

Synthesis and Structure of a Neutral SiAl₁₄ Cluster

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Abstract: A metastable AlCl solution obtained by co-condensation of the high-temperature molecule AlCl and a mixture of toluene/diethyl ether reacted with SiCp*₂ or SiCl₄/AlCp*, giving a unique SiAl₁₄ cluster species that bears six Cp* ligands protecting the compound from disproportionation and formation of the bulk material (elemental Al or an Si/Al alloy). The structure of the SiAl₁₄ core represents a section of the body-centered packing where a Si atom resides in the center of an Al cube. Each of the six faces of the cube is capped by an additional Al(η^5 Cp*) moiety. This cluster compound was investigated by mass spectrometry, X-ray diffraction, ²⁷Al NMR spectroscopy, and ab initio theory. The solid-state structure contains minor amounts of molecules with additional Cl atoms bonded to the Al atoms at the corners of the cube, and the presence of Cl-containing molecules in the crystal is rationalized on basis of the suggested reaction path.

Introduction

Metastable solutions of aluminum(I) halides have been proved to be powerful starting materials for a new area in Al chemistry.¹ These solutions are metastable with respect to disproportionation into the solid Al metal and normal trivalent Al compounds. Employing these solutions, it was possible to synthesize a number of new species, such as a unique Al₇₇ cluster stabilized by 20 bulky ligands, which is the largest metal atom cluster characterized by X-ray diffraction so far.² To prepare Al cluster compounds that incorporate Si atoms, which may be important for nanoscale physics, we performed the experiments described herein.

Results

The Cp* compounds of low-valent silicon and aluminum were prepared^{3,4} some years ago, and therefore, we started our investigation by reacting SiCp*₂ and AlCp*, (Al₄Cp*₄ was the first structurally characterized Al₄ cluster). Even at elevated temperatures (100 °C), no reaction was observed and so we substituted AlCp* by a more reactive AlCl solution in toluene/diethyl ether.⁵ Heating a solution of AlCl and SiCp*₂ for 3 h to ~60 °C afforded black hexagonal crystals that grew at room temperature within a few days. In an alternative procedure, these crystals were later obtained in a more simple reaction between AlCl, SiCl₄, and AlCp*. Although we will focus on the black crystals mentioned above, other products characterized in the

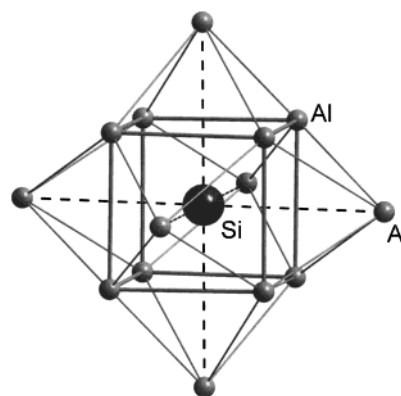


Figure 1. Calculated geometry of SiAl₁₄Cp*₆. The Cp* ligands were omitted for clarity.

same reaction shall be listed: Colorless crystals of Si(AlCl₂·Et₂O)₄ (**2**) were characterized by X-ray methods⁶ and AlCp*Cl₂·Et₂O has been detected in the NMR spectrum.⁷ Both compounds are important for the proposed reaction path. The black crystals, which are of main interest here, were initially investigated by X-ray methods, but even after the data collection of several crystals, some problems concerning the structure refinement still remain.⁸ These problems are the reason for a four-year delay of publication after the first presentation of **1** in 1996.⁹ The preliminary results unambiguously showed the SiAl₁₄ core presented in Figure 1 to be the central unit of this compound (**1**). X-ray fluorescence analysis (EDAX) of the crystals confirmed this composition (Si:Al = 1:16).

To overcome the mentioned crystallographic problems, we first substituted toluene, which was incorporated in the crystals, by *m*-xylene. However, the additional unassigned electron

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(1) Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem.* **1996**, *108*, 141; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129.

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(3) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem.* **1986**, *98*, 163; *Angew. Chem., Int. Ed. Engl.*, **1986**, *23*, 164.

(4) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem.* **1991**, *103*, 594; *Angew. Chem., Int. Ed. Engl.*, **1991**, *30*, 564.

(5) Tacke, M.; Schnöckel, H. *Inorg. Chem.* **1989**, *28*, 2895.

