<sup>+</sup> (eq 2). <sup>d</sup> (MX)<sub>2</sub> + Li<sup>+</sup> → (LiMX<sub>2</sub>) + M<sup>+</sup> (eq 3).

**Table 7. Coulomb Energies [kcal/mol] for Hydrides and Fluorides Computed with an Electrostatic Point Charge Model<sup>a</sup>**

species	$E_{attr}$	$E_{rep}$ X-X	$E_{rep}$ M-M'	$E_{rep}$ tot.	$E_{coulomb}$	$E_{dim.}^b$
LiH	-204.4				-204.4	
NaH	-173.4				-173.4	
KH	-146.9				-146.9	
RbH	-137.4				-137.4	
CsH	-130.4				-130.4	
LiF	-209.3				-209.3	
NaF	-170.6				-170.6	
KF	-149.3				-149.3	
RbF	-139.8				-139.8	
CsF	-136.1				-136.1	
(LiH) <sub>2</sub>	-741.7	121.1	144.1	265.2	-476.5	-67.7 (-48.2)
(NaH) <sub>2</sub>	-623.4	104.5	116.9	221.4	-402.0	-55.2 (-39.4)
(KH) <sub>2</sub>	-537.2	98.3	92.0	190.3	-346.9	-53.1 (-36.6)
(RbH) <sub>2</sub>	-503.8	94.3	84.5	178.8	-325.0	-50.2 (-35.0)
(CsH) <sub>2</sub>	-477.5	93.2	77.7	170.9	-306.6	-45.8 (-34.6)
(LiF) <sub>2</sub>	-767.4	124.8	150.0	274.8	-492.6	-74.0 (-63.7)
(NaF) <sub>2</sub>	-634.7	109.3	115.4	224.7	-410.0	-68.8 (-61.0)
(KF) <sub>2</sub>	-553.3	102.1	94.0	196.1	-357.2	-58.6 (-51.0)
(RbF) <sub>2</sub>	-519.3	98.3	86.5	184.8	-334.5	-54.9 (-48.3)
(CsF) <sub>2</sub>	-497.3	98.7	80.1	178.8	-318.5	-46.3 (-42.2)
(LiNaH <sub>2</sub> )	-685.0	113.4	129.7	243.1	-441.9	
(LiKH <sub>2</sub> )	-643.0	110.5	113.7	224.2	-418.8	
(LiRbH <sub>2</sub> )	-626.7	108.9	108.0	216.9	-409.8	
(LiCsH <sub>2</sub> )	-613.9	108.3	102.7	211.0	-402.9	
(LiNaF <sub>2</sub> )	-703.8	117.6	131.3	248.9	-454.9	
(LiKF <sub>2</sub> )	-663.3	114.7	116.4	231.1	-432.2	
(LiRbF <sub>2</sub> )	-646.6	113.2	110.6	223.8	-422.8	
(LiCsF <sub>2</sub> )	-635.1	113.0	105.6	218.6	-416.5	

<sup>a</sup> Electrostatic Coulomb energies (refs 26e, 35) have been calculated according to  $E = 1/4\pi\epsilon_0 qq'/r$  [kcal/mol] = 332.1/r [kcal/mol], where  $\epsilon_0 = 8.8542 \times 10^{-12}$  F m<sup>-1</sup>,  $q$  = unit charge,  $r$  = interatomic distance [Å] at the MP2(full) optimized geometries. <sup>b</sup> Dimerization energy calculated from the increase in electrostatic energy on going from two monomers to a dimer (/MP2(full) basis B *ab initio* results are given in parenthesis).

calculated as the differences in Coulomb energies for all the species involved in metal exchange (eq 1). Hydrides and fluorides both have anions in which the center of negative charge is close to the position of the

**Table 8. Energy Differences [kcal/mol] for Metal Exchange (eq 1) Computed with an Electrostatic Point Charge Model<sup>a</sup>**

	$\Delta E_{attr}$	$\Delta E_{rep}$ X-X	$\Delta E_{rep}$ M-M'	$\Delta E_{rep}$ tot	$\Delta E_{tot}^b$
M = Na					
X = H	-4.9	+1.2	-1.6	-0.4	-5.3 (-1.6)
X = F	-5.5	+1.1	-2.8	-1.7	-7.2 (-3.5)
M = K					
X = H	-7.1	+1.6	-8.7	-7.1	-14.2 (-7.8)
X = F	-5.9	+2.5	-11.2	-8.7	-14.6 (-9.0)
M = Rb					
X = H	-7.9	+2.4	-12.6	-10.2	-18.1 (-9.8)
X = F	-6.5	+3.3	-15.3	-12.0	-18.5 (11.2)
M = Cs					
X = H	-8.6	+2.3	-16.4	-14.1	-22.7 (-11.4)
X = F	-5.5	+2.5	-18.9	-16.4	-21.9 (-11.5)

<sup>a</sup> See Table 7 for details. <sup>b</sup> /MP2(full) +  $\Delta ZPE$  *ab initio* results are given in parentheses.

nuclei. The results, also separated into attractive and repulsive contributions, are summarized in Table 8.

