ESI

for

Phosphine Complexes of Aluminium(III) Halides – Preparation and Structural and Spectroscopic Systematics

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Table S1. X-ray crystallographic data

Compound	[*o*-$C_6H_4(PMe_2)(PHMe_2)]_2$ [$AlCl_4$][Cl]	[*o*-$C_6H_4(PMe_2)(PHMe_2)]_2$ [$AlBr_4$][Br]	[$Cy_2HP(CH_2)_2PHCy_2$] [$AlCl_4]_2$
Formula	$C_{20}H_{34}AlCl_5P_4$	$C_{20}H_{34}AlBr_5P_4$	$C_{26}H_{50}Al_2Cl_8P_2$
M	602.58	824.88	762.16
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c (no. 15)	C2/c (no. 15)	$P2_1/c$ (no. 14)
a /Å	14.599(5)	14.834(7)	7.073(6)
b /Å	20.672(7)	21.144(8)	17.551(13)
c /Å	11.006(5)	11.274(5)	14.924(13)
α/ °	90	90	90
β /°	115.061(5)	115.646(6)	101.682(15)
γ/°	90	90	90
U /Å^3	3009(2)	3188(2)	1814(3)
Z	4	4	2
μ(Mo-K_α /mm^{-1}	0.733	6.540	0.775
F(000)	1248	1608	796
Total number reflns	18200	13640	10205
Unique reflns	3461	3631	3545
R_{int}	0.0930	0.0306	0.0741
No. of params, restraints	146, 0	146, 0	175, 0
R_1, wR_2 [$I > 2\sigma(I)$] [b]	0.0640, 0.1041	0.0321, 0.0536	0.0884, 0.1658
R_1, wR_2 (all data)	0.0859, 0.1111	0.0382, 0.0555	0.1146, 0.1786

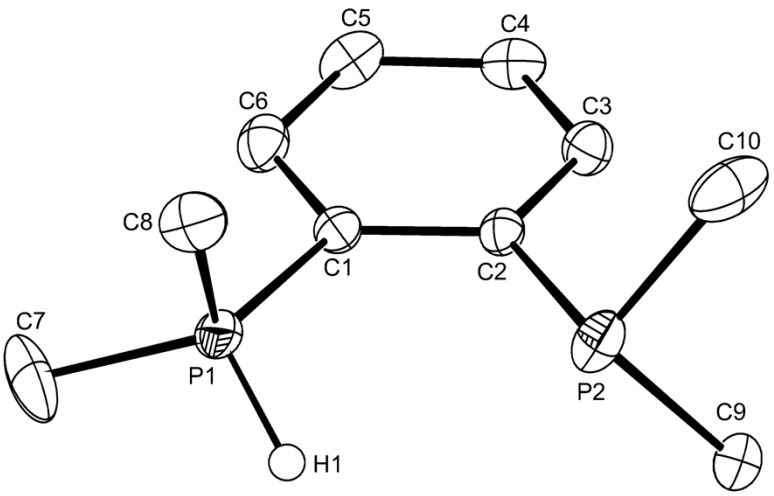

Fig. S1. The structure of the cation in [*o*-$C_6H_4(PMe_2)(PHMe_2)]_2[AlCl_4][Cl]$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms bonded to C are omitted for clarity. Selected bond lengths (Å): P1─C7 = 1.777(4), P1─C8 = 1.783(3), P1─C1 = 1.799(3), P1─H1 = 1.29(3), P2─C10 = 1.836(4), P2─C9 = 1.838(3), P2─C2 = 1.845(3). The cation in the isomorphous [*o*-$C_6H_4(PMe_2)(PHMe_2)]_2[AlBr_4][Br]$ has effectively identical dimensions.

