Complexes of the (Tetramethylcyclobutadiene)cobalt Fragment with Boratabenzene Ligands and an Unprecedented Formation of a Borabenzene Complex − Structures of $(C_4Me_4)Co(3,5\text{-}Me_2C_5H_3BSnMe_3)$ with an Sn−B Bond and of the Dinuclear Complex $[(C_4Me_4)Co(3,5\text{-}Me_2C_5H_3B)]_2O$[‡]

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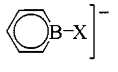
Keywords: Boron / Cobalt / Tin / Borabenzene / Boratabenzene / Cyclobutadiene

The yellow-orange boratabenzene complex $Cb^*Co(3,5\text{-}Me_2C_5H_3BNMe_2)$ (**1**) ($Cb^* = C_4Me_4$) was readily obtained from $[Cb^*Co(NCMe)_3]PF_6$ and $Li(TMEDA)(3,5\text{-}Me_2C_5H_3BNMe_2)$. Methanolysis of **1** afforded $Cb^*Co(3,5\text{-}Me_2C_5H_3BOMe)$ (**2**). Complex **2** reacted with MeLi and with BCl_3 to give the *B*-methyl analogue **3** and the *B*-chloro compound **4**, respectively. The chloro compound **4** reacted with iBu_2AlH, TlF, and $LiSnMe_3$ to afford the *B*-hydrido derivative **5**, the *B*-fluoro complex **6**, and the *B*-(trimethylstannyl) compound **7**, respectively. A single-crystal structure determination of **7** gave an Sn–B bond length of 2.236(5) Å. The B–O–B-linked dinuclear complex $[(C_4Me_4)Co(3,5\text{-}Me_2C_5H_3B)]_2O$ (**8**) was also characterized structurally. The amino compound **1** underwent an unprecedented quaternization with iodomethane to produce $[Cb^*Co(3,5\text{-}Me_2C_5H_3BNMe_3)]I$ (**10**) which possesses a borabenzene–trimethylamine ligand. Compound **10** is the first borabenzene complex of a metal outside the chromium group. When treated with Bu_4NCN in CH_2Cl_2 nucleophilic substitution of the NMe_3 group took place to give the *B*–CN derivative **11** which is the first *B*-cyanoboratabenzene complex.

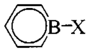
Introduction

In the chemistry of borabenzene derivatives[2] it has become customary to distinguish between boratabenzene ions **A** and neutral borabenzene adducts **B**. The area of boratabenzene salts and complexes, especially those of the low-valent d-metals, is well developed. In the most recent years, the first compounds of Mg,[3] of group-3 metals,[1,4] and complexes of the group-4 metals[4b,5] were described. There are also a few studies of p-element compounds.[6] On the other hand, the scope and number of borabenzene adducts is still rather limited,[7] and very few complexes of these have been prepared. Those that have been synthesised are in all cases tricarbonyl compounds of group-6 metals,[7c,8] such as e.g. $Cr(CO)_3(C_5H_5BNC_5H_5)$ and its homologues of Mo and W.[8c]



A

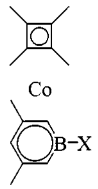
X = e.g. Me, Ph, NMe_2



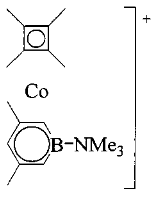
B

X = e.g. py, PMe_3, CN*t*Bu

This paper deals with (boratabenzene)(tetramethylcyclobutadiene)cobalt complexes $Cb^*Co(C_5H_5BX)$ ($Cb = C_4H_4$, cyclobutadiene; $Cb^* = C_4Me_4$). In two previous papers, neutral sandwich complexes $CbCo(C_5H_5BR)$ (R = Me,Ph)[9] and $Cb^*Co(C_5H_5BR)$ (R = Me, Ph) together with derivatives[10] have been described. In this paper we show that the new metallo-electrophile $[Cb^*Co(NCMe)_3]^+$[11] provides an efficient entry into this class of complexes (with the compounds **1**−**8**) and we present an unprecedented formation of a novel borabenzene complex $\mathbf{9}^+$ in the form of its iodide **10** [≡ (**9**)I] and its transformation into a *B*-cyano compound **11**.



