

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/44922412>

Syntheses and X-ray Structures of Anionic Sodicene Sandwiches

ARTICLE *in* ORGANOMETALLICS · JANUARY 1996

Impact Factor: 4.13 · DOI: 10.1021/om950571d · Source: OAI

CITATIONS

39

READS

28

3 AUTHORS, INCLUDING:



Marc Heinrich Prosenc

University of Hamburg

75 PUBLICATIONS 1,265 CITATIONS

SEE PROFILE

Syntheses and X-ray Structures of Anionic Sodicene Sandwiches[†]

Sjoerd Harder,* Marc Heinrich Prosenc, and Ursula Rief

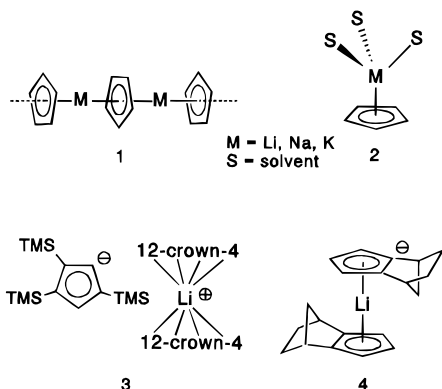
Universität Konstanz, Postfach 5560, M738, 78434 Konstanz, Germany

Received July 24, 1995[®]

While, the lithocene anion (Cp_2Li^-) can simply be generated by reacting 2 equiv of CpLi with PPh_4Cl in THF, the attempted synthesis of the sodocene anion under similar reaction conditions results in the crystallization of $[\text{Cp}^-][\text{PPh}_4^+]$. The structure consists of “naked” Cp anions pinched between *meta*phenyl hydrogens of the phosphonium cations. An *ansa*-sodicene anion in which the two Cp rings are bridged by a $-\text{C}(\text{Me})_2-\text{C}(\text{Me})_2-$ chain is obtained by reaction of $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4\text{Na})_2$ with 1 equiv of PPh_4Cl in THF. Its crystal structure shows a disordered *ansa*-sodicene anion containing a sandwiched sodium cation solvated by a THF molecule. Unbridged Cp_2Na^- was obtained by pushing the $(\text{CpNa} + \text{Cp}^-) \rightleftharpoons \text{Cp}_2\text{Na}^-$ equilibrium to the sodocene anion side. Cell dimensions, space group symmetry, and the molecular structure of $[\text{Cp}_2\text{Na}^-][\text{PPh}_4^+]$ are remarkably similar to that of $[\text{Cp}_2\text{Li}^-][\text{PPh}_4^+]$. The anion can be described as a centrosymmetric $(\eta^5, \eta^5)\text{Cp}_2\text{Na}^-$ sandwich (average C–Na = 2.630(3) Å) with approximate D_{5d} symmetry.

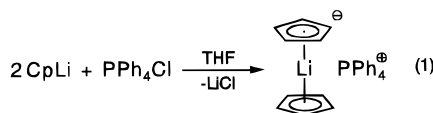
Introduction

X-ray structural studies of alkali metal cyclopentadienide complexes with Li, Na, and K commonly reveal ionic polymeric chain structures (1).¹ Solvation of the



metal cation can break the chain into oligomers or monomeric units (2).² Efficient solvation by crown ethers can even result in cation–anion separation and the formation of “free” cyclopentadienide anions (e.g. 3).³ Gautheron and Paquette *et al.* recently published the structure of the (isodiCp)₂Li anion (4), obtained by specific solvation of only half of the lithium cations by 12-crown-4.⁴

We recently reported the structure of the simplest metallocene sandwich: the lithocene anion, which was obtained by reacting CpLi with 0.5 equiv of PPh_4Cl thus substituting half of the metal cations by noncoordinating phosphonium cations (eq 1).⁵ The structure of the



lithocene anion can be described as a ferrocene-like staggered sandwich molecule with a center of inversion on Li and approximate D_{5d} symmetry. We now focus attention on the syntheses and structure elucidation of the higher alkali metallocene sandwiches.

Results and Discussion

In analogy to the synthesis of the lithocene anion, CpNa was reacted under similar conditions with 0.5 equiv of PPh_4Cl in THF. This results in the immediate formation of a blood-red solution from which dark-red crystals quickly precipitate. Unexpectedly, these crystals appeared to consist of $[\text{Cp}^-][\text{PPh}_4^+]$ instead of the desired $[\text{Cp}_2\text{Na}^-][\text{PPh}_4^+]$ (selected atom coordinates and bond distances and angles are listed in Table 1).⁶ The compound crystallizes in the tetragonal crystal system with alternating phosphonium cations (on 4-fold inversion axes) and Cp anions (on intermediate 2-fold rotation axes) (Figure 1a). The shortest anion contact is 2.719 Å, measured between a *meta*-phenyl hydrogen and

[†] Dedicated, with all best wishes, to Prof. Hans-Herbert Brintzinger on the occasion of his 60th birthday.

