Prototypical arsine–triel adducts (R_3AsEX_3 for E = B, Al, and Ga)

Eamonn Conrad, Janet Pickup, Neil Burford, Robert McDonald, and Michael J. Ferguson

Abstract: Complexes of arsine ligands (R_3As, R = Me, Et, Ph) and Lewis acids of group-13 elements of the form EX_3 (E = B, X = Ph, C_6F_5; E = Al, X = Cl, Br, I; E = Ga, X = Cl) have been isolated and characterized by X-ray crystallography, infrared spectroscopy, ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and ^{27}Al NMR spectroscopy. The compounds are compared with rare arsine–triel adducts.

Key words: arsine–triel (boron, aluminum, gallium) Lewis adducts.

Résumé : Les complexes des ligands d'arsine (R_3As, R = Mé, Ét, Ph) et des acides de Lewis du groupe des éléments 13 de la forme EX_3 (E = B, X = Ph, C_6F_5; E = Al, X = Cl, Br, I; E = Ga, X = Cl) ont été isolés et caractérisés par la cristallographie aux rayons-X, la spectroscopie infrarouge, et la spectroscopie RMN de ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ et ^{27}Al. Les composés sont comparés aux adduits rares d'arsine–triel.

Mots-clés : adduits de Lewis d'arsine–triel (bore, aluminium, gallium).

[Traduit par la Rédaction]

Introduction

Compounds involving bonds between tetracoordinate group-13 elements and tetracoordinate group-15 elements represent prototypical examples of Lewis acid–base adducts and are well-known for compounds involving nitrogen or phosphorus donors. In contrast, examples of adducts involving arsine ligands on Lewis acids of group-13 elements are rare despite the importance of arsenic in the development of semiconducting materials such as gallium arsenide.

Compounds containing a coordinatively unsaturated arsenic center bound to a coordinatively unsaturated boron center are known,[1] but adducts of tetracoordinate arsenic bound to tetracoordinate boron have not been reported. Moreover, although examples of complexes of arsines with alanes,[2–4] gallanes,[5–7] or indanes[7,8] have been spectroscopically or crystallographically characterized, there are limited data available and few acyclic complexes are known that represent prototypical examples of arsines with Lewis acids of group-13 elements and provide fundamental data for the As–E bonds.

Prompted by the recent use of arsine ligands to stabilize pnictogenium cations (PnR^{2+})[9] and diphosphenium dications ($RPPR^{2+}$),[10] we report crystallographic and NMR spectroscopic data for compounds of the form R_3AsEX_3 for E = B, Al, and Ga. Comparisons are made with the rare examples that have been previously reported.

Results and discussion

Reaction mixtures containing an alkyl- or aryl-arsine (R_3As, R = Me, Et, Ph) and an arylborane (BX_3, X = Ph, C_6F_5) in CH_2Cl_2 exhibit a single signal in the $^{11}B\{^1H\}$ NMR spectra (Table 1). The chemical shifts are consistent with those observed for the corresponding solids that are isolated from reaction mixtures and redissolved in CD_2Cl_2 (or CD_3CN). Derivatives containing X = C_6F_5 have chemical shifts in the range observed for those compounds involving $B(C_6F_5)_3$ moieties.[11] Reaction mixtures of arsines (R_3As, R = Me, Et, Ph) with haloalanes (AlX_3, X = Cl, Br, I) in CH_2Cl_2 show a single chemical shift in the ^{27}Al NMR spectra (Table 1) with chemical shifts that are in the range of tetracoordinate aluminum centers.[12]

Crystalline samples of Me_3AsBPh_3, $Et_3AsB(C_6F_5)_3$, $Ph_3AsAlCl_3$, and Ph_3AsAlI_3 have been isolated from the reaction mixtures described above and $Ph_3AsGaCl_3$ was isolated from the reaction of Ph_3As and $GaCl_3$. The compounds have been crystallographically characterized as adducts of arsine ligands on group-13 Lewis acids. The structures all involve slightly distorted tetrahedral geometries at the arsenic and group-13 element centers, as illustrated in Figs. 1–5. There are no significant intermolecular interactions in any of the structures. Selected bond distances and angles are presented in Table 2 and torsional angles are available as Supplementary data.

