Bis(boryl)metallocenes. 2.[1] Syntheses of 1,1′-Bis(boryl)cobaltocenium Complexes

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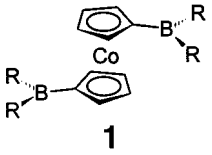
Bis(boryl)cobaltocenes $Co(C_5H_4BR_2)_2$ (**1**) can be made from $CoBr_2$(DME) and alkali metal borylcyclopentadienides $M(C_5H_4BR_2)$ (M = Li, Na) (**2**). The two dialkylamino compounds **1c** (R = NMe_2) and **1d** (R = NEt_2) can be obtained in this way. Oxidation with C_2Cl_6 provides the ionic cobaltocenium chlorides (**1c**)Cl and (**1d**)Cl. Further cobaltocenium compounds can be synthesized by modification of the substituents at boron. Treatment of (**1d**)Cl with excess BCl_3 affords the highly reactive chloride $Co(C_5H_4BCl_2)(C_5H_4BCl_3)$ (**5**). Pinacolysis of **5** then affords the monosubstitution product $Co[C_5H_4B(OCMe_2)_2](C_5H_4BCl_3)$ (**9**) and the disubstitution product $[Co\{C_5H_4B(OCMe_2)_2\}_2]Cl$ [(**1h**)Cl], respectively, depending on stoichiometry and reaction conditions. Reaction of **5** with tetramethyltin replaces two chlorine atoms with methyl groups to give $Co(C_5H_4BMe_2)(C_5H_4BCl_3)$ (**10**), while the more reactive trimethylaluminum replaces four chlorine substituents to give the salt $[Co(C_5H_4BMe_2)_2]AlCl_4$ [(**1b**)$AlCl_4$] and, after metathesis with NBu_4PF_6 in CH_2Cl_2, the more convenient hexafluorophosphate (**1b**)PF_6. The corresponding cobaltocene **1b** is then accessible via conventional amalgam reduction of (**1b**)$AlCl_4$. Reaction of **5** with commercial AsF_3 affords the robust inverse chelate $Co(C_5H_4BF_2)_2(\mu\text{-OH})$ (**11**). Three structural types are encountered for the cobaltocenium derivatives: (i) ionic compounds (type **A**) such as (**1c**,**d**,**h**)Cl, (**1b**)$AlCl_4$, and (**1b**)PF_6; (ii) zwitterionic or semiquaternized compounds (type **B**) with one trigonal and one tetrahedral boron center such as **5**, **9**, and **10**; of these, **5** is fluxional in solution with two effectively equivalent ligands while **9** and **10** display static structures; and (iii) the inverse chelate structure of **11** (type **C**) which is found in the crystal and in solution.

Introduction

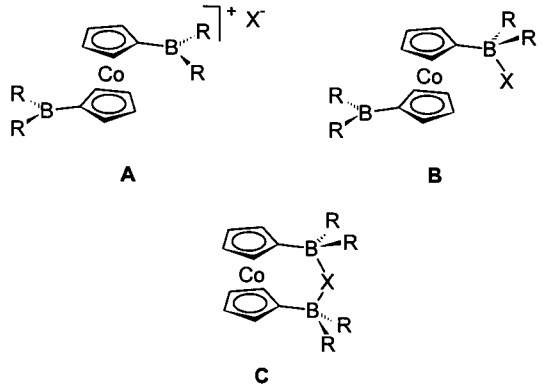
We are currently investigating the anion-binding properties of bis(boryl)metallocenes. The newly accessible class of bis(borylcyclopentadienyl)cobalt complexes such as the paramagnetic uncharged complexes **1** and especially the diamagnetic sandwich cations $\mathbf{1}^+$ represent the focus of our interest.



1

a, R = Pr^i; **b**, R = Me; **c**, R = NMe_2; **d**, R = NEt_2; **e**, R = F; **f**, R = Cl; **g**, R = OMe; **h**, R = $^1/_2(OCMe_2)_2$.

In the first paper of this series[2] we have shown that the cation $\mathbf{1a}^+$ may display three kinds of relationships to the anion: type **A**, purely ionic as in the hexafluorophosphate $[Co(C_5H_4BPr^i_2)_2]PF_6$ [(**1a**)PF_6]; type **B**, semiquaternized or zwitterionic as in the chloride $Co(C_5H_4BPr^i_2)(C_5H_4BPr^i_2Cl)$ [(**1a**)Cl] with two different boron centers; and type **C**, chelating as in the hydroxide $Co(C_5H_4BPr^i_2)_2(\mu\text{-OH})$ [(**1a**)OH]. In all three cases these structures were verified for the solid state by X-ray crystallography. In solution the chloride (**1a**)Cl was found to be fluxional, showing only time-averaged NMR signals for the ligands.



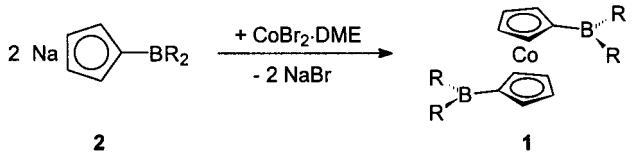
A **B** **C**

The type of cation−anion interaction encountered will depend on the electronic nature and the bulk of the substituents at boron as well as on the nature of the anion. For a more detailed investigation on the anion-binding properties of cations $\mathbf{1}^+$ we needed a set of differently substituted derivatives for a comprehensive comparison. The intention of this work is to establish a general synthetic entry to a wide variety of bis(borylcyclopentadienyl)cobalt complexes. Essentially two strategies can be envisaged: first the direct synthesis starting from borylcyclopentadienides, if these are available,[4] and second the modification of cationic

(1) Part 1: See ref 2.
(2) Herberich, G. E.; Fischer, A.; Wiebelhaus, D. *Organometallics* **1996**, *15*, 3106.

