Solid State Structures of Cyclopentadienyllithium, -sodium, and -potassium. Determination by High-Resolution Powder Diffraction[†]

Robert E. Dinnebier, Ulrich Behrens, and Falk Olbrich*

Chemisches Institut, Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2,
D-39106 Magdeburg, Germany

Received January 8, 1997[⊗]

Summary: The structures of MCp (M = Li, Na, K; Cp = cyclopentadienyl), some of the most important precursors in synthetic organometallic chemistry, have been investigated. All three compounds form polymeric "multidecker structures". In LiCp and NaCp the metal atoms form a "string of pearls" whereas the potassium atoms in KCp are arranged in a zigzag chain that interacts with neighboring chains.

Introduction

The investigation of cyclopentadienyl alkali metal compounds has always been a field of interest in organometallic chemistry.[1−3] The compounds MCp (M = Li, Na, K), known for 95 years, are important precursors in synthetic organometallic chemistry. Therefore it is very surprising that the solid state structures of these compounds are not yet known. Unfortunately, it is not possible to grow sufficiently large single crystals of solvate-free cyclopentadienyl alkali metal compounds for single-crystal structure analysis. Structure determinations were usually carried out on base adducts of these compounds with nitrogen- or oxygen-containing ligands (i.e., [LiCp(12-crown-4)],[4] $[NaCp(tmeda)]_n$,[5] or $[KCp(Et_2O)]_n$.[6] The only exceptions are the two compounds $[MC_5H_4SiMe_3]_n$ (M = Li, K);[7,8] their crystal structures were determined by single-crystal diffraction methods. Recently, a few complexes containing alkali metallocene anions, such as $[MCp_2]^-$ (M = Li, Na)[9−11] and $[Cs_2Cp_3]^-$,[12] have been structurally characterized by employing single crystals. The different structural aspects of these compounds are discussed in previous literature.[3,9,11] If single crystals of sufficient size are not available, structure determinations can, alternatively, be carried out on powders.

Table 1. Crystallographic Data for 1−3

	1	**2**	**3**
formula	C_5H_5Li	C_5H_5Na	C_5H_5K
fw (g mol^{-1})	72.04	88.08	104.19
cryst syst	orthorhombic	orthorhombic	tetragonal
space group	*Pnam*	*Pnam*	$P\bar{4}2_1c$
a (Å)	10.2626(3)	10.1339(9)	9.9742(4)
b (Å)	11.1286(3)	11.0064(10)	
c (Å)	3.9366(1)	4.7128(2)	10.5035(3)
V (Å^3)	449.59 (2)	525.66(7)	1044.94(6)
Z	4	4	8
density (calcd, g cm^{-3})	1.064	1.113	1.325
2θ range (deg)	10.0−53.4	6.0−61.8	7.0−60.0
$\delta 2\theta$ (deg; s)[a]	0.01; 5.1	0.02; 6.1	0.01; 9.1
λ (Å)	1.149 37(1)	1.150 00(2)	1.149 37(1)
no. of ref[b]	141	252	260
no. of params	21	21	23
R_{wp}	0.059	0.043	0.046
R_p	0.035	0.034	0.034
R_{F2}	0.073	0.089	0.084

[a] Scan steps with seconds for each step. [b] From Le-Bail fit.

Here we report the results of a crystallographic investigation on the parent compounds in this field. The structures of the base-free unsubstituted compounds LiCp (**1**), NaCp (**2**), and KCp (**3**) were solved through powder diffraction methods using high-resolution synchrotron radiation.

Results and Discussion

The very similar cell parameters of cyclopentadienyllithium (LiCp, **1**) and cyclopentadienylsodium (NaCp, **2**) indicate great structural similarity between these two compounds (Figures 1 and 2). Thus, we found that LiCp and NaCp are isomorphous (Table 1). Both compounds form "multidecker structures" in the direction of the short c-axis. The metal atoms are linearly coordinated by two η^5-bonded cyclopentadienyl rings. Crystallographic mirror planes are found perpendicular to the c-axis. The metal atoms as well as the carbon and hydrogen atoms lie in these mirror planes. Consequently the cyclopentadienyl anions are orientated in an absolutely coplanar and eclipsed fashion. The coordination of the cyclopentadienyl rings to the lithium and sodium atoms is not absolutely symmetric. A line between the center of the Cp rings (abbreviated

---

[†] Dedicated to Professor Dr. E. Weiss on the occasion of his 70th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

(1) (a) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217. (b) Jutzi, P. *Pure Appl. Chem.* **1989**, *61*, 1731. (c) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1.

