Supplementary Material (ESI) for Chemical Communications

Preparation of $[C_{10}Me_{10}P_2I][GaI_4]$ (1)

"GaI" was prepared by literature methods[i] by sonicating a mixture of I_2 (1.26 g, 10 mmol) and gallium metal (0.693 g, 10 mmol) in toluene (10 mL) at 50 °C. To the resulting "GaI" suspension was added Cp^*PCl_2 (1 ml, 1 M in hexane, 10mmol) dropwise at room temperature. All volatiles were removed *in vacuo* and the resulting red oil was redissolved in dichloromethane (20 mL). On standing, a small amount of grey solid was precipitated (presumably elemental gallium) which was filtered (porosity 3 sinter with Celite). The reaction yields a quantitative amount of cation by ^{31}P NMR spectroscopy; however, the counterion in the reaction solution was shown by ^{71}Ga NMR to be a mixture of $[GaX_nY_{4-n}]^-$ monoanions (X = Cl, Y = I), which by visual inspection is dominated by $[GaCl_4]^-$ and tapering down to $[GaI_4]^-$.

A small yield of colourless $[C_{20}H_{30}P_2I][GaI_4]$ as single crystals for X-ray crystallography was obtained from a dichloromethane/hexane solution mixture kept at -18 °C for two weeks. The following data were taken from these isolated crystals.

^{71}Ga NMR (91.5 MHz, $CDCl_3$, 25 °C) δ = - 452 ppm.

^{31}P NMR (121.4 MHz, $CDCl_3$, 25 °C) δ = 68.7 (d, J_{PP} = 231.1 Hz, P(1)), = 29.0 (d, J_{PP} = 231.1 Hz, P(2)).

^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 146.3 (d, J_{PC} = 15.5 Hz, C(1)), 144.0 (d, J_{PC} = 13.0 Hz, C(8)), 131.1 (dd, J_{PC} = 10.9 Hz, J_{PC} = 6.5 Hz, C(9)), 130.3 (dd, J_{PC} = 11.8 Hz, J_{PC} = 1.6 Hz, C(5)), 76.7 (dd, J_{PC} = 11.8 Hz, J_{PC} = 1.6 Hz, C(6)), 70.1 (dd, J_{PC} = 16.4 Hz, J_{PC} = 3.1 Hz, C(10)), 69.6 (dd, J_{PC} = 29.2 Hz, J_{PC} = 4.0 Hz, C(7)), 68.5 (d, J_{PC} = 4.3 Hz, C(4)), 67.8 (dd, J_{PC} = 4.7 Hz, J_{PC} = 3.1 Hz, C(2)), 65.7 (dd, J_{PC} = 14.0 Hz, J_{PC} = 7.4 Hz, C(3)), 20.0 (dd, J_{PC} = 34.8 Hz, J_{PC} = 26.4 Hz, C(31)), 18.7 (d, J_{PC} = 2.5 Hz, C(41)), 17.9 (d, J_{PC} = 2.8 Hz, C(21)), 16.1 (dd, J_{PC} = 26.4 Hz, J_{PC} = 4.7 Hz, C(71)), 13.6 (d, J_{PC} = 5.3 Hz, C(11)), 13.1 (d, J_{PC} = 5.0 Hz, C(81)), 12.6 (d, J_{PC} = 7.8 Hz, C(61)), 12.4 (d, J_{PC} = 1.4 Hz, C(91)), 11.5 (d, J_{PC} = 1.6 Hz, C(51)), 11.0 (d, J_{PC} = 1.9 Hz, C(101)).

^{1}H NMR (300.4 MHz, $CDCl_3$, 25 °C) δ = 1.77 (s, H(91)), 1.73 (s, H(11)), 1.69 (s, H(81)), 1.63 (s, H(51)), 1.60 (d, J_{HP} = 17.8 Hz, H(71)), 1.39 (d, J_{HP} = 25.2 Hz, H(41)), 1.31 (d, J_{HP} = 18.6 Hz, H(101)), 1.30 (d, J_{HP} = 15.9 Hz, H(31)), 1.14 (s, H(21)), 1.00 (s, H(61)).

