Alkali Metal Cation−π Interactions Stabilized Solely by $[M\{N(SiMe_3)_2\}_3]^-$ Anions (M = Mg or Zn): The Competing Influence of Alkali Metal···C(Me) Agostic Interactions

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A series of $[K(ar)_2]^+$ and $[Rb(toluene)_3]^+$ cations (ar = benzene, toluene, *o*-xylene, or *p*-xylene) has been synthesized and crystallized in the presence of $[M\{N(SiMe_3)_2\}_3]^-$ anions (M = Mg or Zn). In the solid state all form either extended supermolecular, dimeric or supramolecular, polymeric structures. Only $[K(toluene)_2][Mg\{N(SiMe_3)_2\}_3]$ was found to exist as both suprastructural isomers. Introducing cyclopentadienyl to the system gave a similar zincate with the unusual $[K_2Cp]^+$ cation. The absence of any traditional Lewis bases facilitates short metal-to-arene contact distances and makes these species excellent candidates for the study of alkali metal cation−π interactions. It is shown that K−π interactions and to a lesser extent Rb−π interactions are heavily influenced by the number and nature of agostic methyl interactions, especially when the electron-donating ability of these is maximized by adoption of near-linear geometries. These features combine so that the weakest potassium-to-arene interaction observed is that with benzene.

Introduction

Cation−π interactions of alkali metals with arenes are now thought to be one of the fundamental forces underpinning the structural chemistry—and hence the reactivity characteristics—of a wide range of materials. We recently showed that the selectivity of superbases can be linked to their ability to precoordinate aromatic substrates[1] and it is well-known that many zeolite-supported processes also involve such cation−π interactions.[2] Potentially most importantly, it has been realized that the interaction of Na and K with the aromatic side chains of biopolymers such as proteins can dramatically affect molecular conformation.[3] To fully understand the nature of cation−π interactions, much effort has been given to gathering thermodynamic data from model compounds and to modeling studies attempting to rationalize these.[4] Taken together these results indicate that the strength of such interactions decreases with decreasing metal Lewis acidity. Thus lithium-to-benzene binding is stronger than sodium-to-benzene binding and so on down group 1. Even for potassium, however, the interaction is still of a reasonable strength (typically 15 to 20 kcal mol^{-1}). As an illustration, this rivals the strength of a $K-OH_2$ bond and indeed in mass spectroscopic studies $K(OH_2)_x(benzene)_x$ compounds have been detected.[4a,d] Some excellent studies of alkali metal−π interactions in the solid state do exist, such as the work of Gokel et al. utilizing lariat crown ethers,[5] but relating the data gathered to modeling studies has been hampered somewhat by several factors. A main problem is the large range of metal-to-arene distances found in crystal structures[6] and that these are generally much longer than those predicted for gas-phase models (typical is the modeled range 2.60−2.85 Å for the monoligated $[K(benzene)]^+$ cation[4g]). This leads to difficulty both in assessing the usefulness and accuracy of the models and in deciding what is a meaningful, attractive interaction and what is no more than the random presence of arene solvents of crystallization. Presumably, competition from the other stronger Lewis bases which are commonly present[6] weakens or destroys the alkali metal−π interaction and thus favors long separation distances. This extra complexity obviously also hinders modeling of the cation−π interaction and so examples of structures with the cation bound by simple, neutral arenes but free from other Lewis bases are at a premium for study. Herein we present a series of such compounds based upon the ability of magnesates and

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Table 1. Selected Geometric Parameters (Å and deg)

	1	2a	2b	3	4	5	6	9
				anion				
M−N1	2.024(2)	2.017(3)	2.020(1)	2.021(1)	1.964(1)	2.019(3)	1.962(2)	1.961(3)
M−N2	2.026(2)	2.023(3)	2.021(1)	2.027(1)	1.966(1)	2.026(3)	1.973(2)	1.961(3)
M−N3	2.034(2)	2.028(3)	2.026(1)	2.030(1)	1.974(1)	2.030(3)	1.973(2)	1.989(5)
N1−M−N2	119.31(8)	119.6(1)	120.84(6)	120.41(5)	121.01(5)	119.3(1)	119.5(1)	123.3(2)
N1−M−N3	120.71(8)	121.0(1)	119.95(6)	119.64(6)	119.09(5)	119.6(1)	119.5(1)	118.4(1)
N2−M−N3	119.96(8)	119.4(1)	119.21(6)	119.96(6)	119.89(6)	121.0(1)	120.9(1)	118.4(1)
				cation				
M···C(Me)	3.228(3)	3.227(4)	3.128(2)	3.177(2)	3.132(2)	3.544(4)	3.578(3)	3.216(10)
M···C(Me)[a]	3.292(3)	3.345(4)	3.399(2)	3.323(2)	3.355(2)	3.619(4)	3.626(3)	3.328(10)
M···C(Me)[a]		3.345(4)	3.856(2)	3.418(2)	3.865(2)			3.433(10)
M−$C_{C.}$	3.027	2.884	2.935	2.983	2.903	3.100	3.088	2.699
M−C_C	3.041	2.937	2.936	3.023	2.937	3.117	3.112	2.699
M−C_C						3.125	3.113	
C_C-M−C_C	163.5	114.0	116.1	126.3	121.2	118.6	118.6	178.4
C_C−M−C_C						118.4	118.4	
C_C−M−C_C						122.9	122.9	
M−C(ar) max/min	3.237−3.414	3.124−3.273	3.194−3.295	3.104−3.521	3.169−3.276	3.367−3.421	3.351−3.414	2.917−2.957
M−C(ar) max/min	3.277−3.368	3.149−3.345	3.216−3.283	3.138−3.541	3.216−3.291	3.375−3.437	3.372−3.433	
M−C(ar) max/min						3.322−3.499	3.314−3.485	