(2) (a) Weiss, E. *Angew. Chem.* **1993**, *105*, 1565. (b) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501.

(3) (a) Stalke, D. *Angew. Chem.* **1994**, *106*, 2256. (b) Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2168.

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

(5) Aoyagi, T.; Shearer, H. M. M.; Wade, K.; Whitehead, G. *J. Organomet. Chem.* **1979**, *175*, 21.

(6) Jordan, V.; Behrens, U.; Olbrich, F.; Weiss, E. *J. Organomet. Chem.* **1996**, *517*, 81.

(7) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3903.

(8) (a) Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem.* **1987**, *99*, 563. (b) Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 583.

(9) (a) Harder, S.; Prosenc, M. H. *Angew. Chem.* **1994**, *106*, 1830. (b) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744.

(10) (a) Wessel, J.; Lork, E.; Mews, R. *Angew. Chem.* **1995**, *107*, 2565. (b) Wessel, J.; Lork, E.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2376.

(11) Harder, S.; Prosenc, M. H.; Rief, U. *Organometallics* **1996**, *15*, 118.

(12) (a) Harder, S.; Prosenc, M. H. *Angew. Chem.* **1996**, *108*, 101. (b) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 97.

S0276-7333(97)00012-5 CCC: $14.00

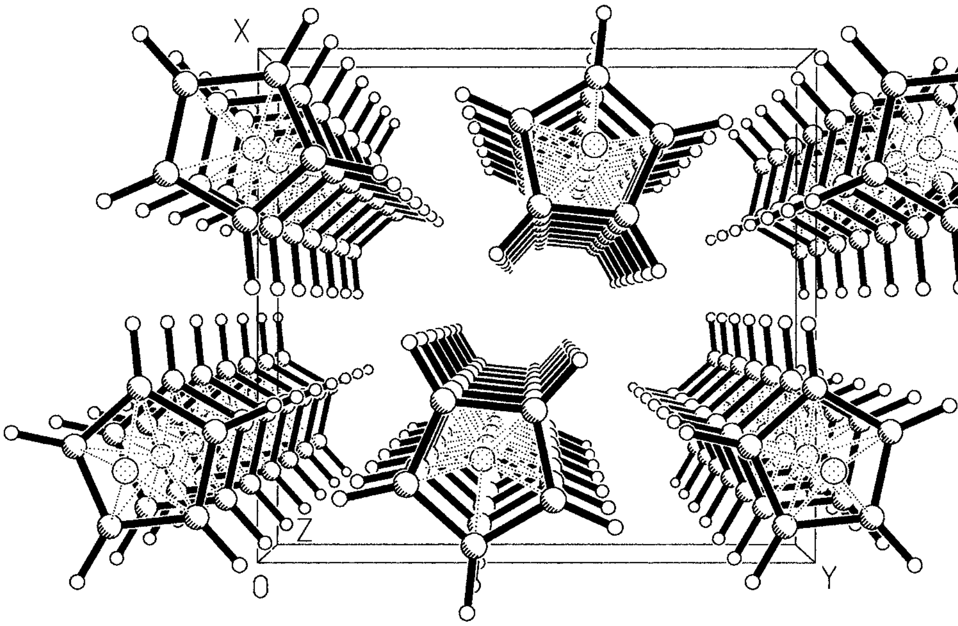

Figure 1. Drawing of the unit cell of NaCp (**2**): View along the *c*-axis. The unit cell of LiCp (**1**) shows the same drawing.

