Supporting Information

Phosphinopnictinophosphonium Frameworks

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Experimental Section

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 Aldrich and were used as received. All chemicals were purchased from Aldrich and solids sublimed before use. Me_3SiOTf was purchased from Aldrich and distilled prior to use. ANCl (10-chloro-5-hydrophenarsazine) was prepared from literature methods.[1]

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). $^{13}C\{^{1}H\}$-NMR (125.76 MHz) chemical shifts were referenced to δ_{TMS} = 0.00, $^{31}P\{^{1}H\}$-NMR (202.46 MHz, 101.26 MHz) to $\delta_{H3PO4\ (85\%)}$ = 0.00. Chemical shifts (δ) are reported in ppm. NMR spectra on samples were obtained by transferring an aliquot of sample in appropriate deuterated solvent into a 5 mm sample tube. The tubes were capped and sealed with parafilm prior to removal from the inert atmosphere.

The solid state NMR experiments were carried out on a Bruker Avance NMR spectrometer with a 9.4T magnet (400 MHz proton Larmor frequency, 162.02MHz ^{31}P Larmor frequency). The experimental parameters for the 31P cross-polarization (CP) / magic angle spinning (MAS) experiments with TPPM proton decoupling were optimized on $NH_4H_2PO_4$, whose resonance also served as external, secondary chemical shift standard at 0.81ppm. The crystalline samples were packed into rotors of 4mm diameter in a MBraun glovebox and kept under nitrogen until the start of the experiments. For the ^{31}P CP/MAS NMR spectra of the samples 32 scans were accumulated, using 500 μs and 2 ms

CP contact times, 24.5s recycle delays, and 7.00, 11.00 and 12.00 kHz MAS frequencies.. Sample were prepared by packing crystalline samples into router and sealed with cap and parafilm in an MBraun glovebox under nitrogen.

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 FT-IR 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. Elemental analysis of selected samples were performed by Canadian Microanalytical Services Ltd. Delta, British Columbia, Canada. X-ray diffraction data were collected on Bruker PLATFORM/SMART 1000 CCD using Mo Kα radiation (α = 0.71073 Å). Crystals were selected under oil, mounted on glass fibres, and placed in a cold stream of N_2. Structures were solved by direct methods and refined using full matrix least squared on F^2. Hydrogen–atom positions were calculated.

Preparation of [(CyP)$_4$(AN)][OSO$_2$CF$_3$] ANCl (139 mg, 0.500 mmol) and $Me_3SiOSO_2CF_3$ (150 μL, 0.600 mmol) was stirred in CH_2Cl_2 (3 mL) for 30 minutes resulting in a purple solution. (CyP)$_4$ (228 mg, 0.500 mmol) was added to the reaction mixture resulting in a dark orange solution. The solution was stirred for 30 minutes then layered with hexanes and crystals formed after 24 hours at -25˚C. The solution was decanted and the solid was washed with hexanes (3 x 3 mL). Yield: 297 mg, 70% Melting point: 196-198°C. FTIR (cm^{-1}, ranked intensities): 3944 (20), 3417 (21), 3054 (5), 2987 (8), 2934 (13), 2834 (18), 2685 (16), 2411 (22), 2306 (11), 1595 (14), 1574 (15), 1461 (3), 1422 (4), 1263 (2), 1162 (6), 1030 (12), 896 (2), 746 (1), 650 (9), 514

(17), 443 (19), 286 (10). ^{31}P CP/MAS spectra of [$(CyP)_4(AN)$][SO_3CF_3] are shown in Figure S1. ^{31}P{^{1}H}-NMR (CH_2Cl_2, 101.3 MHz, 293 K): -58 ppm (*bs*, solution) ^{1}H-NMR (CD_2Cl_2, 500 MHz, 293 K): 1.08-1.51 (20 H), 1.70-2.15 (24 H), 7.16 (*t*, $^3J_{HH}$ = 9 Hz, 3 H), 7.41-7.53 (*m*, 3 H), 7.56 (*bt*, 2H), 7.92 (*s*, 1H). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125.8 MHz, 293 K): Elemental Analysis: Calculated for $C_{37}H_{53}AsF_3NO_3P4_S$: Calcd. (Found) C, 52.42 (52.76); H, 6.30 (6.14).

Preparation of [$(CyP)_4(AN)$][$GaCl_4$] ANCl (139 mg, 0.500 mmol) and $GaCl_3$ (108 mg, 0.600 mmol) was stirred in CH_2Cl_2 (3 mL) for 30 minutes resulting in a purple solution. $(CyP)_4$ (228 mg, 0.500 mmol) was added to the reaction mixture resulting in a dark orange solution. The solution was stirred for 30 minutes then layered with hexanes and crystals formed after 24 hours at -25˚C. The remaining solvent was removed and the solid was washed with hexanes (3 x 3 mL) and remaining solvents were removed *in vacuo*. Yield: 324 mg, 68 %. Melting Point: 218-219°C. FTIR (cm^{-1}, ranked intensities): 3347 (12), 2916 (2), 2848 (4), 1596 (7), 1572 (8), 1481 (15), 1460 (3), 1439 (6), 1343 (9), 1262 (10), 1234 (13), 1064 (11), 1026 (16), 997 (17), 750 (5), 597 (14), 506 (14), 369 (1). ^{31}P CP/MAS spectra of [$(CyP)_4(AN)$][$GaCl_4$] are shown in Figure S2. ^{31}P{^{1}H}-NMR (CH_2Cl_2, 101.3 MHz, 293 K): -58 ppm (*bs*, solution). ^{1}H-NMR ($CDCl_3$, 500 MHz, 293 K): ^{13}C{^{1}H}-NMR ($CDCl_3$, 125.8 MHz, 293 K): Elemental Analysis: Calculated for $C_{36.5}H_{54}AsCl_5GaNP_4$: Calcd. (Found) C, 45.88 (44.90); H, 5.70 (5.84).