(6) Purath, A.; Dohmeier, C.; Baum, E.; Köppe, R.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2144.

(7) Ecker, E. Dissertation, Faculty of Chemistry, University of Karlsruhe, 1996.

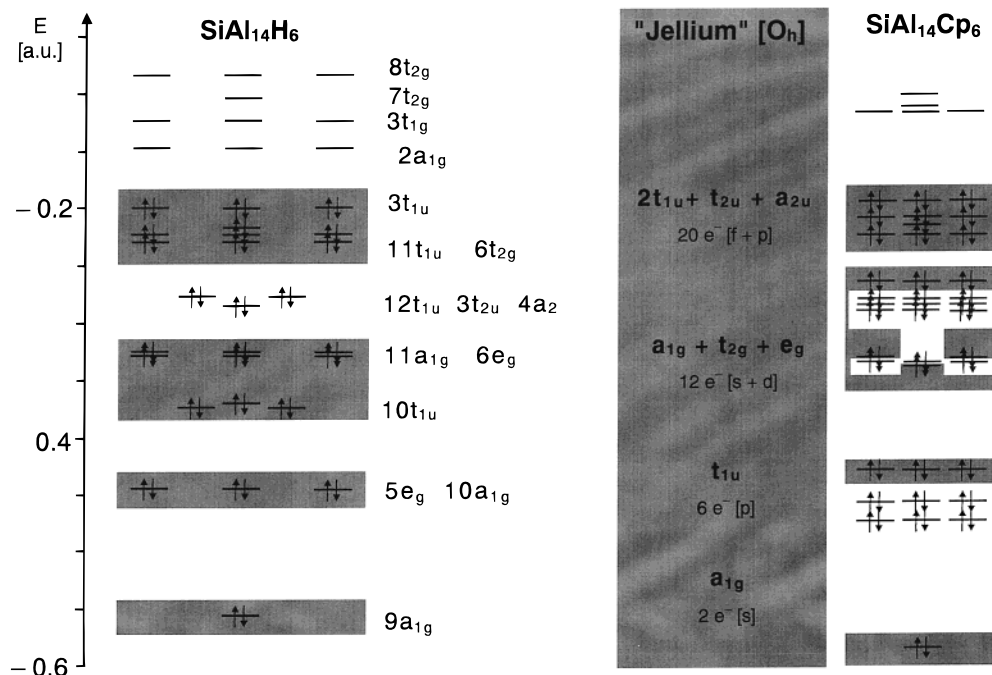


Figure 2. MOs of the $\text{SiAl}_{14}\text{H}_6$ and $\text{SiAl}_{14}\text{Cp}_6$ species. The expected MO separation concluded from the Jellium model is added. The delocalized cluster orbitals are gray-shaded, the remaining are ligand orbitals. For $\text{SiAl}_{14}\text{Cp}_6$ only the 18 π -MOs of the Cp ligands are mentioned.

density remained. In a further experiment, the conditions of crystallization were changed to a higher temperature and with these crystals the problems of the crystal structure determination decreased: The electron density within the Al_8 cube disappeared for every experiment while that residing on the diagonal corners was assigned to impurities containing additional Cl atoms. These new findings will be discussed later in more detail.

Simultaneously with the X-ray investigation, mass spectroscopic evidence for the SiAl_{14} cluster was obtained. A laser desorption mass spectrum demonstrated that **1** can be vaporized and ionized without decomposition,¹⁰ thus proving **1** to be a relatively stable species. Two peaks were detected: The molecular ion of **1** (M^+) at 1217 *m/e* (M^+) and another species lacking one Cp* fragment ($\text{M}^+ - \text{Cp}^*$) at 1081 *m/e*.¹¹ This independent method was a strong confirmation for our initial X-ray result. Moreover, EDAX analysis and chemical intuition favor the formulation as a SiAl_{14} species, especially since the

(8) In the structure refinement of **1**, the $\text{Cp}^*_6\text{M}_{15}$ clusters, which occupy positions with site symmetry $2/m$, are well behaved. However, apart from the solvent molecules, electron density peaks (2.2 and 1.1 $\text{e}^-/\text{\AA}^3$) are observed on the diagonals 218 pm from Al2 and 233 pm from Al1, respectively. Furthermore, there was a second confusion; some of the crystals obtained via rapid crystallization exhibited additional electron density ($8\times$) within the M_{15} entity (1.69–3.21 $\text{e}^-/\text{\AA}^3$). Since so far we have no explanation for these latter mentioned electron densities, they are omitted in this publication. Obviously the generation of crystals of this special kind depends strongly on the reaction conditions. A superlattice as the basis for the additional electron density could be excluded with the help of monochromatic Buerger Precession Method. To exclude phase transformations as the reason for the difficulties, the crystals were measured at different temperatures (200, 210, and 293 K).