[®] Abstract published in *Advance ACS Abstracts*, November 1, 1995.

(1) (a) Aoyagi, T.; Shearer, H. M. M.; Wade, K.; Whitehead, G. *J. Organomet. Chem.* **1979**, *175*, 21. (b) Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem.* **1987**, *99*, 563; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 583. (c) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3903. (d) See for reviews: Weiss, E. *Angew. Chemie* **1993**, *105*, 1565; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501.

(2) (a) Lappert, M. F.; Singh, A.; Engelhardt, L. M.; White, A. H. *J. Organomet. Chem.* **1984**, *262*, 271. (b) Jutzi, P.; Schlüter, E.; Pohl, S.; Saak, W. *Chem. Ber.* **1985**, *118*, 1959. (c) Hammel, A.; Schwarz, W.; Weidlein, J. *Acta Crystallogr.* **1990**, *C46*, 2337. (d) Chen, H.; Jutzi, P.; Leffers, W.; Olmstead, M. M.; Power, P. *Organometallics* **1991**, *10*, 1282.

(3) Chen, H.; Jutzi, P.; Leffers, W.; Olmstead, M. M.; Power, P. P. *Organometallics* **1991**, *10*, 1282.

(4) Zaegel, F.; Gallucci, J. C.; Meunier, P.; Gautheron, B.; Sivik, M. R.; Paquette L. A. *J. Am. Chem. Soc.* **1994**, *116*, 6466.

(5) (a) Harder, S.; Prosenc M. H. *Angew. Chem.* **1994**, *106*, 1830; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744. (b) See also for a review: Stalke, D. *Angew. Chem.* **1994**, *106*, 2256; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2168.

(6) Crystals are only soluble in highly polar organic solvents like pyridine or acetonitrile. However, dissolving the crystals in such solvents leads to H/D scrambling and therefore no reliable $\text{PPh}_4^+/\text{Cp}^-$ ratio could be obtained by NMR analysis. All crystals show a uniform color and habitus. Analyses of several crystals on an X-ray machine gave similar cell constants.

Table 1. Atom Coordinates (*x/a*, *y/b*, *z/c*), Bond Distances (Å), and Angles (deg) for the Anion in [Cp⁻][PPh₄⁺]^a

Atom Coordinates			
atom	<i>x</i>	<i>y</i>	<i>z</i>
C1	0	1/2	0.8799(7)
C2	0.0574(2)	0.4284(2)	0.7717(5)
C3	0.0357(3)	0.4557(3)	0.5963(5)
Bond Distances and Angles			
C1–C2	1.384(4)	C1–C2–C3	108.3(3)
C2–C3	1.389(5)	C2–C3–C3'	107.8(2)
C3–C3'	1.388(6)	C2–C1–C2'	107.8(4)

^a A 2-fold axis passing through C1 generates the atoms C2' and C3' by the symmetry operation $-x, 1-y, z$.

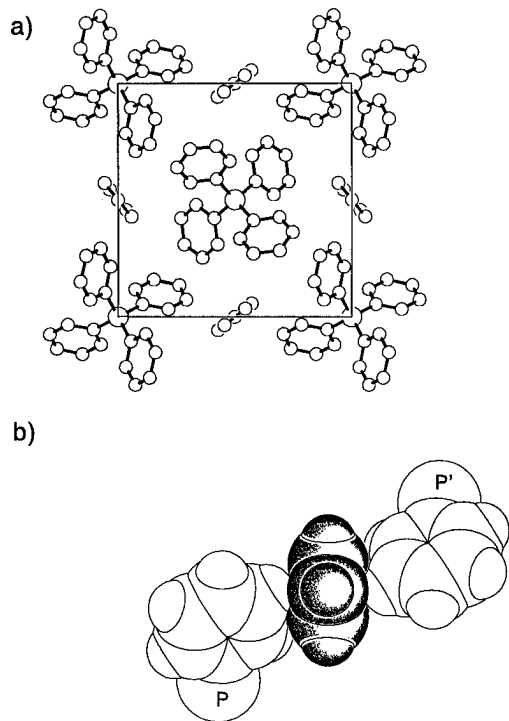
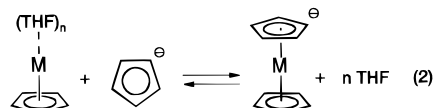


Figure 1. (a) Unit cell for [Cp⁻][PPh₄⁺] viewed along the *c*-axis. (b) CPK model of the partial structure showing the interaction of the Cp anion with two *meta*-phenyl hydrogens of the tetraphenylphosphonium cation.

