

Supporting information

Carbaborane-based alkynylphosphines and phospholes

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1. Computational studies

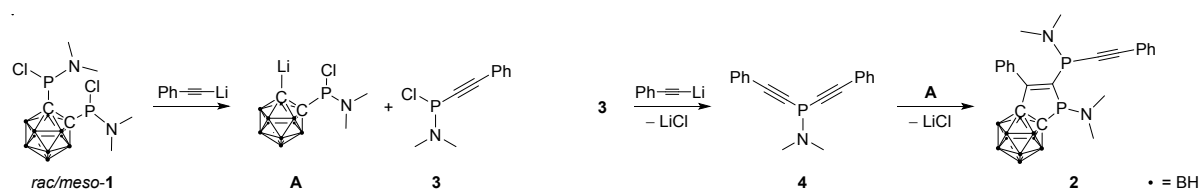


Figure 1. Proposed mechanism for the formation of **2** and the observed by-product **4**.

A relaxed potential energy surface (PES) scan along the decreasing coordinate between one of the P atoms in **1** and the *ipso*-C of lithiated phenylacetylene (LiC_2Ph) using a 0.1 Å step and including one solvent molecule did not lead to the expected mono-substituted compound but showed a $\text{P-C}_{\text{cluster}}$ bond cleavage, leading to intermediates **A** and **3**. The appropriate PES scan coordinates have been used in subsequent calculations, in order to obtain the Gibbs free energies at each critical point along the corresponding reaction path (Figure 2). The second equivalent of LiC_2Ph most probably reacts with **3** to give **4**, through a well understood mechanism (Figure 3). **4** has been identified by ^{31}P NMR spectroscopy in the reaction solution and shows a signal at 8.8 ppm (see main text). Lastly, the $\text{Li-C}_{\text{cluster}}$ bond of **A** inserts into one of the carbon-carbon triple bonds of **4** and **2** is formed after LiCl elimination via a two-step reaction (Figure 4). During the first step, the $\text{Li-C}_{\text{cluster}}$ bond of **A** inserts into a $\text{C}\equiv\text{C}$ bond of **4**, leading to intermediate **IM**. The addition of organolithium compounds to carbon-carbon triple bonds has been described in the literature.^[1] During the second step, LiCl is eliminated from **IM** and the five-membered heterocycle is formed (Figure 4).

All calculations have been carried out with the Gaussian 09 program package^[2] at the M06-2X/6-31+G(d,p) level of theory^[3] and using the SMD solvent model (diethyl ether).^[4]

