Supporting Information for

Synthesis and Reactivity of a Parent Phosphathioethynolatoborane and a Boraarsaketene

Malte Jürgensen,^{a,b} Tanja Kunz,^{a,b} Merle Arrowsmith,^{a,b} Maximilian Dietz,^{a,b} Stephan Hagspiel,^{a,b} and Holger Braunschweig^{a,b,*}

^a Institute for Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. ^b Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

Contents

Methods and materials	2
Synthetic procedures	3
NMR spectra of isolated compounds	9
IR spectra	46
UV-vis spectra	53
X-ray crystallographic data	56
Computational details	60
References	100

Methods and materials

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves.

Liquid-phase NMR spectra were acquired on a Bruker Avance 400 (¹¹B: 128.5 MHz), a Bruker Avance 500 (¹H: 500.1 MHz, ¹¹B: 160.5 MHz, ¹³C: 125.8 MHz, ¹⁹F: 470.6 MHz or a Bruker Avance 600 (¹H: 600.2 MHz, ¹¹B: 192.6 MHz, ¹³C: 150.9 MHz, ³¹P: 243.0 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and internally referenced to the carbon nuclei (¹³C{¹H}) or residual protons (¹H) of the solvent. Heteronuclei NMR spectra are referenced to external standards (¹¹B: BF₃·OEt₂). Resonances are given as singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m) or broad (br). All ¹³C{¹H} NMR resonances are singlets unless stated otherwise.

Microanalyses (C, H, N, S) were performed on an Elementar vario MICRO cube elemental analyzer. All isolated compounds were submitted a minimum of three times for microanalyses but some were too sensitive to yield useful results.

High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer.

UV-vis spectra were acquired on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer at room temperature.

Solid-state IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox.

Solvents and reagents were purchased from Sigma-Aldrich, ABCR or Alfa Aesar. (SIMes)BH₃ (SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene),¹ (CAAC^{Me})BH₂(OTf) (**1-CAAC^{Me}**) (CAAC^{Me} = 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene, OTf = triflate),² Na(diox)_x[PCS] (diox = 1,4-dioxane),^{3, 4} [CpCo(C₂H₄)₂] (Cp = η^5 -cyclopentadienyl),⁵ PPB (= pentaphenylborole),⁶ CBBF (= 9-(1-methyl-1,2-dicarba-*closo*-dodecaboranyl)-9-borafluorene),⁷ Na(diox)_x[AsCO]⁸ were synthesised using literature procedures.

Synthetic procedures

Synthesis of 1-SIMes

A solution of MeOTf (629 mg, 3.83 mmol) in DCM (16 mL) was added dropwise to a solution of (SIMes)BH₃ (1.12 g, 3.48 mmol) in DCM (50 mL) under gas evolution at 0 °C and the clear colourless solution was stirred for 17 h at room temperature. All volatile components were removed in vacuo and the resulting colourless solid was suspended in pentane (100 mL), then filtered and washed again with pentane (40 mL). Final drying in vacuo yielded 1-SIMes as a colourless solid (1.45 g, 3.10 mmol, 89%). Single crystals of 1-SIMes suitable for X-ray diffraction (XRD) analysis were obtained by slow evaporation of a saturated benzene/DCM mixture (9:1) at room temperature. ${}^{1}H{}^{11}B$ NMR (500 MHz, CD₂Cl₂, 297 K): $\delta = 6.98$ (m, 4H, Mes-m-H), 4.04 (s, 4H, NHC-CH₂), 2.36 (br s, 2H, BH₂), 2.32 (s, 6H, Mes-p-CH₃), 2.30 (s, 12H, Mes-*o*- CH₃) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): $\delta = 185.7$ (br s, C_{carbene}), 139.5 (Mes-ipso-C), 135.6 (Mes-o-CH), 133.5 (Mes-p-CCH₃), 129.8 (Mes-m-CH), 119.2 (q, ${}^{1}J_{\text{FC}} = 319.5 \text{ Hz}, CF_3$, 51.00 (CAAC-*C*H₂), 21.2 (Mes-*p*-CCH₃), 17.7 (Mes-*o*-CCH₃) ppm. ${}^{11}\text{B}$ NMR (160 MHz, CD₂Cl₂, 297 K): $\delta = -9.1$ (t, ${}^{1}J_{\text{HB}} = 105$ Hz, BH₂OTf) ppm. 19 F NMR (471 MHz, CD₂Cl₂, 297 K) $\delta = -76.7$ (t, ${}^{4}J_{\text{HF}} = 1.3$ Hz, CF₃) ppm. HRMS LIFDI for $[C_{13}H_{16}BF_3N_2O_3S]^+ = [M-mesitylene]^+: calcd. 448.0921; found 448.0917. Elemental analysis$ for $[C_{22}H_{28}BF_3N_2O_3S]$ (M_w = 468.34): calcd. C 56.42, H 6.03, N 5.98, S 6.85%; found C 56.27, H 6.12, N 6.12, S 7.03%. FT-IR (solid-state): \tilde{v} (B–H) = 2437 cm⁻¹.

