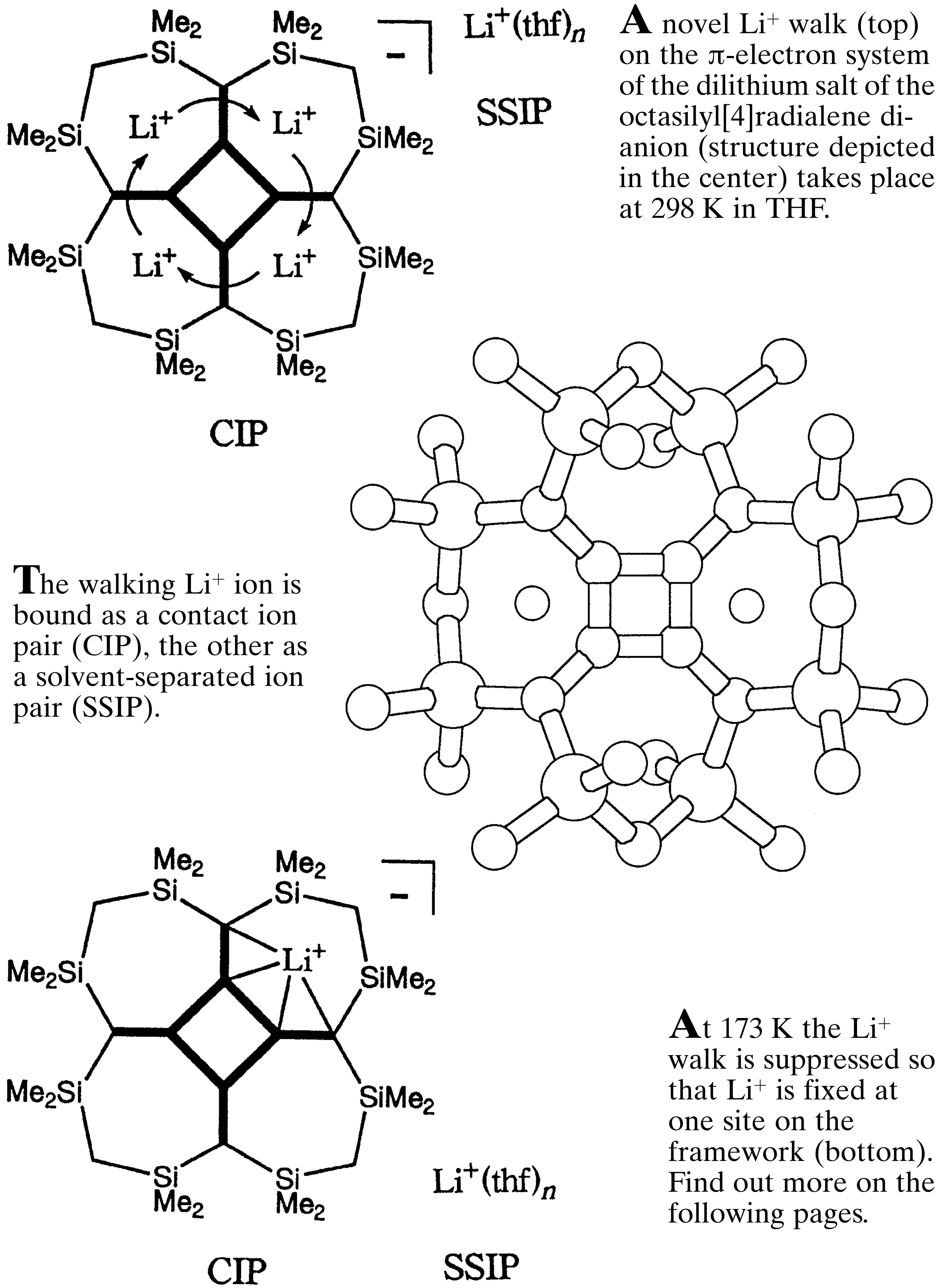

A novel Li^+ walk (top) on the π-electron system of the dilithium salt of the octasilyl[4]radialene dianion (structure depicted in the center) takes place at 298 K in THF.

The walking Li^+ ion is bound as a contact ion pair (CIP), the other as a solvent-separated ion pair (SSIP).

At 173 K the Li^+ walk is suppressed so that Li^+ is fixed at one site on the framework (bottom). Find out more on the following pages.