10.1021/om980465m CCC: $15.00
Publication on Web 09/22/1998

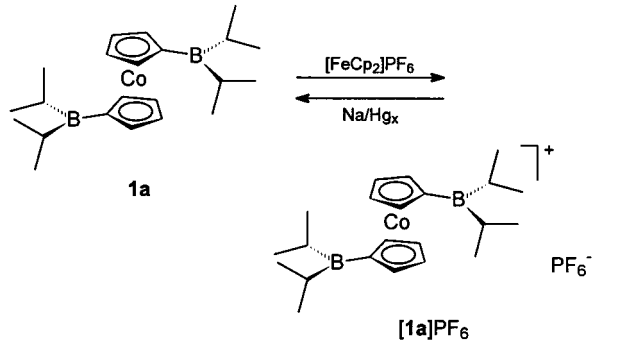
Scheme 1



2 **1**

a, R = Pr^i; **c**, R = NMe_2; **d**, R = NEt_2.

Scheme 2



[1a]PF_6

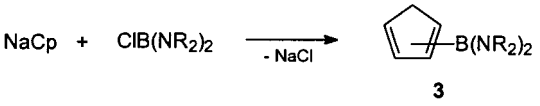
complexes such as **1c**−**h**$^+$ by exchange of the hetero substituents at boron. The potential use of the resulting derivatives is quite varied for the different substituents at boron. While **1c**$^+$ and **1d**$^+$ are easily accessible but comparatively unreactive, **1f**$^+$ is expected to be a highly reactive species and a useful intermediate for the preparation of a large number of derivatives. Finally **1a**$^+$ and **1b**$^+$ should be relatively inert strong Lewis acids with great anion-binding potential.

Results and Discussion

Syntheses from Borylcyclopentadienides. If the required borylcyclopentadienides **2** are available,[4] the corresponding 1,1′-bis(boryl)cobaltocenes **1** can easily be prepared by reaction with $CoBr_2$(DME).[5] This direct synthesis has already been described for **1a**[2] and functions equally well for **1c**; a slight excess of **2** is used to avoid product loss due to oxidation by an excess of the cobalt(II) salt.The neutral metallocenes **1** and their cations **1**$^+$ are readily interconverted. Oxidation[6] of **1a** with [$FeCp_2$]PF_6, C_2Cl_6, or $Cu(OH)_2$ yields the abovementioned cobaltocenium compounds (**1a**)PF_6, (**1a**)Cl, and (**1a**)OH, respectively.[2] Conversely, reduction[6] of (**1a**)PF_6 with sodium amalgam produces the neutral **1a**.Reaction of **1c** with C_2Cl_6 affords the ionic chloride (**1c**)Cl (type **A**). The nitrogen substituents at boron greatly diminish the Lewis acidity in **1c**$^+$. Consequently no sign of semiquaternization as in (**1a**)Cl (type **B**) is detected for (**1c**)Cl. In particular there is no upfield shift in the ^{11}B NMR spectrum, which would be indicative of a quaternization. The ^{11}B chemical shift of 30 ppm is in the usual region for di(amino)organoboranes.[7]

The preparation of the analogous diethylamino compounds later turned out to be necessary for the intended subsequent modification reactions. This seemingly trivial duplication in the amino series displayed two unexpected details. Whereas chloro(dimethylamino)-

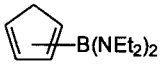
Scheme 3



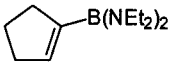
3

c, R = Me; **d**, R = Et.

borane reacts smoothly with NaCp at room temperature in THF to give **3c**,[4] no reaction is observed for the analogous ethyl compound $BCl(NEt_2)_2$. Heating to reflux causes detrimental ether cleavage and gives only a low yield of **3d**. If the same reaction is carried out in DME at 70 °C, **3d** can be isolated in excellent yield (96%). As in the case of **3c**, the resulting mixture of vinyl isomers shows no tendency to undergo Diels−Alder dimerization.Reaction of **3d** with elemental sodium in THF gives the borylcyclopentadienide **2d** together with the cyclopent-1-enylborane **4**. This is quite surprising since an analogous hydrogenation product cannot be detected when **3c** is metalated with elemental sodium.[4] Deprotonation with LDA is successful for both **3c**[4] and **3d**, yielding **2c**[4] and **2d**, respectively. The subsequent metallocene synthesis of **1d** and oxidation to the salt (**1d**)Cl are completely analogous to the procedures described for the corresponding dimethylamino derivatives.



3d

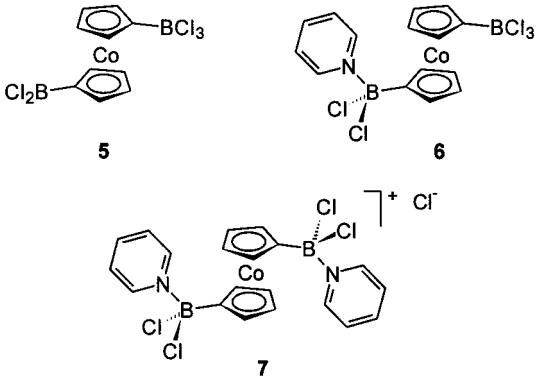


4

Modification by Exchange of the Hetero Substituents at Boron. When (**1c**)Cl was treated with excess BCl_3 only three of the four NMe_2 groups can be removed (NMR), and the resulting material is inert to further treatment with BCl_3.[8] However, treatment of the diethylamino compound (**1d**)Cl with excess BCl_3 results in formation of the desired chloro compound $Co(C_5H_4BCl_2)_2Cl$ (**5**). This substitution is partially reversed when the excess BCl_3 is removed under vacuum. However, on pouring the reaction mixture into a large volume of cold hexane, **5** precipitates as a pale yellow, microcrystalline, and extremely moisture-sensitive solid and can be isolated in high yield (91%). Numerous attempts to grow crystals of **5** suitable for X-ray diffraction remained unsuccessful. Its constitution was rationalized from NMR data, in particular from its ^{11}B NMR spectrum. In CD_2Cl_2 a single ^{11}B resonance is observed at 28.0 ppm. This is midway between the expected limiting values for BCl_2 and BCl_3 groups bonded to sp^2-carbon centers. Reference data for the former are available [δ(^{11}B) 51 ppm for $C_5H_4BCl_2$,[9] δ(^{11}B) 55 ppm for $PhBCl_2$[7]], while for the latter a representative chemical shift can be derived from the reaction of **5** with pyridine. The first equivalent of Lewis base is cleanly coordinated to give the monoadduct **6**, whereas an excess of pyridine gives rise to a slow