Preparation of [$(CyP)_4SbCl_2$][Al_2Cl_7] $SbCl_3$ (91.2 mg, 0.400 mmol), $AlCl_3$ (98.4 mg, 0.800 mmol) and $(CyP)_4$ (182.4 mg, 0.400 mmol) was stirred in toluene (5 mL) for 30 minutes resulting in a yellow solution. The solution was stirred for 30 minutes further then layered with pentane and crystals formed after 24 hours at -25˚C. The remaining solvent was removed and the solid was washed with hexanes (3 x 3 mL). Melting Point: 94-96°C FTIR (cm^{-1}, ranked intensities): 3034 (16), 2918 (1), 2848 (3), 2662 (19), 2329 (20), 1851 (21), 1867 (22), 1811 (23), 1607 (15), 1495 (8), 1443 (4), 1383 (2), 1341 (7), 1295 (10), 1264 (5), 1176 (9), 1120 (17), 1015 (18), 1001 (6), 889 (2), 850 (12), 812 (16), 727 (11), 692 (13). ^{1}H-NMR (CD_2Cl_2, 500 MHz, 293 K): 1.15-1.60 (21 H), 1.71- 2.19 (21 H), 2.56 (bs, 2H). Chemical shifts are reported in regions as there are many overlapping shifts in the ^{1}H NMR spectra. Approximate integrations reported in brackets. ^{13}C{^{1}H}-NMR (CD_2Cl_2, 125.8 MHz, 293 K): 31.1 (*s*), 30.9 (*s*), 29.9 (*s*), 29.4 (*s*), 27.8 (*s*), 26.5 (*s*), 26.3 (*s*), 25.9 (*s*), 25.8 (*s*), 25.2 (*s*), 25.1 (*s*), 24.9 (*s*). ^{31}P{^{1}H}-NMR ($CD_3C_6D_5$, 101.3 MHz, 200 K): See Figure **S7**. While single crystals could be isolated, bulk samples could not be separated from a yellow oily residue, precluding elemental analysis, therefore yields are not included.

Preparation of $[\{(CyP)_4\}_2(Sb_2Cl_2)][AlCl_4]_2$ $SbCl_3$ (68.4 mg, 0.300 mmol), $AlCl_3$ (75.8 mg, 0.600 mmol) and $(CyP)_4$ (91.2 mg, 0.200 mmol) was stirred in toluene (1.5 mL) for 12 hours resulting in an orange solution. The solution was then layered with pentane and crystals formed after 24 hours at -25˚C. The solution was decanted and the solid was washed with hexanes (3 x 3 mL). Melting Point: 161-164°C; FTIR (cm-1, ranked intensities): 3034 (16), 2918 (1), 2848 (3), 2662 (19), 2329 (20), 1851 (21), 1867 (22), 1811 (23), 1607 (15), 1495 (8), 1443 (4), 1383 (2), 1341 (7), 1295 (10), 1264 (5), 1176 (9), 1120 (17), 1015 (18), 1001 (6), 889 (2), 850 (12), 812 (16), 727 (11), 692 (13); ^{31}P{^{1}H}-NMR ($CD_3C_6D_5$, 101.3 MHz, 200 K): 2.9 (*t*, $^{1}J_{PP}$ = 220 Hz), -68.5 (*t*, $^{1}J_{PP}$ = 220 Hz). While single crystals could be isolated, bulk samples could not be separated from an impurity (-36.5 ppm) tentatively assigned as $(CyP)_4$-$AlCl_3$,[2,3] precluding elemental analysis. This reasons is also why yields are not included.

