of H$^-$ and CO. The angular deformations have been rationalized in terms of steric effects. Furthermore, in the three series of complexes studied, the general tendency of l(M–P) to vary in the same direction as $\langle \nu(CO) \rangle$ indicates that an increase in the metal Lewis basicity, as inferred from a decrease in $\langle \nu(CO) \rangle$, favors a shortening of the M–P bonds. Our interpretation of the bond length variations is that π bonding might provide a substantial contribution to the changes observed.

Acknowledgment. The authors wish to thank Professors J. Takats and C. Dittmer for providing the IR data pertaining to complexes **8**, **9** and **11**, M. E. Pippy for assistance with the computations, and the Natural Sciences and Engineering Research Council of Canada for financial support to J.L.A.R.

Registry No. $[Fe(P(C_6H_5)_3)_2(CO)_2(NO)]^+[BF_4]^-\cdot CH_2Cl_2$, 96689-06-4.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters for the non-hydrogen atoms, and the geometries of the phenyl rings, disordered BF_4^- anion, and CH_2Cl_2 solvent molecule (32 pages). Ordering information is given on any current masthead page.

Contribution from the Institute of Inorganic Chemistry,
University of Munich, D-8000 Munich 2, Federal Republic of Germany

Competition between Adduct and Cation Formation in Reactions between Diorganylborane Derivatives and Pyridine or Lutidines[1]

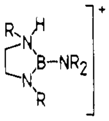
CHAITANYA K. NARULA† and HEINRICH NÖTH*

Received October 9, 1984

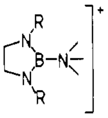
1:1 coordination compounds are formed in the reaction of pyridine and 2,4-lutidine with dibutylboron triflate, 9-(((trifluoromethyl)sulfonyl)oxy)-9-borabicyclo[3.3.1]nonane, and 9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene. In contrast, 2,6-lutidine yields the borenium(1+) triflates **1a**,**b**, with the first two boron triflates. Neutral addition compounds result from the three bases and dibutylboron chloride, 9-chloro-9-borabicyclo[3.3.1]nonane, and 9-chloro-9-borafluorene, respectively. Their interaction with $GaCl_3$ or $AlCl_3$ as chloride acceptors leads to nitrogen base exchange in most cases, but $GaCl_3$ abstracts Cl$^-$ from 9-chloro-9-borafluorene–pyridine ($C_{17}H_{13}BClN$, triclinic, $a = 9.721$ (2) Å, $b = 11.439$ (2) Å, $c = 13.767$ (3) Å, $\alpha = 92.55$ (2)°, $\beta = 103.27$ (2)°, $\gamma = 105.46$ (6)°, space group $P\bar{1}$, $Z = 4$) to form the red 9-borafluorenium tetrachlorogallate–pyridine compound **12**, while 9-chloro-9-borafluorene–acridine and aluminum chloride yield the dark red tetrachloroaluminate **14**, whose structure has been determined by X-ray crystallography ($C_{25}H_{17}AlBCl_4N$, triclinic, $a = 9.401$ (5) Å, $b = 9.621$ (6) Å, $c = 16.183$ (9) Å, $\alpha = 103.71$ (5)°, $\beta = 92.86$ (4)°, $\gamma = 117.15$ (4)°, space group $P\bar{1}$, $Z = 2$). The cation in **14** shows almost planar acridine and 9-borafluorene moieties, whose planes form an interplanar angle of 62°. Characteristic for the cation are short B–C bonds (1.46 Å) and a very long C–C single bond (1.66 Å) of the five-membered borole ring. The formation of base-stabilized diorganylborenium(1+) ions depends on steric and electronic effects.

Introduction

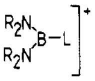
Recent studies have firmly established the existence of tricoordinated borenium salts of type A–C.[2-4] Obviously, the nitrogen atoms help to stabilize these cations by π back-bonding to boron, thus delocalizing the positive charge. This effect decreases as the amino groups are replaced by aryl or alkyl groups, and consequently, salts containing cations of type $R_2N(R')BL^+$ (L = ligand) are considerably less stable.[5] Our current interest in tricoordinated borenium salts, which results from attempts to better understand the mechanism of substitution at tricoordinated boron atoms, and scanty reports on these ions in the literature,[6-8] the majority of which have been found by us to be incorrect,[9] prompted us to study reactions between selected diorganylborane derivatives and suitable donor molecules in order to find limiting factors for the competition between adduct and salt formation according to eq 1.



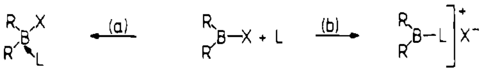
A



B



C



(1)

Experimental Section

All experimental manipulations were conducted under rigorously anhydrous conditions in a high-vacuum system and/or by the Schlenk tube technique in an oxygen-free nitrogen atmosphere. Solvents were dried by standard techniques and stored under nitrogen. Pyridine, 2,4- and 2,6-lutidine, and acridine were commercial products. They were dried, distilled, or recrystallized before use. Trifluoromethanesulfonic acid and silver triflate were purchased from Fluka Corp. and used as supplied. Dibutylboron triflate and 9-(((trifluoromethyl)sulfonyl)oxy)-9-borabicyclo[3.3.1]nonane were prepared according to literature procedures,[10] and the same holds for the chlorides.[10] The 9-borafluorene derivatives have been obtained via o,o'-biphenylmercury and BCl_3.[11]

NMR spectra were recorded on a JEOL FX 90 or a Bruker WP 200 PFT multinuclei NMR spectrometer. Chemical shifts refer to Me_4Si (^1H) and $BF_3\cdot OEt_2$ (^{11}B), respectively. Positive δ values correspond to frequencies higher than the standard. A SYNTEX R3 automated four-circle diffractometer was used for intensity data collection, and computations were performed on a NOVA 3 computer using SHELXTL programs. Elemental analyses were obtained from the Institute's microanalytical laboratory.

General Procedure. A solution of the diorganylborane was cooled to −78 °C, and the solution of the base, usually in the same solvent, was

---

† Aldexander von-Humboldt Fellow.

(1) Contribution to the Chemistry of Boron. 150. For contribution 149 in this series see ref 3.

(2) Narula, C. K.; Nöth, H. *Inorg. Chem.* **1984**, *23*, 4147.

(3) Narula, C. K.; Nöth, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1023.

(4) Nöth, H.; Rasthofer, B., unpublished results. See also: Rasthofer, B. Dissertation, University of Munich, 1984.

(5) An example of this type is $[tmpB(CH_3)py]AlCl_4$ (tmp = 2,2,6,6-tetramethylpiperidino), which decomposes at −20 °C. Weber, S. Thesis, University of Munich, 1981.

(6) Davidson, J. M.; French, C. M. *J. Chem. Soc.* **1958**, *144*; **1962**, 3364. Moodie, R. B.; Elliel, B. *Chem. Ind.* (*London*) **1966**, 761. Armstrong, D. R.; Perkins, P. G. *J. Chem. Soc. A* **1966**, 1026.

(7) Köster, R. "Houben-Weyl, Methoden der Organischen Chemie", 4th ed.; G. Thieme: Stuttgart, New York, 1983; Vol. 13/3b, p 414.

(8) Shchegoleva, T. A.; Mikhailov, B. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 714.

(9) Narula, C. K.; Nöth, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *B38*, 1161. See also unpublished results for these authors.

(10) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 3099.

(11) Narula, C. K.; Nöth, H. *J. Organomet. Chem.* **1985**, *281*, 131.

slowly added with stirring. In most cases a precipitate formed (in some cases only two liquid phases). The mixture was then allowed to warm to room temperature, and a sample was used for ^{11}B NMR studies. Usually a quantitative reaction was noted. Volatiles were either partly removed in vacuo, if a solid had formed, or quantitatively, if the product was an oil. The compounds were washed with cold pentane and dried in vacuo. Results are summarized in Table I.

Pyridine–9-Borafluorenium(1+) Tetrachlorogallate (12). A solution of $GaCl_3$ (0.50 g, 2.8 mmol) in dichloromethane (10 mL) was added to a stirred solution of the adduct **11a** (0.80 g, 2.9 mmol) in the same solvent (40 mL) at −78 °C. A red precipitate separated, which was isolated after gradually warming the suspension to ambient temperature: yield 0.82 g of **12** (63%); mp 142 °C dec. anal. Calcd for $C_{17}H_{13}BCl_4GaN$: C, 45.0; H, 2.9; N, 3.1. Found: C, 44.1; H, 3.4; N, 3.0.

