Experimental Section

1: $[(Cp^*_2ZrH_3Li)_3]$[19] (0.1 g, 0.27 mmol) was dissolved in THF (3 mL), $PH_2CH_2CH_2PH_2$ (1.0 g, 10.87 mmol) was added dropwise to the stirred, colorless solution which became green, then aquamarine, and finally blue, over a period of 30 min. The reaction was stirred for 72 h, until it became colorless. Solvent was removed in vacuo, leaving a white solid which was dissolved in hexane, filtered, and placed in a freezer (−35 °C). Colorless, X-ray quality crystals (0.86 g, 87 % yield) precipitated from solution, over 24 h. ^{1}H NMR (C_6D_6): $\delta = 3.65$ (dt, 2H, $^1J_{P,H} = 330$, $^3J_{H,H} = 10$ Hz), 2.43 (m, 2H), 1.87 (m, 2H), 1.14 (m, 2H), 0.74 (m, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 38.36, 30.66$; ^{31}P NMR (C_6D_6): $\delta = -22.5$ (P_1: $^1J_{P1,P1} = -237$, $^1J_{P1,P0} = -186$, $^2J_{P1,P0} = 20$ Hz), -65.4 (P_0: $^1J_{P1,P1} = -237$, $^1J_{P1,P0} = -186$, $^2J_{P1,P0} = 20$ Hz); elemental analysis (%) calcd for $P_4C_4H_{10}$: C 26.39, H 5.54; found: C 26.18, H 5.42.

2: A 10 % by weight solution of $[GaMe_3]$ in hexane (378 mg, 0.33 mmol) was added to a vial containing **1** (30 mg, 0.16 mmol), with stirring. A very fine white precipitate was evident in the clear colorless solution after 10 min. An aliquot of the reaction mixture was used immediately for ^{31}P NMR spectroscopic characterization. This compound rapidly degraded on standing. ^{31}P NMR (C_6D_6): $\delta = -19.4$ (m), -65.1 (m).

3: A 2 M hexane solution of $[AlMe_3]$ (0.14 mL, 0.28 mmol) was quickly added to a stirred toluene (1 mL) solution of **1** (20 mg, 0.11 mmol). The reaction mixture was heated to 80 °C in a sealed reaction vessel for 1 week, during which time the solution turned a very pale orange. Solvent was removed in vacuo, and the resulting white solid was dissolved in a 1:1 mixture of THF and hexane, and placed in a freezer (−35 °C) until clear, colorless, cubic crystals of **3** precipitated from solution in 64 % yield. ^{1}H NMR (C_7D_8): $\delta = 2.3$ (brs, 2H), 1.8 (brs, 2H), 1.2 (brs, 3H), 1.1 (brs, 2H), 0.8 (brs, 3H), 0.6 (brs, 2H), -0.2 (brs, 3H), -0.3 (9H), -0.7 (brs, 3H); ^{31}P NMR (C_6D_6): $\delta = 1.9$ (brm), -50.9 (brm), -67.1 (brm) -88.8 (brm); elemental analysis (%) calcd for $C_{11}H_{29}P_4Al_3$: C 36.08, H 7.98; found: C 35.88, H 7.78.

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Experimental and Theoretical Observations of Aromaticity in Heterocyclic XAl_3^- (X = Si, Ge, Sn, Pb) Systems**

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The concept of aromaticity may seem foreign for metallic systems. After all, aromaticity usually refers to cyclic, planar, or conjugated organic molecules which possess $(4n+2)$ π electrons and have a specific chemical and structural stability. Nevertheless, aromaticity has been extended to include

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heterosystems[1–3] and organometallic compounds.[4–6] In particular, Robinson and co-workers have synthesized organometallic compounds that contain a cyclic Ga_3 group stabilized by three large organic ligands.[4] However, aromaticity has never been considered in pure all-metal species. We recently reported experimental and theoretical evidence of aromaticity in an all-metal system, the Al_4^{2-} dianion in a series of bimetallic and ionic clusters MAl_4^- (M = Li, Na, or Cu).[7] The Al_4^{2-} dianion, both as an isolated species and in the bimetallic molecules (MAl_4^-), is square planar and possesses two delocalized π electrons, thus conforming to the structural criterion and the $(4n+2)$ electron-counting rule for aromaticity. The delocalization of the two π electrons is critical for the planar structure and aromaticity of Al_4^{2-}. Herein we explore the possibility of aromaticity in a series of heterosystems, XAl_3^- (X = Si, Ge, Sn, and Pb), which are isoelectronic with Al_4^{2-}. All the XAl_3^- species have two lowest singlet isomers: a four-membered heterocyclic structure (C_{2v}) and a pyramidal structure (C_{3v}). The heterocyclic structure is aromatic, with two delocalized π electrons, analogous to Al_4^{2-}. The substitution of one Al in Al_4^{2-} by Si, Ge, Sn, and Pb allowed us to investigate systematically how the delocalized π orbital, and thus aromaticity, affects the relative stabilities and properties of the heterocyclic and pyramidal structures.