[a] For **2a**, **2b**, **3**, and **4** these are to the “chelated” HMDS.

zincates to stabilize M^+ species.[7] The compounds $[K(ar)_2][ML_3]$ (M = Mg, ar = benzene (**1**), toluene (**2**), or *p*-xylene (**3**); M = Zn, ar = *o*-xylene (**4**)) and $[Rb(toluene)_3][ML_3]$ (M = Mg (**5**) or Zn (**6**)), where L is hexamethyldisilazide (HMDS), have been synthesized and characterized by X-ray crystallography. A search of the Cambridge Structural Database[8] for similar $K(ar)_x$ or $Rb(ar)_x$ species containing no K or Rb to Lewis base (e.g. O, N, S, P, halide, carbanion) interactions and where the aromatic ring is neutral (e.g. not the relatively common anionic species[6] such as cyclopentadienyl or BPh_4^-) and where there is no molecular strap or connection holding the aromatic rings together found very few relevant compounds and none with Rb-to-arene contacts or multiple K-to-arene contacts. An early work by Atwood et al.[9] on the $[Al_7O_6Me_{16}]$ anion featured a [K(benzene)] cation (**7**) and Purdy and George[10] characterized the extremely relevant zincate $[K(benzene)][Zn(CH_2Bu^t)_3]$ (**8**). However, neither has a particularly short K-to-benzene distance. The structures of a series of solvated group 1 salts of carbaboranes are also known[11] but these were rejected as disorder in the benzene rings limits their usefulness. Another compound worthy of consideration is the complex between K and the carbanion $[C(SiMe_3)_2(SiMe_2Ph)]$.[12] One of the two K sites in this compound does not interact with the carbanion C. It interacts instead with a benzene molecule and two phenyl rings (whose partially anionic nature initially ensured rejection by our search conditions above). It is, however, the only one of the literature compounds above to exhibit a K-to-C_C (ring centroid) distance that approaches those found by modeling studies (2.97 Å).

Results and Discussion

The compounds **1** to **3** were easily and reproducibly synthesized by addition of 1,1,1,3,3,3-hexamethyldisilazane to a mixture of butyl-potassium and butylmagnesium and then adding the appropriate arene while **4** to **6** were synthesized by the direct reaction of the hexamethyldisilazide M(HMDS) with its divalent counterpart $M'(HMDS)_2$ (M = group 1 metal, M′ = Mg or Zn) in the presence of arene. Colorless crystals were grown by cooling warm hexane solutions. In the case of **2** repetition of this procedure produced two supramolecular isomers **2a** and **2b**. Introducing the cyclopentadienyl anion, Cp, from dicyclopentadiene to the system gives a markedly different reaction from which and with some difficulty only small amounts of $[K_2Cp][Zn(HMDS)_3]$, **9**, could be isolated. We have previously shown that similar reactions with lithium rather than a heavier alkali metal typically give dimeric species of the type $[(HMDS)Mg(\mu\text{-}HMDS)_2Li(S)]$ (S = solvent or vacant site),[13] while the presence of water or oxygen allows the inverse crown ethers $[K_2M_2(HMDS)_4(O_2)]$[14] to be isolated. Finally, exchanging the amine for the more basic 2,2,6,6-tetramethylpiperidide (TMP) gives inverse crowns of the type $[K_6Mg_6(TMP)_{12}(ar)_6]$[15] where six arene molecules are deprotonated and encapsulated at the center of the ring. Both Mg and Zn are known to have an affinity for trigonal-metalate $[ML_3]^-$ formation,[7] and it is believed that for the new complexes herein the steric bulk and relatively low basicity of HMDS favors the $[M(HMDS)_3]^-$ anion over the $[M(amide)_2X]$ fragments observed in the previously studied systems. This stable metalate anion formation separates the divalent metals from the group 1 metals and so disrupts the heterometallic M−N−M′ linkage that seems crucial to

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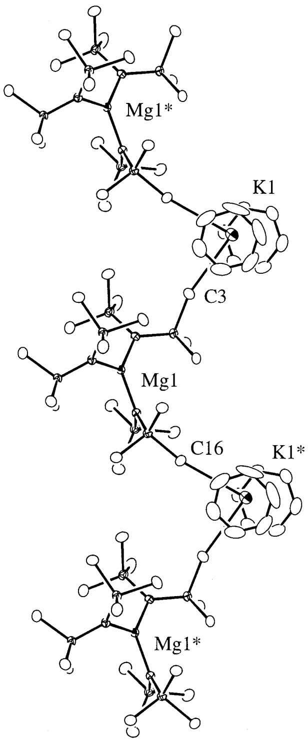

Figure 1. The chain structure of **1** with H-atoms omitted for clarity.

the unusual reactivity profiles of the inverse crown systems. The geometries of the magnesate and zincate anions are unexceptional with all the examples showing near perfect trigonal planar geometry about the metal (see Table 1). Although the $[Mg(HMDS)_3]$ ion is fairly common in the literature only two previous examples of structures with the $[Zn(HMDS)_3]$ ion are known.[16] As with other[14] cases the similarity in size and oxidation state of Zn and Mg leads to the adoption of very similar structures, with only a slight shortening of the M−N bond lengths for Zn (by approximately 0.05 Å) showing any difference between the two.

