Adducts of the Heavier Group 13 Element Halides with Aminoiminoboranes [1]

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2,2,6,6-Tetramethylpiperidino-*tert*-butylimino borane, **1a**, and 2,2,6,6-tetramethyl-piperidino-2,6-diisopropylphenylimino borane (**1b**), react with the trichlorides of Al, Ga and In or with $AlBr_3$ to 1:1 to give the addition products tmp=B=N(ECl_3)*t*Bu (E = Ga (**2a**), In (**2b**) and tmp = B = N($EHal_3$)(C_6H_3,2,6-*i*Pr_2), (E = Al, Hal = Cl, (**2c**), E = Al, Hal = Br (**2d**)). E = Ga, Hal = Cl (**2e**). All these compounds have an allene type structure with short BN bonds as shown by the determination of the crystal structures of **2a, b**. NMR data are in accord with this structure. No isomerization to tmp-BHal-NR-$EHal_2$ has been observed at temperatures up to their melting points.

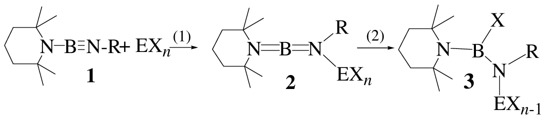
Key words: ECl_3 Adducts, Aminoiminoborane, NMR Spectra, X-Ray Diffraction

Introduction

The reactions of iminoboranes with covalent main group element halides and hydrides follow an addition-insertion mechanism as shown in eqs. (1) and (2) [2, 3]. In most cases, the first step cannot be observed as found for the chlorides of boron, silicon, germanium, tin, and phosphorus [2 – 6]. However, in case of $AlCl_3$, $AlBr_3$, and $GaCl_3$ [7] as well as of AsI_3, $SbBr_3$, SbI_3, and $BiCl_3$ [8] adducts of type **2** were isolated for 2,2,6,6-tetramethylpiperidino-*tert*-butyliminoborane (**1a**), and characterized by NMR spectroscopy and for the group 15 element halides also by X-ray structure analysis [8]. Also, adducts of this aminoiminoborane were obtained with metal carbonyl fragments [9] or $PdCl_2$ [10]. These complexes have also been characterized by X-ray methods. However, no molecular structures could so far be determined for the adducts of any of the trihalides of group 13 elements. Therefore, we investigated the reactions of a more bulky aminoiminoborane **1b** with trihalides of Al and Ga, as well as of **1a** with $GaCl_3$ and $InCl_3$, expecting more stable compounds and, particularly, with hope to be able to grow single crystals.

Experimental Section

Experiments were conducted under anhydrous conditions using Schlenck techniques. **1a** was prepared as cited in [4], and **1b** as described in [11]. $GaCl_3$ and $InCl_3$ were obtained by reacting the metals in a stream of purified chlorine. NMR: Bruker ACP-200 and Jeol GSX 270; IR: Nicolet TF-IR spectrometer; X-ray structure analysis: Siemens P4 diffractometer equipped with a CCD detector and LT2 low temperature device (**2a**) or IPDS, Stoe diffractometer (**2b**). Mo-K_α-radiation, graphite monochromator.



1 **2** **3**

R =	CMe$_3$	C$_6$H$_3$(2,6-(*i*Pr)$_2$
	1a	**1b**

R =	CMe$_3$	C$_6$H$_3$(2,6-*i*Pr)$_2$
$AlCl_3$		**2c**
$AlBr_3$		**2d**
$GaCl_3$	**2a**	**2f**
$InCl_3$	**2b**	