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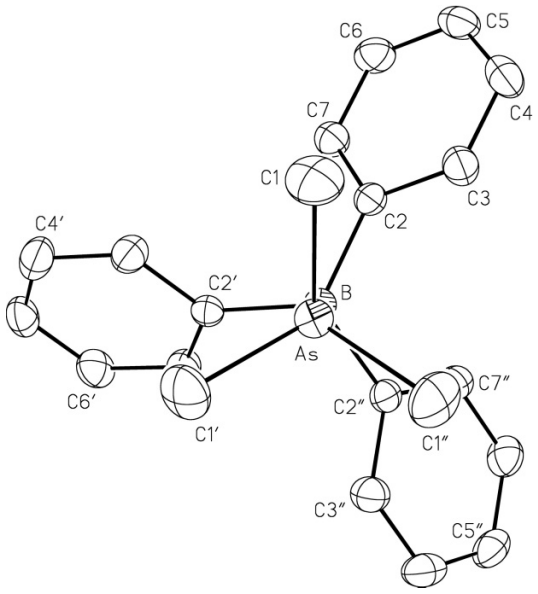
Table 1. $^{11}B\{^1H\}$ NMR and ^{27}Al NMR chemical shifts (ppm) in reaction mixtures of R_3As with EX_3 and for crystalline samples of adducts redissolved.

Compound	$^{11}B\{^1H\}$ or ^{27}Al (δ, ppm)
Me_3AsBPh_3	53.6 (s)
Et_3AsBPh_3	36.3 (s)
Ph_3AsBPh_3	67.8 (s)
$Me_3AsB(C_6F_5)_3$	–11.0 (s)
$Et_3AsB(C_6F_5)_3$	–11.8 (s)
$Ph_3AsB(C_6F_5)_3$	–11.6 (s)
$Me_3AsAlCl_3$	104.3 (s)
$Et_3AsAlCl_3$	110.3 (s)
$Ph_3AsAlCl_3$	104.1 (s)
$Me_3AsAlBr_3$	112.9 (s)
$Et_3AsAlBr_3$	104.8 (s)
$Ph_3AsAlBr_3$	108.4 (s)
Me_3AsAlI_3	110.5 (s)
Et_3AsAlI_3	111.2 (s)
Ph_3AsAlI_3	103.8 (s)

Fig. 1. Crystallographic view of Me_3AsBPh_3. Nonhydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level.



The As–B bond lengths in Me_3AsBPh_3 (2.148(3) Å) and $Et_3AsB(C_6F_5)_3$ (2.1905(18) Å) are longer than the sum of the covalent radii for arsenic and boron (2.09 Å). Both adducts adopt a close to eclipsed conformation (smallest C–As–B–C torsion angle in Me_3AsBPh_3 = 24.03(8)°, in $Et_3AsB(C_6F_5)_3$ = 9.89(13)°), which compares with the conformation observed in the phosphine–borane analogue, $Et_3PB(C_6F_5)_3$ (smallest C–P–B–C torsion angle = 15.7(3)°).[11]

Adducts $Ph_3AsAlCl_3$ and Ph_3AsAlI_3 are isomorphous with both Ph_3PGaI_3 and Ph_3AsGaI_3.[7] As for the arsine–borane adducts, the As–Al bond lengths ($Ph_3AsAlCl_3$, 2.5191(9) Å; Ph_3AsAlI_3, 2.517 Å) are slightly longer than the sum of the covalent radii for aluminum and arsenic (2.47 Å). Nevertheless, the As–Al bonds are shorter than those in *i*-Pr_3AsAl-*t*-Bu_3 (2.839(1) Å) and TMS_3AsAl-*t*-Bu_3 (2.654(2) Å),[3] likely due

Fig. 2. Crystallographic view of $Et_3AsB(C_6F_5)_3$. Nonhydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level.

