Supplementary Information

"Synthesis of ternary group 13/15 chain compounds"

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Content

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Experimental Section

General: All working procedures were conducted under rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen/argon atmosphere. Solvents were dried and freshly distilled before use. NMR spectra were recorded on a BRUKERAVANCEHD 300, BRUKERDRX400 or BRUKERAVANCE 500 and visualized with MESTRENOVA.[1] IR vibrational spectra were gathered with a BRUKER ALPHA ATR-FT-IR. The starting material *t*Bu_2PNH_2 (**1**) was prepared by reported methods.[2]

***t*Bu$_2$PCl (6)**: Magnesium (12.2 g, 502.0 mmol, 2.5 equiv.) was suspended in 200 mL of diethylether. *t*BuCl (55.1 mL, 500.0 mmol, 2.5 equiv.) dissolved in 150 ml of diethylether was added to the suspension dropwise at room temperature. The *Grignard* solution was added to a solution of PCl_3 (17.5 mL, 201.0 mmol, 1.0 equiv.) in 400 mL of diethylether dropwise at -40 °C. The resulting solid was filtrated and washed twice with 40 mL *n*-pentane each. The solvent was removed *in vacuo* and the product was obtained as a colourless liquid (18.0 g, 100.0 mmol, 50% yield) via fractional distillation at 10 mmHg at 63 °C. **^{1}H-NMR** (300.13 MHz, C_6D_6): δ / ppm = 1.09 [d, $^3J_{HP}$ = 12.1 Hz, 18H, CH_3]; **^{13}C{^{1}H}-NMR** (75.47 MHz, C_6D_6): δ / ppm = 27.9 [d, $^2J_{CP}$ = 17.1 Hz, *C*H_3], 35.9 [d, $^1J_{CP}$ = 41.3 Hz, C_{quart}]; **^{31}P{^{1}H}-NMR** (121.54 MHz, C_6D_6): δ / ppm = 148.1 [s].

***t*Bu$_2$PNH$_2$ (1):** *t*Bu_2PCl (10 g, 554.0 mmol, 1.0 equiv.) was dissolved in 10 mL of diethylether. At -50 °C, ammonia was passed into the solution for one hour. The formed colourless solid was filtrated and washed twice with 10 mL of *n*-pentane each. The solvent was removed *in vacuo* and the product was obtained as a colourless liquid (8.06 g, 500.0 mmol, 90% yield) via fractional distillation at 5 mmHg and 55 °C. **^{1}H-NMR** (300.13 MHz, C_6D_6): δ / ppm = 0.92 [s, 2H, N*H*], 1.03 [d, $^3J_{H,P}$ = 11.2 Hz, 18H, CH_3]; **^{13}C{^{1}H}-NMR** (75.47 MHz, C_6D_6): δ / ppm = 28.1 [d, $^2J_{C,P}$ = 15.4 Hz, *C*H_3], 33.0 [d, $^1J_{C,P}$ = 21.5 Hz, C_{quart}]; **^{31}P{^{1}H}-NMR** (121.54 MHz, C_6D_6): δ / ppm = 63.0 [s].

***t*Bu$_2$P(NH$_2$)BH$_3$ (2)**: *t*Bu_2PNH_2 (100.0 mg, 0.62 mmol, 1.0 equiv.) was suspended in 5 mL of thf and cooled to -50 °C. A 1M solution of BH_3:thf (0.62 mL, 0.62 mL, 1.0 equiv.) in thf was added dropwise and the solution was allowed to warm to room temperature. After removal of the solvent *in vacuo*, crystalline needles were obtained with a yield of 92%. **^{1}H-NMR** (300.13 MHz, Tol-d^8): δ / ppm = 1.05 [d, $^3J_{H,P}$ = 12.8 Hz, 18H, PC(CH_3)$_3$], 1.52 [m, 3H, BH_3], NH_2 could not be observed; **^{11}B{^{1}H}-NMR** (96.33 MHz, Tol-d^8): δ / ppm = -40.6 [d, $^1J_{B,P}$ = 66.1 Hz, P*B*H_3]; **^{13}C{^{1}H}-NMR** (75.47 MHz, Tol-d^8): δ / ppm = 27.1 [d, $^2J_{C,P}$ = 2.5 Hz, PC(*C*H_3)$_3$], 33.6 [d, $^1J_{C,P}$ = 30.9 Hz, C_{quart}]; **^{31}P{^{1}H}-NMR** (121.54 MHz, Tol-d^8): δ / ppm = 77.1 [q, $^1J_{P,B}$ = 66.5 Hz]. **IR** (solid): ν / cm^{-1} = 3402 (m, N-H), 3317 (m, N-H), 3118 (vw), 2986 (m), 2963 (m), 2946 (m), 2899 (m), 2867 (m, BH3), 2372 (s), 2308 (w), 2269 (vw), 1563 (m), 1475 (m), 1417 (w), 1389 (m), 1365 (w), 1336 (w), 1278 (w), 1259 (w), 1200 (m, BH3), 1160 (m), 1140 (m, BH3), 1077 (m), 1021 (m), 935 (m), 895 (m), 813 (s), 765 (m), 710 (vw), 644 (vs), 616(s), 547 (m), 474 (m), 446 (m). **CHN** [%] calculated: C, 54.89; H, 13.24; N, 8.00; found: C, 54.82; H, 13.11; N, 7.89.

