Borylcyclopentadienides

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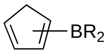
The cyclopentadienylboranes $C_5H_5BR_2$ **1−4** (R = NMe_2, $^1/_2(OCMe_2)_2$, Pr^i, Me) are synthesized from alkali metal cyclopentadienides MCp (M = Li, Na) and $BCl(NMe_2)_2$, $ClB(OCMe_2)_2$, $BClPr^i_2$, and $BBrMe_2$, respectively. Compound **1** reacts with lithium dialkylamides ($LiNMe_2$, LDA, LiTMP) in THF or with elemental sodium to give the salts $M[C_5H_5B(NMe_2)_2]$ [M(**5**) with M = Li, Na]. Compounds **2** and **3** are metalated by LiTMP, and compounds **3** and **4** by cyclopentadienides MCp (M = Li, Na) to give borylcyclopentadienides or boratafulvenes $M[C_5H_5BR_2]$ M(**6**)−M(**8**) (R = $^1/_2(OCMe_2)_2$, Pr^i, Me). Estimated (NMR) room temperature equilibrium constants for the systems **1−4**/LiCp in THF are 0.5, 4, >300, and >300, respectively; they show that dialkylboryl substituents stabilize cyclopentadienide ions markedly. The triclinic THF solvate Na(THF)(**5**) (≡**10**) forms an approximately trigonal helix with alternating $Na(THF)^+$ and anion units, while the tetragonal tetrahydropyran solvate Na(THP)(**5**) (≡**11**) forms a tetragonal helix. The monoclinic solvate Li(12-crown-4)(**6**) (≡**12**) is molecular, and the orthorhombic $Na(THP)_2$(**8**) (≡**13**) displays a chain structure. The B−C1 distances [154.5(2) for **11**, 148.8(8) for **12**, and 150.8(4) pm for **13**], lengthened C1−C2/C1−C5 distances (av) (142.5 for **11**, 142.1 for **12**, and 143.6 pm for **13**), slightly lengthened C3−C4 distances (140.0 for **11**, 141.1 for **12**, and 143.5 pm for **13**), and shortened C2−C3/C4−C5 distances (av) (140.3 for **11**, 137.3 for 12, and 137.9 pm for **13**) are caused by π interactions (**11** < **12**, **13**) between the C_5 ring and the boryl function. These interactions are weak in the case of the $B(NMe_2)_2$ group and quite marked for the $B(OCMe_2)_2$ and BMe_2 groups.

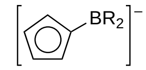
Introduction

Functionalized cyclopentadienides constitute a well-developed family of aromatic systems.[1] Most functionalities increase the C−H acidity of cyclopentadiene and stabilize the corresponding cyclopentadienide ions. It has long been known that boryl groups stabilize carbanions,[2,3] yet there is only one report on a preparation of a borylcyclopentadienide. In 1973, Onak et al. communicated the synthesis of lithium (dichloroboryl)cyclopentadienide in hexane solution and gave ^1H and ^{11}B NMR data as supporting evidence.[4]

It seemed desirable to have a practical synthesis of alkali metal borylcyclopentadienides. These compounds should be useful as building blocks in organic and organometallic chemistry. In addition, we wished to obtain information on the interaction between the aromatic cyclopentadienide ring and the boryl substituent and on the extent of the presumed anion stabilization. In this paper we describe the syntheses of the cyclopentadienylboranes **1−4**, their metalation chemistry, and the alkali metal salts of the anions **5**$^-$−**8**$^-$.



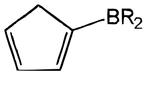
1: R = NMe_2
2: 2R = $(OCMe_2)_2$
3: R = Pr^i
4: R = Me



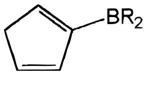
5: R = NMe_2
6: 2R = $(OCMe_2)_2$
7: R = Pr^i
8: R = Me

Results and Discussion

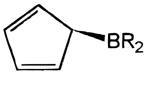
Cyclopentadienylboranes. A number of boranes with *C*-unsubstituted cyclopentadienyl groups are known and have been characterized by NMR spectroscopy. These include compounds with two *B*-hydrocarbyl substituents (Me,[5] Et,[6] Pr,[7] and Ph[7]), with two *B*-alkoxy groups [OMe,[7,8a] OEt,[9] $O(CH_2)_2O$,[8a] and $O(CH_2)_3O$[8b]], Onak's dichloro derivative,[4] and the bis(dimethylamino) derivative **1**.[7]



A



B



C

Cyclopentadienylboranes can exist as three constitutional isomers **A−C** which can be interconvert by sigmatropic rearrangements.[10] Spangler obtained the

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

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[2] (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834. (b) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804. (c) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854. Kow, R.; Rathke, M. W. *J. Am. Chem. Soc.* **1973**, *95*, 2715.

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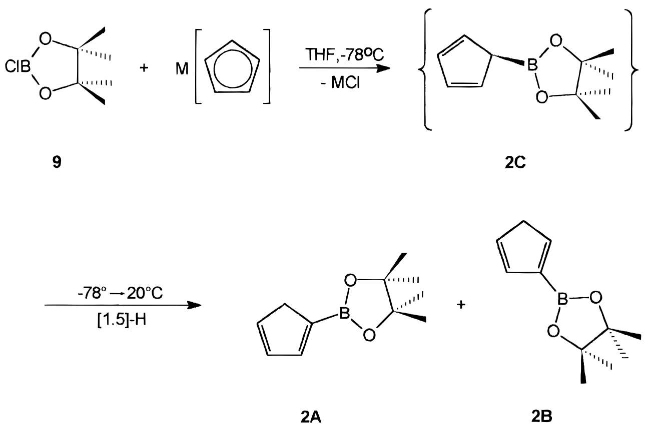
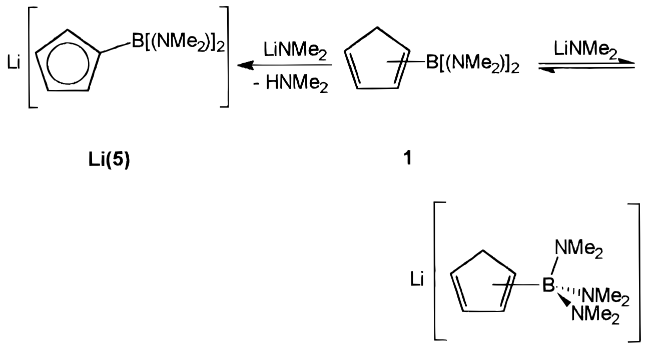
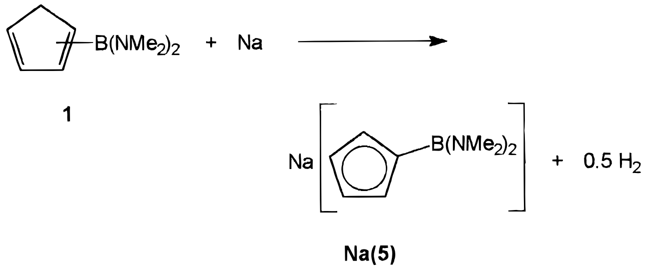
Scheme 1



Scheme 2



Scheme 3



dimethylboryl compound **4** from $HgCp_2/BClMe_2$ at −78 °C as 5-isomer **4C**.[5] This molecule is fluxional, displaying fast sigmatropic migration of the BMe_2 group. At temperatures above −15 °C a [1,5] sigmatropic hydrogen shift comes into play and allows the isomerization of **4C** to the more stable vinyl isomers (**4A**,**B**, unspecified, no data).[5]

Having metalation reactions in mind we chose the compounds **1**−**3** as synthetic goals. They all can be made from alkali metal cyclopentadienides MCp (M = Li, Na) and chloroboranes $[BCl(NMe_2)_2$, the pinacol-derived 1,3,2-dioxaborolane $ClB(OCMe_2)_2$ (**9**), and $BClPr^i{}_2]$. The problems encountered are ether cleavage, particularly with the more Lewis-acid halides, and Diels−Alder dimerization of the product.

Thus, **1** was obtained from NaCp or LiCp in THF at −15 °C by addition of $BCl(NMe_2)_2$; distillative workup gave an isomer mixture **1A**/**1B** (1/1). Similarly, **2** was made from NaCp and $BCl(OCMe_2)_2$ (**9**) in THF at −78 °C. Monitoring the reaction mixture by ^{11}B and ^{13}C NMR spectroscopy demonstrates the primary formation of the nonfluxional (at least up to 5 °C) allylic isomer **2C** [$\delta(^{11}B)$ 32] which rearranges at temperatures above −10 °C to give a mixture of the more stable vinyl isomers **2A**/**2B** (9/1) [$\delta(^{11}B)$ 29] (Scheme 1). Diels−Alder dimerization during distillative workup is a severe problem in this case. The required and known, 1,3,2-dioxaborolane **9**[11] could be obtained efficiently from BCl_3/pinacol in pentane at −30 °C.