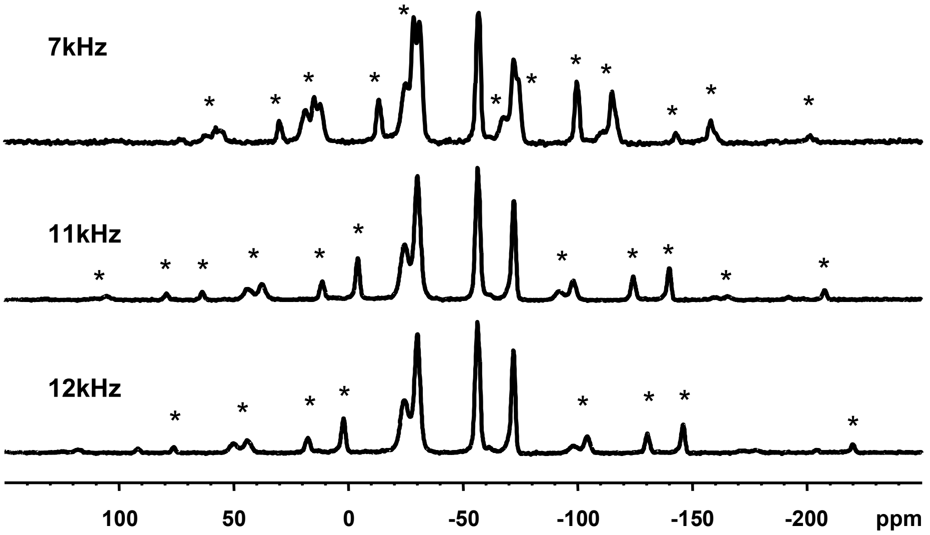

Figure S1: ^{31}P CP/MAS spectra of $[(CyP)_4(AN)][SO_3CF_3]$ at 7, 11, and 12 KHz. Spectra gives rise to 4 isotropic shifts with integrations (-24.6392 [1P], -30.1169 [1P], -56.4063 [1P], -71.9315 [1P]) consistent with crystallographically observed structure. The stars indicate spinning sidebands.

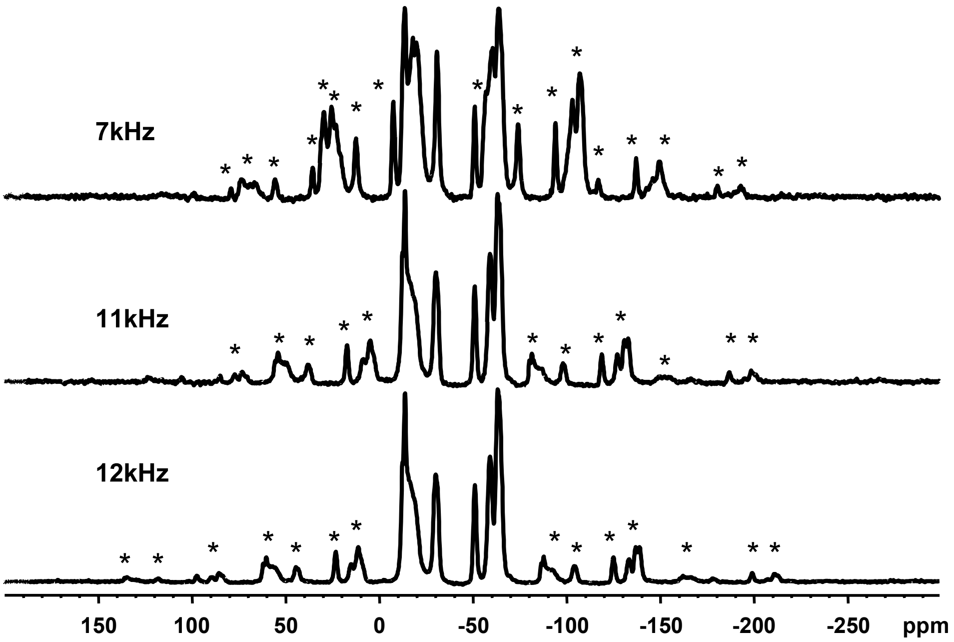

Figure S2: ^{31}P CP/MAS of [(CyP)$_4$(AN)][GaCl$_4$] at 7, 11, and 12 KHz. Due to the similarity of the chemical structure, i.e., the ^{1}H – ^{31}P distances and the chemical shift anisotropies, the integration of the ^{31}P CP/MAS spectra are meaningful. There are three isotropic shifts with integrations of one phosphorus (-29.843, -50.785, -58.930), and one region each with integrations of two (-63.012) and three (-13.618) phosphorus. This total integration of eight is consistent with the crystallographically observed structure. The stars indicate spinning sidebands.

X-Ray Crystallography

X-ray diffraction data were collected on 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*[4]) or Patterson search/structure expansion (*DIRDIF-2008*[5]), and refined using full matrix least squares on F^2 (*SHELXL-97*[4]). Hydrogen atom positions were calculated from the sp^2 or sp^3 hybridization geometries of their attached atoms.

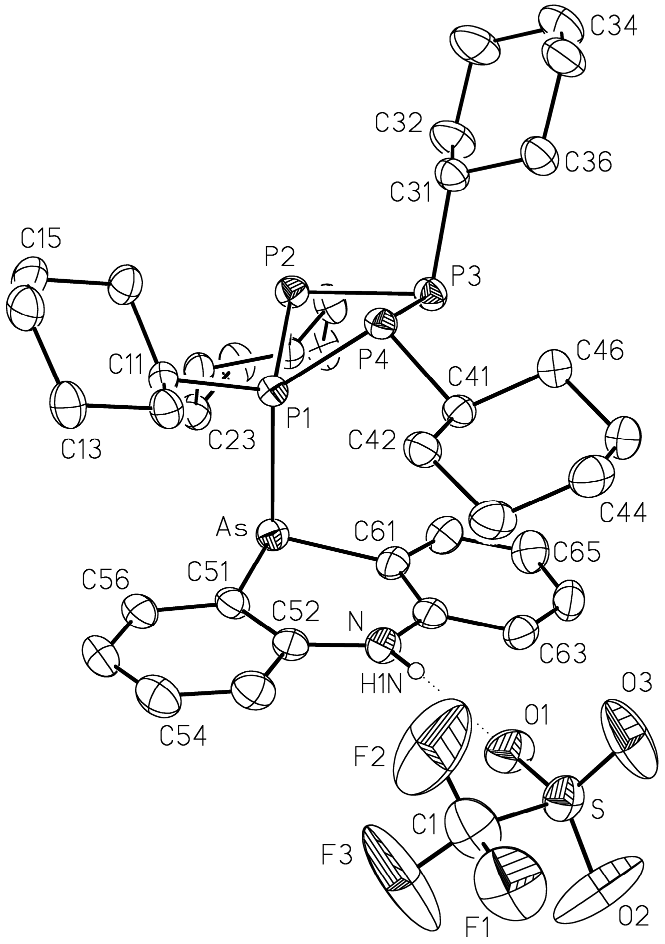

Figure S3: Perspective view of $[(CyP)_4(AN)][SO_3CF_3]$ showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50%

probability level. The hydrogen atom attached to the nitrogen atom is shown with an arbitrarily small thermal parameter; all other hydrogens are not shown.