Reaction of 9-Chloro-9-borabicyclo[3.3.1]nonane–Pyridine (7d) with Gallium Chloride. A solution of 0.19 g of **7d** in 5 mL of dichloromethane was mixed with a solution of 0.14 g of pyridine (0.8 mmol) in 10 mL of CH_2Cl_2. No apparent reaction took place, but the ^{11}B NMR spectrum (δ 69.7, 58.5, 6.1; ratio 3:2:2) shows it to be a mixture of compounds.

A 0.129-g amount of **7d** was added to a freshly prepared solution of $GaCl_3 \cdot py$ (0.147 g of $GaCl_3$, 0.06 g of pyridine) in 5 mL of dichloromethane. An ^{11}B NMR spectrum showed only one signal at $\delta(^{11}B)$ = 58.5 1 h after mixing. It is comparatively broad. One day later a signal at 6 ppm of low intensity appeared; however, no signal at 69.7 ppm could be detected.

Reaction of 9-Chloro-9-borabicyclo[3.3.1]nonane–2,4-Lutidine (7e) with Gallium Chloride. A 0.17-g amount of **7e** (0.64 mmol) was dissolved in 5 mL of dichloromethane. On addition of 0.11 g of $GaCl_3$ in 10 mL CH_2Cl_2 a clear solution was produced. The ^{11}B NMR spectrum showed a signal at 58.5 ppm.

Reaction of 9-Chloro-9-borafluorene–2,4-Lutidine (11b) with Gallium Chloride. To a solution of **11b** (0.34 g, 1.1 mmol) in 5 mL of CH_2Cl_2 was added a solution of 0.192 g of $GaCl_3$ in 10 mL of CH_2Cl_2 at −78 °C. After the solutions were mixed and warmed to room temperature, three ^{11}B NMR signals were observed, indicating the presence of a mixture of compounds. On removal of solvent a solid remained; however, on attempt to recrystallize from dichloromethane–hexane, only an oil was obtained. The ^{11}B NMR spectrum of this oil showed only one signal at 8.5 ppm, but its ^{1}H spectrum exhibited two sets of signals for 2,4-lutidine molecules. The data suggest the formation of a mixture of **11b** with 2,4-lutidine–gallium chloride.

Reaction of 9-Chloro-9-borafluorene–2,6-Lutidine (11c) with Gallium Chloride. The experiment was carried out as for the previous one. A 0.44-g amount of **11c** (1.44 mmol) was reacted with 0.25 g of $GaCl_3$ (1.43 mmol) in 50 mL of CH_2Cl_2. Only a single signal at $\delta(^{11}B)$ = 61 was observed, showing the formation of 9-chloro-9-borafluorene (**10**) (lit.[11] $\delta(^{11}B)$ = 61.5).

Acridine–9-Borafluorenium(1+) Tetrachloroaluminate (14). On slow addition of a solution of acridine (0.78 g, 4.36 mmol) in 10 mL of CH_2Cl_2 to 9-chloro-9-borafluorene (0.87 g, 4.38 mmol) in 50 mL of hexane at −78 °C a yellow precipitate separated, which was filtered, washed with hexane, and dried in vacuo; yield 1.28 g of **13** (78%). Anhydrous, freshly sublimed $AlCl_3$ (0.45 g, 3.37 mmol) was added to a solution of this acridine adduct (0.450 g, 3.37 mmol) in 30 mL of CH_2Cl_2 at −78 °C. The mixture was vividly stirred until dissolution of $AlCl_3$ was complete at room temperature. The ^{11}B NMR spectrum of the orange solution showed a broad signal at 43.5 ppm. The solution was then layered with hexane (30 mL). After 24 h crystallization was complete and the crystalline material was isolated, washed with pentane (10 mL), and dried. This material showed the presence of yellow, orange, and red crystals. Mechanical separation was possible. The yellow crystals, mp 156 °C, showed a fairly sharp ^{27}Al NMR signal at 103.8 ppm ($h_{1/2}$ = 38 Hz) and proved to be the acridine adduct of $AlCl_3$ (by independent synthesis). The orange crystals were too few for full characterization. The bulk (~70%) of the material consisted of red plates, which were characterized by X-ray analysis (vide infra) to be 9-borafluorenium tetrachloroaluminate–9-Acridine (**14**): $\delta(^{27}Al)$ = 104.0, $h_{1/2}$ = 46 Hz (CH_2Cl_2 solution).

Crystal Structure Determination of 11a and 14. Relevant information concerning the crystallographic study of **11a** and **14** is represented in Table II. Single crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **11a** and **14** under an argon atmosphere. Only large plates of **14** were obtained, and a fragment cut from one of the plates was used. Crystals were mounted under argon in glass capillaries. The setting angles of 25 automatically centered reflections (2θ = 20–30°) were used to determine the orientation matrices and cell dimensions, which were checked by axial photographs. Graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å) was used.

Intensity data were collected in the ω mode ($\pm h,+k,+l$ for **11a** and $+h,\pm k,\pm l$ for **14**). Two control reflections were monitored every 48 reflections (intensity decrease in both cases <3%, but less than 0.2% between every 48 reflections).

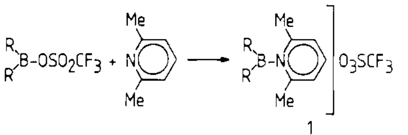
The structures were solved by direct methods.[12] All non-hydrogen atoms were located in the best E map of **11a**. Isotropic refinement converged in eight cycles of a full-matrix least-squares calculation to R = 0.13, and anisotropic refinement with blocked-cascade calculations proceeded to R = 0.07. The function $\sum w\Delta^2$ was minimized. The positions of the hydrogen atoms were then located in a difference Fourier map and included with individual isotropic temperature factors in the final refinement.

The best E map of **14** revealed the positions of the $AlCl_4$ and the 9-borafluorene units and part of the acridine molecule. All atoms of the last species were found in a difference Fourier map. After isotropic and anisotropic refinement all but three hydrogen atoms could be located. Therefore, all hydrogen positions were calculated (d(C–H) = 0.98 Å) and included in the final refinement with a fixed U_i = 0.08 for all hydrogen atoms. A total of 290 parameters were refined, and the calculations converged at R = 0.109, R_w = 0.108. Definitions are $R = \sum|\Delta F|/\sum|F_o|$, $R_w = \sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|$, and $w = (\sigma(F_o) + 0.0003F_o^2)^{-1}$ for both structure determinations.

Atomic scattering factors as implemented in the SHELXTL program package were used, and those of Al were taken from ref 30. Final atomic coordinates for the non-hydrogen atoms, including U_{eq} values ($^1/_3$ of the trace of the orthogonalized anisotropic U_{ii} tensor) are given in Table III and IV. Coordinates of the hydrogen atoms and other material is available as supplementary material.

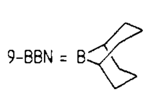
Results and Discussion

Three methods have so far been used by us to generate tricoordinated borenium salts: (i) the reaction of superacids with aminoboranes,[1-3] (ii) attack of a base on adducts of $AlCl_3$ with 2-halo-1,3-dimethyl-1,3,2-diazaborolidines,[2] and (iii) nucleophilic attack on a boron atom in a borane derivative carrying an excellent leaving group such as a triflate group.[2,3] The third method was now found to be suitable for generating diorganylborenium salts. However, this reaction requires *steric assistance* as shown in eq 2 because both pyridine and 2,4-lutidine react with dibutylboron triflate or 9-(((trifluoromethyl)sulfonyl)oxy)-9-borabicyclo[3.3.1]nonane, 9-BBN-OTf, only with the formation of classical 1:1 acid–base adducts containing tetracoordinated boron as shown in eq 3.



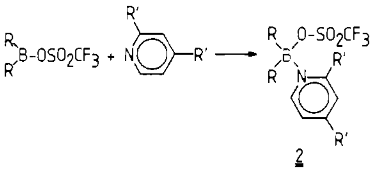
1

(2)



Bu ■ n-C_4H_9

	1a	**1b**
R_2B	Bu_2B	9-BBN



2

(3)

	2a	**2b**	**2c**	**2d**
R_2B	Bu_2B	Bu_2B	9-BBN	9-BBN
R'	H	CH_3	H	CH_3

The ionic compounds **1a,b** are soluble in chlorinated hydrocarbons such as dichloro- and trichloromethane but are insoluble in hydrocarbons. Although solid at −40 °C, they are viscous oils at ambient temperatures. One reason that these compounds are not solid seems to be due to the fact that they exist in solution

---

(12) Sheldrick, G. M. "Shelx-76 Program for Crystal Structure Determination"; Cambridge University: Cambridge, England, 1976.