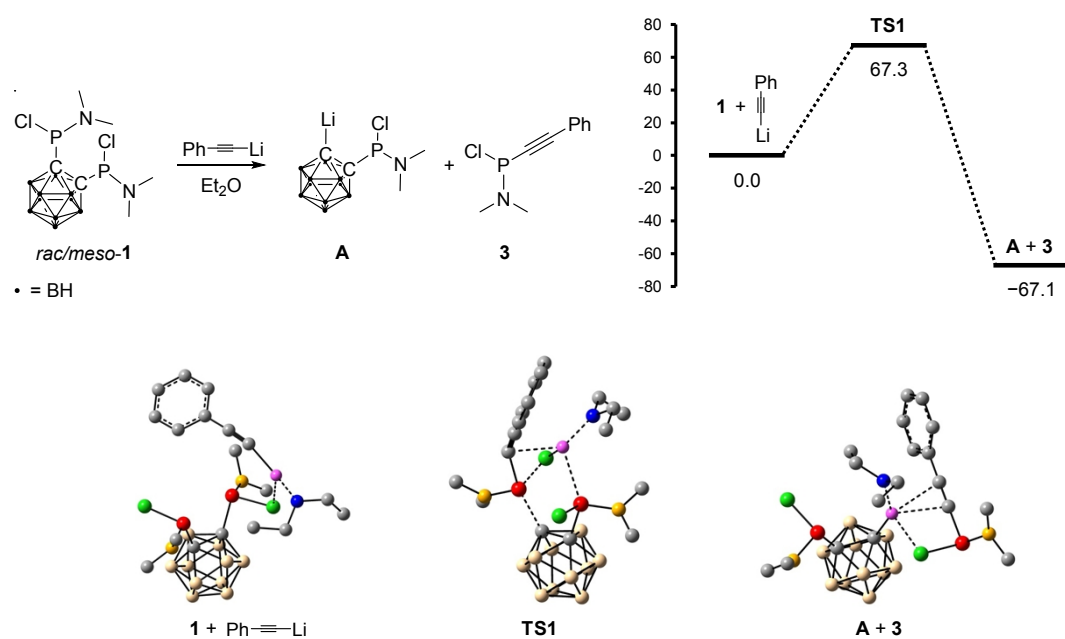


Figure 2. The reaction leading to the intermediates **A** and **3** (B: tan, C: grey, N: orange, O: blue, P: red, Cl: green, Li: purple; hydrogen atoms are not shown, Gibbs free energies in kJ mol⁻¹).

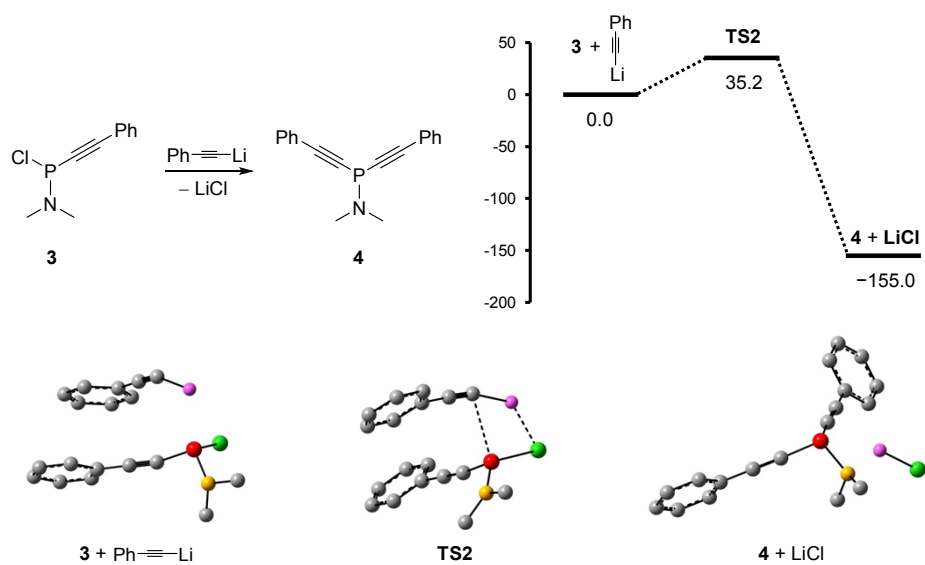


Figure 3. The reaction leading to **4** (C: grey, N: orange, O: blue, P: red, Cl: green, Li: purple; hydrogen atoms are not shown, Gibbs free energies in kJ mol⁻¹).

