Crystal Structure of a Silicon-Bridged Anionic Sodocene Complex: Evidence for Alkene−Na⁺ π-Bonding

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Summary: The (allyl)₂Si-bridged Cp₂Na anion crystallizes as a polymeric chain structure in which Na cations bridge [(allyl)₂Si(C₅H₄)₂]²⁻ units. One of the allyl substituents of the Si bridge shows alkene−Na⁺ π-bonding interactions.

Introduction

The anions Cp_2Li^- and Cp_2Na^- show highly symmetric sandwich structures with an approximate D_{5d} symmetry and, although crystallized from THF, do not exhibit solvation of the metal cation (**1**).[1] In contrast, the C−C-bridged *ansa*-sodocene anion **2**[1c] is bent and the Na cation is solvated by one THF molecule. We here report the structure of the Si-bridged sodocene anion **3**.
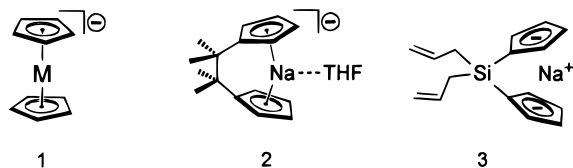

Silicon-bridged metallocenes generally show large deformation of the $R_2Si(C_5H_4)_2$ ligand, i.e. squeezing of the C−Si−C angle (α in **4**) and tilting of the Cp plane in respect to the Si−C$_{ipso}$ axis (β in **4**). These deformations can be quite extreme for small metals (e.g. $Ph_2Si(C_5H_4)_2Fe$ shows squeeze and tilt angles α = 99.1° and β = 40.0°),[2] giving rise to easy metalla-ring-opening reactions and interesting organometallic polymers (**5**).[3] It can be calculated that even the largest metal cation (Cs^+, ionic radius 1.67 Å) is too small to fit in a fully relaxed $R_2Si(C_5H_4)_2{}^{2-}$ ligand.[4]

This leaves three possibilities for the structure of [R_2-$Si(C_5H_4)_2Na$]⁻:

(i) The Si-bridged ligand is distorted from its fully relaxed geometry, as depicted in **4**.

(ii) The Cp−Na bonding is distorted from its favorable $η^5$-Cp−metal bonding geometry, thus relaxing strain in
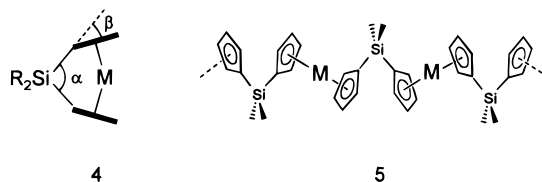
the complex. This situation is observed in the structure of [$Me_2Si(fluorenyl)_2Li$]⁻ (**6**), in which the smaller Li cation has moved toward the Si bridge and only fits within the ligand when both fluorenyl rings coordinate in a $η^1$-fashion.[4]
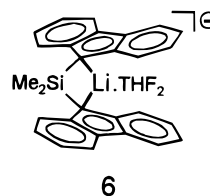
(iii) [$R_2Si(C_5H_4)_2Na$]⁻ builds a strain-free polymeric structure, such as **5**, in which the metal cations bridge the *exo* sides of the $R_2Si(C_5H_4)_2$ ligand.

Results and Discussion

During our investigations on Si-bridged alkali-metal metallocene anions, we isolated a crystalline complex with the composition [$(allyl)_2Si(C_5H_4)_2Na$]⁻[Ph_4P]⁺. The crystal structure shows collinear polymer chains of [$(allyl)_2Si(C_5H_4)_2Na$]⁻ units separated by phosphonium cations. These chains consist of $R_2Si(C_5H_4)_2{}^{2-}$ units bridged at the *exo* sides by Na cations (Figure 1a) and are comparable to the linear polymers **5** obtained when Si-bridged ferrocenes are heated.[3]

The cyclopentadienyl C−Na bond distances in the [$(allyl)_2Si(C_5H_4)_2Na$]⁻$_∞$ chain range from 2.638(5) to 2.744(5) Å (average 2.691(6) Å), which indicate $η^5$-Cp−Na bonding. This preference for $η^5$-Cp−Na bonding is large (the $η^5$-Cp−Na → $η^1$-Cp−Na shift needs 10.4 kcal/mol)[5] and explains why a Si-bridged sandwich structure, similar to **6**, is unlikely. The two similar Cp_c−Na (Cp_c represents the geometric center of the Cp ring) distances of 2.407(5) and 2.414(5) Å show symmetric bonding of Na^+ between the Cp rings.

