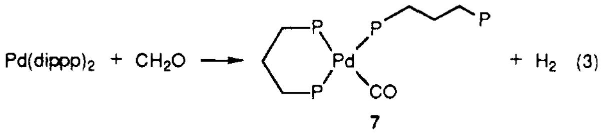
The strict stoichiometry of reaction 2 is readily explained by assuming that the hydrido complex **6** and the carbonyl complex **5** are in equilibrium with the 14e Pd(dippp), whereas the very stable **2** serves as a thermodynamic sink, its formation being essentially irreversible.

In support of the proposed mechanism we observe that paraformaldehyde undergoes decarbonylation with Pd(dippp)$_2$, leading to complex **7** (eq 3). Aldehyde oxidative addition to Pd(0) complexes is not common and may be driven to completion in this case by $H_2$ elimination.



In a probe of the feasibility of generation of **2** from **5** and **6**, Pd(dippp)$_2$ was reacted with 0.5 equiv of gaseous HCl, followed by reaction with CO. Immediate formation of **2** was observed. The same reaction takes place when CO is added prior to HCl (eq 4). A similar reaction of HPd(PPh$_3$)$_4^+$ and CO was reported.[6a,c] Although generation of a dimeric Pd(I) complex from the reaction between Pd(II) and unsaturated Pd(0) complexes is documented,[8] no reaction takes place between **3** and **5** to yield a chloro-bridged analogue of **2**. This suggests that the hydride plays an important role in the coupling process. Mechanistically, this can be viewed as an interaction between an electrophilic hydride and an unsaturated, electron-rich Pd(0) center, as contrasted with the well-known reaction involving coupling of a nucleophilic hydride with an electrophilic metal center.[15]

$$2\text{Pd(dippp)}_2 + \text{HCl} + \text{CO} \rightarrow \mathbf{2} + \text{dippp} \qquad (4)$$

Another point of interest is the role of dippp in this process. Equilibria involving chelate opening undoubtedly promote the $\beta$-elimination, migration, and reductive-elimination processes, all of which are dissociative with square planar Pd(II) complexes.[16] The ability of dippp to function in both mono- and bidentate modes plays an important role in Pd(dippp)$_2$ catalysis.[2] Compatible with this notion, we observe that reaction of (dippe)Pd(Ph)Cl (dippe = 1,2-bis(diisopropylphosphino)ethane) with methanol is considerably slower that that of **1**, although it eventually leads to an analogous complex.

Although the exact role of complex **2** and analogous Pd(I) complexes in catalysis is not yet clear,[17] the unprecented transformation reported here suggests that their formation and function should be considered in reactions involving organopalladium(II) intermediates in alcoholic media. If we take into consideration the high stability of **2**, an intriguing possibility is that some of these processes may actually involve binuclear catalysis.

The observation of reaction 1 has already led us to develop a method for efficient catalytic reduction of aryl chlorides under mild conditions using alcohol as the reducing agent.[18]

**Acknowledgment.** This research was supported by the Fund for Basic Research, administered by the Israel Academy of Sciences and Humanities, and by the U.S.-Israel Binational Science Foundation (BSF), Jerusalem, Israel.

**Supplementary Material Available:** Text describing the data collection, refinement, and crystal data and tables of atom coordinates, anisotropic temperature factors, hydrogen atom coordinates, bond lengths, bond angles, and torsion angles (11 pages); a table of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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[15] (a) Albinati, A.; Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6825. (b) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064. (c) Paonessa, R. S.; Trogler, W. C. *Inorg. Chem.* **1983**, *22*, 1038. (d) Conroy-Lewis, F. M.; Simpson, S. J.; Brammer, L.; Orpen, A. G. *J. Organomet. Chem.* **1991**, *406*, 197.

[16] See, for example: Yamamoto A. *Organotransition Metal Chemistry*; Wiley: New York, 1985; pp 240–249.

[17] Participation of hydrido-bridged palladium complexes in catalysis has been proposed: (a) Reference 6c. (b) Min'kov, A. I.; Eremenko, N. K.; Merkur'eva, S. E.; Efimov, O. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 1347. (c) Min'kov, A. I.; Efimov, O. A.; Eremenko, N. K.; Klimenko, E. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 2076.