2,2,6,6-Tetramethylpiperidino-*tert*-butyliminoborane gallium trichloride (**2a**): $GaCl_3$ (0.76 g, 4.3 mmol) was dissolved in diethyl ether (20 ml). The solution was cooled to −78 °C and a solution of **1a** in hexane (36.3 ml, 0.119 M, 4.3 mmol) was added with stirring. A precipitate occurred immediately. After allowing the suspension to attain room temperature most of the solvents were removed from the solid by a cannula. The solid was dried in vacuo, and was then dissolved in toluene (20 ml). The resulting solution was layered with hexane (10 ml). After some days colorless crystals of **2a** were isolated. Yield: 1.52 g (92%), m. p. 95 °C (dec.). IR (Nujol/Hostaflon): ν(NBN) = 1812 st (cm^{-1}). MS (EI, 80 °C, 70 eV): 398 (7%, $M^{\cdot+}$), 207 (80%, M^+-Me), 126 (70%, tmp-Me^+). $C_{13}H_{27}N_2BCl_3Ga$ (398.25): calcd. C 39.17, H 6.78, N 7.03; found C 38.42, H 6.96, N 6.58.

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Table 1. Chemical shifts for the ^{1}H, ^{11}B, ^{13}C and ^{27}Al resonances (in ppm) and line widths (in Hz), given in parenthesis for compounds **2a – e**. Data recorded in deuterated toluene.

	δ^{11}B	δ^{27}Al	δ^{1}H					
			H2,3,4	H6/7	H11-13	H16-18	H20[a]	H21,22
2a	33.7 (448)		1.09 – 1.38 m	0.96 s, 1.22 s	1.33 s			
2b	33.3 (470)		1.15 – 1.37 m	1.08 s, 1.29 s	1.38			
2c	31.3 (550)	103.6 (75)	1.1 – 1.40 m	1.41 s, 1.72 s		7.07 – 7.12 m	3.53[b]	1.23 d, 1.29 d
2d	33.6 (955)	93.4 (50)	1.14 – 1.44 m	1.35 s		6.98 – 7.07 m	3 – 34[c]	1.18 d, 1.51 d
2e	30.6 (305)		1.03 – 1.60 m	1.41 s, 1.74 s		7.09 – 7.13 m	3.61[d]	1.26 d, 1.33 d

δ^{13}C	C1/5	C2/4	C3	C6/7	C10	C11/13	C15/19	C17	C16/18	C20	C21/22	C14
2a	55.3	36.4	16.4	29.7, 31.1	55.8	32.7						
2b	51.2	38.8	17.8	29.5, 32.4	56.4	33.2						
2c	59.5	35.8	16.0	28.2, 32.5			129.3	124.2	136.8	29.1	24.1, 25.3	142.8
2d	57.6	37.5	16.3	31.1			128.9	125.6	134.1	28.6	25.39, 25.4	144.4
2e	57.1	37.3	16.3	31.1			128.2	125.2	133br	28.6	25.2, 25.4	145.2

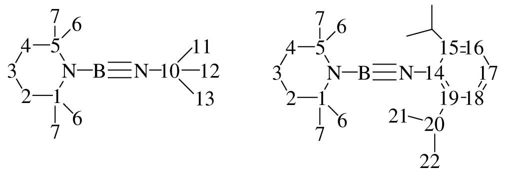
[a] septets, [b] $^{1}J(H,H) = 6.35$ Hz, [c] $^{1}J(H,H) = 6.60$ Hz, [d] broad.

2,2,6,6-Tetramethylpiperidino-*tert*-butyl-iminoborane indium trichloride (**2b**): As described for **2a**, a suspension of $InCl_3$ (0.442 g, 2.0 mmol) in diethyl ether (25 ml) was cooled to −78 °C and was allowed to react with a hexane solution of **1a** (30 ml, 0.07 M, 3.0 mmol). The mixture was stirred for 30 h at ambient temperature. No ^{11}B NMR signal could then be detected in the solution. The product was isolated by filtration, dissolved in toluene (20 ml) and the solution layered with hexane (20 ml). Colorless crystals of **2b** formed during standing for one night. Yield: 0.56 g, (63%), m. p. 105 °C. IR (Nujol/Hostaflon): 1808 st (cm^{-1}). – $C_{13}H_{27}N_2BCl_3In$ (443.35): calcd. C 35.19, H 6.09, N 6.23; found C 34.78, H 6.16, N 6.32.