Crystal data for $[(CyP)_4(AN)][OSO_2CF_3]$ (CCDC 747681): $C_{37}H_{53}AsF_3NO_3P_4S$, M_r = 847.66, orange plates, 0.41 × 0.34 × 0.07 mm^3, triclinic, $P\bar{1}$ (No. 2), a = 11.5413(7) Å, b = 11.5635(7) Å, c = 15.3553 (9) Å, α = 99.0907(8)º, β = 96.0351(8)º, γ = 91.1938(8)º, V = 2010.9(2) Å^3, Z = 2, ρ_{calcd} = 1.400 g cm^{-3}, μ = 1.106 mm^{-1}, Mo Kα (0.71073 Å), T = 173(1) K, $2\theta_{max}$ = 54.96º, 16803 total data collected, 9010 independent data (R_{int} = 0.0329), structure solution: direct methods (*SHELXS-97*[4]), R_1 = 0.0405 (for 6730 data with $I \geq 2\sigma(I)$), wR_2 = 0.0988 (for all 9010 unique data), $\Delta\rho_{min,max}$ = 0.717, –0.536 e Å^{-3}.

Selected bond lengths [Å] (^{a}Nonbonded distance) and bond angles [˚] (^{a}Angle includes nonbonded As···O interaction): As-P1 2.4660(7), As-C51 1.913(3), As-C61 1.921(3), As-O2’ 3.391(3)^a, P1-P2 2.2054(10), P1-P4 2.2053(9), P1-C11 1.847(2), P2-P3 2.2327(10), P2-C21 1.855(3), P3-P4 2.2306(10); P1-As-C51 96.81(8), P1-As-C61 99.66(8), P1-As-O2’ 133.96(6)^{b,} C51-As-C61 97.19(11), C51-As-O2’ 127.71(10)^b ,C61-As-O2’ 87.11(9)^b ,As-P1-P2 110.59(3), As-P1-P4 129.11(3), As-P1-C11 106.35(8), P2-P1-P4 86.11(3), P2-P1-C11 111.67(9), P4-P1-C11 111.16(8), P1-P2-P3 84.94(3), P1-P2-C21 103.63(9), P3-P2-C21 105.13(8), P2-P3-P4 84.86(3), P2-P3-C31 99.94(9), P4-P3-C31 100.84(9), P1-P4-P3 84.99(3), P1-P4-C41 108.14(8), P3-P4-C41 105.60(9).

