A “Lithium-Bonded” Cyclopropyl Edge: The X-ray Crystal Structure of $[Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2]_6$ and Computational Studies

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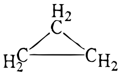
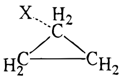
Abstract: The short Li−C distances ($Li_1-C_2 = 2.615(3)$ Å, $Li_1-C_3 = 2.644(3)$ Å) in the X-ray crystal structure of $[Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2]_6$ (**7**)$_6$ characterize Li−cyclopropane edge coordinations. The Li−cyclopropane interactions increase the C_2-C_3 distances (1.519(3) Å) relative to those of the free cyclopropyl edges ($C_2-C_4 = C_6-C_7 = 1.499(2)$ Å) by 0.02 Å. The bent bonds of cyclopropane give rise to an electrostatic potential pattern, which strongly favors edge coordination as is observed experimentally in (**7**)$_6$, but also permits a metastable Li^+ face complex. The cyclopropane edge also is the favored site for hydrogen bonding, but not for protonation. The C−C bond length elongations, the coordination energies E_{coord}, and the charge redistributions upon metal cation edge interactions all are related to the distances between the cyclopropane C−C bond centers and the cations. This is evaluated for the alkali metal cation−cyclopropane complexes (cation = Li^+ to Cs^+). More generally, the cyclopropane C−C bond length variations can be employed as a structural measure for the magnitudes of electrostatic interactions.

Introduction

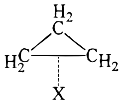
Complexes of cyclopropane (**1**) with various electrophiles and nucleophiles exhibit unusual molecular structures (**2**−**4**).[1−10] Computations on corner- (**2a-asym** C_s, **2a-sym** C_s) and edge-protonated cyclopropane (**3a**, C_{2v}) reveal an extremely flat potential energy surface.[1] The ability of cyclopropanes to participate as hydrogen-bonding proton acceptors, first demonstrated inter- and intramolecularly by Schleyer et al. using IR spectroscopy,[2] has been confirmed recently by MW spectroscopy.[3−6] Like the π-systems in unsaturated hydrocarbons, the cyclopropane “bent bonds”[7] act (edge coordination mode **3**) as proton acceptors for HOR,[2] H_2O,[3] HF,[4] HCl,[5] and HCN.[6] The breaking of hydrogen bonds between water molecules by cyclopropane (**1**) is said to be responsible for the anaesthetic activity of **1**.[8] However, in weaker van der Waals complexes, NH_3,[9] $HNMe_2$,[10] and NMe_3[10] are located above the cyclopropane ring plane (face coordination mode **4**).



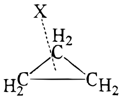
1
free



2
corner



3
edge



4
face

X =	H^+ **2a-asym** C_s, **2a-sym** C_s	H^+ **3a** C_{2v}	H^+ **4a** C_{3v}
	Li^+ **2b** C_{2v}	Li^+ **3b** C_{2v}	Li^+ **4b** C_{3v}
		Na^+ **3c** C_{2v}	
		K^+ **3d** C_{2v}	
		Rb^+ **3e** C_{2v}	
		Cs^+ **3f** C_{2v}	

As the closest congener of hydrogen, lithium can form “lithium bonds” in analogy to hydrogen bonds.[11] Similar to hydrogen, free ions, ion pairs, and atoms of lithium and heavier alkali metals all coordinate to hydrocarbon π-systems.[12] These alkali metal π-interactions have been studied extensively, in particular because of their role in biochemistry,[13] e.g. in ion

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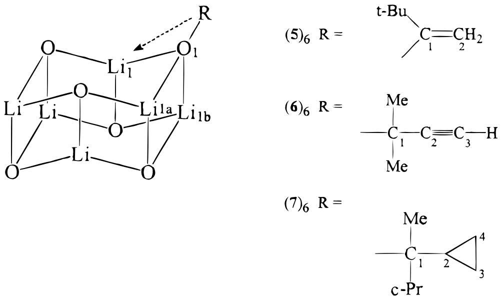
Scheme 1. Electrostatic Interactions in Hexameric Lithium Alkoxide Clusters (Table 1)



channels, and in electrostatic catalyses of pericyclic reactions.[14] The π-contacts appear with phenyl groups in aryl-,[15] alkyl-,[16] and amidolithiums,[17] as well as in vinyl-[18] and ethynyllithiums.[19] Similar π-interactions are found in the lithium alkoxides $[Li-O-C(t\text{-}Bu){=}CH_2]_6$[20] (**5**)$_6$ and $[Li-O-C(Me)_2-C{\equiv}CH]_6$[19] (**6**)$_6$ (Scheme 1). Short Li H−C distances ("agostic"[21] interactions) are apparent in the structures of $[i\text{-}PrLi]_6$,[22] $[n\text{-}BuLi]_6$,[23] $[t\text{-}BuLi]_6$,[23] and $[c\text{-}(CHCMe_2CMe_2)CH_2Li]_6$.[24] Despite the early discovery of hydrogen-bonded cyclopropanes,[2] a "lithium-bonded" cyclopropane edge has not been observed hitherto.

Interactions of (transition) metals with neutral hydrocarbon fragments are involved in catalytic C−H and C−C bond activations.[25] Hence, studies of complexes of cyclopropane and alkali metals provide insights into the electrostatic component of metal C−C interactions.

The present combined experimental and theoretical study on alkali metal ion interactions with cyclopropyl groups focuses on the X-ray crystal structure of $[Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2]_6$ (**7**)$_6$. This reveals edge-coordinated cyclopropyllithium arrangements. High-level computations on the molecular and electronic structures as well as the energies of alkali metal cation−cyclopropane complexes help interpret the experimental results and reveal details of electrostatic metal cation C−C interactions.

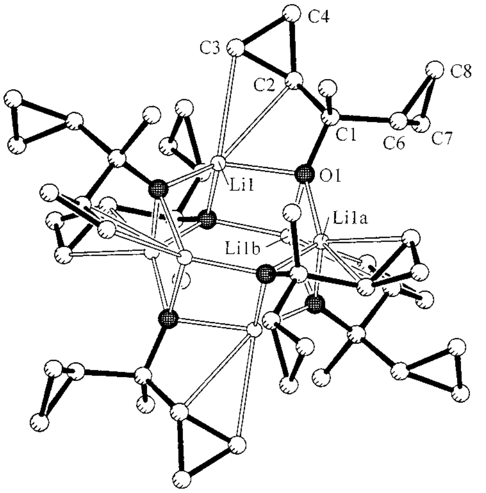


Figure 1. The X-ray crystal structure of $[Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2]_6$ (**7**)$_6$. Hydrogen atoms are omitted. See Table 1 for Li−C and Table 2 for C−C distances.