(13) The results of these reactions will be published in due course, a typical example being the 1:1 adduct of triflic acid with 2-dimethylamino-1,3-dimethyl-1,3,2-diazaborolidine.

Table I

a. Experimental Data Concerning the Reaction of Diorganylboranes with Pyridine Bases[c]

no.	compd	amt of borane, g (mmol)	amt of base, g (mmol)	solvent (amt, mL)	yield, g (%)	mp, °C	formula	anal. calcd (found)		
								% C	% H	% N
1a	2,6-lutidine–dibutylborenium triflate	3.35 (12.2)	1.38 (12.8)	CH_2Cl_2 (30)	4.5 (100)	*a*	$C_{16}H_{27}BF_3NO_3S$		*b*	
1b	2,6-lutidine-9-boreniabicyclo[3.3.1]nonyl triflate	0.54 (2.0)	0.22 (2.0)	CH_2Cl_2 (10)	0.67 (88)	*a*	$C_{16}H_{23}BF_3NO_3S$		*b*	
						a				
3	bipyridine–dibutylboronium triflate	0.52 (1.9)	0.30 (1.9)	CH_2Cl_2 (50)	0.76 (92)	74	$C_{19}H_{26}BF_3N_2O_3S$	53.0 (50.1)	6.1 (5.1)	3.7
2b	dibutyl(((trifluoromethyl)sulfonyl)oxy)borane–2,4-lutidine	0.56 (2.0)	0.22 (2.0)	pentane (40)	0.67	*a*	$C_{16}H_{27}BF_3NO_3S$	50.4 (48.5)	7.1 (6.7)	3.7 (4.0)
2d	9-(((trifluoromethyl)sulfonyl)oxy)-9-borabicyclo[3.3.1]nonane–2,4-lutidine	0.59 (2.2)	0.24 (2.2)	pentane	0.69	77	$C_{16}H_{23}BF_3NO_3S$	50.9 (52.6)	6.1 (6.4)	3.7 (3.8)
2c	9-(((trifluoromethyl)sulfonyl)oxy)-9-borabicyclo[3.3.1]nonane–pyridine	0.99 (3.7)	0.29 (3.7)	hexane (15)	1.03 (80)	192	$C_{14}H_{19}BF_3NO_3S$	48.2 (45.3)	5.5 (5.3)	4.0 (4.8)
2a	dibutyl(((trifluoromethyl)sulfonyl)oxy)borane–pyridine	0.76 (2.8)	0.22 (2.8)	hexane (10)	0.80 (81)	*a*	$C_{14}H_{23}BF_3NO_3S$	47.6 (43.8)	6.56 (5.94)	3.97 (4.39)
	9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene–pyridine	0.53 (1.7)	0.13 (1.7)	hexane (50)	1.45 (68)	137	$C_{18}H_{13}BF_3NO_3S$	55.27 (52.4)	3.35 (4.33)	3.58 (3.62)
	9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene–2,4-lutidine	0.68 (2.2)	0.23 (2.1)	hexane	0.36 (40)	62	$C_{20}H_{17}BF_3NO_3S$	57.30 (52.1)	4.09 (4.33)	3.34 (3.26)
	9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene–2,6-lutidine	1.02 (3.26)	0.35 (3.26)	hexane	1.00 (73)	*a*	$C_{20}H_{17}BF_3NO_3S$	57.30 (52.6)	4.09 (3.95)	3.34 (2.36)
7a	dibutylchloroborane–pyridine	0.657 (4.0)	0.32 (4.0)	hexane	0.63 (65)	*a*	$C_{13}H_{23}BClN$		*b*	
7b	dibutylchloroborane–2,4-lutidine	0.332 (2.06)	0.22 (2.05)	hexane (15)	0.31 (56)	*a*	$C_{15}H_{27}BClN$		*b*	
7c	dibutylchloroborane–2,6-lutidine	0.404 (2.51)	0.27 (2.51)	hexane (15)	0.49 (73)	*a*	$C_{15}H_{27}BClN$		*b*	
7d	9-chloro-9-borabicyclo[3.3.1]nonane–pyridine	0.83 (5.3)	0.42 (5.3)	pentane (35)	0.81 (65)	139	$C_{13}H_{19}BClN$	66.28 (63.3)	8.13 (7.6)	5.95 (5.75)
7e	9-chloro-9-borabicyclo[3.3.1]nonane–2,4-lutidine	0.45 (2.8)	0.31 (2.9)	pentane	0.43 (57)	194	$C_{15}H_{23}BClN$	68.30 (63.7)	8.79 (8.0)	5.31 (5.1)
7f	9-chloro-9-borabicyclo[3.3.1]nonane–2,6-lutidine	0.80 (5.0)	0.55 (5.1)	pentane	0.15 (11)	226	$C_{15}H_{23}BClN$	68.30 (52.9)	8.79 (6.57)	5.31 (5.4)
11a	9-chloro-9-borafluorene–pyridine	1.17 (5.9)	0.47 (5.9)	hexane	1.17 (71)	165	$C_{17}H_{13}BClN$	73.56 (71.7)	4.72 (4.9)	5.07 (5.1)
11b	9-chloro-9-borafluorene–2,4-lutidine	0.733 (3.69)	0.395 (3.69)	hexane (20)	0.87 (77)	192	$C_{19}H_{17}BClN$	74.67 (72.9)	5.61 (5.78)	4.58 (4.49)
11c	9-chloro-9-borafluorene–2,6-lutidine	0.94 (4.74)	0.49 (4.6)	hexane	1.12 (80)	186	$C_{19}H_{17}BClN$	74.67 (71.2)	5.61 (5.8)	4.58 (4.25)

b. NMR Data of the Products[d]

compd	$\delta(^{11}B)$	$\delta(^{1}H)$	solvent
1a	54.7	0.71–1.26 m (18 H), 2.57 s (8 H), 7.38–8.08 m (3 H)	$CDCl_3$
1b	59.2, 36.8	1.07–1.81 m (14 H), 2.68 s (6 H), 7.37–8.13 m (3 H)	$CDCl_3$
3	10.9	0.52–1.26 m (18 H), 8.02–9.04 m (8 H)	$CDCl_3$
2b	9.0	0.85–1.15 m (18 H), 1.75 s (3 H), 2.09 s (3 H), 7–8.23 m (3 H)	C_6D_6
2d	14.8	1.93–2.67 m (17 H), 2.98 s (3 H), 7.08–9.13 (3 H)	C_6D_6
2c	13.4	1.15–1.85 m (14 H), 7.6–8.95 m (5 H)	$CDCl_3$
2a	12.2	0.71–1.29 m (18 H), 6.5–8.13 m (5 H)	C_6D_6
9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene–pyridine	9.3	7.06–8.82 m	$CDCl_3$
9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene–2,4-lutidine	9.9	2.23 s, 2.47 s, 2.57 s, 2.75 s, 7.0–8.92 m	$CDCl_3$
9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene–2,6-lutidine	14.1	2.42 s (6 H), 6.93–7.81 m (11 H)	$CDCl_3$
7a	10.8	0.71–1.06 m (18 H), 7.49–8.84 m (5 H)	$CDCl_3$
7b	15.3	0.71–1.25 m (18 H), 2.48 s (3 H), 2.86 s (3 H)	$CDCl_3$
7c	31.5	0.77–1.43 (18 H), 2.88 s (6 H), 7.17–8.13 m (3 H)	$CDCl_3$
7d	9.9	1.19–2.33 m (14 H), 7.26–8.88 m (5 H)	$CDCl_3$
7e	11.3	1.2–1.81 (14 H), 2.44 bs (3 H), 2.87 s (3 H)	$CDCl_3$
7f	59.2	1.37–1.96 m (14 H), 2.99 s (6 H), 7.27–8.18 m (3 H)	$CDCl_3$
11a	6.3	6.94–8.92 m	$CDCl_3$
11b	6.3	2.0 s (3 H), 2.40 s (3 H), 6.98–9.84 (11 H)	$CDCl_3$
11c	24.6	2.83 s (6 H), 7.09–8.11 m (11 H)	CH_2Cl_2

[a] Oil at 20 °C. [b] Analyses considerably low although no impurity in ^{1}H NMR. Anal. Calcd for 1a: Cl, 13.25. Found: Cl, 12.82. Calcd for 7b: Cl, 13.25. Found: Cl, 12.47. Calcd for 7a: Cl, 14.80. Found: Cl, 13.88. [c] Elemental analyses are often low although no impurities were detected by NMR spectroscopy. [d] Standards: $BF_3 \cdot O(C_2H_5)_2$, Me_4Si.