GooF=1.054, 451 parameters, Temperature 173K, CCDC-747681

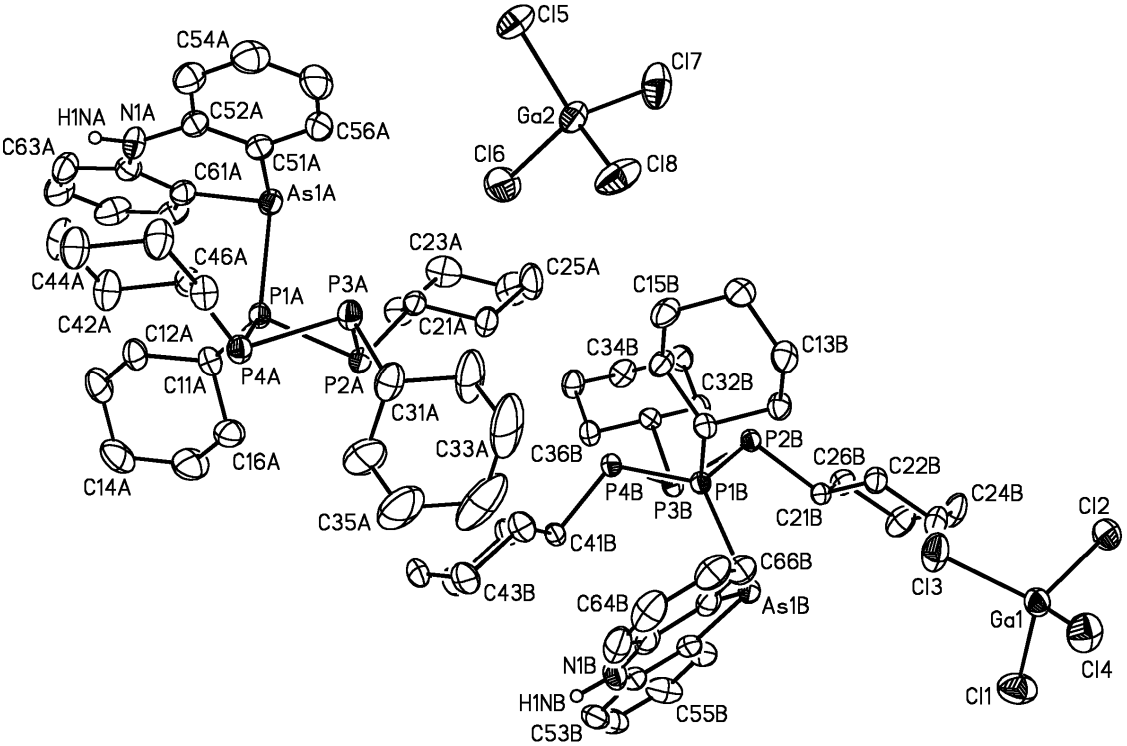

Figure S4: ORTEP view of both crystallographically independent cations and anions in $[(CyP)_4(AN)][GaCl_4]$. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. The nitrogen-bound hydrogen atom is shown with an arbitrarily small thermal parameter; all other hydrogens are not shown.

Crystal data for $[(CyP)_4(AN)][GaCl_4]\cdot 1/2CH_2Cl_2$ (CCDC 747680): $C_{36.5}H_{54}AsCl_5GaNP_4$, *M*r = 952.58, orange blocks, 0.44 × 0.22 × 0.16 mm3, triclinic, $P\bar{1}$ (No. 2), *a* = 11.2986(8) Å, *b* = 16.5069(12) Å, *c* = 23.6544(17) Å, α = 92.1892(9)°, β = 100.9413(9)°, γ = 96.1712(9)°, *V* = 4298.6(5) Å3, *Z* = 4, ρcalcd = 1.472 g cm-3, μ = 1.891 mm-1, Mo Kα(0.71073 Å), *T* = 173(1) K, 2θmax = 55.12°, 37853 total data collected, 19554 independent data (*R*int = 0.0311), structure solution: Patterson search/structure expansion (*DIRDIF-2008*[5]), *R*1 = 0.0363 (for 14412 data with $I \geq 2\sigma(I)$), *wR*2 = 0.1059 (for all 19554 unique data), $\Delta\rho$min,max = 0.896, –0.427 e Å-3.

Selected bond lengths [Å] and bond angles [°]:As1A-P1A 2.4501(8), As1A-C51A

1.917(3), As1A-C61A 1.919(3), P1A-P2A 2.2057(10), P1A-P4A 2.1996(10), P1A-C11A 1.842(3), P2A-P3A 2.2415(11), P2A-C21A 1.860(3), P3A-P4A 2.2334(10), P3A-C31A 1.870(3), P4A-C41A 1.857(3), As1B-P1B 2.4545(7), As1B-C51B 1.920(3), As1B-C61B 1.917(3), P1B-P2B 2.2045(9), P1B-P4B 2.2000(9), P1B-C11B 1.850(3), P2B-P3B 2.2417(9), P2B-C21B 1.862(3), P3B-P4B 2.2294(9), P3B-C31B 1.869(3), P4B-C41B 1.853(3); P1A-As1A-C51A 101.82(8), P1A-As1A-C61A 97.93(9) , C51A-As1A-C61A 97.13(12), As1A-P1A-P2A 110.12(3), As1A-P1A-P4A 127.61(4), As1A-P1A-C11A 107.50(10), P2A-P1A-P4A 84.78(4), P2A-P1A-C11A 112.56(10), P4A-P1A-C11A 112.13(10), P1A-P2A-P3A 81.70(4), P1A-P2A-C21A 103.66(9), P3A-P2A-C21A 105.68(9), P2A-P3A-P4A 83.16(4), P2A-P3A-C31A 104.97(11), P4A-P3A-C31A 103.59(11), P1A-P4A-P3A 82.01(4), P1A-P4A-C41A 111.19(10), P3A-P4A-C41A 102.81(10), P1B-As1B-C51B 99.24(8), P1B-As1B-C61B 97.21(8), C51B-As1B-C61B 97.76(12), As1B-P1B-P2B 111.29(3), As1B-P1B-P4B 127.27(3), As1B-P1B-C11B 108.47(9), P2B-P1B-P4B 85.93(3), P2B-P1B-C11B 111.04(9), P4B-P1B-C11B 110.55(9), P1B-P2B-P3B 84.45(3), P1B-P2B-C21B 104.41(8), P3B-P2B-C21B 104.27(9), P2B-P3B-P4B 84.35(3), P2B-P3B-C31B 99.86(9), P4B-P3B-C31B 99.06(9), P1B-P4B-P3B 84.85(3), P1B-P4B-C41B 107.63(9), P3B-P4B-C41B 109.75(9).

