The coordination chemistry of *o,o′-i*-$Pr_2C_6H_3$-bis(imino)acenaphthene to group 13 trihalides

Hilary A. Jenkins, Carla L. Dumaresque, Dragoslav Vidovic, and Jason A. C. Clyburne

Abstract: The preparation of several complexes of the diimine ligand *o,o′-i*-$Pr_2C_6H_3$-bis(imino)acenaphthene (Ar-BIAN (**1**)) with group 13 trihalides (EX_3, E = B, Al, Ga; X = Cl, Br) is reported. Four compounds with the general formula $[(\text{Ar-BIAN})(EX_2)][EX_4]$ (**2**) have been prepared and isolated. Two complexes have been crystallographically characterized: $[(\text{Ar-BIAN})(BCl_2)][BCl_4]$ (orthorhombic, $P2_12_12_1$, a = 10.408(3) Å, b = 14.376(4) Å, c = 30.908(8) Å, Z = 4) and $[(\text{Ar-BIAN})(GaCl_2)][GaCl_4]$ (monoclinic, $P2_1/m$, a = 9.0822(7) Å, b = 15.390(1) Å, c = 15.458(1) Å, β = 92.519(2)°, Z = 2). Attempts to prepare diazametaloles via reduction of the $[(\text{Ar-BIAN})(EX_2)][EX_4]$ compounds using sodium or potassium have thus far been unsuccessful.

Key words: boron, aluminium, gallium, complex, crystal structure, heterocycle.

Résumé : On a préparé plusieurs complexes du ligand diimide *o,o′-i*-$Pr_2C_6H_3$-bis(imino)acénaphtène (Ar-BIAN (**1**)) avec des halogénures d'éléments du groupe 13 (EX_3, E = B, Al, Ga; X = Cl, Br). On a spécifiquement préparé et isolé quatre composés de formule générale $[(\text{Ar-BIAN})(EX_2)][EX_4]$ (**2**). On a caractérisé deux de ces complexes par diffraction des rayons X, le $[(\text{Ar-BIAN})(BCl_2)][BCl_4]$ (orthorhombique, $P2_12_12_1$, a = 10,408(3), b = 14,376(4) et c = 30,908(8) Å, Z = 4) et le $[(\text{Ar-BIAN})(GaCl_2)][GaCl_4]$ (monoclinique, $P2_1/m$, a = 9,0822(7), b = 15,390(1) et c = 15,458(1) Å, β = 92,519(2)°, Z = 4). On n'a pas réussi à préparer des diazamétaloles par le biais d'une réduction des composés $[(\text{Ar-BIAN})(EX_2)][EX_4]$ à l'aide du sodium ou du potassium.

Mots clés : bore, aluminium, gallium, complexes, structure cristalline, hétérocycle.

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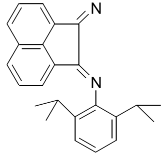
Introduction

Hydroborations are an important class of reaction in synthetic organic chemistry because the B—H bond readily adds across a wide variety of unsaturated fragments, including C=O and C=N bonds (1). Recently, reactions involving chloroboration (B-Cl addition) have been identified (2). To our knowledge, these reactions have not been extended to heavier group 13 elements, although enhanced reactivity would be anticipated for Al—Cl and Ga—Cl bonds as compared with the B—Cl bonds.

Our interest in group 13 element chemistry (3) led us to look at the synthesis of suitable heterocyclic systems as precursors to compounds that may engage in reactions analogous to hydroboration and haloboration. The ideal candidates for such reactions would be heterocyclic compounds, with donor substituents bound to the group 13 metal site; these donors would stabilize a tricoordinate metal centre via delocalization. The presence of a bulky substituent would facilitate synthesis and enhance the thermal stability of the complex. Currently there is great interest in unusual main group element heterocycles, including B (4, 5), Al (6), and Ga (7, 8) derivatives.

It became apparent to us that the bulky diimine ligand **1** (9) would be ideal for our studies since it is both a good donor and extremely bulky.