Metal mixing (eq 1) results in more favorable overall attractive contributions ( $\Delta E_{attr}$ , Table 8). However, these, like the small positive anion–anion repulsion contribution ( $\Delta E_{rep}$  XX), are rather constant in the entire Na–Cs series. These terms compensate to some extent. Hence, the variations in total electrostatic energies ( $\Delta E_{tot}$ ) in Table 8 are dominated by the metal–metal repulsion term ( $\Delta E_{rep}$  MM'). This increases in magnitude considerably from –2.8 kcal/mol for M = Na to –18.9 kcal/mol for the M = Cs, X = F system. The total electrostatic energy changes for the exchange process in eq 1 are higher than the calculated *ab initio* reaction energies (shown in parenthesis in the last column of Table 8, especially for the heavier alkali metals K–Cs, where polarization effects (which were not included in the treatment) can be expected to be most significant.

We also recalculated the dimerization energies, as the increase in Coulomb energy on going from two monomers to one dimer for the alkali metal hydrides and fluorides. The energies are given in Table 7, together with *ab initio* (/MP2(full) basis B) data. In contradiction to earlier results,<sup>26e</sup> the electrostatic dimerization energies are too exothermic. Diffuse augmented basis sets are essential for the description of free anions.<sup>18</sup> The 6-31++G\*\* basis set used in this paper gives energies of aggregation which reproduce experimental values within the limits of the experiment.<sup>33b</sup> The discrepancy between high level *ab initio* calculations and electrostatic point charge models emphasizes that such models are an oversimplification; nevertheless, they are helpful to describe dimeric alkali metal compounds qualitatively.

To summarize, Na and K dimer exchange processes are exothermic due to a combination of LiX bond

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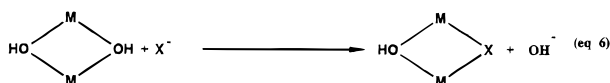
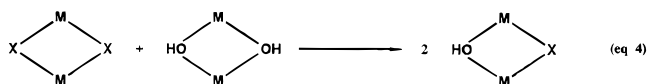
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strengthening and the decrease of MM' repulsions, whereas the exchange energies for the heavier alkali metal dimers (Rb, Cs) are dominated by the decrease in the MM' repulsions.

### Anion Exchange

The energies (Table 9) of the exchange of anions from the (MX)<sub>2</sub> and (MOH)<sub>2</sub> dimers (eq 4), are much smaller than the energies for metal exchange (eq 1, Table 6). Anion exchange results in smaller changes in geometry (compare bonded and nonbonded distances in Tables 2 and 4) because the anion radii in the H, CH<sub>3</sub>, NH<sub>2</sub>, OH, F series vary less than the metal radii in the Li–Cs series (cations radii range from 0.73 to 2.02 Å).<sup>30</sup> Anion exchange energies decrease along the Li–Cs series, *i.e.* with decreasing importance of MX bond strength. The very small reaction energies for anion exchange complicate the qualitative analysis of the bonding in mixed anion aggregates.

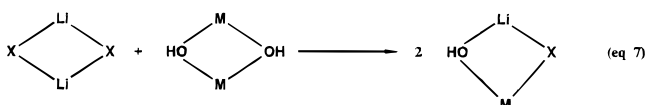


The anion exchange of eq 4 can be separated into two individual exchange processes, eqs 5 and 6. Exchange of one X<sup>-</sup> anion in a MX dimer by OH<sup>-</sup> is exothermic (eq 5, Table 9). The exothermicity is largest for hydrides and for methyl compounds, *i.e.* those species in which the MX bond is considerably weaker than the MOH bond (compare BDE's for MH, MCH<sub>3</sub> and MOH in Table 1).

The second exchange process (OH<sup>-</sup> is replaced by X<sup>-</sup> in (MOH)<sub>2</sub> to give (MOH/MX) and OH<sup>-</sup>, (eq 6, Table 9) is endothermic. The endothermicity is largest for X = H, CH<sub>3</sub>, as they form the weakest MX bonds. The total energies for eq 6 are smaller than those calculated for eq 5, but the difference is mostly small. Adding eqs 5 and 6 leads to the slightly exothermic anions exchange reaction of eq 4.