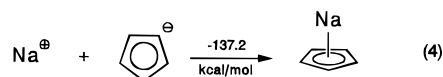
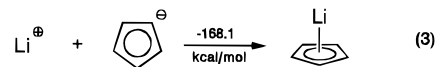
one of the Cp carbon atoms. The cpk model in Figure 1b shows that the Cp anion is pinched between two *meta*-phenyl hydrogens resulting in an inverse sandwich: C^{δ-}–H^{δ+}...Cp⁻...H^{δ+}–C^{δ-}. The distances between the Cp carbons and this phenyl hydrogen (2.719, 2.847, 2.937, 3.131, and 3.185 Å) are smaller or close to the sum of the carbon and hydrogen van der Waals radii (≈2.90 Å). Such C–H...π-system interactions have also been observed theoretically^{7a} and experimentally^{7b} in T-shaped benzene dimers and are considered to be weak but important forces determining crystal packing.^{7c} The structural identification of a (nearly) “naked” unsubstituted Cp anion is not new, and several X-ray structures including an “η⁰-Cp” have been reported.⁸ However, Cp anions in these structures are commonly disordered and

no accurate geometries have been obtained. The C–C bond distances in the current structure are in the narrow range 1.384(4)–1.389(5) Å (average: 1.387(5) Å). The C–C–C bond angles are in the range 107.8(2)–108.3(3)° (average: 108.0(3)°).

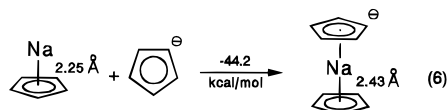
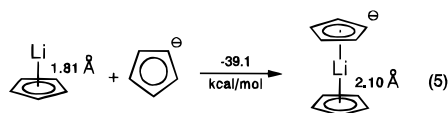
The formation of crystalline [Cp⁻][PPh₄⁺] suggests some stability of the free cyclopentadienide anion in THF solution. The addition of 0.5 mol equiv of PPh₄Cl to a CpM solution results in the generation of free cyclopentadienide anions which can function as effective ligands and interact with the remaining CpM monomer to form the sandwich anion. In THF solution this is presumably an equilibrium which will be dependent on M–THF bond strength and the energy involved in Cp–M bonding (eq 2).



The Cp-alkali metal bond is highly ionic and weakens according to Coulomb's law with increasing Cp⁻–M⁺ distance, *i.e.* along the series M = Li, Na, K. *Ab initio* calculations (eqs 3, 4) indeed show that association of a free Cp anion with Li⁺ is more exothermic than association with Na⁺ and are in agreement with results obtained earlier.⁹



The weaker Cp–Na bond could be a reasonable explanation for the low stability of the sodocene anion and the observed crystallization of the [Cp⁻][PPh₄⁺] in the attempted synthesis. However, calculations on the actual metallocene anions show that bonding of the second Cp anion is more exothermic for Na than for Li (eqs 5, 6). The reason for the weaker Cp–metal bond



in the lithocene anion is the more strongly repulsive Cp⁻...Cp⁻ interaction which outweighs the advantage of stronger Cp⁻–Li⁺ bonding. The importance of the repulsive Cp⁻...Cp⁻ interaction in the lithocene anion is evident from comparison of the CpM bond lengthening for M = Li (eq 5) with that of M = Na (eq 6).

Solvation of the alkali metal will play a dominant role in the equilibrium of eq 2, and therefore it is not straightforward to estimate the position of this equilibrium. The possible existence of higher oligomeric Cp-MCpM structures or triple-decker anions, CpMCpMCp⁻, complicates the solution equilibrium which is continuously changing due to Cp⁻ withdrawal.

(7) (a) Karlström, G.; Linse, P.; Wallquist, A.; Jönsson B. *J. Am. Chem. Soc.* **1983**, *105*, 3777. (b) Steed, J. M.; Dixon, F. A.; Klemperer W. J. *J. Chem. Phys.* **1979**, *70*, 4940. (c) Miyamuro, K.; Mihara, A.; Fujii, T.; Gohshi, Y.; Ishii, Y. *J. Am. Chem. Soc.* **1995**, *117*, 2377.

(8) (a) Butts, M. D.; Bergman R. G. *Organometallics* **1994**, *13*, 1899 and references cited therein. (b) Wessel, J.; Behrens, U.; Lork, E.; Mews, R. *Angew. Chem.* **1995**, *107*, 516; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 443.

(9) Lambert, C.; Schleyer, P. v. R. *Angew. Chem.* **1994**, *106*, 1187; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129.