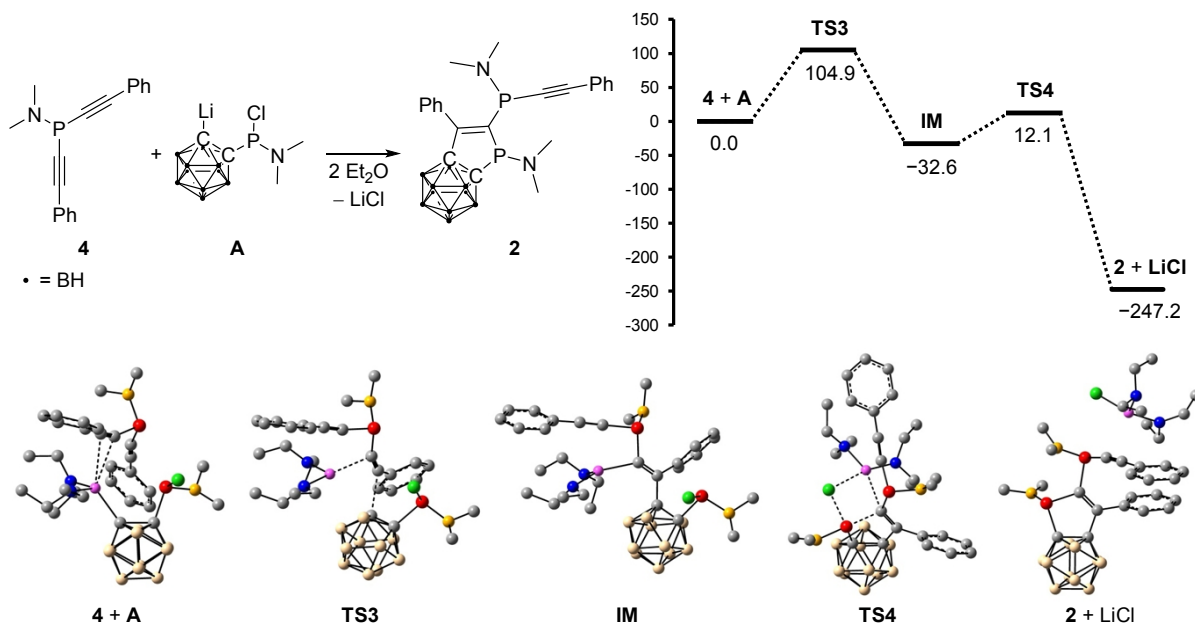


Figure 4. The two-steps reaction leading to **2** (B: tan, C: grey, N: orange, O: blue, P: red, Cl: green, Li: purple; hydrogen atoms are not shown, Gibbs free energies in kJ mol⁻¹).

2. Cyclic voltammetry

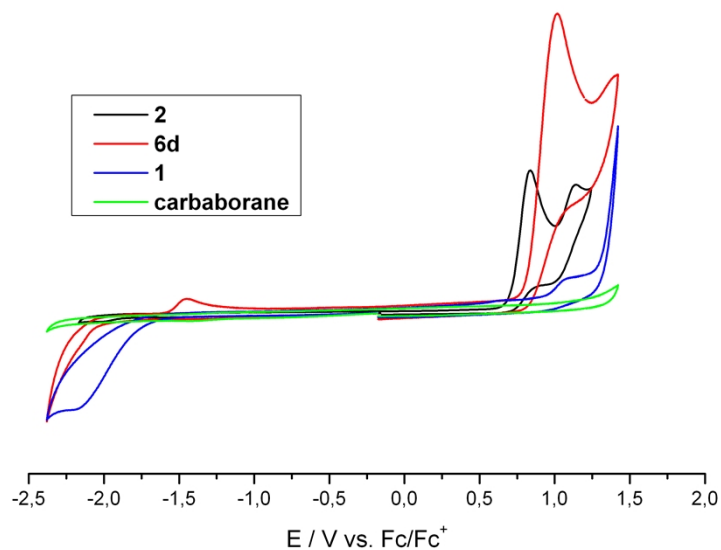


Figure 5. Cyclic voltammograms ($\nu = 100$ mV/s) of 1 mM solutions of **1**, **2**, **6d** and 1,2-dicarba-*closo*-dodecaborane(**12**) in CH₂Cl₂ with 0.1 M NBu₄PF₆ as supporting electrolyte.

