Experimental Section

1: [(Cp∗2ZrH3Li)3][19] (0.1 g, 0.27 mmol) was dissolved in THF (3 mL), CH3C6H4CH2CH2;P (1.0 g, 10.87 mmol) was added to a stirred toluene (1 mL) solution of 1. The reaction mixture was heated to 80 °C, 1.87 (m, 2 H), 1.14 (m, 2 H), 0.74 (m, 2 H); 13C{1H} NMR (C6D6): δ = 65.1 (m), 67.2 (m), 68.8 (br m), 0.2 (br s, 3 H), 0.7 (br s, 3 H); elemental analysis (%) calcd for P 4C4H10: C 26.39, H 5.54; found: C 26.18, H 5.42.

2: A 10% by weight solution of [GaMe3] in hexane (378 mg, 0.33 mmol) was quickly added to a stirred toluene (1 mL) solution of [AlMe3] (0.14 mL, 0.28 mmol) was quickly placed in a freezer (−20 °C). 3: A 2 M hexane solution of [AlMe3] (0.14 mL, 0.28 mmol) was quickly added to a stirred toluene (1 mL) solution of [AlMe3] (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 P were precipitated from solution in 64% yield. 4H NMR (C6D6): δ = 2.3 (brs, 2 H), 1.8 (brs, 2 H), 1.2 (brs, 3 H), 1.1 (brs, 2 H), 0.8 (brs, 3 H), 0.6 (brs, 2 H), 0.2 (brs, 3 H), −0.3 (9 H), −0.7 (brs, 3 H); 13P NMR (C6D6): δ = −1.9 (brm), −50.9 (brm), −67.1 (brm) −88.8 (brm); elemental analysis (%) calcd for C14H14P3AlC1: C 36.08, H 7.98; found: C 35.88, H 7.98.

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[20] Diffraction experiments were performed on a Siemens SMART System CCD diffractometer and solved with the SHELXL-97 software package.

Experimental and Theoretical Observations of Aromaticity in Heterocyclic XAl3− (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...
heterosystems[1–3] and organometallic compounds[4–6] In particular, Robinson and co-workers have synthesized organo-
metallic compounds that contain a cyclic Ga3 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 aromatic-
ity in an all-metal system, the Al42− dianion in a series of bimetallic and ionic clusters MA1− (M = Li, Na, or Cu).[7] The
Al42− dianion, both as an isolated species and in the bimetallic molecules (MA1−), is square planar and possesses two
delocalized π electrons, thus conforming to the structural criterion and the (4n + 2) electron-counting rule for aromatic-
ity. The delocalization of the two π electrons is critical for the planar structure and aromaticity of Al42−. Herein we
explore the possibility of aromaticity in a series of hetero-
systems, XAl3− (X = Si, Ge, Sn, and Pb), which are isoel-
ectrionic with Al42−. All the XAl3− species have two lowest
singlet isomers: a four-membered heterocyclic structure (C2v) and a pyramidal structure (Cn). The heterocyclic structure is
aromatic, with two delocalized π electrons, analogous to Al42−. The substitution of one Al in Al42− 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 XAl3− anions were produced by laser vaporization of the respective alloy targets.[9] The anionic species from the
cluster source were analyzed using a time-of-flight mass spectrometer.[9] The XAl3− anions of interest were selected and
decelerated before being subjected to photodetachment. Photoelectron spectra of the four XAl3− 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
energy resolution was about 25 meV for 1-eV electrons. The
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 SiAl3− and GeAl3−. The X and A features overlapped heavily and were
resolved only in the 355-nm spectrum of PbAl3−. 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 PbAl3−. 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.[7–11] To search for the global
minima of XAl3−, we first performed ab initio calculations on a wide variety of singlet and triplet structures of SiAl3−
by using three different and sophisticated theoretical meth-
ods.[12, 13] For the heavier XAl3− species, we focused only on the two low-lying singlet structures (a C2v cyclic and a Cn
pyramidal structure) initially obtained for SiAl3−. We found that the most stable structure for all four XAl3− species is the