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(5) Harder, S. Unpublished *ab initio* calculations at the MP2/6-31+G* level. Note that an $η^5$-Cp−Li → $η^1$-Cp−Li shift costs 19.6 kcal/mol at the same level of theory. The $η^1$-fluorenyl−Li coordination in **6** is due to the very shallow potential surface of the fluorenyl anion: Hoffmann, D.; Hampel, F.; Schleyer, P. v. R. *J. Organomet. Chem.* **1993**, *13*, 456.

a)   b)
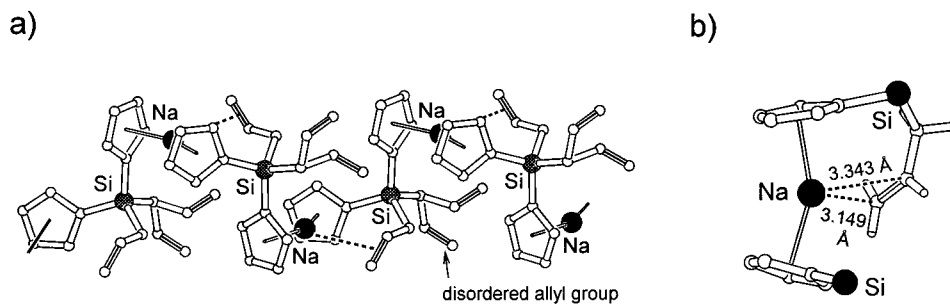
Figure 1. (a) Coordination polymer of [(allyl)$_2$Si(C$_5$H$_4$)$_2$Na]$^-$ units. The weak intramolecular alkene−Na$^+$ π-interaction is indicated by dashed lines. (b) Selected partial structure showing intramolecular alkene−Na$^+$ π-bonding.

An interesting detail in the structure of [(allyl)$_2$Si-(C$_5$H$_4$)$_2$Na]$^-_\infty$ is the alkene−Na$^+$ π-interaction, which has been indicated in Figure 1 with dashed lines. This interaction is quite remarkable if one considers the fact that this compound was crystallized from the strong Lewis base THF. The distances between the alkene carbons and Na$^+$ (3.149(5) and 3.343(5) Å) are considerably longer than the C−Na bond distances to the Cp rings (average value 2.691(5) Å). Nevertheless, several arguments are consistent with alkene···Na$^+$ bonding.

(i) The longer alkene···Na$^+$ interaction is a bond between a *neutral* alkene and Na$^+$, whereas the short Cp$^-$−Na$^+$ interaction represents a much stronger cation−anion bond. Alkene···Na$^+$ bonding is of electrostatic nature (there is no significant electron donation from the alkene to Na$^+$), and its energy falls off slowly with a 1/*r* dependence. For this particular reason there is no distinct cutoff value between a bonding and a nonbonding situation.

(ii) The average Cp$_c$−Na distance of 2.411(5) Å is significantly longer than the corresponding values obtained for the structurally known [Cp$_2$Na]$^-$ (2.329(3) and 2.366(3) Å).[1b,c] It is believed that the alkene···Na$^+$ π-interaction is responsible for the somewhat elongated Cp$_c$−Na distances (alkene···Cp$^-$ repulsion). This π-interaction likewise causes a slight bending of the Cp−Na−Cp unit. The Cp rings in [Cp$_2$Na]$^-$ are coplanar, but the Cp$_c$−Na−Cp$_c$ unit in [(allyl)$_2$Si(C$_5$H$_4$)$_2$Na]$^-$ is bent with an angle of 151.4(4)°.