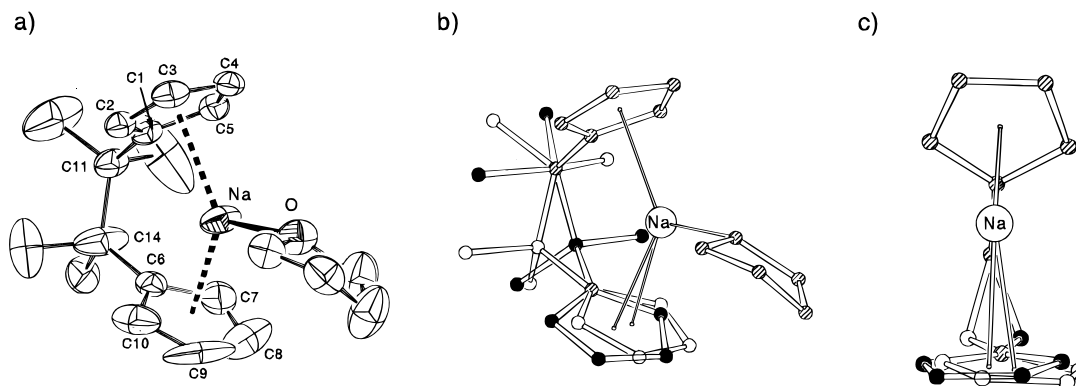
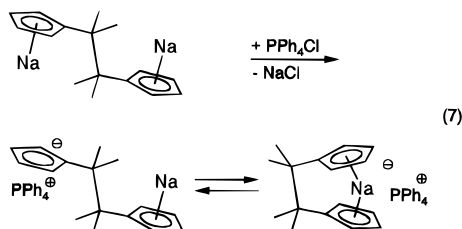


Figure 2. (a) Anisotropically refined structure of $[\text{Me}_4\text{C}_2\text{Cp}_2\text{Na} \cdot \text{THF}][\text{PPh}_4]^+$ showing extraordinary large displacement parameters for the disordered part of the structure (50% probability plot). (b) Plot of the disorder model. Disorder model *a* is refined to 76% occupation and is indicated by black atoms, and model *b* (24% occupation) is indicated by white atoms; striped atoms and Na are anisotropically refined with full occupation. (c) Front view of the partial structure showing ring slippage of the disordered Cp ring *b* (white atoms). Me groups have been omitted for clarity.

One approach to overcome withdrawal of the Cp anion from the reaction mixture is to tie this anion to the CpM fragment, *i.e.* to synthesize an anionic *ansa*-sodocene sandwich (eq 7). The red crystals obtained this way now



must contain both, the CpNa and the Cp anion functionalities. NMR analysis¹⁰ of the crystals shows the composition $[\text{Me}_4\text{C}_2\text{Cp}_2\text{Na} \cdot \text{THF}][\text{PPh}_4]^+$, which was confirmed by X-ray analysis. Anisotropic refinement resulted in extremely large displacement parameters for some of the atoms incorporated in the *ansa*-metallocene bridge and one of the Cp rings (Figure 2a). This indicates disorder which can be described with a model (Figure 2b) in which the bridge and the disordered ring pivot around the carbon atoms C11 and C6, both atoms with relatively small displacement parameters. Such a disorder is also apparent from the larger displacement parameters for C8 and C9 when compared to those of C7 and C10. Refinement with this model yields a better crystallographic description (see Experimental Section; selected atom coordinates and bond distances and angles are listed in Table 2).

The nondisordered Cp ring and the disordered ring with the higher occupation (model *a*) are both bonded to Na with C–Na bond distances in a close range (Table 2). The C–Na bond distances for the Cp ring with lower occupation (model *b*) show stronger variation. One short and two long C–Na bonds indicate η^3 -coordination. However, it should be noted that this ring with only 24% occupation is not very well defined. Moreover, the disorder in the Cp rings also induces an enlarged displacement factor on Na in the same direction as the ring slippage (Figure 2a). Therefore, the observed (η^3)-Cp–Na coordination is probably not as distorted from η^5 -geometry as the model shows. The Cp–Na bond

Table 2. Selected Atom Coordinates (*x/a*, *y/b*, *z/c*) and Bond Distances (Å) for $[\text{Me}_4\text{C}_2\text{Cp}_2\text{Na} \cdot \text{THF}][\text{PPh}_4]^+$ ^a

Atom Coordinates			
atom	<i>x</i>	<i>y</i>	<i>z</i>
Na	0.8432(1)	0.1316(1)	0.9318(1)
O	0.8788(2)	−0.0397(2)	0.9005(2)
C1	0.8406(2)	0.3364(3)	0.8997(2)
C2	0.9225(5)	0.3013(3)	0.8985(2)
C3	0.9254(3)	0.2356(3)	0.8354(2)
C4	0.8450(3)	0.2292(3)	0.7958(2)
C5	0.7932(2)	0.2913(3)	0.8356(2)
C6	0.7749(2)	0.2439(3)	1.0329(2)
C11	0.8116(2)	0.4101(3)	0.9589(2)
C7a	0.7232(3)	0.1571(3)	1.0104(3)
C8a	0.7615(4)	0.0634(4)	1.0401(3)
C9a	0.8370(3)	0.0954(4)	1.0822(3)
C10a	0.8459(3)	0.2058(4)	1.0788(3)
C14a	0.7543(2)	0.3603(3)	1.0117(2)
C7b	0.7007(5)	0.1900(8)	1.0084(8)
C8b	0.7155(7)	0.0821(8)	1.0240(7)
C9b	0.7965(7)	0.0679(7)	1.0617(7)
C10b	0.8320(6)	0.1693(7)	1.0678(8)
C14b	0.8027(5)	0.3606(4)	1.0369(3)