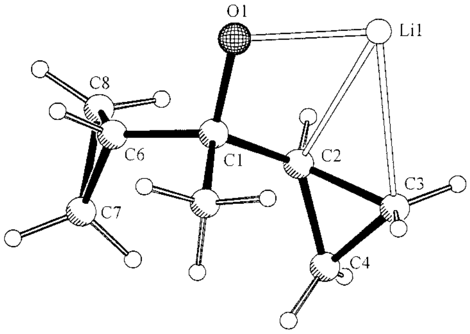


Figure 2. Asymmetric unit in the X-ray crystal structure of $[Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2]_6$ (**7**)$_6$. See Table 1 for Li−C and Table 2 for C−C distances.

Results and Discussion

The X-ray Crystal Structure of $[Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2]_6$ (7)$_6$. Despite the widespread use of alkali metal alkoxides in syntheses as well as in catalytic and ceramic processes, surprisingly little structural information is available.[12,26] The lithiums in the X-ray structures of **5**[20] and **6**[19] interact electrostatically with organic π-systems (Scheme 1). To probe the possible electrostatic interactions between the positively charged lithium centers in a $(LiO)_x$ cluster and the C−C bonds of a cyclopropyl group, we synthesized and crystallized $Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2$ (**7**) from the non-polar solvent hexane.[27] The unsubstituted cyclopropyl rings in **7** facilitate coordination with the lithiums.[24] The 2:1 cyclopropyl:lithium ratio results in both coordinated and free cyclopropyl groups. The latter serve as "internal standards" to assess the structural effects of Li coordination.

Single-crystal X-ray analysis of $Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2$ (**7**) revealed a hexameric aggregate (crystallographic S_6 symmetry), as in (**5**)$_6$[20] and (**6**)$_6$.[19] Electrostatic interactions in (**7**)$_6$ between the Li centers and the cyclopropyl groups are shown clearly in Figures 1 and 2. The Li atoms are coordinated 5-fold by three O atoms in the $(LiO)_6$ core and by two C atoms ($Li_1-C_2 = 2.615(3)$ Å, $Li_1-C_3 = 2.644(3)$ Å) of the cyclo-

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Table 1. Selected X-ray Crystal Data for $[Li-O-C(t\text{-}Bu)=CH_2]_6$ $(\mathbf{5})_6$,[a] $[Li-O-C(Me)_2-C\equiv C-H]_6$ $(\mathbf{6})_6$,[b] and $[Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2]_6$ $(\mathbf{7})_6$ (Scheme 1)

	$(\mathbf{5})_6$[c]	$(\mathbf{6})_6$	$(\mathbf{7})_6$
Li_1-O_1 (Å)	1.976 (9)	1.955 (5)	1.937 (3)
$Li_{1a}-O_1$ (Å)	1.869 (9)	1.877 (5)	1.881 (3)
$Li_{1b}-O_1$ (Å)	1.954 (9)	1.923 (5)	1.926 (3)
$Li_1-O_1-C_1$ (deg)	88.0 (9)	105.3 (2)	105.6 (1)
$Li_{1a}-O_1-C_1$ (deg)	140.0 (4)	130.8 (2)	132.6 (1)
$Li_{1b}-O_1-C_1$ (deg)	132.9 (4)	134.2 (2)	135.1 (1)
Li_1-C_1 (Å)	2.349 (9)	2.687 (5)	2.680 (3)
Li_1-C_2 (Å)	2.420 (8), 2.53[d]	2.443 (5)	2.615 (3)
Li_1-C_3 (Å)		2.749 (6)	2.644 (3)

[a] Reference 20. [b] Reference 19. [c] One of two asymmetric units in the unit cell with approximate S_6 symmetry. [d] Average value of the two asymmetric units.

Table 2. C−C Distances (Å) in the Li-Coordinated and the Free $[Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2]_6$ $(\mathbf{7})_6$ Cyclopropyl Groups

$c\text{-}CHCH_2CH_2$ (Li-coord)		$c\text{-}CHCH_2CH_2$ (free)	
C_2-C_3	1.519 (3)	C_6-C_7	1.499 (2)
C_2-C_4	1.499 (2)	C_6-C_8	1.493 (2)
C_3-C_4	1.508 (3)	C_7-C_8	1.498 (3)

propyl groups. Other cyclopropyl moieties are free from such interactions. The $Li_1-C_2-C_3-C_4$ dihedral angle 176.0° documents the nearly coplanar arrangement of the $Li_1-C_2-C_3$ and $C_2-C_3-C_4$ faces and the cyclopropane edge coordination (Figure 2). As in $[Li-O-C(t\text{-}Bu)=CH_2]_6$ $(\mathbf{5})_6$[20] and $[Li-O-C(Me)_2-C\equiv CH]_6$ $(\mathbf{6})_6$[19] (Scheme 1), this coordination in $(\mathbf{7})_6$ results in a tilt of the organic fragment O_1-C_1 toward Li_1 ($Li_1-O_1-C_1 = 105.6(1)°$, $Li_{1a}-O_1-C_1 = 132.6(1)°$, $Li_{1b}-O_1-C_1 = 135.1(1)°$) and leads to a differentiation in the $Li-O_1$ distances ($Li_1-O_1 = 1.937(3)$ Å, $Li_{1a}-O_1 = 1.881(3)$ Å, $Li_{1b}-O_1 = 1.926(3)$ Å, Table 1).[19] This "lithium bonding"[11] to the cyclopropane edge in $(\mathbf{7})_6$ results in increased C−C bond lengths of the cyclopropyl rings: The coordinated cyclopropyl edges ($C_2-C_3 = 1.519(3)$ Å) are 0.02 Å longer than the equivalent free edges C_2-C_4 (1.499(2) Å) and $C_6-C_7 = (1.499(2)$ Å) and are 0.026 Å longer than C_6-C_8 (1.493(2) Å) (Table 2); C_3-C_4 (1.508(3) Å) is slightly elongated by 0.01 Å relative to C_7-C_8 (1.498(3) Å).[28]