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Synthesis and Characterization of the Dilithium Salt of the Octasilyl[4]radialene Dianion: Evidence for a Lithium Walk on the Eight-Center, Ten-Electron π-Electron System**

Akira Sekiguchi,* Tsukasa Matsuo, and Hideki Sakurai

Over the last few years, the structures of various anions in the solid state and in solution have been reported that are either a component of a solvent-separated ion pair (SSIP) or part of a solvent-shared contact ion pair (CIP).[1] However, in most of these systems, the dynamic behavior of the countercation in solution has not been appreciably revealed.[2] We have observed a novel Li$^+$ ion walk on the π-electron system of the dilithium salt of a [4]radialene dianion. In a solvating medium such as tetrahydrofuran (THF), the two Li$^+$ ions are not fixed to the π-electron system, and one of the Li$^+$ ions dissociates to yield an ion pair (CIP and SSIP). Herein, we report the isolation, characterization, and molecular structure of the dilthium salt of the octasilyl[4]radialene dianion, which has as an eight-center, ten-electron π-electron system, on which Li$^+$ ions undergo a novel walk.

[4]Radialene exhibits a special eight π-electron system. We prepared the [4]radialene dianion from the persilylated [4]radialene (**1**).[3, 4] Reduction of **1** with excess lithium metal in dry oxygen-free THF at room temperature led to the formation of a red solution of the dianion of **1** (Scheme 1).[5] Crystallization from toluene afforded the air- and moisture-sensitive dark red crystals of the dilithium salt **2**.

The molecular structure of **2** was determined by X-ray diffraction (Figure 1).[6] The dianion has an inversion center at the center of the C1-C2-C1*-C2* four-membered ring. The dilithium salt **2** is monomeric and forms bis-contact ion pairs in the crystals. Li1 and Li1* are located above and below the ring, and are bonded to the four carbon atoms of the radialene skeleton as well as to the oxygen atoms of THF molecules. The distances between Li1 and the carbon atoms (C1, C2, C3, and C4) range from 2.245 to 2.315 Å (av 2.279 Å, Figure 2). Two of the seven-membered rings, which lie opposite to each other in the projection shown in Figure 1 and contain the Me$_2$SiCH$_2$SiMe$_2$ fragments, exhibit a twist conformation, and the other two exhibit a boat conformation.

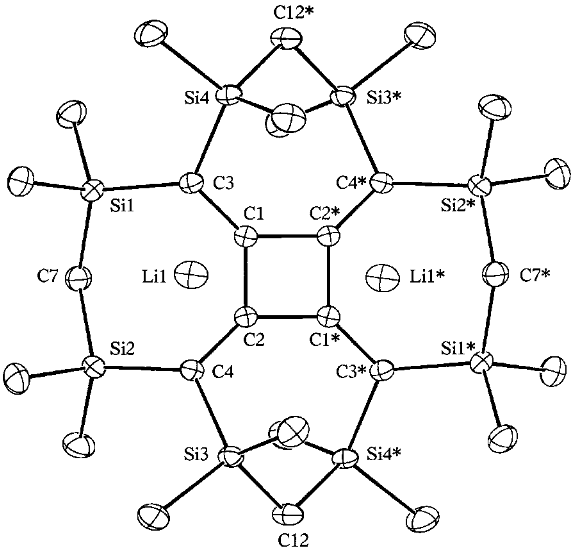
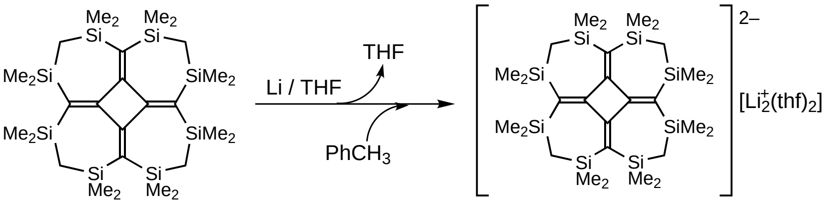


Figure 1. An ORTEP representation of the structure of **2** (THF and hydrogen atoms are omitted for the clarity). Selected bond lengths [Å] and angles [°]: C1–C2 1.473(1), C1–C2* 1.485(1), C1–C3 1.406(1), C2–C4 1.412(1), C3–Si1 1.854(1), C4–Si2 1.851(1), C4–Si3 1.867(1), C3–Si4 1.868(1), Li1–C1 2.246(2), Li1–C2 2.245(2), Li1–C3 2.315(2), Li1–C4 2.309(2); C1-C2-C1* 90.2(1), C2-C1-C2* 89.8(1), C2-C1-C3 134.1(1), C1-C2-C4 133.9(1), C3-C1-C2* 135.0(1), C4-C2-C1* 134.7(1).



