bishomotropylium cation **9** (16.6 kcal mol^{-1} more stable than **4**), was confirmed to be bishomoaromatic by Cremer based on geometric and magnetic criteria.[15] The NICS at the geometric center of **9** (-11.8) and $\Lambda = -18.5$ ppm cgs (i.e., similar to that of **4**[16]), corroborate this conclusion. This cation reacts to give the observed *cis*-8,9-dihydroindenes **3** (X = OH or Cl).[4,5]

In summary, the geometric and magnetic criteria (NICS and Λ) exhibited by **4** now reveal this species to be the first Möbius aromatic system in the Heilbronner sense, for which there is experimental evidence.[4,5] Without such evidence, the nature of **4** was not recognized originally. Furthermore, early speculations were incorrect: While conformation **6** is avoided, transition state **7** is not high in energy.[5b] The complete scrambling of the deuterium label, observed for **3** even at $-66\,^{\circ}$C, is consistent with the low barrier computed for **7**, permitting rapid interconversion of the helical **4** enantiomers. Ninefold repetition of the enantiomerization results in complete distribution of a deuterium label in **4**. In conclusion, the experimental findings reported nearly three decades ago[4,5] are explained by assuming that the $(CH)_9^+$ intermediates were 4*n*-electron Möbius aromatic systems. Our prediction that **4** is the most stable monocyclic $(CH)_9^+$ cation might be verified by applying modern experimental techniques such as laser flash photolysis, which has been employed to observe short-lived carbocations.[17]

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$Cp^*_3Al_5I_6$: An Intermediate in Reactions Leading to Elemental Aluminum and Al^{III} Species?**

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Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

As we have demonstrated in earlier work, Al^{I} species are reactive both in solid noble gases and under preparative synthetic conditions,[1] and often react to give thermodynamically more stable Al^{III} products and metallic aluminum. $[Cp^*_2Al]^+[Cp^*AlCl_3]^-$ is thus formed as the final product from Cp*Al and $AlCl_3$ with simultaneous deposition of aluminum. This isomer of the sesquichloride $[Cp^*_3Al_2Cl_3]$ contains the aluminocenium ion $[Cp^*_2Al]^+$ as a structural peculiarity.[2] To understand this reaction mechanism and to find out how Al^{I} species can react in general, we carried out investigations with the aim of capturing intermediate products of the disproportionation.

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To prepare as stable an intermediate as possible, we selected AlI_3 instead of $AlCl_3$ and treated the iodide with [{Cp*Al}$_4$] under the exclusion of donors; that is, we provided soft substituents that have a proven capability for stabilizing elements in low oxidation states. It became apparent that the presence of Al_2I_6 dramatically increased the tendency of [Cp*Al] to disproportionate: Whereas pure [Cp*Al] can be heated in solution to almost 90 °C without visible decomposition, it disproportionates in the presence of Al_2I_6 even below room temperature. This means that even a relatively stable Al^I compound such as [Cp*Al] reacts so rapidly at room temperature that intermediate products cannot normally be intercepted.[3] In view of this, proof of the participation of other Al^I species in the reaction between Al^0 and Al^{III} should be even more difficult if not altogether impossible to obtain. Therefore, the structurally characterized intermediate product presented here—[$Cp^*_3Al_5I_6$] (**1**), which could be isolated at −20 °C—is of particular significance (Figure 1a).

Compound **1** is formed from a suspension of [{Cp*Al}$_4$] and Al_2I_6 (molar ratio 1:2) in toluene at −20 °C. It is a colorless substance and very sensitive to hydrolysis. Crystals of **1** thus obtained contain toluene such that the formula may be written as **1**·0.5C_7H_8. The X-ray structure analysis[5] at −73 °C shows that **1** has a cagelike framework comprising five Al and two I atoms, in which the aluminum atom Al(1) is coordinated in a tetrahedral fashion by two iodine atoms (Al(1)–I(1) 257, Al(1)–I(2) 254 pm) and two Cp*-substituted aluminum atoms (Al(2), Al(3); Al–Al 252–253, Al–C 214–224 pm) (Figure 1a). The iodine atoms I(3) and I(4) lie at a considerably larger distance from Al(1) (Al(1)–I(3) 398, Al(1)–I(4) 388 pm) and form a plane with I(1) and I(2); Al(1) also lies in this plane.