	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**11**
X	NMe_2	OMe	Me	Cl	H	F	$SnMe_3$	$O_{1/2}$	CN



$\mathbf{9a}^+$

[‡] Borabenzene Derivatives, 38. − Part 37: Ref.[1]

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Table 1. Overview of reactions

Substrate	Reagent	Product
$Cb^*Co(3,5\text{-}Me_2C_5H_3BNMe_2)$ (**1**)	MeOH (neat)	$Cb^*Co(3,5\text{-}Me_2C_5H_3BOMe)$ (**2**)
$Cb^*Co(3,5\text{-}Me_2C_5H_3BOMe)$ (**2**)	MeLi in Et_2O	$Cb^*Co(3,5\text{-}Me_2C_5H_3BMe)$ (**3**)
$Cb^*Co(3,5\text{-}Me_2C_5H_3BOMe)$ (**2**)	BCl_3 in CH_2Cl_2	$Cb^*Co(3,5\text{-}Me_2C_5H_3BCl)$ (**4**)
$Cb^*Co(3,5\text{-}Me_2C_5H_3BCl)$ (**4**)	AlH*i*Bu$_2$ in toluene	$Cb^*Co(3,5\text{-}Me_2C_5H_3BH)$ (**5**)
$Cb^*Co(3,5\text{-}Me_2C_5H_3BCl)$ (**4**)	TlF, suspension in CH_2Cl_2	$Cb^*Co(3,5\text{-}Me_2C_5H_3BF)$ (**6**)
$Cb^*Co(3,5\text{-}Me_2C_5H_3BCl)$ (**4**)	$LiSnMe_3$ in THF	$Cb^*Co(3,5\text{-}Me_2C_5H_3BSnMe_3)$ (**7**)
$Cb^*Co(3,5\text{-}Me_2C_5H_3BSnMe_3)$ (**7**)	O_2, trace	$[Cb^*Co(3,5\text{-}Me_2C_5H_3B]_2O$ (**8**)
$Cb^*Co(3,5\text{-}Me_2C_5H_3BNMe_2)$ (**1**)	MeI in THF	$[Cb^*Co(3,5\text{-}Me_2C_5H_3BNMe_3)]I$ (**10**)
$[Cb^*Co(3,5\text{-}Me_2C_5H_3BNMe_3)]I$ (**10**)	Bu_4NCN in CH_2Cl_2	$Cb^*Co(3,5\text{-}Me_2C_5H_3BCN)$ (**11**)

Results and Discussion

Synthesis of $Cb^*Co(3,5\text{-}Me_2C_5H_3BNMe_2)$ (1)

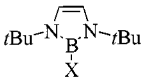
Reaction of the metallo-electrophile $[Cb^*Co(NCMe)_3]PF_6$ [11] with the lithium boratabenzene $Li(TMEDA)(3,5\text{-}Me_2C_5H_3BNMe_2)$[12] in acetonitrile at ambient temperature resulted in the smooth formation of the sandwich complex **1**, which could be isolated as a yellow-orange crystalline solid in high yield (78%). The complex is highly soluble in most common organic solvents and is markedly sensitive to air and humidity. Because of its ready availability complex **1** has become the starting point for the syntheses described below; Table 1 gives an overview of the reactions involved.

Nucleophilic Substitution at the Boron Atom

Complex **1** can readily be modified by nucleophilic substitution at the boron atom. This is a well-known type of reaction that was observed for the first time in 1971[13] and was later established as a versatile and general synthetic method, e.g. in work with boratabenzene ligands,[14] with 2,5-dihydro-1,2,5-thiadiboroles,[15] with 1,4-diboracyclohexadienes,[16] and with 1*H*-borole ligands.[17]

Methanolysis of **1** takes place in refluxing methanol to give the methoxy compound **2** which is more reactive than **1** and a useful synthetic intermediate. Complex **2** readily reacts with MeLi in ether to afford the 1,3,5-trimethyl compound **3**, and with BCl_3 in dichloromethane solution to produce the *B*-chloro derivative **4**, which, to the best of our knowledge, is the first *B*-chloroboratabenzene complex. Complex **4** can be treated with diisobutylaluminium hydride to give a *B*-hydrido complex **5**. We note in this context, that the first *B*-hydrido complex $Fe(C_5H_5BH)_2$ to be described was prepared by a similar nucleophilic substitution reaction.[14] Reaction of **4** with TlF produced the *B*-fluoro complex **6**; the B−F bond in this molecule is seen as a doublet in the $^{11}B\{^1H\}$ NMR spectrum with $^1J(^{19}F-^{11}B) = 55$ Hz. The only previous example of a *B*-fluoroboratabenzene complex is $[Ir(PEt_3)_3(3,5\text{-}Me_2C_5H_3BF)](BF_4)_2$ which was obtained from an iridabenzene precursor and BF_3.[18] The nucleophiles used up to this point are of largely different character and the yields obtained are generally quite satisfactory (70−86%).