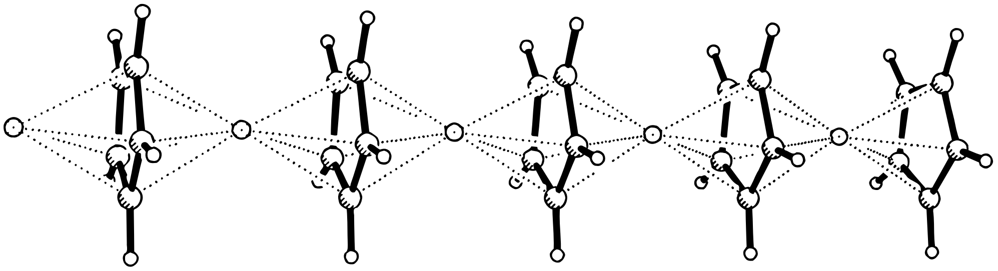

Figure 2. Plot of the polymeric structure of LiCp (**1**, five LiCp units). Distances (Å): Li−C(1) 2.335(9), Li−C(2) 2.331(12), Li−C(3) 2.293(14), Li−C(4) 2.275(6), Li−C(5) 2.301(15), Li−Cp$_{centroid}$ 1.969, C−C 1.413(2) (equal C−C distance for all bonds in the five-membered ring). Angles (deg): Li′−Li−Li″ 180.0, Cp$_{centroid}$−Li−Cp$_{centroid}$′ 176.4. A plot of the molecular structure of NaCp (**2**) is identical. Distances (Å): Na−C(1) 2.671(6), Na−C(2) 2.654(11), Na−C(3) 2.631(12), Na−C(4) 2.633(4), Na−C(5) 2.658(14), Na−Cp$_{centroid}$ 2.357, C−C 1.423(3) (equal C−C distances for all bonds in the five-membered ring). Angles (deg): Na′−Na−Na″ 180.0, Cp$_{centroid}$−Na−Cp$_{centroid}$′ 177.7.

Cp$_{centroid}$) and the metal atoms is slightly bent (angle Cp$_{centroid}$−Li−Cp$_{centroid}$′ 176.4°; Cp$_{centroid}$−Na−Cp$_{centroid}$′ 177.7°). Within the *ab* plane the metal atoms are surrounded by four more cyclopentadienyl anions.

As expected, the *c*-axis for NaCp (4.713(1) Å) is longer than that for LiCp (3.937(1) Å). The value of this *c*-axis is identical with the distance between successive Cp rings along the multidecker chain. Contrarily the *a*- and *b*-axes for NaCp are approximately 1% shorter than those for LiCp. This finding can be explained by the repulsion of the negatively charged Cp rings in adjacent Cp ring stacks. As the Na$^+$ ion is larger than the Li$^+$ ion, the individual Cp rings of the multidecker chains are more distant in NaCp as compared to LiCp. Because adjacent Cp ring stacks approach each other in the planes of the metal ions, the negatively charged repulsive Cp rings can approach each other more in the *ab* plane of the sodium compound.

The distances and angles of the MCp unit (M = Li, Na) which we obtained from our powder diffraction data are in the same range as those found for related compounds which were investigated by single-crystal analyses. We observed Li−C distances between 2.275(6) and 2.335(9) Å (mean value 2.307 Å; Li−Cp$_{centroid}$ 1.969(1) Å). The C−C bonds measure 1.413(2) Å. In the base-free polymeric compound [LiC$_5$H$_4$SiMe$_3$]$_n$, very similar bond lengths were found: Li−C 2.275(6)−2.346(7) Å (mean value 2.309 Å) and Li−Cp$_{centroid}$ 1.957−1.982 Å.[7] Also in the same range are the values observed for the [LiCp$_2$]$^-$ anions (Li−C 2.260(2)−2.366(4) Å, Li−Cp$_{centroid}$ 1.969−2.008 Å).[9,10] Here, the conformation of the η^5-coordinated Cp rings is staggered. In the solvated monomeric LiCp complexes, i.e., [LiCp(12-crown-4] or [LiC$_5$H$_4$SiMe$_3$(tmeda)], the observed Li−Cp$_{centroid}$ distances lie in the range 1.79−2.06 Å[3,4,13] and a calculated Li−Cp$_{centroid}$ distance for a hypothetical solvate-free monomeric LiCp is 1.790 Å.[14]

Because of the larger radius of the Na$^+$ ions, the metal−carbon distances are significantly longer in compound **2**. We observed the following bond lengths: Na−C 2.631(12)−2.671(6) Å (mean value 2.649 Å), Na−Cp$_{centroid}$ 2.357(1) Å, and C−C 1.423(3) Å. Structural data of solvate-free NaCp complexes have yet not been described in the literature. Reported distances for two [NaCp$_2$]$^-$ anions are a little below those found in compound **2** ([NaCp$_2$]$^-$ anions: Na−C 2.584(3)−2.670(3) Å).[10,11] In the polymeric zigzag chain of the compound [NaCp(tmeda)]$_n$, considerably longer Na−C bond lengths

---

(13) Lappert, M. F.; Singh, A.; Engelhardt, L. M.; White. A. H. *J. Organomet. Chem.* **1984**, *262*, 271.

(14) Blom, R.; Faegri, K., Jr.; Midtgaard, T. *J. Am. Chem. Soc.* **1991**, *113*, 3230.