### Metal and Anion Exchange

In contrast to metal exchange (eq 1) and to anion exchange (eq 4), reactions involving mixing of both the metal cations and the anions (eq 7) are not isodesmic. Thus zero point vibrational energies must be included to obtain accurate results.<sup>18</sup>



Interaggregate exchange of anions and cations within (LiX)<sub>2</sub> and (MOH)<sub>2</sub> dimers results in the formation of two LiO and two MX contacts at the expense of two MO

**Table 9. Reaction Energies [kcal/mol] and Changes in MX and MO Distances for Eqs 4–6 at MP2(full) (+ΔZPE)<sup>a</sup>**

	eq 4 <sup>b</sup>	eq 5 <sup>c</sup>	eq 6 <sup>d</sup>	ΔMX [Å]	ΔMO [Å]
M = Li					
X = H	-2.6	-31.9	29.3	-0.013	-0.016
X = CH <sub>3</sub>	-3.4	-26.3	22.9	-0.001/+0.009	-0.022/-0.025
X = NH <sub>2</sub>	-2.0	-6.5	4.5	+0.002	-0.010
X = F	-0.8	-6.3	5.5	-0.003	+0.002
M = Na					
X = H	-1.7	-23.0	21.3	-0.014	-0.003
X = CH <sub>3</sub>	-1.0	-20.0	19.0	+0.002/+0.001	-0.007/-0.019
X = NH <sub>2</sub>	-0.6	-4.4	3.8	-0.005	+0.001
X = F	-0.4	-4.8	4.4	-0.004	+0.001
M = K					
X = H	-2.2	-24.6	22.4	+/-0.00	-0.005
X = CH <sub>3</sub>	-1.0	-21.5	22.5	+0.024/+0.007	-0.004/-0.017
X = NH <sub>2</sub>	-0.4	-6.0	5.6	-0.003	+0.001
X = F	-0.2	-2.7	2.5	-0.003	+0.002
M = Rb					
X = H	-1.7	-23.0	21.3	-0.002	-0.003
X = CH <sub>3</sub>	-0.9	-20.4	19.5	+0.025/+0.007	-0.004/-0.015
X = NH <sub>2</sub>	-0.2	-6.1	5.9	-0.004	+0.001
X = F	-0.1	-2.2	2.1	-0.005	+0.003
M = Cs					
X = H	-1.1	-22.9	21.8	+0.006	-0.003
X = CH <sub>3</sub>	-0.6	-20.2	19.6	+0.026/+0.006	-0.004/-0.016
X = NH <sub>2</sub>	-0.3	-6.9	6.6	-0.002	+/-0.00
X = F	-0.2	-1.9	1.7	-0.006	+0.004

<sup>a</sup> See footnotes in Tables 1 and 2. <sup>b</sup> (MX)<sub>2</sub> + (MOH)<sub>2</sub> → 2(M<sub>2</sub>OHX) (eq 4). <sup>c</sup> (MX)<sub>2</sub> + OH<sup>-</sup> → (M<sub>2</sub>OHX) + X<sup>-</sup> (eq 5). <sup>d</sup> (MOH)<sub>2</sub> + X<sup>-</sup> → (M<sub>2</sub>OHX) + OH<sup>-</sup> (eq 6).

**Table 10. Reaction Energies [kcal/mol] and Changes in LiX and MO Distances for Eq 7<sup>a</sup> at MP2(full) (+ΔZPE)<sup>b</sup>**

	ΔE (kcal/mol)	ΔLiX (Å)	ΔMO (Å)
M = Na			
X = H	-11.9	-0.013	+0.013
X = CH <sub>3</sub>	-9.1	-0.010/+0.022	+0.001
X = NH <sub>2</sub>	-4.3	-0.009	+0.018
X = F	-5.9	-0.028	+0.009
M = K			
X = H	-16.0	-0.047	+0.018
X = CH <sub>3</sub>	-13.9	-0.035/-0.003	+0.002
X = NH <sub>2</sub>	-8.2	-0.020	+0.033
X = F	-12.2	-0.034	+0.027
M = Rb			
X = H	-19.0	-0.050	+0.021
X = CH <sub>3</sub>	-17.1	-0.036/-0.004	+0.006
X = NH <sub>2</sub>	-9.8	-0.022	+0.039
X = F	-14.5	-0.036	+0.034
M = Cs			
X = H	-19.8	-0.057	+0.023
X = CH <sub>3</sub>	-18.9	-0.042/-0.010	+0.010
X = NH <sub>2</sub>	-9.6	-0.024	+0.050
X = F	-16.2	-0.038	+0.047

<sup>a</sup> (LiX)<sub>2</sub> + (MOH)<sub>2</sub> → (LiMOHX) (eq 7). <sup>b</sup> See footnotes in Tables 1 and 2.

and two LiX bonds. Metal-exchange and anion-exchange processes in (LiX)<sub>2</sub> as well as in (MOH)<sub>2</sub> are involved. The energies of eq 7 should be related to the sum of the calculated metal exchange energies (eq 1) and anion-exchange energies (eq 4).

