Supplementary material for:

Germylenes and Stannylenes Stabilized within the N_2PE Rings (E= Ge or Sn): Combined Experimental and Theoretical Study.

Jan Vrána, Sergey Ketkov, Roman Jambor, Aleš Růžička, Antonín Lyčka and Libor Dostál

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1) General consideration and syntheses

General remarks: ¹H, ⁷Li, ¹³C, ³¹P and ¹¹⁹Sn NMR spectra were recorded on Bruker Avance 500 MHz spectrometer or Bruker Ultrashield 400 MHz, using 5 mm tuneable broad-band probe. Appropriate chemical shifts in ¹H and ¹³C NMR spectra were related to the residual signals of the solvent (C₆D₆: $\delta(^{1}H) = 7.27$ ppm and $\delta(^{13}C) = 77.23$ ppm; THF-d₈: $\delta(^{1}H) = 3.58$ ppm and $\delta(^{13}C) = 67.57$ ppm). ⁷Li, ³¹P and ¹¹⁹Sn NMR spectra were related to external standard LiCl in D₂O, 85% H₃PO₄ and Me₄Sn, respectively. Elemental analyses were performed on an LECO-CHNS-932 analyzer.

Synthesis of [PhP(NH*t*-Bu)(N*t*-Bu)]Li(tmeda). (2)A solution of *n*-BuLi (1.51mL, 2.5M, 3.8mmol) in hexane was added dropwise to a stirred solution of PhP(NH*t*-Bu)₂ (0.955 g, 3.8mmol) in hexane (10 mL) at -50°C. The yellow solution was slowly warmed to room temperature and tmeda (0.57 mL, 3.8 mmol) was added forming yellow suspension of (2). The precipitate was re-dissolved by heating to 70°C and the solution was slowly cooled to room temperature and left one day for crystallization. X-Ray quality crystals were decanted and dried in *vacuo*. Yield (0.950 g, 67%).¹H NMR (500 MHz, C₆D₆, 294 K): δ 1.34 (s, 9H, C(CH₃)₃), 1.61 (s, 9H, C(CH₃)₃), 2.02 – 2.16 (m, 16H, tmeda), 7.15 (m, 1H, *p*-Ar*H*), 7.36 (m, 2H, *m*-Ar*H*), 8.06 (m, 2H, *o*-Ar*H*), N*H* not observed.¹³C{¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 32.6 (d, ³*J*_{PC} = 9.9 Hz, C(CH₃)₃), 37.1 (d, ³*J*_{PC} = 12.8 Hz, C(CH₃)₃), 46.5 (s, N(CH₃)₂), 51.7 (d, ²*J*_{PC} = 19.1 Hz, C(CH₃)₃), 52.9 (d, ²*J*_{PC} = 29.9 Hz, C(CH₃)₃), 58.3 (s, NCH₂), 126.4 (s, *p*-Ar*C*), 127.8 (s,*m*-Ar*C*), 130.4 (d, ²*J*_{PC} = 17.5 Hz, *o*-Ar*C*), 159.8 (d, ¹*J*_{PC} = 39.9 Hz, *ipso*-Ar*C*). ³¹P{¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 89.7. ⁷Li NMR (194.3 MHz, C₆D₆, 294 K): 1.10. Mp 78-79 °C. Anal. Calcd for C₂₀H₄oLiN₄P (374.47): C 64.2; H 10.8. Found: C 64.2; H 10.8.

Synthesis of [PhP(N*t*-Bu)(N-2,6-*i*-Pr₂C₆H₃)]Li₂(Et₂O) (3). A solution of *n*-BuLi (1.72mL, 2.5M, 4.3mmol) in hexane was added dropwise to a stirred solution of PhP(NH*t*-Bu)(NH-2,6-*i*-Pr₂C₆H₃) (0.767 g, 2.2mmol) in diethylether (10 mL) at -50°C. The yellow solution was slowly warmed to room temperature yielding slightly yellow suspension. The suspension was filtered off and the solid was dried in *vacuo*. X-Ray quality crystals were obtained by recrystallization from diethylether. Yield (0.819 g, 86%). ³¹P{¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 103.8, 114.6, 121.5. Dp 218-219 °C. Anal. Calcd for C₂₆H₄₁Li₂N₂OP (442.48): C 70.6; H 9.3. Found: C 70.8; H 9.4.

Synthesis of [PhP(NHt-Bu)(N-2,6-i-Pr₂C₆H₃)]Li(tmeda) (4). A solution of *n*-BuLi (1.31mL, 2.5M, 3.3mmol) in hexane was added dropwise to a stirred solution of PhP(NHt-Bu)(NH-2,6-i-Pr₂C₆H₃) (1.166 g, 3.3mmol) in hexane (15 mL) at -50°C. The yellow suspension was slowly warmed to room temperature and TMEDA (0.57 mL, 3.8 mmol) was added forming yellow suspension of (4). The precipitate was re-dissolved by adding toluene (10 mL) and heating to 70°C and the solution was slowly cooled to room temperature and left one day for crystallization. X-Ray quality crystals were decanted and dried in *vacuo*. Yield (0.861 g, 55%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 1.26 (d, ³J_{HH} = 6.4 Hz, 6H, CH(CH₃)₂), 1.27 (s, 9H, C(CH₃)₃), 1.58 (d, ${}^{3}J_{HH} = 6.4$ Hz, 6H, CH(CH₃)₂), 1.85 (m, 16H, tmeda), 4.36 (sept, ${}^{3}J_{HH} = 6.4$ Hz, 2H, CH(CH₃)₂), 7.00 (m, 1H, *p*-ArH), 7.15 (m, 1H, *p*-ArH), 7.24 (m, 2H, ArH), 7.27 (m, 2H, ArH), 7.93 (m, 2H, o-ArH), NH not observed. ¹³C{¹H} NMR (125.76 MHz, C_6D_6 , 294 K): δ 26.1 (s, CH(CH_3)₂), 26.6 (d, J_{PC} = 5.2 Hz, CH(CH₃)₂), 29.0 (d, J_{PC} = 4.7 Hz, $CH(CH_3)_2$, 32.7 (d, ${}^{3}J_{PC} = 9.2$ Hz, $C(CH_3)_3$), 46.1 (s, $N(CH_3)_2$), 51.8 (d, ${}^{2}J_{PC} = 19.6$ Hz, $C(CH_3)_3$), 56.9 (s, NCH₂), 118.4 (s, ArC), 123.7 (s, ArC), 127.8 (s, ArC), 128.4 (d, ${}^{3}J_{PC} = 4.9$ Hz, $m-C_{6}H_{5}$), 129.9 (d, $^{2}J_{PC} = 23.4 \text{ Hz}, o-C_{6}\text{H}_{5}$, 144.1 (d, $^{3}J_{PC} = 4.3 \text{ Hz}, o-C_{6}\text{H}_{3}$), 153.5 (d, $^{2}J_{PC} = 20.8 \text{ Hz}, ipso-C_{6}\text{H}_{3}$), 157.2 (d, ${}^{1}J_{PC} = 43.9$ Hz, *ipso-C*₆H₅). ${}^{31}P{}^{1}H{}$ NMR (202.46 MHz, C₆D₆, 294 K): δ 95.5.⁷Li NMR (194.3MHz, C₆D₆, 294 K): δ 1.07. Mp 109-111°C. Anal. Calcd for C₂₈H₄₈LiN₄P (478.62): C 70.3; H 10.1. Found: C 70.3; H 10.1.