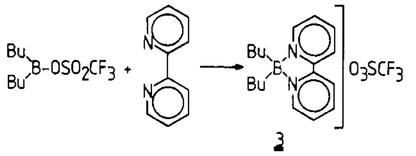
Table II. Crystallographic Data of **11a** and **14** and Information on Data Collection (at 18 °C)

	11a	**14**
formula	$C_{17}H_{13}BClN$	$C_{25}H_{17}AlBCl_4N$
fw	277.56	511.02
cryst dimens, mm	0.2 × 0.3 × 0.45	0.3 × 0.2 × 0.4
unit cell constants (18 ∓ 1 °C)		
a, Å	9.721 (2)	9.401 (5)
b, Å	11.439 (2)	9.621 (6)
c, Å	13.767 (3)	16.183 (9)
α, deg	92.55 (2)	103.71 (5)
β, deg	103.27 (2)	92.86 (4)
γ, deg	105.46 (6)	117.15 (4)
V, Å^3	1426.9 (5)	1245.1 (12)
Z	4	2
D_{calcd}, g cm^{-3}	1.292	1.363
space group	$P\bar{1}$	$P\bar{1}$
μ, cm^{-1}	2.52	5.25
2θ range, deg	2–50	2–50
scan rate, deg min^{-1}	2.5–29.3	1.5–29.3
scan width, deg	0.8	0.9
no. of indep reflcns	5378	4376
no. with $I > 3\sigma(I)$	4243	2901
no. of refined variables	465	290
final R	0.0421	0.109
final R_w	0.0434	0.108

in an equilibrium with their starting materials. Thus, the ^{11}B NMR spectrum of **1b** in CH_2Cl_2 solution shows two signals at 59 and 37 ppm (ratio 1:8), while **1a** produces only a single, broad signal at 55 ppm. Therefore, exchange of the 2,6-lutidine seems faster on the NMR time scale for **1a** than for **1b**. This is substantiated by the fact that only a single signal is observed even at −78 °C for the methyl groups of 2,6-lutidine in the ^1H NMR spectra. A single broad quartet for a CF_3 group at $\delta(^{13}C) = 119$ provides evidence for exchange between free and bonded triflate. Free triflate is reported to exhibit a ^{13}C chemical shift of 120.6 ppm,[14] whereas the triflate group of 9-BBN-OTf shows a ^{13}C NMR signal at 118.1 ppm. In CH_2Cl_2 an equivalent conductance of 9.7 Ω cm^{-1} was determined for **1a**.

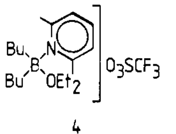
If dibutylboron triflate is treated with only $^1/_2$ equiv of 2,6-lutidine, then two well-separated CH_3 proton NMR signals can be observed at −78 °C in dichloromethane solution, and these coalesce at −20 °C, resulting in a single sharp line at 25 °C. Therefore, **1a** exhibits base exchange at room temperature.

When diethyl ether is added to a solution of **1a** in CH_2Cl_2, a solid precipitates, which, on removal of excess solvent in vacuo, leaves unchanged **1a**. The ^{11}B NMR signal of **1a** in the ether solution was found at $\delta(^{11}B) = 7$. This shift is comparable with $\delta(^{11}B) = 10.9$ recorded for bipyridine–dibutylboronium(1+) triflate (**3**), formed according to eq 4. Therefore, NMR provides evidence for a tetracoordinated boronium salt **4** containing loosely bound diethyl ether.

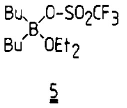


3

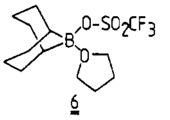
(4)



4



5



6

Dibutylboron triflate, on the other hand, gives a nonconducting solution in diethyl ether and exhibits an ^{11}B chemical shift of 22 ppm in ether solution, indicating weakly coordinated ether in a coordination compound (**5**). The same holds true for a solution of 9-BBN-OTf in tetrahydrofuran ($\delta(^{11}B) = 18$), and we suggest the formation of **6** in solution. However, polymerization prevented further exploration of these solutions.[15]

Table III. Fractional Atomic Coordinates (×10^4) for Non-Hydrogen Atoms and Equivalent Anisotropic Parameters of the Temperature Factor Exponent (Å^2 × 10^3) for 9-Chloro-9-borafluorene–Pyridine (**11a**)[a]

	x/a	y/b	z/c	U_{eq}
		Molecule A		
Cl	5443 (1)	2697 (1)	5487 (1)	62 (0)
B	4046 (2)	1706 (2)	6092 (2)	43 (1)
N	2758 (2)	860 (1)	5177 (1)	41 (1)
C1	4559 (2)	1251 (2)	7834 (1)	43 (1)
C2	4780 (2)	937 (2)	6896 (1)	42 (1)
C3	5563 (2)	96 (2)	6829 (1)	52 (1)
C4	6123 (2)	−419 (2)	7669 (2)	57 (1)
C5	5899 (2)	−94 (2)	8589 (2)	56 (1)
C6	5115 (2)	734 (2)	8680 (2)	51 (1)
C7	3708 (2)	2153 (2)	7758 (1)	43 (1)
C8	3257 (2)	2669 (2)	8520 (2)	58 (1)
C9	2426 (3)	3481 (2)	8297 (2)	64 (1)
C10	2072 (2)	3796 (2)	7330 (2)	62 (1)
C11	2551 (2)	3300 (2)	6574 (2)	51 (1)
C12	3371 (2)	2473 (2)	6772 (1)	43 (1)
C21	2171 (2)	−332 (2)	5235 (2)	49 (1)
C22	1023 (2)	−1047 (2)	4492 (2)	57 (1)
C23	432 (2)	−548 (2)	3666 (2)	51 (1)
C24	1024 (2)	669 (2)	3607 (1)	54 (1)
C25	2178 (2)	1350 (2)	4365 (1)	50 (1)
		Molecule B		
Cl	1035 (1)	−432 (1)	8982 (0)	50 (2)
B	469 (2)	−2168 (2)	8804 (2)	40 (1)
N	1167 (2)	−2587 (1)	9861 (1)	42 (1)
C1	−341 (2)	−3396 (2)	7171 (1)	48 (1)
C2	941 (2)	−2664 (2)	7861 (1)	43 (1)
C3	2280 (2)	−2431 (2)	7600 (2)	56 (1)
C4	2347 (3)	−2923 (2)	6673 (2)	69 (1)
C5	1075 (3)	−3637 (2)	6008 (2)	76 (1)
C6	−273 (3)	−3881 (2)	6247 (2)	65 (1)
C7	−1665 (2)	−3473 (2)	7553 (2)	47 (1)
C8	−3146 (3)	−4107 (2)	7108 (2)	67 (1)
C9	−4206 (3)	−4038 (3)	7614 (3)	78 (1)
C10	−3841 (3)	−3353 (2)	8531 (2)	71 (1)
C11	−2389 (2)	−2715 (2)	8961 (2)	55 (1)
C12	−1284 (2)	−2767 (2)	8490 (1)	43 (1)
C21	1005 (2)	−2105 (2)	10719 (1)	50 (1)
C22	1466 (3)	−2526 (2)	11628 (2)	60 (1)
C23	2126 (3)	−3436 (2)	11669 (2)	72 (1)
C24	2306 (3)	−3928 (2)	10790 (2)	79 (1)
C25	1810 (3)	−3493 (2)	9893 (2)	62 (1)

[a] Estimated standard deviations in parentheses.

Chemical shifts $\delta(^{11}B)$ in the range 9–15 were observed for the 1:1 adducts of pyridine and 2,4-lutidine with dibutylboron and 9-BBN-OTf, and this is good evidence that the adducts contain tetracoordinated boron. The boron nuclei in the borenium salts **1a,b** are deshielded with respect to the coordination compounds **2a–d**, and this demonstrates the importance of steric effects to stabilize the cations.

Dibutylboron chloride ($\delta(^{11}B) = 77.0$) and 9-chloro-9-borabicyclo[3.3.1]nonane (9-BBN-Cl) ($\delta(^{11}B) = 82$)[16] furnish only

---

(14) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470.

(15) It has been claimed that 9-((methylsulfonyl)oxy)-9-borabicyclo[3.3.1]nonane in THF solution yields 9-tetrahydrofuran-9-boreniabicyclo[3.3.1]nonyl methanesulfonate (Köster, R.; Dahlhoff, W. In ref 7, p 420). In the absence of any supporting data we believe this compound to be a coordination compound in analogy of **6**, based on the fact that the CH_3SO_3 group is not a better leaving group than CF_3SO_3. Another possible explanation is the formation of 9-BBN-$OC_4H_8OSO_2CH_3$ in analogy with the reaction of 9-BBN-Cl with THF. Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1.