Mp: 148-152 °C (decomp.).

Elemental Analysis: $[C_{20}H_{30}P_2I][GaI_4]$ requires C 23.17 H 2.92 %; found: C 24.20 H 2.47 %.

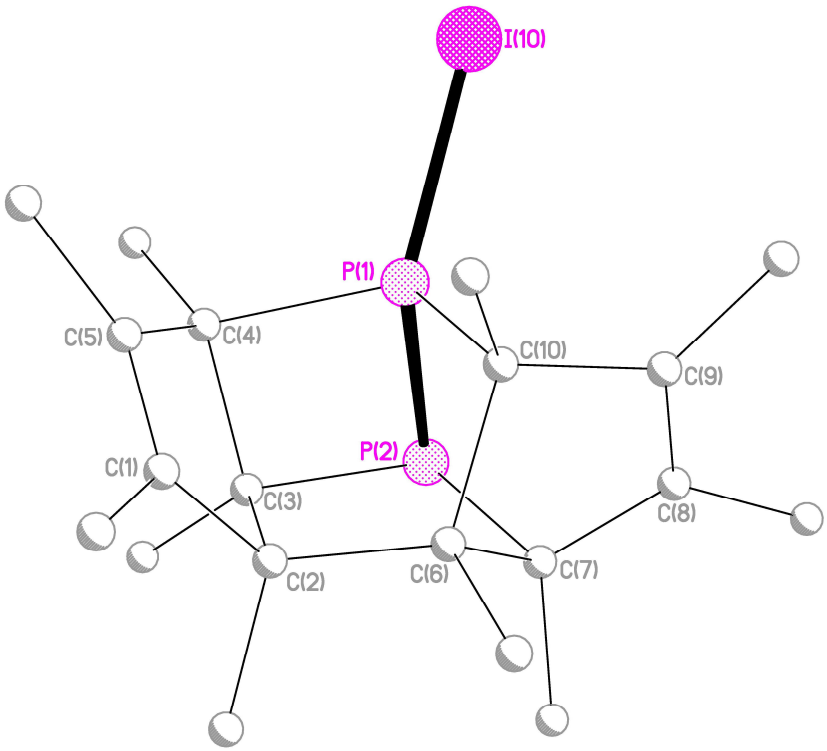

Fig. 1a The molecular structure of **1**; all hydrogen atoms and the $[GaI_4]^-$ anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)-C(5) 1.36(2), C(1)-C(2) 1.46(2), C(2)-C(6) 1.59(2), C(2)-C(3) 1.59(2), C(7)-C(8) 1.43(2), C(7)-C(6) 1.59(2), C(7)-P(2) 1.91(2), C(6)-C(10) 1.64(2), C(9)-C(8) 1.36(2), C(3)-C(4) 1.62(2), C(3)-P(2) 1.95(2), C(5)-C(4) 1.45(2), C(4)-P(1) 1.89(2), C(10)-P(1) 1.88(2), I(10)-P(1) 2.375(4), P(1)-P(2) 2.178(6); C(5)-C(1)-C(2) 113.5(1), C(1)-C(2)-C(6) 116.7(1), C(1)-C(2)-C(3) 102.4(1), C(6)-C(2)-C(3) 106.2(1), C(8)-C(7)-C(6) 105.8(1), C(8)-C(7)-P(2) 108.9(1), C(6)-C(7)-P(2) 102.1(9), C(2)-C(6)-C(7) 113.5(1), C(2)-C(6)-C(10) 112.6(1), C(7)-C(6)-C(10) 95.9(1), C(8)-C(9)-C(10) 109.5(1), C(2)-C(3)-C(4) 99.2(1), C(2)-C(3)-P(2) 109.5(9), C(4)-C(3)-P(2) 101.8(9), C(1)-C(5)-C(4) 110.5(1), C(5)-C(4)-C(3) 103.6(1), C(5)-C(4)-P(1) 114.3(1), C(3)-C(4)-P(1) 88.4(9), C(9)-C(10)-C(6) 101.4(1), C(9)-C(10)-P(1) 100.9(1), C(6)-C(10)-P(1) 99.5(1), C(9)-C(8)-C(7) 111.4(1), C(10)-P(1)-C(4) 110.7(7), C(10)-P(1)-P(2) 98.1(6), C(4)-P(1)-P(2) 85.8(5), C(10)-P(1)-I(10) 112.5(6), C(4)-P(1)-I(10) 116.3(5), P(2)-P(1)-I(10) 129.9(2), C(7)-P(2)-C(3) 94.2(7), C(7)-P(2)-P(1) 88.4(5), C(3)-P(2)-P(1) 72.8(5).