HB{N(H)P*t*Bu$_2$BH$_3$}$_2$ (3): *t*Bu_2PNH_2 (0.18 g, 1.10 mmol, 1.0 equiv.) was dissolved in 5 mL of *n*-pentane and cooled to -20 °C. Me_2S:BH_3 (0.16 mL, 1.65 mmol, 1.5 equiv.) was added dropwise. The solution was allowed to warm to room temperature and then heated to 40 °C for 5 h. The reaction was cooled to room temperature and after removal of the solvent *in vacuo*, the product was obtained as a colourless solid with a yield of 73%. **^{1}H-NMR** (300.13 MHz, Tol-d^8): δ / ppm = 0.97 [br s, 18H, PC(CH_3)$_3$], 1.23 [br s, 18H, PC(CH_3)$_3$], 1.60 [m, 3H, BH_3], 4.75 [s, 1H, NH-B*H*-NH], N*H* could not be observed; **^{11}B{^{1}H}-NMR** (96.33 MHz, Tol-d^8): δ / ppm = -40.9 [d, $^1J_{B,P}$ = 68.1 Hz, P*B*H_3], 32.1 [br s, NH-*B*H-NH]; **^{13}C{^{1}H}-NMR** (75.47 MHz, Tol-d^8): δ / ppm = 27.5 [s, PC(*C*H_3)$_3$], 34.5 [d, $^1J_{CP}$ = 30.6 Hz, C_{quart}]; **^{31}P{^{1}H}-NMR** (121.54 MHz, Tol-d^8): δ / ppm = 79.7 [m, *P*BH_3], 88.5 [m, *P*BH_3]. **IR** (solid): ν / cm^{-1} = 3305 (m), 2983 (m), 2963 (m), 2904 (w), 2870 (w), 2586 (w), 2381 (m), 2312 (m), 2166 (w), 1475 (m), 1439 (m), 1416 (s), 1393 (s), 1376 (m), 1359 (m), 1247 (m), 1186 (w), 1152 (w), 1100 (m), 1072 (m), 1021 (m), 934 (w), 884 (s), 813 (s), 778 (m), 754 (m), 671 (m), 633 (s), 565 (m), 538 (w), 519 (w), 431 (m). **CHN** [%] calculated: C, 53.39; H, 12.60; N, 7.78; found: C, 52.91; H, 12.48; N, 7.80.

***t*Bu$_2$PN(H)Al*t*Bu$_2$N(H)P(H)*t*Bu$_2$ (4):** *t*Bu_2PNH_2 (0.15 mg, 0.90 mmol, 1.0 equiv.) was dissolved in 5 mL of *n*-pentane and cooled to -50 °C. A 1M solution of Al^tBu_3 (0.92 mL, 0.92 mmol, 1.0 equiv.) in heptane was added dropwise. The solution was allowed to warm to room temperature and the solvent was removed *in vacuo*. The formed solid was washed with *n*-pentane and dried *in vacuo*. The product was obtained as a colourless solid with a yield of 79%. **^{1}H-NMR** (300.13 MHz, Tol-d^8): δ / ppm = 0.93 [s,br, 18H, PC(CH_3)$_3$], 1.21 [s,br, 18H, PC(CH_3)$_3$], 1.36 [s, 18H, AlC(CH_3)$_3$], 5.63 [d, $^1J_{H,P}$ = 445.0 Hz, 1H, P*H*], N*H* could not be observed; **^{13}C{^{1}H}-NMR** (75.47 MHz, Tol-d^8): δ / ppm = 26.8 [s, PC(*C*H_3)$_3$], 29.6 [s, PC(*C*H_3)$_3$], 33.5 [s, AlC(*C*H_3)$_3$], 33.5 [s, C_{quart}], 34.9 [s, C_{quart}], AlC_{quart} could not be observed; **^{31}P{^{1}H}-NMR** (121.54 MHz, Tol-d^8): δ / ppm = 62.9 [s, *P*H], 65.4 [s, *P*]; **^{31}P-NMR** (121.54 MHz, Tol-d^8): δ / ppm = 62.9 [d, $^1J_{P,H}$ = 445.0 Hz, *P*H], 65.4 [s, *P*]. **IR** (solid): ν / cm^{-1} = 3332 (w), 2927 (m), 2857