[18] Ben-David, Y.; Portnoy, M.; Gozin, M.; Milstein, D. Submitted for publication.

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# Synthesis and Structure of Silicon-Containing Cage Molecules

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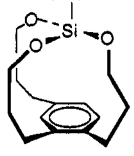
*Summary:* Triarmed cyclophanes **1** and **2** have been synthesized by $i$-Bu$_3$Al/TiCl$_4$-catalyzed cyclotrimerization of $t$-BuSi(OCH$_2$CH$_2$CH$_2$C≡CH)$_3$ and characterized by single-crystal X-ray, $^1$H and $^{13}$C NMR, and elemental analysis. Macrocyclic cage **1** has a distorted benzene ring, while that of **2** is nearly planar. In **1** and **2** the silicon atom is 3.50 and 3.58 Å above the mean plane of the benzene ring. Additional cyclotrimerization studies of this catalyst system are reported.

We wish to report the synthesis of **1** and **2**, the first examples of silicon-containing triarmed cyclophanes in which the silicon substituents are outside of the cage.[1] The syntheses of **1** and **2** are the first steps toward pre-



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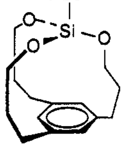

2

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[†] University of Colorado at Denver.

[‡] University of Colorado at Boulder.

[1] L'Esperance, R. P.; West, A. P., Jr.; Van Engen, D.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 2672–2676. This reference reports the first silicon-containing member of this series. Other related compounds are referenced in subsequent citations of Pascal and co-workers. In all of these studies, the hydrogen substituent is on the inside of the macrocycle.

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paring silicon-containing macrocycles which have variable sizes and structures.

The synthesis of 1 and 2 depends on the assembly of a silicon tripod triyne, $t$-BuSi(OCH$_2$CH$_2$CH$_2$C≡CH)$_3$, which can then be cyclotrimerized by metal catalysis to the desired aromatic ring.[2-4] We have prepared $t$-BuSi(OCH$_2$CH$_2$CH$_2$C≡CH)$_3$ in 70% isolated yield by reaction of $t$-BuSiCl$_3$ and HOCH$_2$CH$_2$CH$_2$C≡CH in the presence of copper powder and pyridine in benzene (eq 1).[5] While

$$t\text{-BuSiCl}_3 + 3\mathrm{HOCH_2CH_2CH_2C{\equiv}CH} \rightarrow t\text{-BuSi}(\mathrm{OCH_2CH_2CH_2C{\equiv}CH})_3 \quad (1)$$

recognizing that cyclotrimerization would lead to both 1,2,4- and 1,3,5-trisubstituted benzene isomers,[2,3] we hoped that the yields in the macrocyclization step would be sufficiently good to allow us to isolate both isomers, as has proved to be the case. The cyclotrimerization was effected by $i$-Bu$_3$Al/TiCl$_4$,[2-4] giving about 30% isolated yield of a ~7/1 mixture of 1 and 2 (eq 2).[6] Although 1 and 2 have

$$t\text{-BuSi}(\mathrm{OCH_2CH_2CH_2C{\equiv}CH})_3 \xrightarrow[\mathrm{TiCl_4}]{i\text{-}\mathrm{Bu_3Al}} 1 + 2 \quad (2)$$

very similar properties, they can be separated by flash chromatography and individually characterized.[6] The $^{13}$C NMR spectrum of compound 1 shows 17 distinctly different carbon peaks, demonstrating the asymmetric nature of the substitution pattern and uniquely characterizing this isomer. Thus, the nine carbon atoms bridging the silicon to the benzene ring, the six benzene carbons, and the two different carbons of the $t$-Bu group prove to be magnetically nonequivalent. In contrast, the $^{13}$C NMR spectrum of 2 shows only the seven carbon resonances expected for its symmetrical structure.