Preparation of $[C_{10}Me_{10}P_2Cl][InCl_4]$ (2)
To a suspension of InCl (0.15 g, 1 mmol) in dichloromethane (10 mL) was added Cp^*PCl_2 (0.024 g, 1 mmol), dropwise and at room temperature. The mixture was stirred for half an hour and the resulting red solution was filtered (porosity 3 sinter with Celite). The reaction is quantitative amount by ^{31}P NMR spectroscopy. Single crystals for X-ray crystallography were obtained from a concentrated solution in dichlorobenzene, layered with hexane and left for one month.

^{31}P NMR (121.4 MHz, $CDCl_3$, 25 °C) δ = 126.5 (d, J_{PP} = 245.6 Hz, P(1)), 24.7 (d, J_{PP} = 245.6 Hz, P(2)).
^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 145.7 (d, J_{PC} = 15.5 Hz, C(1)), 144.2 (d, J_{PC} = 12.4 Hz, C(8)), 129.4 (dd, J_{PC} = 13.0 Hz, J_{PC} = 1.9 Hz, C(5)), 128.9 (dd, J_{PC} = 12.1 Hz, J_{PC} = 6.8 Hz, C(9)), 78.6 (dd, J_{PC} = 8.4 Hz, J_{PC} = 2.2 Hz, C(6)), 73.3 (dd, J_{PC} = 6.4 Hz, J_{PC} = 3.6 Hz, C(4)), 69.8 (dd, J_{PC} = 28.9 Hz, J_{PC} = 3.1 Hz, C(7)), 69.4 (dd, J_{PC} = 9.9 Hz, J_{PC} = 4.0 Hz, C(10)), 68.0 (dd, J_{PC} = 4.7 Hz, J_{PC} = 2.8 Hz, C(2)), 62.7 (dd, J_{PC} = 14.6 Hz, J_{PC} = 9.6 Hz, C(3)), 17.7 (dd, J_{PC} = 39.1 Hz, J_{PC} = 27.3 Hz, C(31)), 17.6 (d, J_{PC} = 2.2 Hz, C(21)), 16.3 (dd, J_{PC} = 26.4 Hz, J_{PC} = 5.0 Hz, C(71)), 15.1 (d, J_{PC} = 4.7 Hz, C(41)), 13.4 (d, J_{PC} = 5.6 Hz, C(11)), 12.8 (dd, J_{PC} = 4.4 Hz, J_{PC} = 0.9 Hz, C(81)), 12.4 (dd, J_{PC} = 1.4 Hz, J_{PC} = 1.4 Hz, C(51)), 11.6 (d, J_{PC} = 8.4 Hz, C(61)), 11.5 (d, J_{PC} = 1.6 Hz, C(91)), 8.6 (d, J_{PC} = 2.8 Hz, C(101)).
^{1}H NMR (300.4 MHz, $CDCl_3$, 25 °C) δ = 1.83 (ddd, J_{HP} = 7.6 Hz, J_{HP} = 2.1 Hz, J_{HH} = 1.1 Hz, H(81)), 1.81 (ddd, J_{HP} = 10.6 Hz, J_{HP} = 1.2 Hz, J_{HH} = 1.2 Hz, H(11)), 1.79 (dd, J_{HP} = 5.1 Hz, J_{HH} = 1.2 Hz, H(51)), 1.77 (d, J_{HP} = 4.9 Hz, J_{HH} = 1.0 Hz, H(91)), 1.70 (dd, J_{PP} = 17.3 Hz, J_{PP} = 1.6 Hz, H(71)), 1.68 (d, J_{HP} = 24.7 Hz, H(41)), 1.55 (d, J_{PP} = 18.6 Hz, H(101)), 1.43 (dd, J_{PP} = 14.8 Hz, J_{PP} = 1.1 Hz, H(31)), 1.22 (s, H(21)), 1.01 (d, J_{PP} = 2.0 Hz, H(61)).