The LiX and LiO bond lengths in the mixed dimers (LiOH/MX) are shortened with respect to those in (LiX)<sub>2</sub> and in (LiOH)<sub>2</sub>. On the other hand, MO and MX bonds in the mixed dimers (LiOH/MX) are generally longer than those in (MX)<sub>2</sub> and (MOH)<sub>2</sub> (except MX distances for LiOH/NaH and LiOH/NaNH<sub>2</sub>). The amount of LiX/LiO bond shortening and MX/MO bond elongation increases steadily on going down the group from Na to

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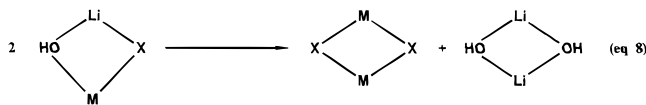
**Table 11. Reaction Energies [kcal/mol] and Changes in LiO and MX Distances for Eq 8<sup>a</sup> at MP2(full) (+ΔZPE)<sup>b</sup>**

	ΔE (kcal/mol)	ΔLiO (Å)	ΔMX (Å)
M = Na			
X = H	-4.9	0.033	0.019
X = CH <sub>3</sub>	-0.9	0.044	0.035/-0.005
X = NH <sub>2</sub>	2.0	0.028	0.001
X = F	3.6	0.014	-0.016
M = K			
X = H	2.1	0.033	-0.048
X = CH <sub>3</sub>	7.6	0.039	-0.043/-0.005
X = NH <sub>2</sub>	9.6	0.039	-0.004
X = F	5.8	0.023	-0.033
M = Rb			
X = H	2.3	0.037	-0.057
X = CH <sub>3</sub>	8.7	0.040	-0.051/-0.004
X = NH <sub>2</sub>	11.6	0.043	-0.005
X = F	7.3	0.026	-0.039
M = Cs			
X = H	3.3	0.038	-0.081
X = CH <sub>3</sub>	10.3	0.043	-0.076/-0.014
X = NH <sub>2</sub>	13.3	0.047	-0.018
X = F	7.3	0.030	-0.048

<sup>a</sup> 2(LiMOHX) → (LiOH)<sub>2</sub> + (MX)<sub>2</sub> (eq 8). <sup>b</sup> See footnotes in Tables 1 and 2.

Cs. A mixed aggregate (LiOH/MX) can be viewed as a bent triple anion X–Li–OH<sup>-</sup> interacting with a heavier metal cation M<sup>+</sup>. Bond distances in this triple anion depend strongly on the cation M<sup>+</sup> and decrease along the series M = Na–Cs.

All exchanges (eq 7, Table 10) are exothermic. In each set the reaction energy order in X is H > CH<sub>3</sub> > F > NH<sub>2</sub>. The perpendicular conformation of the NH<sub>2</sub> group enables multicenter interaction (the filled p-orbital on nitrogen is polarized by both alkali metals). This is most important in LiNH<sub>2</sub> aggregates;<sup>26e,29</sup> exchange with higher alkali metals reduces this favorable interaction. The greater stability of mixed aggregates is due to decreased cation–cation repulsion and increased lithium–anion attraction.



Reaction energies for disproportionation of the mixed aggregate to the fully transmetalated products also have been calculated (eq 8, Table 11). This disproportionation is exothermic only for (LiOH/NaH) and for (LiOH/NaCH<sub>3</sub>). All other species prefer mixed aggregates at equilibrium.

### Solvation Effects

Superbases are normally generated in THF or in the presence of TMEDA. A mixed solution of an organolithium compound and an heavier alkali alkoxide in an indifferent solvent like hexane gives a microcrystalline precipitate of the pure organometallic compound of the heavier alkali metal, whereas the resulting lithium alkoxide remains in solution.<sup>5</sup> In THF however, clear solutions with superbasic qualities are obtained. This observation stresses the importance of solvation effects on the mixed alkali compounds. To what extent does solvation influence the equilibria we have presented in this paper?

We modeled the effects of solvents by calculating the (MOH)<sub>2</sub>/(LiCH<sub>3</sub>)<sub>2</sub> (M = Na, K) equilibria, involving mixed aggregates (LiOH/MCH<sub>3</sub>) and transmetalated products (LiOH)<sub>2</sub>/(MCH<sub>3</sub>)<sub>2</sub> with one O(CH<sub>3</sub>)<sub>2</sub> molecule on each metal. Table 12 gives the total energies and Table 13 the total solvation energies. Figure 1 shows the species involved, together with relative energies.