3. Experimental section

General: All reactions were carried out under dry high-purity nitrogen by using standard Schlenk techniques. Solvents were purified and degassed with an MBRAUN Solvent Purification System SPS-800. The NMR spectra were recorded at 25 °C with a BRUKER Avance DRX 400 MHz spectrometer (^1H NMR 400.13 MHz, ^{11}B NMR 128.38 MHz, ^{13}C NMR 100.63 MHz, ^{31}P NMR 161.98 MHz). SiMe_4 (TMS) was used as internal standard in the ^1H NMR spectra and all other spectra were referenced to TMS by using the Ξ scale.^[5] $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained as APT (Attached Proton Test) spectra, mass spectra with a VG12-250 apparatus (EI), and FTIR spectra with a PerkinElmer Spectrum 2000 FTIR spectrometer in the range of 400 – 4000 cm^{-1} in KBr. X-ray data were collected on a Gemini diffractometer (Agilent Technologies) by using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), ω -scan rotation. Data reduction was performed with CrysAlis Pro^[6] including the program SCALE3 ABSPACK for empirical absorption correction. Elemental analyses were performed with a Heraeus VARIO EL instrument CHN-O-S Analyser. The melting points were determined with a Gallenkamp apparatus on samples sealed under nitrogen in glass capillaries and are uncorrected. Bis(*N,N*-dimethylamidochlorophosphanyl)-1,2-dicarba-*closo*-dodecacaborane (**1**),^[7] bis-*N,N*-dimethylaminophenylethynylphosphane^[8] and *N,N*-dimethylaminodichlorophosphane^[9] were prepared according to literature methods. Phenylacetylene, 1,2-dicarba-*closo*-dodecacaborane(**12**), *n*-butyllithium, and HCl in Et_2O are commercially available.

Synthesis of 2:

n-Butyllithium (4.6 mL, 1.5 M in *n*-hexane, 2.0 equiv) was added to a solution of phenylacetylene (0.70 g, 6.9 mmol, 2.2 equiv) in diethyl ether (25 mL) at $-40 \text{ }^\circ\text{C}$. The colorless solution was stirred for 1 h and warmed up to $-5 \text{ }^\circ\text{C}$, and then *rac/meso*-**1** (1.2 g, 3.2 mmol, 2.0 equiv) was added. The reaction mixture was stirred for 24 h and LiCl was filtered off. The solvent was removed in vacuum, the black residue extracted with *n*-hexane ($3 \times 25 \text{ mL}$) and the solution filtered over silica gel to give a yellow solution. After concentration of the solution and cooling to $-20 \text{ }^\circ\text{C}$, yellow crystals of compound **2** were obtained.

Yield: 20 % (0.31 g, 0.62 mmol); M.p.: $153.2\text{--}154.0 \text{ }^\circ\text{C}$; elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{32}\text{B}_{10}\text{P}_2\text{N}_2$: C 53.43, H 6.52 N 5.66; found: C 53.15, H 6.60, N 5.41; IR (KBr): $\tilde{\nu} = 3060$ (w, CH), 2925 (m, CH), 2892 (s, CH), 2843 (m, CH), 2798 (w, BH), 2589 (s, BH), 2152 (m), 1596 (w), 1573 (w), 1542 (w), 1487 (s), 1442 (m), 1409 (w), 1281 (m), 1263 (m), 1187 (m), 1072 (s), 988 (s), 831 (m), 792 (m), 756 (s), 690 (s), 539 (m), 406 (m) cm^{-1} ; MS (ESI, pos, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$): m/z (%) = 494.3 (100) $[\text{M}]^+$, $\text{C}_{22}\text{H}_{32}\text{B}_{10}\text{P}_2\text{N}_2$. ^1H NMR (C_6D_6): $\delta = 2.35$ (d,

$^3J_{\text{HP}} = 10.2$ Hz, 6H, N(CH₃)₂); 2.56 (d, $^3J_{\text{HP}} = 9.2$ Hz, 6H, N(CH₃)₂); 6.91–7.19 (m, 10H, C₆H₅); 1.90–3.60 (m, 10H, B₁₀H₁₀) ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (C₆D₆): $\delta = -2.8$ (br s, 1B); -4.7 (br s, 1B); -7.0 (br s, 2B); -7.9 (br s, 2B); -11.1 (br s, 4B) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆): $\delta = 42.0$ (d, $^2J_{\text{CP}} = 3.8$ Hz, N(CH₃)₂); 42.2 (d, $^2J_{\text{CP}} = 3.9$ Hz, N(CH₃)₂); 78.1 (d, $^1J_{\text{CP}} = 90.0$ Hz, C13); 84.6 (d, $^1J_{\text{CP}} = 20.5$ Hz, C1); 88.0 (d, $^2J_{\text{CP}} = 6.8$ Hz, C2); 108.3 (d, $^3J_{\text{CP}} = 4.2$ Hz, C14); 122.6 (d, $^3J_{\text{CP}} = 1.7$ Hz, C15); 128.0, 128.1, 128.3, 128.4, 128.7, 128.9, 131.7 (all s, 2x C₆H₅); 134.6 (m, C7); 149.2 (dd, $^1J_{\text{CP}} = 43.1$ Hz, $^1J_{\text{CP}} = 43.3$ Hz, C3); 150.0 (dd, $^2J_{\text{CP}} = 5.1$ Hz, $^2J_{\text{CP}} = 5.6$ Hz, C3) ppm; ^{31}P NMR (C₆D₆): $\delta = 35.3$ (d, $^2J_{\text{PP}} = 20.7$ Hz, P2); 87.6 (d, $^2J_{\text{PP}} = 20.7$ Hz, P1) ppm.