The diisopropyl derivative **3** was obtained by treatment of NaCp with $BClPr^i{}_2$ in pentane (not THF!) at −70 °C. The primary product is again of the allylic type **3C** [$\delta(^{11}B)$ 86]; this isomer is fluxional like **4C**,[5] even at −105 °C in toluene. Workup as usual affords a mixture of the vinylic isomers **3A**/**3B** (11/1) [$\delta(^{11}B)$ 72]. We mention in passing that the different behavior of **2C** and **3C** with respect to boryl migration is as expected: The barrier to sigmatropic boryl migration increases with increasing π interaction between the boron and the substituents at boron;[12] it is also calculated (MNDO) to be larger for Cp than for C_5Me_5-derived compounds.[13]

As it turned out later, our attempts to characterize a salt of anion $\mathbf{7}^-$ by crystallography remained unsuccessful. Therefore we chose the dimethylboryl species **4** and $\mathbf{8}^-$ as alternatives. Samples of **4** were synthesized by much the same method that was used for **3**. Treatment of a suspension of NaCp in decalin with $BBrMe_2$ at −20 °C gave a solution of **4** in the hydrocarbon. After filtration, distillation afforded **4A** as a volatile pyrophoric liquid which contained a 10% admixture of decalin and varying amounts of Diels−Alder dimers; conclusive evidence for the presence of isomer **4B** could not be obtained. Pentane may also be used as reaction medium and is more suitable when samples are needed for subsequent metalation experiments.

The cyclopentadienylboranes **1**−**4** were characterized by NMR spectroscopy. Assignments are based on literature data[9,14,15] and were confirmed in the cases of **1A**/**1B** and **3A**/**3B** by (H,H)-NOE techniques, (H,C)-HETCOR spectra, and simulations.

Metalation Reactions and Borylcyclopentadienides. In most structural situations organoboranes react with bases under quaternization at boron. This reaction is often irreversible or may be followed by detrimental B−C bond breaking. Three effects may help to achieve metalation of unsaturated organoboranes: (i) Rathke and Kow metalated boranes with sterically protected boron by the action of bulky bases.[2b] This "double steric hindrance" amounts to steric destabilization of the borate and prohibits its formation. (ii) The quaternization at boron can become reversible when the borane is sufficiently stabilized by π interactions with the substituents at boron, furthermore when lithium amides are used rather than carbon bases. The reversibility may then open the route to slower metalation processes. The recently reported metalation of bis(dialkylamino)(2,4-pentadienyl)boranes with formation of boratabenzene species exemplifies this situation.[16] (iii) The rare situation of high Brönsted acidity

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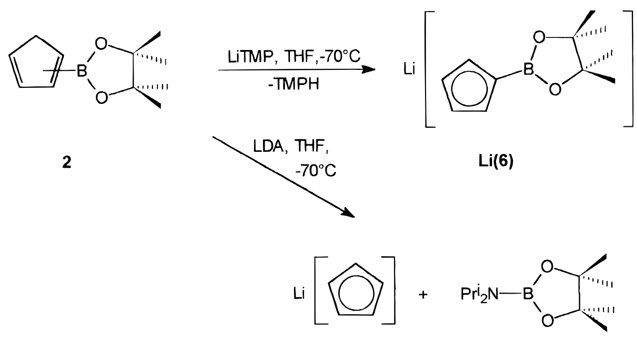
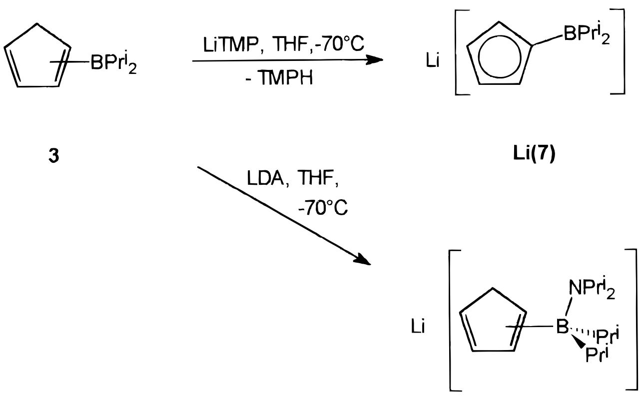
Scheme 4



Scheme 5



of the organoborane can favor deprotonation over quaternization as in Ashe and Shu's metalation of 1-(phenylbora)-2,5-cyclohexadiene.[2a]

The metalation of the cyclopentadienylboranes **1**−**4** turned out to be feasible, although only the case of the bis(dimethylamino) derivative **1** is really simple. Treatment of **1** in THF with LiNMe$_2$, LDA, or LiTMP in THF produces Li(**5**) in near-quantitative yields. Spectroscopically a trace of LiCp (2%−4%) is found, indicating some deborylation with formation of cyclopentadienide. The successful use of LiNMe$_2$ as base is quite remarkable in that neither the organoborane nor the base exerts steric hindrance. In earlier work borate formation in the system MeB(NMe$_2$)$_2$/LiNMe$_2$ was found to be an equilibrium reaction at ambient temperature.[16] Presumably the same is true for the system **1**/LiNMe$_2$. However, if the borate formation is reversible it will not impede the very fast deprotonation of **1** by lithium dialkylamides. This interpretation is summarized in Scheme 2.

The reaction of **1** with sodium sand in pentane or THF produces the sodium salt Na(**5**) under evolution of hydrogen gas (Scheme 3). The salt is isolated as a white solid by pumping off the solvent and may readily be prepared in large runs. This method is particularly simple from a synthetic point of view. Crystallization from pentane/THF affords the solvate Na(THF)(**5**) (≡**10**) in large colorless crystals while from pentane/tetrahydropyran (THP) the solvate Na(THP(**5**) (≡**11**) is obtained. Crystals of **10** and **11** suitable for crystallographic characterization were obtained in this way.

The metalation of **2** can be achieved with LiTMP in THF to produce Li(**6**) in high yield, while attempted metalation with LDA as base resulted in fast deborylation (Scheme 4). Both reactions are highly chemoselective. These observations stress the importance of double steric hindrance in this case. With 12-crown-4 the salt Li(**6**) forms a solvate Li(12-crown-4)(**6**) (≡**12**) as colorless needles. When **2** is treated with elemental sodium, two parallel reactions take place with approximately equal weight: formation of Na(**6**) under hydrogen evolution and deborylation with formation of NaCp. This reaction is therefore of no practical value.

A similar situation obtains with **3**. Deprotonation can be effected with LiTMP in THF to give Li(**7**), whereas with LDA fast and quantitative borate formation is observed (Scheme 5). Deborylation is not observed in this case. Of the three isomeric borates only the one corresponding to the higher-energy isomer **3C** will readily undergo B−C bond breaking. It seems thatborate formation of the lower-energy isomers **3A** and **3B** is irreversible (at least up to room temperature), and as a consequence, the borate Li[**3C**·NPr$^i_2$] becomes kinetically inaccessible. The borane **3** also reacts with elemental sodium; as in the case of **2**, a product mixture of Na(**7**) and NaCp in an approximate 1/1 ratio is formed.

Because of the high Brönsted acidity of **3**, LiCp and NaCp may also be used as bases to produce the corresponding salts Li(**7**) and Na(**7**); this method is both cheaper and more convenient than the deprotonation by LiTMP. With 12-crown-4, the salt Li(**7**) gives colorless needles of Li(12-crown-4)(**7**), which, however, did not yield to X-ray structure determination.

In the same manner the dimethylboryl derivative **4** reacts with LiCp and NaCp in THF to produce Li(**8**) and Na(**8**), respectively, as white solids. Addition of 15-crown-5 to a THF solution of the sodium salt Na(**8**) gives the solvate Na(15-crown-5)(**8**) as large colorless orthorhombic crystals which are disordered in the crown ether part. Crystallization of Na(**8**) from pentane/THP at low temperature affords the low-melting solvate Na(THP)$_2$(**8**) (≡**13**).

All alkali metal borylcyclopentadienides are colorless solids. They are highly sensitive to oxygen and water. Solutions give purple colors with traces of oxygen, just like solutions of NaCp. They often contain varying small admixtures of LiCp and NaCp. Their solvates crystallize free of these impurities.