(3) Wiebelhaus, D. Doctoral Dissertation, Technische Hochschule Aachen, Aachen, Germany, 1998.
(4) Herberich, G. E.; Fischer, A. *Organometallics* **1996**, *15*, 58.
(5) Heyn, B.; Hipler, B.; Kreisel, G.; Schreer, H.; Walther, D. *Anorganische Synthesechemie*; Springer-Verlag: Berlin, 1986.
(6) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
(7) For reference data see: (a) Nöth, H.; Wrackmeyer, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978; Vol. 14. (b) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61. (c) Siedle, A. R. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 205.
(8) It is well-known that $BCl_2(NMe_2)$ readily dimerizes to give a robust four-membered ring compound, while the higher homologue $BCl_2(NEt_2)$ does not, presumably for steric reasons. We believe that the presumed intermediate $Co(C_5H_4BCl_3)(C_5H_4BCl(NMe_2))$ dimerizes in the same fashion.
(9) Lockman, B.; Onak, T. *J. Org. Chem.* **1973**, *38*, 2552.

equilibrium between monoadduct **6** and the ionic bis-adduct **7**. The quaternized ^{11}B nuclei in **6** and **7** display chemical shifts near 6 ppm.

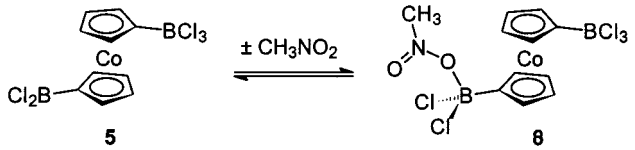


These reference values support the assumption of a type **B** structure for **5**. In solution this structure is fluxional as observed for (**1c**)Cl and gives rise to NMR spectra corresponding to effective C_{2v} symmetry. If there was a significant share of type **C** structure (which would possess true C_{2v} symmetry) in dynamic equilibrium, one would expect a strong temperature dependence of this equilibrium and the resulting $\delta(^{11}B)$ chemical shift in solution. Between room temperature and −60 °C no such temperature dependence is found. Hence we have to conclude that a nondegenerate equilibrium cannot be present, and solely a type **B** structure remains for **5**.

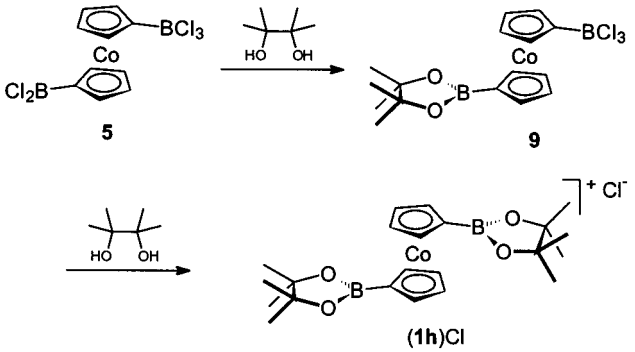
A different situation emerges on changing the solvent to nitromethane. Now a single resonance is found at much higher field (12.7 ppm) in the ^{11}B NMR spectrum at room temperature. Moreover, this resonance displays a strong temperature dependence between −20 (8.6 ppm) and +80 °C (22.1 ppm). This observation cannot be explained by an equilibrium between different forms of **5** (types **A**−**C**) because the more polar solvent would favor the more polar forms of the solute (type **A** > **B** > **C**). Thus a larger ^{11}B chemical shift would be expected in $MeNO_2$ than in CH_2Cl_2. However, the opposite is observed experimentally. Consequently, another equilibrium must be operative in nitromethane.

Although nitromethane is frequently considered a noncoordinating solvent, its donicity (as defined by V. Gutman)[10] is significantly larger than that of dichloromethane (2.7 vs 0). Regarding the interaction of these two solvents with dissolved boron trifluoride, the difference is even more pronounced [$\Delta H(BF_3)$ −10.0 kJ·mol^{-1} for CH_2Cl_2 and −37.6 kJ·mol^{-1} for $MeNO_2$].[11] Thus coordination of $MeNO_2$ to the unquaternized boryl substituent in **5** seems a reasonable explanation for the above observations. If the temperature-dependent NMR data are analyzed on the basis of an equilibrium between **5** and its nitromethane adduct **8** and if sensible assumptions are made about the ^{11}B chemical shifts involved, crude thermodynamic data for the equilibrium can be extracted. The association process is exothermic ($\Delta_R H$ −34 ± 12 kJ·mol^{-1}) and exotropic ($\Delta_R S$ −129 ± 35 J·mol^{-1}·K^{-1}). The fact that the reaction enthalpy found is of the same magnitude as the above-mentioned enthalpy for the adduct formation between $MeNO_2$ and BF_3 lends support to our interpretation of the observed temperature dependence and demonstrates the high Lewis acidity of **5**.

Scheme 4



Scheme 5



While developing the synthesis of **5** we also treated the salts (**1c**,**d**)Cl with hydrogen chloride. This led to rather stable bis(amine) adducts, analogous to **7**, in mixture with ammonium salts. The reaction is synthetically unattractive, as neither liberation of **5** from these adducts nor separation from the ammonium salts could be achieved. The chloro compound **5** may be used as a versatile synthetic intermediate which opens the route to derivatives with further heterosubstituents at boron.

Alcoholysis. Reaction of **5** with pinacol results in stepwise alcoholysis. The monosubstitution product Co-$[C_5H_4B(OCMe_2)_2](C_5H_4BCl_3)$ (**9**) can be isolated by choosing the correct stoichiometry or, if an excess of pinacol is used, by interrupting the reaction after a few minutes at room temperature. After prolonged reaction times and with at least 2 equiv of the diol the disubstitution product $[Co\{C_5H_4B(OCMe_2)_2\}_2]Cl$ [(**1h**)Cl] is formed in near quantitative yield.