Synthesis of [*t*-**BuP**(N-2,6-*i*-**Pr**₂C₆H₃)₂]**L**i₂(**E**t₂**O**)₂ (5). A solution of *n*-BuLi (1.58mL, 2.5M,5.8mmol) in hexane was added dropwise to a stirred solution of *t*-BuP(NH-2,6-*i*-Pr₂C₆H₃)₂ (1.277 g, 2.9mmol) in diethylether (15 mL) at -10°C. The yellow solution was slowly warmed to room temperature forming white suspension of (5.2Et₂O). The precipitate was re-dissolved by heating to 55°C and then left at room temperature for one day, yielding colorless X-ray quality crystals. Yield (0.976 g, 55%).¹H NMR (500 MHz, C₆D₆, 294 K): δ 0.91 (d, ³*J*_{HH} = 9.6 Hz, 9H, C(*CH*₃)₃), 0.97 (t, ³*J*_{HH} = 6.8 Hz, 12H, CH₂CH₃), 1.23 (m broad, 6H, CH(*CH*₃)₂), 1.39 (d, ³*J*_{HH} = 6.8 Hz, 12H, CH(*CH*₃)₂), 3.21 (q, ³*J*_{HH} = 6.8 Hz, 8H, CH₂CH₃), 3.96 (m broad, 2H, CH(CH₃)₂), 4.27 (m broad, 2H, CH(CH₃)₂), 6.96 (t, ³*J*_{HH} = 7.4 Hz, 2H, *p*-ArH), 7.16 (m broad, 4H, ArH).¹³C {¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 15.4 (s, OCH₂CH₃), 24.9 (d, ²*J*_{PC} = 18.6 Hz, C(CH₃)₃), 26.0, 26.7, 27.5, 28.0 (s broad, CH(CH₃)₂), 30.4 (s broad, CH(CH₃)₂), 40.1 (d, ¹*J*_{PC} = 64.9 Hz, C(CH₃)₃), 66.2 (s,

OCH₂CH₃), 118.1, 123.3, 125.0, 141.2, 142.6 (s, Ar*C*), 153.6 (d, ${}^{2}J_{PC} = 10.3$ Hz, *ipso*-Ar*C*).³¹P{¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 139.4. ⁷Li NMR (194.3MHz, C₆D₆, 294 K): δ 1.38. Dp 152 °C. Anal. Calcd for C₃₆H₆₃Li₂N₂O₂P (600.75): C 72.0; H 10.6. Found: C 72.1; H 10.7.

Synthesis of [*t***-BuP(N-2,6-***i***-Pr₂C₆H₃)₂]Li₂(tmeda)₂ (5a). A solution of** *n***-BuLi (1.58mL, 2.5M, 4.0mmol) in hexane was added dropwise to a stirred solution of** *t***-BuP(NH-2,6-***i***-Pr₂C₆H₃)₂ (0.872 g, 2.0mmol) in toluene (15 mL) at -10°C. The yellow solution was slowly warmed to room temperature and tmeda (0.59 mL, 4.0 mmol) was added forming yellow suspension of (5a). The suspension was filtered off and the powder was dried in** *vacuo***. Yield (1.234 g, 91%).¹H NMR (500 MHz, C₆D₆, 294 K): δ 0.64 (d, {}^{3}J_{PH} = 9.6 Hz, 9H, C(CH₃)₃), 1.06 (d, {}^{3}J_{HH} = 7.0 Hz, 12H, CH(CH₃)₂), 1.16 (d, {}^{3}J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 2.14 (s, 24H, N(CH₃)₂), 2.30 (s, 8H, NCH₂), 4.75 (m, 4H, CH(CH₃)₂), 5.94 (t, {}^{3}J_{HH} = 7.3 Hz, 2H,** *p***-Ar***H***), 6.52 (d, {}^{3}J_{HH} = 7.3 Hz, 2H,** *m***-Ar***H***).¹³C {¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 25.9 (s, CH(CH₃)₂), 26.4 (s, CH(CH₃)₂), 26.6 (s, CH(CH₃)₂), 27.7 (d, {}^{2}J_{PC} = 13.9 Hz, C(CH₃)₃), 39.1 (d, {}^{1}J_{PC} = 43.8 Hz, C(CH₃)₃), 46.3 (s, N(CH₃)₂), 58.9 (s, NCH₂), 109.5 (s, Ar***C***), 122.6 (s, Ar***C***), 140.1 (s,** *o***-Ar***C***), 158.4 (d, {}^{2}J_{PC} = 15.6 Hz,** *ipso***-Ar***C***). ³¹P {¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 129.8. ⁷Li NMR (194.3MHz, C₆D₆, 294 K): δ -0.04 broad. Dp 118 °C. Anal. Calcd for C₄₀H₇₅Li₂N₆P (684.92): C 70.1; H 11.0. Found: C 70.1; H 11.1.**