The ^{11}B and ^{13}C chemical shift data of the anions **5**$^-$−**8**$^-$ give insight into the charge distribution in these systems. The carbon chemical shifts of monocyclic aromatic ring systems are highly correlated with the π electron density per carbon atom.[17] Alkali metal cyclopentadienides MCp (M = Li, Na, K) show chemical shifts δ(^{13}C) 103.4−104.8 with little influence of the cation.[18] The resonances of the unsubstituted carbon atoms in **5**$^-$−**8**$^-$ are all shifted to lower field. This effect is more pronounced in the 2- and 5-positions and less so in the 3- and 4-positions. Furthermore, it increases in the order **5**$^-$ < **6**$^-$ < **7**$^-$, **8**$^-$. These observations demonstrate transfer of π electron density from the Cp ring onto the boron. For **7**$^-$ and **8**$^-$ the same effect is seen in the ^{11}B NMR spectra. The deprotonation of the dialkylboryl compounds **3** and **4** is accompanied by a

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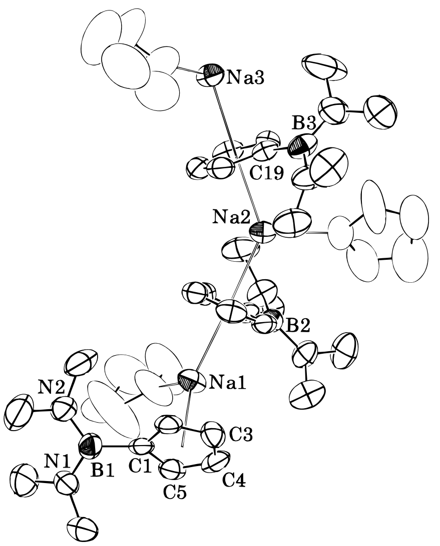
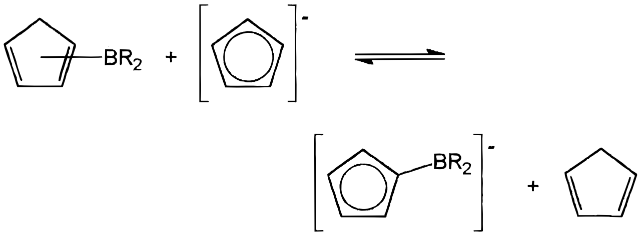


Figure 1. ORTEP diagram (50% probability) of the asymmetric unit (three independent formula units) of **10**.

Scheme 6



$$K = \frac{[\mathrm{CpH}][\mathrm{C_5H_4BR_2}^-]}{[\mathrm{C_5H_5BR_2}][\mathrm{Cp}^-]}$$

Table 1. Atomic Coordinates of Non-Hydrogen Atoms for 10

atom	x	y	z	B_{eq}[a]
Na1	0.0818(3)	0.1743(2)	0.6974(2)	5.18(9)
Na2	0.1068(3)	−0.1581(2)	0.8117(2)	4.99(8)
Na3	0.3093(3)	−0.4831(2)	0.7691(2)	4.86(8)
O1	−0.0576(9)	0.1628(5)	0.5823(3)	8.9(2)
O2	−0.0311(9)	−0.1772(5)	0.9006(4)	9.0(2)
O3	0.5419(6)	−0.4700(5)	0.7616(4)	8.6(2)
N1	0.3850(8)	0.2861(6)	0.5811(4)	6.3(2)
N2	0.2573(8)	0.4334(5)	0.5513(4)	6.2(2)
N3	−0.2788(7)	−0.0883(5)	0.6836(3)	5.0(2)
N4	−0.2772(7)	0.0543(5)	0.7676(3)	5.1(2)
N5	0.4034(8)	−0.2277(6)	0.9883(4)	6.1(2)
N6	0.299(1)	−0.3973(6)	0.9881(4)	7.8(3)
C1	0.2384(9)	0.3497(5)	0.6722(4)	4.0(2)
C2	0.112(1)	0.3811(5)	0.6854(5)	4.7(3)
C3	0.101(1)	0.3637(6)	0.7575(6)	5.4(3)
C4	0.221(1)	0.3233(6)	0.7908(4)	5.1(3)
C5	0.3031(9)	0.3120(5)	0.7397(5)	4.6(2)
C6	0.396(1)	0.1835(7)	0.6091(6)	8.5(4)
C7	0.491(1)	0.3107(8)	0.5396(6)	10.0(4)
C8	0.245(1)	0.4226(7)	0.4723(5)	9.0(4)
C9	0.217(1)	0.5322(7)	0.5716(5)	8.4(4)
C10	−0.0369(8)	−0.0003(5)	0.7444(4)	3.6(2)
C11	0.0545(9)	0.0430(5)	0.8080(4)	4.0(2)
C12	0.192(1)	0.0367(6)	0.7966(5)	5.0(3)
C13	0.1886(9)	−0.0084(6)	0.7284(5)	4.6(3)
C14	0.0503(9)	−0.0300(5)	0.6971(4)	3.9(2)
C15	−0.2220(9)	−0.1794(6)	0.6598(5)	6.8(3)
C16	−0.420(1)	−0.0769(7)	0.6419(5)	7.8(3)
C17	−0.225(1)	0.1561(7)	0.7951(5)	7.6(3)
C18	−0.4091(9)	0.0245(8)	0.7905(5)	7.5(3)
C19	0.2778(8)	−0.3132(5)	0.8649(4)	4.0(2)
C20	0.3447(9)	−0.2642(6)	0.8121(5)	5.0(3)
C21	0.260(1)	−0.2800(6)	0.7433(4)	5.1(3)
C22	0.141(1)	−0.3374(6)	0.7517(5)	5.3(3)
C23	0.1523(9)	−0.3570(5)	0.8251(5)	4.6(3)
C24	0.396(1)	−0.1255(7)	0.9636(5)	8.0(3)
C25	0.499(1)	−0.2325(9)	1.0569(5)	9.0(4)
C26	0.276(2)	−0.5012(8)	0.9575(6)	12.6(5)
C27	0.276(1)	−0.3956(9)	1.0620(6)	11.1(5)
C28	−0.036(2)	0.215(1)	0.5222(7)	17.3(6)
C29	−0.144(2)	0.1925(9)	0.4648(6)	11.4(5)
C30	−0.215(1)	0.103(1)	0.4806(7)	11.7(5)
C31	−0.174(1)	0.099(1)	0.5595(7)	12.4(5)
C32	−0.157(1)	−0.135(1)	0.8994(7)	11.2(5)
C33	−0.187(2)	−0.146(2)	0.972(1)	22(1)
C34	−0.101(2)	−0.222(1)	1.0038(8)	14.2(6)
C35	−0.002(2)	−0.230(1)	0.9650(8)	18.1(8)
C36	0.603(2)	−0.526(1)	0.7146(9)	15.5(7)
C37	0.746(2)	−0.497(2)	0.7248(8)	14.0(7)
C38	0.778(1)	−0.423(1)	0.783(1)	14.5(7)
C39	0.640(1)	−0.3906(9)	0.7937(8)	11.3(5)
B1	0.294(1)	0.3564(8)	0.6013(5)	5.1(3)
B2	−0.201(1)	−0.0109(7)	0.7314(5)	4.3(3)
B3	0.328(1)	−0.3129(8)	0.9478(6)	5.3(3)

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents ($^4/_3$)[$a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}$]; in 10^4 pm^2.

large high-field shift of the ^{11}B resonance [$\delta(^{11}\mathrm{B})$ 72 for **3** and 45 for **7**$^-$; $\delta(^{11}\mathrm{B})$ 68 for **4** and 40 for **8**$^-$]. These high-field shifts again indicate transfer of π electron density onto the boron.

Equilibria. It was already seen above that protolysis reactions of the cyclopentadienylboranes with LiCp and NaCp are useful synthetically. To assess the relative stabilities of the various cyclopentadienides we have studied equilibria of the boranes **1**−**4** with LiCp in THF in NMR tube experiments at ambient temperature (Scheme 6). Spectra were measured after 2, 24, 50, and 70 h after preparation of the samples. Equilibrium was established in less than 2 h for **1** and **2** and within 3 days for **3** and **4**.

The equilibrium constant is $K = 0.5$ for **1** and $K = 4$ for **2** at ambient temperature, whereas in the cases of **3** and **4** the protolysis reaction goes to completion, corresponding to an estimated lower limit of $K > 300$ (or p$K < -2.5$). Thus only the dialkylboryl groups are seen to stabilize cyclopentadienide ions markedly.