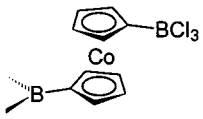
The disubstitution product (**1h**)Cl is ionic in character (type **A**). Its ^{11}B chemical shift of 30.4 ppm is in the region expected for di(alkoxy)organoboranes.[7] As for the amino derivatives (**1c**,**d**)Cl, there is no indication of partial quaternization. Again this is in agreement with the assumed low Lewis acidity, now due to the oxygen substituents at boron. In contrast to this situation, the unsymmetrical compound **9** shows two resonances in the ^{11}B NMR spectrum consistent with a static zwitterionic structure (type **B**). The more acidic chloro-substituted boryl group is quaternized by coordination of the anion. The observation of a type **B** structure readily explains why the second step of the alcoholysis is so much slower than the first one.

Alcoholysis of **5** with methanol essentially yields the bis(dialkoxyboryl) compound $[Co\{C_5H_4B(OMe)_2\}_2]Cl$ [(**1g**)-Cl], analogous to (**1h**)Cl. This same compound is also obtained from the chloride **5** and excess Me_3SiOMe. Isolation of the pure product is hampered by the fact that it undergoes a slow decomposition with formation of B−O−B bridged species.

(10) (a) Gutman, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: NewYork, 1978. (b) Gutman, V. *Pure Appl. Chem.* **1979**, *51*, 2197.

(11) Maria, P.-C.; Gal, J.-F. *J. Chem. Phys.* **1985**, *89*, 1296.

Alkylation. On treatment of **5** with $SnMe_4$ a 2-fold alkylation takes place at room temperature to give the unsymmetrical $Co(C_5H_4BMe_2)(C_5H_4BCl_3)$ (**10**). Further methylation is not observed even with a large excess of $SnMe_4$ and over prolonged reaction times. Purification of **10** by crystallization (for X-ray analysis) was unsuccessful, but its NMR data leave no doubt as to its constitution. As in the case of **9**, two ^{11}B resonances are observed for **10**, which confirm its unsymmetrical structure. While the quaternized boron atom gives rise to a signal at 5.3 ppm, the second resonance at 78.1 ppm is consistent only with an unquaternized BMe_2 group. The alternative constitution with a BCl_2 group would show a chemical shift around 51 ppm.[7] This conclusion is in agreement with the chemical notion that the more Lewis acidic chloro-substituted boron center coordinates the Lewis base Cl^- in preference to the methyl-substituted group.

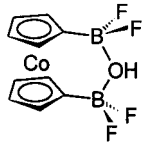


10

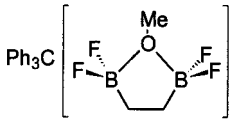
If trialkylaluminum compounds AlR_3 are used as alkylation agent, complete substitution of **5** is achieved. Stoichiometric amounts of trimethylaluminum transform **5** into the salt $[Co(C_5H_4BMe_2)_2]AlCl_4$ [(**1b**)$AlCl_4$]. A small excess of $AlMe_3$ leads to an admixture of $[Co(C_5H_4BMe_2)_2]AlMeCl_3$. Both compounds are easily purified by crystallization from CH_2Cl_2, and subsequent anion metathesis with NBu_4PF_6 affords the more convenient hexafluorophosphate (**1b**)PF_6. The analogous reaction of **5** with $AlEt_3$ gives $[Co(C_5H_4BEt_2)_2]AlCl_4$ as a spectroscopically pure brown oil in quantitative yield; attempted crystallization proved impossible in this case. For all these salts ^{11}B chemical shifts of above 76 ppm prove type **A** structures with trigonal planar boron centers [cf. (**1a**)PF_6[2]].

The salt (**1b**)$AlCl_4$ can be reduced to the cobaltocene **1b** with sodium amalgam just as described above for the analogous isopropyl derivative (**1a**)PF_6. The reader may wonder why the complexes of the methyl series **b** were not made by the same simple route that was used for the synthesis of the isopropyl compounds **a**. The reasons are of a purely practical nature. The direct route would require the handling of the isomer mixture of the (dimethylboryl)cyclopentadienes, which, in addition to being extremely sensitive and pyrophoric, can only be kept in dilute solutions at low temperatures.[4,12]

Fluoridation. When **5** was treated with a commercial and to a small extent hydrolyzed sample of AsF_3 (NMR), the robust fluoro derivative $Co(C_5H_4BF_2)_2(\mu$-OH)(**11**) was obtained. Its single ^{11}B resonance at 3.1 ppm indicates two equally quaternized boron atoms. Moreover the temperature independence of ^{11}B and ^1H NMR spectra between room temperature and 90 °C rules out the existence of a nondegenerate equilibrium. Thus a structure of type **C** must be present in solution. This structure is closely akin to the one proposed for compound **12**, which represents the very first example of anion chelation (1966).[13] Exchange between the hydroxylic proton in **11** and CF_3CO_2H is slow on the NMR time scale but fast on the laboratory time scale, as shown by deletion of its proton resonance with CF_3CO_2D.



11



12

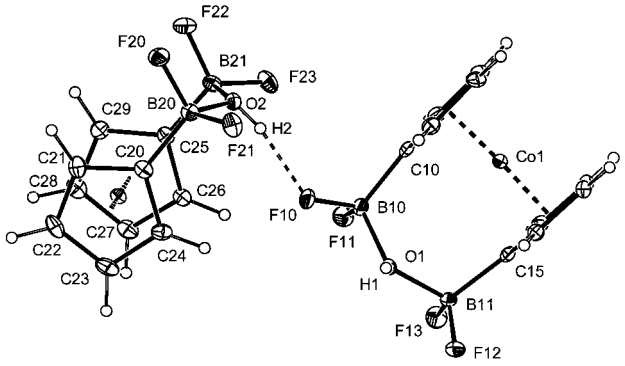


Figure 1. PLATON diagram of **11** (30% probability, arbitrary radius for hydrogen atoms).

