SUPPLEMENTARY INFORMATION

Cationic phosphorus/carbon/pnictogen cages isolobal to $[C_5R_5]^+$

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Synthesis of [1][$Al\{OC(CF_3)_3\}_4$]

To a stirred solution of $C_2Bu^t_2P_2PCl$ (0.5 mmol, 0.13 g) in dichloromethane (10 mL) was added $Li[Al\{OC(CF_3)_3\}_4]$ (0.5 mmol, 0.067 g) resulting in a yellow solution. A $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed that all of the starting material had reacted. The product was dissolved in 2 mL dichloromethane and layered with 4 mL *n*-hexane in a long thin Young's tube to yield a good crop of light yellow crystals whose identity was confirmed by X-ray crystallography.

$^{31}P\{^1H\}$ NMR (121.42 MHz, 21 °C, CD_2Cl_2): no signal observed

^1H NMR (270.16 MHz, 21 °C, CD_2Cl_2): δ=1.16 ppm (s, $C(CH_3)_3$)

$^{13}C\{^1H\}$ NMR (100.54 MHz, 21 °C, CD_2Cl_2): δ 29.9 ppm (br $C(\mathit{C}H_3)_3$), δ 34.0 ppm (br, $\mathit{C}(CH_3)_3$), δ 110.0 ppm (br, $\mathit{C}_2Bu^t_2P_2$); $\mathit{C}_2Bu^t_2P_2$ not observed, δ 79.0 ppm (br, $Al\{O\mathit{C}(CF_3)_3\}_4$), δ 121.2 ppm (q, $^1J_{PP}$ 292 Hz, $Al\{OC(\mathit{C}F_3)_3\}_4$;

^{19}F NMR (282.20 MHz, 21 °C, CD_2Cl_2): δ = -75.7 ppm (s, $[Al\{OC(CF_3)_3\}_4]$); ^{29}Al δ 37.3 ppm (s, $[\{Al\{OC(CF_3)_3\}_4]$).

Syntheses of $[2]^+[X]^-$

For X = $AlCl_4$: $C_2Bu^t_2P_2AsCl$ (0.5 mmol, 0.15 g) was dissolved 10 mL dichloromethane (Schlenk tube) and reacted with $AlCl_3$ (0.5 mmol, 0.067 g) for 15 mins resulting in yellow solution. Removal of the solvent in vacuo gave an off white solid which redissolved in an *n*-hexane-dichloromethane mixture (1 mL: 3 mL); cooling to –15 °C for 15 hours yielded pale yellow blocks of $[AsP_2C_2Bu^t_2][AlCl_4]$.

$^{31}P\{^1H\}$ NMR (121.42 MHz, 21 °C, CD_2Cl_2): δ 169.9 ppm

^1H NMR (270.16 MHz, 21 °C, CD_2Cl_2): δ 1.22 ppm (s, $C(CH_3)_3$)

$^{13}C\{^1H\}$ NMR (100.54 MHz, 21 °C, CD_2Cl_2): δ 31.2 ppm (t, $^3J_{CP}$ 3 Hz, $C(\mathit{C}H_3)_3$), δ 35.1 ppm (t, $^2J_{CP}$ 5 Hz, $\mathit{C}(CH_3)_3$), δ 53.7 ppm (t, $^1J_{CP}$ 27 Hz, $\mathit{C}_2Bu^t_2P_2$)

^{29}Al NMR (78.15 MHz, 21 ^oC, CD_2Cl_2): δ 106.1 ppm (s, [$AlCl_4$]).

For X = Al{OC(CF_3)$_3$}$_4$: A dichloromethane solution of $C_2Bu^t{}_2P_2AsCl$ (0.5 mmol, 0.15 g) was reacted with Li[Al{OC(CF_3)$_3$}$_4$] (0.5 mmol, 0.067 g) resulting in a yellow solution. A $^{31}P\{^1H\}$ NMR spectrum indicated that all of the starting material had been consumed to form [$AsP_2C_2Bu^t{}_2$][Al{OC(CF_3)$_3$}$_4$].