The Cyclopropane Edge as a Structural Probe for Electrostatic Interactions. A variety of complexes between alkali metal ions[12] and saturated as well as unsaturated hydrocarbons have been studied both experimentally[29] and computationally.[30] The metal cation binding energies (E_{coord}, as in eq 1) in these species decrease from Li^+ to Cs^+ [29a] and are large for aromatics (E_{coord} $C_6H_6-Li^+ = 37$ kcal/mol),[29b] but they are substantial even for saturated hydrocarbons such as cyclohexane (E_{coord} $C_6H_{12}-Li^+ = 24$ kcal/mol).[29b] Methyl substitution of unsaturated hydrocarbons increases the Li^+ coordination energy.[29b] Whereas protonated species are strongly covalent, the analogous Li^+ complexes are bound largely ionically.[14,29b,30c] The potential energy surface of protonated cyclopropane has been investigated extensively,[1] but studies of Li^+-cyclopropane interactions are rare.[31]

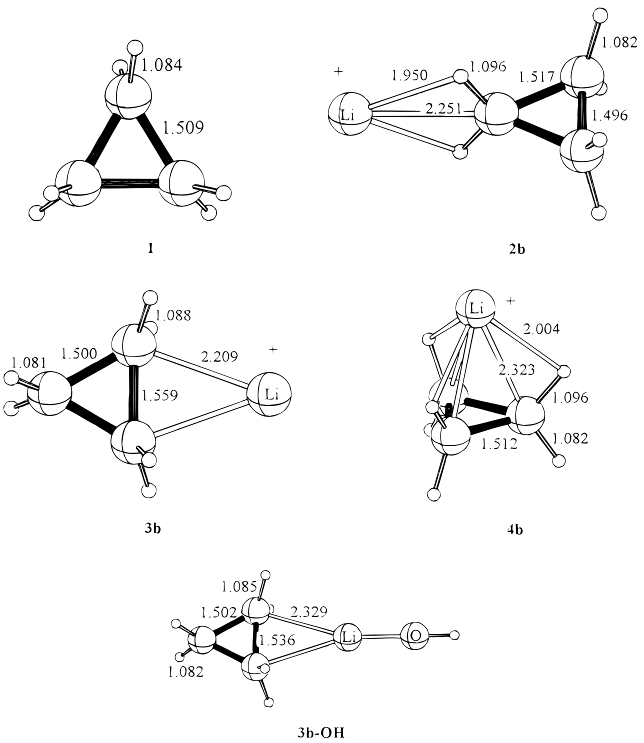

Figure 3. Cyclopropane **1** D_{3h} and Li^+ and LiOH cyclopropane complexes **2b** C_{2v}, **3b** C_{2v}, **4b** C_{3v}, and **3b−OH** C_{2v}; RB3LYP/6-311+G** (C, H, O), /6-31G* (Li) optimized geometries. The bond distances are given in angstroms.

The geometries of the lithium-bonded cyclopropyl groups in the X-ray crystal structure of **7** (Figure 2) are confirmed computationally: Consistent with results on hydrogen-bonded cyclopropane species,[2−6] the edge complex **3b** ($E_{\text{coord}} = 22.9$ kcal/mol) is the most stable minimum on the Li^+-cyclopropane potential surface; the corner transition structure (**2b**) ($E_{\text{coord}} = 13.2$ kcal/mol) and the face isomer (**4b**) ($E_{\text{coord}} = 11.6$ kcal/mol) are 9.7 and 11.3 kcal/mol less stable (Figure 3, Tables 3 and 4).

Comparisons between **3b** and **4b** and the analogous H^+ species (**3a**, **4a**, Figure 4) bring out significant differences (Tables 3 and 4): **3a** is a transition structure and close in energy to the corner-protonated minimum **2a-asym**. In contrast to **4b**, face-protonated **4a** is a high-energy second-order saddle point (Tables 3 and 4). Whereas the protonated hydrocarbons exhibit strong covalent or multicenter bonding (see the H^+ natural population analysis (NPA) charges in Table 3),[29b,30c] electrostatic interactions provide the basis for the stable Li^+ locations in **3b** and **4b**. The C−C bent bonds[7] of **1** result in areas of negative electrostatic potential outside the ring (Figures 5 and 6a), which favor the Li^+ edge coordination of **3b** over the Li^+ corner position in **2b**. The positively charged H atoms result in three electrostatic potential maxima above the ring plane of **1**, surrounding a lower but still positive area (Figure 6b). This explains the "meta"-stable Li^+ position in **4b**. As in both the Li^+ (**3b**) and the LiOH complex (**3b−OH**), electrostatics dominate the Li−cyclopropane interactions (see the Li NPA charges in Table 3); Li^+ is a valid model for lithium-bonded species.

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[28] These $C_\alpha-C_\beta$ elongations by $C_\alpha-C_\alpha$ coordination are not reproduced computationally (see below) and may arise from substituent effects and asymmetric edge coordination of the cyclopropyl groups in $(\mathbf{7})_6$. No significant interactions between the $(\mathbf{7})_6$ clusters are apparent in the crystal.

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Table 3. Coordination Energies and Natural Charges of Protonated and Lithium-Complexed Hydrocarbons[a]