The dimethyl ether complexation energies (see Table 13) decrease regularly on going from Li to K. For the dimeric methyl compounds, complexation is more exothermic than for the dimeric hydroxides. Solvation is less important in dimers with strong MX bonds and high dimerization energies (e.g. the alkoxides). Therefore transmetalation involving a mixture of (LiCH<sub>3</sub>)<sub>2</sub>·2O(CH<sub>3</sub>)<sub>2</sub> and (MOH)<sub>2</sub>·2O(CH<sub>3</sub>)<sub>2</sub> to give (LiOH)<sub>2</sub>·2O(CH<sub>3</sub>)<sub>2</sub> and (MCH<sub>3</sub>)<sub>2</sub>·2O(CH<sub>3</sub>)<sub>2</sub> results in a loss of solvation

**Table 12. Total Energies and Selected Bond Distances<sup>a</sup>**

dimer	PG	//RHF basis A		bond distances <sup>c</sup>							
		BECKE3LYP basis D <sup>b</sup>	//RHF basis A	MC	MO	MO <sub>solv</sub>	MM	CC	OO	CO	
(LiCH <sub>3</sub> ) <sub>2</sub>	C <sub>2h</sub>	-94.10114	-94.89812	2.147			2.189	3.685			
(LiCH <sub>3</sub> ) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	C <sub>2h</sub>	-402.28712	-405.08241	2.139		1.962	2.260	3.739			
(NaCH <sub>3</sub> ) <sub>2</sub>	C <sub>2h</sub>	-402.85863	-404.41722	2.188			2.707	4.221			
(NaCH <sub>3</sub> ) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	C <sub>2h</sub>	-711.03317	-714.58989	2.511			2.745	4.267			
(KCH <sub>3</sub> ) <sub>2</sub>	C <sub>2h</sub>	-135.23530	-136.46160	2.503			3.522	4.591			
(KCH <sub>3</sub> ) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	C <sub>2h</sub>	-443.39906	-446.62300	2.539		2.324	3.529	4.702			
(LiOH) <sub>2</sub>	D <sub>2h</sub>	-165.93379	-166.91953	2.914	1.778		2.255		2.749		
(LiOH) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	D <sub>2h</sub>	-474.11274	-477.09672	2.872	1.807	1.964	2.313		2.777		
(NaOH) <sub>2</sub>	D <sub>2h</sub>	-474.67427	-476.41890	2.955	2.134		2.820		3.203		
(NaOH) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	D <sub>2h</sub>	-782.84403	-786.58813	2.924	2.158	2.333	2.844		3.248		
(KOH) <sub>2</sub>	D <sub>2h</sub>	-207.05270	-208.46651	2.955	2.498		3.473		3.593		
(KOH) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	D <sub>2h</sub>	-515.21018	-518.62276	2.924	2.523	2.834	3.454		3.679		
(LiCH <sub>3</sub> /NaOH)	C <sub>s</sub>	-284.39496	-285.66544	2.148	1.755		2.450				3.417
(LiCH <sub>3</sub> /NaOH)·2O(CH <sub>3</sub> ) <sub>2</sub>	C <sub>s</sub>	-592.57004	-595.83947	2.516	2.127		2.577				3.449
(LiCH <sub>3</sub> /KOH)	C <sub>s</sub>	-150.59025	-151.69325	2.222	1.803	1.991	2.577				3.449
(LiCH <sub>3</sub> /KOH)·2O(CH <sub>3</sub> ) <sub>2</sub>	C <sub>s</sub>	-458.756027	-461.85905	2.513	2.133	2.324	2.577				3.449
				2.127	1.766		2.871				3.513
				2.931	2.469		2.972				3.528
				2.200	1.819	2.009	2.972				3.528
				2.901	2.474	2.804					

<sup>a</sup> See footnotes in Tables 1 and 2. <sup>b</sup> Basis D: Li, Na, H, C, O (6-311+G\*), K: 9VE-ECP MWB 6s6p2d/5s5p2d. <sup>c</sup> //RHF basis A.