As shown in Figure 1 the benzene complex, **1**, forms a polymeric, linear chain via two K···Me interactions (K···C(Me) 3.228 and 3.292 Å) that involve two of the three HMDS ligands. The benzene rings lie approximately trans to each other across K (C_c-K-C_c 163.5 °) and each chain has a cationic $K(ar)_2$ side and an anionic MgL_3 side. The toluene and xylene $K(ar)_2$ species **2**−**4** adopt one of two supramolecular architectures and all have much tighter C_c-K-C_c angles (range 114.0 to 126.3°). In **2a** and **3** the K ions are bridged by the magnesate anions via three K···Me contacts to again form polymeric, linear chains similar to **1** (see Figure 2). Now, however, one HMDS ligand provides one short contact (K···C(Me) range 3.177 to 3.227 Å) while a second HMDS ligand forms two longer contacts in a chelating fashion (K···C(Me) range 3.323 to 3.418 Å, see Table 1 for details). This forms a six-membered (KCSiNSiC) "chelate" ring. **2b** and **4** are essentially mutually isomorphous and isostructural and feature an extended structure that is strictly supermolecular rather than supramolecular in character. K···Me contacts

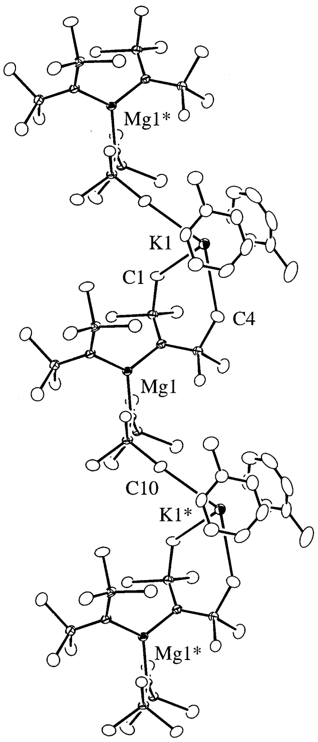

Figure 2. The chain structure of **2a** with H-atoms omitted for clarity.

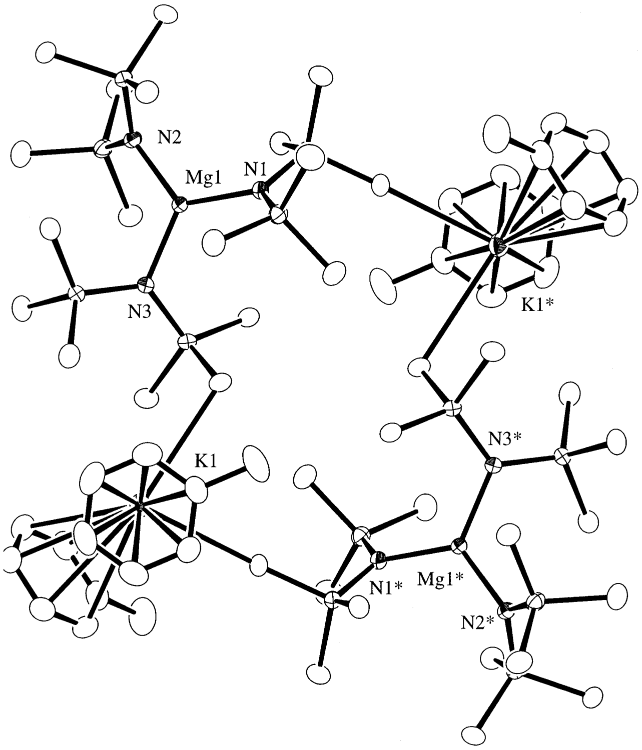

Figure 3. The dimeric structure of **2b** with H-atoms omitted for clarity.

again link the cations and anions but do so to form discrete $\{[K(ar)_2][ML_3]\}_2$ rings (see Figure 3). Each K ion forms only two short K···C(Me) contacts (range 3.128 to 3.399 Å), but some degree of "chelation" is retained as in addition one H atom from a third methyl group also makes a close approach (K···H 3.036 and 3.021, respectively). The C atoms of these third interactions