(iii) One of the −CH$_2$CH=CH$_2$ substituents at Si is disordered in a 70/30 ratio (see Figure 1a; disordered allyl substituents are very common); however, the Na$^+$-bound allyl group shows a perfectly ordered structure. Likewise, statistical analysis of thermal vibrations in terminal −C≡CH substituents has shown that weak −C≡CH···X hydrogen bonds are responsible for a reduction of the displacement factors in the participating groups.[6] Also, weak intermolecular CH···π interactions have been shown to influence the ordering of long butyl substituents.[7]

(iv) Comparison of the structure of [(allyl)$_2$Si(C$_5$H$_4$)$_2$Na]$^-$ with the structures of the half-sandwich complexes of Ge (**7**)[8] and Sn (**8**)[9] shows that all three structures contain a subunit, C=C−C−Si−CpM, in which the alkene π-system is directed toward the metal.

a)

b)
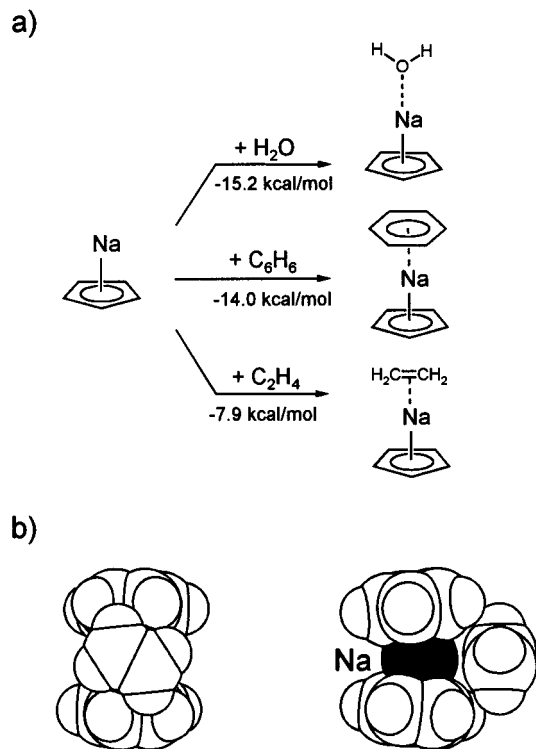
Figure 2. (a) *Ab initio* calculated coordination complexes of CpNa with H$_2$O, benzene, and ethylene (MP2/6-31+g*). (b) Space-filling representation of the calculated structure for the complex [Cp$_2$Na]$^-$···(ethylene).
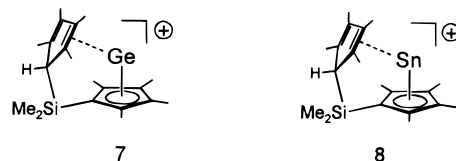
The alkene−M distances in all three complexes show a striking similarity (Ge···C distances, 3.18(1) and 3.34(1) Å; Sn···C distances, 3.169(6) and 3.301(1) Å; Na···C distances, 3.149(5) and 3.343(5) Å). However, the radii of the metals are quite different, as reflected in the different Cp−M distances (Cp$_c$−Ge, 1.93 Å; Cp$_c$−Sn, 2.22 Å; Cp$_c$−Na, 2.41 Å). This suggests that the alkene−M distances in all three complexes are dictated by limits in the conformation of the C=C−C−Si−CpM unit.

The alkene−Na$^+$ interaction reported here is weak. Ab initio calculations (MP2/6-31+G*) show the interaction energies between CpNa and ethylene to be small in comparison to those with water and benzene (Figure 2a). The interaction between [Cp$_2$Na]$^-$ and ethylene is

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even weaker: a bonding energy of 2.6 kcal/mol has been calculated. Optimization of the $[Cp_2Na]^-$–ethylene complex could be performed at an MP2 level (the RHF level showed dissociation) using tight convergence criteria. A very shallow minimum has been found only for a C_2-symmetric species (C_{2v}- and C_s-symmetric complexes dissociate during optimization). The ethylene molecule is twisted in order to avoid repulsive interaction with the Cp rings (Figure 2b) and shows long C···Na$^+$ contacts of 3.786 Å, i.e. longer than the sum of their van der Waals radii. The angle Cp_c–Na–Cp_c measures 168.9°. The C–Na distances vary from 2.679 to 2.686 Å with an average of 2.682 Å, which is slightly larger than the calculated C–Na distance of 2.667 Å in $[Cp_2Na]^-$ (D_{5d}).