Synthesis of [*t*-BuP(NH-2,6-*i*-Pr₂C₆H₃)(N-2,6-*i*-Pr₂C₆H₃)]Li(tmeda) (6). A solution of *n*-BuLi (0.54mL, 2.5M, 1.4mmol) in hexane was added dropwise to a stirred solution of *t*-BuP(NH-2,6-*i*-Pr₂C₆H₃)₂ (0.598 g, 1.4mmol) in hexane (10 mL) at -10°C. The yellow solution was slowly warmed to room temperature and tmeda (0.20 mL, 1.4 mmol) was added forming slightly yellow suspension of (6). The suspension was filtered off and the powder was dried in *vacuo*. Yield (0.695 g, 91%).¹H NMR (500 MHz, THF-d₈, 294 K): δ -0.93 (d, ³*J*_{PH} = 10.5 Hz, 9H, C(CH₃)₃), 1.06 (d, ³*J*_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 1.08 (d, ³*J*_{HH} = 6.6 Hz, 6H, CH(CH₃)₂), 1.13 (d, ³*J*_{HH} = 6.7 Hz, 6H, CH(CH₃)₂), 1.17 (d, ³*J*_{HH} = 6.4 Hz, 6H, CH(CH₃)₂), 2.14 (s, 12H, N(CH₃)₂), 2.29 (s, 4H, NCH₂), 3.67 (m broad, 2H, CH(CH₃)₂), 4.11 (s, 1H, NH), 4.23 (m broad, 2H, CH(CH₃)₂), 6.35 (t, ³*J*_{HH} = 7.2 Hz, 1H, *p*-ArH), 6.65 (t, ³*J*_{HH} = 7.6 Hz, 1H, *p*-ArH), 6.72 (d, ³*J*_{HH} = 7.4 Hz, 2H, *m*-ArH), 6.35 (d, ³*J*_{HH} = 7.4 Hz, 2H, *m*-ArH). ¹³C{¹H} NMR (125.76 MHz, THF-d₈, 294 K): δ 24.7 (s, CH(CH₃)₂), 25.4 (s, CH(CH₃)₂), 25.5 (s,

CH(CH₃)₂), 25.9 (d, ${}^{5}J_{PC} = 3.4$ Hz, CH(CH₃)₂), 26.2 (d, ${}^{2}J_{PC} = 17.2$ Hz, C(CH₃)₃), 28.1 (d, ${}^{4}J_{PC} = 8.7$ Hz, CH(CH₃)₂), 29.2 (d, ${}^{4}J_{PC} = 8.7$ Hz, CH(CH₃)₂), 37.7 (d, ${}^{1}J_{PC} = 32.1$ Hz, C(CH₃)₃), 46.4 (s, N(CH₃)₂), 59.1 (s, NCH₂), 120.5 (s, ArC), 122.9 (s, ArC), 123.4 (s, ArC), 124.1 (s, ArC), 139.1 (s, ArC), 142.3 (s, ArC), 144.1 (s, ArC), 154.9 (d, ${}^{2}J_{PC} = 12.4$ Hz, *ipso*-ArC). ${}^{31}P\{{}^{1}H\}$ NMR (202.46 MHz, THF-d⁸, 294 K): δ 127.7. ⁷Li NMR (194.3MHz, THF-d₈, 294 K): δ 0.17. Mp 47°C. Anal. Calcd for C₃₄H₆₀LiN₄P (562.78): C 72.6; H 10.8. Found: C 72.8; H 10.9.

Synthesis of [PhP(N*t*-Bu)₂]Ge (7). Asolution of 1 (0.555 g, 2.1 mmol) in THF (20 mL) was added dropwise to a stirred suspension of GeCl₂.diox (0.491 g, 2.1 mmol) in diethylether (20 mL) at -50°C. The yellow solution was slowly warmed to room temperature and stirred for 2 hours. The solvent was removed under reduced pressure and the product was re-dissolved in hexane (30 ml). The solution was filtered off to remove lithium chloride and the solvent was removed under reduced pressure producing orange-red oil. Yield (0.622 g, 91%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 1.13 (s, 18H, C(C*H*₃)₃), 7.18 – 7.23 (m, 3H, Ar*H*), 7.65 (t, ³*J*_{HH} = 1.6 Hz, 2H, *o*-Ar*H*). ¹³C {¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 34.1 (d, ³*J*_{PC} = 6.9 Hz, C(CH₃)₃), 54.5 (d, ²*J*_{PC} = 7.8 Hz, C(CH₃)₃), 128.7 (d, ³*J*_{PC} = 7.0 Hz, *m*-ArC), 130.4 (d, ²*J*_{PC} = 25.8 Hz, *o*-ArC), 130.8 (s, *p*-ArC), 147.2 (d, ¹*J*_{PC} = 44.7 Hz, *ipso*-ArC). ³¹P {¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 138.3. Anal. Calcd for C₁₄H₂₃GeN₂P (322.96): C 52.1; H 7.2. Found C 52.2; H 7.3.

Synthesis of [PhP(Nt-Bu)(N2,6-i-Pr₂C₆H₃)]Ge (8).A solution of 3 (1.504 g, 3.4mmol) in THF (20 mL) was added dropwise to a stirred suspension of GeCl₂.diox (0.780 g, 3.4mmol) in diethylether (20 mL) at -50 °C. The yellow solution was slowly warmed to room temperature and stirred for 1 hour. The solvent was removed under reduced pressure and the product was re-dissolved in hexane (30 mL). The suspension was filtered to remove lithium chloride and the solvent was removed to third of its volume under reduced pressure. The orange solution was stored at -30°C to give orange X-Ray quality crystals. Yield (1.089 g, 75%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 1.05 (d, ³J_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 1.35 (s, 9H, C(CH₃)₃), 1.46 (d, ³J_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 3.77 (m, 2H, CH(CH₃)₂), 7.10 – 7.26 (m, 6H, Ar*H*), 7.67 (m, 2H, *o*-C₆H₅).¹³C {¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 25.5 (s, CH(CH₃)₂), 26.6 (s, CH(CH₃)₂), 29.0 (d, ⁴J_{PC} = 4.5 Hz, CH(CH₃)₂), 34.2 (d, ³J_{PC} = 6.5 Hz, C(CH₃)₃),

55.0 (d, ${}^{2}J_{PC} = 8.2$ Hz, $C(CH_{3})_{3}$), 123.9 (s, ArC), 125.6 (s, ArC), 128.7 (s, ArC), 130.5 (d, ${}^{2}J_{PC} = 25.4$ Hz, $o-C_{6}H_{5}$), 131.0 (s, ArC), 139.7 (d, $J_{PC} = 4.3$ Hz, ArC), 144.6 (d, ${}^{1}J_{PC} = 46.2$ Hz, *ipso-C*₆H₅), 146.1 (s, ArC). ${}^{31}P{}^{1}H{}$ NMR (202.46 MHz, C₆D₆, 294 K): δ 158.3. Mp 107-109 °C. Anal. Calcd for C₂₂H₃₁GeN₂P (427.11): C 61.9; H 7.3. Found: C 62.0; H 7.4.