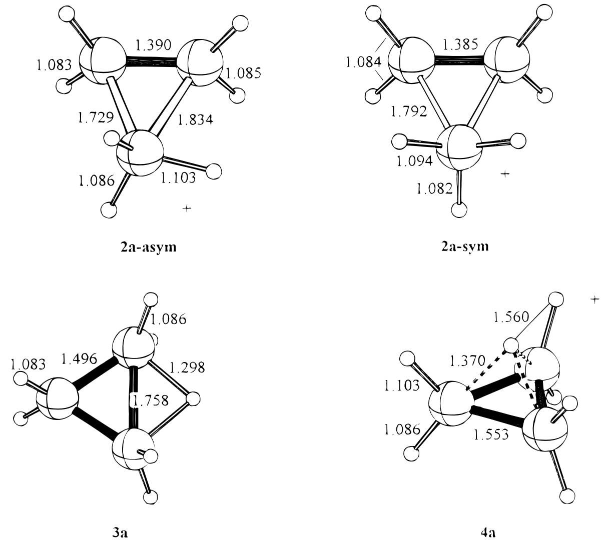
	PG (NIMAG)[b]	E_{coord} (kcal/mol)[c]	q H^+ or q Li^+ (au)[d]
1	D_{3h} (0)		
2a-asym	C_s (0)	179.83	+0.321
2a-sym	C_s (1)	179.80	+0.311
2b	C_{2v} (1)	13.18	+0.985
3a	C_{2v} (1)	177.07	+0.336
3b	C_{2v} (0)	22.91	+0.982
3b-OH	C_{2v} (0)	8.86	+0.953
4a	C_{3v} (2)	95.85	+0.660
4b	C_{3v} (0)	11.63	+0.974
8	D_{3h} (1)		
8−Li$^+$	C_{2v} (1)	15.01	+0.981
9	D_{4h} (1)		
9−Li$^+$	C_{2v} (1)	19.40	+0.979
10	C_s (0)		
10−Li$^+$	C_1 (0)	23.33	+0.969
11	D_{2h} (0)		
11−Li$^+$	C_{2v} (0)	19.62	+0.967

[a] B3LYP/6-311+G** (C, H, O), /6-31G* (Li) optimized geometries. [b] Point groups and (in parentheses) number of imaginary frequencies, obtained from B3LYP frequency calculations. [c] H^+ or Li^+ coordination energies E_{coord} (ZPE corrected, eq 1) of the protonated or Li^+-complexed species. [d] Natural charges (ref 42) of coordinated H^+ or Li^+.

Table 4. Relative Energies (kcal/mol) and Numbers of Imaginary Frequencies of Protonated and Li^+-Complexed Cyclopropanes[a]

	corner		edge		face	
H^+	**2a-asym**	0.00 (0)	**3a**	2.76 (1)	**4a**	83.98 (2)
Li^+	**2b**	9.73 (1)	**3b**	0.00 (0)	**4b**	11.28 (0)

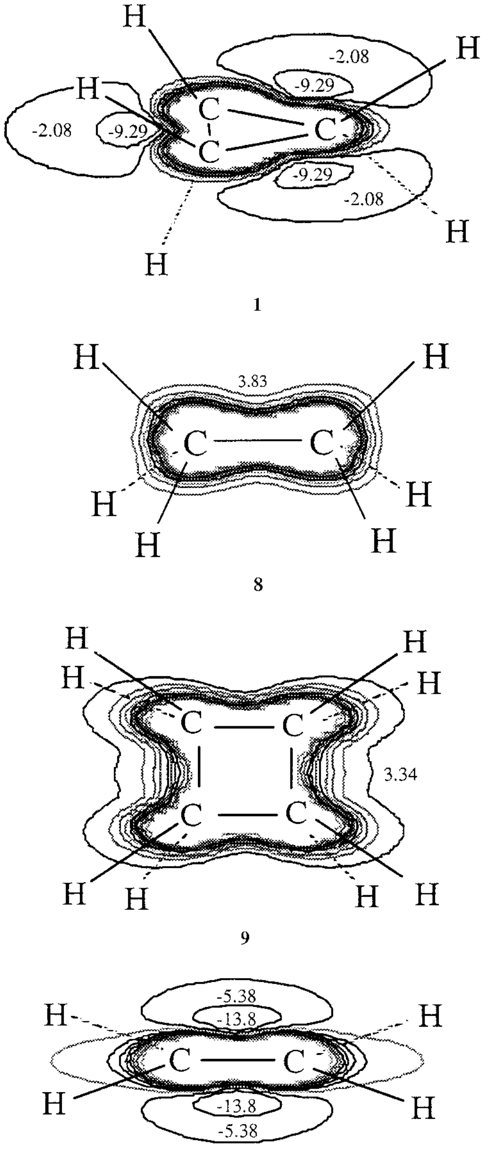
[a] See Table 3.



2a-asym 2a-sym 3a 4a

Figure 4. Protonated cyclopropanes **2a-asym** C_s, **2a-sym** C_s, **3a** C_{2v}, **4a** C_{3v}; RB3LYP/6-311+G** (C, H) optimized geometries. The bond distances are given in angstroms.

The special bent bond[7] character in **1** is also apparent from a comparison with eclipsed ethane (**8**) and planar cyclobutane (**9**). The $-H_2C-CH_2-$ topologies in **1**, **8**, and **9** are very similar (Figure 7). Due to their higher polarizability, larger (and unsaturated) hydrocarbons exhibit usually higher Li^+ E_{coord} than smaller ones.[29b] However, the Li^+ E_{coord} of **3b** (22.91 kcal/mol) is higher than the E_{coord} of **8−Li**$^+$ (15.0 kcal/mol), of **9−Li**$^+$ (19.4 kcal/mol), and of the Li^+−ethene complex **11−Li**$^+$ (19.6 kcal/mol) and even approaches the E_{coord} of the Li^+−propene complex **10−Li**$^+$ (23.3 kcal/mol, Table 3, Figure 7). Consistent with the lower Li^+ affinity of **8** and **9**, no negative electrostatic potential areas of the C−C bonds are apparent in **8** and **9** (Figure 5). In **1**, the negative electrostatic potential lobes, caused by the C−C bent bonds,[7] resemble those of the π-electrons in ethene **11** (Figure 5).



1

8

9

11

Figure 5. Electrostatic potential maps (RHF/6-31+G**//B3LYP/6-311+G**) of the C−C bonds in cyclopropane **1** D_{3h}, eclipsed ethane **8** D_{3h}, planar cyclobutane **9** D_{4h}, and ethene **11** D_{2h}. Energies in kcal/mol.