Table 1. Selected Bond Distances and Bond Angles for 11

(a) Bond Distances (Å)

F10−B10	1.423(3)	O2−B20	1.529(3)
F11−B10	1.373(3)	O2−B21	1.557(3)
F12−B11	1.390(3)	B10−C10	1.611(4)
F13−B11	1.367(4)	B11−C15	1.615(4)
F20−B20	1.373(3)	B20−C20	1.602(4)
F21−B20	1.416(3)	B21−C25	1.609(4)
F22−B21	1.376(4)	O1−H1	0.81(3)
F23−B21	1.386(3)	O2−H2	0.82(3)
O1−B10	1.521(3)	H1−F21	1.88(3)
O1−B11	1.556(3)	H2−F10	1.84(3)

(b) Bond Angles (deg)

B10−O1−B11	126.8(2)	F21−H1−O1	163(3)
B20−O2−B21	126.0(2)	F10−H2−O2	167(3)

Crystal Structure of 11. To verify the type **C** structure for **11** in the solid state, a single-crystal X-ray study was undertaken. Suitable crystals were grown from a nitromethane solution. Complex **11** crystallizes in the centered monoclinic space group *C*2/*c* and contains two independent molecules per unit cell. A PLATON representation[14] of the molecules is shown in Figure 1, and selected structural data are given in Table 1.

Complex **11** possesses the same chelating type **C** structure in the solid state that was found in solution.[15] The inverse bidentate anion ligand is slightly distorted to accommodate the small hydroxide ion. The B−B distance is shortened from 3.27 Å (ring−ring distance of an undistorted cobaltocenium moiety) to 2.752(4) Å. This is achieved by tilting the two eclipsed cyclopentadienyl rings by about 4° and additionally by bending

(12) Johnson, H. D.; Hartford, T. W.; Spangler, C. W. *J. Chem. Soc., Chem. Commun.* **1978**, 242.

(13) Biallas, M. J.; Shriver, D. F. *J. A. Chem. Soc.* **1966**, *88*, 375.
(14) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
(15) Only one of the two independent molecules is discussed, as the two are not different within standard deviations.

the boron substituent toward the anion [angle Z−C-1−B 5.4° and 3.8°, where Z denotes the geometrical center of the C_5 ring]. The resulting B−O bond lengths of 1.521(3) and 1.556(3) Å are in the normal range for tetrahedral boron (1.50−1.58 Å, excluding pure oxygen substitution).[16] A significantly longer B−O distance of 1.605(6) Å in (**1a**)(μ-OH)[2] indicates a stronger OH^- chelation in the fluoro compound **11** as compared to the isopropyl derivative.

The anionic OH group is directed toward the next neighboring molecule to allow a hydrogen bridge to be formed to one of its fluorine atoms. Thus an overall tetrameric packing motif around the 2-fold axes is generated from the two independent molecules in the asymmetric unit. The resulting B−F distance of the hydrogen-bonded fluorine atom [1.423(3) Å] is significantly longer than the B−F distances of the other fluorine atoms without a hydrogen bridge [1.367(4)−1.390(3) Å]. A similar situation was noted for the crystal structure of $MeOH{\cdot}BF_3$.[17]

Concluding Remarks. It was the aim of this paper to give an overview of the synthetic chemistry of both cationic and neutral bis(borylcyclopentadienyl)cobalt complexes. These complexes can be made either by a direct synthesis from alkali metal borylcyclopentadienides or, alternatively, by subsequent modification of the substituents at boron.

^{11}B NMR spectroscopy plays a key role in the elucidation of the solution structures involved. It should be noted that the chloride **5** is fluxional, in contradistinction to the chlorides **9** and **11**, which display apparently static structures. Cation **1f**$^+$ possesses two identical Lewis acid centers. Hence the chloride counterion may be considered to move in a symmetrical double-minimum potential resulting in the fluxionality of chloride **5**. In the case of **10**, the corresponding cation [Co($C_5H_4BMe_2$)($C_5H_4BCl_2$)]$^+$ possesses two different Lewis acidic groups or, in other words, an unsymmetrical double-minimum potential, and the counterion is bonded to the more acidic boron center in the product **10**. The case of **9** is, of course, completely analogous to that of **10**.

The next paper of this series will be devoted to a systematic study of the interactions of the two cations **1a**,**b**$^+$ with various anions. We will then be able to comment on some of the factors governing the structural preferences and also on the mechanisms underlying the fluxionality of complexes such as the chlorides (**1a**)Cl[2] and (**1b**)Cl.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk technique. Hexane was distilled from potassium, THF from sodium benzophenone ketyl, and dichloromethane from calcium hydride. Nitromethane was filtered through a column of activated alumina and condensed from a vacuum. Silica and alumina were heated under vacuum at 300 °C and kept under dinitrogen.

NMR spectra were recorded on a Varian Unity 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 126 MHz), a Varian VXR 300 (^{1}H, 300 MHz; ^{13}C, 76 MHz), and a Rototec/Piccinotti Mini-FID (^{11}B, 29 MHz) and calibrated using referenced solvent signals. Chemical shifts are given in ppm. Assignments were made with the help of (^{1}H,^{13}C)-HETCOR, (^{1}H,^{13}C)-HMQC, and NOE difference spectra.[3] Mass spectra were recorded on a Finnigan MAT-95 spectrometer. Elemental analyses were determined by Analytische Laboratorien Malissa and Reuter, Lindlar, Germany.

Preparation of $C_5H_5B(NEt_2)_2$ (3d). Cyclopentadiene (52.0 g, 0.79 mol) was added dropwise to a stirred suspension of NaH (17.3 g, 0.72 mol) in DME (800 mL). The reaction was brought to completion by heating to 70 °C for 2 h. Then $BCl(NEt_2)_2$ (135.5 g, 0.71 mol) was added at room temperature, and the reaction mixture was stirred at 50 °C for 15 h. DME was carefully removed under vacuum (20 mbar), and the residual solution was condensed into another flask. The nonvolatile residue was extracted with hexane (5 times with 100 mL), and the combined extracts were liberated from the solvent. The product solutions were distilled to yield **3d** (151.6 g, 96%) as a colorless liquid of vinyl isomers; bp 80−94 °C/1 mbar.