Synthesis of [*t***-BuP(N-2,6-***i***-Pr₂C₆H₃)₂] Ge (9). A solution of 5 (0.796 g, 1.3 mmol) in THF (15 mL) was added dropwise to a stirred solution of GeCl₂.diox (0.307 g, 1.3 mmol) in THF (15 mL) at -80°C. The reaction mixture was slowly warmed to room temperature and stirred for 1 hour. The solvent was removed under reduced pressure and the product was re-dissolved in hexane (10 ml) at 0°C. The solution was filtered off and the solvent was removed under reduced pressure to give orange oil of 9. Yield (0.312 g, 46%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 0.85 (d, ³***J***_{PH} = 12.8 Hz, 9H, C(CH₃)₃), 1.18 (d, ³***J***_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 1.27 (d, ³***J***_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 1.36 (d, ³***J***_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 1.54 (d, ³***J***_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 4.06 (sept, ³***J***_{HH} = 6.8 Hz, 2H, C***H***(CH₃)₂), 4.39 (sept, ³***J***_{HH} = 6.8 Hz, 2H, C***H***(CH₃)₂), 7.04-7.18 (m, 6H, Ar***H***). ¹³C {¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 23.5 (s, CH(CH₃)₂), 24.0 (s, CH(CH₃)₂), 24.1 (s, CH(CH₃)₂), 26.0 (d, ⁴***J***_{PC} = 4.4 Hz, CH(CH₃)₂), 27.2 (s, CH(CH₃)₂), 28.4 (d, ²***J***_{PC} = 14.7 Hz, C(CH₃)₃), 30.0 (d, ⁴***J***_{PC} = 16.8 Hz, CH(CH₃)₂), 36.8 (d, ²***J***_{PC} = 41.6 Hz, C(CH₃)₃), 124.2 (s, ArC), 124.7 (s, ArC), 125.5 (s, ArC), 140.4 (d,** *J***_{PC} = 4.0 Hz, ArC), 143.9 (s, ArC), 144.8 (s, ArC). ³¹P {¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 189.2. Anal. Calcd for C₂₈H₄₃GeN₂P (511.27): C 65.8; H 8.5. Found: C 65.8; H 8.5.**

Synthesis of [PhP(N*t*-Bu)₂]Sn (10). A solution of 1 (0.745 g, 2.8 mmol) in THF (20 mL) was added dropwise to a stirred solution of SnCl₂ (0.535 g, 2.8 mmol) in THF (20 mL) at -50°C. The red solution was slowly warmed to room temperature and stirred for 2 hours. The solvent was removed under reduced pressure and the product was re-dissolved in hexane (30 mL). The solution was filtered off to remove lithium chloride and the solution was concentrated to third of its volume under reduced pressure. The red solution was stored at -30°C to give orange X-Ray quality crystals. Yield (0.320 g, 31%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 1.15 (s, 9H, C(CH₃)₃), 1.25 (s, 9H, C(CH₃)₃), 7.20 (m, 1H, *p*-Ar*H*), 7.28 (m, 2H, *m*-Ar*H*), 7.70 (m, 2H, *o*-Ar*H*). ¹³C {¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 36.2 (d, ³*J*_{PC} = 7.8 Hz, C(CH₃)₃), 54.9 (d, ²*J*_{PC} = 14.0 Hz, C(CH₃)₃), 128.8 (d, ²*J*_{PC} = 12.8 Hz, *o*-Ar*C*),

129.9 (s, *p*-Ar*C*), 130.1 (d, ${}^{3}J_{PC} = 5.8$ Hz, *m*-Ar*C*), 151.3 (d, ${}^{1}J_{PC} = 52.9$ Hz, *ipso*-Ar*C*). ${}^{31}P\{{}^{1}H\}$ NMR (202.46 MHz, C₆D₆, 294 K): δ 135.0. ${}^{119}Sn\{{}^{1}H\}$ NMR (149.2 MHz, C₆D₆, 294 K): δ 698.7. Dp 93-95 °C. Anal. Calcd for C₁₄H₂₃SnN₂P (369.03): C 45.6; H 6.3. Found: C 45.6; H 6.3.

Synthesis of [*t***-BuP(N-2,6-***i***-Pr₂C₆H₃)₂]Sn (11).** A solution of 5 (0.691 g, 1.2mmol) in THF (15 mL) was added dropwise to a stirred solution of SnCl₂ (0.218 g, 1.2mmol) in THF (20 mL) at -80°C. The reaction mixture was slowly warmed to room temperature and stirred for 1 hour. The solvent was removed under reduced pressure and the product was re-dissolved in hexane (20 mL). The solution was filtered off to remove lithium chloride and the solvent was removed under reduced pressure to give red oil of **11**. Yield (0.482 g, 75%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 0.88 (d, ³*J*_{PH} = 12.2 Hz, 9H, C(C*H*₃)₃), 1.17 (d, ³*J*_{HH} = 7.0 Hz, 6H, CH(C*H*₃)₂), 1.34 (d, ³*J*_{HH} = 6.9 Hz, 6H, CH(C*H*₃)₂), 1.49 (d, ³*J*_{HH} = 7.0 Hz, 6H, CH(C*H*₃)₂), 1.69 (d, ³*J*_{HH} = 6.7 Hz, 6H, CH(C*H*₃)₂), 4.08 (sept, ³*J*_{HH} = 6.9 Hz, 2H, C*H*(CH₃)₂), 4.57 (m, 2H, C*H*(CH₃)₂), 7.05 (m, 4H, Ar*H*), 7.28 (m, 2H, Ar*H*). ¹³C {¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 23.6 (s, CH(CH₃)₂), 24.1 (s, CH(CH₃)₂), 24.3 (s, CH(CH₃)₂), 26.8 (d, ⁴*J*_{PC} = 5.9 Hz, CH(CH₃)₂), 123.8 (s, ArC), 124.4 (s, ArC), 124.7 (s, ArC), 142.9 (d, *J*_{PC} = 5.9 Hz, ArC), 143.1 (s, ArC), 144.4 (s, ArC). ³¹P {¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 191.3 (s, ²*J*_{Sn} = 74.8 Hz). ¹¹⁹Sn {¹H} NMR (149.2 MHz, C₆D₆, 294 K): δ 592.6. Anal. Calcd for C₂₈H₄₃N₂PSn (559.35): C 60.1; H 7.8. Found: C 60.2; H 7.9.