Bond Distances			
Na–C1	2.650(4)	Na–C6	2.647(4)
Na–C2	2.614(4)	Na–C7a	2.574(6)
Na–C3	2.657(4)	Na–C8a	2.625(6)
Na–C4	2.705(4)	Na–C9a	2.713(6)
Na–C5	2.693(4)	Na–C10a	2.757(6)
Na–C6	2.647(4)	C1–C2	1.411(5)
Na–C7b	2.94(1)	C2–C3	1.397(5)
Na–C8b	2.89(1)	C3–C4	1.401(5)
Na–C9b	2.64(1)	C4–C5	1.411(6)
Na–C10b	2.48(1)	C1–C5	1.402(5)
C6–C7a	1.408(6)	C6–C7b	1.404(9)
C7a–C8a	1.406(7)	C7b–C8b	1.41(1)
C8a–C9a	1.406(8)	C8b–C9b	1.41(2)
C9a–C10a	1.405(7)	C9b–C10b	1.41(1)
C6–C10a	1.404(6)	C6–C10b	1.41(1)
C1–C11	1.523(5)	C11–C14a	1.544(6)
C11–C14b	1.539(6)	C6–C14a	1.544(5)
C6–C14b	1.543(7)	Na–O	2.329(3)

^a Numbering scheme shown in Figure 2. Atoms indicated by *a* and *b* are disordered and have a site occupation factor of 0.76 and 0.24, respectively.

distances are comparable to the Cp–metal distances in the isoelectronic Ca analogue, $\text{Me}_4\text{C}_2\text{Cp}_2\text{Ca}$.¹¹ The diagonal relationship between these alkali and alkaline

(10) The compound is slightly soluble in THF, and a $\text{Me}_4\text{C}_2\text{Cp}/\text{PPh}_4/\text{THF}$ ratio could be determined.

(11) Rieckhoff, M.; Pieper, U.; Stalke, D.; Edlmann, F. T. *Angew. Chem.* **1993**, 105, 1102; *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1079.

Table 3. Atom Coordinates (*x/a*, *y/b*, *z/c*), Bond Distances (Å), and Angles deg for the Anion in [Cp₂Na⁻][PPh₄⁺]^a

Atom Coordinates			
atom	<i>x</i>	<i>y</i>	<i>z</i>
Na	1	1/2	1/2
C1	0.8252(3)	0.4720(5)	0.5784(2)
C2	0.9268(3)	0.4050(6)	0.6275(1)
C3	0.9604(2)	0.2375(5)	0.5994(2)
C4	0.8769(3)	0.2038(5)	0.5322(2)
C5	0.7953(2)	0.3487(7)	0.5209(2)
Bond Distances and Angles			
Na—C1	2.621(4)	C5—C1—C2	108.1(3)
Na—C2	2.670(3)	C1—C2—C3	108.1(3)
Na—C3	2.664(4)	C2—C3—C4	107.0(3)
Na—C4	2.609(4)	C3—C4—C5	107.5(3)
Na—C5	2.584(3)	C4—C5—C1	109.3(3)

^a The sodicene anion is located on an inversion center (1, 1/2, 1/2).

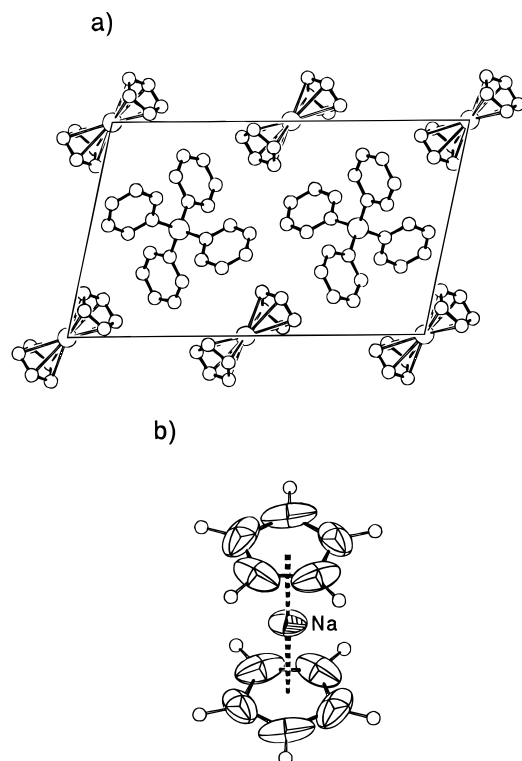


Figure 3. (a) Unit cell for [Cp₂Na⁻][PPh₄⁺] viewed along the *b*-axis. (b) ORTEP plot of the anionic sodicene sandwich (50% probability ellipsoids).

earth metals is due to the similar ionic radii of Na⁺ (0.97 Å) and Ca²⁺ (0.99 Å).