Experimental – Preparation of $C_{10}Me_{10}P_2{\cdot}GaCl_3$ (3)
To gallium metal (634 mg, 9.72 mmol) in a Schlenk tube with a Teflon stopcock was added toluene (20 ml) and Cp^*PCl_2 (534 mg, 2.25 mmol). The tube was sealed and heated to 50°C for 10 days. After filtering the solution and concentrating it, $C_{10}Me_{10}P_2{\cdot}GaCl_3$ was obtained as colourless crystals (450 mg, 78 %) on storage at -30 °C.
^{31}P NMR (162.0 MHz, THF-d_8, 25 °C) δ = 17.8 (d, J_{PP} = 149.1 Hz), –10.8 (d, J_{PP} = 149.1 Hz).
^{13}C NMR (100.6 MHz, THF-d_8, 25 °C) δ = 139.8 (d, J_{PC} = 3.9 Hz), 137.2 (d, J_{PC} = 7.8 Hz), 133.7 (dd, J_{PC} = 5.9, 2.0 Hz), 133.7 (s), 67.6 (dd, J_{PC} = 22.5, 2.9 Hz),67.0 (d, J_{PC} = 3.9 Hz), 61.5 (d, J_{PC} = 34.2 Hz), 61.2 (dd, J_{PC} = 5.4, 5.4 Hz), 46.2 (dd, J_{PC} = 6.8, 6.8 Hz), 25.5 (dd, J_{PC} = 20.5, 20.5 Hz), 19.8 (d, J_{PC} = 23.5 Hz), 17.4 (d, J_{PC} = 21.5 Hz), 17.0 (s), 16.0 (d, J_{PC} = 25.4Hz), 13.2 (d, J_{PC} = 15.7 Hz), 12.1 (s), 11.1 (s), 11.0 (s), 9.5 (d, J_{PC} = 4.9 Hz), 9.3 (s)
^{1}H NMR (400.1 MHz, THF-d_8, 25 °C) δ = 1.67 (dq, J_{HP} = 1.6 Hz, J_{HH} = 0.9 Hz), 1.52-1.49 (m, 6 H), 1.51 (d, J_{HP}=14.9 Hz, 3 H), 1.45 (dq, J_{HP} = 1.1, J_{HH} = 1.1 Hz, 3 H), 1.21 (d, J_{HP} = 15.4 Hz, 3 H), 1.19 (dd, J_{HP} = 11.7, 0.6 Hz, 3 H), 1.13 (s, 3 H), 0.91 (d, J_{HP} = 14.0 Hz, 3 H), 0.82 (s, 3 H)
Elemental analysis: $C_{20}H_{30}Cl_3GaP_2$ requires C 47.24 % H 5.95 %; found C 46.36 % H 6.15 %.
EI-MS (170 °C) *m*/*z* (%) = 473 (2) [M^+ – Cl], 332 (100) [M^+ – $GaCl_3$], 166 (2) [$C_{10}H_{15}P^+$].

[i] M. L. H. Green, P. Mountford, G. J. Smout, S. R. Speel, *Polyhedron*, 1990, **9**, 2763.