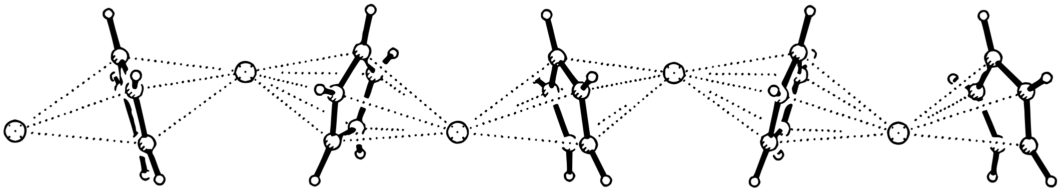

Figure 3. Structure of the polymeric chain of KCp (**3**, five KCp units). Distances (Å): K−C(1) 3.033(7), K−C(2) 3.058(7), K−C(3) 3.080(7), K−C(4) 3.069(4), K−C(5) 3.040(7), K−C(1)′ 3.018(7), K−C(2)′ 2.955(5), K−C(3)′ 3.032(7), K−C(4)′ 3.140(6), K−C(5)′ 3.131(7), K−Cp$_{centroid}$ 2.816, K−Cp$_{centroid}$′ 2.816, C−C 1.395(3) (equal C−C distances for all bonds in the five-membered ring). Angles (deg): K′−K−K″ 138.0, K−Cp$_{centroid}$−K′ 174.6.

have been observed: 2.829(14)−3.033(12) Å (mean value 2.924 Å) and Na−Cp$_{centroid}$ 2.667 Å.[5]

The solid state structure of KCp (**3**) is very different from those of the lighter homologues **1** and **2**. The structure shown in Figure 3 can also be described as a multidecker structure with two Cp rings η^5 coordinated to each potassium atom. Instead of forming a “string of pearls” as in **1** and **2**, the metal atoms in **3** form a zigzag chain (angle K′−K−K″ 138.0°).

Similar to the LiCp and NaCp structures, a line connecting the K atoms does not intersect the plane of the Cp unit at the center of the ring (angle K−Cp$_{centroid}$−K′ 174.6°).

The structure of **3** is related to the structures of [KC$_5$H$_4$SiMe$_3$]$_n$ and the single example of a base adduct of unsubstituted KCp, the complex [KCp(Et$_2$O)]$_n$.[6,8] In all three examples polymeric zigzag chains have been observed. We made an analogous observation for the structures of RbCp and CsCp.[15,16] Because of the bent chain of K$^+$ ions, the potassium atoms are exposed to one side and can be easily coordinated here by Lewis bases. This could be an ether molecule, as realized in the compound [KCp(Et$_2$O)]$_n$, or a η^2-coordinated Cp ring from a neighboring chain, as shown in the compound [KC$_5$H$_4$SiMe$_3$]$_n$. In **3** the K′−K−K″ angle is, with 138.0°, very small compared to those in [KCp(Et$_2$O)]$_n$ (145.3°) and [K$_5$H$_4$SiMe$_3$]$_n$ (150.7°). Therefore, on the backside of the potassium atom in **3**, more space is available than in the other compounds and, thus, we found, in addition to the two η^5-coordinated Cp rings, two η^2(C,C) interactions with Cp rings of two adjacent chains. As a result, all K atoms in **3** are coordinated in a distorted tetrahedral geometry by two η^5- and two η^2-bonded cyclopentadienyl rings (Figure 4). The K−C distances to the η^5-bonded Cp rings are in the range 2.955(5)−3.140(6) Å (mean value 3.056 Å). The K−C(η^2) bond lengths are significantly longer (3.331(7) Å and 3.391(8) Å to “ring 3”, 3.546(7) and 3.663(8) Å to “ring 4”, cf. Figure 4). Compared to **3**, the K−C(η^5) distances in the complex [KC$_5$H$_4$SiMe$_3$]$_n$ are 2.988−3.079 Å and only one η^2(C,C) interaction with K−C(η^2) bond lengths of 3.666 Å and 3.678 Å could be observed. In the ether adduct [KCp(Et$_2$O)]$_n$ the K−C(η^5) distances are 2.991(2)−3.032(2) Å.[6,8] The K−Cp$_{centroid}$ distances lie in the same range for all three examples: KCp 2.816 Å, [KC$_5$H$_4$SiMe$_3$]$_n$ 2.787 Å, and [KCp(Et$_2$O)]$_n$ 2.768 Å. The new type of coordination geometry found for the potassium atom in **3** is related to the coordination sphere of the calcium atom in the structure of CaCp$_2$.[17] Herein the Ca atom is also coordinated by four cyclopentadienyl rings ($\eta^5\eta^5\eta^2\eta^1$). A related type of structure has been previously reported for InCp and TlCp.[18] These compounds are also composed of a polymeric “multidecker structure”.