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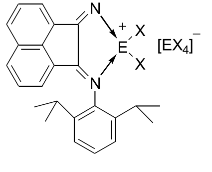

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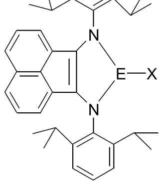

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E = B, Al, Ga; X = Cl, Br

Diimines are bidentate ligands consisting of two nitrogen atoms bridged by at least two carbon atoms, and having two C=N double bonds (10). The bis(arylimino)acenaphthene

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This paper is dedicated to Professor Tristram Chivers for his many contributions to main group chemistry.

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diimine ligand (**1**) is different from other diimine ligands as it has both better σ-donating and π-accepting properties than nonrigid diimines (9). Therefore, **1** could serve as an ideal starting material for the preparation of stable heterocyclic metal-containing ions (metal = boron, aluminium, and gallium) (**2**), which would serve as precursors to the requisite heterocycles (**3**). The nitrogen atoms are locked into a rigid *s-cis* conformation due to the presence of the naphthalene backbone, thus allowing for better metal coordination. Brookhart and co-workers (11) have recently reported Ni(II) and Pd(II) complexes of **1** that catalyze the polymerization of ethylene. These catalysts have activities similar to those of the early transition metal catalysts; however, they produce polymers with different structures and properties. Despite extensive use in transition metal chemistry ligand design, **1** has not been used in main group chemistry.

Herein we report our synthetic and structural studies on a series of bulky diazametalolium (**2**) complexes. A series of reactions involving **1** with EX_3 (E = B, Al, Ga; X = Cl, Br) has been examined, and the reaction products have been isolated and characterized. The products have the general formula $[(Ar\text{-}BIAN)(EX_2)][EX_4]$ (**3**). Attempts to prepare molecules such as **3** via reduction of **2** have thus far been unsuccessful.

Experimental methods

An MBraun UL-99–245 dry box and standard Schlenk techniques on a double manifold vacuum line were used in the manipulation of air- and moisture-sensitive compounds. Anhydrous solvents were used as received from Aldrich Chemical Company. NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer in 5-mm quartz tubes. ^1H chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and were calibrated to the residual signal of the solvent. Infrared spectra were obtained using a Bomem MB spectrometer with the % transmittance reported in cm^{-1}. Melting points were measured using a Mel-Temp apparatus and are uncorrected. Ligand **1** was prepared using the published procedure (9). Note that ^{13}C NMR spectra were not obtained due to decomposition and low solubility of the ionic compounds.

Synthesis of $[(Ar\text{-}BIAN)(BCl_2)][BCl_4]$

Ar-BIAN (1.20 g, 2.5 mmol in 10 mL CH_2Cl_2) was added to a solution of 25 mL CH_2Cl_2 and 5 mL (5.0 mmol) of 1 M BCl_3 in hexanes, resulting in the formation of a dark red solution. The volume of solvent was reduced to ca. 25% of the original volume, and then the solution was cooled to –30°C. Small red crystals were obtained and the supernatant was removed via cannula under an atmosphere of argon. Yield: 1.05 g (1.47 mmol, 59%), decomposition temperature ≈ 140°C. IR (Nujol mull) (cm^{-1}): 1643, 1600, 1569, 1418, 1366, 1318, 1260, 854, 835, 802, 774, 691, 658, 634, 546. ^1H NMR (CD_2Cl_2) δ (ppm): 1.14 (broad, 12H), 1.42 (d, J_{HH} = 6 Hz, 12H), 3.01 (m, 4H), 6.9 (d, 7 Hz), 7.6 (m, 2H), 8.28 (d, J_{HH} = 8 Hz, 2H), 7.3–7.8 (6H aryl). Anal. calcd. for $C_{36}H_{40}B_2Cl_6N_2$: C 58.82, H 5.48, N 3.81; found: C 59.16, H 5.60, N 3.64.