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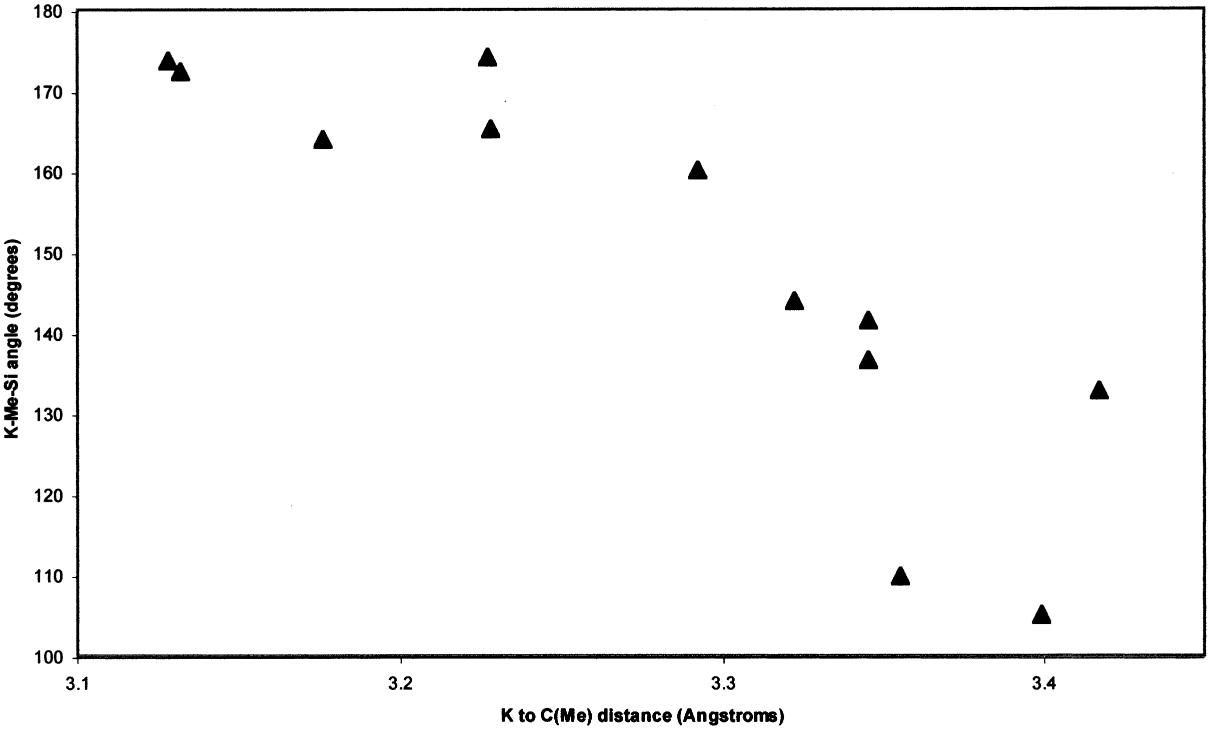

Figure 4. Plot of the K···C(Me) distance vs K···C(Me)−Si angle for the intermolecular contacts of less than 3.5 Å found in compounds **1**−**4**.

are too far from K (3.856 and 3.865 Å) to be considered as of the same type as the K···Me interactions above.

In his authoritative paper[17] Klinkhammer describes how such *s*-block "agostic" interactions (as opposed to conventional transition metal agostic interactions)[18] may be described as consisting of an electrostatic interaction between dipoles and a donor−acceptor interaction between the C−H bonding density and the metal cation. Thus the agostic interaction should be strongest when the Si−C···M angle approaches linearity (which both maximizes the number of K···H interactions, and hence the electron donating power of the methyl, while also minimizing the electrostatically favorable C-to-metal approach). Examination of Figure 4 seems to support this with the K···Me interactions falling into distinct groups with a trend that correlates linearity with short separation distances. Both the contacts of **1** and the shorter, nonchelated interactions in **2** to **4** have Si−C···M angles >160 ° and in their structures all three H atoms of the methyl are seen to contact the metal. The remaining contacts are longer, bent interactions with only two H···K contacts per methyl. The two H-only contacts seen in **2b** and **4** form a separate group outside the range of Figure 4 (Si−C···M angles 124.0 and 125.7 °) further indicating that these interactions are of a different type from the others. Klinkhammer also noted that the Si−C distance for those methyl groups involved in agostic interactions was slightly elongated. The examples here support this with the shortest Si−C distance being 1.884 Å for methyls showing agostic interactions and 1.867 Å for those that do not. Disorder in the HMDS groups of **9** preclude detailed discussion of its agostic interactions but it can be seen from Figure 5 that the extra metal bridging possibilities given by the inverse sandwich $[K_2Cp]$ cation give a material with a higher dimensional polymeric network. This may explain the difficulty encountered in preparing suitable crystals. The figure also shows that designating the cation as $[K_2Cp]$ is largely a formalism. The structure is perhaps better viewed as a three-dimensional polymeric network with Cp anions trapped at the centers of large ring motifs.