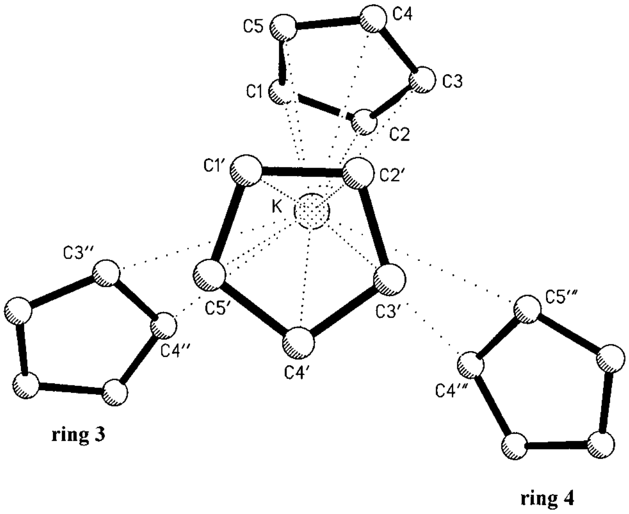

Figure 4. View of the distorted tetrahedral coordination of four Cp rings around the K atoms in KCp (**3**). The H atoms are omitted. Distances (Å): K−C(η^5) (see Figure 3), K−C(3)″ 3.331(7), K−C(4)″ 3.391(8), K−C(4)‴ 3.663(8), K−C(5)‴ 3.546(7).

It is worth mentioning that a short time ago Gillespie et al. presented charge density calculations for both MgCp$_2$ and CaCp$_2$.[19] It was conclusively shown that the linear geometry of MgCp$_2$ and the bent structure of CaCp$_2$ can be understood using arguments where ligand−ligand, CCC−ligand (CCC = core charge concentration), and CCC−CCC interactions are minimized, in keeping with the spirit of the VSEPR model. We think that similar arguments can explain the linear and bent geometries of LiCp, NaCp, and KCp, respectively.

Experimental Section

General Procedures. All reactions were carried out under purified argon by Schlenk techniques. Diethyl ether and cyclopentane were dried over Na/K alloy (benzophenone) and THF over K (benzophenone). The solvents were distilled under nitrogen. Cyclopentadiene was freshly distilled before each reaction. All cyclopentadienyl alkali metal compounds were obtained as white solids which must be handled under absolutely dry and anaerobic conditions due to their extreme sensitivity to moisture and oxygen. To make sure that no

---

(15) Dinnebier, R. E.; Olbrich, F.; van Smaalen, S; Stephens, P. W. *Acta Crystallogr., Sect. B* **1997**, *53*, 153.

(16) Dinnebier, R. E.; Olbrich, F.; Bendele, G. *Acta Crystallogr., Sect. C*, in press.

(17) Zerger, R.; Stucky, G. *J. Organomet. Chem.* **1974**, *80*, 7.

(18) (a) Frasson, E.; Menegus, F.; Panattoni, C. *Nature (London)* **1963**, *199*, 1087. (b) Beachley, O. T., Jr.; Pazik, J. C.; Glassman, T. E.; Churchill, M. R.; Fettinger, J. C.; Blom, R. *Organometallics* **1988**, *7*, 1051.

(19) Bytheway, I; Popelier, P. L. A.; Gillespie, R. J. *Can. J. Chem.* **1996**, *74*, 1059.

coordinating solvents (diethyl ether or THF) remained in our base-free compounds, purity was checked by IR spectroscopy, by ^{1}H-NMR spectroscopy, and in the case of KCp by C,H analysis as well. None of these analyses indicated any impurities.

Synthesis of LiCp (1).[20] ^{n}BuLi (24 mL of a 1.6 M ^{n}BuLi/hexane solution; 38 mmol) was added to a solution of cyclopentadiene (3 mL, 2.4 g, 36 mmol) in diethyl ether (50 mL) at 0 °C, yielding a white suspension. The precipitate was filtered and redissolved in THF (65 mL). After the volume of the filtered solution was reduced to ca. 5 mL, cyclopentane (50 mL) was added. The precipitate was isolated and dried at 75 °C and 10^{-4} Torr for 8 h. Yield: 1.55 g (60%). IR (ν, Nujol): 3086, 1759, 1643, 1259, 1005, 750, 521 cm^{-1}.