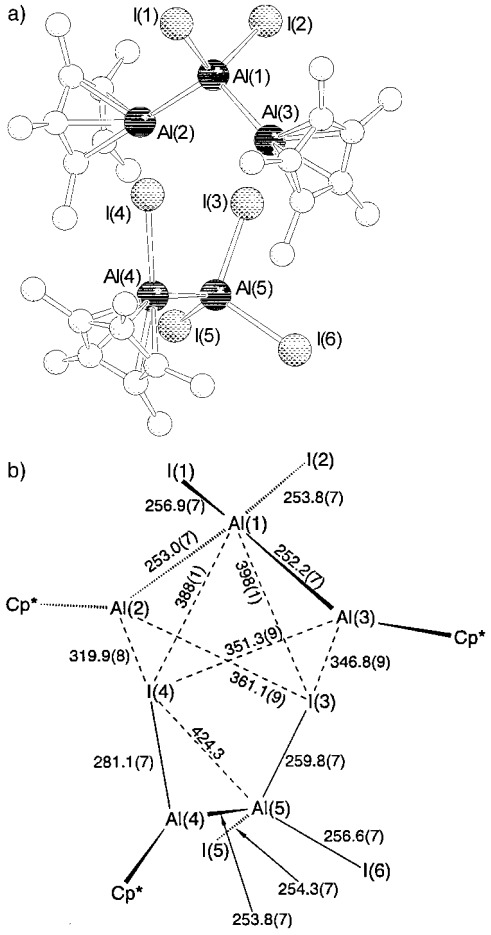
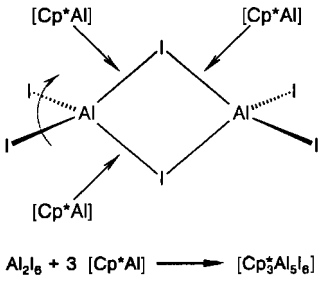


Figure 1. a) Structure of **1** in the crystal (SCHAKAL[4]). Hydrogen atoms are not shown. b) Schematic representation of the structure of **1** with several distances [pm]. Further distances [pm] and angles [°]: Al(2)–Al(3) 407(1), Al(2)/Al(3)–C_{Cp^*} 214.4(6)–224.4(7), Al(4)–C(21) 233.6(6), Al(4)–C(22) 227.1(6), Al(4)–C(23) 215.2(5), Al(4)–C(24) 215.6(6), Al(4)–C(25) 225.3(7), Al(1)–Al(5) 597(2), Al(1)–Al(4) 608(2); Al(2)-Al(1)-Al(3) 107.23(7), I(1)-Al(1)-I(2) 111.73(9), C_{Cp^*}-Al-Al(1) 117.3(2)–176.9(2), Al(5)-Al(4)-I(4) 104.83(7), Al(4)-Al(5)-I(6) 111.10(8), Al(4)-Al(5)-I(3) 111.27(7), I(6)-Al(5)-I(3) 108.04(13).

An Al_2 unit (Al(4), Al(5); Al–Al 254 pm) is arranged almost perpendicular to the Al_3 group. One of the metal atoms of this Al_2 unit is coordinated by three iodine atoms (Al(5)–I(3) 260, Al(5)–I(5) 254, Al(5)–I(6) 257 pm), and the other by one iodine atom and a Cp* substituent (Al(4)–I(4) 281, Al(4)–C 215–234 pm). The iodine atoms I(3) and I(4) occupy an eclipsed conformation with respect to the Al_2 unit. In addition, there are interactions between these iodine atoms and the Al atoms Al(2) and Al(3) of the Al_3 unit. The atomic distances are shown in Figure 1b.[6] In agreement with the average oxidation number 1.8 for aluminum, the Al–Al and Al–I distances in **1** resemble those in donor-stabilized aluminum(II) diiodides.[10] The structure of **1** provides a first indication of the reaction mechanism for the reaction of [Cp*Al] with Al_2I_6 (Scheme 1).