Synthesis of N,N-dimethylaminochloro(phenylethynyl)phosphane (3)

A solution of hydrogen chloride (9.1 mL, 2M in diethyl ether, 2.0 equiv) was added dropwise to a solution of bis(*N,N*-dimethylamino)(phenylethynyl)phosphane (2.0 g, 9.1 mmol, 1.0 equiv) in diethyl ether (40 mL) at -70 °C. The resulting white suspension was allowed to warm to room temperature. After 3 h the suspension was filtered and the solvent was evaporated in vacuum. Fractional distillation gave **3** (0.5 g, 0.24 mmol, 26 %) as a colorless liquid (b.p. 94–95 °C, 0.5 mbar).

^1H NMR(CDCl₃): $\delta = 2.89$ (d, 6H, N(CH₃)₂, $^3J_{\text{HP}} = 14.5$ Hz), 7.33–7.37 (m, 3H, C₆H₅), 7.50 (d, 2H, C₆H₅) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 40.5$ (d, N(CH₃)₂, $^2J_{\text{CP}} = 12.6$ Hz); 87.9 (d, C1, $^1J_{\text{CP}} = 33.9$ Hz); 108.4 (d, C2, $^2J_{\text{CP}} = 7.6$ Hz); 121.5 (d, *ipso*-C, $^3J_{\text{CP}} = 2.1$ Hz, C₆H₅); 128.8 (s, C₆H₅); 130.2 (s, C₆H₅); 132.2 (d, *o*-C, $^4J_{\text{CP}} = 2.3$ Hz, C₆H₅) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 104.2$ (s) ppm.

Synthesis of N,N-dimethylamino-bis(phenylethynyl)phosphane (4)

A solution of *n*-butyllithium (8.8 mL, 1.6 M in *n*-hexane, 2.05 equiv) was added dropwise to a solution of phenylacetylene (1.5 ml, 13.8 mmol, 2.0 equiv) in diethyl ether (10 mL) at -78 °C. After 2 h, *N,N*-dimethylaminodichlorophosphane (1.0 g, 6.9 mmol, 1.0 equiv) in diethyl ether (10 mL) was added dropwise to the lithiated phenylacetylene at -78 °C. The reaction mixture was stirred for 2 h at -78 °C. After evaporation of the solvent at -70 °C, **4** (0.5 g, 0.18 mmol, 26 %) was obtained as a yellow oil.

^1H NMR (CDCl₃): $\delta = 2.80$ (d, 6H, N(CH₃)₂, $^3J_{\text{HP}} = 12.7$ Hz); 7.31 (br m, 6H, C₆H₅); 4.32 (d, 4H, C₆H₅) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 41.6$ (d, N(CH₃)₂, $^2J_{\text{CP}} = 14.0$ Hz); 85.3 (d, C1,

$^1J_{\text{CP}} = 13.4$ Hz); 105.4 (d, C2, $^2J_{\text{CP}} = 5.6$ Hz); 122.4 (s, *ipso*-C, C₆H₅); 128.4 (s, C₆H₅); 129.1 (s, C₆H₅); 131.8 (s C₆H₅) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 8.8$ (s) ppm.