Synthesis of $[(Ar\text{-}BIAN)(BBr_2)][BBr_4]$

Ar-BIAN (1.20 g, 2.5 mmol in 10 mL of CH_2Cl_2) was added to a solution of 25 mL of CH_2Cl_2 and 5 mL (5.0 mmol) of 1 M BBr_3 in CH_2Cl_2 to produce a dark red solution. The volume of solvent was reduced to ca. 25% of the original volume, and then the solution was cooled to –30°C. Solvent was removed under an argon atmosphere and dark red crystals were isolated in the dry box. Yield: 1.35 g (1.38 mmol, 55%), decomposition temperature ≈ 185°C. IR (Nujol mull) (cm^{-1}): 1635, 1597, 1570, 1319, 834, 733, 615, 588, 541. ^1H NMR (CD_2Cl_2, poor solubility) δ (ppm): 1.0 (d, J_{HH} = 6Hz, 12H), 1.45 (d, J_{HH} = 6 Hz, 12H), 3.3 (broad, 4H), aromatic region broad and not resolved. Anal. calcd. for $C_{36}H_{40}B_2Br_6N_2$: C 43.16, H 4.02, N 2.80; found: C 42.80, H 3.92, N 2.65.

Synthesis of $[(Ar\text{-}BIAN)(AlCl_2)][AlCl_4]$

Aluminium trichloride (1.0 g, 7.50 mmol) was added to an oven-dried Schlenk flask containing 40 mL of CH_2Cl_2. Ar-BIAN (1.80 g, 3.75 mmol) in 5 mL of CH_2Cl_2 was added, and the solution turned dark red. Half of the solvent was removed under vacuum, and the reaction was cooled to –30°C in the freezer. A microcrystalline powder was obtained, and this material was washed with CH_2Cl_2. Yield: 0.95 g (1.27 mmol, 34%), decomposition temperature ≈ 185°C. IR (Nujol mull) (cm^{-1}): 1626, 1617, 1569, 1418, 1366, 1318, 1221, 854, 835, 802, 774, 490, 460. ^1H NMR (CD_2Cl_2) δ (ppm): 1.14 (d, J_{HH} = 6Hz, 12H), 1.30 (d, J_{HH} = 6 Hz, 12H), 3.0 (m, 4H), 7.2 (d, J_{HH} = 7 Hz, 4H), 7.3–7.8 (6 H aryl), 7.70 (m, 2H), 8.50 (d, J_{HH} = 8 Hz, 2H). Anal. calcd. for $C_{36}H_{40}Al_2Cl_6N_2$: C 56.34, H 5.25, N 3.65; found: C 56.20, H 5.11, N 3.59.

Synthesis of $[(Ar\text{-}BIAN)(GaCl_2)][GaCl_4]$

Gallium trichloride (1.00 g, 5.68 mmol) in 15 mL of CH_2Cl_2 was added to an oven-dried Schlenk flask. Ar-BIAN (1.37 g, 2.84 mmol in 5 mL of CH_2Cl_2) was added to this colourless solution, which turned dark red. Another 5 mL of CH_2Cl_2 was added, and this solution was then cooled to –30°C. Flat red crystals were obtained and isolated after removal of the supernatant, via cannula, under an atmosphere of argon. Yield: 1.75 g (2.10 mmol, 74%), decomposition temperature ≈ 140°C. IR (Nujol mull) (cm^{-1}): 1621, 1596, 1572, 1488, 1420, 1366, 1300, 1270, 1055, 803, 777, 734, 584, 545. ^1H NMR (CD_2Cl_2) δ (ppm): 1.02 (broad, s, 12H), 1.45 (d, J_{HH} = 6 Hz, 12H), 3.1 (m, 4H), 6.90 (d, J_{HH} = 7 Hz, 2H), 7.3–7.8 (6 H aryl), 7.64 (m, 2H) 8.42 (d, J_{HH} = 8 Hz, 2H). Anal. calcd. for $C_{36}H_{40}Ga_2Cl_6N_2$: C 50.70, H 4.73, N 3.28; found C 50.54, H 4.63, N 3.15.

Attempts to reduce the compounds above in THF (1 to 2 mmol scale) with sodium or potassium were made, but unfortunately in our hands no pure compounds could be isolated from the reaction mixtures. The only compound identified (by NMR and melting point) was Ar-BIAN. Likewise, attempts were made to exchange the $[EX_4]$ anions with the weakly coordinating anion $[B(C_6F_5)_4]$ by treating **3** with $Li[B(C_6F_5)_4]$ in CH_2Cl_2 solution. In general, these attempts were unsuccessful, resulting in the formation of dark coloured solutions, from which the only pure compound isolated was Ar-BIAN.