The other alkali metal cation−cyclopropane complexes **3c−f** document further the energetic, electronic, and structural effects of the edge coordination mode (**3**). All alkali metal cations in **3b−f** have nearly unit charges (Table 5) and hence serve as good "point charge models".[12] The computed coordination energies E_{coord} (eq 1) decrease in **3b−f** with increasing distances r between the cyclopropane edge and the cations M^+ (Table 6). The best correlation is obtained between E_{coord} and $1/r^{2.5}$ for **3b−f** (Figure 8). Ion/quadrupole interactions (the potential energy V of interacting n- and m-poles varies with the distance; see eq 2)[32] are discussed as dominant contributions in cation benzene π-bondings.[13,33] For these π-interactions, however, a $1/r^x$ ($x < 2$) dependence is found.[13b] To estimate the electrostatic contribution of the metal cation binding in **3b−f**, the metal centers are replaced by dummy charges and the electrostatic potentials (EP) at these points are computed (Table 6).[13a] A

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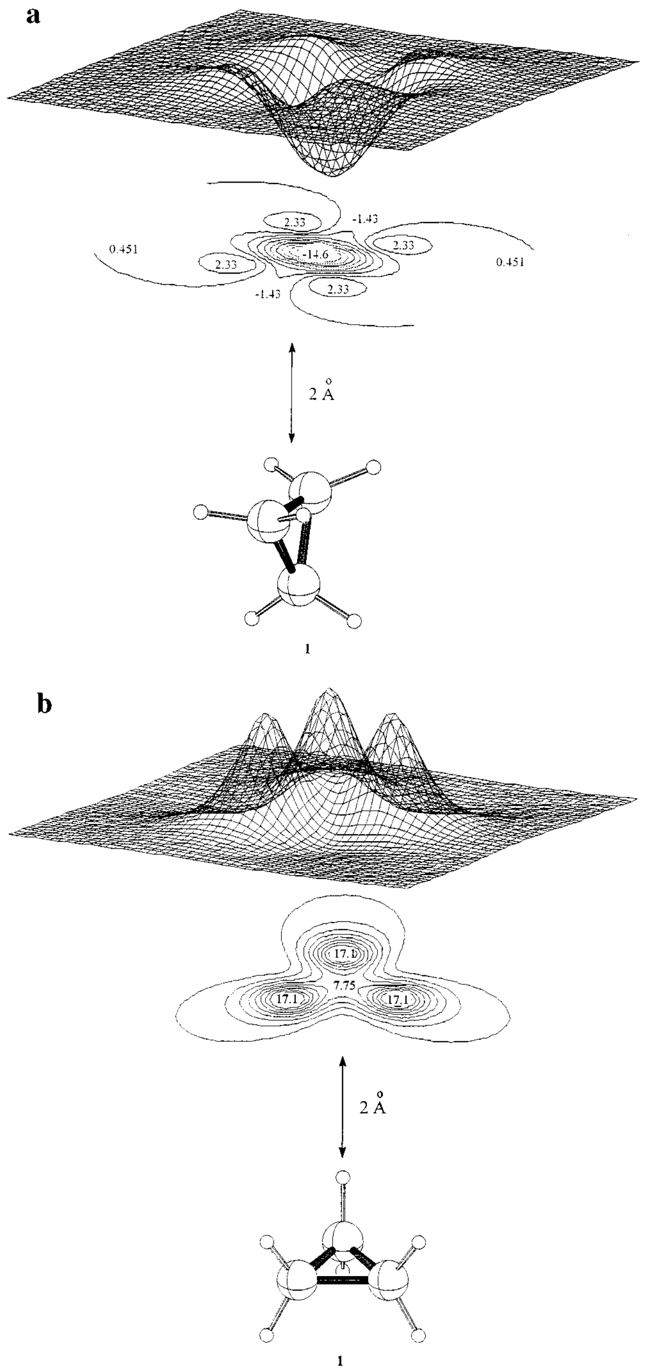

Figure 6. (a) Electrostatic potential surface and contour map (RHF/6-31+G**//B3LYP/6-311+G**) of a C−C bond in cyclopropane (**1**, D_{3h}) in a distance of 2 Å from the center of the CCC ring. Energies in kcal/mol. (b) Electrostatic potential surface and contour map (RHF/6-31+G**//B3LYP/6-311+G**) of the cyclopropane (**1**, D_{3h}) face in a distance of 2 Å above the CCC ring plane. Energies in kcal/mol.

correlation between E_{coord} and EP reveals a slope of 1.5 (Figure 9), which accounts for the increasing electrostatic contributions with increasing metal cation sizes (compare the NPA charges in Table 5).

$$\mathrm{HC} + \mathrm{X}^+ \rightarrow \mathrm{HC{-}X}^+ + E_{\text{coord}}$$

$$(\mathrm{HC} = \text{hydrocarbon; } \mathrm{X} = \mathrm{H}^+, \mathrm{Li}^+ \text{ to } \mathrm{Cs}^+) \tag{1}$$

$$V \propto 1/r^{(n+m-1)} \tag{2}$$

$$F_{\text{el}} = q/(4\pi\epsilon_0)r^2 \propto 1/r^2 \tag{3}$$

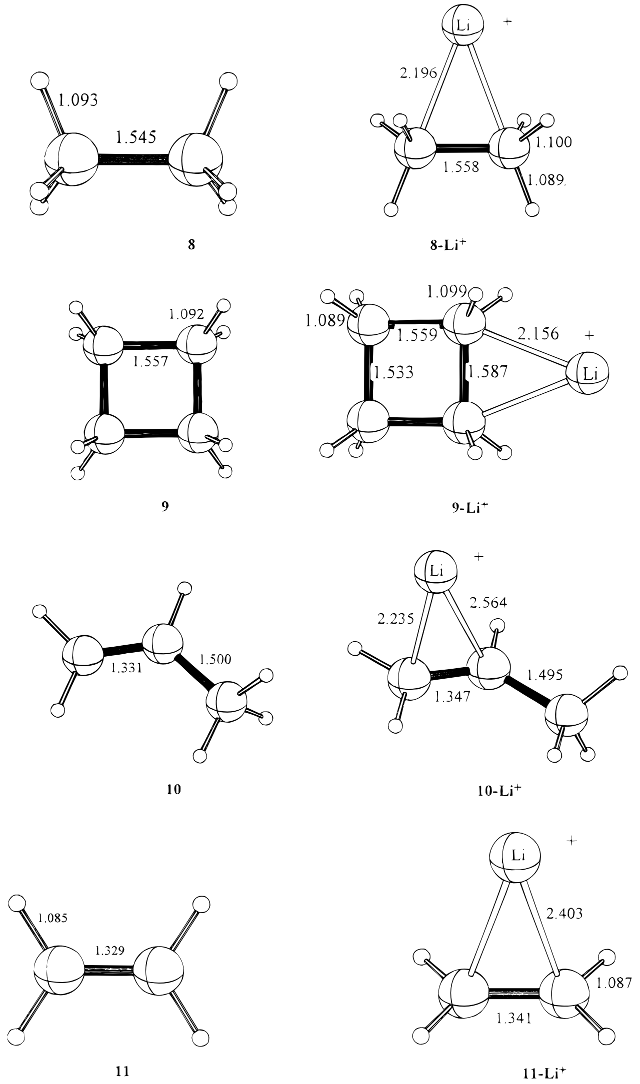

Figure 7. Hydrocarbons and their Li$^+$ complexes: eclipsed ethane **8** D_{3h}, **8−Li$^+$** C_{2v}, planar cyclobutane **9** D_{4h}, **9−Li$^+$** C_{2v}, propene **10** C_s, **10−Li$^+$** C_1, ethene **11** D_{2h}, **11−Li$^+$** C_{2v}; RB3LYP/6-311+G** (C, H), /6-31G* (Li) optimized geometries. The bond distances are given in angstroms.