Structures. One of our main objectives was the structural characterization of the borylcyclopentadienides. We report here the structures of the THF solvate Na(THF)(**5**) (≡**10**) (Tables 1 and 2, Figure 1), of the corresponding tetrahydropyran solvate Na(THP)(**5**) (≡**11**) (Tables 3 and 4, Figures 2 and 3), of the crown ether solvate Li(12-crown-4)(**6**) (≡**12**) (Tables 5 and 6, Figure 4), and of the tetrahydropyran solvate (Na(THF)$_2$(**8**) (≡**13**) (Tables 7 and 8, Figure 5).

The four structures represent four different building patterns. The dioxaborolanyl derivative **12** forms monoclinic van der Waals crystals of Li(12-crown-4)(**6**) molecules, a situation previously observed for the parent compound Li(12-crown-4)Cp.[19] The distance Li−Cp (208 pm) is slightly longer than in the parent compound (206 pm), and this may be understood as a first structural hint to the electron-withdrawing nature of the dioxaborolanyl substituent.

The dimethylboryl derivative **13** forms low-melting orthorhombic crystals with a chain motif and pseudotetrahedral coordination around sodium as previously observed for Na(TMEDA)Cp[20] and for the 2-furfuryl compound Na(THF)($\mathrm{C_5H_4CH_2C_4H_3O}$).[21] The bending

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[19] Chen, H.; Jutzi, P.; Leffers, W.; Olmstaed, M. M.; Power, P. P. *Organometallics* **1991**, *10*, 1282.

Table 2. Selected Bond Distances (pm) for 10

N1−B1	143(1)	N2−B1	142(1)
C1−B1	154(1)	C1−C2	140(1)
C2−C3	140(1)	C3−C4	137(1)
C4−C5	138(1)	C1−C5	142(1)
N3−B2	143(1)	N4−B2	143(1)
C10−B2	158(1)	C10−C11	143(1)
C11−C12	141(1)	C12−C13	139(1)
C13−C14	138(1)	C10−C14	141(1)
N5−B3	143(1)	N6−B3	141(1)
C19−B3	154(1)	C19−C20	144(1)
C20−C21	140(1)	C21−C22	139(1)
C22−C23	139(1)	C19−C23	139(1)
Na1−C1	280.6(8)	Na1−C10	276.5(8)
Na1−C2	276.0(7)	Na1−C11	278.4(8)
Na1−C3	271.2(8)	Na1−C12	276.0(9)
Na1−C4	272.5(8)	Na1−C13	273.6(8)
Na1−C5	272.7(8)	Na1−C14	270.8(7)
Na2−C10	279.6(7)	Na2−C19	282.4(8)
Na2−C11	275.2(7)	Na2−C20	280.4(9)
Na2−C12	270.1(8)	Na2−C21	274(1)
Na2−C13	273.2(9)	Na2−C22	267.8(9)
Na2−C14	277.1(8)	Na2−C23	271.5(8)
Na3−C1	280.5(7)	Na3−C19	292.5(8)
Na3−C2	278.1(8)	Na3−C20	297.8(8)
Na3−C3	276.3(9)	Na3−C21	280.6(9)
Na3−C4	272.4(9)	Na3−C22	261.6(9)
Na3−C5	275.9(7)	Na3−C23	267.9(9)

Table 3. Atomic Coordinates of Non-Hydrogen Atoms for 11

atom	*x*	*y*	*z*	B_{eq}[a]
Na	0.18063(5)	0.19554(5)	−0.825	3.96(2)
B	0.0510(2)	0.2990(1)	−0.7117(2)	3.46(5)
C1	0.1251(1)	0.2740(1)	−0.7047(1)	3.19(4)
C2	0.1848(1)	0.3069(1)	−0.7342(1)	3.98(5)
C3	0.2425(1)	0.2687(2)	−0.7139(2)	5.04(6)
C4	0.2205(1)	0.2110(2)	−0.6727(2)	5.03(5)
C5	0.1495(1)	0.2144(1)	−0.6668(1)	4.00(5)
N1	0.0298(1)	0.3402(1)	−0.7776(1)	4.19(4)
N2	0.0006(1)	0.2827(1)	−0.6535(1)	4.20(4)
C6	0.0635(2)	0.3408(2)	−0.8537(2)	5.53(7)
C7	−0.0225(2)	0.3915(2)	−0.7733(2)	6.38(8)
C8	0.0158(2)	0.2616(2)	−0.5730(2)	5.72(7)
C9	−0.0715(1)	0.2753(2)	−0.6701(2)	5.44(6)
O	0.08116(9)	0.1330(1)	−0.8367(1)	4.68(4)
C10	0.0311(2)	0.1403(2)	−0.8971(2)	5.50(7)
C11	−0.0346(2)	0.1654(2)	−0.8641(2)	5.31(6)
C12	−0.0604(2)	0.1186(2)	−0.7991(2)	5.18(6)
C13	−0.0044(2)	0.1069(2)	−0.7394(2)	5.05(6)
C14	0.0604(2)	0.0857(1)	−0.7782(2)	4.89(6)

[a] See footnote *a* in Table 1.

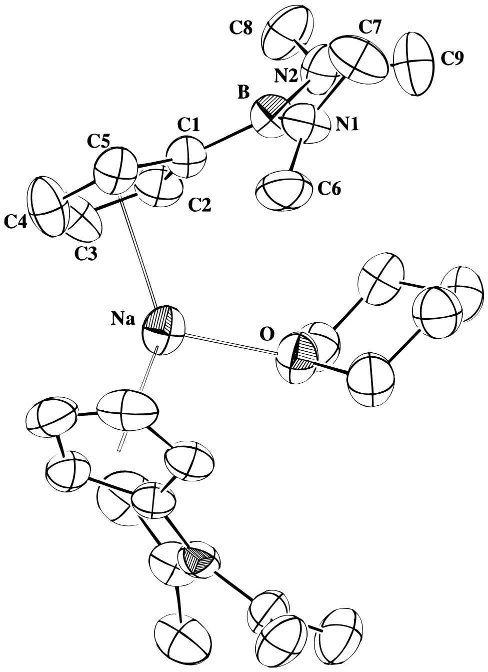

Figure 2. ORTEP diagram (50% probability) of a fragment (asymmetric unit and one anion in addition) of the structure of **11**.

Table 4. Selected Bond Distances and Bond Angles for 11

(a) Bond Distances (pm)

B−N1	144.0(2)	B−N2	143.4(2)
B−C1	154.5(2)	C1−C2	143.0(2)
C2−C3	140.5(2)	C3−C4	140.0(2)
C4−C5	140.4(2)	C1−C5	142.0(3)
Na−O	232.0(2)		
Na−C1	278.4(1)	Na′−C1	273.8(1)
Na−C2	268.2(1)	Na′−C2	270.4(1)
Na−C3	266.8(1)	Na′−C3	270.8(1)
Na−C4	271.8(2)	Na′−C4	273.8(2)
Na−C5	277.9(2)	Na′−C5	273.4(2)

(b) Bond Angles (deg)

Na−B−N2	117.2(1)	C2−C1−C5	104.7(1)
C1−B−N1	120.8(1)	C1−B−N2	121.9(1)
B−C1−C2	127.2(1)	B−C1−C5	128.1(1)
C1−C2−C3	109.7(1)	C1−C5−C4	110.0(2)
C2−C3−C4	107.8(1)	C3−C4−C5	107.8(2)

angle X1−Na−X2 (where X1 and X2 are the centroids of the C_5 rings) amounts to 131°. The distances Na−Cp (258 and 263 pm) are again slightly longer than in Na(THF)($C_5H_4CH_2C_4H_3O$) (258 and 257 pm).[21]

The triclinic THF solvate **10** shows an approximately trigonal helix of alternating cations Na(THF)$^+$ and ring anions and a pseudotrigonal coordination around sodium. This structural motif has not previously been found for cyclopentadienides. As the space group is $P\bar{1}$, this arrangement implies the presence of three independent formula units in the asymmetric unit. The bending angle amounts to 136.0° (av). Unfortunately the THF ligands show large anisotropic thermal parameters for C-3/4 perpendicular to the ring plane. These are due to the frequently encountered conformational disorder of saturated five-membered rings. This disorder and the large size of the asymmetric unit limit the accuracy of the structural parameters obtained.

The structure of the corresponding tetragonal tetrahydropyran solvate **11** consists of tetragonal helices with tetragonal crystallographic symmetry (Figure 3). The sodium possesses the same pseudotrigonal coordination as in **10** and a bending angle of 140.6°. The values of the Na−Cp distances are rather small (245 and 248 pm) as compared to the values for the dimethylboryl derivative **13**, the difference being caused by the lower coordination number of the Na$^+$ ion.[19,22]

The main question concerns the extent of π interaction between the aromatic cyclopentadienide and the boryl group attached to it. This interaction may be described by two resonance formulae: a borylcyclopentadienide formula “without” π interaction and a boratafulvene formula with a B−C “double bond”. Obviously the bond lengths of the C_5B skeleton will provide

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

(21) Zhang, S.; Liu, J.; Wei, G.; Lin, G.; Chen, W. *Polyhedron* **1993**, *12*, 2771.