2,6-Diisopropylphenylimino-2,2,6,6-tetramethylpiperidinoborane aluminum trichloride (**2c**): A suspension of $AlCl_3$ (0.65 g, 4.6 mmol) in pentane (15 ml) was cooled to −60 °C. Then a solution of **1b** (1.53 g, 4.5 mmol) in pentane (20 ml) was added while stirring. Stirring was continued at ambient temperature over night, the insoluble **2c** isolated by filtration and dried in vacuo. Yield: 1.22 g (58%), m. p. 118 – 120 °C (dec). IR (nujol): 1768 st, 1830 m (cm^{-1}). – $C_{21}H_{35}N_2AlBCl_3$ (459.65): calcd. C 54.87, H 7.76, N 6.09, Cl 23.12; found C 52.48, H 7.77, N 5.62, Cl 22.0.

2,6-Diisopropylphenylimino-2,2,6,6-tetramethylpiperidinoborane aluminum tribromide (**2d**): To a suspension of $AlBr_3$ (0.68 g, 2.5 mmol) in hexane (10 ml) was added at −50 °C with vigorous stirring a solution of **1b** (0.98 g, 3.0 mmol) in hexane (15 ml). The suspension was allowed to slowly attain room temperature. The yield of isolated **2d** was 1.126 g (75%), m. p. 145 °C (dec.). IR (Nujol): 1815 st. 1760 vst, (νBN_2), 461, 410 (ν_s, ν_{as} $AlBr_3$) (cm^{-1}). – $C_{21}H_{35}N_2AlBBr_3$ (593.03): calcd. C 42.43, H 5.59, N 4.72; found C 39.84, H 5.90, N 4.35.

2,6-Diisopropylphenylimino-2,2,6,6-tetramethylpiperidinoborane gallium trichloride (**2e**): As described for **2d** from $GaCl_3$ (0.34 g, 1.9 mmol) an **1b** (0.64 g, 1.9 mmol) in a total of 25 ml of hexane. **2e** was obtained as a slightly pink solid. Yield: 0.77 g (80%), m. p. 117 – 120 °C (dec.). IR (Nujol): 1837 m, 1777 st (νBN_2), 388, 360 (ν_s, ν_{as} $AlBr_3$) (cm^{-1}). – $C_{21}H_{35}N_2BCl_3Ga$ (502.42): calcd. C 50.20, H 7.02, N 5.85; found C 48.85, H 7.49, N 5.89.



Scheme. Labels of the C- and H-atoms in Table 1.

X-ray structure determination. Single crystals were selected and fixed on a glass fiber. Cell constants were calculated from the reflections on a set of 60 frames using the program SMART [12]. Data collection was performed at −80 °C in the hemisphere mode. For data reduction the program SAINT [12] was used. The structures were solved and refined by applying the program SHELX97 [13]. Crystallographic data are deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCD 229830 and 229831. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44 1223-336033 or e-mail: deposit@ccdc.ca.ac.uk.

Results and Discussion

$GaCl_3$ and $InCl_3$ were found to react with the aminoiminoborane **1a** to give the adducts **2a, b**. These are the first adducts of group 13 element trihalides of **1a** of which single crystals for X-ray structure analysis could be obtained. The aminoiminoborane **1b** was shown to add $AlCl_3$, $AlBr_3$ and $GaCl_3$ quite readily to produce adducts **2c, d, e**, which proved to be sparingly soluble in hexane or diethyl ether.

Table 2. Selected bonding parameters of **2a**, **b**. Bond lengths are given in Å, bond angles in °, e.s.d's in parenthesis.

	B1-N2	B1-N1	N2-E	av. E-Cl
2a	1.317(4)	1.343(4)	1.937(1)	2.173(1)
2b	1.312(2)	1.345(2)	2.139(1)	2.348(1)
	N1-B1-N2	C10-N2-E	B1-N2-E	τC10N2E1/C1N2C5
2a	178.9(2)	123.2(2)	116.3(2)	97.0
2b	177.9(2)	120.9(1)	115.8(1)	97.3

Sum of bond angles at N1, N2 and B1 in all cases 360°.