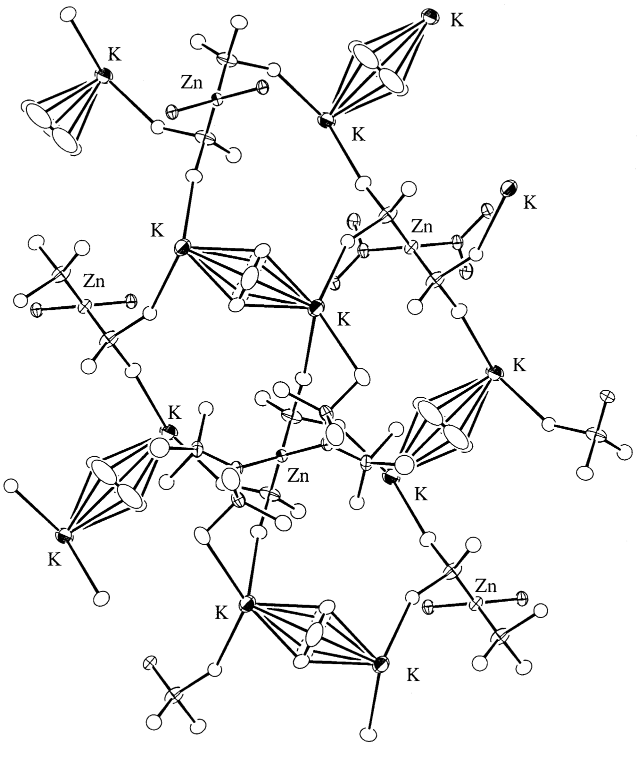

Figure 5. Part of the extended polymeric network structure of **9**.

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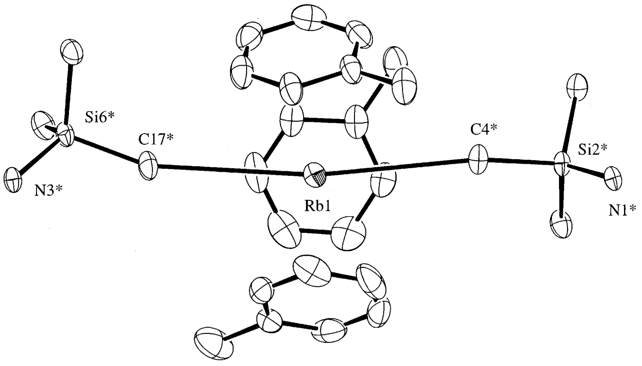

Figure 6. Detail of the structure of **5**, showing the coordination around Rb.

Examination of the geometric parameters summarized in Table 1 shows that the K-to-benzene coordination is different from the coordination of the other neutral arenes. The aromatic rings in **1** sit approximately on opposite sides of the metal (C_c-K-C_c 163.5 °) while in the other compounds they are much more adjacent with the corresponding angles spread around 120°. Also the K−benzene centroid distances are clearly longer than the others, although all are of course much longer than those to the charged Cp rings ($K-C_c$ 2.699 Å for **9**). As usual the factors that must be considered can be categorized as steric or electronic. Benzene is smaller than toluene or the xylenes and benzene does not have methyl groups donating additional electron density to its aromatic ring. Some insight into why benzene acts differently can be gained by examining the other structures. There is no evidence that the xylene groups systematically bind more strongly than toluene. In fact, apart from in **1** the next longest K-to-centroid distances appear in **3**, the *p*-xylene complex. This may be due to steric strain, an argument that is supported by the ring binding being furthest from symmetrical in **3** and its C_c-K-C_c angle widening with respect to those in **2a**, **2b**, and **4**. The K-to-centroid distances of **4** are intermediate to those of **2a** and **2b**. This mitigates against electron donation from methyl being the dominant factor. Similarly there is no evidence for systematic shortening of the K-to-C(ipso) contacts or indeed any other indication of K preferentially bonding to a particular ring position. Again this is not what would be expected if substituent electron donation was dominant. What is apparent is that **2a** has one K-to-centroid distance that is significantly shorter than those of its isomer **2b**. The major difference between the two is that the linear polymer **2a** makes three K···C agostic contacts but **2b** makes only two. However, each only makes one short, linear contact and that of **2b** is shorter than its isomer. We suggest that the methyl groups making short, linear agostic contacts (those with electron donation from three C−H bonds) are more powerful “Lewis bases” than those involved in bent agostic contacts and that they have the greatest influence on the $K-C_c$ distances. **1** is the only structure herein to allow two of these short, linear agostic contacts (perhaps because of the smaller size of benzene) and it clearly has the longest K-to-arene contacts. In the literature compounds **7** and **8**, despite K being coordinated by only one benzene, the $K-C_c$ distances are longer than those of **1** to **4** (3.34 Å for **8**). Both compounds have five agostic interactions.

The Rb complexes **5** and **6** differ from each other only by substituting Mg by Zn and are unsurprisingly both isomorphous and isostructural. The Rb coordination can be described as trigonal bipyramidal with (Figure 6) three toluene molecules in the equatorial positions and two fairly linear (Rb−C(Me)−Si range 158.0 to 161.9 °) agostic methyl contacts in the axial positions. This produces a zigzag linear polymer (Figure 7). Comparatively little modeling has been carried out on the Rb-to-π interaction [4a] but it is indicated that its lesser Lewis acidity means that the Rb−benzene interaction is about 4 kcal mol^{-1} less attractive than K−benzene and that as usual the energy gained by adding successive ligands is less than that of the first. As expected for the larger atom the Rb bond lengths are greater than those for the K species. Intriguingly though, the $Rb-C_c$ distances are only around 0.15 Å longer than the $K-C_c$ distances (despite there now being three arenes per metal) while the agostic interactions are around 0.3 Å longer than