Data for bis(diethylamino)cyclopenta-1,3-dienylborane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (m, 4-H), 6.57 (m, 3-H), 6.56 (m, 2-H), 3.03 (m, 2H, 5-H), 3.00 (q, ^3J = 7.0 Hz, 4 CH_2), 1.08 (t, ^3J = 7.0 Hz, 4 Me); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.97 (C-3), 134.09 (C-2), 132.94 (C-4), 45.72 (C-5), 42.05 (NC), 15.64 (Me).

Data for bis(diethylamino)cyclopenta-1,4-dienylborane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (m, 5-H), 6.46 (m, 4-H), 6.42 (m, 2-H), 3.04 (m, 2H, 3-H), 3.03 (q, ^3J = 7.0 Hz, 4 CH_2), 1.08 (t, ^3J = 7.0 Hz, 4 Me);^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 137.42 (C-5), 136.43 (C-4), 131.31 (C-2), 42.73 (C-3), 42.16 (NC), 15.69 (Me).

Data for **3d** (mixture): MS (EI) *m*/*z* (I_{rel}) 220 (75, M^+), 205 (65, $M^+ - Me$), 191 (30, $M^+ - Et$), 155 (88, $M^+ - Cp$), 148 (100, $M^+ - NEt_2$); ^{11}B{^{1}H} NMR (29 MHz, $CDCl_3$) δ 33.1.

Preparation of Li[$C_5H_4B(NEt_2)_2$] [Li(2d)]. Compound **3d** (50.4 g, 0.23 mol) was added to a solution of LDA (21.5 g, 0.20 mol) in THF (200 mL) at −78 °C. The solution was allowed to warm to room temperature, and stirring was continued for a further 3 h. The volatiles were removed under vacuum. The powder so obtained was suspended in hexane (100 mL), collected by filtration, washed with hexane (two times with 70 mL), and finally dried under vacuum to give Li(**2d**) as a white powder (41.8 g, 93%). Anal. Calcd for $C_{13}H_{24}BLiN_2$: C, 69.06; H, 10.70. Found: C, 69.27; H, 10.43.

Data for Li(**2d**): ^{1}H NMR (300 MHz, [D_8]THF) δ 5.95 (m, *N* = 5.0 Hz, 2-/5-H), 5.78 (m, *N* = 5.0 Hz, 3-/4-H), 3.17 (q, ^3J = 7.0 Hz, 4 NCH_2), 1.00 (t, ^3J = 7.0 Hz, 4 Me); ^{13}C{^{1}H} NMR (76 MHz, [D_8]THF) δ 113.21 (C-2/5), 104.56 (C-3/4), 41.32 (NCH_2), 14.46 (Me); ^{11}B{^{1}H} NMR (29 MHz, $CDCl_3$) δ 34.8.

Preparation of Co[$C_5H_4B(NMe_2)_2$]$_2$ (1c). A solution of $CoBr_2$(DME) (1.50 g, 4.9 mmol) in THF (60 mL) was added dropwise to a solution of Na(**2c**) (5.83 g, 31.3 mmol) in THF (40 mL) held at −78 °C. The solution was allowed to warm to room temperature, and all volatiles were removed under vacuum. The solid residue was suspended in toluene (20 mL) and filtered over silica. After washing with toluene (3 times 20 mL) the combined filtrates were concentrated under vacuum. Crystallization at −30 °C gave **1c** as a black solid (4.76 g, 79%). Anal. Calcd for $C_{18}H_{32}B_2CoN_4$: C, 56.30; H, 8.38. Found: C, 56.30; H, 8.44. MS (EI): *m*/*z* (I_{rel}) 385 (100, M^+), 287 (5, $M^+ - B(NMe_2)_2$).

Preparation of Co[$C_5H_4B(NEt_2)_2$]$_2$ (1d). The procedure described for **1c** using Li(**2d**) (19.94 g, 88.2 mmol) and $CoBr_2$(THF) (12.48 g, 42.9 mmol) gave **1d** as black crystals (18.84 g (88%). Anal. Calcd for $C_{26}H_{48}B_2CoN_4$: C, 62.80; H, 9.73. Found: C, 62.66; H, 9.51. MS (EI): *m*/*z* (I_{rel}) 497 (14, M^+).

Preparation of [Co{$C_5H_4B(NMe_2)_2$}$_2$]Cl [(1c)Cl]. C_2Cl_6 (5.02 g, 21.2 mmol) was added to compound **1c** (7.41 g, 19.2

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mmol) in toluene (150 mL) under vigorous stirring. A yellow powder began to precipitate immediately, and stirring was continued for 4 h. The product was collected on a frit and kept under high vacuum until weight constancy was achieved to give pure (**1c**)Cl (7.99 g, 99%). Crystallization from CH_2Cl_2/hexane (1/1, v/v) afforded clear brown cubes; mp 140−150 °C (dec). Anal. Calcd for $C_{18}H_{32}B_2ClCoN_4$: C, 51.42; H, 7.67; N, 13.32. Found: C, 51.35; H, 7.70; N, 13.24.

Data for (**1c**)Cl: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.09 (s, 4H, 3-/4-H), 5.55 (s, 4H, 2-/5-H), 2.75 (s, 4 NMe_2); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 91.91 (C-2/5), 86.86 (C-3/4), 41.36 (NMe_2); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2) δ 29.7.

Preparation of [Co{$C_5H_4B(NEt_2)_2$}$_2$]Cl [(1d)Cl]. As described for (**1c**)Cl, the reaction of C_2Cl_6 (9.86 g, 41.65 mmol) with **1d** (18.81 g, 37.83 mmol) gave (**1d**)Cl as a yellow powder (19.69 g, 98%); mp 92−97 °C (dec). Anal. Calcd for $C_{26}H_{48}B_2ClCoN_4$: C, 58.62; H, 9.08. Found: C, 58.33; H, 9.10.