1 **2**

Scheme 1. Synthesis of **2**.

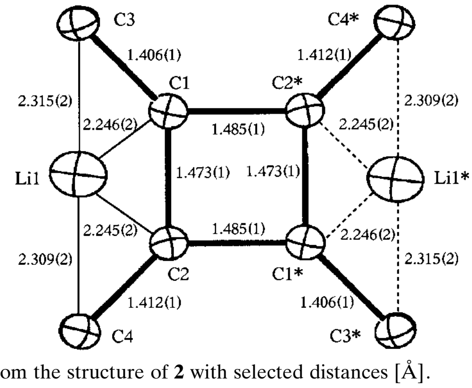


Figure 2. Section from the structure of **2** with selected distances [Å].

The structural features of **2** are quite interesting. The eight carbon atoms that contribute to the π-electron system of the skeleton of **2** are almost coplanar as a consequence of the delocalization of the negative charge. The four-membered ring is planar and almost square, as determined by the internal

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[*] Prof. Dr. A. Sekiguchi, Dipl.-Chem. T. Matsuo
Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305–8571 (Japan)
Fax: (+81) 298-53-4314
E-mail: sekiguch@staff.chem.tsukuba.ac.jp

Prof. Dr. H. Sakurai
Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda
Chiba 278–0022 (Japan)
Fax: (+81) 471-23-8984
E-mail: sakurai@koura01.ci.noda.sut.ac.jp

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bond angles of 89.8 to 90.2° (av 90.0°) and the sum of the bond angles (358.8 to 358.9° for C1, C2, C1*, and C2*). The average length of the exocyclic bonds (C1 – C3 and C2 – C4) is 1.409 Å and that of the endocyclic bonds (C1 – C2 and C1 – C2*) is 1.479 Å.

The NMR data on the structure of **2** in [D$_8$]toluene indicate a very highly symmetric bis-contact ion pair formation in solution. Thus, the ^{1}H NMR spectrum of **2** in [D$_8$]toluene shows only one signal for the methyl ($\delta = 0.32$) and methylene ($\delta = 0.13$) groups, respectively, together with the signals for THF. The ^{6}Li NMR spectrum of **2** displays only one signal at $\delta = -0.66$, and the ^{29}Si NMR spectrum shows a signal at $\delta = -11.8$, which is shifted upfield relative to that of **1** ($\delta = -7.8$). The ^{13}C NMR signal of the exocyclic carbon atoms ($\delta = 73.2$) is shifted significantly upfield relative to that of **1** ($\delta = 167.5$). Thus, the negative charge is largely delocalized on the four exocyclic carbon atoms C3, C4, C3*, and C4*. In contrast, the signal of the endocyclic carbon atoms C1, C2, C1*, and C2* is shifted downfield and appears at $\delta = 182.8$ ($\delta = 134.7$ for **1**). These spectral data suggest that the two Li$^+$ ions of **2** are not fixed to the π-electron skeleton, but are fluxional; the two Li$^+$ ions are walking on the skeleton on the NMR time scale.[7]

However, one of the Li$^+$ ions dissociates to yield an ion pair in [D$_8$]THF such that **2** is present as CIP and SSIP. The Li$^+$ walk is evidenced in [D$_8$]THF.[8] The ^{6}Li NMR spectrum of **2** shows two signals with the same intensity at $\delta = -0.38$ and -0.66, and the ratio of the peaks is independent of the concentration (0.03 to 0.13 M). The signal at $\delta = -0.38$ is assigned to the THF-solvated species [Li(thf)$_n$]$^+$, whereas the other signal is assigned to the Li$^+$ ion that is bonded to the π-electron system.[9] The exchange of the two Li$^+$ ions was not observed in the temperature range between 173 and 298 K. Thus, one Li$^+$ ion of **2** forms a SSIP and the other one forms a CIP in [D$_8$]THF. Consequently, the skeleton of **2** has a different environment above and below the plane; at room temperature therefore doublets appear in the ^{1}H NMR spectrum for the methylene protons with a geminal coupling of 12.6 Hz, and two signals for SiMe$_2$ in the ^{13}C NMR spectrum. These spectroscopic data clearly reveal that the Li$^+$ of CIP coordinates with one side of the framework and that it can walk freely on the π-electron system of the framework (Figure 3, left).