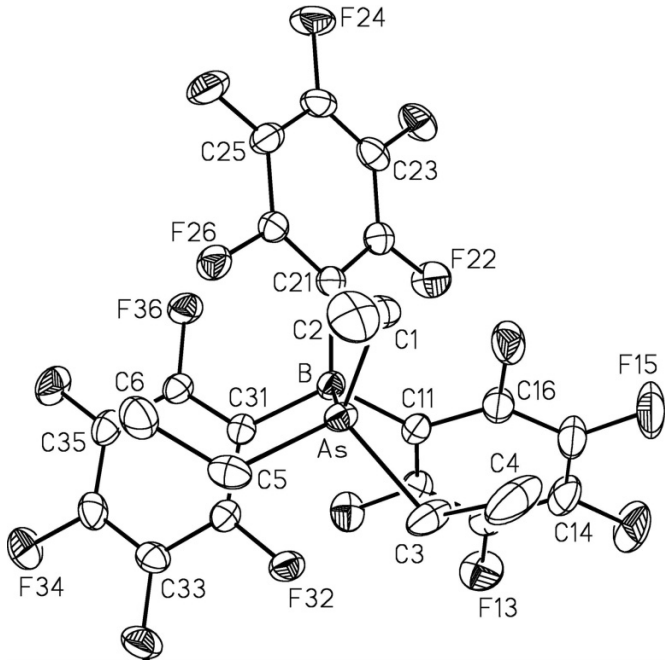
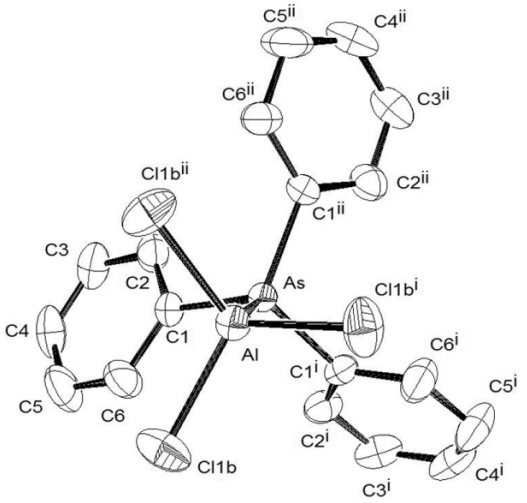


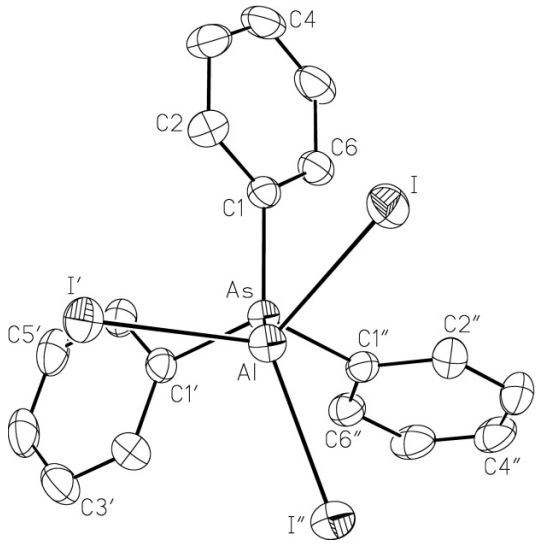
Fig. 3. Crystallographic view of the $Ph_3AsAlCl_3$ molecule showing the atom labelling scheme. Nonhydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.



to the lower steric repulsion in the organoalane derivatives and the inductive influence of the halogens on the Lewis acidity of the alane in the haloalane. The alane adducts $Ph_3AsAlCl_3$ and Ph_3AsAlI_3 adopt a more staggered conformation about the As–Al bond axis (smallest C–As–Al–C torsion angle in $Ph_3AsAlCl_3$ = 32.58(6)°, in Ph_3AsAlI_3 = 38.83(6)°) than the borane adducts Me_3AsBPh_3 and $Et_3AsB(C_6F_5)_3$.

Crystals of $Ph_3AsGaCl_3$ are isomorphous with both Ph_3PGaI_3 and Ph_3AsGaI_3[7] and there are two crystallographically independent molecules in the unit cell (Fig. 5). The As–Ga bond lengths (2.540(6) Å and 2.449(6) Å) are close to the sum of the covalent radii for arsenic and gallium

Fig. 4. Crystallographic views of Ph_3AsAlI_3. Nonhydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level.



(2.47 Å), and to that in Ph_3AsGaI_3.[7] The torsion angles about the As–Ga bond (smallest C–As–Ga–Cl torsion angles for molecule A = 29.9(3)°, for molecule B = –53.4(3)°) are more staggered than in the arsine–borane adducts.

Summary

Prototypical examples of compounds containing As → B, As → Al, and As → Ga coordinate bonds have been isolated from reaction mixtures of an arsine Lewis base with a triel Lewis acid. The compounds provide fundamental spectroscopic and structural data. While bond length trends are as expected, As → B < As → Al < As → Ga, the torsion angles are generally smaller for As → B complexes than for the As → Al and As → Ga complexes.