Data for (**1d**)Cl: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.04 (m, 4H, 3-/4-H), 5.48 (m, 4H, 2-/5-H), 3.12 (q, ^3J = 7.2 Hz, 8 NCH_2), 1.08 (t, ^3J = 7.2 Hz, 8 Me); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 91.38 (C-2/5), 86.99 (C-3/4), 42.06 (NCH_2), 15.11 (Me); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2) δ 30.7.

Preparation of Co($C_5H_4BCl_2$)($C_5H_4BCl_3$) (5). Liquid BCl_3 (−78 °C, 30 mL) was poured into a stirred solution of compound (**1d**)Cl (18.7 g, 35.1 mmol) in CH_2Cl_2 (300 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature under evaporation of excess BCl_3 and kept stirring at ambient temperature for a further hour. The mixture was quickly poured into vigorously stirred hexane (800 mL) held at −78 °C. The precipitate formed was collected by filtration and dried in a high vacuum to give **5** as pale yellow powder (12.3 g, 91%); mp 188−192 °C (dec). Anal. Calcd for $C_{10}H_8B_2Cl_5Co$: C, 31.12; H, 2.09. Found: C, 31.31; H, 2.22.

Data for **5**: ^{1}H NMR (500 MHz, CD_3NO_2) δ 5.69 (m, 4H, 2-/5-H), 5.67 (m, 4H, 3-/4-H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3NO_2) δ 105 (br, C-1), 89.14 (C-2/5), 88.46 (C-3/4); $^{11}B\{^1H\}$ NMR (160 MHz, CD_3NO_2) δ 12.7; $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2) δ 28.0.

Pinacolysis of 5 and Synthesis of Co[$C_5H_4B(OCMe_2)_2$]($C_5H_4BCl_3$) (9). Pinacol (57.1 mh, 0.483 mmol) in CH_2Cl_2 (10 mL) was added to a stirred suspension of **5** (183.2 mg, 0.475 mmol) in CH_2Cl_2 (10 mL). After 5 min the now clear solution was liberated from all volatiles. The yellow powdery residue was kept under vacuum for 2 h. The material was redissolved in CH_2Cl_2 (5 mL). The solution was filtered, diluted with an equal volume of Et_2O, and cooled to −30 °C to give **9** as yellow crystals (186.0 mg, 91%); mp 183 °C.

Data for **9**: MS (SIMS, 18-crown-6/tetraethylene glycol dimethyl ether) positive ions, *m*/*z* (I_{rel}) 395 (19, $M^+ - Cl$); negative ions, 430 (35, M^-), 35 (38, Cl^-); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (m, *N* = 3.7 Hz, 3′-/4′−H), 5.74 (m, *N* = 3.7 Hz, 2-/5-H), 5.70 (m, *N* = 3.7 Hz, 2′-/5′−H), 5.35 (m, *N* = 4.0 Hz, 3-/4-H), 1.37 (s, 4 Me); dashed H and C atoms belong to the $C_5H_4B(OCMe_2)_2$ ligand; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 89.13 (C′-3/4), 88.99 (C′-2/5), 87.55 (C-2/5), 85.30 (OC), 83.82 (C-3/4), 24.88 (Me); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 30.6, 5.2.

Pinacolysis of 5 and Synthesis of [Co{$C_5H_4B(OCMe_2)_2$}$_2$]Cl [(1h)Cl]. Pinacol (171.2 mg, 1.449 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of **5** (270.9 mg, 0.702 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at ambient temperature for 6 h. The volatiles were removed under vacuum. The yellow powdery residue was suspended in hexane (20 mL), collected on a frit, washed with hexane twice, and finally dissolved in CH_2Cl_2 (10 mL). After mixing the solution with the same volume of toluene, cooling to −30 °C gave (**1h**)Cl as fine yellow needles (329.9 mg, 99%); mp 212 °C (dec).

Data for (**1h**)Cl: MS (SIMS, 18-crown-6/tetraethyleneglycol dimethyl ether) positive ions, *m*/*z* (I_{rel}) 441 (100%, $M^+ - Cl$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.24 (m, *N* = 3.7 Hz, 4H, 3-/4-H), 5.72 (m, *N* = 3.4 Hz, 4H, 2-/5-H), 1.36 (s, 8 Me); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 89.86 (C-2/5), 89.55 (C-3/4), 85.47 (OC), 24.82 (Me); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 30.4.

Table 2. Crystal Data, Data Collection Parameters, and Refinement Results for 11

formula	$C_{10}H_9B_2CoF_4O$
fw/g·mol^{-1}	301.73
cryst size	0.55 × 0.40 × 0.20 mm
T/K	203
cryst syst	monoclinic
space group	*C*2/*c* (No. 15)
a / Å	28.715(3)
b / Å	7.6072(8)
c / Å	23.501(3)
β/deg	125.895(9)
Z	16
V/Å^3	4159(1)
d_{calc}/g·cm^{-3}	1.928
μ/cm^{-1}	16.81
λ/Å	Mo Kα, 0.710 73
F(000)	2400
scan mode	$\Omega-2\theta$
total no. of data	6989
no. of unique obsd data	3888 ($I > 1\sigma$)
scan range/deg	$2.0 < \theta < 27.0$
sec extinction	0.520×10^{-7}
abs corr	empirical − Ψ-scans
no. of variables	334
R	0.0367
R_w	0.0388
GOF	1.104

Methylation of 5 with $SnMe_4$ and Synthesis of Co($C_5H_4BMe_2$)($C_5H_4BCl_3$) (10). $SnMe_4$ (0.70 mL, 5.05 mmol) was added to a suspension of **5** (608.4 mg, 1.58 mmol) in CH_2Cl_2 (20 mL). After stirring at room temperature for 3 days all volatiles were removed under vacuum to give **10** as a pale yellow powder (468.7 mg, 86%). Attempted further purification was unsuccessful.

Data for **10**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.88 (m, *N* = 4.0 Hz, 3-/4-H′), 5.75 (m, *N* = 4.0 Hz, 2-/5-H′), 5.62 (m, *N* = 3.7 Hz, 2-/5-H), 5.31 (m, *N* = 4.0 Hz, 3-/4-H), 1.11 (s, 2 Me); dashed H and C atoms belong to the $C_5H_4BMe_2$ ligand; $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 90.69 (C′-3/4), 90.26 (C′-2/5), 87.58 (C-2/5), 83.99 (C-3/4), 12.2 (br, Me); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2) δ 78.1, 5.3.