The XAl_3^- anions were produced by laser vaporization of the respective alloy targets.[8] The anionic species from the cluster source were analyzed using a time-of-flight mass spectrometer.[9] The XAl_3^- anions of interest were selected and decelerated before being subjected to photodetachment. Photoelectron spectra of the four XAl_3^- species were taken at two detachment laser wavelengths (355 and 266 nm, Figure 1) by using a magnetic bottle type analyzer,[9] and were calibrated with the known spectra of Cu^-. The photoelectron energy resolution was about 25 meV for 1-eV electrons. The spectra of the four species are similar, each with an intense threshold peak (X and A), followed by another intense peak (B) and a relatively weaker feature (C) only observed in the 266-nm spectra for X = Ge, Sn, and Pb, and also for X = Si in both 266 and 355 nm spectra. Weak low-binding energy features seem to be present in the spectra of $SiAl_3^-$ and $GeAl_3^-$. The X and A features overlapped heavily and were resolved only in the 355-nm spectrum of $PbAl_3^-$. Whereas the binding energies of the X and A features decrease from X = Si to Pb, those of the B and C features increase, leading to the well-separated spectra of $PbAl_3^-$. The vertical detachment energies (VDEs) of the four spectral features measured from the peak maxima are listed in Table 1 and are compared to the values obtained from ab initio calculations.

We have found that combining photoelectron spectroscopy and ab initio calculations offers a particularly powerful approach to investigate the structure and bonding of novel molecular and cluster species.[7, 8, 10, 11] To search for the global minima of XAl_3^-, we first performed ab initio calculations on a wide variety of singlet and triplet structures of $SiAl_3^-$ by using three different and sophisticated theoretical methods.[12, 13] For the heavier XAl_3^- species, we focused only on the two low-lying singlet structures (a C_{2v} cyclic and a C_{3v} pyramidal structure) initially obtained for $SiAl_3^-$. We found that the most stable structure for all four XAl_3^- species is the

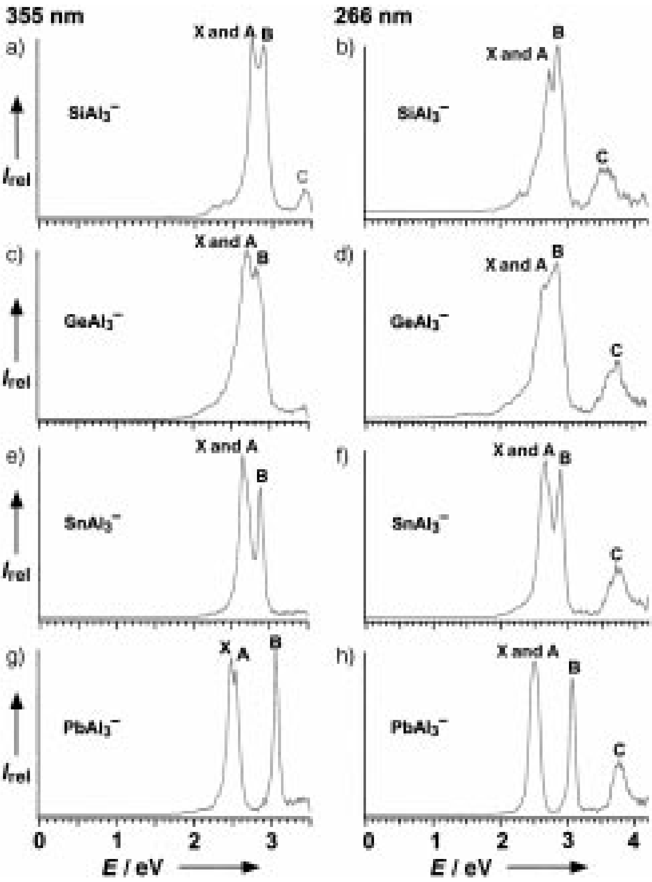

Figure 1. Photoelectron spectra at 355 nm (3.496 eV) of a) $SiAl_3^-$, c) $GeAl_3^-$, e) $SnAl_3^-$, and g) $PbAl_3^-$, and at 266 nm (4.661 eV) of b) $SiAl_3^-$, d) $GeAl_3^-$, f) $SnAl_3^-$, and h) $PbAl_3^-$. The spectra are plotted in order of increasing electron-binding energies.