(m), 2812 (m), 2682 (w), 2410 (w), 1461 (m), 1395 (w), 1373 (m), 1357 (m), 1260 (w), 1154 (m), 1014 (s), 1000 (s), 934 (m), 880 (s), 808 (s), 639 (m), 592 (m), 577 (m), 547 (m), 507 (m), 452 (m), 408 (m). **CHN** [%] calculated: C, 62.31; H, 12.42; N, 6.05; found: C, 61.85; H, 12.24; N, 6.07.

***t*Bu$_2$(H)PN(H)Ga*t*Bu$_3$ (5):** *t*Bu$_2$PNH$_2$ (0.21 mg, 1.28 mmol, 1.0 equiv.) was dissolved in 5 mL of *n*-pentane and cooled to -65 °C. Ga^{t}Bu$_3$ (0.31 mL, 1.00 mmol, 0.79 equiv.) was added dropwise. The solution was allowed to warm to room temperature and the solvent was removed *in vacuo*. The formed solid was washed with *n*-pentane and dried *in vacuo*. The product was obtained as a colourless solid with a yield of 69%. **^{1}H-NMR** (300.13 MHz, C_6D_6): δ / ppm = 0.76 [d, $^3J_{HP}$ = 15.4 Hz, 18H, PC(CH_3)$_3$], 1.50 [s, 27H, GaC(CH_3)$_3$], 5.54 [dd, $^1J_{H,P}$ = 460.2 Hz, $^3J_{H,H}$ = 16.3 Hz, 1H, P*H*], N*H* could not be observed; **^{13}C{^{1}H}-NMR** (75.47 MHz, C_6D_6): δ / ppm = 28.1 [d, = 15.4 Hz, PC(*C*H$_3$)$_3$], 34.0 [s, GaC(*C*H$_3$)$_3$], 35.4 [d, $^1J_{C,P}$ = 46.2 Hz, C_{quart}], GaC_{quart} could not be observed; **^{31}P{^{1}H}-NMR** (121.54 MHz, C_6D_6): δ / ppm = 64.3 [s, *P*H]; **^{31}P-NMR** (121.54 MHz, C_6D_6): δ / ppm = 64.3 [d, $^1J_{P,H}$ = 461.1 Hz, *P*H]. **IR** (solid): ν / cm^{-1} = 3344 (w), 2955 (m), 2930 (m), 2867 (m), 2815 (m), 2688 (w), 2399 (w), 1550 (w), 1464 (m), 1393 (w), 1368 (m), 1355 (w), 1260 (m), 1130 (m), 1093 (m), 1014 (s), 998 (s), 935 (m), 905 (m), 806 (s), 699 (w), 660 (w), 632 (m), 586 (w), 520 (m), 448 (m). **CHN** [%] calculated: C, 59.71; H, 11.78; N, 3.48; found: C, 59.67; H, 11.53; N, 3.62.

Crystal Structure Data

Data collection was performed using a BRUKER D8 QUEST diffractometer at 100(2) K with MoK$_\alpha$ radiation and graphite monochromatization (λ = 0.71073). Structure solution was realised by direct methods, refinement with full-matrix-least-squares against F^2 using SHELXL-14 and Olex2 software.[3,4] The presentation of crystal structures was done with DIAMOND 4.2.2.[5] *For crystallographic data see also: CCDC* 1818069 (**3**), 1818070 (**2**), 1818071 (**4**) and 1818072 (**5**).

Single crystals of **2** were obtained by removing the solvent of the reaction in vacuum.