**Table 13. Solvation Energies  $E_{\text{solv}}$  [kcal/mol]<sup>a</sup>**

dimer	//RHF basis A	BECKE3LYP basis D //RHF basis A
(LiCH <sub>3</sub> ) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	-34.1	-29.4
(NaCH <sub>3</sub> ) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	-26.9	-22.1
(KCH <sub>3</sub> ) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	-20.1	-15.0
(LiOH) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	-29.6	-24.9
(NaOH) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	-23.9	-19.9
(KOH) <sub>2</sub> ·2O(CH <sub>3</sub> ) <sub>2</sub>	-16.2	-11.8
(LiCH <sub>3</sub> /NaOH)·2O(CH <sub>3</sub> ) <sub>2</sub>	-27.2	-22.9
(LiCH <sub>3</sub> /KOH)·2O(CH <sub>3</sub> ) <sub>2</sub>	-21.6	-17.8

<sup>a</sup> See footnotes in Tables 1, 2, and 12.

energy. As stated above, mixed aggregates are favored due to a synergistic effect, relative to the two individual homo dimers. The strong bonds get stronger and the weak bonds get weaker, but not as much as the strong bonds get stronger. Thus, mixed aggregates have the smallest solvation energies of all lithium aggregates in this study.

The influence of dimethyl ether complexation on the calculated equilibria is shown in Figure 1. For the (LiCH<sub>3</sub>)<sub>2</sub> and (NaOH)<sub>2</sub> combination, solvation decreases the energy difference between mixed aggregates and transmetalated compounds but does not change the order. For the composition (LiCH<sub>3</sub>)<sub>2</sub> and (KOH)<sub>2</sub> complexation also reduces the difference in relative energies and changes the order. Transmetalation is now favored by 1 kcal/mol relative to mixed aggregates.

Solvation energies per ligand decrease regularly, for steric and electronic reasons, with every added solvent molecule. Lower energies of solvation result with higher degrees of aggregation.<sup>31</sup> Therefore the differences in complexation energies are expected to be less pronounced in higher aggregated or in completely solvated species. The need for THF or TMEDA either as solvent or as cosolvent in the generation of superbases may well be to prevent the least soluble species (*i.e.* the heavier alkalimetal organic compound) from precipitating. Otherwise heterogeneous mixtures of the transmetalated species without superbasic qualities would result.

### Conclusions

Many different species may be in equilibrium in superbasic mixtures of an organolithium compound and an heavier alkali metal alkoxide. Table 14 summarizes the relative energies for all possible combinations which can result from anion and/or cation exchange processes. The energies for the most stable species are given in bold type.

Metal mixing between (LiX)<sub>2</sub> and (MOH)<sub>2</sub> (eq 1) is exothermic for all species studied here. The mixed metal dimers are more stable due to a combination of LiX/LiO bond strengthening and the decrease of the metal-metal repulsions. The decrease in metal-metal repulsion seems to be the main factor in mixed dimers involving the heavier alkali metals (Rb, Cs).

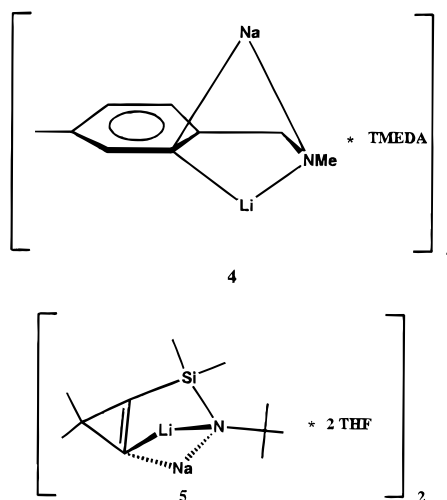
Anion mixing between (LiX)<sub>2</sub> and (MOH)<sub>2</sub> (eq 4, Table 9) is only slightly exothermic, except for X = H and X = CH<sub>3</sub>, with M = Na. In the latter cases, the anion-cation bond-strengths appear to be responsible.

Exchange of both metal and cation (eq 7) results in mixed aggregates (LiOH/MX) which are almost always the most stable species considered (Table 14). The LiX and LiO bonds in such mixed aggregates are stronger

than those in homo dimers. The greater stabilities of the mixed aggregates are due to these stronger cation-anion interactions combined with decreased metal-metal repulsions.

Complete transmetalation rather than mixed aggregate formation (see Table 14) is favorable only for (LiOH/NaH) and for (LiOH/NaCH<sub>3</sub>). Complete transmetalation from (LiNH<sub>2</sub>)<sub>2</sub> + (MOH)<sub>2</sub> into (MNH<sub>2</sub>)<sub>2</sub> + (LiOH)<sub>2</sub> is endothermic for the heavier alkali metals (M = K, Rb, Cs). The endothermicity is a consequence of the importance of multicenter interaction among the metal and the filled p-orbital on nitrogen in (LiNH<sub>2</sub>)<sub>2</sub>.<sup>26c,29</sup>