(9) Preliminary results have already been presented at the XVII Conference on Organometallic Chemistry, Brisbane, 1996.

(10) Friedrich, J. Diplomarbeit, Faculty of Chemistry, University of Karlsruhe, 1996.

(11) Positive ion LDI results in a broad near-Gaussian mass peak centered at 1217 (± 1) amu (fwhm 6 amu). The isotopic structure was not resolved. This was unexpected according to the instrumental mass resolution of $m/\Delta m > 1000$ in the corresponding mass range. The observed mass peak is also significantly wider and more symmetric than expected for a poorly resolved isotopomer distribution of **1**. Whether this is due to a substance-specific LDI peak broadening mechanism (e.g., delayed ionization) or to the presence of several molecular ions with similar mass but different composition cannot be decided at present.

distances of the central atom to the eight Al atoms of the cube are in very good agreement with this choice.

Ab Initio DFT Calculations. Before starting ab initio calculations on this rather large molecule, simple electron counting gave the first hint of the stability of **1** and its unexpected existence in the gas phase. With the assumption that the 6 outer Al atoms each contribute 2 electrons and each of the remaining 8 Al atoms adds 3 electrons while the central silicon atom contributes 4 electrons to the SiAl_{14} cluster core, 40 electrons result for the whole entity. A metal cluster containing 40 electrons fulfills the prescription of a stable Jellium state,¹² and therefore, the stability of **1** is plausible. To confirm this hypothesis with more certainty, DFT calculations were performed. The sequence of the MOs mainly constituting the SiAl_{14} core is in accordance with the simple Jellium model and is evident by inspection of Figure 2 in which the MOs for the species $\text{SiAl}_{14}\text{H}_6$ and $\text{SiAl}_{14}\text{Cp}_6$ are compared. The expected MO separation according to the simple Jellium model is added. The optimized geometry of these calculations is included in Table 1.¹³

The calculated distances of the Cp* containing species are in line with the preliminary experimental X-ray data. The Si–Al distance (calcd 252.4 pm) is close to the average between the normal Si–Si (234 pm; $\text{Si}(\text{SiMe}_3)_4$)¹⁴ and Al–Al (266 pm; $[\text{AlCH}(\text{SiMe}_3)_2]_2$)¹⁵ bond lengths. The distance between the Al

(12) The Jellium model implies that the high stability of clusters is corresponding to particular closed-shell electronic configurations. It describes the cluster electronic structure by considering only the valence electrons, which are assumed to move “freely” in a smooth attractive spherical field potential. A crucial approximation is that the detailed positions of nuclei do not play a significant role: Heer, W. A. de; Knight, W. D.; Chou, M. Y.; Cohen, M. L. *Solid State Phys.* **1987**, *40*, 93.

(13) Furthermore, some species in which additional Al atoms are substituted by Si atoms have been calculated. However, all compounds containing an even number of Al atoms were much more unsymmetrical and did not fit with the experimental results obtained so far. Species containing an odd number of Al atoms could be excluded because of the lack of an ESR signal. That means, only for **1** are the calculated distances in good agreement with the preliminary results from the X-ray investigations.

(14) Heine, A.; Herbst-Irmer, R.; Sheldrick, G. M.; Stahlke, D. *Inorg. Chem.* **1993**, *32*, 2694.