GooF=1.040, 884 parameters, Temperature 173 K, CCDC-747680

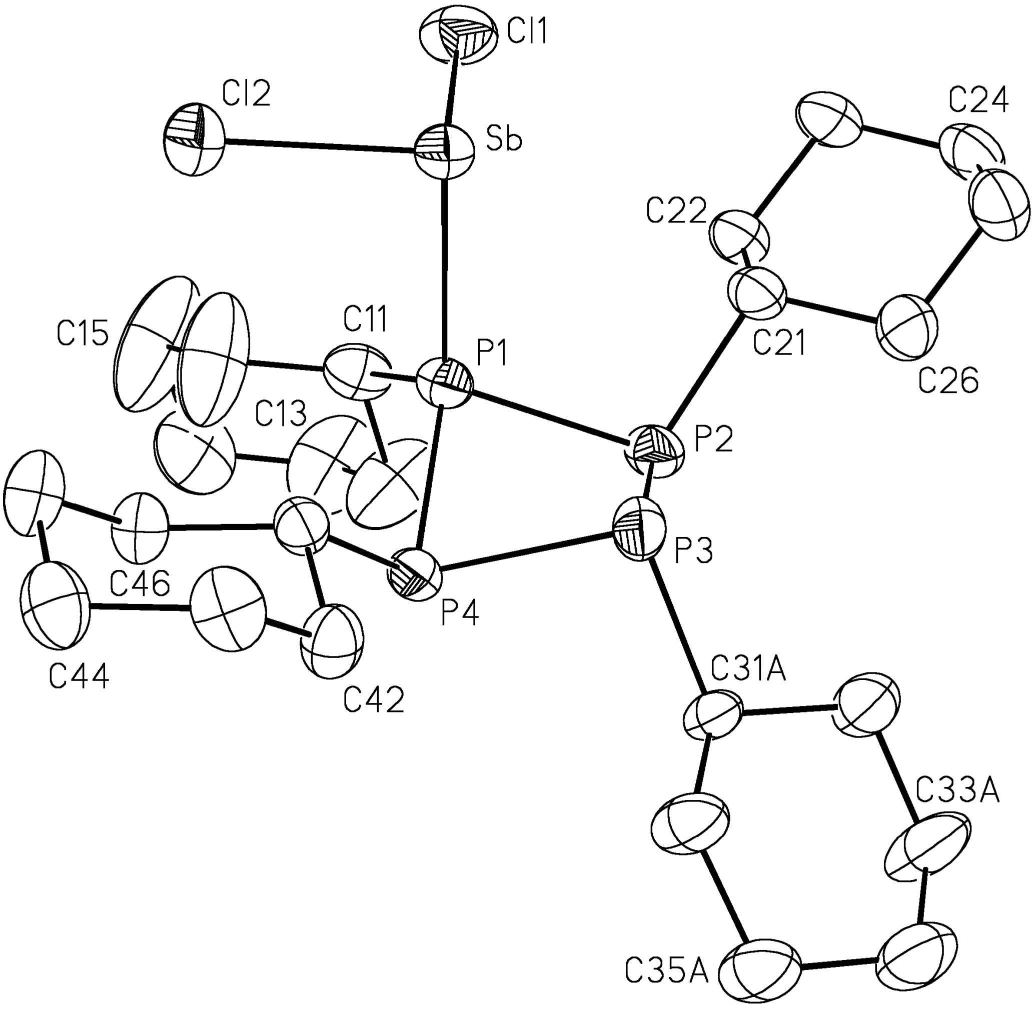

Figure S5: Perspective view of the $[(CyP)_4SbCl_2]^+$ ion in $[(CyP)_4SbCl_2][Al_2Cl_7]$ showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Only one orientation of the disordered cyclohexyl group (C31A to C36A) is shown for clarity. Hydrogen atoms are not shown.

Crystal data for $[(CyP)_4SbCl_2][Al_2Cl_7]$ (CCDC 747678): $C_{24}H_{44}Al_2Cl_9P_4Sb$, $M_r = 951.23$, yellow blocks, 0.56 × 0.27 × 0.20 mm^3, monoclinic, $P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14]), $a = 11.9912(5)$ Å, $b = 21.7620(9)$ Å, $c = 15.6538(7)$ Å, $\beta = 91.0720(10)$°, $V =$

4084.2(3) Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.547$ g cm^{-3}, $\mu = 1.481$ mm^{-1}, Mo Kα (0.71073 Å), T = 173(1) K, $2\theta_{\mathrm{max}} = 54.28°$, 34739 total data collected, 9046 independent data (R_{int} = 0.0205), structure solution: direct methods (*SHELXS-97*[4]), R_1 = 0.0332 (for 7749 data with $I \geq 2\sigma(I)$), wR_2 = 0.0882 (for all 9046 unique data), $\Delta\rho_{\mathrm{min,max}}$ = 0.796, –0.578 e Å^{-3}. The model was well-behaved enough to allow anisotropic refinement of even the disordered cyclohexyl group carbons.

Selected bond lengths [Å] and bond angles [°]: Sb-Cl1 2.3397(8), Sb-Cl2 2.3333(8), Sb-P1 2.6178(7), P1-P2 2.1897(10), P1-P4 2.1966(10), P1-C11 1.834(3), P2-P3 2.2226(11), P2-C21 1.862(3), P3-P4 2.2336(10), P3-C31A 1.959(6), P3-C31B 1.816(7), P4-C41 1.860(3); Cl1-Sb-Cl2 96.45(3), Cl1-Sb-P1 88.89(3), Cl2-Sb-P1 94.83(3), Sb-P1-P2 108.91(3), Sb-P1-P4 112.15(3), Sb-P1-C11 115.94(10), P2-P1-P4 86.29(4), P2-P1-C11 111.61(11), P4-P1-C11 117.87(10), P1-P2-P3 82.55(4), P1-P2-C21 104.68(9), P3-P2-C21 108.07(10), P2-P3-P4 84.62(4), P2-P3-C31A 92.7(2), P2-P3-C31B 111.4(3), P4-P3-C31A 95.9(2), P4-P3-C31B 108.2(2), P1-P4-P3 82.14(3), P1-P4-C41 106.06(9), P3-P4-C41 103.31(9)