Based on our *ab initio* results on model dimers, mixed aggregates might well be expected in superbasic mixtures. In almost every case, mixed dimeric aggregates are more stable than other combinations. According to our study mixed aggregated species might also be expected for superbasic lithium diisopropylamide/M-alkoxide (M = Na-Cs) systems, used for selective deprotonations of organic compounds.<sup>2</sup> Indeed we recently were able to crystallize two mixed Li/Na carbanion-amide complexes (**4**·TMEDA)<sub>4</sub><sup>33a</sup> and (**5**·2THF)<sub>2</sub>.<sup>36</sup>



The central core of (**4**·TMEDA)<sub>4</sub> is a tetrameric cluster of units in which Li and Na cations bridge the carbanion and amide functionalities. The same type of bridging was found for the centrosymmetric dimer of (**5**·2THF)<sub>2</sub>.<sup>36</sup>

The effects of the degree of aggregation, higher bulky organic substituents and higher degrees of solvation or ligation were not evaluated in this study but will certainly influence the nature of such species and are therefore currently under investigation.<sup>33b</sup>

Our findings differ from HOESY and MNDO results of Bauer and Lochman.<sup>6</sup> Their model compounds, trityllithium and cesium 3-ethyl-3-heptoxide, were cho-

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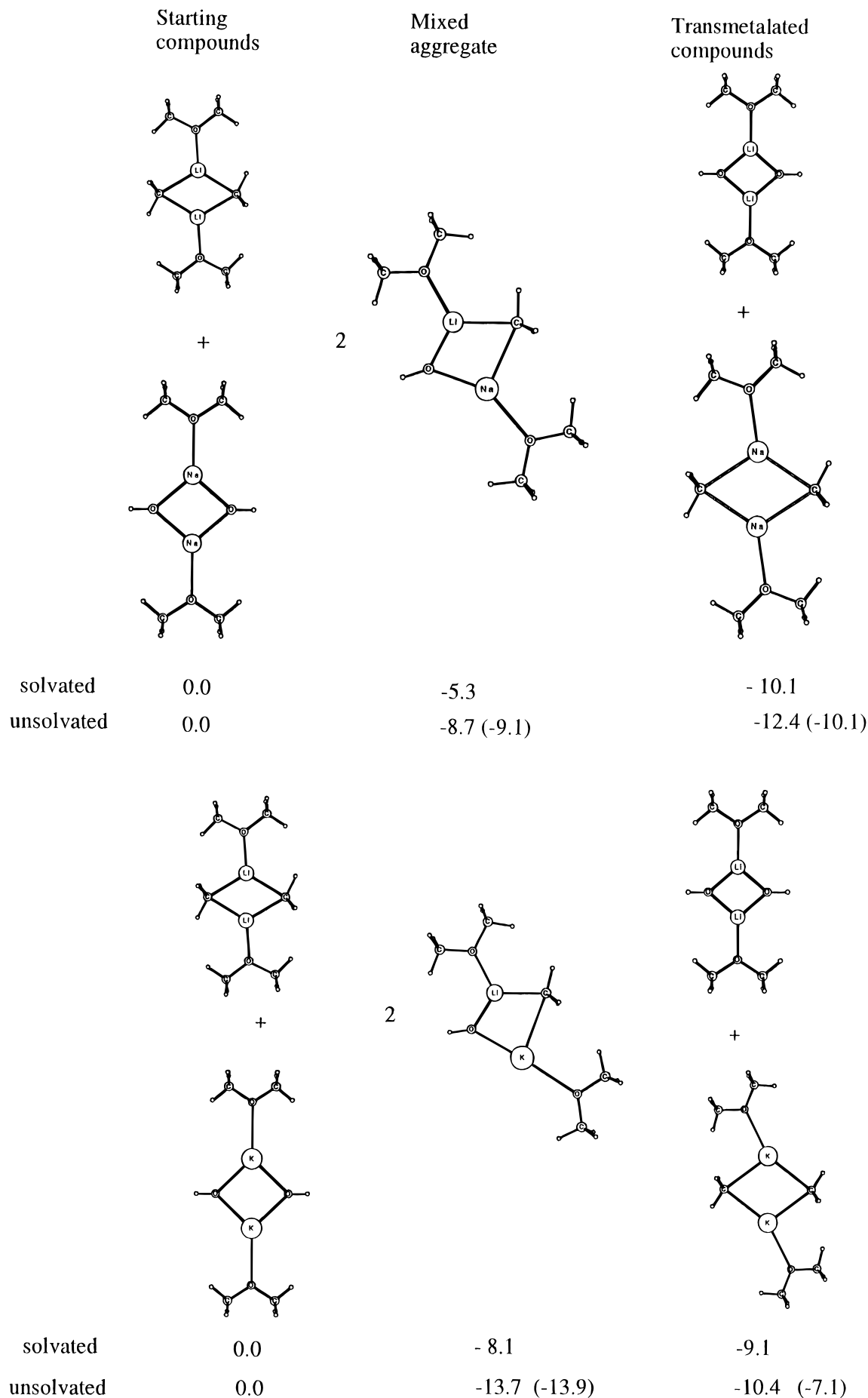
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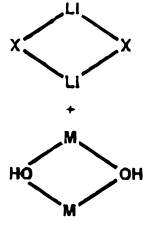
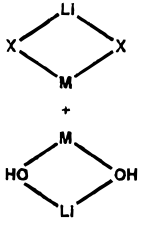
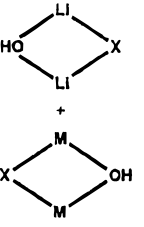
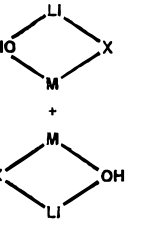
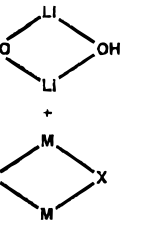
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**Figure 1.** Relative energies for dimethyl ether solvated mixtures compared to the uncomplexed species at BECKE3LYP basis D/RHF basis A. (/MP2(full) basis B energies for the unsolvated equilibria are given in parentheses).