Table 1. Structural Data Obtained Experimentally and by Means of DFT Calculations for **1**

distances (pm)	X-ray structure	DFT calculation
<i>d</i> (Al–Cl)	218–233	
<i>d</i> (Al–C)	222–234	233.8
<i>d</i> (Al–Si)	249–251	252.4
<i>d</i> (Al _C –Al _C)	290	291.7
<i>d</i> (Al _C –Al _{Cp*})	279–281	283.6
<i>d</i> (Al _{C/Cl} –Al _{Cp*})	287	

atoms coordinated by Cp* ligands and the Al atoms of the Al₈-cube (calcd 283.6 pm) is slightly longer than the Al–Al distance in (AlCp*)₄ (expt 277 pm,⁴ calcd 281.7 pm) due to the lower coordination number and therefore shorter Al–Al distances in (AlCp*)₄. The remaining Al–Al distances within the Al₈ cube are 291.7 pm (calcd) and thus slightly longer than those in Al metal (287 pm). In a very rough topological description, the heavy atoms (Si, Al) of **1** occupy the positions of a body-centered cubic structure (distorted rhombic dodecahedron) giving a molecular Si/Al alloy that is stabilized against the formation of the bulk material by the sterically demanding Cp* ligands.

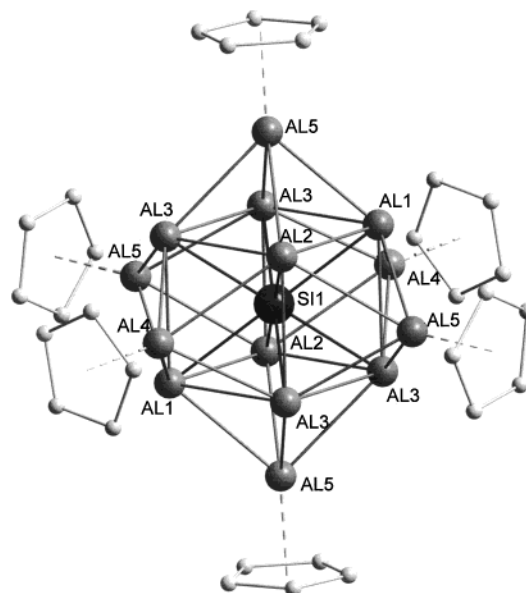
To obtain further evidence for the proposed structure of **1**, the ²⁷Al and ²⁹Si NMR shifts have been calculated and measured. On the basis of our experiences with several AlCp* compounds, the Al atoms bonded η⁵ to the Cp* ligands should give a sharp resonance. Therefore, we initially concentrated on the calculation of the shift of the corresponding six Al nuclei. Their signal was calculated to appear at δ²⁷Al = –29, which is in reasonable agreement with a weak resonance at δ²⁷Al = –17 observed in the solution of a reaction between SiCp*₂ and AlCl. Simultaneously we studied the signals of the remaining eight Al atoms. The resonances were calculated to appear at δ²⁷Al = –273, which—to our knowledge—is a unprecedented region at high field. However, in a new NMR experiment, a signal at δ²⁷Al = –280 was observed which is a further support for the validity of our model. We never measured signals at these positions (δ²⁷Al = –17 and δ²⁷Al = –273) in any of the large number of experiments using AlCp*.

The unique position of the central electron-rich Si atom within the coordination sphere of eight plus six Al atoms should also be reflected in its ²⁹Si NMR spectrum. And indeed, the calculated shift at δ²⁹Si = –480 occurs in a range similar to that of the divalent SiCp*₂ (C.N = 10; δ²⁹Si = –481 (calcd), δ²⁹Si = –392 (expt)¹⁵). Based on these calculations, a measurement of the ²⁹Si NMR spectrum appeared to be important as the structural proof of **1** and for the understanding of its bonding. However, the very low solubility of **1** prevented the measurement of a solution NMR spectrum of the low natural abundance nucleus ²⁹Si (4.70%) in an environment of eight Al atoms. Moreover, we cannot provide the relatively large amounts of crystals necessary for solid-state NMR investigations.

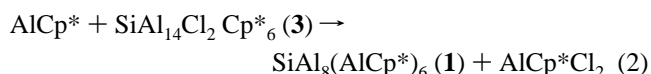
Mechanism of the Formation of 1. We are convinced that Si(AlCl₂)₄ (**2**) (cf. above) is an essential precursor in the formation of **1**. The reaction of **2** with AlCl may generate SiAl₈-Cl₈ in a first step.