Experimental procedures

Reactions were carried out in an MBraun glovebox under atmosphere of dry N_2. Solvents were dried on an MBraun solvent purification system and stored over 4 Å molecular sieves. Deuterated solvents were purchased from Sigma-Aldrich and were used as received. Experimental details relating to the single crystal X-ray diffraction studies are summarized in Table 3. X-ray diffraction data were collected on a Bruker APEX II CCD area detector/D8 diffractometer. Crystals were coated with Paratone-N oil, mounted on glass fibres, and placed in a cold stream of N_2. Structures were solved by direct methods (SHELXS-97)[14] or Patterson search/structure expansion (DIRDIF-2008),[15] and refined using full-matrix least-squares on F^2 (SHELXL-97).[14] Hydrogen atom positions were calculated from the sp^2 or sp^3 hybridization geometries of their attached atoms. NMR spectra were obtained at room temperature, unless otherwise stated, on a Bruker AVANCE 500 ^{1}H (500.13 MHz, 11.7 T) and Bruker/Tecmag AC250 ^{1}H (250.06 MHz, 5.9 T). $^{13}C\{^1H\}$ NMR (125.76 MHz) chemical shifts were referenced to $\delta_{TMS} = 0.00$, as were $^{11}B\{^1H\}$ NMR (160.42 MHz) and ^{27}Al-NMR (130.29 MHz). Chemical shifts (δ) are reported in ppm. NMR spectra of samples were obtained by transferring an aliquot of sample in an appropriate deuterated solvent into a 5 mm sample tube. The tubes were capped and sealed with Parafilm prior to removal from the inert atmosphere. IR spectra were obtained from powdered and crystalline samples dissolved in CH_2Cl_2 and spotted on CsI plates. Data collection was on a Bruker Vertex FTIR spectrometer. Peaks are reported in wavenumbers (cm^{-1}) with ranked intensities in parenthesis beside the value, where a value of one is indicative of the most intense peak in the spectrum. Melting points were recorded on an Electrothermal melting point apparatus in sealed capillary tubes under N_2.

Caution

All arsines are known carcinogens and must be handled using appropriate procedures.

Preparation of Me_3AsBPh_3

A solution of Me_3As (52.0 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of BPh_3 (121.0 mg, 0.50 mmol) in CH_2Cl_2 and the mixture was stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. A white precipitate was isolated and washed with hexanes (3 × 3 mL). Crystals were obtained by CD_3CN/ether diffusion at –25 °C over 48 h. Yield: 65%, 117 mg; mp 144–146 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 3058 (1), 2917 (3), 2849 (4), 1590 (12), 1430 (13), 1261 (11), 1238 (10), 1096 (9), 1020 (8), 802 (5), 746 (6), 696 (2), 636 (7). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 1.23 (s, 9H), 7.52–7.57 (m, 6H), 7.58–7.63 (m, 3H), 7.65–7.70 (m, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273K, 125.76 MHz) δ: 8.4 (s), 128.0 (s), 130.6 (s), 138.3 (s). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 273 K, 160.42 MHz) δ: 53.6 (s).

Preparation of $Me_3AsB(C_6F_5)_3$

A solution of Me_3As (52.0 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of $B(C_6F_5)_3$ (256.0 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. A white precipitate formed immediately. The solid was isolated and washed with ether (3 × 3 mL) and has poor solubility. Crystals were obtained by CD_3CN/ether diffusion at –25 °C over 48 h. Yield: 78%, 236 mg; mp 257–259 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 2917 (1), 2703 (14), 1644 (10), 1516 (4), 1446 (1), 1370 (6), 1163 (16), 1117 (15), 1087 (5), 979 (3), 960 (2), 780 (9), 770 (8), 730 (17), 667 (7), 617 (11). ^{1}H NMR (CD_3CN, 273 K, 500 MHz, ppm) δ: 0.96 (s, 9H). $^{11}B\{^1H\}$ NMR (CD_3CN, 273 K, 160.42 MHz) δ: –11.0 (s).

Preparation of Et_3AsBPh_3

A solution of Et_3As (70.5 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of BPh_3 (121.0 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with ether and stored at –25 °C overnight. Clear colourless crystals were obtained by CD_3CN/ether diffusion at –25 °C over 48 h and were isolated and washed with ether (3 × 3 mL). Yield: 66%, 133 mg; mp 86–88 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 3666 (14), 3061 (1), 2425 (4), 1953 (13), 1642 (2), 1554 (12), 1462 (11), 1453 (10), 1260 (5), 1098 (7), 1020 (6), 847 (3), 699 (9), 613 (8). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 1.17 (t, $^3J_{HH}$ = 7.0 Hz, 9H), 1.68 (q, $^3J_{HH}$ = 7.0 Hz, 6H), 7.48–7.54 (m,

Fig. 5. Crystallographic views of the two crystallographically independent conformers (a and b) of the disordered structure of $Ph_3AsGaCl_3$. Nonhydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level.