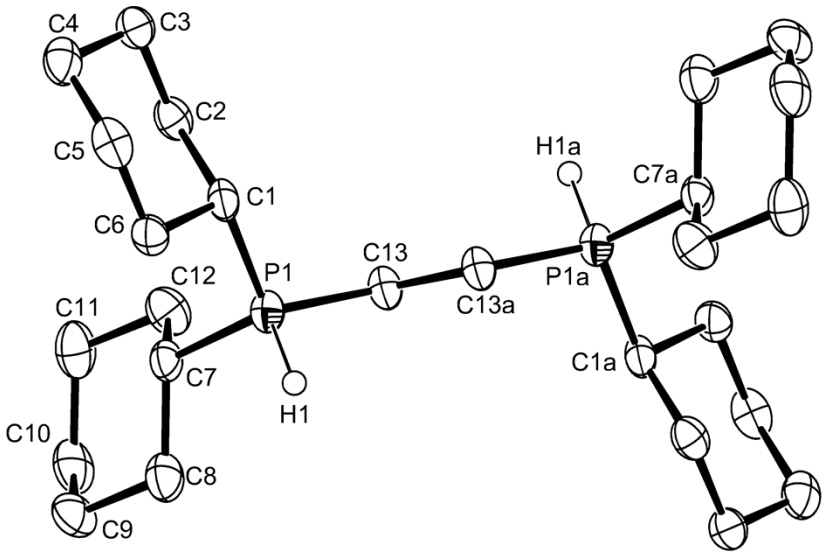

Fig. S2. The structure of the centrosymmetric cation in $[Cy_2HP(CH_2)_2PHCy_2][AlCl_4]_2$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms bonded to C are omitted for clarity. Symmetry operation: a = 1 – x, 1 – y, 2 – z. Selected bond lengths (Å): P1─C13 = 1.811(6), P1─C1 = 1.812(6), P1─C7 = 1.822(6), P1─H1 = 1.36(6).

These phosphonium salts were formed either by trace hydrolysis or as by-products (through reaction with the solvent) of the reactions of the diphosphanes with AlX_3 as described in the main text. The spectroscopic data are listed below:-

$[Cy_2HP(CH_2)_2PHCy_2][AlCl_4]_2$: ^{31}P NMR (CD_2Cl_2, 295 K): δ = 26.8 (d, $^1J_{PH}$ = 462 Hz).

$[o\text{-}C_6H_4(PMe_2)(PHMe_2)]_2[AlCl_4][Cl]$: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = –4.2 (d, $^4J_{PP}$ = 56 Hz), –51.9 (d, $^4J_{PP}$ = 56 Hz). ^{31}P NMR: δ = –4. 2 (d, $^1J_{PH}$ = 540 Hz).

Analysis of M−X Bond Lengths in $[MX_4]^-$ (M = Al, Ga, I): Data taken from the Cambridge Structural Database (CSD version 5.34; latest update = May 2013) on the 21st January 2014. The data were analysed in Legacy Vista (version 2.1). The REFcodes used all contained discrete $[MX_4]^-$ molecules – those containing bonds to other atoms and structures containing any disorder were omitted.