As another approach to prepare anionic sodicene sandwiches, the equilibrium in eq 2. can be directed toward the side of the metallocene anion by varying the reactant concentrations. Increasing the overall absolute concentration favors the formation of [Cp₂Na⁻], and with an additional increase of the CpNa concentration (CpNa/Cp⁻ is 3/1) it prohibits the crystallization of the Cp anion. This approach results in the formation of orange-brown needlelike crystals which not only differ in color but also in habit from crystals of [Cp⁻][PPh₄⁺].

A single-crystal X-ray diffraction study on these orange-brown needles reveals the structure of [Cp₂Na⁻][PPh₄⁺] (Figure 3a). Cell dimensions, space group symmetry, crystal packing, and the molecular structure of [Cp₂Na⁻][PPh₄⁺] are remarkably similar to

that of [Cp₂Li⁻][PPh₄⁺]. The sodicene anions are situated on crystallographic inversion centers (Figure 3a). This implies that their Cp rings are coplanar and staggered. However, high anisotropy in the ring thermal parameters indicates rotational disorder in the positions of the Cp carbon atoms and a small energy difference between staggered and eclipsed conformations (see Figure 3b). Since the C—Na bond distances are in the narrow range of 2.584(3)–2.670(3) Å (average 2.630(3) Å), the structure can be described as a (η⁵, η⁵)Cp₂Na⁻ sandwich with approximate *D*_{5d} symmetry.

Although the fragment CpNaCp⁻ can be considered as a substructure of the polymeric chain [CpNa]_∞, the Cp_{centroid}—Na distance of 2.366(3) Å is remarkably shorter than that of 2.65 Å previously observed in the zigzag chain polymer [CpNa(tmeda)]_∞.^{1a} The larger Cp—Na distances in the latter are due to the effect of additional Na⁺...Na⁺ repulsions and solvation of the cation by a chelating diamine. Solvation of Na⁺ forces the molecule to bend which results in stronger Cp⁻...Cp⁻ repulsion and consequently a larger average Cp—Na distance. In THF solution, the sodicene anion will be most likely in equilibrium with its THF solvate, Cp₂Na⁻·THF, with a structure analogous to that of Me₄C₂Cp₂Na⁻·THF.

The solid state structure of the sodicene anion is comparable with the structures of [Cp₂Li⁻]⁵ and Cp₂Mg.¹² Crystalline Cp₂Ca, however, forms a polymer in which Ca is surrounded by four Cp groups (η⁵, η⁵, η³, η¹).¹³ Despite the similar ionic radii of Na⁺ and Ca²⁺, the diagonal relationship between alkali and alkaline earth metals apparently does not hold here. The 2-fold positive charge on alkaline earth cations, and therefore the *a priori* stronger electrostatic Cp—metal bonding, is probably a more profound stimulus for the formation of coordination polymers.

Experimental Procedures

All experiments were carried out in an inert argon atmosphere using Schlenk techniques and syringes. Solvents were freshly distilled from sodium/benzophenone prior to use. NMR spectra were recorded on a Bruker AC250 (250 MHz) machine and frequencies were referenced internally to the solvent (¹H-NMR: CD₃CN, 1.93; THF, 1.73; pyridine, 8.71. ¹³C-NMR: CD₃CN, 1.3; THF, 25.2; pyridine, 123.5).

Ab initio calculations were performed using the program Turbomol¹⁴ and a split valence basis set with diffuse orbitals only on carbon (Li, Na, H, 6-31G*; C, 6-31+G*). Optimized structures and energies (hartree): Li⁺ (-7.235 480); Na⁺ (-161.659 277); Cp⁻ (C_{5h}, -192.218 386); CpLi (C_{5v}, -199.721 676); CpNa (C_{5v}, -354.096 236); Cp₂Li⁻ (D_{5d}, -392.002 348); Cp₂Na⁻ (D_{5d}, -546.385 025). All structures were checked by frequency analysis and found to be real minima.

Crystals were measured on a Siemens R3m/V diffractometer and structure solution followed with the SHELXTL program. Plots and geometry calculations were made with the EUCLID package.¹⁵

Synthesis of [Cp⁻][PPh₄⁺]. Addition of CpNa (0.30 g, 3.41 mmol) dissolved in 10 mL of THF to a suspension of anhydrous

(12) Bänder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, 92, 1.

(13) Zenger, R.; Stucky, G. *J. Organomet. Chem.* **1974**, 80, 7.

(14) Turbomole: Ahlrichs, R.; Bär, M.; Häser, M.; Kölmel, C. Electronic structure calculations on workstation computers: the program system Turbomole. *Chem. Phys. Lett.* **1989**, 162, 165.

(15) Spek, A. L. The EUCLID package. *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, U.K., 1982.