**Table 14. Summary of Computational Results on Intermolecular Exchange Reactions at MP2(full) (+ΔZPE)<sup>a</sup> [kcal/mol]**

					
	<i>starting compounds</i>	<i>cations exchange</i>	<i>anions exchange</i>	<i>mixed aggregates</i>	<i>transmetalated compounds</i>
	$E_{rel} = 0.0$				
<b>M=Li</b>					
X=H		0.0	<b>-2.6</b>	<b>-2.6</b>	0.0
X=CH <sub>3</sub>		0.0	<b>-3.4</b>	<b>-3.4</b>	0.0
X=NH <sub>2</sub>		0.0	<b>-2.0</b>	<b>-2.0</b>	0.0
X=OH		0.0	0.0	0.0	0.0
X=F		0.0	<b>-0.8</b>	<b>-0.8</b>	0.0
<b>M=Na</b>					
X=H		-10.2	-10.5	-11.9	<b>-16.8</b>
X=CH <sub>3</sub>		-6.3	-7.3	-9.1	<b>-10.1</b>
X=NH <sub>2</sub>		-2.9	-2.6	<b>-4.3</b>	-2.6
X=OH		<b>-2.0</b>	0.0	<b>-2.0</b>	0.0
X=F		-4.0	-1.8	<b>-4.8</b>	-2.6
<b>M=K</b>					
X=H		-14.4	-9.5	<b>-16.0</b>	-14.1
X=CH <sub>3</sub>		-11.8	-5.8	<b>-13.9</b>	-7.1
X=NH <sub>2</sub>		-6.5	-0.9	<b>-8.2</b>	+0.6
X=OH		<b>-6.8</b>	0.0	<b>-6.8</b>	0.0
X=F		-11.2	-3.8	<b>-12.2</b>	-6.5
<b>M=Rb</b>					
X=H		-17.6	-10.6	<b>-19.0</b>	-16.9
X=CH <sub>3</sub>		-15.1	-6.8	<b>-17.2</b>	-9.3
X=NH <sub>2</sub>		-8.1	-0.7	<b>-9.8</b>	+1.0
X=OH		<b>-8.6</b>	0.0	<b>-8.6</b>	0.0
X=F		-13.6	-4.2	<b>-14.5</b>	-7.4
<b>M=Cs</b>					
X=H		-18.7	-10.0	<b>-19.8</b>	-16.4
X=CH <sub>3</sub>		-16.9	-6.7	<b>-18.9</b>	-9.4
X=NH <sub>2</sub>		-8.5	+0.1	<b>-9.9</b>	+2.5
X=OH		<b>-9.5</b>	0.0	<b>-9.5</b>	0.0
X=F		-14.7	-4.6	<b>-15.6</b>	-8.2

<sup>a</sup> See footnotes in Tables 1 and 2.

sen because of their good solubility in THF at room temperature and their stability. However, these large systems might be sterically too demanding to build mixed aggregates (trityllithium·2Et<sub>2</sub>O is monomeric in the solid state!).<sup>34</sup> Additional MNDO calculations (using monomeric tritylorganic compounds and tetrameric alkoxides solvated by dimethyl ether as model compounds)<sup>6</sup> support the NMR results, but the deficiencies of the lithium parametrization<sup>32a</sup> (overestimation of Li, C and Li, H interactions) are well known<sup>32b</sup> and might be responsible.

Although mixed aggregates may well exist in superbasic mixtures, their enhanced reactivity remains to be explained. This will be the subject of a future paper.<sup>33c,37</sup>

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