Table 1. Crystal data and structure refinement for [(Ar-BIAN)BCl_2][BCl_4]·1.25 CH_2Cl_2 and [(Ar-BIAN)$GaCl_2$][$GaCl_4$].

Compound	[(Ar-BIAN)BCl_2][BCl_4]·1.25 CH_2Cl_2	[(Ar-BIAN)$GaCl_2$][$GaCl_4$]
Empirical formula	$C_{37.26}H_{42.50}B_2Cl_{8.5}N_2$	$C_{37}H_{40}Cl_8Ga_2N_2$
Formula weight (g ml^{-1})	841.18	935.75
Temperature (K)	223(2)	223(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/m$
a (Å)	10.408(3)	9.0822(7)
b (Å)	14.376(4)	15.390(1)
c (Å)	30.908(8)	15.458(1)
α (°)	90	90
β (°)	90	92.519(2)
γ (°)	90	90
Volume ($Å^3$)	4625(2)	2158.5(3)(2)
Z	4	2
Density (calculated) mg m^{-3}	1.239	1.440
Absorption coefficient (μ) (mm^{-1})	0.572	1.771
$F(000)$	1780	948
Crystal size (mm^3)	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.30
θ range for data collection (°)	1.32–25.00	1.87–25.00
Index ranges	$9 \le h \le 12$	$-10 \le h \le 8$
	$-16 \le k \le 17$	$-18 \le k \le 18$
	$-29 \le l \le 36$	$-17 \le l \le 18$
Reflections collected	24 923	10 799
Independent reflections	8146	3907 (R_{int} = 0.0608)
Absorption correction	none	none
Max and min transmission	0.745 and −0.392	0.447 and −0.597
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8137/3/516	3907/0/251
Goodness-of-fit on F^2	1.162	1.018
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1152, wR_2 = 0.2798	R_1 = 0.0534, wR_2 = 0.1094
R indices (all data)	R_1 = 0.2117, wR_2 = 0.3222	R_1 = 0.1092, wR_2 = 0.1290
Extinction coefficient	0.018(4)	0.0014(5)

Crystallographic studies

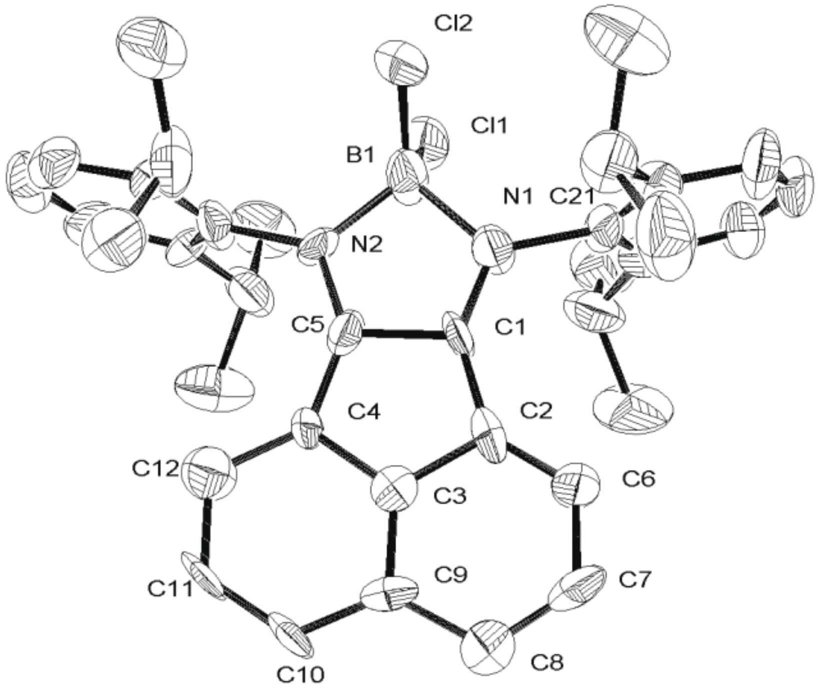
A single crystal of either [(Ar-BIAN)BCl_2][BCl_4]·1.25[CH_2Cl_2] or [(Ar-BIAN)$GaCl_2$][$GaCl_4$] was mounted on a glass fibre and centred on a Seimens 1K SMART/CCD diffractometer. Data were collected at –50°C using Mo (Kα) radiation. Lorentz and polarization corrections were applied, and data were also corrected for absorption using redundant data and the SADABS program. Direct methods and Fourier techniques were used to solve the crystal structures. Refinement was conducted using full-matrix least-squares calculations and SHELX-TL PC V 5.03. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in calculated positions and were refined using a riding model. In the final stages of the refinement of [(Ar-BIAN)BCl_2][BCl_4]·1.25[CH_2Cl_2], R_1 = 0.1152, wR_2 = 0.2798, and the largest peak was 0.745 e $Å^{-3}$ and was associated with one of the methylene chloride solvent molecules. In the final stages of refinement of [(Ar-BIAN)$GaCl_2$][$GaCl_4$]· [CH_2Cl_2], R_1 = 0.0534, wR_2 = 0.1094, and the largest residual peak was 0.447 e $Å^{-3}$ and was associated with the residual methylene chloride solvent. Full crystallographic details can be found in Table 1.