Figure S3. Al−Cl Bond Length Distribution in $[AlCl_4]^-$

Data points = 915 from 184 REFcodes

Range = 2.055 – 2.216 Å

Mean Al−Cl bond length = 2.126±0.018 Å

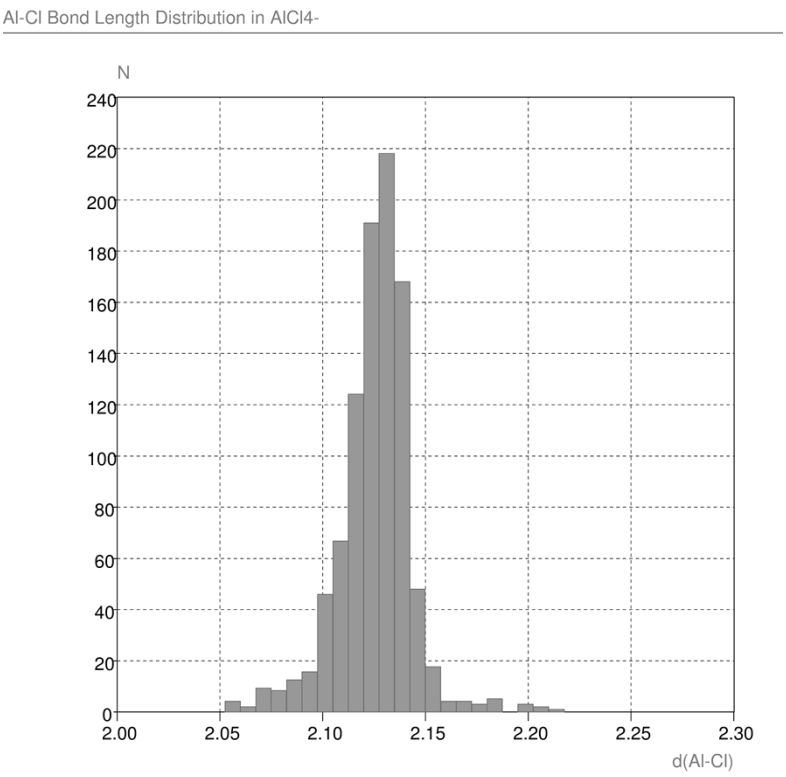

Figure S4. Al−Br Bond Length Distribution in $[AlBr_4]^-$

Data points = 64 from 13 REFcodes

Range = 2.244 – 2.320 Å

Mean Al−Br bond length = 2.289±0.015 Å

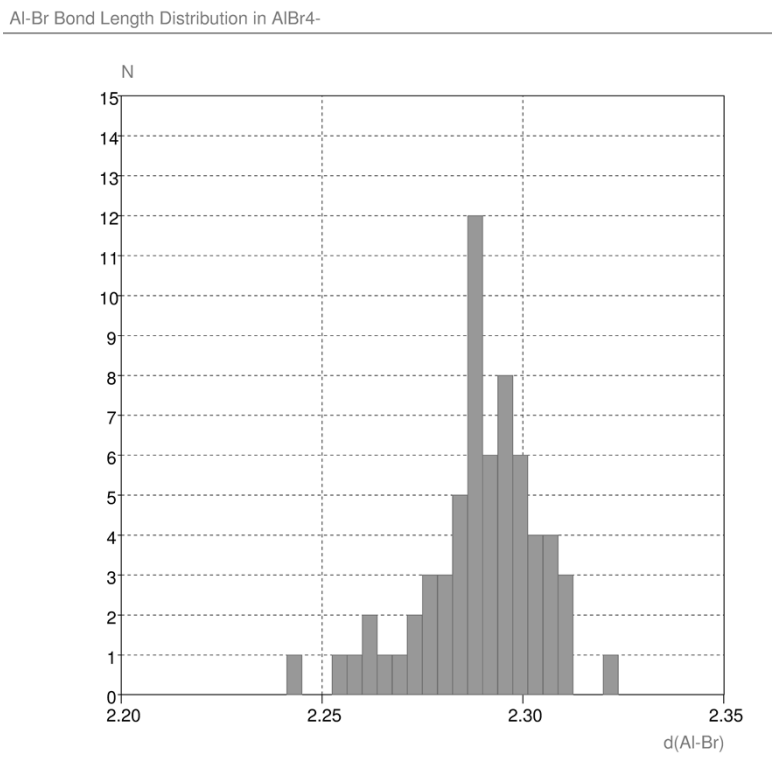

Figure S5. Al−I Bond Length Distribution in $[AlI_4]^-$

Data points = 12 from 3 REFcodes

Range = 2.506 – 2.555 Å

Mean Al−I bond length = 2.527±0.012 Å

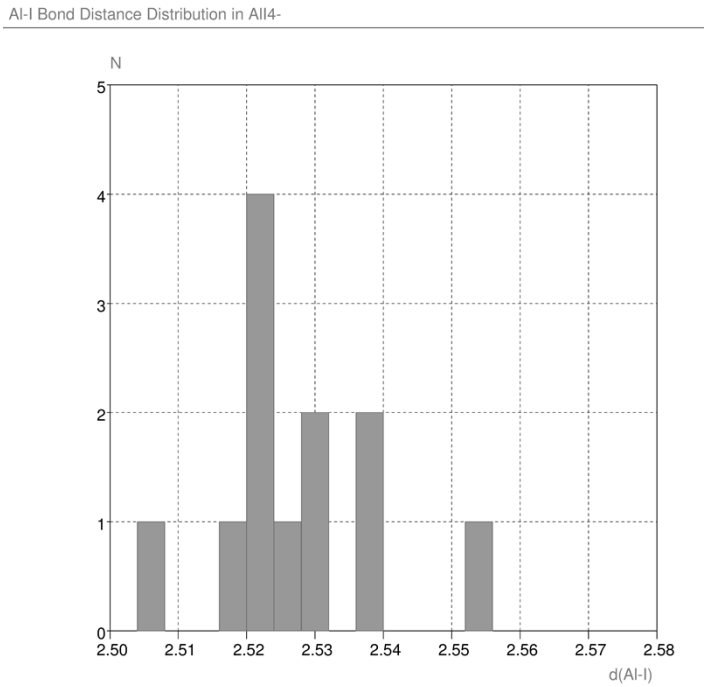