Single-crystal X-ray structures of 1 and 2 are shown in Figures 1 and 2.[7,8] Several aspects of the crystal structures of 1 and 2 deserve comment. For compound 1, (1) the benzene ring is slightly distorted from planarity, (2) the

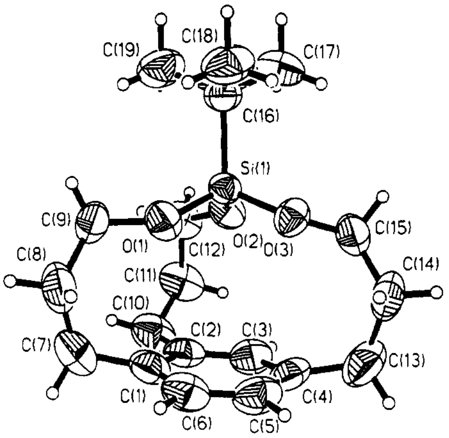

**Figure 1.** Anisotropic ellipsoid plot of 1 at the 50% probability level showing the numbering scheme adopted. The disordered C(9′) atom (occupancy = 0.23) is omitted for clarity. Selected bond lengths and angles (Å, deg) are as follows: Si(1)–O(1), 1.604 (2); Si(1)–O(2), 1.621 (2); Si(1)–O(3), 1.612 (2); Si(1)–C(16), 1.865 (3); O(1)–C(9), 1.402 (5); O(1)–C(9′), 1.245 (21); O(2)–C(12), 1.410 (3); O(3)–C(15), 1.416 (4); C(1)–C(2), 1.392 (5); C(1)–C(6), 1.386 (5); C(1)–C(7), 1.496 (5); C(2)–C(3), 1.387 (5); C(2)–C(10), 1.526 (5); C(3)–C(4), 1.382 (4); C(4)–C(5), 1.379 (6); C(4)–C(13), 1.506 (6); C(5)–C(6), 1.368 (5); O(1)–Si(1)–O(2), 114.2 (1); O(1)–Si(1)–O(3), 104.3 (1); O(2)–Si(1)–O(3), 106.9 (1); O(1)–Si(1)–C(16), 110.9 (1); O(2)–Si(1)–C(16), 109.7 (1); O(3)–Si(1)–C(16), 110.5 (1); Si(1)–O(1)–C(9), 137.3 (2); Si(1)–O(2)–C(12), 132.4 (2); Si(1)–O(3)–C(15), 130.0 (2); C(2)–C(1)–C(6), 118.2 (3); C(2)–C(1)–C(7), 124.9 (3); C(6)–C(1)–C(7), 116.6 (3); C(1)–C(2)–C(3), 119.0 (3); C(1)–C(2)–C(10), 123.5 (3); C(3)–C(2)–C(10), 117.5 (3); C(2)–C(3)–C(4), 122.4 (3); C(3)–C(4)–C(5), 117.5 (3); C(3)–C(4)–C(13), 120.0 (3); C(5)–C(4)–C(13), 122.0 (3); C(4)–C(5)–C(6), 120.8 (3); C(1)–C(6)–C(5), 121.7 (3); C(1)–C(7)–C(8), 114.1 (3); O(1)–C(9)–C(8), 112.5 (3); O(2)–C(12)–C(11), 112.9 (3); O(3)–C(15)–C(14), 112.5 (3).