Treatment of the *B*-chloro complex **4** with $LiSnMe_3$ [19] afforded the anticipated *B*-(trimethylstannyl) derivative **7**, again as yellow-orange crystals. The presence of an Sn−B bond is readily seen in the $^{11}B\{^1H\}$ NMR spectrum of **7**, in the form of tin satellites, and in the $^{119}Sn\{^1H\}$ NMR spectrum, which displays a quadruplet with $^1J(^{119}Sn-^{11}B) = 869$ Hz. This may be compared with the 2,3-dihydro-1*H*-1,3,2-azadiborole **12a** that has an Me_3Sn-B single bond with a trigonal boron atom, and displays $^1J(^{119}Sn-^{11}B) = 1031$ Hz.[20] Alternatively, this may be compared to $Li[H_3BSnMe_3]$ with a tetrahedral boron atom showing $^1J(^{119}Sn-^{11}B) = 554$ Hz.[21] Direct coupling constants qualitatively reflect the amounts of s-orbital contribution to the bonding between the two atoms involved. Thus, the data show that the s-orbital contribution of the boron atom in the Sn−B bond of **7** is only moderately reduced as compared to situations with truly trigonal boron atoms and, on the other hand, confirm that the boron orbital involved in the Co−B bonding largely retains its p-orbital character.



12a: X = $SnMe_3$, **b:** X = CN

Compound **7** is sensitive to air, but not more so than the more sensitive examples **1**, **4**, and **5**. When compound **7** was recrystallized, crystals appeared in the mother liquor that were identified by single-crystal structure determination as the *B*,*B′*-oxo linked dinuclear complex **8**.

Quaternization at the *B*-Amino Group

The *B*-amino group of **1** constitutes a Lewis basic reaction center. Treatment of **1** in THF with iodomethane at ambient temperature resulted in a slow quaternization and formation of the iodide (**9**)I ≡ **10**. This unusual reaction transforms a boratabenzene ligand into a borabenzene−trimethylamine ligand, or in more general terms, a ligand of type **A** into a ligand of type **B**. It also provides access to the first borabenzene complex outside the chromium triad. It is likely that other 1-aminoboratabenzene complexes will display an analogous reactivity, provided the nucleophilicity of the *B*-amino group is not reduced by strong π-interactions with the boron center or by the presence of sterically hindering *N*-alkyl groups.

A broad range of nucleophilic substitution reactions has been reported for the borabenzene adduct $C_5H_5BPMe_3$;[8b] the corresponding tricarbonylchromium complex $Cr(CO)_3(C_5H_5BPMe_3)$ is much more reactive, at least when treated with $LiC{\equiv}CSiMe_3$.[8b] We found that the NMe_3 group of **10** could readily be substituted on treatment with tetrabutylammonium cyanide in dichloromethane at ambient temperature. The reaction afforded the *B*-cyanoboratabenzene complex **11**, which is the first *B*-cyanoboratabenzene complex to be described.

We are not aware of other sandwich or half-sandwich complexes with a *B*-cyano group as part of a boron ring ligand. The ^{11}B chemical shift of **11** is at remarkably high field, as often observed for compounds with triple-bond systems (CO, CN, and CCR) attached to a boron atom.[22] A comparison of compounds **12a** and **12b** provides a pertinent example with $\delta(^{11}B) = 25.8$ for **12a** and $\delta(^{11}B) = 11.9$ for **12b**.[20] Note that the value for **12a** is in the typical range for this class of compounds,[22] while the value for **12b** is again at unusually high field.

Structure of $Cb^*Co(3,5\text{-}Me_2C_5H_3BSnMe_3)$ (7)

Crystals of **7** that were suitable for single-crystal X-ray work were obtained by slow crystallization from hexane (Figure 1, Table 2). The main aim of this study was the determination of the Sn−B bond length. The structure is described in some detail because of the high quality of the data obtained.

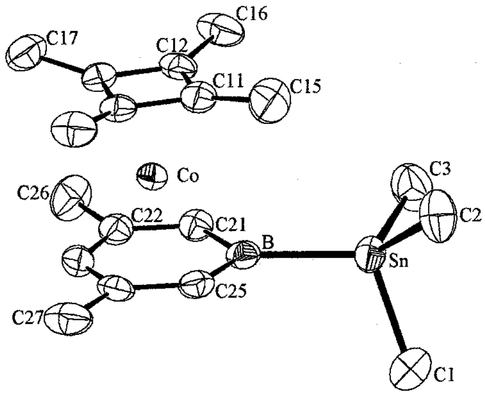


Figure 1. Molecular structure (PLATON plot, see ref.[23] at the 50% probability level) of **7** in the crystal