Table 1. Experimental and theoretical vertical detachment energies (VDE) in eV for $SiAl_3^-$, $GeAl_3^-$, $SnAl_3^-$, and $PbAl_3^-$.

Exp. Features	Exp. VDE	C_{2v} MO	C_{2v} VDE[a]	C_{3v} MO	C_{3v} VDE[a]
		$SiAl_3^-$			
X&A	2.73 ± 0.08	$4a_1$	2.64 (0.86)	2e	2.48 (0.86)
		$1b_1$	2.70 (0.86)	3a	2.72 (0.86)
B	2.88 ± 0.05	$2b_2$	2.82 (0.86)	$2a_1$	4.64 (0.80)
C	3.54 ± 0.10	$3a_1$	3.33 (0.86)		
		$GeAl_3^-$			
X&A	2.70 ± 0.09	$4a_1$	2.61 (0.87)	2e	2.46 (0.86)
		$1b_1$	2.65 (0.86)	3a	2.56 (0.86)
B	2.83 ± 0.08	$2b_2$	2.81 (0.86)	$2a_1$	4.66 (0.79)
C	3.65 ± 0.18	$3a_1$	3.43 (0.86)		
		$SnAl_3^-$			
X	2.66 ± 0.04	$1b_1$	2.47 (0.86)	2e	2.24 (0.86)
A	2.70 ± 0.04	$4a_1$	2.51 (0.86)	$3a_1$	2.43 (0.86)
B	2.88 ± 0.02	$2b_2$	2.71 (0.86)	$2a_1$	5.10 (0.74)
C	3.72 ± 0.06	$3a_1$	3.63 (0.85)		
		$PbAl_3^-$			
X	2.484 ± 0.020	$1b_1$	2.36 (0.86)	2e	2.11 (0.86)
A	2.538 ± 0.020	$4a_1$	2.41 (0.87)	$3a_1$	2.33 (0.86)
B	3.054 ± 0.010	$2b_2$	2.61 (0.86)	$2a_1$	5.79 (0.00)
C	3.76 ± 0.06	$3a_1$	3.74 (0.85)		

[a] The theoretical VDEs were calculated at the OVGF/6-311 + G(2df) or OVGF/4s4p2d1f levels of theory. The numbers in the parentheses indicate the pole strength, which characterizes the validity of the one-electron detachment picture. The ionization processes from the $1b_1$ and $4a_1$ orbitals are too close in energy, and their order cannot be definitely established in our calculations.

C_{2v} cyclic structure (Figure 2a, 2c, 2e, and 2g). The C_{3v} pyramidal structure is a low-lying isomer for all XAl_3^- species (Figure 2b, 2d, 2f, and 2h). The optimized geometries, vibrational frequencies, and relative energies agreed well at the three levels of theory used in this work for all four XAl_3^- species. At our highest level of theory, the global minimum C_{2v} cyclic structure is more stable than the C_{3v} pyramidal structure by 14.7, 18.4, 29.2, and 33.4 kcal mol^{-1} for X = Si, Ge, Sn, and Pb, respectively.