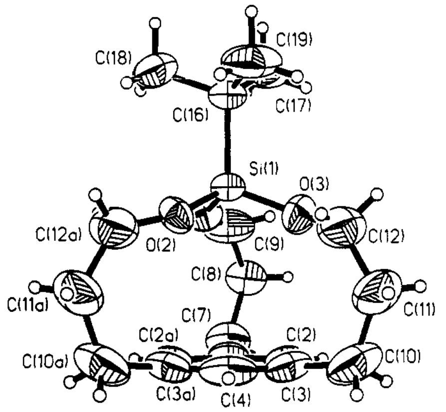

**Figure 2.** Anisotropic ellipsoid plot of 2 at the 50% probability level showing the numbering scheme adopted. Atom O(1), which is behind atom O(2), and atom C(1), which is behind atom C(4), are not labeled. The molecules sit on a crystallographic mirror plane which passes through Si(1), C(1), C(4), C(7), and C(16). The molecule is therefore disordered. For clarity only one orientation is shown. Selected bond distances and angles (Å, deg) follow: Si(1)–O(1), 1.610 (5); Si(1)–O(2), 1.617 (7); Si(1)–O(3), 1.580 (7); Si(1)–C(16), 1.863 (6); O(1)–C(9), 1.319 (7); O(2)–C(12A), 1.253 (9); O(3)–C(12), 1.303 (10); C(1)–C(2), 1.382 (6); C(1)–C(7), 1.498 (8); C(2)–C(3), 1.383 (6); C(3)–C(4), 1.377 (6); C(3)–C(10), 1.474 (8); O(1)–Si(1)–O(2), 107.1 (3); O(1)–Si(1)–O(3), 108.7 (3); O(2)–Si(1)–O(3), 109.8 (3); Si(1)–O(1)–C(9), 137.9 (4); Si(1)–O(2)–C(12A), 140.4 (6); Si(1)–O(3)–C(12), 139.1 (6); C(2)–C(1)–C(7), 120.4 (3); C(2)–C(1)–C(2A), 118.8 (6); C(7)–C(1)–C(2A), 120.4 (3); C(1)–C(2)–C(3), 121.2 (5); C(2)–C(3)–C(4), 118.3 (5); C(2)–C(3)–C(10), 121.0 (5); C(4)–C(3)–C(10), 120.5 (5); C(3)–C(4)–C(3A), 122.1 (6).

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(2) Hubert, A. J. *J. Chem. Soc.* **1967**, 6–10.

(3) Hubert, A. J. *J. Chem. Soc.* **1967**, 11–12.

(4) Hubert, A. J. *J. Chem. Soc.* **1967**, 13–14.

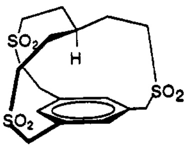
(5) Tamborski, C.; Post, H. W. *J. Org. Chem.* **1952**, *17*, 1400–1404.

(6) Compounds 1 and 2 were prepared by adding 15.0 g (0.045 mol) of the *tert*-butyl tripod (eq 1) dissolved in 25 mL of hexane to a mixture of 1.5 mL (0.014 mol) of TiCl$_4$ and 7.5 mL (0.030 mol) of $i$-Bu$_3$Al dissolved in 600 mL of hexane. The addition to the refluxing, stirred catalyst solution was carried out by syringe pump over 56 h. After the addition, the reaction flask was cooled, 15 mL of isopropyl alcohol was added, and the contents were filtered through a silica gel bed to remove any solid residue. A liquid (12.6 g), which later partially solidified, was obtained by rotoevaporation. Gas chromatographic analysis shows this to be a mixture of about 7/1 1/2. Compounds 1 and 2 were isolated from this material by flash chromatography through a 40-mm column containing a 23-cm height of silica gel by elution with a 95/5% mixture of hexane-/ethyl acetate. We obtained 1.23 g of pure 1 and 0.14 g of pure 2 as well as 3.05 g of a mixture of these isomers (total yield ~30%). Characterization of 1: $^1$H NMR (300 MHz, CDCl$_3$) 0.79 ppm (s, 9 H), 1.62–2.06 (m, 6 H), 2.34–3.11 (m, 6 H), 3.70–4.18 (m, 6 H), 6.96–7.16 (m, 3 H); $^{13}$C NMR (300 MHz, CDCl$_3$) 19.40, 26.29, 28.57, 30.09, 30.33, 32.30, 34.11, 35.46, 63.65, 63.76, 65.73, 125.27, 129.69, 129.98, 136.89, 137.46, 138.62 ppm; mass spectrum shows base peak at $m/z$ 277, which is the loss of a *tert*-butyl group. Anal. Calcd for C$_{19}$H$_{30}$O$_3$Si: C, 68.22; H, 9.04. Found: C, 67.87; H, 8.90. Characterization of 2: $^1$H NMR (300 MHz, CDCl$_3$) 0.73 ppm (s, 9 H), 1.87–1.96 (m, 6 H), 2.68 (t, 6 H, $J$ = 6.6 Hz), 3.70–3.76 (m, 6 H), 6.88 (s, 3 H); $^{13}$C NMR (300 MHz, CDCl$_3$) 19.70, 26.21, 32.46, 34.66, 62.91, 128.30, 139.85 ppm; mass spectrum shows base peak at $m/z$ 277, which is the loss of a *tert*-butyl group. Anal. Calcd for C$_{19}$H$_{30}$O$_3$Si: C, 68.22; H, 9.04. Found: C, 67.19; H, 8.83.