GooF=1.079, 442 parameters, Temperature 173 K. CCDC-747678

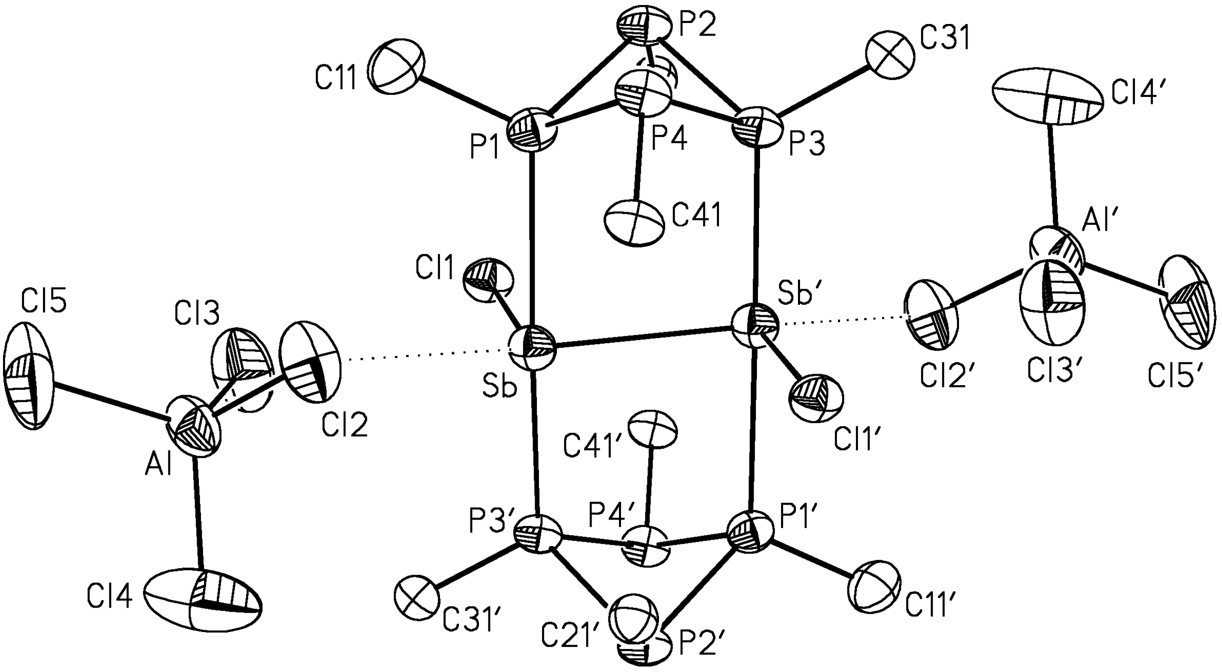

Figure S6: Perspective view of the $[Cl_2Sb_2(\mu\text{–tetracyclohexyltetraphosphetane})_2][AlCl_4]_2$ tetrachloroaluminate ions showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms are not shown. Primed atoms are related to unprimed ones via the crystallographic inversion center (1/2, 1/2, 1/2) at the midpoint of the Sb–Sb' bond. Only the phosphorus-bound carbons of the cyclohexyl groups are shown.

Crystal data for $[\{(CyP)_4\}_2(Sb_2Cl_2)][AlCl_4]_2$ (CCDC 747679): $C_{55}H_{96}Al_2Cl_{10}P_8Sb_2$, M_r = 1657.04, orange blocks, 0.55 × 0.38 × 0.19 mm^3, monoclinic, $P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14]), a = 12.0664(7) Å, b = 21.3906(13) Å, c = 14.9019(9) Å, β = 104.6473(7)°, V = 3721.3(4) Å^3, Z = 2, ρ_{calcd} = 1.479 g cm^{-3}, μ = 1.314 mm^{-1}, Mo Kα (0.71073 Å), T = 173(1) K, $2\theta_{max}$ = 53.10°, 28434 total data collected, 7740 independent data (R_{int} = 0.0332), structure solution: Patterson search/structure expansion (*DIRDIF-2008*[5]), R_1 = 0.0538 (for 6589 data with $I \geq 2\sigma(I)$), wR_2 = 0.1295 (for all 7740 unique data), $\Delta\rho_{\mathrm{min,max}}$ = 1.405, –0.845 e Å^{-3}. Attempts were made to refine the disordered cyclohexyl group carbons with anisotropic displacement parameters, but these refined quite unsatisfactorily, giving wildly divergent ranges of bond lengths (1.26–1.61 Å), angles (104.7–120.8°), and displacement parameter U_{eq}'s (0.056–0.338 Å^2), plus some severely elongated thermal ellipsoids. Forcing the U_{ij} values to be equal or similar for pairs of analogous atoms (e.g. C12A and C12B, C13A and C13B, etc.) tames the wild behaviour of the U_{eq}'s, but the distortions of ring geometry (bond lengths and angles) remain. From the appearance of the thermal ellipsoids for the 'unsplit' carbons of this ring, the group appears to be disordered via slight rotation about the P1–C11 bond, so instead of two (or three, or four, ...) discrete conformers there is most likely a continuum. The model presented herein combines the most satisfactory results (in terms of group geometry and displacement parameter behaviour) with the least amount of geometric or U_{ij} restraints (i.e. *none*).