Table 5. Natural Charges *q* (au) of Alkali Metal Cation−Cyclopropane Edge Complexes[a]

	q M	q C$_\alpha$	q H(C$_\alpha$)	q C$_\beta$	q H(C$_\beta$)
1 (D_{3h})		−0.404	+0.202	−0.404	+0.202
3b (C_{2v})	+0.980	−0.529	+0.235	−0.340	+0.240
4b (C_{3v})	+0.973	−0.501	+0.208	−0.501	+0.302
3c (C_{2v})	+0.988	−0.492	+0.222	−0.356	+0.233
3d (C_{2v})	+0.997	−0.468	+0.212	−0.363	+0.226
3e (C_{2v})	+0.999	−0.454	+0.208	−0.369	+0.223
3f (C_{2v})	+0.999	−0.446	+0.206	−0.373	+0.221

[a] RB3LYP/6-31+G** (C, H), /6-31G(2d) (Li, Na), /LanL2DZ(2d) ECP (K, Rb, Cs) optimized geometries. The B3LYP/6-31++G** (C, H), /6-31G(2d) (Li, Na), /LanL2DZ(2d) ECP (K, Rb, Cs) wave functions are used for the natural population analysis, ref 42.

As is apparent from C$_\alpha$, C$_\beta$ charges (Table 5), the polarization of negative charge decreases in **3b−f** with increasing distance *r* (Figure 10a). The best correlation is found between the C$_\alpha$, C$_\beta$ charges and $1/r^2$ (Figure 10b), reflecting the distance dependence of the electric fields F_{el} of the cations (eq 3).[32]

In accord with our experimental observations on (**7**)$_6$, Li$^+$ cation−cyclopropane edge coordination increases the C$_\alpha$−C$_\alpha$ bond lengths in **3b−f** relative to the length in **1** (Table 6, Figure 11a). This bond elongation (ΔC$_\alpha$−C$_\alpha$) decreases linearly with increasing distance *r* in **3b−f** (Figure 11b). Hence, the structural change in the coordinated cyclopropane C−C edge is related to the coordination energy E_{coord} and the changes in the charge

Table 6. Energies (kcal/mol) and Bond Distances (Å) of Alkali Metal Cation−Cyclopropane Edge Complexes[a]

	E_{coord}[b]	EP[c]	M−C$_\alpha$	M−(C−C)[d]	C$_\alpha$−C$_\alpha$	Δ(C$_\alpha$−C$_\alpha$)	C$_\alpha$−C$_\beta$
1 (D_{3h})					1.510		1.510
3b (C_{2v})	−22.48	−16.51	2.188	2.044	1.560	0.050	1.503
4b (C_{3v})	−10.56	+4.99	2.286	2.112[e]	1.513	0.003	1.513
3c (C_{2v})	−12.95	−10.78	2.579	2.460	1.551	0.041	1.503
3d (C_{2v})	−6.26	−6.31	3.065	2.967	1.535	0.025	1.506
3e (C_{2v})	−4.07	−4.63	3.374	3.286	1.530	0.020	1.506
3f (C_{2v})	−2.84	−3.59	3.636	3.555	1.526	0.016	1.507

[a] RB3LYP/6-31+G** (C, H), /6-31G(2d) (Li, Na), /LanL2DZ(2d) ECP (K, Rb, Cs) optimized geometries. [b] Coordination energies E_{coord} (ZPE corrected, eq 1) of the M$^+$-complexed species. [c] Electrostatic potential energies at the metal centers, which were replaced by dummy charges. [d] Distances r from the centers of the C$_\alpha$−C$_\alpha$ bonds to the cations. [e] Distance from the center of the ring to the cation.

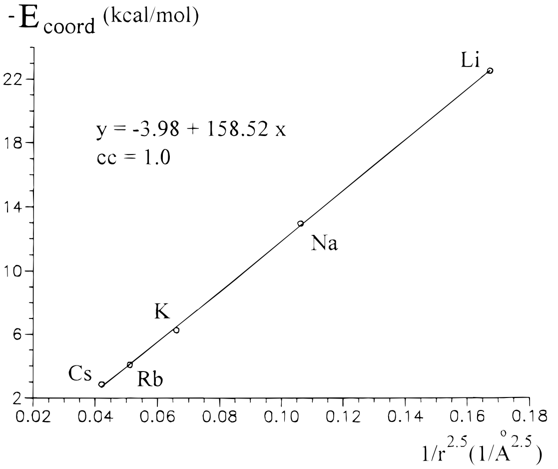

Figure 8. Correlation between the metal cation coordination energies E_{coord} (eq 1) and the metal cation edge distances r of **3b**−**f**.

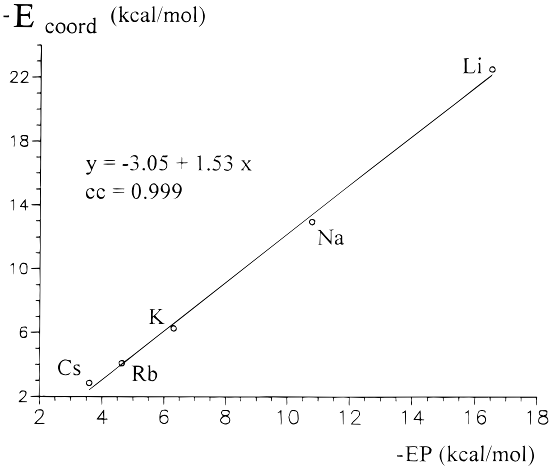

Figure 9. Correlation between the metal cation coordination energies E_{coord} (eq 1) and the electrostatic potentials EP at the replaced metal centers of **3b**−**f**.

distribution of the cyclopropyl group due to counterion complexation.