(7) Crystal data for 1, the 1,2,4-isomer of C$_{19}$H$_{30}$O$_3$Si: formula weight 334.5, orthorhombic, $P2_12_12_1$, $a$ = 8.196 (2) Å, $b$ = 11.573 (4) Å, $c$ = 19.792 (6) Å, $V$ = 1877 (1) Å$^3$, $Z$ = 4, $D_{\mathrm{calc}}$ = 1.184 g/cm$^3$. Intensity data: Nicolet P3F autodiffractometer, data collected at room temperature, Mo K$\alpha$ ($\lambda$ = 0.71073 Å), $\theta$–$2\theta$ scan mode, $3.0 < \theta < 45.0$, 3641 reflections measured, of which 2852 were unique ($R_{\mathrm{int}}$ = 0.016) and 2157 were observed [$F > 6\sigma(F)$]. The structure was solved by direct methods and refined using full-matrix least-squares techniques. Final residues $R$ = 0.037 and $R_w$ = 0.046.

Si–O–C bond angles are all between 130 and 137°, (3) there is a jawlike opening in the cage because of the 1,2,4-substitution pattern, and (4) the silicon atom is 3.50 Å from the mean plane of the benzene ring. Compound 2 has (1) its benzene ring essentially planar, (2) Si–O–C bond angles between 138 and 140°, and (3) a 3.58-Å silicon-to-benzene ring distance.

Pascal and co-workers have studied several related macrocyclics.[1,9-11] Two of these, 3 and 4, also have three four-atom arms making them analogous to 2.[1,9] The X-ray structures of 3, 4, and related molecules show that their methine hydrogens are directed inside the macrocycle. Molecular mechanics calculations indicate that the "in" hydrogen isomer is the more stable one.[10,11]



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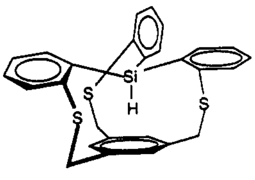

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In compounds 1 and 2, the bulky *tert*-butyl group precludes formation of the "in" isomer. Ours are the first X-ray structures of such small *out*-cyclophanes. Pascal and co-workers have reported evidence of strain in 4 in that the benzylic carbon atoms are 0.39 Å above the nearly planar basal benzene ring. Pascal's compound 3 has its benzylic carbons averaging 0.16 Å above the nearly planar basal benzene ring. Analysis of 2 reveals distortions that are essentially the same as 3 with the benzylic carbons averaging 0.16 Å above the mean plane of the benzene ring. In 1 we find that the para-situated benzylic carbons average 0.32 Å above the mean plane of the slightly distorted benzene ring, indicating, as can be readily seen in Figure 1, a boatlike benzene ring.

Other cyclotrimerization reactions in this and related systems have also been studied. While the $i$-$Bu_3Al/TiCl_4$ catalyst system gives high yields for cyclotrimerizations of 1-hexyne, 3-hexyne, 5-chloro-1-pentyne, and $t$-$Bu(CH_3)_2SiOCH_2CH_2CH_2C{\equiv}CH$, it does not work for $CH_3Si(OCH_2CH_2CH_2C{\equiv}CH)_3$ or $HOCH_2CH_2CH_2C{\equiv}CH$. Somewhat surprisingly, $(CH_3)_3SiOCH_2CH_2CH_2C{\equiv}CH$ is cyclotrimerized to a ~4/1 ratio of 1,2,4/1,3,5 in only about 10% yield. Thus, it appears that the effectiveness of this catalyst system is quite sensitive to the presence of oxygen in the alkyne. The $i$-$Bu_3Al/TiCl_4$ catalyst also fails to cyclotrimerize $ClCH_2CH_2CH_2C{\equiv}CSi(CH_3)_3$ and $(CH_3)_3SiOCH_2CH_2CH_2C{\equiv}CSi(CH_3)_3$.

**Acknowledgment.** We wish to thank the National Science Foundation (Grant CHE-8921522) for generous support of this work. We are also particularly indebted to Martin E. Ashley for expert help with the NMR analysis.