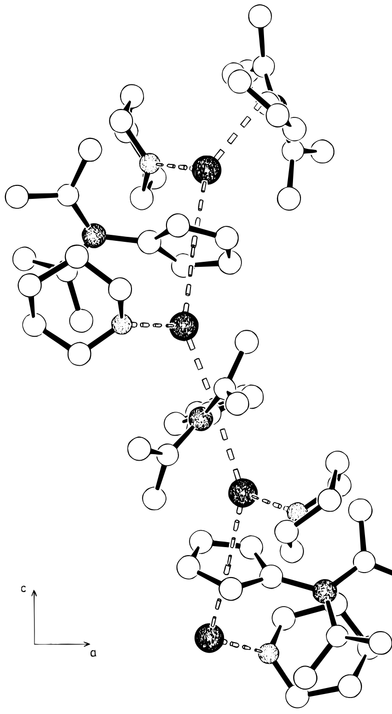


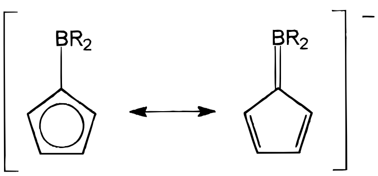
Figure 3. Ball-and-stick representation of a helical fragment (four asymmetric units) of the structure of **11**.

Table 5. Atomic Coordinates of Non-Hydrogen Atoms for 12

atom	x	y	z	B_{eq}[a]
B	0.3977(6)	−0.0825(7)	0.1127(2)	3.9(1)
Li	0.1467(7)	−0.330(1)	0.1220(3)	3.9(2)
C1	0.2567(4)	−0.0702(5)	0.1080(2)	3.3(1)
C2	0.1814(5)	−0.0414(5)	0.1468(2)	3.4(1)
C3	0.0536(5)	−0.0483(6)	0.1263(2)	4.1(1)
C4	0.0453(5)	−0.0951(9)	0.0900(2)	5.9(2)
C7	0.6122(5)	−0.0977(8)	0.1490(2)	5.3(2)
C8	0.6625(8)	−0.231(2)	0.0651(3)	14.2(4)
C9	0.6339(7)	0.083(1)	0.0696(3)	10.2(3)
C10	0.6511(8)	−0.276(1)	0.1713(3)	11.6(3)
C11	0.6960(8)	0.038(1)	0.1763(3)	12.1(3)
O1	0.4633(3)	−0.1085(5)	0.0724(1)	5.4(1)
O2	0.4847(3)	−0.0645(5)	0.1586(1)	5.7(1)
O10	0.2047(4)	−0.4458(4)	0.2042(1)	5.1(1)
O11	−0.0321(3)	−0.4584(4)	0.1446(2)	5.7(1)
O12	0.0853(4)	−0.5119(4)	0.0623(1)	5.4(1)
O13	0.3223(4)	−0.4948(5)	0.1203(2)	5.6(1)
C20	0.1158(7)	−0.5699(8)	0.2161(2)	6.7(2)
C21	−0.0072(7)	−0.4952(8)	0.1999(3)	6.4(2)
C22	−0.0726(5)	−0.6029(7)	0.1142(3)	6.1(2)
C23	−0.0489(6)	−0.5608(7)	0.0628(2)	5.3(2)
C24	0.1625(7)	−0.6553(7)	0.0605(2)	6.4(2)
C25	0.2974(6)	−0.5795(7)	0.0691(2)	5.6(2)
C26	0.3554(6)	−0.6051(8)	0.1623(3)	6.4(2)
C27	0.3346(7)	−0.5101(7)	0.2080(2)	6.1(2)

[a] See footnote *a* in Table 1.

the most direct evidence for the π interaction in question.



The B−C1 bond lengths amount to 154.5 for **11**, 148.8 for **12**, and 150.8 pm for **13**.[23] The typical B(sp^2)−C(sp^2) single-bond length is 158 pm (cf. BPh_3[24a] and $BMes_3$[24b]), while the typical B(sp^2)−C(sp^2) double-bond distance in a borataethene ion [cf. Li[$H_2C{=}B(Mes)_2$]][23a] is close to 144 pm.[25] We conclude from these data that the boratafulvene formula is highly weighted in **12** and **13** while the π interaction in **11** is rather less important.

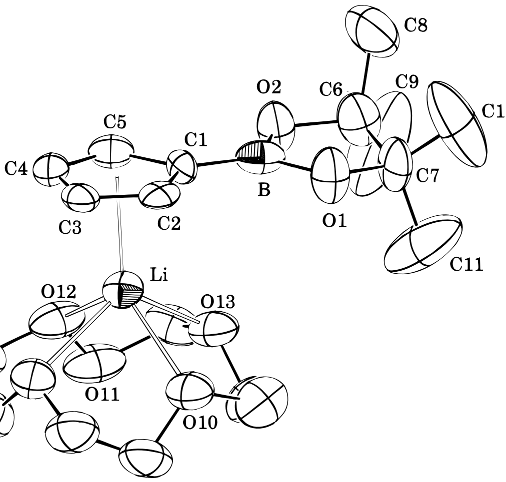


Figure 4. ORTEP diagram (50% probability) of a molecule of **12**.

Table 6. Selected Bond Distances and Bond Angles for 12

(a) Bond Distances (pm)			
B−C1	148.8(8)	C6−C7	154.1(8)
B−O1	138.7(7)	C6−C8	146(1)
B−O2	140.1(6)	C6−C9	154(1)
C1−C2	142.3(8)	C6−O1	143.6(6)
C1−C5	141.8(6)	C7−C10	152(1)
C2−C3	137.7(7)	C7−C11	148(1)
C3−C4	141.1(9)	C7−O2	144.7(7)
C4−C5	136.9(8)		
Li−C1	237.8(9)	Li−O10	233.3(9)
Li−C2	232.8(9)	Li−O11	231.5(9)
Li−C3	239.6(9)	Li−O12	212.7(8)
Li−C4	245.4(9)	Li−O13	226.8(9)
Li−C5	243.5(9)		
(b) Bond Angles (deg)			
O1−B−O2	109.5(5)	C2−C1−C5	104.3(4)
C1−B−O1	125.4(4)	C1−B−O2	125.0(5)
B−C1−C2	129.4(4)	B−C1−C5	126.3(5)
C1−C2−C3	110.6(5)	C1−C5−C4	109.9(5)
C2−C3−C4	106.6(5)	C3−C4−C5	108.6(5)
B−O1−C6	110.4(4)	B−O2−C7	109.4(4)
C7−C6−O1	104.1(5)	C6−C7−O2	104.2(4)

The same bonding picture is borne out by considering the intraring C−C bond lengths. The distances C1−C2/C1−C5 (av) (142.5 for **11**, 142.1 for **12**, and 143.6 pm for **13**) are lengthened, the distances C3−C4 (140.0 for **11**, 141.1 for **12**, and 143.5 pm for **13**) are slightly lengthened, while the distances C2−C3/C4−C5 (av) (140.3 for **11**, 137.3 for 12, and 137.9 pm for **13**) are shortened. The differences observed are pronounced for **12** and **13**; for **11** only the distance C1−C2/C1−C5 (av) shows a significant (on a 3σ level) lengthening.

The dihedral angles between the cyclopentadienide ring and the boryl function amount to 5° for **12**, 8° for **13**, and 29° for **11**. The near coplanarity of the two groups may be understood as a consequence of the π interactions evidenced above. It seems not purely accidental that the largest deviation from coplanarity

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(22) (a) Jutzi, P. *Pure Appl. Chem.* **1989**, *61*, 1731. (b) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1.

is found for **11**, which is expected to have the lowest barrier to internal rotation between the ring and the boryl group.