Synthesis of [Ph(H)P(Nt-Bu)₂]GeCl (12). A solution of 2 (0.812 g, 2.2 mmol) in diethylether (10 mL) was added dropwise to a stirred suspension of GeCl₂.diox (0.502 g, 2.2 mmol) in diethylether (15 mL) at -80°C. The reaction mixture was slowly warmed to room temperature and stirred for 1 hour. The solvent was removed under reduced pressure and the product was re-dissolved in toluene (25 mL). The solution was filtered off to remove lithium chloride and then concentrated to third of its volume. The slightly yellow solution was stored at -30°C to give colorless X-Ray quality crystals. Yield 0.312 g, 40%. ¹H NMR (500 MHz, C₆D₆, 294 K): δ overlapped signals 1.09 (s broad, 18H, C(CH₃)₃), 7.00 (m, 3H, Ar*H*), 7.98 (m, 2H, Ar*H*); major set: 8.25 (d, ¹J_{PH} = 469.8 Hz, 1H, P*H*); minor set: 8.59 (d, ¹J_{PH} = 462.2 Hz, 1H, P*H*). ³¹P{¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ major signal 33.9

(d, ${}^{1}J_{PH} = 469.8$ Hz); minor signal 36.4 (d, ${}^{1}J_{PH} = 462.2$ Hz). Mp 140 °C. Anal. Calcd for $C_{14}H_{24}ClGeN_2P$ (359.42): C 46.8; H 6.7. Found: C 46.9; H 6.8.

Synthesis of [P(N-2,6-*i*-Pr₂C₆H₃)₂]Li(tmeda) (13). A suspension of 5a (0.990 g, 1.4 mmol) was heated at 90°C for two hours giving orange solution. The solvent was removed under reduced pressure and the solid was recrystallized from diethylether (10 mL) giving colorless crystals of 13. Yield (0.372 g, 51%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 1.40 (d, ³*J*_{HH} = 7.0 Hz, 24H, CH(CH₃)₂), 1.61 (s,4H, NC*H*₂), 1.83 (s, 12H, N(C*H*₃)₂), 3.68 (sept, ³*J*_{HH} = 7.0 Hz, 4H, C*H*(CH₃)₂), 7.09 (t, ³*J*_{HH} = 7.6 Hz, 2H, *p*-Ar*H*), 7.27 (d, ³*J*_{HH} = 7.6 Hz, 4H, *m*-Ar*H*). ¹³C{¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 25.3 (s broad, CH(CH₃)₂), 28.7 (s, CH(CH₃)₂), 45.2 (s, N(CH₃)₂), 56.4 (s, NCH₂), 121.4 (s, ArC), 123.3 (s, Ar*C*), 140.4 (d, ³*J*_{PC} = 5.9 Hz, *o*-Ar*C*), 145.9 (d, ²*J*_{PC} = 14.5 Hz, *ipso*-Ar*C*). ³¹P{¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 335.9. ⁷Li NMR (194.3MHz, C₆D₆, 294 K): δ 2.39. Dp 135°C. Anal. Calcd for C₃₀H₅₀LiN₄P (504.66): C 71.4; H 10.0. Found: C 71.5; H 10.1.

Synthesis of $[P(N-2,6-i-Pr_2C_6H_3)_2]_2$ Ge (14). A solution of 13 (1.004 g, 2.0mmol) in THF (15 mL) was added dropwise to a stirred solution of GeCl₂.diox (0.230 g, 1.0mmol) in THF (20 mL) at -80°C. The reaction mixture was slowly warmed to room temperature and stirred for 1 hour. The solvent was removed under reduced pressure and the yellow powder was washed with hexane (10 ml). The product was then extracted with toluene (20 mL). The orange solution was stored at -30°C to give orange X-ray quality crystals of 14. Yield (0.299 g, 36%). ¹H NMR (500 MHz, Tol-d₈, 294 K): δ 0.58 (m broad, 6H, CH(CH₃)₂), 0.95 (m broad, 12H, CH(CH₃)₂), 1.21 (m broad, 18H, CH(CH₃)₂), 1.37 (m broad, 6H, CH(CH₃)₂), 1.48 (m broad, 6H, CH(CH₃)₂), 3.18 (m broad, 4H, CH(CH₃)₂), 3.49 (m broad, 2H, CH(CH₃)₂), 3.82 (m broad, 2H, CH(CH₃)₂), 6.85 (m broad, 2H, ArH), 6.98 (m broad, 8H, ArH), 7.11 (m broad, 2H, ArH). ¹H NMR (500 MHz, Tol-d₈, 338 K): δ 1.11 (m broad, 48H, CH(CH₃)₂), 3.40 (m broad, 8H, CH(CH₃)₂), 6.95 (m broad, 12H, ArH). ³¹P{¹H} NMR (202.46 MHz, Tol-d₈, 294 K): δ 341.7. ³¹P{¹H} NMR (202.46 MHz, Tol-d₈, 294 K): δ 343.0. Mp 204 °C. Anal. Calcd for C₄₈H₆₆GeN₄P₂ (835.77): C 69.0; H 8.2. Found: C 69.2; H 8.4.

Synthesis of $[P(N-2,6-i-Pr_2C_6H_3)_2]_2Sn$ (15). A solution of 13 (1.161 g, 2.3mmol) in THF (15 mL) was added dropwise to a stirred solution of $SnCl_2$ (0.218 g, 1.2 mmol) in THF (20 mL) at -80°C. The

reaction mixture was slowly warmed to room temperature and stirred for 1 hour. The solvent was removed under reduced pressure and the yellow powder was re-dissolved in hexane (30 mL). The yellow solution was stored at 4°C to give yellow X-ray quality crystals of **15**. Yield (0.385 g, 38%). ¹H NMR (500 MHz, Tol-d₈, 338 K): δ 1.12 (s broad, 48H, CH(CH₃)₂), 3.43 (s broad, 8H, CH(CH₃)₂), 6.92 (t, ${}^{3}J_{HH} = 7.4$ Hz, 4H, Ar*H*), 6.99 (m, 8H, Ar*H*) ppm. ${}^{13}C{}^{1}H$ NMR (125.76 MHz, Tol-d₈, 338 K): δ 24.3 (s, CH(CH₃)₂), 29.4 (s, CH(CH₃)₂), 123.7 (s, ArC), 125.0 (s, ArC), 139.8 (d, $J_{PC} = 15.2$ Hz, ArC), 142.6 (s, ArC). ${}^{31}P{}^{1}H$ NMR (202.46 MHz, C₆D₆, 294 K): δ 350.0 (s, ${}^{2}J_{SnP} = 120.0$ Hz). ${}^{119}Sn{}^{1}H$ NMR (149.2 MHz, C₆D₆, 294 K): δ -204.7 (s). Mp 145-146 °C. Anal. Calcd forC₄₈H₆₈N₄P₂Sn (881.74): C 65.4; H 7.8. Found: C 66.4; H 7.9.