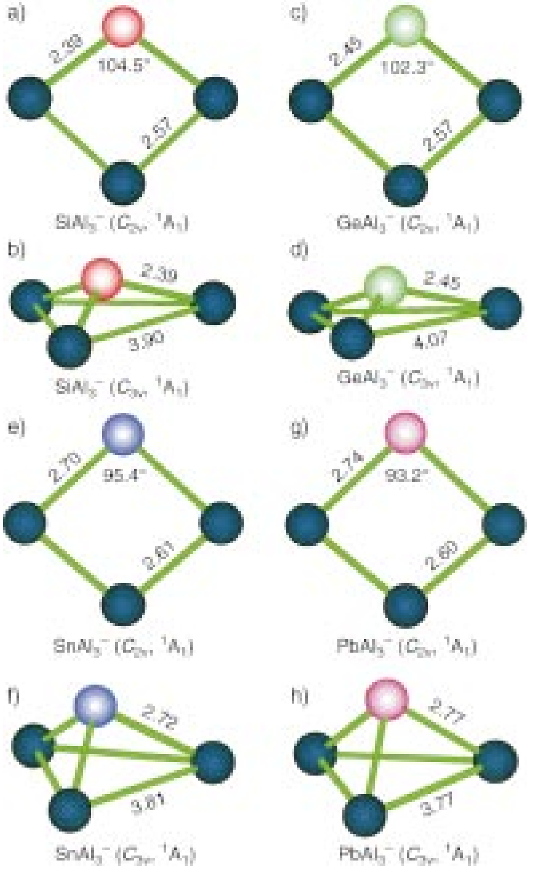

Figure 2. Optimized structures of XAl_3^- at the CCSD(T)/6-311 + G* and CCSD4s4p1d level of theory. Bond lengths are given in Å. a) Cyclic planar $SiAl_3^-$ (C_{2v}, $^1A_1$), b) pyramidal $SiAl_3^-$ (C_{3v}, $^1A_1$), c) cyclic planar $GeAl_3^-$ (C_{2v}, $^1A_1$), d) pyramidal $GeAl_3^-$ (C_{3v}, $^1A_1$), e) cyclic planar $SnAl_3^-$ (C_{2v}, $^1A_1$), f) pyramidal $SnAl_3^-$ (C_{3v}, $^1A_1$), g) cyclic planar $PbAl_3^-$ (C_{2v}, $^1A_1$), and h) pyramidal $PbAl_3^-$ (C_{3v}, $^1A_1$).

Theoretical calculations of the four lowest-lying vertical one-electron detachment processes for the cyclic and pyramidal species are compared with the experimental VDEs in Table 1. Excellent agreement was obtained for all four anions between the predicted VDEs of the C_{2v} cyclic structures and the experimental spectra, whereas the predicted VDEs of the low-lying pyramidal isomers do not agree with the experimental data. The highest occupied molecular orbital (HOMO) of the C_{3v} isomer consists of two degenerate orbitals (2e), which have lower VDEs than those of the HOMO of the C_{2v} cyclic structure. The photoelectron spectra of $SiAl_3^-$ and $GeAl_3^-$ (Figure 1) both exhibited lower binding energy features, which suggests a significant population of the C_{3v} isomer. Similar lower binding-energy features seemed to also exist in the spectra of $SnAl_3^-$ and $PbAl_3^-$, but they are weakened significantly along the $SiAl_3^- \rightarrow GaAl_3^- \rightarrow SnAl_3^- \rightarrow PbAl_3^-$ series. This observation is in complete agreement with the results of our ab initio calculations, which showed that the relative energy of the C_{3v} isomer steadily increased along the same direction. Both this observation and the excellent agreement between the calculated spectra of the cyclic structures and the experimental spectra provide conclusive evidence for the cyclic global minima structures of the XAl_3^- species.

The stability of the C_{2v} cyclic structure relative to the pyramidal structure is related to the $1b_1$ orbital, HOMO-1 in $SiAl_3^-$ and $GeAl_3^-$, and HOMO in $SnAl_3^-$ and $PbAl_3^-$ (Figure 3). Clearly the $1b_1$ orbital is a delocalized π orbital. However, in $SiAl_3^-$ the electron density of the $1b_1$ orbital is heavily concentrated at the Si site. When Si is substituted by the more metallic Ge, Sn, or Pb atoms, the $1b_1$ molecular orbital steadily expands towards the terminal Al atom (Figure 3). Consequently, the stability of the cyclic isomer is enhanced relative to the pyramidal structure. In our previous study of the lighter CAl_3^- species,[14] we found that the pyramidal isomer was the only minimum. The instability of the CAl_3^- planar cyclic isomer is a result of the complete localization of the two π electrons on the C atom, because it is much more electronegative than Al. The series of the XAl_3^-