Synthesis of N,N-diethylaminochloro(phenylethynyl)phosphane (5a)

Same method as for the synthesis of **3**; 1.6 g (5.8 mmol, 1.0 equiv) bis(*N,N*-diethylamino)(phenylethynyl)phosphane and 5.8 ml hydrogen chloride solution (2 M in diethyl ether, 11.6 mmol, 2.0 equiv) were used. Removal of the solvent yielded 0.84 g (3.5 mmol, 60%) of **5a**.

^1H NMR (CDCl₃): $\delta = 1.23$ (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, N(CH₂CH₃)₂); 3.23–3.51 (m, 4H, N(CH₂CH₃)₂); 7.33–7.52 (m, 5H, C₆H₅) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 14.3$ (d, $^3J_{\text{CP}} = 6.7$ Hz, N(CH₂CH₃)₂); 44.9 (s br, N(CH₂CH₃)₂); 87.8 (d, $^1J_{\text{CP}} = 34.0$ Hz, P–C≡C); 107.6 (d, $^2J_{\text{CP}} = 8.2$ Hz, P–C≡C); 121.4 (d, $^3J_{\text{CP}} = 2.6$ Hz, *ipso*-C, C₆H₅); 128.3 (s, *m*-C, C₆H₅); 129.7 (s, *p*-C, C₆H₅); 131.9 (d, $^4J_{\text{CP}} = 2.5$ Hz, *o*-C, C₆H₅) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 99.7$ (s) ppm.

Synthesis of N,N-diethylaminochloro(3,3-dimethylbutynyl)phosphane (5b)

Same method as for the synthesis of **3**; 2.9 g (11.0 mmol, 1.0 equiv) bis(*N,N*-diethylamino(3,3-dimethylbutynyl)phosphane, and 11.0 ml hydrogen chloride solution (2 M in diethyl ether, 22.0 mmol, 2.0 equiv) were used. Removal of the solvent yielded 2.36 g (10.7 mmol, 97%) **5b**.

^1H NMR (CDCl₃): $\delta = 1.10$ (t, $^3J_{\text{HH}} = 6.8$ Hz, 6H, N(CH₂CH₃)₂); 1.24 (s, 9H, C(CH₃)₃), 3.07–3.43 (m, 4H, N(CH₂CH₃)₂) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 14.3$ (s, N(CH₂CH₃)₂); 28.5 (s, C(CH₃)₃); 30.2 (s, C(CH₃)₃); 44.5 (s br, N(CH₂CH₃)₂); 77.8 (d, $^1J_{\text{CP}} = 29.7$ Hz, P–C≡C); 118.6 (d, $^2J_{\text{CP}} = 7.3$ Hz, P–C≡C) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 102.4$ (s) ppm.

Synthesis of N,N-diethylaminochloro(trimethylsilylethynyl)phosphane (5c)

Using the method for the synthesis of **3**, 3.1 g (11.4 mmol, 1.0 equiv) bis(*N,N*-diethylamino)(trimethylsilylethynyl)phosphane and 11.4 ml (2 M in diethyl ether, 22.8 mmol, 2.0 equiv) hydrogen chloride were used. Removal of the solvent yielded 2.25 g (9.5 mmol, 84%) **5c**.

^1H NMR (CDCl₃): $\delta = 0.12$ (s, 9H, Si(CH₃)₃); 1.07 (t, $^3J_{\text{HH}} = 7.5$ Hz, 6H, N(CH₂CH₃)₂); 3.07–3.28 (m, 4H, N(CH₂CH₃)₂) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 96.6$ (s) ppm.

Synthesis of rac/meso-bis(N,N-diethylamino(phenylethynyl)phosphanyl)dicarba-closo-dodecaborane(12) (6a)

A solution of *n*-butyllithium (7.5 mL, 11.6 mmol, 1.55 M in *n*-hexane, 2.0 equiv) was added dropwise to a solution of 0.84 g (5.8 mmol, 1.0 eq) 1,2-dicarba-*closo*-dodecaborane(12) in 30 ml diethyl ether at 0 °C. After 2 h at room temperature, the suspension was added slowly to a solution of **5a** in 20 ml of diethyl ether at 0 °C. The suspension was stirred overnight and then LiCl was filtered off. The solvent was removed in vacuum and the residue was purified by column chromatography (ethyl acetate/*n*-hexane, 5/1, v/v) to give **6a** as a yellow oil.