As the temperature was lowered, the ^{13}C NMR signals of the endocyclic and exocyclic carbon atoms broadened and split into two singlets ($\delta = 185.9$, 177.8 and $\delta = 83.5$, 50.2, respectively). The temperature-dependent change of the ^{13}C NMR signals of the endocyclic carbon atoms in [D$_8$]THF must have resulted from the dynamics of the Li$^+$ walk on the [4]radialene framework. Experimental and simulated spectra for the ^{13}C NMR signals of the endocyclic carbon atoms are shown in Figure 4. From the Arrhenius and Eyring plots, the values $E_a = 13.1$ kcal mol^{-1}, $\Delta H^{\ddagger} = 12.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 4.5$ cal mol^{-1} K^{-1} can be estimated for the Li$^+$ walk. The present Li$^+$ walk is accompanied by the twist-boat interconversion of the two seven-membered rings that contain the Me$_2$SiCH$_2$SiMe$_2$ fragments, which presents a high barrier to internal migrations of the Li$^+$ ion. At 173 K, the Li$^+$ ion walk of the CIP is suppressed so that Li$^+$ is fixed at one site on the framework (Figure 3, right).[10]

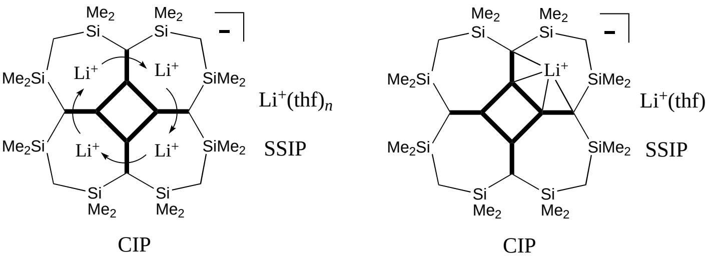

Figure 3. Schematic representation of the Li$^+$ walk on the π-electron system of **2** in [D$_8$]THF at 298 K (left) as well as the position of the Li$^+$ ion at 173 K (right).

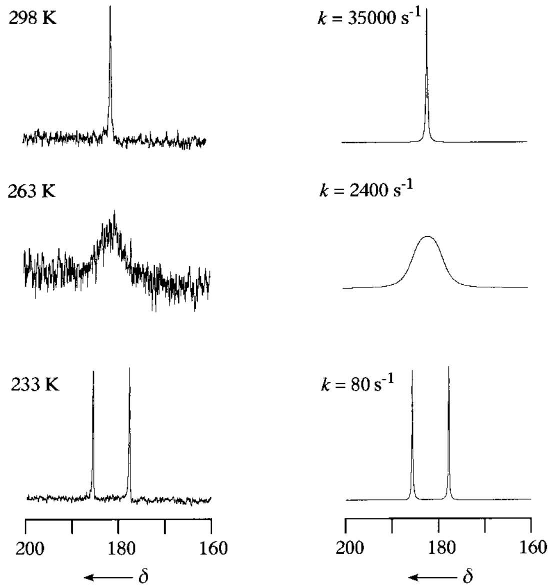

Figure 4. Observed (left) and simulated (right) ^{13}C (125 MHz) line shapes of the endocyclic carbon atoms of **2** in [D$_8$]THF.