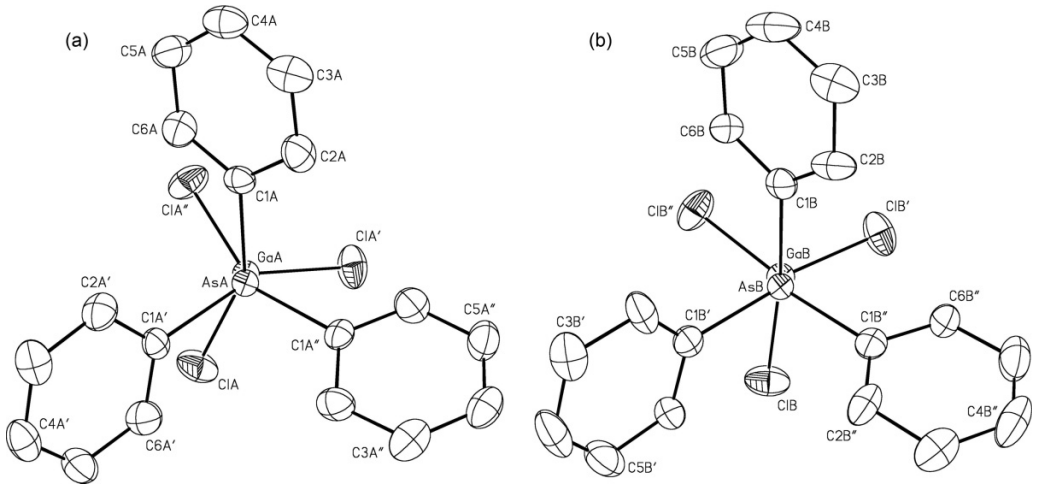


Table 2. Selected bond lengths (Å) and angles (°) in Ph_3BAsMe_3, $Et_3AsB(C_6F_5)_3$, $Ph_3AsAlCl_3$, Ph_3AsAlI_3, $Ph_3AsGaCl_3$, and related compounds.

Compound	E—As (Å)	C–As–E (°)	X–E–As (°)
Me_3AsBPh_3	2.148(3)	115.80(6)	104.83(10)
$Et_3AsB(C_6F_5)_3$	2.1905(18)	114.70(7)	103.35(10)
		112.75(8)	107.52(10)
		117.02(7)	104.56(11)
$\{(t\text{-}Bu)_2As\}_2BPh$[1]	2.064(5)	106.9(2)	124.3(5)
$Ph_3AsAlCl_3$[a]	2.5191(9)	114.17(5)	101.76(4)
			108.76(4)
Ph_3AsAlI_3	2.5140(10)	113.78(6)	102.48(2)
$Ph_3AsGaCl_3$[b]	2.540(6)	113.1(2)	106.29(16)
	2.449(6)	113.4(2)	107.40(16)
Ph_3AsGaI_3[7]	2.490(1)	113.21(7)	102.97(2)
TMS_3AsGaI_3[13]	2.509	—	—
$i\text{-}Pr_3AsAl\text{-}t\text{-}Bu_3$ [3]	2.839(1)	106.3(1)	111.5(2)
		100.5(1)	121.8(1)
		105.4(1)	110.2(1)
$TMS_3AsAlEt_3$ [3]	2.654(2)	Si–As–Al	C–Al–As
		113.5(1)	106.0(2)
		113.3(1)	102.9(2)
		113.2(1)	104.2(2)
$[TMS_2AsAlEt_2]_2$[4]	2.539(2)	Si–As–Al	C–Al–As
		114.10(6)	112.5(2)
		114.79(6)	114.7(2)
			110.3(2)
			112.5(2)
$TMS_3AsGaPh_3$[6]	2.671(1)	Si–As–Ga	C–Ga–As
		114.45(7)	103.3(2)
		110.74(7)	104.6(2)
		113.98(7)	105.3(2)

[a]Disorder in structure.
[b]Two crystallographically independent molecules in the asymmetric unit.

8H), 7.60–7.65 (m, 7H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 10.2 (s), 16.1 (s), 127.9 (s), 129.1 (s), 137.8 (s), 136.3 (s). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 273 K, 160.42 MHz, ppm) δ: 36.3 (s).