Although only little evidence for interactions between Li$^+$ and *neutral* π-ligands, such as benzene,[10] acetylene,[11] alkene,[12] and a thiophene double bond,[13] has been reported, the much weaker alkene–Na$^+$ interaction has not been hitherto observed. It is presumed, however, that such weak interactions play an important role in addition reactions of organosodium compounds to alkenes and in ion-pair polymerization mechanisms.

Experimental Section

All experiments were carried out under argon with the use of Schlenk techniques and freshly dried and distilled solvents. $(allyl)_2SiCl_2$ was prepared according to a literature procedure.[14]

Synthesis of $(allyl)_2Si(C_5H_5)_2$. A solution of 11.1 g (126.0 mmol) of CpNa in 60 mL of THF was added to a solution of $(allyl)_2SiCl_2$ (10.9 g, 60.0 mmol) in 130 mL of pentane (ambient temperature, 2 h addition time). The reaction was completed by stirring overnight. Removal of the solvents yielded a sticky brown residue which was dried at 0.01 Torr for 2 h. The remaining substance was suspended in 120 mL of pentane and washed with 100 mL of a saturated solution of NH$_4$Cl in water. Subsequently, the organic layer was washed with two 80 mL portions of water and dried over MgSO$_4$. Removal of the pentane and drying at 0.01 Torr for 1 h yielded $(allyl)_2Si(C_5H_5)_2$ as an off-white powder (11.7 g; 49.0 mmol; 82%). The product should be stored below 0 °C in order to prevent polymerization. ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C; ppm): 1.40–1.95 and 3.03 (sp^3 protons of C$_5$H$_5$ and allyl); 4.88–4.98 (m, 4H, =CH$_2$); 5.67–5.82 (m, 2H, =CH–); 6.59–6.69 (sp^2 protons of C$_5$H$_5$). Reaction of this ligand with 2 equiv of NaN-

$(SiMe_3)_2$ in refluxing THF (1 h) quantitatively yields $(allyl)_2Si(C_5H_4Na)_2$ which can be directly used for further reactions or can be isolated by evaporating the solvent and washing the remaining solid with pentane.

Synthesis of $[(allyl)_2Si(C_5H_4)_2Na]^-[Ph_4P]^+$. A solution of $(allyl)_2Si(C_5H_4Na)_2$ (0.20 gg, 0.70 mmol) in 4 mL of THF was added to a suspension of Ph$_4$PCl (0.26 g, 0.70 mmol) in 4 mL of THF. The resulting wine red, slightly turbid solution was centrifuged, and the clear solution was carefully layered with 5 mL of hexane. A red oil of the composition $[(allyl)_2Si(C_5H_4)_2Na]^-[Ph_4P]^+$ separated from the solution. This oil partially crystallized after standing for some weeks. Some needlelike crystals could be isolated. ^{1}H NMR (250 MHz, internal THF reference 1.73 ppm, THF-d_8 and pyridine-d_5 mixture, 25 °C; ppm): 2.20 (d, 2H, ^3J(H,H) = 8.2 Hz, CH$_2$); 4.60–4.88 (m, 3H, H$_2$C=CH–); 5.95 (t, J = 2.0 Hz, Cp); 6.07 (t, J = 2.0 Hz, Cp); 7.50–7.80 (m, 10H, Ph$_4$P$^+$).

Crystal Structure Data: $C_{40}H_{38}NaPSi$; $a = 14.433(2)$ Å, $b = 10.533(1)$ Å, $c = 22.288(3)$ Å, $\beta = 98.46(1)°$; monoclinic, $P2_1/c$; $Z = 4$; $\omega/2\theta$ scans; $T = -120$ °C; refinement on $\sum w(|F_o| - |F_c|)^2$. Final R values: observed data ($I > 2\sigma(I)$), R1 = 0.074 and wR2 = 0.198; all data, R1 = 0.169 and wR2 = 0.304.

Ab initio calculations were performed using the GAUSSIAN 94 program with standard implemented methods (MP2-fc) and basis sets (6-31+G*).[15] The programs SHELXS86[16] and SHELXL93[17] were used for crystal structure determination and refinement. Plots and geometry calculations were made with the EUCLID package.[18]

Supporting Information Available: Tables giving crystal data and refinement details, positional and thermal parameters, and bond distances and angles for $[(allyl)_2Si(C_5H_4)_2Na]^-[Ph_4P]^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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