Scheme 1. Reaction of three molecules of [Cp*Al] with one molecule of Al_2I_6. Schematic representation (top) and reaction equation (bottom).

It is apparent that monomeric [Cp*Al] has a tendency to undergo insertion reactions. Even at −20 °C—that is, at very low [Cp*Al] concentrations[11]—three [Cp*Al] molecules are inserted into bridging Al–I bonds. At the same time, three bridging Al–I bonds of Al_2I_6 are expanded so much that only the weak Al-I-Al bridging interactions mentioned above remain.

To decide whether the experimentally observed species should be described as separated ions [$Cp^*_2Al_3I_2$]$^+$-[$Cp^*Al_2I_4$]$^-$, as an ion pair, or as a donor–acceptor complex, we carried out extensive quantum-chemical calculations.[9] These show that the calculated geometry parameters (e.g., several Al–I distances and the angle Al_{Cp^*}-Al-Al_{Cp^*}) for isolated ions do not agree with the observed structural data. Additional calculations were therefore carried out for the model compounds [$Cp_3Al_5I_6$] (**1a**), $Br_3Al_5I_6$ (**1b**), and $H_3Al_5I_6$ (**1c**).[9] It became clear that the geometry is decisively influenced by the Cp* groups, because both the hydrogen-

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and the bromine-substituted compounds have quite different Al–I distances in the bridges and very acute Al-Al-Al angles in the Al_3 unit when compared with **1a**. The compounds **1a–c** also differ from one another considerably with regard to the population analyses. Whereas the calculations for **1a** result in a clear charge separation between the Al_3 and Al_2 units (± 0.38) and negatively charged bridging iodine atoms (-0.15), there are virtually no charge separations (Al_3: approx. -0.04; Al_2: ca. $+0.04$). Furthermore, there are only very weakly negatively polarized bridging iodine atoms (ca. -0.04) in **1b** and **1c**.[9e]

The compounds **1a–c** also differ in their energy balance. The insertion of three AlH units into a Al_2I_6 molecule is, with 438 kJ mol^{-1}, highly exothermic, whereas the insertion of the CpAl units leads to an energy gain of just 199 kJ mol^{-1}. These thermodynamic results are plausible in view of the calculated charge separation in **1a**. In conclusion, the quantum-chemical calculations, which in the case of **1a** produce results that are in good agreement with the experimental structural data of **1**, permit the following bonding description for this intermediate. In contrast to the donor–acceptor complexes **1b** and **1c**, **1** and **1a** are best described as contact ion pairs that disproportionate at room temperature to give elemental aluminum and Al^{III} species.[12]

This type of insertion of Al^{I} species can also occur in technically relevant electrochemical reductions[13] of organic aluminum(III) compounds. The resulting primary products can insert themselves into the reagents and react in an analogous manner to **1** to give species rich in aluminum. Unstable intermediates such as these can then spontaneously disproportionate to give elemental aluminum. The starting compound (Al^{III}) is also formed, which can then go through the reaction cycle again. In a similar manner, Al^{I} species could also be important intermediates in the preparation of organic aluminum compounds from aluminum and alkyl halides, whereby the insertion of Al^{I} compounds into Al^{III} species already formed could possibly lead to compounds analogous to **1**.[14]

Experimental Section

AlI_3 (50 mg, 0.12 mmol) was combined with [{Cp*Al}$_4$] (20 mg, 0.03 mmol), and toluene was added. The suspension was stored at $-20\,^{\circ}$C. After a few days clear, colorless crystals of **1** were formed along with solid [{Cp*Al}$_4$]. Elemental aluminum was not deposited under these conditions. To transfer the crystals quickly from the cold suspension onto the goniometer head, they were warmed to room temperature in mineral oil (Aldrich) under an argon stream. (The crystals decompose slowly in this oil; the color changes from colorless to yellow and then to red.) In the cold N_2 stream (200 K) on the goniometer head, a glass-like protective coating is formed around the crystal, thus preventing attack by air and moisture.