The geometric and displacement parameter misbehaviour was even more pronounced for the inversion-disordered solvent toluene molecule, so it was modelled as having an idealized phenyl ring (a regular hexagon with a C–C bond length of 1.39 Å) and a C_{methyl}–C_{ipso} bond length fixed at 1.50 Å. All carbon atoms were refined with a common isotropic displacement parameter.

Selected bond lengths [Å] (^{a}Nonbonded distance) and bond angles [°] (^{b}Angle includes nonbonded Sb···Cl interaction): Sb-Sb' 2.9150(6), Sb-Cl1 2.3654(12), Sb-P1 2.8353(12), Sb-P3' 2.8484(12), Sb-Cl2 3.6489(17)^{a}, P1-P2 2.2161(18), P1-P4 2.2157(17), P1-C11 1.851(6), P2-P3 2.2139(17), P2-C21 1.859(5), P3-P4 2.2180(18), P3-C31 1.856(5), P4-C41 1.868(5); Sb'-Sb-Cl1 93.50(3), Sb'-Sb-P1 87.45(3), Sb'-Sb-P3' 88.56(3) Sb'-Sb-Cl2 145.21(3)^{b}, Cl1-Sb-P1 84.46(4), Cl1-Sb-P3' 83.07(4), Cl1-Sb-Cl2 117.34(4)^{b}, P1-Sb-P3' 166.65(4), P1-Sb-Cl2 80.44(4)^{b}, P3'-Sb-Cl2 109.63(4)^{b}, Sb-P1-P2 118.06(6), Sb-P1-P4 111.67(6), Sb-P1-C11 115.83(19), P2-P1-P4 82.95(6), P2-P1-C11 113.2(2), P4-P1-C11 110.36(19), P1-P2-P3 78.06(6), P1-P2-C21 108.20(17), P3-P2-C21 103.55(16), Sb'-P3-P2 107.17(6), Sb'-P3-P4 120.01(6), Sb'-P3-C31 118.54(16), P2-P3-P4 82.95(6), P2-P3-C31 109.97(16), P4-P3-C31 111.72(17), P1-P4-P3 77.98(6), P1-P4-C41 105.31(16), P3-P4-C41 109.66(16).

GooF=1.114, 318 parameters, Temperature 173 K. CCDC-747679

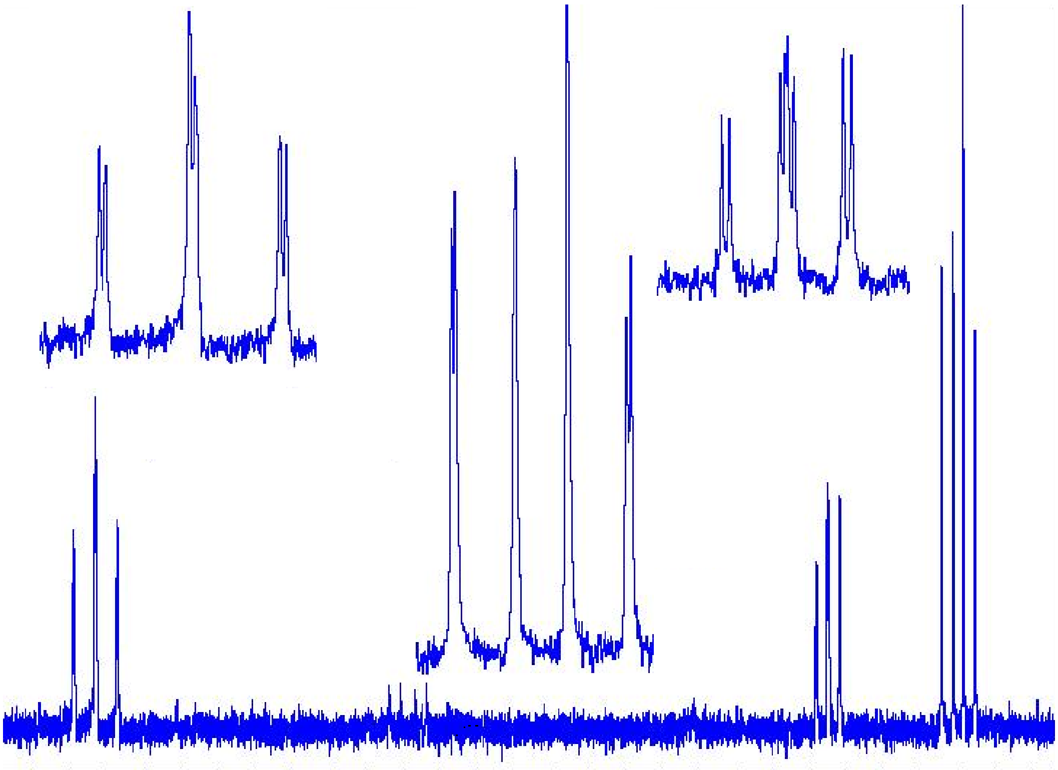

Figure S7: mixture $^{31}P\{^{1}H\}$-NMR ($CDCl_3$, 202.6 MHz, 293 K) spectra showing formation of $[(PCy)_4(SbCl_2)][Al_2Cl_7]$, A_2BX spin system.

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