Table 2. Selected bond lengths [Å] and bond angles [°] of **7**

Co−C11	1.984(5)	Sn−C1	2.158(6)
Co−C12	1.985(4)	Sn−C2	2.150(6)
Co−C13	1.990(4)	Sn−C3	2.148(6)
Co−C14	1.983(4)	Sn−B	2.236(5)
Co−C21	2.122(4)	C21−C22	1.407(6)
Co−C22	2.100(5)	C22−C23	1.415(7)
Co−C23	2.078(5)	C23−C24	1.400(7)
Co−C24	2.122(4)	C24−C25	1.417(7)
Co−C25	2.126(4)	C21−B	1.506(7)
Co−B	2.214(5)	C25−B	1.519(7)
C1−Sn−C2	102.6(3)	C1−Sn−B	109.5(2)
C1−Sn−C3	106.9(3)	C2−Sn−B	121.5(2)
C2−Sn−C3	103.2(3)	C3−Sn−B	111.9(2)
Sn−B−C21	121.4(4)	Sn−B−C25	124.9(3)
C21−B−C25	113.7(4)		

The molecular structure of **7** is that of a typical sandwich complex, and in its details it is typical of an electron-rich 18e complex. The cyclobutadiene ring is planar and the boratabenzene ring is nearly so [maximum deviation from the best plane 0.023(5) Å at B]. The metal atom is shifted away from the boron atom toward the opposite carbon atom [slip distortion: 0.043 Å] and the boron atom is bent away from the metal atom [folding angle of the boratabenzene ring: 3.5(7)°]. On the other hand, the bonding around the boron atom is strictly trigonal planar (angle sum at boron: 360.0°). Both the slip distortion and the folding angle are comparatively small. The two rings are almost perfectly coplanar [interplanar angle: 1.4(3)°], and the distances of the metal atom to the ring planes amount to 1.7026(6) Å for the Cb* ring and to 1.5622(6) Å for the borabenzene ring.

A particularly interesting aspect of the structure is the presence of a $B{-}SnMe_3$ group. The Sn−B distance amounts to 2.236(5) Å and the torsional position of the $SnMe_3$ group is such that one *Sn*−Me substituent adopts a *transoid* position relative to the metal atom. This reduces the transannular repulsion between the remaining two *Sn*−Me substituents and the Cb* counter-ligand. Structurally documented and comparable Sn−B bonds are still rare. The closely related complex $Cp^*Fe(C_5H_5BSnMe_3)$ shows the same Sn−B distance of 2.237(5) Å[24] and the observed Sn−B distance is, for instance, 2.274(5) Å for **12a**,[20] and 2.286 and 2.277(17) Å for (*E*)-$Me_3Sn(iPr_2N)$-$BCHCHB(NiPr_2)SnMe_3$.[25]

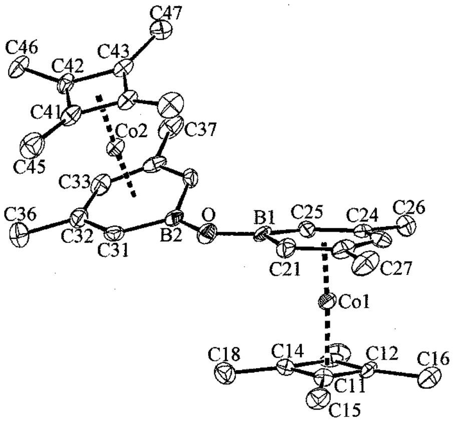


Figure 2. Molecular structure (PLATON plot, see ref.[23] at the 30% probability level) of **8** in the crystal; selected bond lengths [Å] and bond angles [°]: Co−C(Cb*) 1.969 (av.), $Co{-}C_{1,5}(C_5B)$ 2.119 (av.), $Co{-}C_{2,4}(C_5B)$ 2.082 (av.), $Co{-}C_3(C_5B)$ 2.055 (av.), Co1−B1 2.283(9), Co2−B2 2.267(10), O−B1 1.367(10), O−B2 1.404(11); B1−O−B2 131.1(7), O−B1−C21 118.7(8), O−B1−C25 128.8(8), O−B2−C31 120.5(8), O−B2−C35 126.2(8), C21−B−C25 112.0(8), C31−B−C35 112.5(8)

Structure of $[Cb^*Co(3,5\text{-}Me_2C_5H_3B)]_2O$ (8)

Crystals of **8** deposited from the mother liquor of the crystallization of **7** after prolonged standing. Compound **8** had presumably formed from **7** and traces of oxygen. The molecules of **8** (Figure 2) consist of two sandwich units with structural features close to those of **7** and a B−O−B bridge linking the two. The B−O bond lengths and the B−O−B angle are in the expected ranges.[26] The bridging ligand is not planar; the observed twisting of the chain C25,B1,O,B2,C35 reduces the repulsive 1,5-interaction between the carbon atoms C25 and C35.