In a second step, the eight Cl atoms are removed by reacting with AlCl or AlCp* and the six AlCp* units are added to complete the formation of **1**. To test this plausible hypothesis, DFT calculations on SiAl₁₄H₆ containing eight, four, and two

**Figure 3.** Structural model of SiAl₁₄Cp*₆. Methyl groups were omitted for clarity.

additional Cl atoms¹⁷ were performed. We found that the HOMO–LUMO gap increased with a decreasing amount of Cl atoms.¹⁸ A detailed theoretical analysis of the final reaction (eq 2) showed it to be exothermic at about –66 kJ/mol. Guided by



these theoretical investigations we were able to prove our hypothesis by the following experiment: Instead of SiCp*₂ as Si-containing species, we used SiCl₄, and the reaction smoothly proceeded by formation of **1**.

The X-ray structure analysis of the obtained crystals showed the above-described SiAl₁₄Cp*₆ cluster, which is presented in Figure 3, with only small variations in the distances compared to the results of the DFT calculations (Table 1). The additional electron density outside the Al₈ cube may be assigned to incorporated Cl atoms of impurities such as SiAl₁₄Cp*₆Cl_x (Cl connected to Al1 and Al2, respectively). Strong support for such species was obtained by electron ionization mass spectrometry of the gas phase (after heating the black crystals to ~280 °C) where molecular species containing AlCl_x units such as AlCp*Cl₂ were observed. If the additional electron densities were refined as a partial occupation with Cl atoms (average, one Cl atom per cluster), the final agreement factor was *R* = 6.54%. The arrangement of the rhombic dodecahedral-like SiAl₁₄ cluster molecules within the distorted simple hexagonal lattice is shown in Figure 4.

(16) Jutzi, P.; Holtmann, U.; Kanne, D.; Krüger, C.; Blom, R.; Gleiter, G.; Hyla-Kryspin, I. *Chem. Ber.* **1989**, *122*, 1629.

(17) The species SiAl₁₄Cl_nH₆ (*n* = 0, 2, 4, 8) serve as model compounds since the MO scheme of the metal cluster core is similar to the one in the Cp-substituted molecules. The HOMO–LUMO gap as a rough measure of stability in SiAl₁₄Cl_nH₆ decreases gradually going from *n* = 0 (1.41 eV, symmetry *O_h*) to *n* = 2 (1.24 eV, symmetry *D_{3d}*), *n* = 4 (0.90 eV, symmetry *D_{2d}*), and *n* = 8 (0.76 eV, symmetry *O_h*). Amazingly, no analogous structure for *n* = 6 (symmetry *D_{3d}*) was found. In a test calculation of the molecule, SiAl₁₄Cl₆H₆ (symmetry *C₁*) was distorted into a structure incorporating two terminal and four bridging Cl atoms.

(18) Since for the calculations of the large molecules **1** special hardware and software conditions are required, these results have already been published in order to demonstrate the performance of the Parallel Turbomole Program Package.^{21d}

(15) Uhl, W. Z. *Naturforsch.* **1988**, *43B*, 1113.

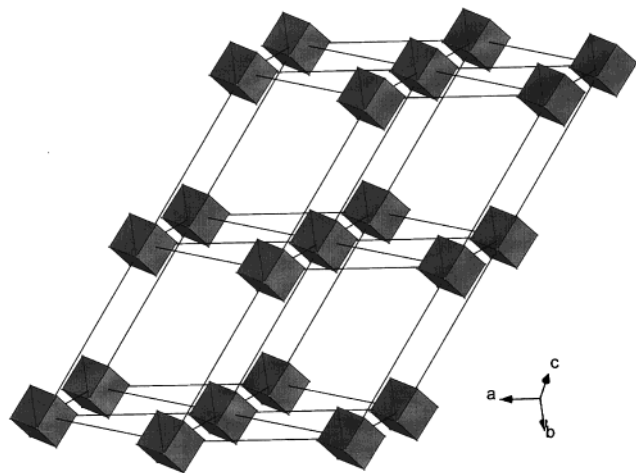


Figure 4. Arrangement of the rhombic dodecahedral-like SiAl_{14} cluster molecules within the distorted simple hexagonal lattice. For clarity only, the SiAl_8 cubes are presented.

In summary, we showed that the molecule $\text{SiAl}_{14}\text{Cp}_6^*$ (**1**) with its unique structure can be obtained by the reaction of SiCp_2^* or $\text{SiCl}_4/\text{AlCp}^*$ (cf. above) and metastable solutions of AlCl_3 . Theoretical and experimental results strongly support this structure, although the X-ray investigations do not allow its rigorous assignment.