$^{31}P\{^1H\}$ NMR (121.42 MHz, 21 ^oC, CD_2Cl_2): δ 183.1 ppm

^1H NMR (270.16 MHz, 21 ^oC, CD_2Cl_2): δ 1.24 ppm (s, C(CH_3)$_3$)

$^{13}C\{^1H\}$ NMR (100.54 MHz, 21 ^oC, CD_2Cl_2): δ 31.2 ppm (t, $^3J_{CP}$ 3 Hz, C(CH$_3$)$_3$), δ 35.5 ppm (t, $^2J_{CP}$ 4 Hz, C(CH_3)$_3$), $C_2Bu^t{}_2P_2$ not observed, δ 79.0 ppm (br, Al{OC(CF_3)$_3$}$_4$), δ 121.2 ppm (q, $^1J_{PP}$ 292 Hz, Al{OC(CF$_3$)$_3$}$_4$

^{19}F NMR (282.20 MHz, 21 ^oC, CD_2Cl_2): δ -75.5 ppm (s, [Al{OC(CF_3)$_3$}$_4$])

^{29}Al NMR (78.15 MHz, 21 ^oC, CD_2Cl_2): δ 37.3 ppm (s, [Al(OC(CF_3)$_3$}$_4$]).

Syntheses of [3]$^+$[X]$^-$

For X = $AlCl_4$: $C_2Bu^t{}_2P_2SbCl$ (0.5 mmol, 0.15 g) was dissolved 10 mL dichloromethane (Schlenk tube) and reacted with $AlCl_3$ (0.5 mmol, 0.067 g) for 15 mins resulting in a lightening of the yellow solution and the precipitation of a small amount of white solid which redissolved upon gentle warming. Storage at –15 °C for 15 hours yielded colourless blocks of [$SbP_2C_2Bu^t{}_2$][$AlCl_4$].

$^{31}P\{^1H\}$ NMR (121.42 MHz, 21 ^oC, CD_2Cl_2): δ 180.3 ppm

^1H NMR (270.16 MHz, 21 ^oC, CD_2Cl_2): δ 1.11 ppm (s, C(CH_3)$_3$)

$^{13}C\{^1H\}$ NMR (100.54 MHz, 21 ^oC, CD_2Cl_2): δ 33.4ppm (t, $^3J_{CP}$ 3 Hz, C(CH$_3$)$_3$), δ 35.9 ppm (t, $^2J_{CP}$ 4 Hz, C(CH_3)$_3$), $C_2Bu^t{}_2P_2$ not observed

^{29}Al NMR (78.15 MHz, 21 ^oC, CD_2Cl_2): δ 106.2ppm (s, [$AlCl_4$])

MS EI [M^+] calculated *m/z* 320.9922 observed *m/z* 320.9914

For X = Al{OC(CF_3)$_3$}$_4$: A dichloromethane solution of $C_2Bu^t{}_2P_2SbCl$ (0.5 mmol, 0.15 g) was reacted with Li[Al{OC(CF_3)$_3$}$_4$] (0.5 mmol, 0.067 g) for 15 minutes to yield [$SbP_2C_2Bu^t{}_2$][Al{OC(CF_3)$_3$}$_4$].