Results and discussion

The Ar-BIAN ligand **1** was treated with a variety of group 13 compounds to prepare Lewis base coordination complexes. Lewis acids studied included BCl_3, BBr_3, $AlCl_3$, and $GaCl_3$. Of these reactions, solid materials were successfully isolated from BCl_3, BBr_3, $AlCl_3$, and $GaCl_3$. In general, treatment of **1** with 2 equiv of EX_3 in CH_2Cl_2 solution, followed by reduction of the solvent volume, resulted in the formation of a solid, bright red material. These compounds were characterized by ^1H NMR and IR spectroscopy. Poor solubility of these ionic compounds made NMR studies difficult, and it was discovered that the compounds decompose in CD_2Cl_2 solution (12). Fortunately, X-ray-quality crystals were obtained from the mother liquors of [(Ar-BIAN)BCl_2][BCl_4] and [(Ar-BIAN)$GaCl_2$][$GaCl_4$].

IR spectroscopic studies were performed on the [(Ar-BIAN)(EX_2)][EX_4] series of compounds. The stretching frequencies observed between 1660 and 1610 cm^{-1} have been tentatively assigned to the ν(C=N) stretches. The assignments for the [(Ar-BIAN)(EX_2)][EX_4] complexes are as follows (cm^{-1}): free ligand (1660 or 1640); E = B, X = Cl (1646); E = B, X = Br (1636); E = Al, X = Cl (1627);

Fig. 1. ORTEP view of cation $[(\text{Ar-BIAN})\text{BCl}_2]^+$ showing the labelling scheme. Thermal ellipsoids are shown at 50% probability level; hydrogen atoms have been removed for clarity.



E = Ga, X = Cl (1621). The C=N stretching frequency in the free ligand cannot be assigned unambiguously because of the presence of C—C stretching frequencies from the naphthalene backbone in this region (9). The absorptions for the C=N stretches in the complexes have been assigned because of the fact that these peaks were discernible as being quite strong and broad, consistent with a C=N stretch. More importantly, the position of this absorption shifts upon complex formation, and is dependent on the Lewis acid used in the complexation reaction.

The absorptions for the E—X bonds are also informative. The IR spectrum for $[(\text{Ar-BIAN})\text{EX}_2][\text{EX}_4]$ reveals two different E—X stretches from the two types of E—X bonds present (i.e., one from the cation and one from the anion). These two stretching bands are present at 691(s-br) and 658(s-br) cm^{-1} (E = B, X = Cl), 588(s) and 541(s) cm^{-1} (E = B, X = Br), and 490(s) and 460(m) cm^{-1} (E = Al, X = Cl). The stretching bands have been assigned based on known E—X stretching regions and intensities (13). The stretches for Ga—Cl bonds were not observed in the IR spectrum of the $[(\text{Ar-BIAN})\text{GaCl}_2][\text{GaCl}_4]$ complex, as Ga—Cl bonds absorb below 450 cm^{-1}.