¹H NMR (CDCl₃): δ = 1.30 (m br, 12H, N(CH₂CH₃)₂); 1.60–3.10 (m, 10H, B₁₀H₁₀); 3.18–3.33 (m, 8H, N(CH₂CH₃)₂); 7.37–7.66 (m, 10H, C₆H₅) ppm; ¹¹B{¹H} NMR (CDCl₃): δ = –7.2 (s br, 6B); –0.9 (s br, 4B) ppm; ¹³C{¹H} NMR (CDCl₃): δ = 15.5 (s, N(CH₂CH₃)₂); 46.5 (s br, N(CH₂CH₃)₂); 81.0 (m, ¹J_{CP} + ²J_{CP} = 95,9 Hz, C₂B₁₀H₁₀); 86.6 (d, ²J_{CP} = 11.1 Hz, P–C≡C); 109.6 (m, ¹J_{CP} = 40.0 Hz, P–C≡C); 122.5 (d, ³J_{CP} = 5.7 Hz, *ipso*-C, C₆H₅); 128.2 (s, *m*-C, C₆H₅); 129.0 (s, *p*-C, C₆H₅); 132.1 (s, *o*-C, C₆H₅) ppm; ³¹P{¹H} NMR (CDCl₃): δ = 42.0 (s); 42.6 (s) ppm. MS (ESI pos., CH₂Cl₂/CH₃CN): *m/z* (%) = 961.6 (100) [2 M + K – N(CH₂CH₃)₂ – PC₆H₅]⁺, 551.4 (15) [M + H]⁺, (80) [M – N(CH₂CH₃)₂]⁺.

Synthesis of rac/meso-bis(N,N-diethylamino-(3,3-dimethylbutynyl)phosphanyl)dicarba-closo-dodecaborane(12) (6b)

Using the method for the synthesis of **6a**, 3.86 g (17.6 mmol, 2.0 equiv) **5b**, 1.27 g (8.8 mmol, 1.0 eq) 1,2-dicarba-*closo*-dodecaborane(12) and 11.3 ml *n*-butyllithium (1.55 M in *n*-hexane, 17.6 mmol, 2.0 equiv). **6b** was purified by column chromatography (ethyl acetate/*n*-hexane, 8:1, v/v) to give a colorless oil.

¹H NMR (CDCl₃): δ = 1.01 (m br, 12H, N(CH₂CH₃)₂); 1.21 (s br, 18H, C(CH₃)₃); 1.66–2.71 (m, 10H, B₁₀H₁₀); 2.83–3.20 (m, 8H, N(CH₂CH₃)₂) ppm; ¹¹B{¹H} NMR (CDCl₃): δ = –7.8 (s br, 6B); –1.7 (s br, 4B) ppm; ¹³C{¹H} NMR (CDCl₃): δ = 14.9 (s, N(CH₂CH₃)₂); 28.6 (s, C(CH₃)₃); 30.2 (s, C(CH₃)₃); 44.8 (s br, N(CH₂CH₃)₂); 85.0 (m, ¹J_{CP} + ¹J_{CP} = 119.2 Hz, C₂B₁₀H₁₀); 86.3 (d, ²J_{CP} = 7.3 Hz, P–C≡C); 118.7 (d, ¹J_{CP} = 29.9 Hz, P–C≡C) ppm; ³¹P{¹H} NMR (CDCl₃): δ = 41.6 (s); 42.2 (s) ppm. MS (ESI pos., CH₂Cl₂/CH₃CN): *m/z* (%) = 429.4 (100) [M–C≡C'Bu]⁺, 511.4 (10) [M + H]⁺.

Synthesis of rac/meso-bis(N,N-diethylamino-(trimethylsilylethynyl)phosphanyl)dicarba-closo-dodecaborane(12) (6c)

Using the method for the synthesis of **6a**, 2.25 g (9.6 mmol, 2.0 eq) **5c**, 0.7 g (4.8 mmol, 1.0 eq) 1,2-dicarba-closo-dodecaborane(12) and 6.0 ml *n*-butyllithium (1.6 M in *n*-hexane, 9.6 mmol, 2.0 eq). **6c** was purified by column chromatography (ethyl acetate/*n*-hexane, 5/1, *v/v*) to give a colorless oil.