Synthesis of $[P(N-2,6-i-Pr_2C_6H_3)_2]_2Pb$ (16). A solution of 13 (0.850 g, 1.7mmol) in THF (15 mL) was added dropwise to a stirred suspension of PbCl₂ (0.234 g, 0.8 mmol) in THF (20 mL) at -80°C. The reaction mixture was slowly warmed to room temperature and stirred for 15 minutes. The solvent was removed under reduced pressure and the yellow powder was re-dissolved in hexane (30 ml). The yellow solution was stored at -6°C to give yellow X-ray quality crystals of 15.Yield (0.474 g, 58%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 1.15 (s broad, 48H, CH(CH₃)₂), 3.45 (m broad, 8H, CH(CH₃)₂), 6.90 (t, ³J_{HH} = 7.7 Hz, 4H, *p*-ArH), 7.07 (d, ³J_{HH} = 7.7 Hz, 8H, *m*-ArH). ¹³C {¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 28.8 (s, CH(CH₃)₂), 29.4 (s, CH(CH₃)₂), 123.6 (s, ArC), 125.1 (s ArC), 140.5 (d, J_{PC} = 11.8 Hz, ArC), 142.6 (s, ArC). ³¹P {¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 349.3 (s, ²J_{PbP} = 138 Hz). Mp 122 °C. Anal. Calcd for C₄₈H₆₈N₄P₂Pb (970.23): C 59.4; H 7.1. Found: C 59.5; H 7.2.

Synthesis of $[P(Nt-Bu)_2]Li(tmeda)$ (17). A solution of *n*-BuLi (0.95 mL, 2.5M, 2.4 mmol) in hexane was added dropwise to a stirred solution of **2** (0.891 g, 2.4mmol) in toluene (20 mL) at -50°C. The yellow emulsion was warmed to room temperature and then heated to 90°C for one week. The volatiles were removed under reduced pressure at 90°C giving slightly yellow oil. Yield (0.670 g, 95%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 1.47 (s, 18H, , C(CH₃)₃), 1.78 (s, 4H, NCH₂), 1.97 (s, 12H, N(CH₃)₂). ¹³C{¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 36.9 (d, ³J_{PC} = 12.1 Hz, C(CH₃)₃), 46.4 (s, N(CH₃)₂), 53.1 (d, ²J_{PC} = 15.5 Hz, C(CH₃)₃), 56.8 (s, NCH₂). ³¹P{¹H} NMR (202.46 MHz, C₆D₆,

294 K): δ 364.70. ⁷Li NMR (194.3MHz, C₆D₆, 294 K): δ 2.44. Anal. Calcd for C₁₄H₃₄LiN₄P (296.36): C 56.7; H 11.6. Found: C 56.7; H 11.6.

Synthesis of {[P(N*t*-Bu)₂]K(tmeda)}₂ (18). A solution of 2 (0.548 g, 1.5 mmol) in THF (20 mL) was added to freshly prepared KC₈ (K: 0.057 g, 1.5 mmol, C: 0.140 g, 11.7 mmol) while stirring. After two hours of stirring at room temperature the solvent was removed by reduced pressure and the product was extracted with toluene (15 mL). The dark red solution was concentrated to half of its volume and stored at -30°C for one week yielding colorless crystals of 18. Yield (0.115 g, 24%). ¹H NMR (500 MHz, C₆D₆, 294 K): δ 1.21 (s, 18H, C(CH₃)₃), 2.14 (s 12H, N(CH₃)₂), 2.29 (s, 4H, NCH₂). ¹³C{¹H} NMR (125.76 MHz, C₆D₆, 294 K): δ 36.8 (d, ³*J*_{PC} = 13.7 Hz, C(CH₃)₃), 46.4 (s, N(CH₃)₂), 53.8 (d, ²*J*_{PC} = 17.7 Hz, *C*(CH₃)₃), 59.0 (s, NCH₂). ³¹P{¹H} NMR (202.46 MHz, C₆D₆, 294 K): δ 351.6. Mp 72 °C. Anal. Calcd forC₁₄H₃₄KN₄P (328.52): C 51.2; H 10.4. Found: C 51.2; H 10.4.

Synthesis of *cis*-[$P(\mu$ -Nt-Bu)₂P(t-BuN)₂]Ge (19). A solution of 17 (0.756 g, 2.6 mmol) in THF (10 mL) was added dropwise to a stirred solution of GeCl₂.diox (0.295 g, 1.3 mmol) in THF (10 mL) at - 80°C. The reaction mixture was slowly warmed to room temperature and stirred for 1 hour. The solvent was removed under reduced pressure and the yellow powder was extracted with diethylether (10 mL). The extract was stored at -30°C giving yellow amorphous precipitate. Yield (0.374 g, 70%). The spectral data were in agreement with the literature.

Synthesis of *cis*-[P(μ -Nt-Bu)₂P(t-BuN)₂]Sn (20). A solution of 17 (0.688 g, 2.3 mmol) in THF (10 mL) was added dropwise to a stirred solution of SnCl₂ (0.219 g, 1.2 mmol) in THF (10 mL) at -80°C. The reaction mixture was slowly warmed to room temperature and stirred for 1 hour. The solvent was removed under reduced pressure and the yellow powder was extracted with hexane (15 mL). The extract was stored at -30°C giving pale yellow amorphous precipitate. Yield (0.351 g, 65%). ¹¹⁹Sn{¹H} (149.2 MHz, C₆D₆, 294 K): δ 430.9 (s). The other spectral data were in agreement with the literature.

2) Computational details.