Crystallographic studies on $[(\text{Ar-BAIN})\text{BCl}_2][\text{BCl}_4]$ and $[(\text{Ar-BAIN})\text{GaCl}_2][\text{GaCl}_4]$

$[(\text{Ar-BIAN})\text{BCl}_2][\text{BCl}_4]\cdot 1.25[\text{CH}_2\text{Cl}_2]$ crystallizes in the uniquely determined orthorhombic space group $P2_12_12_1$, with four molecules in the unit cell. Crystals of this compound were not well-formed, and resulted in overall R values that are somewhat high. The X-ray analysis does show that $[(\text{Ar-BIAN})\text{BCl}_2][\text{BCl}_4]$ exists in the solid state as discrete anions and cations, with no unusual interactions between the ions or the solvent.

The anion ($[\text{BCl}_4]^-$) is a distorted tetrahedron, with bond angles between 100(1)° and 118(1)°, and B—Cl bond lengths ranging from 1.74(3) to 1.95(3) Å. There are no unusual structural features associated with this anion. The closest interactions between ions are between Cl4 and C21 (3.77 Å), and B2 and the centre of the ring formed by C2–C9 (4.25 Å). The primary coordination sphere of the boron centre in the $[(\text{Ar-BIAN})\text{BCl}_2]^+$ cation features two N→B dative bonds from the Ar-BIAN ligand (1.57(2) and 1.54(2) Å). Two B—Cl bonds complete the $[(\text{Ar-BIAN})\text{BCl}_2]^+$ coordination sphere. The B—Cl bond lengths in the cationic fragment, 1.78(2) and 1.89(1) Å, are about the same as those of the anionic fragment. For comparison, the B—Cl bond length in BCl_3 is 1.74 Å.[3] An ORTEP view of the cation $[(\text{Ar-BIAN})\text{BCl}_2]^+$ is shown in Fig. 1, and important bond lengths and angles are presented in Table 2.

$[(\text{Ar-BIAN})\text{GaCl}_2][\text{GaCl}_4]$ crystallizes in the monoclinic space group $P2_1/m$, with two molecules in the unit cell. The X-ray analysis of this complex also revealed that it exists in the solid state as discrete anions and cations. The $[\text{GaCl}_4]^-$ anion is tetrahedral, with Ga—Cl bond angles between 106.54(9)° and 111.26(6)°, and bond lengths between 2.159(2) and 2.175(1) Å. There are no unusual structural features associated with this anion.

The primary coordination sphere of the cationic $[(\text{Ar-BIAN})\text{GaCl}_2]^+$ fragment features two N→Ga dative bonds from the Ar-BIAN ligand (1.985(3) Å). This Ga—N bond

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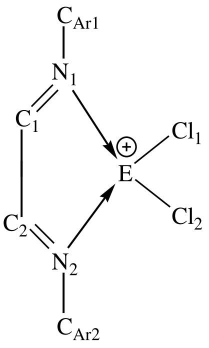
[3] Recently the reaction of a bulky 1,4-diazabutadiene with BCl_3 was reported, and the isolated compound was characterised as a 2,4,5-trichloro-1,3,2-diazaborolidine, which is a covalent alternative to the ionic diazaborolium salt. See reference 12. It is possible that a similar rearrangement occurs in the $[(\text{Ar-BIAN})(\text{EX}_2)][\text{EX}_4]$ compounds reported here.

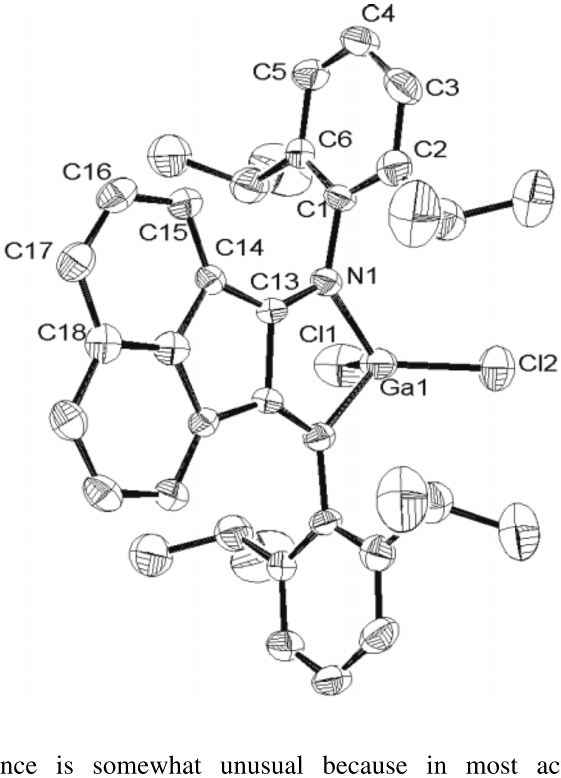
Table 2. Comparison of [(Ar-BIAN)$GaCl_2$][$GaCl_4$], [(Ar-BIAN)BCl_2][BCl_4], and [(DAB)$GaCl_2$][$GaCl_4$].