These experiments showed once more that metastable AlX solutions have a high synthetic potential to prepare new compounds which are unique with respect to unusual Al_x cluster formation and with respect to the ability of the Si atom to coordinate to eight electropositive Al atoms in its direct coordination sphere. To our knowledge, there is no other example of a similar metal atom cluster with a body-centered cubic arrangement other than those that are stabilized by bridging electronegative atoms.¹⁹ **1** was the first example that accounts for the validity of the Jellium model if only species are considered that are stable at room temperature. The stability of a $\text{Ga}_{22}[\text{Si}(\text{SiMe}_3)_3]_8$ cluster (information that we published recently) was also explained on the basis of the Jellium model.²⁰ In addition to its structural singularity, molecules such as **1** and their syntheses may provide an idea of possible preparation methods that lead to other “metallic” or “semiconducting” clusters for which future applications in nanochemistry may be more important than the basic research presented here.

Experimental Section

General Considerations. All manipulations were performed in an atmosphere of dry nitrogen or argon using standard Schlenk techniques or in a glovebox (MBraun MB 150-GI). Solvents were dried and distilled under nitrogen employing standard drying agents. Solutions of AlCl_3 were prepared according to our standard procedure.¹ All ^{27}Al NMR spectra were recorded on a Bruker AMX 300 spectrometer (chemical shifts reported in δ units (ppm) were referenced to ext. $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (0.5 M, 0 ppm, ^{27}Al), ESR spectra were recorded on a Bruker ESP 300 E. Standard mass spectra (EI, 70 eV) were obtained on a Finnigan MS 8230 instrument. M^+ of **1** was detected on a LDI (MALDI)-TOF mass spectrometer using a pulsed nitrogen laser. X-ray fluorescence analysis was carried out with the help of the microanalysis system Link ISIS 200/300 (OXFR Instruments, Wiesbaden).

(19) Clusters such as $\text{Ni}_9(\mu_4\text{-GeEt})_6(\text{CO})_8$ are stabilized via an additional eight CO ligands: Zebrowski, J. P.; Hayashi, R. K.; Bjarnason, A.; Dahl, L. F. *J. Am. Chem. Soc.* **1992**, *114*, 3121.

(20) Schnepf, A.; Weckert, E.; Linti, G.; Schnöckel, H. *Angew. Chem.* **1999**, *111*, 3578; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3381.

Syntheses of 1. (a) A 4-mL sample of freshly prepared AlCl_3 solution (toluene/diethyl ether, 0.25 M) was mixed with 1 mmol of solid SiCp_2^* (298.5 mg) at -78°C . The reaction mixture was slowly heated to 60°C for 3 h. After 10 days at -25°C , black hexagonal crystals had formed. Crystal structure analysis showed the described $\text{Al}_{14}\text{SiCp}_6^*$ species with additional electron density in and outside of the SiAl_{14} cluster entity. ($T = 200\text{ K}$) space group $I 2/m$, $a = 13.241(3)$, $b = 17.909(4)$, $c = 17.048(3)\text{ \AA}$; $\beta = 96.66(3)^\circ$) The crystals are not soluble in benzene, hexane, or diethyl ether. The compound decomposes at temperatures above 180°C and at room temperature in C_6D_6 by treatment with ultrasound for 20 min. LDI-TOF mass spectrum (m/z): 1217 ($\text{M}^+ = [\text{Al}_{14}\text{SiCp}_6^*]^+$), 1081 ($\text{M}^+ - \text{Cp}^*$). Mass spectrum (EI, 280°C , m/z): 162 (100) (AlCp^*), 232 (16) ($^{35}\text{Cl}_2\text{AlCp}^*$) and expected isotopical splitting. EDAX Al: Si 16:1, Yield: 25 mg (24% based on AlCl_3).