The optimization of the 8, syn-12 - 15 molecular geometries was carried out using the Gaussian09 program package^{S1} with the M062X hybrid functional^{S2} and the DGDZVP double- ζ valence polarization basis set.^{S3} The wavefunctions obtained with the AIMALL code^{S4} were used for analysis of the electron density distribution and calculations of the AIM charges based on the Quantum Theory of Atoms in Molecules.^{S5} Deformation densities were obtained with the Multiwfn program^{S6} by subtracting the ρ values of the sphericalized individual atoms from the molecular electron density. The bonding critical point electron densities, ellipticities and potential energy density / kinetic energy density ratios were computed using the Multiwfn suit. The natural bond orbital (NBO) analysis^{S7}was performed with the Gaussian09 package to investigate the Lewis pair structures of complexes, charge distribution and donor-acceptor interactions. To compare the molecular and electronic structures of the tin and lead complexes the DFT calculations were carried out at the M062X/def2-TZVP/DGDZVP level of theory for the 15 and 16 molecules as well as for model complexes 15A and 16A bearing Me groups instead of the Dip fragments. The triple- ζ valence polarization def2-TZVP basis set was used for the Sn and Pb atoms while the DGDZVP functions were taken for C, H, N and P. The charge distributions and MO structures were compared for the optimized molecular geometries.

S11



Figure S1. Positive deformation electron density (DED) contour maps (0.01-0.10 a.u., step 0.01 a.u.) of complexes **8**, *syn*-**12-14** in the NPN plane. The nitrogen atom notations correspond to those in Figures 4, 6-9.



Figure S2. Positive deformation electron density (DED) contour maps (0.01-0.10 a.u., step 0.01 a.u.) of complexes **8**, *syn***-12-14** in the planes orthogonal to NEN and containing the N-P bonds. The nitrogen atom notations correspond to those in Figures4, 6-9.



Figure S3. Positive deformation electron density (DED) contour maps (0.01-0.10 a.u., step 0.01 a.u.) of complexes **8**, *syn*-**12-14** in the NEN plane (E = Li, Ge). The nitrogen atom notations correspond to those in Figures 4, 6-9.



Figure S4. Positive deformation electron density (DED) contour maps (0.01-0.10 a.u., step 0.01 a.u.) of complexes **8**, *syn*-**12-14** in the planes orthogonal to NEN (E = Li, Ge) and containing the N-E bonds. The nitrogen atom notations correspond to those in Figures 4, 6-9.



Figure S5. The optimized M062X/def2-TZVP/DGDZVP geometries of complexes 15 (left) and 16 (right). Hydrogen atoms are omitted for clarity.

Table S1. M062X/DGDZVP/Def2TZVP selected bond lengths d (Å), Mulliken atomic charges q (a.u.) and frontier MO energies E (eV) in complexes **15**, **16** and corresponding model compounds **15A** and **16A** where the Dip fragments are substituted with Me groups.

Molecular parameters ^a	15	16	15A	16A
<i>d</i> (E-N1)	2.40	2.50	2.41	2.54
<i>d</i> (E-N2)	2.26	2.40	2.21	2.33
<i>d</i> (P-N1)	1.60	1.60	1.60	1.60
<i>d</i> (P-N2)	1.63	1.63	1.62	1.62
<i>q</i> (E)	+0.90	+1.03	+1.05	+1.15
<i>q</i> (N1)	-0.80	-0.81	-0.71	-0.72
<i>q</i> (N2)	-0.88	-0.86	-0.74	-0.74
$q(C_{N1})$	+0.11	+0.11	-0.51	-0.51
$q(C_{N2})$	+0.19	+0.18	-0.52	-0.51
E(HOMO)	-6.81	-6.99	-6.76	-7.22
E(LUMO)	-1.18	-1.02	-0.43	-0.28

^aE = Sn for complexes **15**, **15A**, E = Pb for complexes **16**, **16A**. The nitrogen atom notations correspond to those in Figure 9.

Molecule	Level of theory	Energy
8	M062X/DGDZVP	-3384.05939765
syn-12	M062X/DGDZVP	-3535.28060070
anti-12	M062X/DGDZVP	-3535.27918660
13	M062X/DGDZVP	-1740.69181481
14	M062X/DGDZVP	-4847.55795551
15	M062X/DGDZVP	-8796.10355021
	M062X/def2-	
15	TZVP/DGDZVP	-2985.25479774
	M062X/def2-	
16	TZVP/DGDZVP	-2963.76082517
	M062X/def2-	
15a	TZVP/DGDZVP	-1275.40423446
	M062X/def2-	
16a	TZVP/DGDZVP	-1253.90576702

Table S2. Calculated total electronic energies (a.u.) of the complexes studied.

3) Crystallographic data for studied compounds

Suitable single crystals of 2 - 5, 8, 10, 12 - 15 and 18 were mounted on a glass fiber with an oil and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized MoK α radiation ($\lambda = 0.71073$ Å). Corresponding crystallographic data are given in Table S3. The numerical^{S8} absorption correction from crystal shape was applied for all samples except of 5 and 13 where the SADABS multi-scan procedure has been applied.⁵⁹ The structures were solved by the direct method (SIR92^{S10} or ShelXT^{S11} for samples of **5** and **13**) and refined by a full matrix least squares procedure based on F² (SHELXL97^{S12}, ShelXL-2014^{S13} or Olex2.1^{S14}). Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure the uniformity of treatment of crystal, all hydrogen atoms, except of P-H ones, were recalculated into idealized positions (riding model) and assigned temperature factors Hiso(H) = 1.2 Ueq(pivot atom) or of 1.5Ueq for the methyl moiety with C-H = 0.96 Å, 0.97, 0.98, and 0.93 Å for methyl, methylene, methine and hydrogen atoms in aromatic rings, respectively. Heavily disordered coordinated diethylether molecule is found in compound 5, and similar type of disorder has been recognized in the case of coordinated TMEDA molecule in 13. Positional disorders were also detected for the Dip part of 13 and one of *i*-Pr groups in 15, all these disordered parts of molecules were treated by standard procedures and constraints/restraints implemented in Shelxl program package.^{S11} Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 1451458-1451468. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