Preparation of $Et_3AsB(C_6F_5)_3$

A solution of Et_3As (70.5 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of $B(C_6F_5)_3$ (256.0 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. A white precipitate formed immediately. The solid was redissolved in CH_3CN and crystalline material was obtained by CH_3CN/ether diffusion at –25 °C over 48 h. Yield: 44%, 142 mg; mp 204–206 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 2918 (12), 1645 (7), 1518 (4), 1460 (1), 1374 (6), 1283 (8), 1100 (5), 979 (2), 965 (3), 772 (11), 731 (10), 669 (9). ^1H NMR δ: (CD_3CN, 273 K, 500 MHz, ppm) δ: 1.19 (t, $^3J_{HH}$ = 7.5 Hz, 9H), 1.86 (q, $^3J_{HH}$ = 7.5 Hz, 6H). $^{11}B\{^1H\}$ NMR (CD_3CN, 273 K, 160.42 MHz, ppm) δ: –11.8 (s).

Preparation of Ph_3AsBPh_3

A solution of Ph_3As (151.5 mg, 0.50 mmol) in CH_2Cl_2 was added to a solution of BPh_3 (121.0 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. A white powder was isolated and washed with ether (3 × 3 mL). Yield: 55%, 150 mg; decomposes above 100 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 3059 (1), 2429 (10), 2283 (11), 1980 (12), 1642 (2), 1260 (7), 1097 (6), 1019 (5), 910 (4), 804 (3), 734 (9), 694 (8). ^1H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 7.28–8.27 (m, 30H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 128.2 (s), 129.4 (s), 132.1 (s), 134.4 (s), 136.4 (s), 139.2 (s), 140.5 (s), 143.9 (s). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 273 K, 160.42 MHz, ppm) δ: 67.8 (s).

Preparation of $Ph_3AsB(C_6F_5)_3$

A solution of Ph_3As (151.5 mg, 0.50 mmol) in CH_2Cl_2 was added to a solution of $B(C_6F_5)_3$ (256.0 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. A white precipitate formed immediately. The solid was redissolved in CH_3CN and then precipitated by ether diffusion at –25 °C over 48 h. The solid was washed with ether (3 × 3 mL). Yield: 51%, 201 mg; mp 155–157 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 3001 (1), 2342 (17), 1895 (16), 1645 (12), 1464 (2), 1389 (4), 1366 (3), 1260 (9), 1230 (6), 1011 (11), 1020 (10), 950 (7), 923 (8), 888 (15), 850 (14), 802 (13),

Table 3. Crystallographic data for Ph_3BAsMe_3, $Et_3AsB(C_6F_5)_3$, and Ph_3AsEX_3 (E = Al and Ga; X = Cl and I).

Compound	Ph_3BAsMe_3	$Et_3AsB(C_6F_5)_3$	$Ph_3AsAlCl_3$	Ph_3AsAlI_3	$Ph_3AsGaCl_3$
Formula	$C_{21}H_{24}AsB$	$C_{24}H_{15}AsBF_{15}$	$C_{18}H_{15}AlAsCl_3$	$C_{18}H_{15}AlAsI_3$	$C_{18}H_{15}AsCl_3Ga$
Formula weight	362.13	674.09	439.55	713.90	482.29
Crystal system	Trigonal	Monoclinic	Trigonal	Trigonal	Trigonal
Space group	$P\bar{3}$ (No. 147)	$P2_1/n$	$R\bar{3}$ (No. 148)	$R\bar{3}$ (No. 148)	$R\bar{3}$ (No. 148)
a (Å)	11.3230 (6)	12.5167 (4)	13.9920 (12)	14.8705 (6)	14.0065 (7)
b (Å)	11.3230 (6)	10.5712 (3)	13.9920 (12)	14.8705 (6)	14.0065 (7)
c (Å)	8.1329 (4)	18.2940 (5)	16.8498 (14)	16.7263 (6)	16.8497 (9)
α (°)	90	90	90	90	90
β (°)	90	90.2369 (3)	90	90	90
γ (°)	120	90	120	120	120
Crystal size (mm^3)	0.43 × 0.21 × 0.19	0.32 × 0.29 × 0.28	0.67 × 0.60 × 0.34	0.49 × 0.41 × 0.31	0.48 × 0.36 × 0.29
Reflections collected	7754	19 870	7861	9448	8386
Independent reflections (R(int))	1387 (R_{int} = 0.0219)	5564 (R_{int} = 0.0178)	1452 (R_{int} = 0.0196)	1644 (R_{int} = 0.0162)	1470 (R_{int} = 0.0152)
GoF[a]	1.106	1.046	1.072	1.119	1.158
Z	2	4	6	6	6
V ($Å^3$)	903.02 (8)	2420.58 (12)	2856.8 (4)	3203.2 (2)	2862.7 (3)
ρ_{calcd} (mg m^{-3})	1.332	1.850	1.533	2.221	1.679
R_1	0.0199	0.0256	0.0196	0.0147	0.0171
wR_2	0.0534	0.0683	0.0508	0.0358	0.0509

[a] $S = [\sum^w (F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0259P)^2 + 0.3085P]^{-1}$, where $P = [Max(F_o^2, 0) + 2F_c^2]/3$).