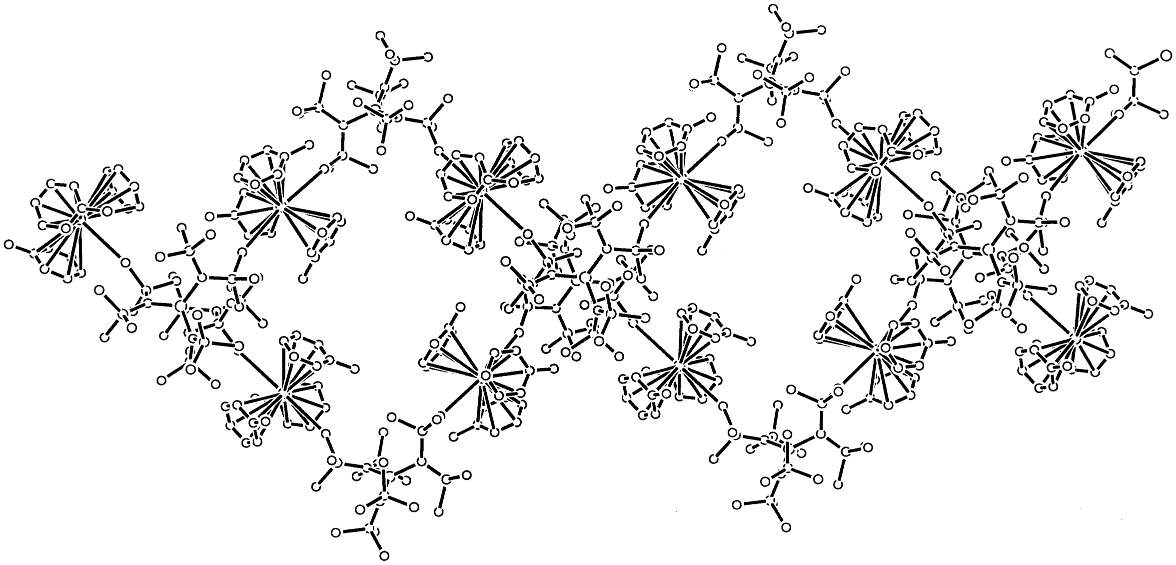

Figure 7. Two extended chains of **6**, showing their relative displacement.

Table 2. Crystallographic Parameters and Refinement Data

	1	**2a**	**2b**	**3**	**4**	**5**	**6**	**9**
formula	$[K(ben)_2][MgL_3]$	$[K(tol)_2][MgL_3]$	$[K(tol)_2][MgL_3]$	$[K(p\text{-}xy)_2][MgL_3]$	$[K(o\text{-}xy)_2][ZnL_3]$	$[Rb(tol)_3][MgL_3]$	$[Rb(tol)_3][ZnL_3]$	$[K_2(Cp)][ZnL_3]$
fw	700.81	728.86	728.86	756.91	797.97	867.36	908.42	689.84
system	monoclinic	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	Pc	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_12_12$
a (Å)	11.6742(2)	11.506(2)	9.6143(8)	11.6299(3)	9.8699(1)	18.8594(4)	18.7511(1)	12.1889(4)
b (Å)	9.9214(2)	11.676(4)	15.765(2)	12.2471(3)	15.9917(2)	14.4985(3)	14.4159(1)	13.3110(6)
c (Å)	18.5938(3)	17.819(5)	16.116(2)	17.4976(5)	16.3728(2)	20.0470(5)	20.0262(2)	11.7458(4)
α (deg)	90	83.78(3)	72.529(10)	84.172(1)	70.518(1)	90	90	90
β (deg)	95.042(1)	74.15(2)	74.898(7)	73.638(1)	76.871(1)	110.136(1)	110.103(1)	90
γ (deg)	90	86.35(2)	77.439(8)	82.401(2)	74.717(1)	90	90	90
V (Å^3)	2145.28(7)	2287.9(11)	2223.6(4)	2364.9(1)	2322.40(5)	5146.5(2)	5083.56(7)	1905.71(12)
Z	2	2	2	2	2	4	4	2
T (K)	123	123	123	123	150	123	123	123
no. of reflns	30377	8479	10285	14302	19972	37157	32337	8446
no of unique reflns	9521	8044	9697	10204	10608	10481	10336	2227
R_{int}	0.0490	0.0453	0.0098	0.0202	0.0200	0.0867	0.0558	0.0704
R	0.0378	0.0532	0.0331	0.0362	0.0297	0.0588	0.0434	0.0454
WR2	0.0830	0.1645	0.0969	0.0778	0.0726	0.1424	0.1165	0.0976

K···C contacts with similar angles. This indicates that the agostic contacts are affected more by the decreased Lewis acidity of the metal than are the metal-to-π interactions and further strengthens the argument that it is the agostic methyl groups that are the dominant "Lewis bases" in these systems.