Figure S6. Ga−Cl Bond Length Distribution in $[GaCl_4]^-$

Data points = 705 from 157 REFcodes

Range = 2.036 – 2.258 Å

Mean Ga−Cl bond length = 2.166±0.018 Å

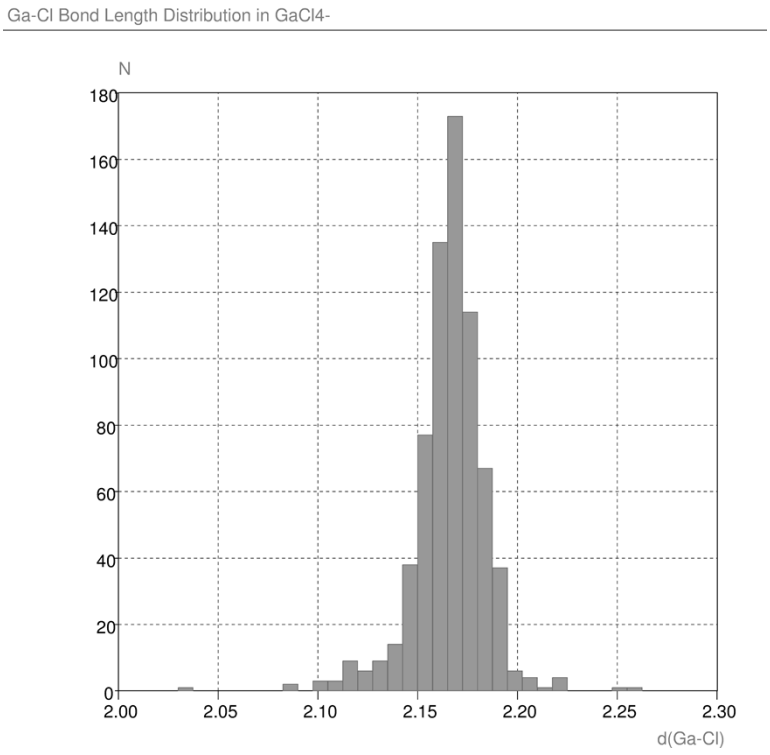

Figure S7. Ga−Br Bond Length Distribution in $[GaBr_4]^-$

Data points = 91 from 27 REFcodes

Range = 2.277 – 2.361 Å

Mean Ga−Br bond length = 2.321±0.016 Å

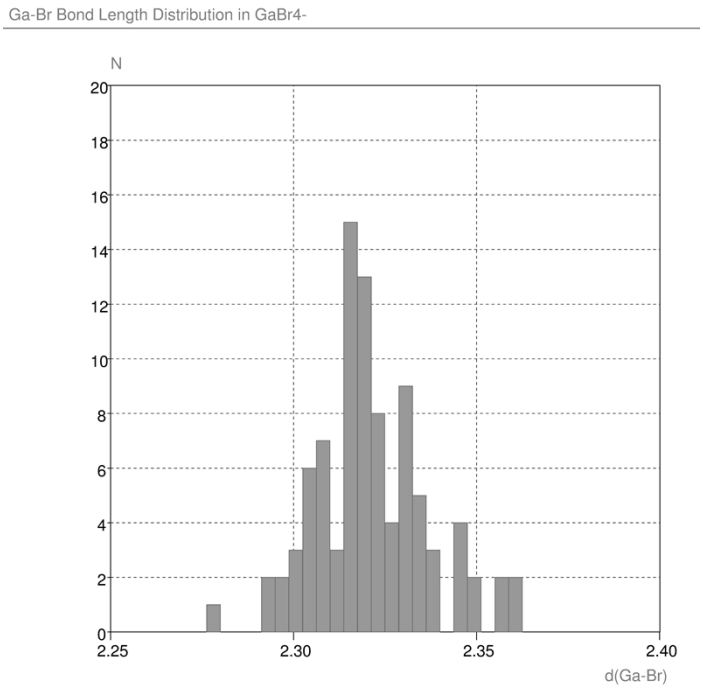

Figure S8. Ga−I Bond Length Distribution in $[GaI_4]^-$

Data points = 31 from 8 REFcodes

Range = 2.506 – 2.586 Å

Mean Ga−I bond length = 2.544±0.018 Å

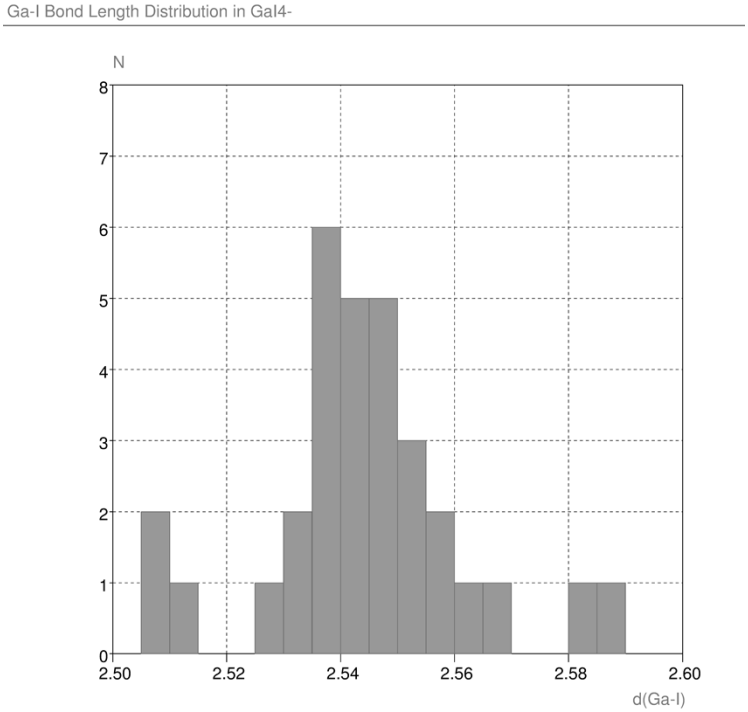