Ph₄PCl (0.64 g, 1.71 mmol) in 10 mL of THF results in immediate formation of an intense red solution and small bright red crystals. The remaining mother liquor is isolated by quick centrifugation. After standing for 2 days at +4 °C, a batch of uniform large dark-red cubelike crystals was isolated and washed with THF (total yield 0.51 g, 74%). The Crystals are insoluble in THF but slightly dissolve in acetonitrile.⁶ ¹H-NMR (CD₃CN, 25 °C): 5.46 (s, Cp); 7.60–7.95 (m, Ph₄P). ¹³C-NMR: 104.3 (Cp); 119.0 (d, ¹J(C,P) = 87.9 Hz, Ph_{ipso}), 131.3 (d, ³J(C,P) = 12.9 Hz, Ph_{meta}), 135.7 (d, ²J(C,P) = 10.4 Hz, Ph_{ortho}), 135.8 (d, ⁴J(C,P) = 3.0 Hz, Ph_{para}).

Synthesis of [Me₄C₂Cp₂Na⁺·THF][PPh₄⁺]. *n*-Butyllithium (4.8 mL, 1.6 M in hexane) was added at –70 °C to a solution of the bridged ligand, CpH-C(Me)₂C(Me)₂-CpH (0.75 g, 3.50 mmol)¹⁶ in 20 mL of THF. The white suspension was slowly warmed to room temperature, and the solvent was evaporated. Washing the precipitate twice with pentane and drying under high vacuum at 60 °C gives a white powder (Me₄C₂Cp₂Li₂; 0.75 g, 95% yield) which is only very slightly soluble in THF. ¹H-NMR (THF-*d*₆, 25 °C): 1.34 (s, 12 H, Me); 5.17 (dd, ³J(H,H) and ⁴J(H,H) = 5.3 Hz, Cp); 5.31 (dd, ³J(H,H) and ⁴J(H,H) = 5.3 Hz, Cp). ¹³C-NMR: 28.6 (Me); 42.3 (C-bridge); 101.1 and 102.6 (Cp); 130.5 (Cp_{ipso}).

A solution of sodium 3-methyl-3-pentanolate (0.70 g; 5.63 mmol) in 10 mL of Et₂O was added to a suspension of Me₄C₂Cp₂Li₂ (0.62 g; 2.74 mmol). The white suspension slowly turns into a slightly yellowish solution which was stirred for 1 h. The solvent was pumped off, and the resulting precipitate was dried at 60 °C under high vacuum. The lithium pentanolate was washed away with three 15 mL portions of hexane. Drying at 60 °C under high vacuum yields the product Me₄C₂Cp₂Na₂ as an off-white powder (0.65 g; 92% yield) which is perfectly soluble in THF. ¹H-NMR (THF-*d*₆, 25 °C): 1.38 (s, 12 H, Me); 5.27 (broad singlet with shoulders, 2 H, Cp); 5.48 (broad singlet with shoulders, 2 H, Cp). ¹³C-NMR: 29.5 (Me); 42.5 (C-bridge); 100.4 and 102.1 (Cp); 130.9 (Cp_{ipso}).

Addition of Me₄C₂Cp₂Na₂ (0.30 g, 1.16 mmol) dissolved in 5 mL of THF to a suspension of anhydrous Ph₄PCl (0.44 g, 1.16 mmol) in 10 mL of THF results in immediate formation of a wine-red solution and large red crystals suitable for X-ray diffraction. Crystals are isolated and washed with THF (yield 0.48 g, 65%). ¹H-NMR (pyridine-*d*₅, 25 °C): 1.60 (m, 4H, THF); 2.09 (s, 12 H, Me); 3.64 (m, 4H, THF); 6.21 (dd, 2H, ³J(H,H) and ⁴J(H,H) = 5.2 Hz, Cp); 6.49 (dd, 2H, ³J(H,H) and ⁴J(H,H) = 5.2 Hz, Cp); 7.60–7.95 (m, 20H, Ph₄P). ¹³C-NMR: 25.8 (THF); 30.6 (Me); 43.4 (C-bridge); 101.3 and 103.2 (Cp); 118.2 (d, ¹J(C,P) = 89.4 Hz, Ph_{ipso}); 130.8 (d, ³J(C,P) = 13.2 Hz, Ph_{meta}); 131.2 (Cp_{ipso}); 134.9 (d, ²J(C,P) = 10.4 Hz, Ph_{ortho}), 135.7 (d, ⁴J(C,P) = 3.1 Hz, Ph_{para}).

Synthesis of [Cp₂Na⁺][PPh₄⁺]. Addition of CpNa (0.30 g, 3.41 mmol) dissolved in 4 mL of THF to a suspension of anhydrous Ph₄PCl (0.32 g, 0.85 mmol) in 4 mL of THF results in immediate formation of a red solution. The reaction mixture was quickly centrifuged, and the clear solution was isolated. After standing overnight at room temperature, large orange-brown needles of [Cp₂Na⁺][Ph₄P⁺] could be isolated and were washed with THF (yield 0.28 g, 68%, calc on PPh₄Cl). Crystals are slightly soluble in THF but dissolve well in acetonitrile.⁶ ¹H-NMR (CD₃CN, 25 °C): 5.52 (s, Cp), 7.60–7.95 (m, Ph₄P). ¹³C-NMR: 104.0 (Cp), 119.0 (d, ¹J(C,P) = 88.0 Hz, Ph_{ipso}), 131.3 (d, ³J(C,P) = 12.9 Hz, Ph_{meta}), 135.7 (d, ²J(C,P) = 10.4 Hz, Ph_{ortho}), 136.3 (d, ⁴J(C,P) = 2.6 Hz, Ph_{para}).