Experimental Section

2: The crystals of **1** (20 mg, 0.03 mmol) and lithium metal (30 mg, 4.3 mmol) were placed in a sealed tube with a magnetic stirrer. After degassing the tube, dry oxygen-free THF (1 mL) was introduced by vacuum transfer and stirred at room temperature to give a red solution of **2** within 1 h. After the solvent was removed in vacuo, degassed toluene was introduced by vacuum transfer. After the lithium metal had been removed from the tube, the solution was cooled to afford dark red crystals of **2** quantitatively. ^{1}H NMR ([D$_8$]toluene, 298 K, TMS): $\delta = 0.13$ (s, 8H, CH$_2$), 0.32 (s, 48H, CH$_3$), 1.26 (br.s, 8H, THF), 3.46 (br.s, 8H, THF); ^{13}C{^{1}H} NMR ([D$_8$]toluene, 298 K, TMS): $\delta = 6.0$ (CH$_3$), 9.5 (CH$_2$), 25.3 (THF), 69.7 (THF), 73.2 (C), 182.8 (C); ^{29}Si{^{1}H} NMR ([D$_8$]toluene, 298 K, TMS): $\delta = -11.8$; ^{6}Li{^{1}H} NMR ([D$_8$]toluene, 298 K, LiCl in MeOH, external): $\delta = -0.66$.

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[3] [4]Radialene (**1**) was isolated as yellow crystals in 11% yield by the intramolecular reaction of hexadecamethyl-3,5,8,10,13,15,18,20-octasilacycloicosa-1,6,11,16-tetrayne with $[(C_5H_4Me)Mn(CO)_3]$ (3 molar equiv) by irradiation ($\lambda > 300$ nm) under reflux in THF. However, when one molar equivalent of the manganese complex was used, the octasilyl-substituted trimethylenecyclopentene derivative was obtained in 17% yield. For π-electron systems, such as **1,** derived from silicon-containing macrocyclic polyacetylene, see H. Sakurai, *Pure Appl. Chem.* **1996**, *68*, 327. For the trimethylenecyclopentene and its tetraanion tetralithium, see: A. Sekiguchi, T. Matsuo, C. Kabuto, *Angew. Chem.* **1997**, *109*, 2572; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2462.

[4] Spectral data for **1**: m.p. 219–220°C; ^{1}H NMR ([D$_1$]chloroform, TMS): $\delta = 0.05$ (s, 8H, CH$_2$), 0.14 (s, 48H, CH$_3$); ^{13}C{^{1}H} NMR ([D$_1$]chloroform, TMS): $\delta = 2.1$ (CH$_3$), 10.8 (CH$_2$), 134.7 (C), 167.5 (C); ^{29}Si{^{1}H} NMR ([D$_1$]chloroform, TMS): $\delta = -7.8$.

[5] The [4]radialene dianion, which was obtained by metalating 1,2-dimethyl-3,4-bismethylenecyclobutene with *n*BuLi/KO*t*Bu or *n*BuLi/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, has been characterized by the quenching experiments, see: W. T. Thorstad, N. S. Mills, D. Q. Bucklew, L. S. Govea, *J. Org. Chem.* **1989**, *54*, 773.

[6] Crystal structure analysis of **2**: A single crystal (0.35 × 0.30 × 0.25 mm) was sealed in a capillary glass tube for the data collection. Diffraction data were collected at 150 K on a Mac Science DIP2020 Image Plate Diffractometer employing graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); $C_{36}H_{72}Li_2O_2Si_8$, $M_r = 767.47$, $a = 9.506(1)$, $b = 22.105(1)$, $c = 11.869(1)$ Å, $\beta = 112.197(1)°$, $V = 2309.20(1)$ Å^3, monoclinic, space group $= P2_1/c$, $Z = 2$, $\rho_{calcd} = 1.164$ g cm^{-3}. The final R factor was 0.031 ($Rw = 0.038$) for 4208 reflections with $I_o > 2\sigma(I_o)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101 602. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] The variable-temperature NMR experiment cannot be conducted in [D$_8$]toluene. When the temperature is lowered, the crystals of the bis-contact ion pair precipitate which hampers the dynamic NMR study.

[8] Spectral data for **2** in [D$_8$]THF: ^{1}H NMR ([D$_8$]THF, 298 K, TMS): $\delta = -0.23$ (d, $J = 12.6$ Hz, 4H, CH$_2$), -0.17 (d, $J = 12.6$ Hz, 4H, CH$_2$), 0.04 (s, 48H, CH$_3$); ^{13}C{^{1}H} NMR ([D$_8$]THF, 298 K, TMS): $\delta = 6.4$ (CH$_3$), 6.9 (CH$_3$), 11.4 (CH$_2$), 66.8(C), 180.7 (C); ^{29}Si{^{1}H} NMR ([D$_8$]THF$_8$, 298 K, TMS): $\delta = -13.5$; ^{6}Li{^{1}H} NMR ([D$_8$]THF, 298 K, LiCl in MeOH, external standard): $\delta = -0.38, -0.66$.