![Figure 1. Photoelectron spectra at 355 nm (3.496 eV) of a) SiAl3−, c) GeAl3−, e) SnAl3−, and g) PbAl3−, and at 266 nm (4.661 eV) of b) SiAl3−, d) GeAl3−, f) SnAl3−, and h) PbAl3−. The spectra are plotted in order of increasing electron-binding energies.](image)

<table>
<thead>
<tr>
<th>Exp. Features</th>
<th>Exp. VDE</th>
<th>MO</th>
<th>( C_{\text{SiAl}^2-} ) VDE[a]</th>
<th>MO</th>
<th>( C_{\text{GeAl}^2-} ) VDE[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X&amp;A</td>
<td>2.73 ± 0.08</td>
<td>4a1</td>
<td>2.64 (0.86)</td>
<td>2e</td>
<td>2.48 (0.86)</td>
</tr>
<tr>
<td>B</td>
<td>2.88 ± 0.05</td>
<td>2b2</td>
<td>2.82 (0.86)</td>
<td>2a1</td>
<td>4.64 (0.80)</td>
</tr>
<tr>
<td>C</td>
<td>3.54 ± 0.10</td>
<td>3a1</td>
<td>3.33 (0.86)</td>
<td>( \text{GeAl}^2- )</td>
<td>( \text{GeAl}^2- )</td>
</tr>
<tr>
<td>X&amp;A</td>
<td>2.70 ± 0.09</td>
<td>4a1</td>
<td>2.61 (0.87)</td>
<td>2e</td>
<td>2.46 (0.86)</td>
</tr>
<tr>
<td>B</td>
<td>2.83 ± 0.08</td>
<td>2b2</td>
<td>2.81 (0.86)</td>
<td>2a1</td>
<td>4.66 (0.79)</td>
</tr>
<tr>
<td>C</td>
<td>3.65 ± 0.18</td>
<td>3a1</td>
<td>3.43 (0.86)</td>
<td>( \text{SnAl}^2- )</td>
<td>( \text{SnAl}^2- )</td>
</tr>
<tr>
<td>X</td>
<td>2.66 ± 0.04</td>
<td>1b1</td>
<td>2.47 (0.86)</td>
<td>2e</td>
<td>2.24 (0.86)</td>
</tr>
<tr>
<td>A</td>
<td>2.70 ± 0.04</td>
<td>4a1</td>
<td>2.51 (0.86)</td>
<td>3a1</td>
<td>2.43 (0.86)</td>
</tr>
<tr>
<td>B</td>
<td>2.88 ± 0.02</td>
<td>2b2</td>
<td>2.71 (0.86)</td>
<td>2a1</td>
<td>5.10 (0.74)</td>
</tr>
<tr>
<td>C</td>
<td>3.72 ± 0.06</td>
<td>3a1</td>
<td>3.63 (0.85)</td>
<td>( \text{PbAl}^2- )</td>
<td>( \text{PbAl}^2- )</td>
</tr>
</tbody>
</table>

[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 1b1 and 4a1 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.

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 $p$ 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 CAI$_3^-$ species,$^{[14]}$ we found that the pyramidal isomer was the only minimum. The instability of the CAI$_3^-$ planar cyclic isomer is a result of the complete localization of the two $\pi$ electrons on the C atom, because it is much more electronreceptive than Al. The series of the XAl$_3^-$
species thus provide unequivocal evidence that the delocalization of the π electrons is responsible for the C₆₀ cyclic structure, rendering the more metallic heterosystems aromatic. Schaefer and co-workers[10] recently performed theoretical studies on model heterocyclic three-membered ring systems related to the Ga₃ 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, XAl₃⁻. 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 heteroatoms differ substantially in their electronegativities, such as C in CAI₃⁻,[14] the cyclic aromatic structure is no longer a minimum.

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

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