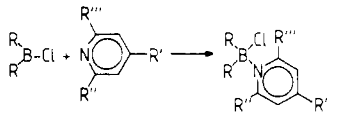
(16) Nöth, H.; Wrackmeyer, B. "Nuclear Magnetic Resonance Spectroscopy of Boron Compounds"; Springer-Verlag: Berlin, Heidelberg, New York, 1978. $\delta(^{11}B) = 82$; see also: Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1.

Table IV. Fractional Atomic Coordinates ($\times 10^4$) for Non-Hydrogen Atoms and Equivalent Anisotropic Parameters of the Temperature Factor Exponent ($Å^2 \times 10^3$) for 9-Acridine–9-Borafluorenium(1+) Tetrachloroaluminate (**14**)[b]

atom	x/a	y/b	z/c	U_{eq}[a]
Al	7604 (3)	1231 (3)	2784 (1)	61 (1)
Cl(1)	7741 (3)	−958 (3)	2625 (2)	116 (2)
Cl(2)	5243 (3)	739 (3)	3052 (2)	104 (1)
Cl(3)	9410 (3)	3171 (3)	3823 (1)	101 (1)
Cl(4)	7898 (4)	1925 (3)	1635 (1)	123 (2)
N	6658 (8)	4306 (7)	7153 (4)	85 (4)
B	7002 (9)	5436 (10)	8159 (6)	66 (4)
C(11)	7505 (8)	7166 (8)	8391 (4)	63 (4)
C(12)	7892 (10)	8253 (9)	7890 (5)	85 (5)
C(13)	8314 (11)	9969 (14)	8358 (10)	136 (7)
C(14)	8312 (12)	10232 (1)	9288 (10)	126 (7)
C(15)	7979 (14)	9036 (21)	9713 (8)	169 (10)
C(16)	7627 (10)	7626 (12)	9286 (6)	101 (6)
C(17)	7182 (9)	5989 (9)	9622 (5)	80 (4)
C(18)	7103 (11)	5762 (12)	10405 (5)	105 (6)
C(19)	6648 (12)	4219 (12)	10491 (5)	104 (7)
C(20)	6276 (11)	2934 (10)	9754 (5)	89 (5)
C(21)	6357 (10)	3205 (8)	8949 (5)	76 (4)
C(22)	6824 (8)	4740 (8)	8892 (4)	68 (4)
C(31)	7556 (8)	3524 (8)	6891 (4)	64 (4)
C(32)	8902 (9)	3694 (8)	7426 (4)	67 (4)
C(33)	9739 (12)	2925 (11)	7143 (6)	94 (6)
C(34)	9400 (13)	2002 (11)	6382 (6)	117 (7)
C(35)	8300 (11)	1751 (9)	5782 (5)	89 (5)
C(36)	7211 (11)	2519 (10)	5995 (5)	108 (5)
C(37)	6058 (15)	2372 (11)	5442 (5)	151 (7)
C(38)	5120 (11)	3119 (9)	5718 (6)	89 (5)
C(39)	3826 (13)	2871 (11)	5064 (5)	112 (6)
C(40)	2976 (11)	3539 (13)	5274 (7)	123 (7)
C(41)	3195 (11)	4485 (11)	6068 (7)	109 (6)
C(42)	4400 (10)	4809 (9)	6736 (5)	83 (5)
C(43)	5401 (9)	4140 (8)	6573 (4)	69 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ii} tensor. [b] Estimated standard deviations in parentheses.

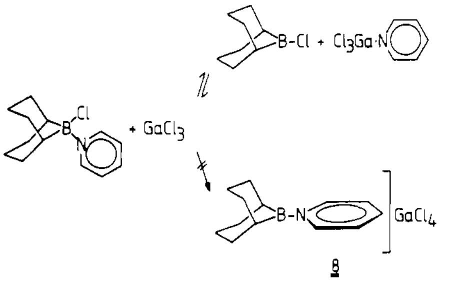
the neutral adducts **7a–f** with pyridine and 2,4- and 2,6-lutidine as shown by eq 5. 2,6-Lutidine is only very weakly bonded to the boron atom in **7c** and **7f**. The latter dissociates in halogenated solvents into its components as deduced from the ^{11}B NMR shifts at 59.2 and 31.6 ppm, respectively, the solutions themselves being electrically nonconducting.



(5)

7

	7a	7b	7c	7d	7e	7f
R_2B	Bu_2B	Bu_2B	Bu_2B	9-BBN	9-BBN	9-BBN
R'	H	CH_3	H	H	CH_3	H
R''	H	CH_3	CH_3	H	CH_3	CH_3
R'''	H	H	CH_3	H	H	CH_3



(6)

(7)

8

When $GaCl_3$ was added to a CH_2Cl_2 solution of **7d**, three ^{11}B NMR signals at 69.7, 58.5, and 6.1 ppm result (intensity ratio 3:2:2). This can be explained in terms of a partial transfer of the ligand pyridine to $GaCl_3$ according to eq 6. The signal at 69.7 ppm may result from the cation 9-BBN·py$^+$. The signal at 58.5 ppm results most likely from an exchange between $GaCl_3$·py and 9-BBN-Cl, the latter being liberated as shown in eq 6. The signal at 6.1 ppm stems from **7d**.

Only a single ^{11}B NMR signal at 58.5 ppm is observed in CH_2Cl_2 solution when $GaCl_3$ is added to **7e** or when gallium trichloride–2,4-lutidine is mixed with 9-BBN-Cl. This signal, which is fairly broad, may result from salt formation or from rapid equilibration according to eq 6. Since the solution is only weakly conducting, the latter explanation is the more likely one. The repression of salt formation in analogy to eq 7 can be understood in terms of greater steric hindrance weakening the strength of the B–N bond both in the adduct and the cation derived thereof, the $GaCl_3$ therefore reacts preferably with the lutidine. Solutions of **7a–c** in dichloro- and trichloromethane exhibit no appreciable ionic dissociation as well as no dissociation into the acid–base components as evidenced by their ^{11}B and ^1H NMR spectra. The $\delta(^{11}B)$ values are very typical for tetracoordinated boron compounds.

The formation of the cations **1a,b** can be rationalized by the weak nucleophilicity of the anions and by steric shielding of the boron atom in **1a,b**. In addition, stabilization of the cations by π bonding between the tricoordinated boron and the heterocyclic base seems to be a contributing factor. Indeed, formation of a Cl_2B·pic cation in solution from Cl_3B·pic and $AlCl_3$ has been reported by Ryschkewitsch et al.[17] The latter effect is very pronounced in the cations of type A–C.

Cation stabilization may also result if the tricoordinated boron atom is part of an aromatic ring system such as 9-borafluorene. Indeed, Köster and Benedikt have reported that the pyridine–9-borafluorenium ion **9** is produced in the reaction of pyridine with 9-chloro-9-borafluorene (**10**) according to eq 8.[18]

We have now found that the coordination compound **11a** is formed instead of **9** as shown by eq 9. Moreover, 2,4- and 2,6-lutidine also yield 1:1 coordination compounds with **10**. The presence of a tetracoordinated boron atom in these adducts is convincingly demonstrated by $\delta(^{11}B) = 6.3$ and 24.6, respectively. The latter value indicates a weakly bonded 2,6-lutidine molecule, resulting from steric crowding.

If a strong chloride ion acceptor such as $GaCl_3$ is added to **11a**, the tetrachlorogallate **12** is formed as a red solid. **12** is insoluble in hydrocarbon solvents and chlorohydrocarbons. The only direct evidence for its ionic nature, as described by eq 10, comes from its IR spectrum: there is a strong band at 373 cm^{-1}, which is typical for $\nu_{as}(GaCl_4)$.[19] However, analogy with the results obtained in the system **10**–$AlCl_3$–acridine supports strongly the ionic nature of **12**. Dissolution of **12** in acetonitrile leads to decoloration and formation of a tetracoordinated boronium salt. When the acridine adduct **13** was reacted with $AlCl_3$, the solution turned red and three compounds were obtained in yellow, orange, and red crystals. Only two of these products were characterized. The yellow crystals are the adduct aluminum chloride–acridine (**15**) and the red crystals the borafluorenium salt **14**. Therefore, the Lewis acid reacts with **13** in at least the two competing reactions (11) and (12) with (11) dominating over (12).