Conclusions

We have synthesized and examined a series of compounds which allow the first systematic, solid-state examination of heavy alkali metal-to-π interactions in the absence of disruptive, strong, conventional Lewis bases. These compounds have shorter metal-to-ring centroid distances than those commonly found in the literature and are thus a better fit to gas-phase models. The arene groups are labile under mild conditions, which should aid thermodynamic measurements of their metal binding energies. Toluene and xylenes are found to form shorter and presumably stronger bonds to K than does benzene and this is attributed to greater competition by short, electron-donating agostic methyl interactions in **1**, perhaps aided by benzene's smaller size. It appears that linearity of these agostic interactions is correlated to strength and there is evidence that even these weakly electron donating interactions lengthen the K−arene distances, but that they are less important in Rb complexes. In their absence an even better fit with calculated distances could be expected. Study of alkali metal cation−π bonding of aromatic residues has previously been driven by a perception of biological significance. It is our belief that the prebinding of arenes to *s*-block metals is of equal significance for the selective reactivity of both inverse crown ethers and superbases, and we are currently working toward utilizing this behavior to produce novel synthetic routes to selectively substituted aromatics.

Experimental Section

General Procedures. Benzene, toluene, *o*-xylene, and *p*-xylene were distilled from Na/benzophenone and stored over 4A molecular sieves. Hexamethyldisilazane was distilled from CaH_2 and stored over 4A molecular sieves. Dicyclopentadiene was stored over 4A molecular sieves and not purified further. KHMDS was purchased from Aldrich. RbHMDS[19] and Zn(HMDS)$_2$[20] were synthesized according to reported procedures and characterized by their ^{1}H NMR spectra. Bu^{n}K[21] was prepared by the metathetical exchange between Bu^{n}Li and KOBu^t.

Physical Measurements. NMR spectral data were recorded on a Bruker DPX 400-MHz spectrometer operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C. Both ^{1}H and ^{13}C NMR shifts are relative to external $SiMe_4$. Microanalysis (C, H, and N) was performed with a Perkin-Elmer 2400 elemental analyzer. Melting point studies were carried out in sealed capillaries and are uncorrected.

Crystallography. Crystals were mounted directly into the cold stream of the diffractometer's low-temperature device using the oil-drop technique. Measurements on **2a** and **2b** were carried out with a Rigaku AFC7S diffractometer ($\lambda = 0.71069$

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Å) and on all other samples with a Nonius Kappa CCD diffractometer ($\lambda = 0.71073$ Å). Data from **5** and **6** were corrected for absorption effects with use of a multiscan method.[22] All non-H atoms were modeled anisotropically. One xylene ring in **4** was treated as disordered over two sites related by translation. Disorder was also modeled in the HMDS ligands of **9**. All geometric parameters in the text refer only to the major disorder component. H atoms of the agostically bound methyls were modeled isotropically. The structures were refined against F^2, using all unique reflections [23] until convergence. Further details are given in Table 2 and in the Supporting Inforamation.

Syntheses of $[\{K(benzene)_2\}^+\{Mg(HMDS)_3\}^-]_\infty$ (1), $[\{K(toluene)_2\}^+\{Mg(HMDS)_3\}^-]_2$ (2a), $[K(toluene)_2\}^+\{Mg(HMDS)_3\}^-]_\infty$ (2b), and $[\{K(p\text{-xylene})_2\}^+\{Mg(HMDS)_3\}^-]_\infty$ (3). Bu^nK (0.48 g, 5 mmol) was suspended in hexane (ca. 15 mL) and subjected to ultrasound for 5 min. To this was added an equimolar amount of $Bu^{n,s}{}_2Mg$ (5 mmol in heptane, 5 mL of a 1.0 M solution) resulting in the formation of a congealed brown/cream mass. Three equivalents of hexamethyldisilazane (3.16 mL, 15 mmol) were then added resulting in a slightly exothermic reaction, which yielded a yellow suspension. To this suspension the relevant arene (ca. 2 mL) was added (benzene for **1**, toluene for **2**, and *p*-xylene for **3**), dissolving the precipitate to give a yellow solution. The solution was heated, allowed to cool slowly to room temperature, and then placed in the refrigerator at 5 °C, resulting in precipitation of colorless crystals overnight.

For **1**: yield 1.85 g, 68% {based on $KMg(HMDS)_3$ as product}; mp 195−196 °C; ^1H NMR $[C_5D_5N]$ δ 0.58 (s, Si*Me*$_3$); ^{13}C NMR $[C_5D_5N]$ δ 9.1 (Si*Me*$_3$). Negligible amounts of benzene were found in both ^1H and ^{13}C NMR spectra, consistent with the fact that benzene was mostly removed in vacuo during the isolation procedure. Microanalysis: the sample was found to lose weight too rapidly during the balance procedure to gain accurate results.

For **2a**: yield 0.58 g, 21% {based on $KMg(HMDS)_3$ as product}; mp 189−191 °C; ^1H NMR $[C_4D_8O]$ δ 0.55 (s, Si*Me*$_3$); ^{13}C NMR $[C_4D_8O]$ δ 6.3 (Si*Me*$_3$). Negligible amounts of toluene were found in both ^1H and ^{13}C NMR spectra, consistent with the observation that toluenee was mostly removed in vacuo during the isolation procedure. Microanalysis: Calcd for $KMg(HMDS)_3$: C, 39.9; H, 10.0; N, 7.7. Found: C, 39.7; H, 10.2; N, 7.4.