Conclusions

The edge interactions of Li ions of the (LiO)$_6$ cluster with the cyclopropyl groups result in ca. 0.02 Å bond length elongations in the X-ray structure of (**7**)$_6$. This finding documents the analogy between hydrogen-bridged and lithium-bonded cyclopropyl groups and emphasizes the "electrostatic component" in C−C bond metal cation coordination and activation. The electrostatic potential pattern of the C−C bonds in cyclopropane (**1**) resembles organic π-systems, such as ethene (**11**), and explains the favorable Li$^+$ edge coordination mode in the X-ray crystal structure (**7**)$_6$ and in **3b**. Furthermore, the electrostatic potential provides the basis for the unusually high Li$^+$ edge coordination energy of **1** (E_{coord} = 22.9 kcal/mol) in comparison to E_{coord} of eclipsed ethane (**8**, 15.0 kcal/mol) and planar cyclobutane (**9**, E_{coord} = 19.4 kcal/mol). Unlike the protonated cyclopropanes (see comparison in Table 4), the Li$^+$−cyclopropane face complex **4b** is predicted to be a 11.3 kcal/mol higher energy minimum, but the corner-lithiated **2b** is a transition structure (9.7 kcal/mol less stable than **3b**). The extent of C−C bond length elongations, the coordination energies E_{coord}, and the cyclopropyl C$_\alpha$, C$_\beta$ charge polarizations all are related to the distances between the C−C edge and the alkali metal cations in **3b**−**f**. Hence, the cyclopropane C−C bond length elongations, as observed experimentally in the X-ray crystal structure (**7**)$_6$, provide a measure for the degree of the electrostatic interaction with edge-coordinating metal cations.

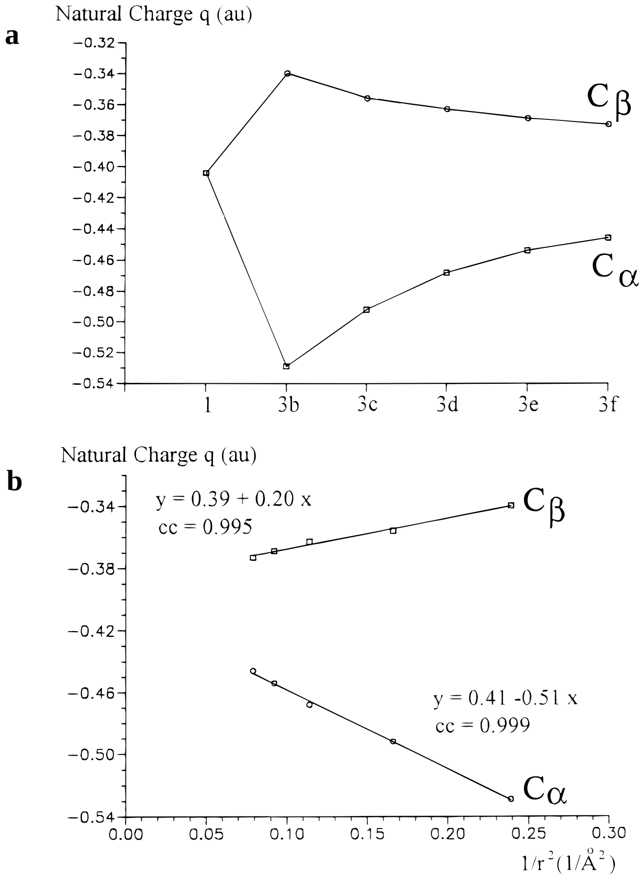

Figure 10. (a) Natural charges of carbon atoms, reflecting the charge polarizations by the metal cations of **3b**−**f**. (b) Correlation between carbon charges and the metal cation edge distances r of **3b**−**f**.

Experimental Section

The experiments were carried out under an argon atmosphere by using standard Schlenk as well as needle/septum techniques. The solvents were freshly distilled from sodium/benzophenone. Dicyclopropyl ketone (Aldrich) was distilled prior to use. The NMR spectra were recorded on JEOL GX and JEOL Alpha 500 (CP-MAS)

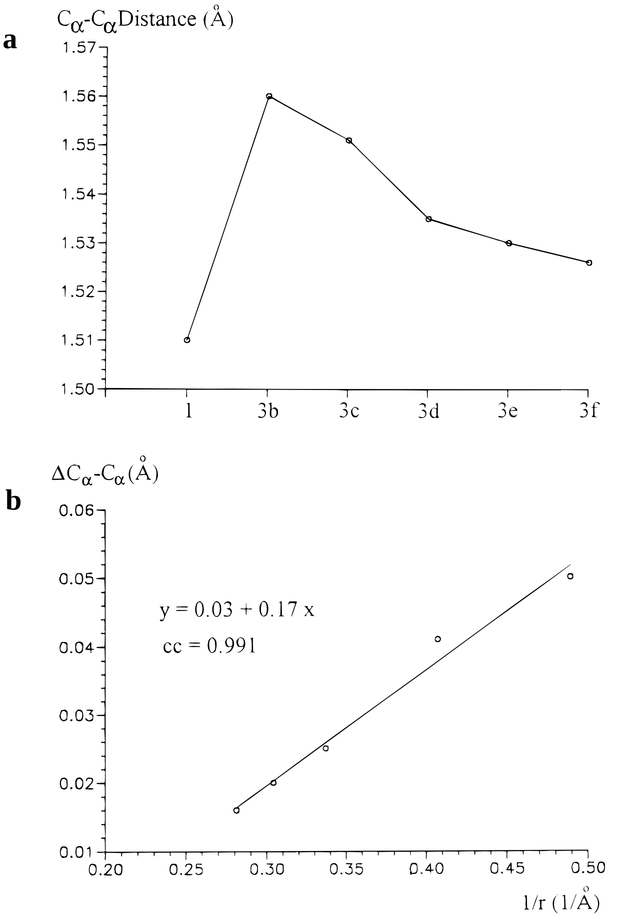

Figure 11. (a) Cyclopropane $C_\alpha-C_\alpha$ edge elongations by metal cation coordinations of **3b**−**f**. (b) Correlation between the cyclopropane edge elongations $\Delta(C_\alpha-C_\alpha)$ and the metal cation edge distances *r* of **3b**−**f**.

spectrometers (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) and referenced to TMS or to adamantane (CP-MAS). IR spectra were determined neat or as Nujol mulls between NaCl disks on a Perkin-Elmer 1420 spectrometer. Mass spectral data were obtained on a Varian MAT 311A spectrometer and the elemental analyses (C, H) on a Heraeus micro automaton.