Crystal Structure Data for [Cp[–]][Ph₄P⁺]: tetragonal, *a* = 12.188(4) Å, *b* = 12.188(4) Å, *c* = 7.535(5) Å, *V* = 1119.3(10) Å³, space group *P*4̄, formula {(C₅H₅)·(C₂₄H₂₀P)}, *M* = 404.5, *Z* = 2, ρ_{calcd} = 1.200 g cm^{–3}, μ(Mo Kα) = 0.13 mm^{–1}; 2686 reflections measured (Mo Kα, graphite monochromator, *T* = –40 °C), 1325 unique reflections after merging (*R*_{int} = 0.021), 1126 observed reflections with *F* > 4.0σ(*F*); solution by direct methods, refinement by minimization of Σw(|*F*_o| – |*F*_c|)² to *R* = 0.035 and *wR* = 0.039 (137 parameters, 1126 data observed) with *w* = 1/(σ²(*F*) + 0.0003(*F*)²). Non-hydrogens were refined anisotropically; all hydrogens were assigned calculated idealized positions and were refined with an overall isotropic thermal parameter.

Crystal Structure Data for [Me₄C₂Cp₂Na⁺·THF][Ph₄P⁺]: monoclinic, *a* = 16.311(6) Å, *b* = 12.647(5) Å, *c* = 17.669(6) Å, β = 97.97(3)°, *V* = 3610(2) Å³, space group *P*2₁/*n*, formula {(C₁₆H₂₀Na)(C₄H₈O)·C₂₄H₂₀P}, *M* = 646.8, *Z* = 4, ρ_{calcd} = 1.190 g cm^{–3}, μ(Mo Kα) = 0.116 mm^{–1}; 6917 reflections measured (Mo Kα, graphite monochromator, *T* = –40 °C), 6345 unique reflections after merging (*R*_{int} = 0.020), 3869 observed reflections with *F* > 4.0σ(*F*); solution by direct methods. Anisotropic refinement of non-hydrogen atoms and inclusion of hydrogens at calculated idealized positions converged to *R* = 0.079 (424 refined parameters). High thermal anisotropy in the bridge and in one of the cyclopentadienyl rings indicated substantial disorder of this part of the structure. Fixing the disordered part in an ideal structure by restraining C–C bonds and nonbonding C···C distances (*i.e.* C–C–C bond angles) and isotropic refinement with 50% occupation resulted in electron density peaks for the complementary disordered part of the structure. Refining the restrained parameters in the final stages converged to *R* = 0.060 and *wR* = 0.059 (refinement by minimization of Σw(|*F*_o| – |*F*_c|)² with *w* = 1/(σ²(*F*) + 0.0003(*F*)²), 429 refined parameters, 3869 data observed). Disordered non-hydrogens were refined isotropically, other non-hydrogens anisotropically; all hydrogens were assigned calculated idealized positions and were refined with an overall isotropic thermal parameter.

Crystal Structure Data for [Cp₂Na⁺][Ph₄P⁺]: monoclinic, *a* = 10.974(4) Å, *b* = 7.007(3) Å, *c* = 17.961(6) Å, β = 102.51(3)°, *V* = 1348.3(9) Å³, space group *P*2₁/*c*, formula {(C₁₀H₁₀Na)·C₂₄H₂₀P}, *M* = 492.6, *Z* = 2, ρ_{calcd} = 1.213 g cm^{–3}, μ(Mo Kα) = 0.133 mm^{–1}; 6551 reflections measured (Mo Kα, graphite monochromator, *T* = –40 °C), 2945 unique reflections after merging (*R*_{int} = 0.022), 2341 observed reflections with *F* > 5.0σ(*F*); solution by direct methods, refinement by minimization of Σw(|*F*_o| – |*F*_c|)² to *R* = 0.045 and *wR* = 0.042 (167 parameters, 2341 data observed) with *w* = 1/σ²(*F*). Non-hydrogens were refined anisotropically; all hydrogens were assigned calculated idealized positions and were refined with an overall isotropic thermal parameter.

Acknowledgment. S.H. thanks the Alexander von Humboldt Foundation and the European Community for a fellowship. Prof. Dr. H.-H. Brintzinger is kindly acknowledged for helpful discussions and for providing laboratory facilities. We thank the computer center from the University of Konstanz for their kind cooperation in providing computer time and memory.

Supporting Information Available: Tables of crystallographic parameters, atom coordinates and thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

(16) Schwemlein, H.; Brintzinger, H. H. *J. Organomet. Chem.* **1983**, *254*, 69.