Conclusion

The recently discovered metallo-electrophile $[Cb^*Co(NCMe)_3]PF_6$ could readily be combined with boratabenzene salts such as $Li(TMEDA)(3,5\text{-}Me_2C_5H_3BNMe_2)$ to produce the *B*−NMe$_2$ complex **1**. This complex may be used as a starting point for the development of bora- and boratabenzene derivatives with the Cb*Co complex fragment. It readily underwent a quaternization with iodomethane to afford complex **11**, which is the first representative of a new type of borabenzene complexes. Nucleophilic substitution at the boron atom has not often been used previously with complex borabenzene derivatives. In this paper we have made use of this type of reaction to synthesize several compounds with uncommon substituents at the boron atom.

Experimental Section

General: Reactions were carried out under dinitrogen by employing conventional Schlenk techniques. Hexane was distilled from potassium, toluene from sodium, THF and Et_2O from sodium benzophenone ketyl, and CH_2Cl_2 from CaH_2. Alumina was heated under high vacuum at 300 °C prior to use and was deactivated (5% H_2O, deoxygenated) after cooling. Melting points were determined in sealed capillaries with a Büchi 510 melting point apparatus and are uncorrected. Elemental analyses were performed by the Analytische Laboratorien, Prof. Dr. H. Malissa and G. Reuter GmbH, 51789 Lindlar. NMR spectra were recorded with a Varian Unity 500 (^1H: 499.6 MHz. $^{13}C\{^1H\}$: 125.6 MHz; $^{11}B\{^1H\}$: 160.3 MHz. ^{19}F: 470.1 MHz; ^{119}Sn: 186.3 MHz) and a Varian VXR 300 (^1H: 300 MHz. $^{13}C\{^1H\}$: 75.4 MHz). Chemical shifts are given in ppm; they were measured at ambient temperature and are quoted relative to internal TMS for ^1H and ^{13}C, relative to external $BF_3{\cdot}OEt_2$ for ^{11}B, to external $CFCl_3$ for ^{19}F, and relative to external $SnMe_4$ for ^{119}Sn. Deuterated solvents for NMR spectroscopy were degassed, dried and stored over molecular sieves (4 Å; Merck). Assignments are based on APT and DEPT spectra. IR spectra were measured with a Nicolet Avatar 360 FT IR instrument.

$Cb^*Co(3,5\text{-}Me_2C_5H_3BNMe_2)$ (1): A freshly prepared solution of $[Cb^*Co(NCMe)_3]PF_6$ [11] (1.66 g, 4.25 mmol) in acetonitrile (40 mL) was added with stirring to $Li(TMEDA)(3,5\text{-}Me_2C_5H_3BNMe_2)$[12] (1.22 g, 4.49 mmol), and stirring was continued at ambient temperature for 5 h. The volatiles were then removed under vacuum and the resulting residue was triturated with hexane. The extract was filtered through a frit covered with alumina (deactivated with 5% H_2O, 5-cm layer) at −80 °C, and the elution was completed with 60 mL of hexane. The volatiles were removed from the hexane solution. The product was crystallized from pentane at −30 °C as yellow-orange crystalline solid. Concentrating the mother liquor and cooling afforded a second crop of **1** (combined yield: 1.05 g, 78%); m.p. 66−67 °C, soluble in all common organic solvents. $C_{17}H_{27}BCoN$ (315.2): calcd. C 64.79, H 8.64, N 4.44; found C 64.71, H 8.77, N 4.90. ^1H NMR (CD_2Cl_2): δ = 1.36 (s, Cb*), 2.18 (s, 3-/5-Me), 3.76 (d, 2-/6-H), 4.77 (t, 4-H, $^4J_{24}$ = 1.2 Hz), 2.76 (s, NMe_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 9.7 ($C_4\mathit{Me}_4$), 22.6 (3-/5-Me), 39.2 (NMe_2), 77.5 (br, C-2,6), 77.8 (C_4Me_4), 85.2 (C-4), 112.4 (C-3,5); reliable spectra could be obtained more easily from toluene solutions of **1** because of the higher solubility of **1** in this solvent. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 22.0.