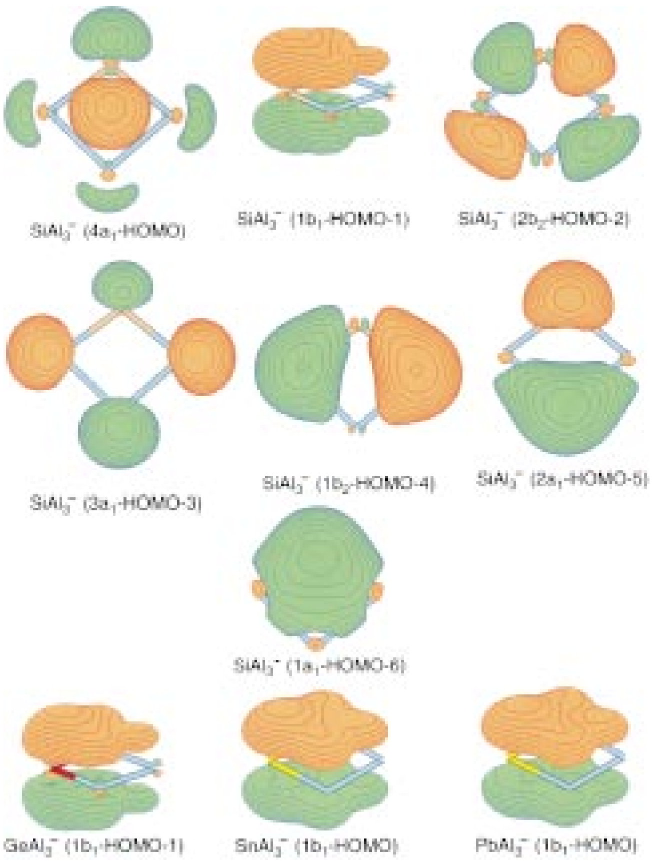

Figure 3. Molecular orbital pictures[15] of cyclic planar $SiAl_3^-$, showing the highest occupied molecular orbital (HOMO, $4a_1$) down to the sixth valence molecular orbital from the HOMO (HOMO-6, $1a_1$), and the delocalized π orbitals ($1b_1$) of $GeAl_3^-$, $SnAl_3^-$, and $PbAl_3^-$.

species thus provide unequivocal evidence that the delocalization of the π electrons is responsible for the C_{2v} cyclic structure, rendering the more metallic heterosystems aromatic. Schaefer and co-workers[16] recently performed theoretical studies on model heterocyclic three-membered ring systems related to the Ga_3 organometallic compounds and concluded that these systems were indeed also aromatic.

Herein we extended the concept of aromaticity to the heterocyclic four-membered ring all-metal systems, XAl_3^-. We showed systematically the importance of the delocalization of the π electrons for the stability of the cyclic aromatic structure. Metallic systems can be aromatic when they are composed of heteroatoms, provided that the heteroatoms have similar electronegativities to the rest of atoms of the ring. However, if the heretoatoms differ substantially in their electronegativities, such as C in CAl_3^-,[14] the cyclic aromatic structure is no longer a minimum.

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[12] We initially optimized the geometries and calculated the frequencies of XAl_3^- by using analytical gradients with polarized split-valence basis sets (6-311 + G*) for Al, Si and Ge in XAl_3^-, and the LANL2DZ basis sets (extending by additional two s, two p and one d functions resulting in (5s5p1d/4s4p1d) basis sets) and the relativistic effective core potentials for Al, Sn, and Pb in XAl_3^-, and a hybrid method known in the literature as B3LYP. Then we refined the geometries and calculated the frequencies at the second-order Møller-Plesset perturbation theory (MP2) level. The two most stable planar cyclic and pyramidal structures were studied further by using the coupled-cluster method (CCSD(T)) with the same basis sets. The energies of the most stable structures were refined by using the CCSD(T) method, the more extended 6-311 + G(2df) basis sets for Al, Si, and Ge, and (5s5p2d1f/4s4p2d1f) valent basis sets and relativistic core potentials for Al, Sn, and Pb. The vertical electron-detachment energies were calculated by using the outer valence Green Function method (OVGF/6-311 + G(2df) for XAl_3^- (X = Si, Ge) and OVGF/4s4p2d1f for XAl_3^- (X = Sn, Pb)), and the CCSD(T)/6-311 + G* and CCSD(T)/4s4p1d geometries, respectively. All calculations were performed by using the Gaussian 98 program[13].

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Template-Directed Synthesis of a [2]Rotaxane by the Clipping under Thermodynamic Control of a Crown Ether Like Macrocycle Around a Dialkylammonium Ion**

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Andrew J. P. White, and David J. Williams*

New synthetic procedures for preparing rotaxanes[1] are appearing in the current literature[2] with ever-increasing regularity as a result of the attention[3] these mechanically interlocked molecules[4] are receiving because of their rapidly growing promise as molecular switches for developing devices[5] on the mesoscale and as linear motor-molecules for constructing artificial molecular machinery[6] on the nanoscale. One of the simplest recognition motifs that produces pseudorotaxanes,[7] complexes that are often the precursors of catenanes and rotaxanes, is the binding[8] of dialkylammonium ions with suitably large macrocycles, for example, dibenzo[24]crown-8. Although this motif has so far yielded rotaxanes by both the threading-followed-by-stoppering[9] and slippage[10] approaches, until now no rotaxanes based on the dialkylammonium ion have been synthesized using a clipping[11] protocol. Here, we report the template-directed synthesis[4c, 12] of a [2]rotaxane by a clipping approach under thermodynamic control and the subsequent conversion of the dynamic products into a kinetically stable [2]rotaxane which

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