Table 3. Crystallographic data for **2a**, **b** and data related to data collection and structure refinement.

Compound	**2a**	**2b**
Chem. formula	C13 H27 B Cl3 Ga N2	C13 H27 B Cl3 In N2
Form. wght.	398.25	443.35
Cryst. size [mm]	$0.10 \times 0.20 \times 0.30$	$0.15 \times 0.20 \times 0.42$
Cryst. system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a, [Å]	14.9850(1)	14.8128(8)
b, [Å]	13.4330(1)	13.7001(9)
c, [Å]	19.2096(1)	19.454(1)
α, [°]	90	90
β, [°]	90	90
γ, [°]	90	90
V, [Å^3]	3866.77(4)	3947.9(4)
Z	**8**	**8**
ρ (calcd.) [Mg/m^3]	1.368	1.492
μ [mm^{-1}]	1.830	1.596
F(000)	1648	1792
Index range	$-16 \le h \le 15$ $-15 \le k \le 15$ $-22 \le l \le 22$	$-19 \le h \le 15$ $-18 \le k \le 18$ $-25 \le l \le 23$
2θ[°]	49.40	55.84
Temp. [K]	193(2)	200(2)
Refl. collected	17265	24355
Refl. unique	3101	4688
Refl. observed (4σ)	2403	3601
R (int.)	0.0487	0.0373
No. variables	188	188
Weighting scheme^a x/y	0.0289/3.0125	0.02330/0
GOOF	1.038	0.944
Final $R(4\sigma)$	0.0311	0.0231
Final $wR2$	0.0671	0.0507
Larg. res. peak [e/Å^3]	0.284	0.533

^{a} $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

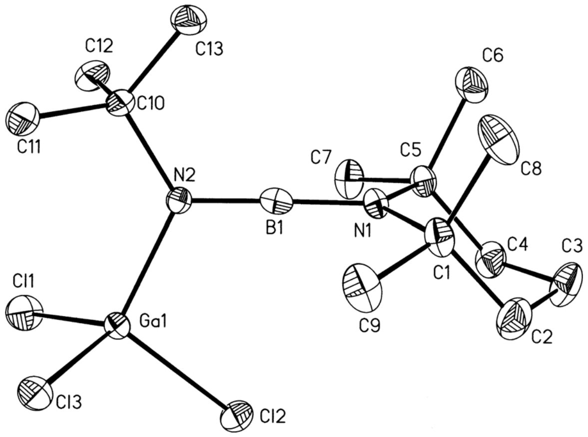


Fig. 1. Molecular structure of compound **2a** in ORTEP description. Thermal ellipsoids are represented with 25% probability. Selected bond lengths (in Å): Ga1-Cl1 2.1616(9), Ga1-Cl2 2.1860(8), Ga1-Cl3 2.1718(8), N1-C1 1.514(3), N1-C5 1.511(4), N2-C10 1.528(3). – Selected bond angles (in °): C1-N1-B1 120.2(2), B1-N2-Ga1 116.3(2), B1-N1-C5 118.9(2), B1-N2-C10 120.5(2), C1-N1-C5 120.8(2), N2-Ga1-Cl1 112.79(7), N2-Ga1-Cl2 104.25(6), N2-Ga1-Cl3 109.41(7). Analogous data for **2b**: In1-Cl1 2.3391(6), In1-Cl2 2.3609(5), In1-Cl3 2.3496(6), N1-C1 1.509(3), N1-C5 1.509(3), N2-C10 1.511(2). – Selected bond angles (°): C1-N1-B1 119.81.2(1), B1-N2-In1 115.8(1), B1-N1-C5 118.9(2), B1-N2-C10 123.2(1), C1-N1-C5 121.3(1), N2-In1-Cl1 112.90(5), N2-In1-Cl2 102.69(4), N2-In1-Cl3 108.62(5).