Table 7. Atomic Coordinates of Non-Hydrogen Atoms for 13

atom	*x*	*y*	*z*	B_{eq}[a]
Na	0.16159(2)	0.35499(8)	0.98962(3)	2.52(1)
O1	0.17262(5)	0.47814(5)	0.88411(5)	2.82(3)
O2	0.15056(5)	0.56443(6)	1.04727(7)	2.71(2)
C1	0.40877(6)	0.2221(1)	0.94177(8)	2.51(4)
C2	0.46891(9)	0.3345(2)	0.97692(8)	2.64(3)
C3	0.44458(8)	0.3285(2)	1.0491(2)	2.99(2)
C4	0.36553(8)	0.20960(9)	1.0627(1)	2.94(4)
C5	0.34632(7)	0.1457(3)	0.99855(7)	2.87(4)
C6	0.3228(1)	0.0704(1)	0.83121(9)	3.81(4)
C7	0.5024(1)	0.27466(2)	0.8101(1)	3.81(5)
C11	0.1268(1)	0.4197(1)	0.81951(7)	2.88(4)
C12	0.0368(2)	0.5138(2)	0.7770(1)	3.31(3)
C13	0.1186(1)	0.6413(1)	0.7626(1)	3.58(5)
C14	0.1808(1)	0.6969(2)	0.8302(1)	3.28(3)
C15	0.26095(8)	0.5914(1)	0.8705(1)	2.99(3)
C21	0.0462(1)	0.6597(2)	1.02644(8)	2.82(3)
C22	0.10713(9)	0.8006(2)	1.02769(8)	3.00(4)
C23	0.16695(9)	0.8324(1)	1.10002(8)	3.02(3)
C24	0.2680(1)	0.72331(8)	1.1239(1)	2.87(3)
C25	0.19867(6)	0.5878(2)	1.1178(1)	2.62(4)
B	0.4108(1)	0.1891(3)	0.8636(1)	3.00(5)

[a] See footnote *a* in Table 1.

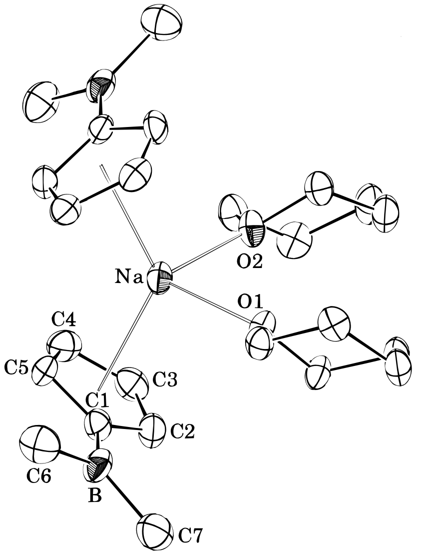
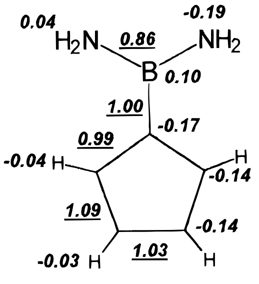


Figure 5. ORTEP diagram (50% probability) of a fragment (asymmetric unit and one anion in addition) of the structure of **13**.

Table 8. Selected Bond Distances and Bond Angles for 13

(a) Bond Distances (pm)			
C6−B	157.9(4)	C7−B	158.3(4)
C1−B	150.8(4)		
C1−C2	142.9(3)	C1−C5	144.3(3)
C2−C3	137.9(4)	C4−C5	137.9(4)
C3−C4	143.5(4)		
Na−O1	234.3(2)	Na−O2	237.3(2)
Na−C1	284.3(2)	Na−C2	292.8(3)
Na−C3	291.7(2)	Na−C4	278.6(2)
Na−C5	274.3(2)		
(b) Bond Angles (deg)			
C1−C2−C3	110.8(2)	C1−C5−C4	110.2(2)
C2−C3−C4	107.4(2)	C3−C4−C5	107.6(2)
C2−C1−C5	104.0(2)	C6−B−C7	117.0(3)
C2−C1−B	128.4(2)	C5−C1−B	127.6(2)
C1−B−C6	122.4(3)	C1−B−C7	120.6(2)
O1−Na−O2	85.39(6)		

EHMO Calculations. The perturbing influence of the various boryl substituents on the cyclopentadienide system will have its origin both in inductive effects and in resonance interactions. To gain more insight we performed a set of comparative EHMO calculations[26] on the three model systems $[C_5H_4B(NH_2)_2]^-$ (**14**), $[C_5H_4B(OH)_2]^-$ (**15**), and $[C_5H_4BMe_2]^-$ (**16**) using the structural data from above. The calculation results are summarized in three diagrams below, with calculated net charges of the atoms and reduced-overlap integrals for the skeletal bonds.



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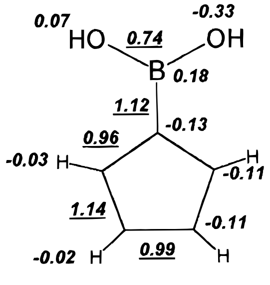

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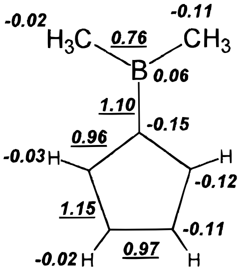

16

The HOMO/LUMO separation (2.92 for **14**, 2.69 for **15**, and 2.57 eV for **16**) indicates increasing perturbations of the aromatic ring in the order **14** < **15** < **16** or NH_2 < OH < Me. The same order is borne out from a comparison of the reduced-overlap integrals which correspond to the observed differences of the intra-ring C−C bond lengths.

The calculated net charges of the ring (−0.88 for **14**, −0.66 for **15**, and −0.71 for **16**) indicate transfer of charge to the boryl group in all three cases; however, this effect is weak for **14**. The calculations also show that the high electron-withdrawing abilities of the $B(OH)_2$ and BMe_2 groups are different in origin: Resonance effects dominate for the dimethylboryl substituent in **16**, while the inductive effect is more important for the dihydroxyboryl group in **15**.

Concluding Remarks. Work currently in progress shows that the methods developed here can be used to make borylcyclopentadienides with several boryl substituents or with further functionalities. The borylcy-

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(23) Note here that the structure of **13** has been determined at lower temperature (−110 °C) than that of **12** (−30 °C). Therefore *all* distances of the C_5B part are apparently shorter for **12** as compared to **13**.

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clopentadienides can also be used to synthesize sandwich-type complexes as, e.g., $M[C_5H_5B(NMe_2)_2]_2$ with M = Fe, Co, Ni, and $Co(C_5H_5BPr^i_2)_2$ and its cation. Of these the Co and Ni complexes are not accessible by previously known synthetic methods. Thus the borylcyclopentadienides open the route to promising new organic and organometallic chemistry.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Pentane was distilled from Na/K alloy, hexane from potassium, and THF from sodium benzophenone ketyl. Kieselgur was heated in a high vacuum at 300 °C prior to use. NMR spectra were used to judge the purity of the new compounds; elemental analyses were not attempted because of the high reactivity of the compounds prepared.

NMR spectra were recorded on a Bruker WP 80 PFT spectrometer (^{1}H, 80 MHz), a Bruker WH 270 PFT (^{13}C, 67.9 MHz), a JEOL NM-PS-100 (^{11}B, 32.08 MHz), a Varian VXR 300 (^{1}H, 300 MHz; ^{13}C, 75.4 MHz), and a Varian Unity 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125.7 MHz). Mass spectra were recorded on a Varian MAT CH-5 and on a Finnigan MAT-95 spectrometer.

Cyclopentadienylbis(dimethylamino)borane (1). $BCl(NMe_2)_2$[27] (134.4 g, 1.00 mol) was added dropwise (45 min) to a stirred solution of NaCp (1.00 mol) in THF (1 L) at −10 °C. The equivalence point was indicated by a color change from pink to yellowish. After the solution had warmed up to ambient temperature, the solvent was removed in a vacuum. Pentane was then added (300 mL). The NaCl formed was filtered off and carefully washed with several portions of pentane. Removal of the pentane in a vacuum and further distillative workup using a Vigreux column (50 cm) gave **1** (95 g, 58%) as colorless liquid; bp 64−68 °C/5 mbar, **1A**/**1B** = 1/1 (NMR). MS (70 eV) *m*/*z* (I_{rel}) 164 (88, M^+), 120 (83, $M^+ - NMe_2$), 99 (100, $M^+ - C_5H_5$); ^{11}B NMR (32 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 30.

1A: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (ddt, J = 4.97, −1.53, −1.22 Hz, 3-H), 6.55 (ddt, J = 1.68, 1.22, −1.22 Hz, 2-H), 6.54 (ddt, J = 4.97, 1.37, 1.22, 4-H), 3.00 (ddd, J = 1.37, −1.53, −1.22 Hz, CH_2), 2.64 (s, 4 Me); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 149 (br, only observed at low temperature, C-1), 137.98 (C-2), 137.52 (C-3), 134.95 (C-4), 45.36 (C-5), 40.85 (NMe_2).