^1H NMR (CDCl_3): $\delta = 0.12$ (s, 18H, $\text{Si}(\text{CH}_3)_3$); 0.90 (m br, 12H, $\text{N}(\text{CH}_2\text{CH}_3)_2$); 1.40–2.85 (m, 10H, $\text{B}_{10}\text{H}_{10}$); 2.86–3.16 (m, 8H, $\text{N}(\text{CH}_2\text{CH}_3)_2$) ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -10.3$ (s br, 6B); -7.5 (s br, 2B); -1.5 (s br, 2B) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -0.5$ (s, $\text{Si}(\text{CH}_3)_3$); 13.5 (s, $\text{N}(\text{CH}_2\text{CH}_3)_2$); 44.0 (s br, $\text{N}(\text{CH}_2\text{CH}_3)_2$); 84.3 (m, $^1J_{\text{CP}} + ^1J_{\text{CP}} = 116.6$ Hz, $\text{C}_2\text{B}_{10}\text{H}_{10}$); 102.8 (d, $^2J_{\text{CP}} = 21.7$ Hz, $\text{P}-\text{C}\equiv\text{C}$); 118.1 (d, $^1J_{\text{CP}} = 34.0$ Hz, $\text{P}-\text{C}\equiv\text{C}$) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 41.1$ (s); 41.6 (s) ppm MS (ESI pos., $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$): m/z (%) = 470.3 (50) $[\text{M} - \text{N}(\text{CH}_2\text{CH}_3)_2]^+$, 445.3 (100) $[\text{M} - \text{C}\equiv\text{CSiMe}_3]^+$

Synthesis of rac/meso-bis(N,N-dimethylamino(phenylethynyl)phosphanyl)-dicarba-closo-dodecaborane(12) (6d)

Using the method for the synthesis of **6a**, 0.324 g (1.54 mmol, 2.0 equiv) **5d**, 0.111 g (0.77 mmol, 1.0 equiv) 1,2-dicarba-closo-dodecaborane(12), and 1.06 ml *n*-butyllithium (1.45 M in *n*-hexane, 1.54 mmol, 2.0 equiv). Purification by column chromatography (hexanes/dichloromethane, 8/1, *v/v*) gave **6d** (189 mg, 0.38 mmol, 50 %) as a yellow oil.

^1H NMR (CDCl_3): $\delta = 1.40$ –3.20 (m, 10H, $\text{B}_{10}\text{H}_{10}$); 2.77–2.86 (m, 12H, $\text{N}(\text{CH}_3)_2$); 7.18–7.48 (m, 10H, C_6H_5) ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -9.9$ (s br, 6B); -7.5 (s br, 2B); -1.1 (s br, 6B) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 39.8$ (s br, $\text{N}(\text{CH}_3)_2$); 83.1; 84.2 (d, $^1J_{\text{CP}} = 19.4$ Hz, *rac*- $\text{C}_2\text{B}_{10}\text{H}_{10}$); 83.7 (d, $^1J_{\text{CP}} = 19.7$ Hz, *meso*- $\text{C}_2\text{B}_{10}\text{H}_{10}$); 85.3–85.6 (m, $\text{P}-\text{C}\equiv\text{C}$); 109.5–110.2 (m, $\text{P}-\text{C}\equiv\text{C}$); 121.9 (d, $^3J_{\text{CP}} = 3.9$ Hz, *ipso*-C, C_6H_5); 128.6 (d, $^4J_{\text{CP}} = 8.1$ Hz, *o*-C, C_6H_5); 129.6 (d, $^5J_{\text{CP}} = 5.6$ Hz, *m*-C, C_6H_5); 131.9 (*p*-C, C_6H_5) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 46.5$ (s); 46.8 (s) ppm. MS (ESI pos., $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$): m/z (%) = 496.4 (30) $[\text{M} + \text{H}]^+$.

4. References

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