$Cb^*Co(3,5\text{-}Me_2C_5H_3BOMe)$ (2): A solution of **1** (0.53 g, 1.68 mmol) in methanol (15 mL, 0.37 mol) was heated under reflux at 65 °C for 24 h. After careful removal of the volatiles, the resulting residue was crystallized from hexane to give **2** (0.43 g, 86%) as an orange crystalline solid; m.p. 46−47 °C. $C_{16}H_{24}BCoO$ (302.1): calcd. C 63.61, H 8.01; found C 63.59, H 8.18. ^1H NMR (CD_2Cl_2): δ = 1.38 (s, Cb*), 2.04 (s, 3-/5-Me), 3.59 (s, OMe), 3.96 (d, 2-/6-H), 4.86 (t, 4-H, $^4J_{24}$ = 1.0 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 9.5 ($C_4\mathit{Me}_4$), 22.8 (3-/5-Me), 53.4 (OMe), 78.2 (C_4Me_4), 80.6 (br, C-2,6), 87.0 (C-4), 113.4 (C-3,5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 25.4.

$Cb^*Co(3,5\text{-}Me_2C_5H_3BMe)$ (3): A solution of MeLi (1.52 mL, 1.6 M in diethyl ether, 2.43 mmol) was added dropwise to a stirred solution of **2** (0.38 g, 1.25 mmol) in diethyl ether (20 mL) at −80 °C. The reaction mixture was stirred for additional 30 min under cold conditions, then allowed to warm to room temperature and stirring was continued for 24 h. After removal of the volatiles in a vacuum, the resulting residue was dissolved in hexane. Filtration and concentration gave **3** (0.31 g, 86%) as an orange-yellow crystalline solid; m.p. 127−128 °C. $C_{16}H_{24}BCo$ (286.1): calcd. C 67.17, H 8.45; found C 66.77, H 8.66. ^1H NMR (CD_2Cl_2): δ = 0.49 (s, BMe), 1.38 (s, Cb*), 2.04 (s, 3-/5-Me), 4.34 (d, 2-/6-H), 5.01 (t, 4-H), $^4J_{24}$ = 1.0 Hz. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 0.6 (br, BMe), 9.5 ($C_4\mathit{Me}_4$), 22.6 (3-/5-Me), 77.9 (C_4Me_4), 88.9 (C-4), 95.0 (br, C-2,6), 112.7 (C-3,5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 22.4.

$Cb^*Co(3,5\text{-}Me_2C_5H_3BCl)$ (4): A solution of BCl_3 in dichloromethane (2.97 mL, 1.56 M, 4.63 mmol) was added dropwise to a stirred solution of **2** (0.47 g, 1.55 mmol) in hexane (20 mL) at 0 °C. Rapid formation of a precipitate was seen. Stirring was continued for 1 h; then the reaction mixture was allowed slowly to warm to room temperature (12 h). After removal of the volatiles, the resulting residue was dissolved in dichloromethane and filtered through alumina (deactivated with 5% H_2O, 3 cm layer) using the same solvent as eluent. Removal of the solvent left **4** (0.33 g, 70%) as a fine microcrystalline, deep yellow solid; m.p. 159−160 °C. $C_{15}H_{21}BClCo$ (306.5): calcd. C 58.78, H 6.91; found C 58.81, H 6.97. ^1H NMR (CD_2Cl_2): δ = 1.39 (s, Cb*), 2.08 (s, 3-/5-Me), 4.50 (d, 2-/6-H), 5.09 (t, 4-H), $^4J_{24}$ = 1.0 Hz. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 9.4 ($C_4\mathit{Me}_4$), 22.3 (3-/5-Me), 80.3 (C_4Me_4), 89.8 (C-4), 91.8 (br, C-2,6), 113.1 (C-3,5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = 23.7.

$Cb^*Co(3,5\text{-}Me_2C_5H_3BH)$ (5): To a stirred solution of **4** (0.24 g, 0.78 mmol) in hexane (40 mL) was added diisobutylaluminium hydride in toluene (2.24 mL, 1 M, 2.24 mmol) at −80 °C. The reaction mixture was stirred for 30 min, then it was allowed slowly to warm to room temperature (12 h). The solvents were evaporated under vacuum, and the residue was dissolved in hexane (10 mL) and cooled to −80 °C. Anhydrous methanol (ca. 6 drops) and pyridine (ca. 4 drops) were added. The mixture was stirred for 30 min and then was allowed to warm to room temperature. Filtration through a cold frit (−80 °C) containing alumina (deactivated with 5% H_2O, 5 cm layer) with diethyl ether as eluent and subsequent concentration of the filtrate gave **5** (0.18 g, 86%) as an orange colored solid; m.p. 138−139 °C. $C_{15}H_{22}BCo$ (272.1): calcd. C 66.22, H 8.15; found C 66.97, H 8.36. ^1H NMR (CD_2Cl_2): $\delta = 1.39$ (s, Cb*), 2.08 (s, 3-/5-Me), 4.65 (dd, $^3J_{12} = 4.1$, $^4J_{24} = 1.1$ Hz, 2-/6-H), 5.11 (t, $^4J_{24} = 1.1$ Hz, 4-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 9.9$ (C_4Me_4), 22.7 (3-/5-Me), 79.3 (C_4Me_4), 90.1 (C-4), 96.6 (br, C-2,6), 112.5 (C-3,5). ^{11}B NMR (CD_2Cl_2): $\delta = 16.8$ [d, $^1J(^{11}B-^1H) = 110.0$ Hz].