$^{31}P\{^1H\}$ NMR (121.42 MHz, 21 ^oC, CD_2Cl_2): δ 176.3 ppm

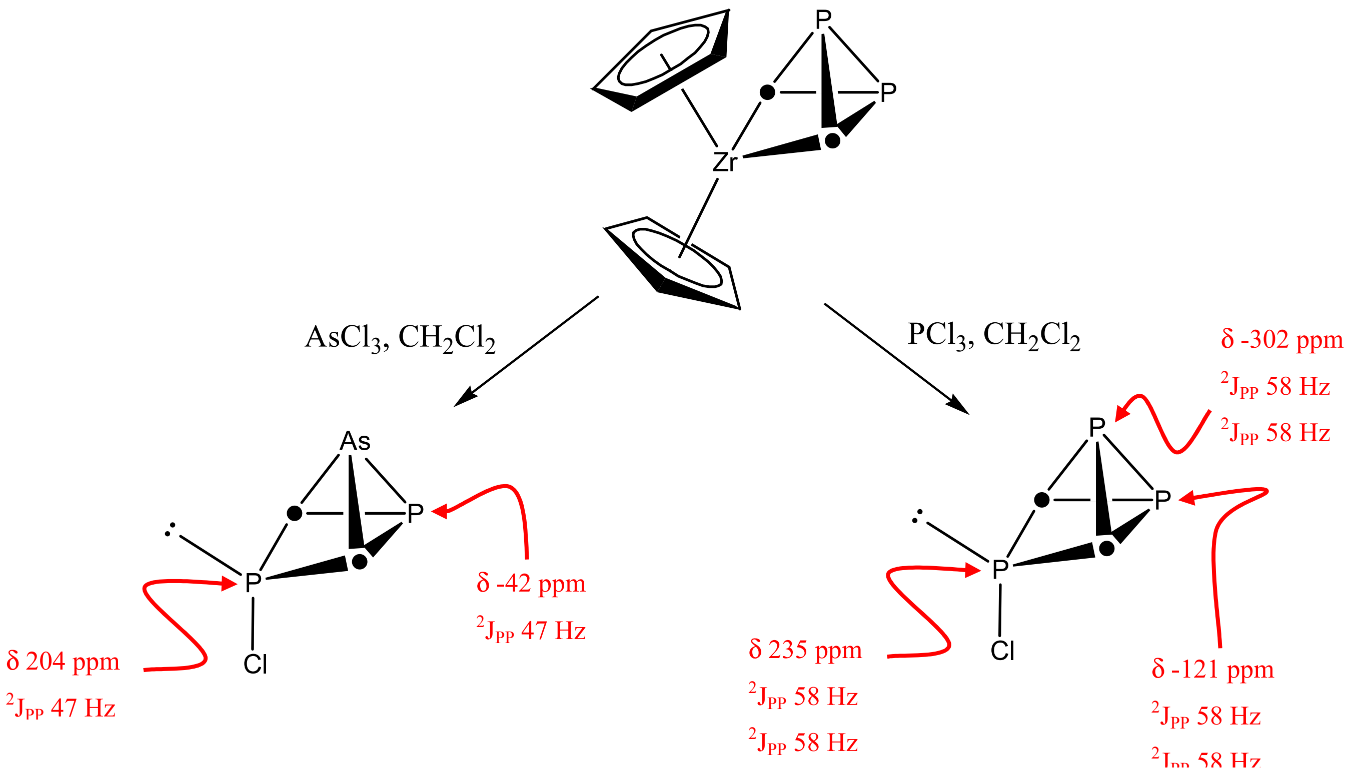
^1H NMR (270.16 MHz, 21 ^oC, CD_2Cl_2): δ 1.26 ppm (s, C(CH_3)$_3$)

^{19}F NMR (282.20 MHz, 21 ^oC, CD_2Cl_2): δ -75.6 ppm (s, [Al{OC(CF_3)$_3$}$_4$])

^{29}Al NMR (78.15 MHz, 21 ^oC, CD_2Cl_2): δ 37.6 ppm (s, [Al{OC(CF_3)$_3$}$_4$]).

Synthesis and Structure of $ClP_2(CBu^t)_2As$

$Cp_2ZrC_2Bu^t{}_2P_2$ (0.21 g, 0.5 mmol) was dissolved in 10 ml *n*-hexane and stirred with one equivalent of arsenic trichloride (0.05 ml, 0.5 mmol) for 2 hours. The by-product (Cp_2ZrCl_2) was separated from the reaction mixture by filtration through Celite® and removal of the solvent afforded a yellow oil. The structure was assigned (see Figure) by comparison with the NMR data of the tricyclic cage $ClP_3(CBu^t)_2$, which exhibits three distinctive and characteristic resonances in the ^{31}P NMR spectrum at δ 234.7 (dd, $^2J_{PP}$ 58 Hz, $^2J_{PP}$ 58 Hz), -121.4 (dd, $^1J_{PP}$ 146 Hz, $^2J_{PP}$ 58 Hz) and -302.2 (dd, $^1J_{PP}$ 146 Hz, $^2J_{PP}$ 58 Hz) ppm.



$^{31}P\{^1H\}$ NMR (121.42 MHz, 21 °C, CD_2Cl_2): δ 204.8 and -42.2 ppm (both d $^2J_{pp}$ 47 Hz)

^1H NMR (270.16 MHz, 21 °C, CD_2Cl_2): δ 1.14 ppm (s, $C(CH_3)_3$)

$^{13}C\{^1H\}$ NMR (100.54 MHz, 21 °C, CD_2Cl_2): δ 30.2 ppm (t, $^3J_{CP}$ 4 Hz, $C(CH_3)_3$) δ 32.4 ppm (t, $^2J_{CP}$ 5 Hz, $C(CH_3)_3$), δ 53.7 ppm (t, $^1J_{CP}$ 27 Hz, $C_2Bu^t{}_2P_2$).