Methylation of 5 with Al_2Me_6. Trimethylaluminum (2 M, in toluene, 1.70 mL, 3.40 mmol) was added to a stirred suspension of **5** (992.0 mg, 2.57 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The suspension brightens immediately, and the resulting clear yellow solution was stirred at room temperature for 2 h. Then all volatiles were removed under vacuum. The residue was dissolved in CH_2Cl_2. The product was precipitated by addition of excess hexane, isolated by filtration, and washed with some hexane. Crystallization from CH_2Cl_2 at −30 °C gave (**1b**)$AlCl_4$ (1.12 g, 99%); mp 159 °C (dec). Anal. Calcd for $C_{14}H_{20}AlB_2Cl_4Co$: C, 38.42; H, 4.61. Found: C, 38.25; H, 4.86. Alternatively 1 equiv of NBu_4PF_6 was added before crystallization to give, after cooling to −30 °C, (**1b**)PF_6 (91%, based on (**1b**)$AlCl_4$); mp 185 °C (dec). Anal. Calcd for $C_{14}H_{20}B_2CoF_6P$: C, 40.63; H, 4.87. Found: C, 40.60; H, 5.11.

Data for (**1b**)$AlCl_4$: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.89 (m, *N* = 4.0 Hz, 4H, 3-/4-H), 5.80 (m, *N* = 3.7 Hz, 4H, 2-/5-H), 1.10 (s, 4 Me); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 93.0 (br, C-1), 90.47 (C-2/5), 89.45 (C-3/4), 13.2 (br, Me); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2) δ 76.6.

Data for **(1b)**PF_6: MS (SIMS, DTE/DTT) positive ions, *m*/*z* (I_{rel}) 269 (100, $M^+ - PF_6$), 229 (4, [CoCp($C_5H_4BMe_2$)]$^+$); negative ions, 145 (100, PF_6^-); ^{1}H NMR (500 MHz, CD_3NO_2) δ 5.95 (m, 8H, 2-/3-/4-/5-H), 1.12 (s, 4 Me); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3NO_2) δ 91.63 (C-2/5), 90.58 (C-3/4), 12.6 (br, Me); $^{11}B\{^1H\}$ NMR (160 MHz, CD_3NO_2) δ 78.1; ^{19}F NMR (470 MHz, CD_3NO_2) δ −73.8 (d, ^1J(P−F) = 707 Hz); $^{31}P\{^1H\}$ NMR (202 MHz, CD_3NO_2) δ −145.1 (sept, ^1J(P−F) = 707 Hz).

Preparation of $Co(C_5H_4BMe_2)_2$ (1b). A solution of (**1b**)-$AlCl_4$ (742.0 mg, 1.79 mmol) in CH_2Cl_2 (30 mL) was added with stirring to sodium amalgam, freshly prepared from sodium sand (39.2 mg, 1.71 mmol) and mercury (4.0 g). The yellow solution turned purple after a few minutes. After 2 h the suspension was left to settle, and the clear, deep purple solution was transferred to another flask with the help of a capillary. The residue was washed with hexane. The combined solutions were freed from solvent, and the purple solid was redissolved in hexane. After filtration over silica the volatiles were removed under vacuum to give **1b** as a deep purple solid (288.9 mg, 64%); mp 63 °C. Anal. Calcd for $C_{14}H_{20}B_2Co$: C, 62.53; H, 7.50. Found: C, 62.88; H, 7.37. MS (EI): *m*/*z* (I_{rel}) 269 (100, M^+), 253 (20, $M^+ - CH_4$), 213 (14, $[Co(C_5H_5BH)_2]^+$), 56 (39, BMe_3).

Preparation of $Co(C_5H_4BF_2)_2(\mu$-OH) (11). Commercial AsF_3 (0.30 mL, 6.14 mmol) was added to a solution of **5** in nitromethane (30 mL). The reaction mixture was stirred for 3 h at room temperature, and then all volatiles were removed under vacuum. The residue was suspended in hexane, transferred to a frit covered with silica, washed several times with small amounts of hexane, and finally eluted with nitromethane. The orange-brown eluate was concentrated to a small volume (5 mL) and cooled to −30 °C to give **11** as somewhat brownish orange crystals (471.5 g, 60%); mp 188 °C (dec). Anal. Calcd for $C_{10}H_9B_2CoF_4O$: C, 39.81; H, 3.01. Found: C, 40.03; H, 2.80.

Spectral data for **11**: ^{1}H NMR (500 MHz, CD_3NO_2) δ 6.44 (s, OH), 5.58 (m, N = 3.7 Hz, 4H, 2-/5-H), 5.53 (m, N = 3.7 Hz, 4H, 3-/4-H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3NO_2) δ 88.71 (C-2/5), 86.50 (C-3/4); $^{11}B\{^1H\}$ NMR (160 MHz, CD_3NO_2) δ 3.1 [t, ^1J(B−F) = 49 Hz]; ^{19}F NMR (470 MHz, CD_3NO_2) δ −145 (br, $\nu_{1/2}$ = 146 Hz).

Crystal Structure of 11. Crystal data, data collection parameters, and refinement results are collected in Table 2. The structure was solved and refined with the help of the SHELXS[18] and the SDP[19] program systems. Non-hydrogen atoms were refined with anisotropic displacement parameters, the hydrogen-bonded atoms H1 and H2 were refined isotropically, and all other hydrogen atoms were treated as riding (C−H = 0.98 Å, $U_H = 1.3U_C$).

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Supporting Information Available: Tables of fractional coordinates of all atoms, anisotropic displacement parameters, and bond distances and angles for **11** (6 pages). Ordering information is given on any masthead page.

OM980465M

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(20) Further details of the crystal structure determination are available on request from the Cambridge Crystallographic Data Centre, on quoting the depository number CCDC-102478.