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be regarded as a donor–acceptor complex, as there is no charge separation between the Al units and the bridging iodine atoms are only weakly charged.[9d] $[H_3Al_5I_6]$ (**1c**; C_1 symmetry): $E = -1282.817496$; Al(1)–Al(2) 259.7, Al(1)–Al(3) 259.7, Al(2)–I(3) 291.9, Al(2)–I(4) 305.3, Al(3)–I(3) 292.2, Al(3)–I(4) 305.4, Al(4)–I(4) 268.4, Al(5)–I(3) 282.0, Al(4)–Al(5) 256.4, Al(2)–Al(3) 333.0; Al(2)-Al(1)-Al(3) 79.8, I(4)-Al(4)-Al(5) 114.2, Al(4)-Al(5)-I(3) 100.2; $\delta(H_{Al(4)}) = -0.02$, $\delta(H_{Al(2)}) = 0.09$, $\delta(H_{Al(3)}) = 0.09$, $\delta(Al(1)) = 0.40$, $\delta(Al(2)) = 0.04$, $\delta(Al(3)) = 0.04$, $\delta(Al(4)) = 0.28$, $\delta(Al(5)) = 0.35$, $\delta(I(3)) = -0.03$, $\delta(I(4)) = -0.05$, $\delta(I(5)) = -0.24$, $\delta(\text{“}Al_3\text{”}) = -0.05$, $\delta(\text{“}Al_2\text{”}) = 0.05$; that is, **1c** should be regarded as a donor–acceptor complex, as there is no charge separation between the Al units and the bridging iodine atoms are only weakly charged.[9d] $Al_2I_6 + 3\,AlH \rightarrow H_3Al_5I_6$: $\Delta E = -438\ kJ\,mol^{-1}$. $Al_2I_6 + 3[CpAl] \rightarrow [Cp_3Al_5I_6]$: $\Delta E = -199\ kJ\,mol^{-1}$. a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283–290; *Chem. Phys. Lett.* **1995**, *242*, 652–660; b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169; c) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577. d) A similar polarization was also calculated for Al_2I_6: donor-acceptor complex; D_{2h} symmetry; $Al-I_{bridge}$ 270.7, $Al-I_{terminal}$ 250.2, Al–Al 367.8; $\delta(I_{bridge}) = -0.05$, $\delta(I_{terminal}) = -0.21$; $\delta(Al) = 0.47$.

[10] a) A. Ecker, E. Baum, M. A. Friesen, M. A. Junker, C. Üffing, R. Köppe, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1998**, *624*, 513–516; b) A. Ecker, H. Schnöckel, *Z. Anorg. Allg. Chem.*, in press.

[11] In the ^{27}Al NMR spectrum, monomeric [Cp*Al] can only be identified in equilibrium with $[\{Cp^*Al\}_4]$ above about 60 °C, because the energy for the tetramerization to $[\{Cp^*Al\}_4]$ is around $-150\ kJ\,mol^{-1}$.[1]