General structure for comparison of bond lengths and angles in Ar-BIAN and DAB complexes

Parameter	[(Ar-BIAN)BCl_2]$^+$	[(Ar-BIAN)$GaCl_2$]$^+$	[(DAB)$GaCl_2$]$^+$
N—E	1.57(2), 1.54(2)	1.985(3)	1.979(5), 1.982(6)
E—Cl	1.78(2), 1.89(1)	2.106(2), 2.124(3)	2.105(2), 2.104(2)
N-E-N	99.6(9)	85.1(2)	84.4(2)
N-E-Cl	115(1), 115(1), 108(1), 110.7(9)	114.1(1), 111.9(1)	Not reported
Cl-E-Cl	108.5(7)	115.9(1)	118.2(1)

Fig. 2. ORTEP view of cation [(Ar-BIAN)$GaCl_2$]$^+$ showing the labelling scheme. Thermal ellipsoids are shown at 50% probability level; hydrogen atoms have been removed for clarity.



distance is somewhat unusual because in most acyclic trialkylamine adducts, the Ga—N bond distances are much longer, being somewhere between 2.1 and 2.2 Å (14). This is, however, not so surprising because N is sp^2 hybridized and therefore has a shorter covalent radius than an sp^3 hybridized nitrogen centre. The coordination sphere around the cationic gallium centre in [(Ar-BIAN)$GaCl_2$]$^+$ is completed by two Ga—Cl bonds of 2.106(2) and 2.124(3) Å. Important bond lengths and angles are reported in Table 2. An ORTEP view of [(Ar-BIAN)$GaCl_2$]$^+$ is presented in Fig. 2. As shown in Table 2, the metrical parameters observed for [(Ar-BIAN)$GaCl_2$][$GaCl_4$] are similar to those reported for [DAB$GaCl_2$][$GaCl_4$] (DAB = *t*-BuN=C(H)-C(H) = N*t*Bu) (14).

There are no unusual long-range interactions between ions, and the closest interactions are the Cl5—C18 distance at 3.582 Å, and the Cl4 — centre of C13-C13A distance of 3.528 Å, and Ga2—C19 at 4.808 Å.

Attempts to prepare [(Ar-BIAN)ECl_2][$B(C_6F_6)_4$] via ion-exchange reactions were unsuccessful. It was hoped that the strong electron donating ability of **1** would facilitate formation of [(Ar-BIAN)ECl]$^{++}$, via ion-exchange and halide abstraction from [(Ar-BIAN)ECl_2]$^+$, but this was not realised. We are currently working on the preparation of amido-substituted derivatives to facilitate the formation of [(Ar-BIAN)ENR_2]$^{++}$, recognising the isoelectronic relationship with, for example, the carbocation [CR_3]$^+$. Finally, attempts to reduce [(Ar-BIAN)(EX_2)][EX_4] using Na or K to generate compounds such as **3** have thus far been unsuccessful.

Conclusions

Several new main group complexes were prepared based upon the *o*,*o*′-*i*-$Pr_2C_6H_3$-bis(imino)acenaphthene ligand. The Ar-BIAN ligand is easily prepared and is a robust ligand for supporting highly Lewis acidic main group element sites. Unfortunately, attempted reduction of [(Ar-BIAN)(EX_2)][EX_4] to produce heterocycles such as **3** were unsuccessful.

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