Optimised structures and total electronic energies (hartree) of all species reported.

$[(CH)_2P_3]^+$ **A** E = −1101.163181

15	-1.285822	0.236188	0.000000
15	0.440036	-0.686954	1.130813
15	0.440036	-0.686954	-1.130813
6	0.440036	1.095481	0.709532
6	0.440036	1.095481	-0.709532
1	0.402911	1.960005	1.372435
1	0.402911	1.960005	-1.372435

$[(CH)_2P_3]^+$ **B (=C)** E = −1101.150631

15	0.000000	0.000000	1.298731
15	-1.405380	0.000000	-0.493491
15	1.405380	0.000000	-0.493491
6	0.000000	1.143675	-0.347068
6	0.000000	-1.143675	-0.347068
1	0.000000	2.227122	-0.255708
1	0.000000	-2.227122	-0.255708

$[(CH)_2P_3]^+$ **F (=E)** E = −1101.122233

15	-0.271856	-0.224895	1.491989
6	-1.283079	-0.224501	0.000000
15	-0.271856	-0.224895	-1.491989
15	1.355816	-0.005482	0.000000
6	-0.271856	1.023541	0.000000
1	-2.359581	-0.050323	0.000000
1	-0.492378	2.085160	0.000000

$[(CH)_2P_3]^+$ **B ↔ C** E = −1101.136021

15	-0.320951	0.000000	1.295395
15	-1.398329	0.000000	-0.543132
15	1.293841	0.000000	-0.886025
6	0.115735	1.143153	-0.195325
6	0.115735	-1.143153	-0.195325
1	0.096985	2.228723	-0.184695
1	0.096985	-2.228723	-0.184695

$[(CH)_2P_3]^+$ **B ↔ F** E = −1101.105745

15	0.000161	1.359537	-0.316159
15	-1.449775	-0.380091	-0.051834
15	1.449667	-0.380222	-0.051750
6	-0.000094	-1.392381	-0.325472
6	-0.000131	0.283008	1.080342
1	0.000642	-2.485879	-0.390795
1	-0.000103	0.153747	2.157709

$[(CH)_2P_2As]^+$ **A** E = −2993.595243

33	1.066701	0.172241	0.000000
15	−0.800180	−0.737581	1.140055
15	−0.800180	−0.737581	−1.140055
6	−0.800180	1.050798	−0.709496
6	−0.800180	1.050798	0.709496
1	−0.796785	1.916955	−1.370563
1	−0.796785	1.916955	1.370563

$[(CH)_2P_2As]^+$ **B** E = −2993.580521

33	0.000000	0.000000	1.075767
15	1.403316	0.000000	−0.853631
6	0.000000	1.154497	−0.714717
1	0.000000	2.239599	−0.657389
6	0.000000	−1.154497	−0.714717
1	0.000000	−2.239599	−0.657389
15	−1.403316	0.000000	−0.853631

$[(CH)_2P_2As]^+$ **C** E = −2993.564353

15	0.600026	−1.698603	0.000000
6	0.251693	−0.355496	1.164614
1	0.160745	−0.415524	2.246025
6	0.251693	−0.355496	−1.164614
1	0.160745	−0.415524	−2.246025
15	−1.376538	−0.572787	0.000000
33	0.251693	1.186905	0.000000

$[(CH)_2P_2As]^+$ **D** E = −2993.586957

15	0.924965	1.266805	−0.041367
6	1.306916	−0.201265	0.984181
1	2.266758	−0.467553	1.428305
15	0.856700	−0.840504	−0.914666
33	−1.137257	0.092528	−0.017877
6	0.118103	−0.972027	1.016628
1	−0.012377	−1.940621	1.497269

$[(CH)_2P_2As]^+$ **E** E = −2993.539122

15	−0.572728	1.377513	−0.016151
33	1.247262	−0.075258	−0.101519
6	−0.242567	−1.277590	−0.090605
1	−0.164871	−2.337865	0.149768
15	−1.825736	−0.431126	−0.305309
6	−0.498115	−0.221364	1.070916
1	−0.573725	−0.380693	2.140389