[9] The signal at $\delta = -0.38$, which is assigned to the solvated Li$^+$ ion, becomes more intense on addition of ^{6}LiBr due to the rapid exchange. However, the intensity of the signal at $\delta = -0.66$ for the Li$^+$ ion of the CIP remains unchanged because this ion is bound to the π-electron system of the framework.

[10] The Li$^+$ ion walk of the CIP is suppressed at 173 K so that Li$^+$ is fixed at one site of the framework. This gives rise to eight ^{13}C NMR signals for SiMe$_2$ and three methylene groups ($\delta = 9.7$, 10.4, and 11.4), two endocyclic carbons ($\delta = 185.9$ and 177.8), and two exocyclic carbons ($\delta = 83.5$ and 50.2). In the ^{29}Si NMR spectrum, four signals were observed at $\delta = -15.7, -14.3, -12.6$, and -11.6.

$[\{(CO)_5Cr\}_6Ge_6]^{2-}$, A Molecular Organometallic Derivative of the Unknown Zintl Ion $[Ge_6]^{2-}$**

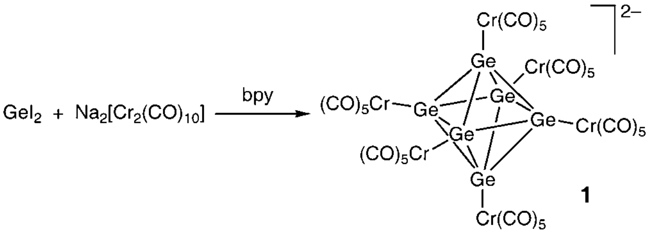
Peter Kircher, Gottfried Huttner,* Katja Heinze, and Gerd Renner

Dedicated to Professor Manfred Weidenbruch
on the occasion of his 60th birthday

The synthesis of $[\{(CO)_5Cr\}_6Sn_6]^{2-}$[1] illustrated that clusters composed exclusively of main group elements could be prepared from organometallic precursors; the resulting cluster is embedded in a matrix of organometallic protective groups. At the same time it was shown that octahedral clusters, which obey the usual counting rules[2] in terms of the structure and the electron count, were not restricted to boron[3] in main group chemistry. Whereas the $[Sn_6]^{2-}$ ion[1] protected by organometallic groups was initially the only example for this, in the meantime octahedral clusters that obey the counting rules[2] have been established as building blocks of solids. Both $[Ga_6]^{8-}$ and $[Tl_6]^{8-}$ exhibit octahedral structures with 14 framework electrons.[4] Two-dimensional corner-sharing indium octahedra are present in Rb_2In_3.[4] The phase KTl contains tetragonally compressed thallium octahedra with 12 framework electrons.[4] All these octahedral clusters are built from elements of Group 13.[5, 6] For elements of other groups the only example to date was the $[Sn_6]^{2-}$ ion, which was protected by organometallic groups.[1]

The reaction principle based on the treatment of pentacarbonylchromate with element halides had with $K_2[Cr(CO)_5]$ and $SnCl_2$ led to the octahedaral cluster $[\{(CO)_5Cr\}_6Sn_6]^{2-}$.[1] The transfer of this principle to other pentacarbonylmetalates and other element halides appeared straightforward; however, numerous attempts proved unsuccessful. We have now found that the reaction of GeI_2 with $Na_2[Cr_2(CO)_{10}]$ leads to the desired anionic cluster $[\{(CO)_5Cr\}_6Ge_6]^{2-}$ (**1**) provided that 2,2′-bipyridine is added to the reaction mixture (Scheme 1).

After the reaction 2,2′-bipyridine (bpy) is mainly contained as ligand in the main product $[\{(CO)_5Cr\}_2Ge(bpy)]$.[7] The role of the 2,2′-bipyridine in the formation of **1** is not clear; however, without it compound **1** is not obtained. Since the



Scheme 1. Synthesis of **1**. bpy = 2,2′-bipyridine.

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[*] Prof. Dr. G. Huttner, Dipl.-Chem. P. Kircher, Dipl.-Chem. K. Heinze, G. Renner
Anorganisch-chemisches Institut der Universität
Im Neuenheimer Feld 270, D-69120 Heidelberg (Germany)
Fax: (+49) 6221-545707

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