**Supplementary Material Available:** Single-crystal structure reports for compounds 1 and 2, including tables of crystal data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters (17 pages); tables of structure factors (11 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for 2, the 1,3,5-isomer of $C_{19}H_{30}O_3Si$: formula weight 334.5, monoclinic, $P2_1/m$, $a$ = 8.533 (2) Å, $b$ = 11.232 (2) Å, $c$ = 10.028 (2) Å, $\beta$ = 95.15 (1)°, $V$ = 957.2 (3) Å$^3$, $Z$ = 2, $D_{calc}$ = 1.161 g/cm$^3$. Intensity data: Nicolet P3F autodiffractometer, data collected at room temperature, Mo K$\alpha$ ($\lambda$ = 0.71073 Å), $\theta$–$2\theta$ scan mode, $3.0 < \theta < 45.0$, 4116 reflections measured, of which 1338 were unique ($R_{int}$ = 0.021) and 1027 were observed [$F > 4\sigma(F)$]. The structure was solved by direct methods and refined using full-matrix least-squares techniques. Final residues $R$ = 0.066 and $R_w$ = 0.088. The model was originally solved and refined in the space group $P2_1$. There was significant disorder present in the acentric space group, and many of the anisotropic displacement parameters and bond lengths were unreasonable. This model converged with $R$ = 0.044 and $R_w$ = 0.053 for 1554 observed data and 246 variables. Examination of the ordered and disordered positions suggested the presence of a mirror plane. Although the final residues are higher in the centrosymmetric space group, the resulting displacement parameters, bond distances, and bond angles are more reasonable. All results presented are for the solution in $P2_1/m$.

(9) Pascal, R. A., Jr.; Grossman, R. B.; Van Engen, D. *J. Am. Chem. Soc.* 1987, *109*, 6878–80.

(10) Pascal, R. A., Jr.; Grossman, R. B. *J. Org. Chem.* 1987, *52*, 4616–17.

(11) Pascal, R. A., Jr.; Winans, C. G.; Van Engen, D. *J. Am. Chem. Soc.* 1989, *111*, 3007–10.

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# Synthesis and Crystal Structure of the First Yttracarborane Sandwich Complex: Analogue of an Yttrocene Derivative

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*Received September 11, 1991*

*Summary:* The first carborane analogue of an yttrocene derivative, 1, was synthesized from $Li^+{}_2[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ and $YCl_3$ in a molar ratio of 2:1 in dry benzene ($C_6H_6$) in 83% yield. Compound 1 consists of a dianionic $\{Y(Cl)(THF)[\eta^5\text{-}(SiMe_3)_2C_2B_4H_4]_2\}^{2-}$ sandwich complexed with an exo-polyhedral $Li(THF)^+$ cation, and the net negative charge is balanced by a discrete cationic $Li^+(THF)_4$ unit outside the coordination sphere as shown by X-ray structure analysis. The ($C_2B_3$ centroid 1)–Y–($C_2B_3$ centroid 2) angle of 129.7°, Y–centroid distance of 2.38 Å, Y–Cl distance of 2.582 (4) Å, Cl–Y–O(THF) angle of 89.5 (3)°, and the bent geometry of 1 all resemble those of an yttrocene analogue. As in the Cp systems, the average (ring centroid)–Y–O(THF) (103°) and (ring centroid)–Y–Cl (111°) angles constitute a distorted-tetrahedral geometry for 1.

The cyclopentadienide anion and a number of its C-substituted derivatives have been the ligands of choice in the production of sandwiched and/or half-sandwiched $\pi$-complexes of both metals and nonmetals. Thus, a wide variety of Cp (Cp = $\eta^5$-$C_5R_5$, R = organic or organometallic group) complexes involving the majority of the s-, p-, d-, and f-block elements have been reported.[1] The dianions of the carboranes, including the $C_2B_9$ and $C_2B_4$ systems, are isoelectronic with the Cp ligands, and while fewer in

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(1) (a) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982. (b) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987. (c) *Dictionary of Organometallic Compounds*; Macintyre, J. E., Ed.; Chapman and Hall: New York, 1984. *Ibid.*, Suppl. Vol. 1-5, 1985–1989. (d) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; and references therein.

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