Typically for the formation of the adducts is the low field shift of the ^{11}B resonance with a concomitant decrease in the line widths (except for **2d**). The difference in shielding is larger for compounds **1a, b** (29.5 and 28.1 ppm, respectively) than for **2c, d, e** (19.2, 21.5 and 18.5 ppm). The line widths are still rather broad, ranging from 385 to 925 Hz, respectively (see Table 1 for NMR data). The aluminum atom in **2c, d** is present in a tetracoordinated state as is shown by a comparison with δ^{27}Al for $AlCl_3 \cdot NMe_3$ [108.9 ppm ($h_{1/2} = 77$ Hz)] and $AlBr_3 \cdot NMe_3$ (103.8, ($h_{1/2} = 94$ Hz) [14]. That the shielding at the Al Atoms is somewhat less than in the trimethylamine adducts is most likely due to the steric effect of the *tert*-butyl group.

Except for **2d** there are two ^{1}H resonances for the CMe_2 groups of the tetramethylpiperidino units in the ^{1}H spectra but, and only one for **2d, e** in the ^{13}C NMR spectra. This is in accord with the allene type structure of these compounds. On cooling solutions of **2d** below 20 °C one observes two signals: the coalescence temperature is 25 °C, and with $\Delta\nu = 13.2$ Hz one arrives at $\Delta G^{\#} = 62 + / - 3$ kJmol^{-1}, indicating a low barrier to rotation about the BN bonds.

In line with the structure of compounds **2** is the strong IR band of the antisymmetric BN_2 vibration at 1812 and 1808 cm^{-1} for **2a, b** and between 1760 and 1777 cm^{-1} for **2c, d, e**. In each case also a $^{10}BN_2$ band in the range of 1815 to 1837 cm^{-1} was observed.

Compounds **2a, b** are isotypic, crystallizing in the orthorhombic system in space group *Pbca*. Relevant crystallographic data are summarized in Table 3. Because the molecular structures of the two compounds are rather similar (of course not for the E-N and E-Cl bonds) only one is presented in Fig. 1. Typical bonding parameters are presented in Table 2.

The NBN bond angle of both compounds is close to 180° and the planes EN2C10/C1N2C5 are twisted by 97.0 and 97.3°, respectively. The tricoordinated N and B atoms reside in a planar environment. In spite of the planar N1 atoms the tetramethylpiperidino rings are present in a chair conformation. The two BN bonds differ significantly in lengths. In both cases the BN bond to the EX_3 bearing nitrogen atom N2 is shorter than to N1 of the tetramethylpiperidino group but the differences in bond lengths are less pronounced than in the complexes with $PdCl_2$ [10] and $M(CO)_5$ [9]. The N-E-Cl bond angles vary from 104.3 to 112.8° for **2a** and from 102.7° to 112.9° for **2b**, while the Cl-E-Cl bond angles are close to the tetrahedral angle.

The Ga-N bond in **2a** is on the short side for Ga-N bonds. Values for comparison are 1.981 and 1.977 Å for the eight membered ring $[Me_2Ga\text{-}NPh\text{-}CPh\text{-}O]_2$ [15]. Also, the In-N bond in **2b** is significantly shorter than those found in $Me_3In\cdot NHCy_2$, and $[Me_3In\text{-}MeHN\text{-}(CH_2)]_2$ (2.38 Å) [16], and the distances of 2.188 – 2.239(3) Å for $ClIn(cyN\text{-}C\mathit{t}Bu\text{-}Ncy)_2$ with a pentacoordinated In atom [17]. The In-N single bond is generally assumed to be 2.28 Å [18, 19]. The short GaN and InN bonds observed for **2a**, **b** can be associated with the inductive effect of the ECl_3 group.

The new adducts are perfectly stable under anhydrous conditions, and the formation of compounds of type **3** have not been observed under relatively mild conditions up to the melting points of the compounds.

Acknowledgements

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