729 (5). ^{1}H NMR δ: (CD_3CN, 273 K, 500 MHz, ppm) δ: 7.34–7.41 (m, 15H). ^{11}B{^{1}H} NMR (CD_3CN, 273 K, 160.42 MHz, ppm) δ: –11.6 (s).

Preparation of $Me_3AsAlCl_3$

A solution of Me_3As (52.0 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of $AlCl_3$ (61.5 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. A white powder formed and was isolated and washed with ether (3 × 3 mL). Yield: 70%, 89 mg; mp 143–145 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 3094 (1), 2921 (2), 2850 (3), 2432 (12), 2361 (11), 1642 (5), 1462 (14), 1412 (10), 1261 (9), 1100 (13), 1018 (8), 925 (4), 848 (7), 651 (6). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 2.21 (s, 9H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 7.9 (s). ^{27}Al NMR (CD_2Cl_2, 273 K, 130.29 MHz, ppm) δ: 104.3 (s).

Preparation of $Me_3AsAlBr_3$

A solution of Me_3As (52.0 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of $AlBr_3$ (133.5 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. A white powder formed and was isolated and washed with ether (3 × 3 mL). Yield: 71%, 137 mg. FTIR (CsI Plates, ranked intensities, cm^{-1}): 3016 (7), 2918 (8), 2848 (9), 1414 (4), 1269 (10), 1011 (11), 989 (12), 962 (13), 921 (1), 835 (6), 790 (2), 698 (3), 626 (5). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 1.59 (s, 9H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 6.9 (s). ^{27}Al NMR (CD_2Cl_2, 273 K, 130.29 MHz, ppm) δ: 112.9 (s).

Preparation of Me_3AsAlI_3

A solution of Me_3As (52.0 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of AlI_3 (204.0 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. Upon completion, the solution was layered with hexanes and allowed to sit at –25 °C overnight. White powder was obtained and washed with ether (3 × 3 mL) and solvents removed in vacuo. Yield: 69%, 184 mg; mp 138–140 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 3000 (1), 2918 (2), 2849 (3), 1641 (9), 1462 (4), 1389 (8), 1365 (7), 1261 (15), 1230 (10), 1094 (14), 1019 (11), 923 (12), 802 (13), 729 (5), 719 (6). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 1.57 (bs, 9H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 7.1 (s). ^{27}Al NMR (CD_2Cl_2, 273 K, 130.29 MHz, ppm) δ: 110.5 (s).

Preparation of $Et_3AsAlCl_3$

A solution of Et_3As (70.5 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of $AlCl_3$ (61.5 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. A white powder formed and was isolated and washed with ether (3 × 3 mL). Yield: 65%, 96 mg; mp 160–162 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 3341 (14), 2972 (4), 2938 (6), 2879 (7), 2304 (13), 2197 (14), 1459 (3), 1416 (9), 1387 (10), 1238 (8), 954 (2), 876 (16), 794 (12), 696 (1), 678 (5). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 1.36 (t, $^3J_{HH}$ = 7.85 Hz, 9H), 2.06 (q, $^3J_{HH}$ = 7.85 Hz, 6H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 9.3 (s), 13.6 (s). ^{27}Al NMR (CD_2Cl_2, 273 K, 130.29 MHz, ppm) δ: 110.3 (s).

Preparation of $Et_3AsAlBr_3$

A solution of Et_3As (70.5 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of $AlBr_3$ (133.5 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. A white powder formed and was isolated and washed with ether (3 × 3 mL) and solvents removed in vacuo. Yield: 62%, 133 mg. FTIR (CsI plates, ranked intensities, cm^{-1}): 2973 (1), 2940 (2), 2880 (3), 2849 (8), 2431 (16), 1640 (14), 1459 (4), 1416 (12), 1389 (13), 1240 (11), 1093 (15), 1022 (9), 923 (17), 793 (3), 744 (10), 706 (5), 678 (5). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 1.59 (t, $^3J_{HH}$ = 9.0 Hz, 9H), 3.07 (q, $^3J_{HH}$ = 9.0 Hz, 6H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 8.7 (s), 26.3 (s). ^{27}Al NMR (CD_2Cl_2, 273 K, 130.29 MHz, ppm) δ: 104.8 (s).