Cb*Co(3,5-Me$_2$C$_5$H$_3$BF) (6): A solution of **4** (0.18 g, 0.58 mmol) in dichloromethane (20 mL) was treated with excess TlF (0.26 g, 1.16 mmol) and stirred at room temperature for 3 d. The reaction mixture was filtered and normal workup gave **6** (0.13 g, 76%) as a yellow crystalline solid; m.p. 151−152 °C. $C_{15}H_{21}BCoF$ (290.1): calcd. C 62.11, H 7.30; found C 62.20, H 7.40. ^1H NMR (CD_2Cl_2): $\delta = 1.40$ (s, Cb*), 2.06 (s, 3-/5-Me), 4.12 (d, 2-/6-H), 4.95 (t, 4-H, $^4J_{24} = 1.0$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 9.5$ (C_4Me_4), 22.5 (3-/5-Me), 79.4 (C_4Me_4), 83.3 (br, C-2,6), 88.1 (C-4), 114.1 (C-3,5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = 27.0$ [d, $^1J(^{19}F-^{11}B) = 55$ Hz]. ^{19}F NMR (CD_2Cl_2): $\delta = -174$ (br, with 90 Hz splitting).

Cb*Co(3,5-Me$_2$C$_5$H$_3$BSnMe$_3$) (7): A solution of **4** (0.22 g, 0.71 mmol) in THF (10 mL) was added dropwise to an ice-cooled solution of $LiSnMe_3$ [prepared from Sn_2Me_6 (0.23 g, 0.70 mmol) in THF (5 mL) and MeLi in diethyl ether (0.43 mL, 1.65 M, 0.70 mmol) at −80 °C].[19] Stirring was continued for 1 h; then the reaction mixture was allowed to warm to room temperature (12 h). After removal of the volatiles under vacuum, the resulting residue was dissolved in hexane and filtered through a cold frit (−80 °C) containing alumina (deactivated with 5% H_2O, 1-cm layer) with hexane as eluent. Concentration of the eluate yielded **7** (0.25 g, 81%) as yellow-orange crystals; m.p. 110−111 °C. $C_{18}H_{30}BCoSn$ (434.9): calcd. C 49.72, H 6.95; found C 49.57, H 7.35. ^1H NMR (CD_2Cl_2): $\delta = 0.02$ [s, $^2J(^{119}Sn-^1H) = 41.4$ Hz, $SnMe_3$], 1.37 (s, Cb*), 2.08 (s, 3-/5-Me), 4.83 (d, 2-/6-H), 5.17 (t, 4-H), $^4J_{24} = 1.5$ Hz. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = -10.4$ [s, $^1J(^{119}Sn-^{13}C) = 201.6$ Hz, $SnMe_3$], 10.1 (C_4Me_4), 22.5 (3-/5-Me), 80.0 (C_4Me_4), 90.8 (C-4), 101.1 (br, C-2,6), 112.1 (C-3,5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = 20.9$ [s, $^1J(^{119}Sn-^{11}B) = 0.86$ kHz]. $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2): $\delta = -105.3$ [q, $^1J(^{119}Sn-^{11}B) = 869$ Hz].

Byproduct 8: On standing, the mother liquor of the above preparation of **7** deposited orange-colored crystals of **8**; m.p. 189−190 °C. The compound was identified and characterized by an X-ray structure determination.