The red color of **12** is a further indication of its ionic structure, since X-ray crystallography proves the ionic nature of **14**, which is also a red compound. Presumably, the color is associated with cation formation and may be due to a π–π^* transition in the 9-borafluorene unit. This assumption, however, needs confirmation.

Earlier MO calculations by Perkins et al.[20] predicted that the 9-borafluorenium ion **16** should be stable. Such an ion would

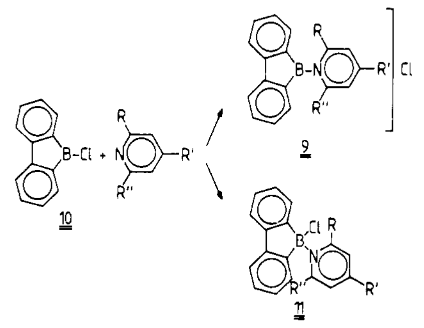
---

(17) Ryschkewitsch, G. E.; Wiggins, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 1790.

(18) Pyridine–9-borafluorenenium(1+) hexachloroantimonate has been reported[7] to be formed from **9** and $SbCl_5$ in $C_2H_2Cl_4$ solution. When a similar reaction was carried out at −78 °C, a blue solution was obtained that sustained the color on raising the temperature to ambient. ^{11}B NMR of the solution shows a signal at $\delta = 7$.

(19) Adams, D. M.; Chatt, J.; Davidson, J. M.; Gerrat, J. *J. Chem. Soc.* **1963**, 2189.

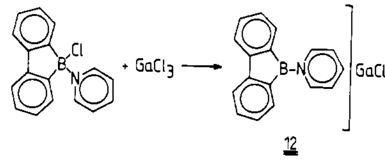
(20) Armstrong, D. R.; Perkins, P. *J. Chem. Soc. A* **1966**, 1026.



(8)

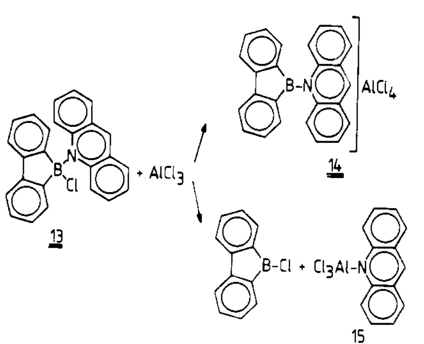
(9)

	9	11a	11b	11c
R	H	H	H	CH3
R'	H	H	CH3	H
R''	H	H	CH3	CH3



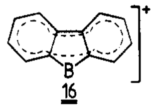
12

(10)

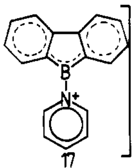


(11)

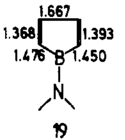
(12)



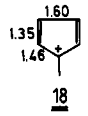
16



17



19



18

contain a dicoordinated boron atom and would be electronically unsaturated because only the p_z orbital of the sp^2-hybridized boron atom could interact with the π system of the ring framework. No compound is known at the present time containing **16**, and this present study indicates that **16** is an unlikely situation. However, if **16** adds a base, stable cations of type **17** result.

In contrast to **1a**,**b**, 9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene adds pyridine and 2,4- and 2,6-lutidine to yield only coordination compounds. Therefore, the steric effect of 2,6-lutidine is insufficient to displace the triflato group from the boron atom in 9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene with salt formation. This result illustrates again that several factors must cooperate in order to achieve cations containing tricoordinated boron and to favorably suppress classical adduct formation.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for 9-Chloro-9-borafluorene–Pyridine (**11a**)[a]

Bond Lengths

	molecule A	molecule B		molecule A	molecule B
B–Cl	1.898 (2)	1.902 (2)	C7–C12	1.408 (3)	1.409 (3)
B–N	1.616 (2)	1.609 (3)	C8–C9	1.386 (4)	1.385 (5)
B–C2	1.602 (3)	1.602 (3)	C9–C10	1.385 (4)	1.376 (5)
B–C12	1.611 (3)	1.604 (3)	C10–C11	1.390 (4)	1.380 (3)
C2–C1	1.404 (3)	1.409 (2)	C11–C12	1.389 (3)	1.383 (3)
C2–C3	1.389 (3)	1.390 (3)	N–C21	1.343 (2)	1.341 (3)
C1–C6	1.394 (3)	1.388 (3)	C21–C22	1.370 (2)	1.381 (3)
C1–C7	1.480 (3)	1.482 (3)	C22–C23	1.371 (3)	1.359 (4)
C3–C4	1.387 (3)	1.394 (4)	C23–C24	1.372 (3)	1.367 (4)
C4–C5	1.385 (3)	1.382 (3)	C24–C25	1.371 (2)	1.384 (3)
C5–C6	1.383 (4)	1.383 (4)	C25–N	1.348 (2)	1.343 (3)
C7–C8	1.390 (3)	1.405 (3)			

Bond Angles

	molecule A	molecule B
Cl–B–N	105.9 (1)	106.3 (1)
Cl–B–C2	112.1 (1)	111.0 (1)
Cl–B–C12	113.7 (1)	113.3 (2)
N–B–C2	113.3 (2)	114.9 (2)
N–B–C12	110.6 (2)	109.9 (2)
C2–B–C12	101.5 (2)	101.6 (1)
B–C2–C1	108.6 (2)	108.3 (2)
B–C2–C3	132.9 (2)	132.7 (2)
C1–C2–C3	118.5 (2)	118.8 (2)
C2–C1–C6	120.8 (2)	120.8 (2)
C2–C1–C7	110.7 (2)	110.9 (2)
C6–C1–C7	128.4 (2)	128.1 (2)
C1–C7–C8	127.6 (2)	129.4 (2)
C1–C7–C12	111.3 (2)	110.8 (2)
C8–C7–C12	121.1 (2)	119.8 (2)
B–C12–C7	107.8 (2)	108.3 (2)
B–C12–C11	133.9 (2)	132.6 (2)
C7–C12–C11	118.3 (2)	119.0 (2)
B–N–C21	120.9 (2)	120.2 (2)
B–N–C25	120.7 (1)	120.8 (2)
C21–N–C25	118.3 (1)	118.8 (2)

[a] Estimated standard deviations in parentheses.

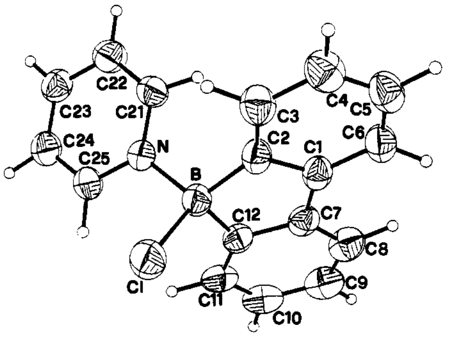


Figure 1. ORTEP plot of one of the two crystallographically independent **11a** molecules. Thermal ellipsoids represent a 50% probability level.

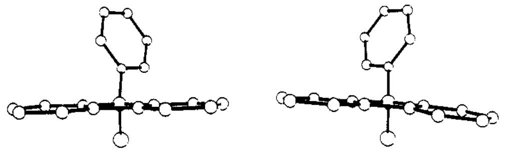


Figure 2. Plots of the two enantiomeric **11a** molecules as viewed down the 9-borafluorene unit, demonstrating the different orientations of the pyridine ring.

X-ray crystal structures of **11a** and the tetrachloroaluminate **14** have been determined in order to establish their constitutions unambiguously and to study the influence of tetra- and tricoordinated boron on the 9-borafluorene ring. Tables V and VI contain selected bond lengths and angles, and Figures 1 and 3 show plots of the molecular structures.

The pyridine adduct of 9-chloro-9-borafluorene crystallizes in the triclinic space group $P\bar{1}$ with two independent enantiomeric molecules in the unit cell. Figure 2 shows projections of these

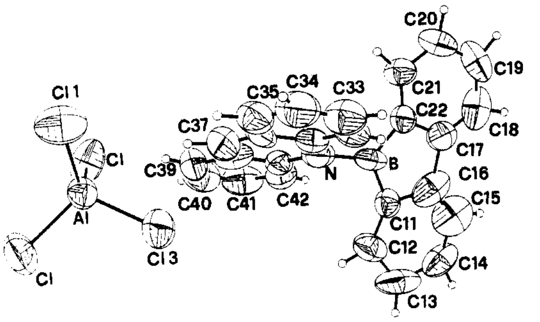


Figure 3. ORTEP plot of one unit of the tetrachloroaluminate **14**. Thermal ellipsoids represent a 50% probability level.

molecules. Inspection of the data in Table V reveals that equivalent bonds in these two molecules are equal within experimental errors. The 9-borafluorene unit is essentially planar. Although all atoms except the boron atom of the five-membered borole ring in the 9-borafluorene heterocycle have to be considered sp^2 hybridized, all bond angles are much smaller than 120°, implying considerable ring strain. The smallest bond angles are those incorporating the boron atom with the C2–B–C12 bond angle deviating from the tetrahedral bond angle by 8°.