$[Li-O-C(Me)-(c\text{-}CHCH_2CH_2)_2]$ (7). Dicyclopropylmethylcarbinol[34] was synthesized by a procedure analogous to that for dicyclopropylcarbinol:[35] A solution of methylmagnesium iodide in 100 mL of diethyl ether was prepared from 6.1 g (0.25 mol) of Mg and 35.5 g (0.25 mol) of methyl iodide.[36] To this Grignard mixture was slowly added 27.5 g (0.25 mol) of dicyclopropyl ketone diluted in 100 mL of diethyl ether. After 1 h of reflux, hydrolysis with H_2O/NH_4Cl, extraction with diethyl ether, and drying over Na_2SO_4, the distillation afforded 26.5 g (0.21 mol) of dicyclopropylmethylcarbinol $HO-C(Me)-(c\text{-}CHCH_2CH_2)_2$ (84% yield): bp 35 °C/1.5 mbar; ^{1}H NMR ($CDCl_3$) δ 1.41 (s, O*H*), 1.10 (s, CH_3), 0.89 (m, C*H*), 0.37 (m, CH_2); $^{13}C\{^1H\}$ NMR/DEPT ($CDCl_3$) δ 69.32 (C), 25.25 (*C*H_3), 19.88 (*C*H), −0.46 (*C*H_2); IR (neat, cm^{-1}) 3460 (ν OH), 3080, 3000, 2960, 2920 (ν CH), 1365, 1155, 1100, 1040, 1010 (δ CCC).[37]

To a stirred solution of 0.24 g (1.9 mmol) of dicyclopropylmethylcarbinol in 1.0 mL of hexane at 0 °C was added 1.17 mL of *n*-BuLi/hexane (1.6 M, Acros). After the solution was stirred for 5 min at room temperature, the white precipitate was separated from the solvent and dried in vacuum: ^{1}H NMR ($CDCl_3$) δ 0.76 (s, CH_3), 0.36 (m, C*H*), 0.29 (m, CH_2); $^{13}C\{^1H\}$ NMR/DEPT ($CDCl_3$) δ 69.01 (C), 24.77 (*C*H_3), 23.44 (*C*H), −0.20 (*C*H_2); ^{13}C CP-MAS δ 70.35 (C), 28.42 (*C*H_3), 20.85 (*C*H), 2.74 (*C*H_2); IR (Nujol mull, cm^{-1}) 3070 (ν CH), 1155, 1130, 1010 (δ CCC); MS (EI, 70 eV, 120 °C) *m*/*e* 403 ($[M]_3 - Li^+$), 271 ($[M]_2 - Li^+$), 139 ($[M]_1 - Li^+$), 111 ($HOC-(c\text{-}CHCH_2CH_2)_2^+$), 98 ($O(c\text{-}CHCH_2CH_2)_2^+$), 43 ($C_3H_7^+$); Anal. Calcd for $C_8H_{13}O_1Li_1$: C, 72.7; H, 9.9. Found: C, 71.9; H, 10.1 Colorless single crystals of **7** were obtained by cooling hexane solutions.

X-ray crystal data for $(\mathbf{7})_6$: $M_r = 132.12$; rhombohedral; space group $R\bar{3}$; $a = b = 12.217(3)$ Å, $c = 26.562(6)$ Å; $V = 3433.1(13)$ Å^3; $D_{calc} = 1.150$ Mg m^{-3}; $Z = 18$; $F(000) = 1296$; Mo Kα ($\lambda = 0.71\,073$ Å); $T = 173(2)$ K; data were collected with a Enraf Nonius CAD4-Mach3 diffractometer on a crystal with the dimensions 0.40 × 0.30 × 0.30 mm using the ω-scan method ($3.0° < 2\theta < 54.0°$). Of the total of 1773 collected reflections, 1556 were unique and 1212 with $I > 2\sigma(I)$ were observed. The structure was solved by direct methods using SHELXS 86; 143 parameters with all data were refined by full matrix least squares on F^2 using SHELXL93 (G. M. Sheldrick, Göttingen, 1993). All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were refined independently and isotropically. The final *R* values were R1 = 0.0492 ($I > 2\sigma(I)$) and R2$_w$ = 0.1385 (all data) with $R1 = \sum|F_o - F_c|/\sum F_o$ and $R2_w = \sum w|(F_o^2 - F_c^2)^2|/\sum(w(F_o^2)^2)^{0.5}$; GOF = 1.110; largest peak (0.287 e Å^{-3}) and hole (−0.208 e Å^{-3}). Further details are available on request from the Director of the Cambridge Crystallographic Data Center, Lensfield Road, GB-Cambridge CB2 1 EW, by quoting the journal citation.

Theoretical Section

All theoretical structures were optimized using the gradient techniques implemented in GAUSSIAN 94[38] with Becke's three-parameter hybrid functional incorporating the Lee−Yang−Parr correlation functional (Becke3LYP).[39] The 6-311+G** and 6-31+G** (C, H, O) as well as 6-31G(d) (Li) and 6-31G(2d) (Li, Na) all-electron basis sets were used. For K, Rb, and Cs 9-valence electron effective core potentials[40] and the LanL2DZ basis sets, K (341/311), Rb (341/321), Cs (341/321), each augmented with two polarization functions,[41] were used. The characters of the stationary points, the zero-point energy corrections, and the harmonic vibration frequencies were obtained from analytical and, for pseudopotential computations of the K, Rb, and Cs systems, from numerical frequency calculations. All partial charges are based on the natural population analysis[42] of the Becke3LYP electron density. The electrostatic potentials were evaluated with RHF/6-31+G** wave functions on optimized B3LYP geometries.

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Supporting Information Available: Tables giving the X-ray crystal data and the zero-point energies of the computed systems (9 pages). See any current masthead page for ordering and Internet access instructions.

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