Figure S9. In−Cl Bond Length Distribution in $[InCl_4]^-$

Data points = 26 from 7 REFcodes

Range = 2.295 – 2.368 Å

Mean In−Cl bond length = 2.337±0.022 Å

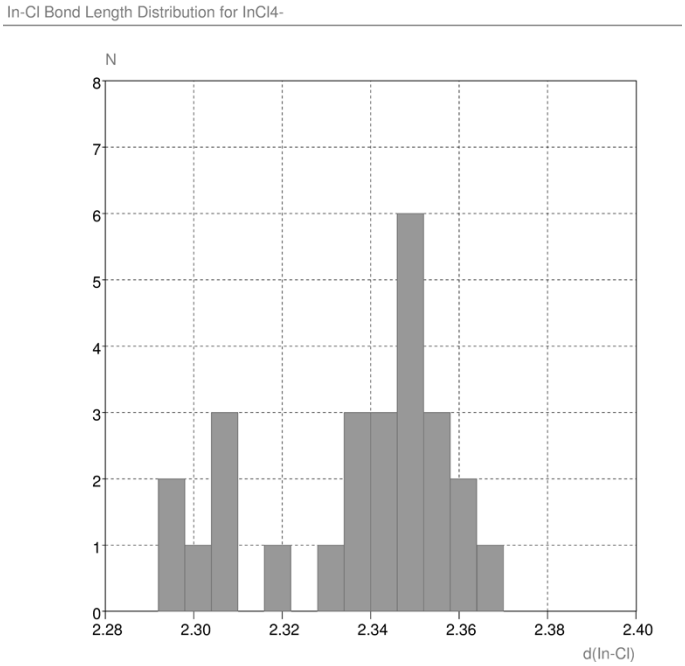

Figure S10. In−Br Bond Length Distribution in $[InBr_4]^-$

Data points = 50 from 11 REFcodes

Range = 2.438 – 2.510 Å

Mean In−Br bond length = 2.484±0.018 Å

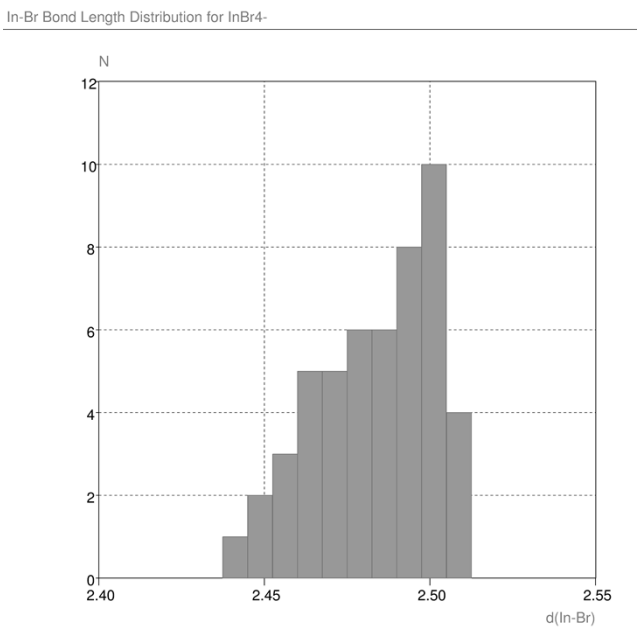

Figure S11. In−I Bond Length Distribution in $[InI_4]^-$

Data points = 35 from 8 REFcodes

Range = 2.663 – 2.731 Å

Mean In−I bond length = 2.702±0.014 Å

In-I Bond Length Distribution in InI4-