For **2b**: the crystal which yielded structure **2b** was removed from a batch of crystals that gave the same analysis as **2a**.

For **3**: yield 0.73 g, 27% {based on $KMg(HMDS)_3$ as product}; mp 199−201 °C; ^1H NMR $[C_6D_5CD_3]$ δ 0.43 (s, Si*Me*$_3$); ^1H NMR $[C_4D_8O]$ δ 0.00 (s, Si*Me*$_3$); ^{13}C NMR $[C_6D_5CD_3]$ δ 7.3 (Si*Me*$_3$); ^{13}C NMR $[C_4D_8O]$ δ 4.1 (Si*Me*$_3$). Negligible amounts of *p*-xylene were found in both ^1H NMR spectra, consistent with the fact that *p*-xylene was mostly removed in vacuo during the isolation process. Microanalysis: the sample was found to lose weight too rapidly during the balance procedure to gain accurate results.

Synthesis of $[\{K(o\text{-xylene})_2\}^+\{Zn(HMDS)_3\}^-]$ (4). KHMDS (1.00 g, 5 mmol) was dissolved in 5 mL of *o*-xylene. To this was added an equimolar amount of $Zn(HMDS)_2$ (1.93 g, 5 mmol). This mixture was allowed to stir overnight. The resultant pale yellow solution was then cooled to 5 °C whereby a modest crop of cube-shaped colorless crystals was formed. Yield 0.92 g, 32% {based on $KZn(HMDS)_3$ as product}; mp 161−162 °C; ^1H NMR $[C_5D_5N]$ δ 0.64 (s, Si*Me*$_3$); ^1H NMR $[C_4D_8O]$ δ 0.08 (s, Si*Me*$_3$); ^{13}C NMR $[C_5D_5N]$ δ 9.4 (Si*Me*$_3$); ^{13}C NMR $[C_4D_8O]$ δ 74.6 (Si*Me*$_3$). *o*-Xylene was removed in vacuo during the isolation process. Microanalysis: Calcd for $KZn(HMDS)_3$: C, 37.1; H, 9.3; N, 7.2. Found: C, 37.3; H, 9.3; N, 7.2.

Synthesis of $[\{K_2Cp\}^+\{Zn(HMDS)_3\}^-]$ (9). KHMDS (1.00 g, 5 mmol) was dissolved with mild heating in 8 mL of dicyclopentadiene. An equimolar amount of $Zn(HMDS)_2$ (1.93 g, 5 mmol) was then added. The mixture was refluxed for 10 min, forming a dark brown solution. Slow cooling of this solution to room temperature yielded a small crop of cube-shaped colorless crystals. Attempts to repeat this reaction have thus far failed.

Syntheses of $[\{Rb(toluene)_3\}^+\{Mg(HMDS)_3\}^-]$ (5) and $[\{Rb(toluene)_3\}^+\{Zn(HMDS)_3\}^-]$ (6). RbHMDS (0.74 g, 3 mmol) was dissolved in 5 mL of toluene. An equimolar amount of $Mg(HMDS)_2$ (1.03 g, 3 mmol) (**5**) or $Zn(HMDS)_2$ (1.16 g, 3 mmol) (**6**) in toluene was then added. The resultant clear, pale yellow solutions were allowed to stir overnight. The solutions were then heated to reflux and cooled slowly to room temperature. After 48 h, modest yields of crystals **5** or **6** were formed.

For **5**: yield 0.41 g, 35% {based on $RbMg(HMDS)_3$ as product}; mp decomposes slowly from 114 °C, melts at 155−156 °C; ^1H NMR $[C_5D_5N]$ δ 0.62 (s, Si*Me*$_3$); ^1H NMR $[C_6D_5CD_3]$ δ 0.53 (s, Si*Me*$_3$); ^{13}C NMR $[C_5D_5N]$ δ 7.2 ($SiMe_3$); ^{13}C NMR $[C_6D_5CD_3]$ δ 7.3 (Si*Me*$_3$). Toluene was removed in vacuo during isolation. Microanalysis: sample was found to lose weight too rapidly during the balance procedure to gain accurate results.

For **6**: yield 0.50 g, 45% {based on $RbZn(HMDS)_3$ as product}; mp 116−117 °C; ^1H NMR $[C_5D_5N]$ δ 0.64 (s, Si*Me*$_3$); ^1H NMR $[C_6D_5CD_3]$ δ 0.51 (s, 36H, Si*Me*$_3$), 0.18 (s, 18H, Si*Me*$_3$); ^{13}C NMR $[C_5D_5N]$ δ 9.4 (Si*Me*$_3$); ^{13}C NMR $[C_6D_5CD_3]$ δ 7.5 (Si*Me*$_3$), 5.1 (Si*Me*$_3$). Toluene was removed in vacuo during isolation. Microanalysis: sample was found to lose weight too rapidly during the balance procedure to gain accurate results.

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Supporting Information Available: Listings giving crystallographic data for **1**, **2a**, **2b**, **3**, **4**, **5**, 6, and **9** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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