Table S1. X-ray measurement, structure solution and refinement details of **2**.

Empirical formula	$C_8H_{23}B_1N_1P_1$
Formula weight /g·mol^{-1}	175.05
Crystal colour, shape	colourless block
Crystal size /mm^3	0.43 x 0.085 x 0.065
Crystal system	triclinic
Space group	*P* -1
a / Å	6.3544(5)
b / Å	8.4271(7)
c / Å	11.7497(9)
α /°	99.059(7)
β /°	95.591(6)°
γ /°	109.064(6)
V /Å^3	579.75(8)
Z	2
ρ_{calc} / g·cm^{-3}	1.003
μ (Mo$_{K\alpha}$) /mm^{-1}	0.187
2 ϑ range /°	3.56 – 56.21
Reflections measured	5915
Independent reflections	2789, R_{int} = 0.0723
R_1 ($I > 2\sigma(I)$)	0.0482
wR_2 (all data)	0.1181
GooF (all data)	1.015
Largest diff. peak and hole /e.Å^{-3}	0.421 and -0.332

Single crystals of **3** were obtained from cyclopentane at 3 °C.

Table S2. X-ray measurement, structure solution and refinement details of **3**.

Empirical formula	$C_{16}H_{45}B_3N_2P_2$
Formula weight /g·mol^{-1}	359.91
Crystal colour, shape	colourless block
Crystal size /mm^3	0.207 x 0.163 x 0.099
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	26.4536(11)
b / Å	8.4495(3)
c / Å	24.1754(10)
β /°	116.853(1)°
V /Å^3	4821.0(3)
Z	8
ρ_{calc} / g·cm^{-3}	0.992
μ ($Mo_{K\alpha}$) /mm^{-1}	0.181
2 ϑ range /°	4.81 – 56.702
Reflections measured	165029
Independent reflections	12019, R_{int} = 0.0654
R_1 ($I > 2\sigma(I)$)	0.0427
wR_2 (all data)	0.0968
GooF (all data)	1.133
Largest diff. peak and hole /e.Å^{-3}	0.351 and -0.286

Single crystals of **4** were obtained from benzene at 7 °C.

Table S3. X-ray measurement, structure solution and refinement details of **4**.

Empirical formula	$C_{24}H_{57}Al_1N_2P_2$
Formula weight /g·mol^{-1}	462.63
Crystal colour, shape	colourless block
Crystal size /mm^3	0.222 x 0.216 x 0.127
Crystal system	monoclinic
Space group	*Pn*
a / Å	16.5685(6)
b / Å	11.5095(4)
c / Å	17.2952(6)
β /°	115.201(1)
V /Å^3	2984.19(18)
Z	4
ρ_{calc} / g·cm^{-3}	1.030
μ ($Mo_{K\alpha}$) /mm^{-1}	0.188
2 ϑ range /°	5.206 – 50.512
Reflections measured	50020
Independent reflections	10696, R_{int} = 0.0474
R_1 ($I > 2\sigma(I)$)	0.0402
wR_2 (all data)	0.0979
GooF (all data)	1.028
Largest diff. peak and hole /e.Å^{-3}	0.826 and -0.400
Flack parameter	0.00(4)

Single crystals of **5** were obtained from benzene at 7 °C.

Table S4. X-ray measurement, structure solution and refinement details of **5**.

Empirical formula	$C_{20}H_{47}Ga_1N_1P_1$, 0.5 (C_6H_6)
Formula weight /g·mol^{-1}	441.33
Crystal colour, shape	colourless block
Crystal size /mm^3	0.529 x 0.485 x 0.22
Crystal system	triclinic
Space group	*P* -1
a / Å	8.7135(5)
b / Å	11.0101(6)
c / Å	15.2569(8)
α /°	71.092(2)
β /°	85.633(3)
γ /°	70.883(2)
V /Å^3	1307.61(13)
Z	2
ρ_{calc} / g·cm^{-3}	1.121
μ ($Mo_{K\alpha}$) /mm^{-1}	1.120
2 ϑ range /°	5.334 – 52.842
Reflections measured	50635
Independent reflections	5365, R_{int} = 0.0211
R_1 ($I > 2\sigma(I)$)	0.0174
wR_2 (all data)	0.0450
GooF (all data)	1.092
Largest diff. peak and hole /e.Å^{-3}	0.313 and -0.258

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