(b) To 1 mL of a SiCl_4 solution (toluene, 0.2 M) was added 5.7 mL of a freshly prepared AlCl_3 solution (toluene/diethyl ether, 0.37 M) at -78°C . The reaction mixture was slowly warmed to 0°C and then added to 324 mg of solid $(\text{AlCp}^*)_4$. Heating the solution for 3 h to 60°C followed by storage at room temperature led to black hexagonal crystals which were characterized by X-ray methods to be the same species as prepared in (a) as well as a gray precipitate of elemental Al. Yield: 33 mg (12% based on SiCl_4)

(c) To 0.33 mmol of SiCp_2^* (100 mg) was added 2.2 mL of a freshly prepared AlCl_3 solution (*m*-xylene/diethyl ether, 0.15 M) at -78°C . The solution was heated for 3 h to 60°C and then stored at room temperature. After 10 days at 20°C , blackish hexagonal crystals were formed. After several weeks, a second crystalline fraction could be obtained from the same solution. The structure analysis of these crystals is presented here. Yield: 12 mg (35% based on AlCl_3)

NMR Experiment. SiCp_2^* (37 mg, 0.125 mmol), 0.5 mL of a freshly prepared AlCl_3 solution (toluene/diethyl ether, 0.25 M), and 0.5 mL of C_6D_6 were mixed together and sealed in a NMR tube. The following ^{27}Al NMR signals were measured: $\delta^{27}\text{Al}$ (20°C , 0 h) +125, +101, +29 (broad, characteristically for AlCl_3 solutions in toluene/ether); $\delta^{27}\text{Al}$ (60°C , 2 h -80 (Al_4Cp_4^*), +86 ($\text{Cp}^*\text{AlCl}_2\text{-OEt}_2$); after 2 d the signal for $(\text{AlCp}^*)_4$ had disappeared and two new signals at $\delta^{27}\text{Al} -17$ and $\delta^{27}\text{Al} -273$ were found; after 2 weeks black crystals formed inside the NMR tube while the two signals at $^{27}\text{Al} -17$ and $\delta^{27}\text{Al} -273$ had disappeared.

X-ray Analysis. Data for $\text{Al}_{14}\text{SiCp}_6^*\text{Cl}_2\cdot 2\text{C}_8\text{H}_{10}$ (**1**) were collected on a STOE IPDS diffractometer using the graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71069\text{ \AA}$). The oil-coated crystal was mounted on a glass fiber and cooled in a nitrogen stream to 200 K: $\text{C}_{76}\text{H}_{110}\text{-Al}_{14}\text{Cl}_2\text{Si}$, $M_r = 1464.9$, black hexagonal plate, monoclinic, space group $I 2/m$, $a = 13.430(3)$, $b = 18.333(4)$, $c = 17.118(3)\text{ \AA}$; $\alpha = 90.0^\circ$, $\beta = 94.86(3)^\circ$, $\gamma = 90.0^\circ$; $V = 4199.5(15)\text{ \AA}^3$; $Z = 2$; $\rho_{\text{cal}} = 1.158\text{ g/cm}^3$, $F(000) = 1558$; μ ($\text{Mo K}\alpha$) = 0.245 mm^{-1} ; $\text{Goof} = 0.985$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of $R1 = 0.0654$ for $I > 2\sigma(I)$, $wR2 = 17.21$ (all data). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in the refinement at calculated positions. The positions of the Cl atoms are partially occupied (Cl1, 33.3% connected with Al2; Cl2, 17% connected with Al2) due to the specified reasons. Two of the Cp^* rings (65/35% sterically dependent on Cl1/Cl2) and both of the *m*-xylene molecules (50/50%) were refined in two different positions.

Computational Details. The DFT investigations on $\text{SiAl}_{14}\text{R}_6$ ($\text{R} = \text{H, Cp}$) and $\text{SiAl}_{14}\text{R}_6\text{Cl}_n$ ($n = 0, 2, 4, 8$) have been performed with help of RI-DFT program of TURBOMOLE package^{21a,b} using the Becke-Perdew functional “BP-86” and split valence basis sets (SVC(P)).^{21c} Determination of the NMR shifts was performed by calculation of SCF-MOs using the DFT optimized geometries. The calculations were run on an IBM RS6000/390 workstation. Furthermore, $\text{SiAl}_{14}\text{Cp}_6^*$ (**1**) was investigated using the parallel version of TURBO-

(21) (a) Turbomole: Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346. (b) RIDFT: Eichhorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652. Eichhorn, K., Weigend, F., Treutler, O., Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119. (c) Becke, A. D. *Phys. Rev. A* **1998**, *38*, 3098. Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. (d) Arnim, M.; Ahlrichs, R. *J. Comput. Chem.* **1998**, *19*, 1746.

MOLE on an IBM SP2 supercomputer of the Computer Center of the University of Karlsruhe.^{21d}

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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