The B–Cl bond length in **11a** corresponds to that observed for chloroborane–2,6-lutidine (1.900 Å)[21] and is therefore significantly longer than in boron trichloride–pyridine (1.835 Å).[22] Since most B–Cl bonds to tetracoordinated boron are shorter (1.76–1.83 Å) than in **11a**, it seems that its B–Cl bond is weaker than in other comparable compounds, and this would account for the ready attack of a chloride acceptor at this bond by breaking it.

Comparing B–N bonds in the series **11a**, chloroborane–2,6-lutidine, and $Cl_3B{\cdot}py$ (1.612, 1.588, and 1.592 Å), one finds the longest bond for **11a**, but differences are quite small and may not be significant enough to draw any conclusions.

The structure of the borafluorene unit shows no unexpected features. Its B–C bond lengths are typical for bonds of tetrahedral boron to tricoordinated carbon as found, e.g., for tetraphenylborate or for complexes of diphenylborinic acid (1.60–1.64 Å).[23-25] It should be noted, however, that the C1–C7 bond of the borole ring in the 9-borafluorene unit is significantly longer (1.48 Å) than the rest of the C–C bonds (1.38–1.41 Å). This lengthening of the bond reflects ring strain in the five-membered ring.

Figure 3 clearly demonstrates that **14** is indeed a salt containing a cation with tricoordinated boron. Its tetrachloroaluminate ion shows no interaction with the boron atom: the boron atom is coplanar with its directly bonded atoms, and the closest Cl···B distance was calculated to be 4.4 Å. The $AlCl_4^-$ ion approaches the tetrahedral symmetry quite closely; it is only slightly distorted.

The main structural difference between the 9-borafluorene units in **11a** and **14** result from the enlarged C–B–C bond angle in **14** (115.2°). As a consequence, the B–C–C and C–C–C bond angles are smaller than in **11a**. More importantly, the C1–C7 bond is now very long, exceeding the C–C *single*-bond lengths by 0.13 Å. Moreover, the B–C bonds in **14** are quite short (1.46 Å), reflecting the positive charge associated with **14** and indicating the incorporation of the boron atom in the π system of the borafluorenium ion as described by **17**. These structural features compare favorably with calculated bond lengths[26] for the cyclopentadienium cation $C_5H_5^+$ (**18**)8 which is isoelectronic with the borenium part **19** in **14**. B–C bonds in neutral trigonal boron compounds such as in phenyl–boron compounds are observed in the range 1.52–1.54 Å.[27,28]

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for 9-Acridine–9-Borafluorenium Tetrachloroaluminate (**14**)[a]

	Bond Lengths		
Al–Cl(1)	2.125 (5)	Al–Cl(2)	2.140 (4)
Al–Cl(3)	2.128 (3)	Al–Cl(4)	2.110 (4)
N–B	1.650 (11)	N–C(31)	1.387 (12)
N–C(43)	1.397 (11)	B–C(11)	1.450 (12)
B–C(22)	1.476 (13)	C(11)–C(12)	1.402 (13)
C(11)–C(16)	1.393 (12)	C(12)–C(13)	1.495 (15)
C(13)–C(14)	1.466 (22)	C(14)–C(15)	1.402 (24)
C(15)–C(16)	1.246 (21)	C(16)–C(17)	1.667 (15)
C(17)–C(18)	1.336 (13)	C(17)–C(22)	1.368 (10)
C(18)–C(19)	1.389 (16)	C(19)–C(20)	1.393 (12)
C(20)–C(21)	1.387 (12)	C(21)–C(22)	1.363 (12)
C(31)–C(32)	1.420 (12)	C(31)–C(36)	1.464 (10)
C(32)–C(33)	1.336 (16)	C(33)–C(34)	1.261 (13)
C(34)–C(35)	1.277 (15)	C(35)–C(36)	1.524 (16)
C(36)–C(37)	1.305 (16)	C(37)–C(38)	1.400 (19)
C(38)–C(39)	1.465 (15)	C(38)–C(43)	1.425 (11)
C(39)–C(40)	1.249 (19)	C(40)–C(41)	1.331 (14)
C(41)–C(42)	1.395 (14)	C(42)–C(43)	1.367 (15)
	Bond Angles		
Cl(1)–Al–Cl(2)	107.3 (1)	Cl(1)–Al–Cl(3)	111.5 (2)
Cl(2)–Al–Cl(3)	109.6 (1)	Cl(1)–Al–Cl(4)	110.1 (2)
Cl(2)–Al–Cl(4)	109.2 (2)	Cl(3)–Al–Cl(4)	109.1 (1)
B–N–C(31)	121.8 (7)	B–N–C(43)	117.4 (7)
C(31)–N–C(43)	120.9 (6)	N–B–C(11)	123.2 (8)
N–B–C(22)	121.6 (7)	C(11)–B–C(22)	115.2 (7)
B–C(11)–C(12)	131.4 (7)	B–C(11)–C(16)	104.5 (8)
C(12)–C(11)–C(16)	124.1 (8)	C(11)–C(12)–C(13)	116.2 (9)
C(12)–C(13)–C(14)	112.8 (11)	C(13)–C(14)–C(15)	124.8 (11)
C(14)–C(15)–C(16)	119.3 (12)	C(11)–C(16)–C(15)	122.7 (12)
C(11)–C(16)–C(17)	108.1 (8)	C(15)–C(16)–C(17)	129.2 (11)
C(16)–C(17)–C(18)	132.3 (8)	C(16)–C(17)–C(22)	105.7 (7)
C(18)–C(17)–C(22)	121.9 (9)	C(17)–C(18)–C(19)	119.8 (8)
C(18)–C(19)–C(20)	119.0 (8)	C(19)–C(20)–C(21)	119.9 (9)
C(20)–C(21)–C(22)	119.3 (7)	B–C(22)–C(17)	106.5 (7)
B–C(22)–C(21)	133.4 (6)	C(17)–C(22)–C(21)	120.0 (7)
N–C(31)–C(32)	124.4 (6)	N–C(31)–C(36)	120.4 (8)
C(32)–C(31)–C(36)	115.0 (8)	C(31)–C(32)–C(33)	122.3 (7)
C(32)–C(33)–C(34)	122.7 (11)	C(33)–C(34)–C(35)	125.3 (13)
C(34)–C(35)–C(36)	118.9 (8)	C(31)–C(36)–C(35)	115.5 (8)
C(31)–C(36)–C(37)	119.5 (10)	C(35)–C(36)–C(37)	125.0 (8)
C(36)–C(37)–C(38)	119.8 (8)	C(37)–C(38)–C(39)	116.7 (8)
C(37)–C(38)–C(43)	123.9 (9)	C(39)–C(38)–C(43)	119.3 (10)
C(38)–C(39)–C(40)	119.1 (8)	C(39)–C(40)–C(41)	123.0 (11)
C(40)–C(41)–C(42)	122.4 (11)	C(41)–C(42)–C(43)	119.1 (8)
N–C(43)–C(38)	115.4 (8)	N–C(43)–C(42)	127.6 (7)
C(38)–C(43)–C(42)	116.9 (8)		

[a] Estimated standard deviations in parentheses.

Surprisingly, the B–N bond in **14** is longer than in **11a** in contrast to expectation. The longer bond may be due to steric interaction of the 9-borafluorene unit with the acridine molecule. The mean planes of the acridine and 9-borafluorene parts of the cation form an angle of 62° with one another. Its two C–N bonds are slightly elongated as compared to those of the neutral molecule,[29] but all other data are similar. Therefore, the striking color change on formation of **14** from the yellow 9-chloro-9-borafluorene acridine adduct must be due to changes in the bonding situation in the 9-borafluorene unit.

Conclusion

The interaction of Lewis acids of boron with pyridines and other aromatic nitrogen bases were so far only considered to result in 1:1 Lewis acid–Lewis base adducts. The only exception reported was the pyridine adduct of 9-chloro-9-borafluorene,[7] for which an ionic structure was suggested. This has now been shown to be incorrect: the compound is a coordination compound. The

---

(21) Clayton, W. R.; Fratini, A. V.; Remmel, R.; Shore, S. G. *Cryst. Struct. Commun.* **1974**, *3*, 151.