1B: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 (ddt, J = 5.19, 1.53, −1.53 Hz, 3-H), 6.45 (ddt, J = 1.83, 1.53, 1.53 Hz, 1-H), 6.40 (ddt, J = 5.19, 1.83, 1.53, 4-H), 3.01 (ddd, J = 1.53, 1.53, −1.53 Hz, CH_2), 2.67 (s, 4 Me); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 146 (br, only observed at low temperature, C-2), 139.73 (C-1), 132.91 (C-3), 131.31 (C-4), 42.92 (C-5), 40.88 (NMe_2).

2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9). BCl_3 (82 mL, 1.00 mol) was added dropwise (30 min) to a stirred solution of dry pinacol in pentane (1.3 L) at −30 °C. The reaction mixture was kept stirring at 20 °C for 1 h. A solid byproduct, $B_2[(OCMe_2)_2]_3$, was removed by filtration. Distillative workup gave **9** (88.3 g, 54%) as a colorless liquid which can be stored as a solid at −30 °C; bp 31−33 °C/5 mbar. ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.2 (s, 4 Me); ^{13}C NMR (68 MHz, $CDCl_3$) δ 86.1 (sept, J = 4 Hz, C-4/5), 24.5 (qq, J = 127, 4 Hz, Me); ^{11}B NMR (32 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 21.

2-Cyclopentadienyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2). A solution of NaCp (5.0 g, 57 mmol) in THF (60 mL) was stirred at −75 °C. Compound **9** was added dropwise until the color of the reaction mixture changed from light-pink to yellowish. The solvent was then pumped off in a vacuum. Cooled pentane (30 mL) was added. The NaCl formed was removed by filtration and washed with cooled pentane, using a cooled flask (−60 °C) to collect the filtrates. After removal of the solvent, the residue was warmed up under vacuum (10^{-6} bar) and **2** was collected by condensation (4.3 g, 40%); colorless liquid at ambient temperature, solid at −30 °C; **2A**/**2B** = 9/1 (NMR). MS (70 eV) *m*/*z* (I_{rel}) 192 (100, M^+), 93 (98, $CpBOH^+$); ^{11}B NMR (32 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 29.

2A: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (ddt, J = 1.83, −1.83, 1.22 Hz, 2-H), 6.71 (ddt, J = 4.88, 1.22, 1.22 Hz, 4-H), 6.61 (ddt, J = 4.88, 1.83, −1.53 Hz, 3-H), 3.14 (ddd, J = −1.83, −1.53, 1.22 Hz, CH_2), 1.28 (s, 4 Me); ^{13}C NMR (68 MHz, $CDCl_3$) δ 146.7 (d, J = 166 Hz, C-2), 140.1 (d, J = 169 Hz, C-4), 133.4 (d, J = 163 Hz, C-3), 83.4 (s, CO), 44.9 (td, J = 126, 9 Hz, C-5), 25.0 (qd, J = 126, 3 Hz, Me), C-1 not observed.

2B: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (ddt, J = 1.9, 1.22, 1.20 Hz, 1-H), 6.73 (ddt, J = 5.10, 1.22, 1.22 Hz, 3-H), 6.42 (ddt, J = 5.10, 1.9, −1.53 Hz, 4-H), 3.06 (ddd, J = −1.53, 1.22, 1.22 Hz, CH_2), 1.29 (s, 4 Me); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.4 (d, C-1), 135.3 (d, C-4), 133.4 (d, C-3), 83.4 (s, CO), 44.1 (t, 125 Hz, C-5), 24.8 (q, 125 Hz, Me), C-2 not observed.

Cyclopentadienyldiisopropylborane (3). $BClPr^i_2$[28] (22.9 g, 173 mmol) was added dropwise (20 min) to a stirred suspension of NaCp (15.2 g, 173 mmol) in hexane (200 mL) at −50 °C. After the solution had warmed up to ambient temperature, NaCl was removed by filtration. Further workup as above gave **3** (21.0 g, 75%) as colorless liquid, fuming in air; bp 47−50 °C/2 mbar, **3A**/**3B** = 10/1 (NMR). MS (70 eV) *m*/*z* (I_{rel}) 162 (23, M^+), 119 (89, $M^+ - Pr^i$), 91 (76, $CpBCH_3^+$), 41 (100, $C_3H_5^+$); ^{11}B NMR (32 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 72.

3A: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (ddt, J = 1.83, −1.53, 1.22 Hz, 2-H), 6.87 (ddt, J = 4.88, 1.53, 1.22 Hz, 4-H), 6.73 (ddt, J = 4.88, 1.83, −1.53 Hz, 3-H), 3.29 (ddd, J = 1.53, −1.53, −1.53 Hz, CH_2), 1.90 (sept, J = 7.32 Hz, 2 BCH), 1.04 (d, J = 7.32 Hz, 4 Me); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (br, C-1), 148.93 (C-2), 142.19 (C-4), 133.46 (C-3), 45.48 (C-5), 21.5 (br, BCH), 18.95 (Me).

3B: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (ddt, J = 1.83, 1.53, 1.22 Hz, 1-H), 6.87 (hidden, 4-H), 6.47 (ddt, J = 5.19, 2.14, −1.53 Hz, 3-H), 3.10 (ddd, J = 1.53, 1.53, −1.53 Hz, CH_2), 1.90 (hidden, 2 BCH), 1.04 (d, J = 7.02 Hz, 4 Me); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.6 (C-1), 136.2 (C-4), 132.2 (C-3), 43.3 (C-5), 18.23 (Me), C-2 and BCH not observed.

Cyclopentadienyldimethylborane (4). $BBrMe_2$[29] (10.3 g, 85 mmol) was added dropwise (20 min) to a stirred suspension of LiCp (6.12 g, 85 mmol) in decalin (50 mL) at −25 °C. The reaction mixture was warmed up to 20 °C; the volatiles were slowly (2−3 h) condensed through a column (0 °C) into a cold flask (−78 °C). The product contained decalin (36%, NMR). A second condensation afforded **4** (5.1 g, 52%, with 10% decalin) as a colorless liquid, spontaneously igniting in air; only isomer **4A** was identified (NMR). MS (70 eV) *m*/*z* (I_{rel}) 106 (18, M^+), 92 (33, $M^+ - CH_2$), 47 (100, ?); ^{11}B NMR (32 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 70 in $CDCl_3$, 68 in THF; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (ddt, J = 1.68, −1.34, 1.01 Hz, 2-H), 6.81 (ddt, J = 5.04, 1.34, 1.01 Hz, 4-H), 6.65 (ddt, J = 5.04, 1.68, −1.68 Hz, 3-H), 3.19 (ddd, J = −1.68, 1.34, −1.34 Hz, CH_2), 0.73 (s br, 2 Me); ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 153 (br, C-1), 148.21 (C-2), 142.70 (C-4), 133.81 (C-3), 44.81 (C-5), 11 (br, Me).

Lithium [Bis(dimethylamino)boryl]cyclopentadienide [Li(5)]. Compound **1** (5.0 g, 30.5 mmol) in THF (80 mL) was mixed with $LiNMe_2$[30] (1.56 g, 30.6 mmol) (alternatively with LDA or LiTMP)[30] in THF (15 mL) at −70 °C within 10 min; the order of addition is not relevant. After the solution had warmed up to ambient temperature, the volatiles were carefully removed in a vacuum. The residue was transferred to a frit with the help of cold pentane and washed with the same

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Table 9. Crystallographic Data, Data Collection Parameters, and Refinement Parameters for 10−13

	10	**11**	**12**	**13**
formula	$NaC_{13}H_{24}BN_2O$	$NaC_{14}H_{26}BN_2O$	$LiC_{19}H_{32}BO_6$	$NaC_{17}H_{30}BO_2$
fw	258.15	272.18	374.22	300.23
cryst syst	triclinic	tetragonal	monoclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$I4_1cd$ (No. 110)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)
a, pm	982(1)	1968(2)	1064.9(2)	947.2(3)
b, pm	1328(1)		770.5(2)	1006.5(6)
c, pm	1883(1)	1691.6(8)	2641.7(3)	1882.2(9)
α, deg	91.30(7)			
β, deg	101.02(7)		99.91(2)	
γ, deg	93.82(9)			
V, nm^3	2.404(8)	6.55(2)	2.135(1)	1.794(2)
d_{calcd}, g/cm^3	1.070	1.104	1.173	1.111
Z	6	16	4	4
F(000)	840.0	2368.0	808.0	656.0
μ, cm^{-1}	0.85	7.4	6.46	7.2
cryst dimens, mm	0.6 × 0.2 × 0.3	0.5 × 0.35 × 0.4	0.4 × 0.2 × 0.2	0.3 × 0.25 × 0.4
radiation (λ, pm)	Mo Kα (70.93)	Cu Kα (154.18)	Cu Kα (154.18)	Cu Kα (154.18)
monochromator	graphite	graphite	graphite	graphite
T, K	253	233	243	163
scan mode	ω	ω	ω	ω
scan range, deg	$3 \le \theta \le 22$	$7 \le \theta \le 74$	$5 \le \theta \le 74$	$5 \le \theta \le 75$
absorption corr		empirical (ψ-scans)		
total no. of data	5585	4157	6413	6401
no. of unique obsd data	5163 (all data)	3077 ($I > 0\sigma(I)$)	4255 ($I > 0\sigma(I)$)	2593 ($I > 1\sigma(I)$)
sec extinction	1.1×10^{-4}	4.1×10^{-6}	7.2×10^{-4}	1.1×10^{-4}
no. of variables	500	276	261	303
R, R_w	0.097, 0.309[a]	0.051, 0.063[b]	0.091, 0.260[a]	0.069, 0.028[b]
max resid density, e 10^{-6} pm^{-3}	0.28	0.35	0.40	0.55