	2	3	4	5	8
chemical formula	C ₂₀ H ₄₀ LiN ₄ P	$C_{52}H_{82}Li_4N_4O_2P_2$	C ₂₈ H ₄₈ LiN ₄ P	$C_{36}H_{63}Li_2N_2O_2P$	$C_{22}H_{31}GeN_2P$
		$C_4H_{10}O$			
crystsyst	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P2_l/c$	$P2_l/c$	$P2_l/c$	Pnma	P-1
a[Å]	16.9831(16)	18.1381(19)	10.5280(4)	20.3440(10)	10.1790(4)
<i>b</i> [Å]	16.3830(13)	11.6450(12)	15.6740(8)	17.6920(15)	10.6229(7)
c[Å]	19.5470(13)	27.5590(17)	18.8041(13)	10.6001(19)	11.3441(5)
α[°]	90	90	90	90	105.523(5)
β[°]	118.911(6)	95.983(6)	106.627(5)	90	101.831(4)
γ[°]	90	90	90	90	99.773(4)
Z	8	4	4	4	2
μ [mm ⁻¹]	0.125	0.118	0.113	0.102	1.442
$D_x [Mg m^{-3}]$	1.045	1.100	1.069	1.046	1.262
cryst size [mm]	0.59x0.27x0.20	0.59×0.37×0.21	0.37×0.36×0.30	0.51×0.32×0.32	0.39×0.30×0.29
θ range, [deg]	1-27.5	1-27.3	1-27.5	1-27.5	1-27.5
T_{min}, T_{max}	0.956, 0.980	0.954, 0.980	0.972, 0.986	0.955, 0.969	0.666, 0.802
no. of reflnsmeasd	47 311	42 677	26 591	27674	26310
no. of unique reflns, R_{int}^{a}	10812, 0.045	12454, 0.085	6612, 0.040	4435, 0.029	5146, 0.025
no. of obsdreflns	7385	7818	4828	3262	4546
no. of params	469	622	307	242	235
S ^b all data	1.157	1.143	1.144	1.070	1.104
final R ^c indices $[I > 2\sigma(I)]$	0.050	0.097	0.051	0.059	0.032
wR2 ^c indices (all data)	0.107	0.194	0.104	0.143	0.074
$\Delta \rho$, max., min. [e Å ⁻³]	0.701, -0.303	0.512, -0.246	0.512, -0.246	0.450, -0.468	0.456, -0.491
${}^{a}R_{\text{int}} = \Sigma F_{o}^{2} - F_{o,n}$	$_{\text{nean}}^{2} /\Sigma F_o^2, b \overline{S} = [2]$	$\Sigma(w(F_{\rm o}^{2} - F_{\rm c}^{2})^{2})/(N_{\rm d})$	$_{\rm iffrs}$ - $N_{\rm params}$)] ^{$\frac{1}{2}$} . ^c R	$R(F) = \Sigma F_{\rm o} - F_{\rm c} $	$ /\Sigma F_{o} ,$

 Table S3.Crystallographic data for studied compounds.

 $wR(F^{2}) = [\Sigma(w(F_{o}^{2} - F_{c}^{2})^{2})/(\Sigma w(F_{o}^{2})^{2})]^{\frac{1}{2}}.$

	10	syn-12	13	14	15
chemical formula	$C_{28}H_{46}N_4P_2Sn_2$	C14H24ClGeN4P	C ₃₀ H ₅₀ LiN ₄ P	$C_{48}H_{68}GeN_4P_2$	$C_{48}H_{68}N_4P_2Sn$
crystsyst	monoclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$Pna2_1$	C12/c1	$C222_1$	$C222_{1}$
a[Å]	10.7590(4)	14.8260(6)	10.463(2)	15.1732(4)	15.4435(7)
<i>b</i> [Å]	11.1479(7)	10.2630(7)	24.322(5)	20.1215(8)	20.2430(3)
	16.5240(5)	11.3191(12)	13.238(3)	15.3980(4)	15.3661(4)
alo	90	90	90	90	90
β[°]	125.839(4)	90	107.28(3)	90	90
γ[°]	90	90	90	90	90
Z	2	4	4	4	4
μ[mm ⁻¹]	1.677	2.017	0.108	0.755	0.633
D_x [Mg m ⁻³]	1.526	1.386	1.042	1.181	1.219
cryst size [mm]	0.45x0.26x0.11	0.40×0.25×0.24	0.43×0.27×0.24	0.36×0.30×0.21	0.58×0.45×0.25
θ range, [deg]	1-27.5	1-27.5	1-27.5	1-27.5	1-27.5
T _{min} , T _{max}	0.720, 0.889	0.641, 0.727	0.628414	0.804, 0.893	0.788, 0.879
no. of reflnsmeasd	12709	13375	12994	21691	15320
no. of unique reflns, R_{int}^{a}	3651, 0.030	3545, 0.031	3671, 0.034	5355, 0.063	5458, 0.030
no. of obsdreflns	2756	3304	2402	4475	4731
no. of params	163	172	241	249	253
$S^{\rm b}$ all data	1.155	1.098	1.044	1.141	1.206
final R ^c indices $[I \ge 2\sigma(I)]$	0.029	0.026	0.057	0.047	0.032
wR2 ^c indices (all data)	0.053	0.054	0.131	0.091	0.073
$\Delta \rho$, max., min. [e Å ⁻³]	0.338, -0.421	0.274, -0.424	0.369, -0.269	1.157, -0.487	1.053, -0.479
${}^{a}R_{int} = \Sigma F_{o}^{2} - F_{o,mean}^{2} / \Sigma F_{o}^{2}, {}^{b}S = [\Sigma (w(F_{o}^{2} - F_{c}^{2})^{2}) / (N_{diffrs} - N_{params})]^{\frac{1}{2}} \cdot {}^{c}R(F) = \Sigma F_{o} - F_{c} / \Sigma F_{o} ,$					

 Table S3 (continue).Crystallographic data for studied compounds.

 $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{\frac{1}{2}}, dcorrected multi-scan method SADABS.$

		18
	chemical formula	$C_{28}H_{68}K_2N_8P_2$
	crystsyst	monoclinic
	space group	C2/c
	a[Å]	14.5542(4)
	<i>b</i> [Å]	15.0050(2)
		19.2902(4)
	α[°]	90
	β[°]	105.712(3)
	γ[°]	90
	Z	4
	μ [mm ⁻¹]	0.439
	$D_{\rm r}$ [Mg m ⁻³]	1.076
	cryst size [mm]	0.52x0.31x0.20
	θ range, [deg]	1-27.5
	T_{min}, T_{max}	0.902, 0.946
	no. of reflnsmeasd	12 934
	no. of unique reflues, R_{int}^{a}	4387, 0.024
	no. of obsdreflns	3616
	no. of params	182
	$S^{\rm b}$ all data	1.100
	final R ^c indices $[I > 2\sigma(I)]$	0.034
	wR2 ^c indices (all data)	0.080
	$\Delta \rho$, max., min. [e Å ⁻³]	0.419, -0.229
$= \Sigma \left F^2 - F \right ^2 / \Sigma F^2$	$b = \sum (w(E^2 - E^2)^2)/(N)$	$\frac{1}{12} \frac{1}{2} 1$

 Table S3 (continue).Crystallographic data for studied compounds.

 $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{\frac{1}{2}}.$

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