Preparation of Et_3AsAlI_3

A solution of Et_3As (70.5 μL, 0.50 mmol) in CH_2Cl_2 was added to a solution of AlI_3 (204.0 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. A pale brown oil was obtained and washed with ether (3 × 3 mL). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 1.36 (t, $^3J_{HH}$ = 7.95 Hz, 9H), 2.06 (q, $^3J_{HH}$ = 7.90 Hz, 6H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 9.3 (s), 13.4 (s). ^{27}Al NMR (CD_2Cl_2, 273 K, 130.29 MHz, ppm) δ: 111.2 (s).

Preparation of $Ph_3AsAlCl_3$

A solution of Ph_3As (151.5 mg, 0.50 mmol) in CH_2Cl_2 was added to a solution of $AlCl_3$ (61.5 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. A white powder formed and was isolated and washed with ether (3 × 3 mL). Crystals were obtained by CH_2Cl_2/pentane layering at –25 °C over 48 h. Yield: 65%, 142 mg; mp 57–59 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 3064 (1), 2432 (14), 1886 (20), 1642 (5), 1578 (11), 1480 (6), 1433 (4), 1336 (18), 1305 (16), 1261 (17), 1184 (14), 1156 (15), 1083 (8), 1074 (9), 1023 (13), 998 (11), 844 (10), 735 (2), 692 (3), 613 (2). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 7.69–7.75 (m, 6H), 7.73–7.83 (m, 6H), 7.86–7.91 (m, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 131.6 (s), 133.1 (s), 133.7 (s), 135.4 (s). ^{27}Al NMR (CD_2Cl_2, 273 K, 130.29 MHz, ppm) δ: 104.1 (s).

Preparation of $Ph_3AsAlBr_3$

A solution of Ph_3As (151.5 mg, 0.50 mmol) in CH_2Cl_2 was added to a solution of $AlBr_3$ (133.5 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. Yellow glassy material was obtained and washed with ether (3 × 3 mL). Yield: 60%, 171 mg. FTIR (CsI plates, ranked intensities, cm^{-1}): 3060 (1), 2905 (2), 2870 (3), 2427 (10), 1642 (4), 1515 (13), 1451 (12), 1260 (8), 1097 (7), 1019 (6), 845 (5), 730 (9), 696 (11). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 7.76–7.77 (m, 6H), 7.83–7.87 (m, 6H), 7.93–7.98 (m, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 273 K, 125.76 MHz,

ppm) δ: 131.8 (s), 133.3 (s), 133.5 (s), 135.8 (s). ^{27}Al NMR (CD_2Cl_2, 273 K, 130.29 MHz, ppm) δ: 108.4 (s).

Preparation of Ph_3AsAlI_3

A solution of Ph_3As (151.5 mg, 0.50 mmol) in CH_2Cl_2 was added to a solution of AlI_3 (204.0 mg, 0.50 mmol) in CH_2Cl_2 and stirred for 30 min. The solution was layered with hexanes and stored at –25 °C overnight. Small yellow crystals were obtained and were washed with ether (3 × 3 mL). Yield: 50%, 179 mg; mp 86–88 °C. FTIR (CsI plates, ranked intensities, cm^{-1}): 3052 (11), 2994 (10), 2917 (9), 2849 (8), 1578 (12), 1481 (4), 1433 (3), 1365 (17), 1261 (13), 1184 (14), 1158 (15), 1082 (5), 1022 (6), 997 (7), 799 (16), 735 (1), 694 (2). ^{1}H NMR (CD_2Cl_2, 273 K, 500 MHz, ppm) δ: 7.69–7.72 (m, 2H), 7.81–7.85 (m, 2H), 7.93–7.97 (m, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 273 K, 125.76 MHz, ppm) δ: 130.9 (s), 132.2 (s), 134.4 (s), 135.6 (s). ^{27}Al NMR (CD_2Cl_2, 273 K, 130.29 MHz, ppm) δ: 103.8 (s).

Preparation of $Ph_3AsGaCl_3$

The procedures were described by Reid and co-workers,[5a] and the characterization data was consistent. Crystalline material was obtained by CH_2Cl_2/pentane layering at –25 °C over 48 h.

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca). CCDCs 759512–759516 contain the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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