(22) Töpel, K.; Hensen, K.; Trömel, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 969.

(23) Trotter, S. *Can. J. Chem.* **1973**, *51*, 1288.

(24) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1974**, *67*, 221.

(25) Rettig, S. J.; Trotter, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2139.

(26) Hehre, W. J.; von Schleyer, P. *J. Am. Chem. Soc.* **1973**, *95*, 5837.

(27) Coffin, K. P.; Bauer, H. S. *J. Phys. Chem.* **1955**, *59*, 193.

(28) Zvonkova, Z. V.; Glushkova, V. P. *Kristallografiya* **1958**, *3*, 559.

(29) Phillips, D. C. *Acta Crystallogr.* **1956**, *9*, 237.

(30) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

present work demonstrates that borenium salts are obtained from dibutylboron triflate and 9-(((trifluoromethyl)sulfonyl)oxy)-9-borabicyclo[3.3.1]borane and sterically demanding bases such as 2,6-lutidine while pyridine and 2,4-lutidine form only Lewis acid–Lewis base adducts with these diorganylboranes as well as with dibutylboron chloride and 9-chloro-9-borabicyclo[3.3.1]nonane. Therefore, there is competition between adduct and salt formation. In addition, diorganylborenium cations of type R_2BL^+ (L = pyridine, acridine) can be generated from the adducts $R_2BCl{\cdot}L$ by halide abstraction with $AlCl_3$ or $GaCl_3$, but base exchange between the diorganylboron halide adduct and the halide acceptor is a competing reaction.

Acknowledgment. C.K.N. gratefully acknowledges a Humboldt Fellowship. We are also grateful to Fonds der Chemischen Industrie and BASF-Aktiengesellschaft for support of our work and to Deutsche Forschungsgemeinschaft for providing us with the Bruker WP 200 NMR spectrometer. Thanks are due to Dr. H. Prigge, A. Bittner, D. Schlosser, and F. Dirschl for recording many NMR spectra, as well as to K. Schönauer and L. Moser, who provided elemental analysis.

Registry No. **1a**, 96806-75-6; **1b**, 96806-77-8; **2a**, 96806-78-9; **2b**, 96806-79-0; **2c**, 96806-80-3; **2d**, 96806-81-4; **3**, 96806-83-6; **4**, 96807-01-1; **5**, 96807-02-2; **6**, 96807-03-3; **7a**, 96806-84-7; **7b**, 96806-85-8; **7c**, 96806-86-9; **7d**, 22086-36-8; **7e**, 96806-87-0; **7f**, 96806-88-1; **10**, 13059-59-1; **11a**, 96825-32-0; **11b**, 96806-89-2; **11c**, 96806-90-5; **12**, 96806-92-7; **13**, 96806-93-8; **14**, 96806-95-0; 9-BBN-OTF, 62731-43-5; 9-BBN-Cl, 22086-34-6; $GaCl_3$, 13450-90-3; $AlCl_3$, 7446-70-0; dibutylboron triflate, 60669-69-4; 2,6-lutidine, 108-48-5; pyridine, 110-86-1; 2,4-lutidine, 108-47-4; 2,2′-bipyridine, 366-18-7; dibutylboron chloride, 1730-69-4; 9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene, 96806-96-1; 9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene–pyridine, 96806-97-2; 9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene–2,4-lutidine, 96806-98-3; 9-(((trifluoromethyl)sulfonyl)oxy)-9-borafluorene–2,6-lutidine, 96806-99-4; acridine, 260-94-6.

Supplementary Material Available: Tables containing fractional coordinates and isotropic thermal parameters of hydrogen atoms, anisotropic thermal parameters of non-hydrogen atoms, and F_o/F_c values (48 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
West Virginia University, Morgantown, West Virginia 26506-6045

Synthesis, Structural Characterization, and Electrochemistry of [1]Metallocenophane Complexes, $[Si(alkyl)_2(C_5H_4)_2]MCl_2$, M = Ti, Zr

CHANDRASEKHAR S. BAJGUR, WAYNE R. TIKKANEN, and JEFFREY L. PETERSEN*

Received November 8, 1984

A series of modified metallocene dichloride compounds, $[SiR_2(C_5H_4)_2]MCl_2$ (M = Ti, R = CH_3; M = Zr, R = CH_3, C_2H_5, n-C_3H_7), have been prepared to evaluate the presence of a dialkylsilyl bridge on their electrochemical behavior. The compounds have been characterized by elemental analysis and ^1H and ^{13}C NMR, and the molecular structures of $[Si(CH_3)_2(C_5H_4)_2]MCl_2$, M = Ti, Zr, have been determined by X-ray diffraction methods. The ^{13}C NMR resonance of the bridgehead carbons is consistently located substantially upfield from the corresponding resonances for the proximal and distal carbons of the rings in these compounds. Cyclic voltammetric measurements have shown that these [1]metallocenophane dichlorides exhibit only one one-electron reversible reduction in THF within a scan range of +1.0 to −3.0 V vs. SCE. Complementary EPR studies were conducted to identify and monitor the stability of the paramagnetic species generated during the electrochemical reduction of $[Si(CH_3)_2(C_5H_4)_2]TiCl_2$ and the sodium naphthalide reduction of $[Si(CH_3)_2(C_5H_4)_2]MCl_2$, M = Ti, Zr. These reduction processes proceed similarly with the formation of only one paramagnetic product, $[Si(CH_3)_2(C_5H_4)_2]MCl_2^-$. The inherent stability observed for these d^1 M(III) monoanions apparently follows directly from the ability of the dimethylsilyl bridge to restrict the mobility of the cyclopentadienyl rings and thereby limit their potential participation in these reduction reactions. The compounds $[Si(CH_3)_2(C_5H_4)_2]MCl_2$, M = Ti, Zr, similarly crystallize in a monoclinic unit cell of $C2/c$ symmetry with the following refined lattice parameters: for M = Ti, $a = 13.309$ (5) Å, $b = 9.871$ (2) Å, $c = 13.337$ (4) Å, $\beta = 132.79$ (1)°, $V = 1285.8$ (7) Å^3, and $\rho_{calcd} = 1.576$ g/cm^3; for M = Zr, $a = 13.391$ (3) Å, $b = 9.965$ (2) Å, $c = 10.922$ (3) Å, $\beta = 113.37$ (2) Å, $V = 1337.8$ (5) Å^3, and $\rho_{calcd} = 1.730$ g/cm^3. Full-matrix least-squares refinement (based on F_o^2) converged with respective final discrepancy indices of $R(F_o) = 0.024$, 0.032 and $\sigma_1 = 1.69$, 1.93 for diffractometry data with $F_o^2 > \sigma(F_o^2)$.

Introduction

One of the most widely studied series of electron-deficient, early-transition-metal organometallic compounds is $Cp^*{}_2MCl_2$, where $Cp^* = C_5H_xMe_{5-x}$, $x = 0$, 1, 5, and M = Ti, Zr, and its derivatives.[1] The two cyclopentadienyl rings in these compounds and their related derivatives typically display a canted arrangement that forms a protective pocket about the metal center. Under appropriate conditions, various investigators have observed that the Cp* ligand in these group 4[42] metallocenes can actively participate in many different chemical reactions. These processes include H/D exchange[2] of ring and methyl protons, ring coupling[3] that leads to the formation of a dinuclear fulvalene complex, ring migration[4] with a C_5H_5 unit acting simultaneously as a σ and π donor to two metal centers, and ring detachment[5] that accompanies the formation of a polynuclear metal complex. This widely diverse behavior of the Cp* ligand, as demonstrated by these aforementioned examples, arises from its inherent ability to venture across the frontier orbital surface of the metal. This premise was demonstrated initially in early-transition-metal chemistry by a classical study performed by Calderon, Cotton, et al.,[6] who ob-

---

(1) (a) Wailes, P. C.; Coutts, R. S. P.; Weigold, H. "Organometallic Chemistry of Titanium, Zirconium, and Hafnium"; Academic Press: New York, 1974. (b) Bottrill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; pp 271–431. (c) Cardin, D. J.; Lappert, M. F.; Raston, C. L.; Riley, P. I. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; pp 549–633.

(2) (a) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (b) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136.

(3) (a) Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182. (b) Davison, A.; Wreford, S. S. *J. Am. Chem. Soc.* **1974**, *96*, 3017. (c) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 7870. (d) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1976**, *98*, 4137.

(4) (a) Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072. (b) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703.

(5) Huffman, J. C.; Stone, J. G.; Krussel, W. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829.

0020-1669/85/1324-2539$01.50/0