[Cb*Co(3,5-Me$_2$C$_5$H$_3$BNMe$_3$)]I (10): MeI (0.16 g, 1.12 mmol) in THF (10 mL) was added dropwise to a solution of **1** (0.35 g, 1.11 mmol) in the same solvent (20 mL) with stirring. A yellow precipitate appeared after ca. 40 min and stirring was continued at ambient temperature for 10 h. The crude product was collected on a frit, washed with THF (2 × 5 mL), then with diethyl ether (2 × 10 mL), and dried under vacuum. The product was dissolved in hot chloroform; subsequent slow cooling to −30 °C yielded **10** (0.43 g, 86%) as yellow microcrystals; m.p. 198−199 °C, soluble in chloroform, dichloromethane, acetone, and methanol. $C_{18}H_{30}BCoIN$ (457.1): calcd. C 47.03, H 6.62; found C 46.78, H 6.62. ^1H NMR (CD_2Cl_2): $\delta = 1.42$ (s, Cb*), 2.18 (s, 3-/5-Me), 3.29 (s, NMe_3), 4.71 (d, 2-/6-H), 5.30 (t, 4-H, $^4J_{24} = 1.0$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 10.3$ (C_4Me_4), 22.4 (3-/5-Me), 54.0 (NMe_3), 82.5 (C_4Me_4), 83.4 (br, C-2,6), 93.2 (C-4), 114.4 (C-3,5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = 25.3$.

Cb*Co(3,5-Me$_2$C$_5$H$_3$BCN) (11): A solution of tetrabutylammonium cyanide (0.20 g, 0.74 mmol) in dichloromethane (10 mL) was added dropwise to a solution of **10** (0.30 g, 0.66 mmol) in the same solvent (10 mL). The reaction mixture was stirred for 24 h. After removal of the volatiles, the residue was extracted in toluene (40 mL). Filtration through alumina (deactivated with 5% H_2O, 3-cm layer) using toluene/diethyl ether (95:5, v/v) as eluent, subsequent removal of the volatiles under vacuum, and recrystallisation from dichloromethane/diethyl ether (1:1) yielded **11** (0.15 g, 79%) as a yellow-orange solid; m.p. 155−156 °C. $C_{16}H_{21}BCoN$ (297.1): calcd. C 64.69, H 7.12, N 4.71; found C 65.12, H 7.24, N 5.08. ^1H NMR (CD_2Cl_2): $\delta = 1.42$ (s, Cb*), 2.11 (s, 3-/5-Me), 4.87 (d, 2-/6-H), 5.27 (t, 4-H, $^4J_{24} = 1.5$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −50 °C): $\delta = 9.4$ (C_4Me_4), 22.0 (3-/5-Me), 81.4 (C_4Me_4), 91.4 (C-4), 96.7 (br, C-2,6), 112.2 (C-3,5), 131.4 (br, CN). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = 7.4$. IR (CD_2Cl_2): $\nu(CN) = 2198\ cm^{-1}$.

X-ray Crystal Structure Determinations: Diffraction intensity data were collected with ENRAF-Nonius CAD4 diffractometers equipped with graphite monochromators. Crystal data, data collection parameters, and convergence results are listed in Table 3. Before averaging over symmetry-related reflections, numerical[27] or empirical absorption[28] corrections were applied to the data sets. Structures were solved by direct methods with the help of the SHELXS-97 program[29] and refined on reflection intensities (F^2) using the SHELXL-97 program.[30] In the final least-squares refinements, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms were included as riding with

Table 3. Crystal data, data collection parameters, and convergence results for **7** and **8**

	7	**8**
Empirical formula	$C_{18}H_{30}BCoSn$	$C_{30}H_{42}B_2Co_2O$
Molecular weight	434.87	558.16
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Radiation (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)
a [Å]	7.321(1)	15.907(2)
b [Å]	10.285(1)	13.664(3)
c [Å]	13.6514(8)	14.581(1)
α [°]	77.861(7)	90
β [°]	82.530(7)	115.750(6)
γ [°]	82.98(1)	90
V [Å^3]	991.6(2)	2854.5(8)
Z	2	4
$d_{calcd.}$ [g/cm^3]	1.46	1.30
$F(000)$	440	1176
μ [mm^{-1}]	20.99	11.79
Absorption correction	numerical	empirical
Max./min. transmission	0.622/0.523	1.000/0.886
θ range [°]	3.1−28.0	3.1−26.0
Temperature [K]	223	233
Scan mode	ω−2θ	ω−2θ
Crystal size [mm]	0.50 × 0.31 × 0.20	0.50 × 0.45 × 0.40
Reflections collected	9522	9361
Reflections unique	4766	5031
Reflections observed	3531	2205
Criterion for observation	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$
Variables	199	328
R_1 [a], observed (all data)	0.049 (0.069)	0.079 (0.187)
wR_2[b], observed (all data)	0.118 (0.124)	0.131 (0.152)
GOF[c]	1.01	0.89
Max. resd. density [e/Å^3]	1.85	0.54

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n - p)]^{1/2}$.

fixed displacement parameters [C−H = 0.98 Å, U_{iso}(H) = 1.3 U_{eq}(C)]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-167066 (**7**) and -167065 (**8**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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