Synthesis of NaCp (2).[20] Cyclopentadiene (2.9 mL, 2.32 g, 35 mmol) was added to a gray suspension of NaH (0.69 g, 29 mmol, washed with cyclopentane) in diethyl ether (75 mL), yielding a white suspension after 14 h of stirring at room temperature. The precipitate was collected by filtration and dissolved in THF (10 mL). The obtained solution was filtered, half of the THF was distilled off, and cyclopentane (50 mL) was added. The product was isolated and dried at 75 °C and 10^{-4} Torr for 8 h. Yield: 1.92 g (75%). IR (ν, Nujol): 3071, 1708, 1580, 1001, 718 cm^{-1}.

Synthesis of KCp (3).[20] Cyclopentadiene (2.1 mL, 1.68 g, 25 mmol) was added to a gray suspension of KH (0.84 g, 21 mmol, washed with *n*-hexane) in diethyl ether (50 mL), yielding a colorless solution. After filtration, 40 mL of the solvent was removed under reduced pressure and cyclopentane (25 mL) was added. The resulting precipitate was isolated and dried at 50 °C and 10^{-4} Torr for 5 h. Yield: 1.78 g (48%). IR (ν, Nujol): 3063, 3051, 3023, 1705, 1568, 1009, 733, 702 cm^{-1}. Anal. Calcd (found) for C_5H_5K (**3**): C, 57.6 (56.6); H, 4.8 (5.2).

X-ray Crystallography. The crystal data of **1**−**3** were obtained through powder diffraction methods. For this purpose the colorless air-sensitive compounds were sealed in 1.0 mm capillaries under argon. The data were collected at room temperature with high-resolution synchrotron radiation in transmission geometry (SUNY X3B1 beamline, National Synchrotron Light Source, Brookhaven National Laboratory). The powder patterns were indexed with the program ITO.[21] Systematic absences and crystallographic considerations led to the results provided in Table 1. We used the program SIRPOW92 and direct methods to obtain the positions of the metal and carbon atoms.[22] The hydrogen positions were calculated using a C−H distance of 1.05 Å. Final Rietveld refinements were carried out with the program package GSAS.[23] The metal atoms were refined anisotropically, and the C atoms were refined using the same isotropic thermal parameter. The lengths of all C−C bonds within the C_5 unit were restrained to have the same value (rigid body refinement). We could not find any nonfitting peaks from other crystalline phases, as we observed in RbCp,[15] nor amorphous backgrounds in the Rietveld refinement plots. The final *R*-values are as follows. **1**: $R_{wp} = 0.059$, $R_p = 0.035$, $R_{F2} = 0.073$. **2**: $R_{wp} = 0.043$, $R_p = 0.034$, $R_{F2} = 0.089$. **3**: $R_{wp} = 0.046$, $R_p = 0.034$, $R_{F2} = 0.084$.

Acknowledgment. The authors thank Prof. Dr. P. W. Stephens for his help during data collection. Research was carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. The SUNY X3 Beamline at NSLS is supported by the DOE Office of Basic Energy Sciences under Grant DE-FG02-86ER45231.

Supporting Information Available: Crystallographic details, tables of all bond lengths and angles, atom coordinates and equivalent thermal parameters, anisotropic thermal parameters (for metal atoms only), and Rietveld plots for **1**−**3** (21 pages). Ordering information is given on any current masthead page.

OM9700122

---

[20] The compounds were prepared in a similar way. (a) LiCp and KCp: Wagner, B. O.; Ebel, H. F. *Tetrahedron* **1970**, *26*, 5155. (b) NaCp: Fehlhammer, W. P.; Herrmann, W. A.; Oefele, K. *Handbuch der Präparativen Anorganischen Chemie*, 3rd ed.; Brauer, G., Ed.; Ferdinand Enke Verlag: Stuttgart, Germany, 1981; Vol. 3, p 1810.

[21] Visser, J. W. *J. Appl. Crystallogr.* **1969**, *2*, 89.

[22] Cascarano, G.; Favia, L.; Giacovazzo, C. *J. Appl. Crystallogr.* **1992**, *25*, 310.

[23] von Dreele, R. B.; Larson, A. C. *Los Alamos Natl. Lab., Rep.* **1990**, *LAUR 86−748.*