[12] The NMR spectrum of a mixture of $[\{Cp^*Al\}_4]$ and Al_2I_6 in deuterated toluene shows signals at the following shifts: ^1H NMR (Bruker AC-250 spectrometer (250.134 MHz); room temperature; reference: $\delta(C_7D_7H)$): $\delta = 2.09$; ^{27}Al NMR (Bruker AMX-300 spectrometer; room temperature; external reference: $\delta([Al(H_2O)_6]^{3+})$): $\delta = 0$. After a reaction period of a few days at −20 °C: ^1H NMR: δ ($\omega_{1/2}$[Hz]) = 2.07 (10), 2.03 (10) (both with low intensity), 1.93 (2), 1.85 (3), 1.78 (3), 1.60 (3) (the latter in a ratio of about 3:3:2); ^{27}Al NMR: δ ($\omega_{1/2}$[Hz]) = 110 (br, weak), −21 (550), −83 (260). After about one month at −20 °C: ^1H NMR: δ ($\omega_{1/2}$[Hz]) = 1.85 (2), 1.74 (2), 1.60 (2) (in a ratio of about 2:3:4); ^{27}Al NMR: δ ($\omega_{1/2}$[Hz]) = 110 (br, weak), −21 (520), −82 (260). After about three months and intermediate tempering at 120 °C: ^1H NMR: δ ($\omega_{1/2}$[Hz]) = 1.57 (sharp, s); ^{27}Al-NMR: δ ($\omega_{1/2}$[Hz]) = −19 (500, weak), −81 (360), −114 (very weak, $[Cp^*_2Al]^+$).[2a] These NMR spectroscopic results indicate a more complex reaction sequence than for the reaction between $[\{Cp^*Al\}_4]$ and $AlCl_3$.[2a]

[13] See, for example, the electrochemical reduction of Al^{III} species to elemental aluminum or the preparation of simple organic aluminum(III) compounds from aluminum and alkyl halides: K. Ziegler, H. Lehmkuhl, *Z. Anorg. Allg. Chem.* **1956**, *283*, 414–424; W. Kautek, W. Fromberg, J. A. de Hek, *Metalloberfläche* **1992**, *46*, 67–74; J. Fischer, *Metalloberfläche* **1996**, *50*, 183–184; A. Ecker, H. Schnöckel, *VDI-Nachrichten* **1996**, *50*, 22; H. Köhnlein, H. Schnöckel, *Aluminum* **1997**, *73*, 766–767.

[14] Additional Al^{III} species are formed by their subsequent disproportionation. This should lead to an increase in the reaction rate for the formation of the desired end products.

Average Octet Radical Polymer: A Stable Polyphenoxyl with Star-Shaped π Conjugation**

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The search for syntheses of organic molecules with very high spin resulting from intramolecular through-bond magnetic ordering is driven by the desire to realize magnetism based purely on organic components.[1] High-spin alignment in the ground state has been demonstrated for cross-conjugated polyradicals or radical polymer main chains, such as poly(1,3-phenylenecarbene)[1b] and poly(1,3-phenylenephenylmethine).[1c] Pseudo-two-dimensional branched, cyclic, and ladder homologues have also been synthesized to increase the spin quantum number S at low temperature.[2] The aim was to diminish the damage of a radical or spin defect, which is fatal for the cross-conjugated polyradicals. In addition, these polyradicals lacked chemical stability at room temperature.

There is another approach to the high-spin molecules that makes use of π-conjugated linear polymers bearing pendant radical groups on the polymer backbone which are π-conjugated with the backbone to ensure the ferromagnetic connectivity of the radicals.[1e] In this type of polyradical, the spin alignment between the pendant unpaired electrons is not sensitive to a spin defects, which are unavoidable for radical polymers of increasing molecular size because the magnetic interaction is transmitted through the π-conjugated polymer backbone. A further advantage is that the pendant, built-in radical groups could be chosen from a series of chemically stable organic radicals. We recently synthesized poly(1,2-phenylenevinylene) containing di-*tert*-butylphenoxyl as the pendant radical group (**1**) which has a through-conjugated backbone bond and allows long-range ferromagnetic exchange interaction between the pendant unpaired electrons: With a spin concentration of 0.7 per monomer unit, **1** displays values for S of 4/2 to 5/2.[3] We report here our successful improvement of both S and the stability of the polyradical by extending **1** to the star-shaped homologue **2** (Scheme 1).

The precursor acetoxypolymer **2″** was synthesized in a one-pot reaction by the Pd-catalyzed Heck reaction of styrene **3** with 1,3,5-triiodobenzene (**4**), the core of the star-shaped polymer (see the Experimental Section). The molecular weight and degree of polymerization ($DP = l + m + n + 6$ for **2**) of the star-shaped polymer was controlled by the feed ratio of **3** to **4** during the polymerization. The iodide groups had completely reacted in every polymer. The DP measured by

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