$[(CH)_2P_2As]^+$ **F** E = −2993.548806

15	0.201571	−0.649215	1.509816
33	0.032180	1.114901	0.000000
6	−1.040692	−0.648858	0.000000
1	−2.098630	−0.882909	0.000000
15	0.201571	−0.649215	−1.509816
6	0.201571	−1.637588	0.000000
1	0.024278	−2.713701	0.000000

$[(CH)_2P_2As]^+$ **B ↔ C** E = −2993.555277

33	0.812342	0.831416	0.000000
15	-0.187667	-1.841187	0.000000
6	-0.187667	-0.498131	1.162482
1	-0.239143	-0.513011	2.246745
6	-0.187667	-0.498131	-1.162482
1	-0.239143	-0.513011	-2.246745
15	-1.417465	0.478978	0.000000

$[(CH)_2P_2As]^+$ **B ↔ F** E = −2993.528473

33	1.140989	-0.000004	-0.128645
15	-0.756110	-1.460438	-0.044092
6	-1.697394	0.000070	-0.473297
1	-2.773456	-0.000184	-0.684366
6	-0.245741	-0.000068	1.149527
1	-0.537391	-0.000065	2.194561
15	-0.756087	1.460463	-0.044061

$[(CH)_2P_2Sb]^+$ **A** E = −765.250051

51	0.978443	0.140370	0.000000
15	-1.131021	-0.771821	1.142211
15	-1.131021	-0.771821	-1.142211
6	-1.131021	1.018925	-0.707975
6	-1.131021	1.018925	0.707975
1	-1.198856	1.884338	-1.366915
1	-1.198856	1.884338	1.366915

$[(CH)_2P_2Sb]^+$ **B** E = −765.234532

51	0.000000	0.000000	0.986415
15	-1.396168	0.000000	-1.190604
6	0.000000	1.162091	-1.039872
1	0.000000	2.248575	-1.055286
6	0.000000	-1.162091	-1.039872
1	0.000000	-2.248575	-1.055286
15	1.396168	0.000000	-1.190604

$[(CH)_2P_2Sb]^+$ **C** E = −765.211112

51	0.192436	1.078046	0.000000
15	0.594307	-2.006826	0.000000
6	0.192436	-0.703098	1.192881
1	0.084156	-0.846345	2.265852
6	0.192436	-0.703098	-1.192881
1	0.084156	-0.846345	-2.265852
15	-1.413759	-0.983206	0.000000

$[(CH)_2P_2Sb]^+$ **D** E = −765.234381

15	1.214629	1.309827	0.003154
6	1.633475	-0.189915	0.966903
1	2.619456	-0.416074	1.376276
15	1.244720	-0.776445	-0.940329
51	-1.037729	0.038836	-0.010867
6	0.514382	-1.060629	1.000552
1	0.527359	-2.062056	1.430827

$[(CH)_2P_2Sb]^+$ **E** E = −765.190904

15	-0.965147	1.383300	0.004269
51	1.128206	-0.038714	-0.061956
6	-0.578467	-1.304238	-0.017391
1	-0.570497	-2.360708	0.252634
15	-2.151774	-0.453748	-0.375339
6	-0.941257	-0.235785	1.073187
1	-1.095836	-0.368023	2.138423

$[(CH)_2P_2Sb]^+$ **F** E = −765.198679

15	0.119452	-1.001279	1.534316
51	0.088864	1.014141	0.000000
6	-1.099594	-0.957861	0.000000
1	-2.156573	-1.199994	0.000000
15	0.119452	-1.001279	-1.534316
6	0.119452	-1.951896	0.000000
1	-0.078199	-3.024267	0.000000

$[(CH)_2P_2Sb]^+$ **B ↔ C** E = −765.204211

51	0.703126	0.797624	0.000000
15	-0.364423	-2.088365	0.000000
6	-0.364423	-0.765598	1.184420
1	-0.480492	-0.838304	2.262183
6	-0.364423	-0.765598	-1.184420
1	-0.480492	-0.838304	-2.262183
15	-1.670600	0.100694	0.000000

$[(CH)_2P_2Sb]^+$ **B ↔ F** E = −765.175134

51	-1.045475	-0.000066	-0.068356
15	1.107036	1.476739	-0.046804
6	1.977408	0.000154	-0.561756
1	3.043777	0.000730	-0.822616
6	0.686047	-0.000031	1.152910
1	1.077159	0.000108	2.166621
15	1.107469	-1.476618	-0.046847