[a] Refinement on I; $R = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $(F > 4\sigma(F))$; $R_w^2 = \{\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (P1 * P)^2]$ with $P = (\max(F_o^2, 0) + 2F_c^2)/3$; ***10***: $P1 = 0.1865$ and ***12***: $P1 = 0.1276$. [b] Refinement on F; $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\sum w(F_o)^2$; $w = 1/\sigma^2(F_o)$.

solvent (total ≤25 mL). Drying gave Li(**5**) (4.7 g, 90%) as a white powder, highly sensitive to air and humidity. ^{11}B NMR (32 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 30; ^{1}H NMR (500 MHz, d_8-THF) δ 6.07 (AA′BB′ system, J = 5.0, 3.5, 1.5, 1.2 Hz, 2/5-H) and 5.80 (3/4-H), 2.78 (s, 4 Me), assignment based on a (H,H)-NOE experiment; ^{13}C NMR (75 MHz, [D_8-THF) δ 115.7 (d′q′, J = 157, 6 Hz, C-2/5), 105.5 (d′q′, J = 158, 7 Hz, C-3/4), 42.4 (qq, J = 132, 5, Me).

Sodium [Bis(dimethylamino)boryl]cyclopentadienide [Na(5)]. Compound **1** (49.2 g, 0.300 mol) was added slowly to a suspension of sodium powder (14 g, 0.6 mol) in pentane (400 mL). The reaction mixture was stirred at 0 °C for 4 h and then for 24 h at 20 °C. The solids were transferred onto a frit (G4) covered with a layer of dried (300 °C/10^{-6} bar) Kieselgur and washed twice with pentane. The product was then washed through the frit with THF. Removal of the volatiles, in the last stage in a vacuum (10^{-6} bar), gave Na(**5**) (50.0 g, 90%) as a white powder.

Crystallization of Na(THF)(5) and Na(THP)(5). Na(**5**) (0.3 g) was dissolved in THF (3 mL). Dropwise addition of pentane (ca. 0.7 mL) and cooling to 0 °C gave the THF solvate **10** as large colorless crystals. The THP solvate **11** was obtained in the same way.

Lithium [4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl]cyclopentadienide [Li(6)]. Compound **2** (1.80 g, 9.4 mmol) in THF (25 mL) was mixed with LiTMP[30] (9.4 mmol) prepared in THF/hexane (15 mL) at −70 °C within 10 min. Workup as described for Li(**5**) gave a quantitative yield of Li(**6**), contaminated by the amine HTMP. The subsequent washing step to remove HTMP caused considerable losses and gave pure Li(**6**) (1.45 g, 78%) as a white powder, extremely sensitive to air and humidity. ^{1}H NMR (500 MHz, d_8-THF) δ 6.20 (AA′BB′ system, J = 4.8, 3.6, 1.6, 1.4 Hz, 2/5-H) and 5.79 (3/4-H), 1.19 (s, 4 Me); ^{13}C NMR (126 MHz, APT, d_8-THF) δ 118.3 (C-2/5), 110.3 (C-3/4), 27.4 (CO), 22.7 (Me).

Crystallization of Li(12-crown-4) (6). Li(**6**) (0.2 g) and 12-crown-4 were dissolved in THF (5 mL). Cooling to −30 °C afforded the crown ether solvate **12** as almost colorless small needles.

Lithium (Diisopropylboryl)cyclopentadienide [Li(7)] by Metalation with LiTMP. Compound **3** (4.05 g, 25 mmol) was added dropwise to LiTMP[30] (25 mmol), prepared from HTMP (3.53 g, 25 mmol) in THF (25 mL) and LiBu in hexane, at −70 °C. Workup as described for Li(**5**) gave Li(**7**) (3.27 g, 78%) as a (light-yellow) powder, extremely sensitive to air and humidity. ^{11}B NMR (32 MHz, $CDCl_2$, $BF_3{\cdot}OEt_2$ external) δ 40, half-width 320 Hz; ^{1}H NMR (500 MHz, d_8-THF) δ 6.47 (AA′BB′ system, J = 5.1, 3.5, 1.5, 1.2 Hz, 2/5-H) and 5.82 (3/4-H), 1.88 (sept, J = 7.3 Hz, 2 BCH), 1.08 (d, J = 7.3 Hz, 4 Me); ^{13}C NMR (75 MHz, d_8-THF) δ 122 (br, C-1), 117.3 (d′q′, J = 159, 7 Hz, C-2/5), 110.4 (d′q′, J = 158, 7 Hz, C-3/4), 21.6 (qquin, J = 124, 6 Hz, Me), 21.2 (d br, J = 117 Hz, BCH).

Li(7) and Na(7) by Metalation with LiCp or NaCp. Compound **3** (3.24 g, 20 mmol) was added to LiCp (1.44 g, 20 mmol) in THF (50 mL). The usual workup afforded Li(**7**) (3.08 g, 92%) as a powder with a yellowish tinge, contaminated by 4% LiCp. Na(**7**) is obtained by the same procedure (yield 90%).

Li(8) by Metalation with LiCp. As described for Li(**7**), **4** reacted with LiCp to give Li(**8**) (yield 95%) as a white pyrophoric powder. ^{11}B NMR (32 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 45; ^{1}H NMR (500 MHz, d_8-THF) δ 6.46 (AA′BB′ system, J = 5.0, 3.5, 1.5, 1.3 Hz, 2/5-H) and 5.93 (3/4-H), 0.69 (s, 2 Me); ^{13}C NMR (68 MHz, d_8-THF) δ 116.0 (d′q′, J = 158, 7 Hz, C-2/5), 110.4 (d′q′, J = 158, 7 Hz, C-3/4), 14.3 (br, Me), C-1 not observed.

Na(8) by Metalation with NaCp. As described for Li(**8**), Na(**8**) was obtained from **4** and NaCp (yield 92%) as a white powder, extremely sensitive to air and humidity.

Crystallization of Na(THP)$_2$(8). Solutions of Na(**8**) in pentane/THP deposited large needles of the bis(solvate) **13** upon cooling to −30 °C. The crystals are extremely sensitive to air and humidity, and melt above 0 °C. Therefore the X-ray diffraction data for **13** were collected at −110 °C.

X-ray Structure Determinations. Suitable crystals of **10**−**14** were grown as described above. Crystallographic data, data collection, and refinement parameters are collected in

Table 9. The structures were solved and refined with the help of the SDP[31] and the SHELXS program systems.[32]

10: In the final full-matrix refinement, non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were treated as riding (C−H = 98 pm, $B_H = 1.3B_C$).[33]

11: Non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were refined with their positional parameters and isotropic thermal parameters.[33]

12: Non-hydrogen atoms were refined with anisotropic thermal parameters, the Cp ring hydrogen atoms were refined with their positional parameters and isotropic thermal parameters, and all other hydrogen atoms were fixed ($B_H = 1.3B_C$).[33]

13: Non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were refined with their positional parameters. Most hydrogen atoms were refined with isotropic thermal parameters; for the ring atoms H3 and H4 and five hydrogen atoms of the THP ligands, the isotropic thermal parameter B_{iso} was set to 0.2×10^4 pm^2.[33]

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Supporting Information Available: ^{1}H, ^{13}C, and ^{11}B NMR and mass spectra for **1**−**4**, Li(**5**), Li(**6**), Li(12-crown-4) **7**, and Na(THP)$_{0.2}$ **8** and tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **10**−**13** (61 pages). Ordering information is given on any masthead page.

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(33) Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-404255 for **13**, CSD-404256 for **12**, CSD-404257 for **11**, and CSD-404258 for **10**, the names of the authors, and this journal citation.