Synthesis of 2-SIMes

1-SIMes (200 mg, 427 µmol) was dissolved in benzene (12 mL) and a freshly prepared solution of Na(diox)_{3.6}[SCP] (177 mg, 427 µmol) in THF (4 mL) was added at room temperature, resulting in an orange suspension. After stirring the reaction mixture for 30 min all volatile components were removed *in vacuo*. The orange solid was suspended in pentane (12 mL), the solvent was removed *in vacuo* and the resulting solid was extracted with benzene (3 x 10 mL). Subsequently, the solvent was removed *in vacuo* and the resulting solid was extracted with benzene (3 x 10 mL). Subsequently, the solvent was removed *in vacuo* and the residual solid washed with hexane (4 x 5 mL). Final drying *in vacuo* yielded **2-SIMes** as an orange powder (145 mg, 368 µmol, 86%). Yellow single crystals of **2-SIMes** suitable for XRD analysis were obtained by layering a saturated benzene solution with hexane at room temperature. ¹H{¹¹B} NMR (600 MHz, C₆D₆, 297 K): $\delta = 6.73$ (s, 4H, Mes-*m*-H), 3.08 (s, 4H, NHC-CH₂), 2.39 (s, 2H, BH₂), 2.26 (s, 12H, Mes-*o*-CH₃), 2.07 (s, 6H, Mes-*p*-CH₃) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 297 K): $\delta = 189.7$ (br s, *C*_{carbene}, identified by HMBC), 174.0 (d, ¹J_{PC} = 12.4 Hz, SCP), 138.8 (Mes-*p*-CCH₃),

135.9 (Mes-*ipso*-*C*), 134.3 (Mes-*o*-*C*CH₃), 129.9 (Mes-*m*-*C*), 49.7 (NHC-*C*H₂), 21.0 (Mes-*p*-CCH₃), 18.5 (Mes-*o*-CCH₃) ppm. ¹¹B NMR (193 MHz, C₆D₆, 297 K): $\delta = -20.2$ (br t, ¹J_{HB} = 98 Hz, *B*H₂) ppm. ³¹P NMR (243 MHz, C₆D₆, 297 K): $\delta = -43.7$ (s, SC*P*) ppm. HRMS ASAP for [C₂₂H₂₈BN₂PS]⁺ = [M]⁺: calcd. 394.1798; found 394.1796. FT-IR (solid-state): $\tilde{\nu}$ (B–H) = 2390 cm⁻¹, $\tilde{\nu}$ (C=P) = 1508 cm⁻¹.

Synthesis of 2-CAAC^{Me}

1-CAAC^{Me} (20.0 mg, 44.7 µmol) was dissolved in C₆D₆ (0.4 mL) and a freshly prepared solution of Na(diox)_{3.1}[SCP] (17.0 mg, 44.7 µmol) in THF (0.2 mL) was added at room temperature, resulting in a yellow suspension. After stirring the reaction mixture for 30 min all volatile components were removed in vacuo. The yellow solid was extracted with benzene (0.5 mL). Subsequently, the solvent was removed in vacuo and the residual solid washed with hexane (3 x 0.7 mL). Final drying *in vacuo* yielded **2-CAAC**^{Me} as a yellow powder (9.2 mg, 24.6 µmol, 55%). ¹H{¹¹B} NMR (600 MHz, C₆D₆, 297 K): δ = 7.08 (t, ³J_{HH} = 7.8 Hz, 1H, Dipp*p-H*), 6.94 (d, ${}^{3}J_{HH} = 7.8$ Hz, 2H, Dipp-*m-H*), 2.73 (s, 2H, BH₂), 2.49 (sept, ${}^{3}J_{HH} = 6.6$ Hz, 2H, *i*Pr-CH(CH₃) ₂), 1.69 (s, 6H, CAAC-NC(CH₃)₂), 1.40 (s, 2H, CAAC-CH₂), 1.25 (d, ${}^{3}J_{\text{HH}} = 6.6 \text{ Hz}, 6\text{H}, i\text{Pr-CH}(CH_{3})_{2}, 1.06 \text{ (d, } {}^{3}J_{\text{HH}} = 6.6 \text{ Hz}, 6\text{H}, i\text{Pr-CH}(CH_{3})_{2}, 0.76 \text{ (s, 6H, })_{2}$ CAAC-C(CH₃)₂) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 297 K): $\delta = 231.1$ (br s, C_{carbene}, identified by HMBC), 173.1 (d, ${}^{1}J_{PC} = 12.0$ Hz, SCP), 144.9 (Dipp-o-C), 132.6 (Dipp-ipso-C), 129.9 (Dipp-p-C), 125.0 (Dipp-m-C), 77.7 (CAAC-C(CH₃)₂), 53.3 (CAAC-NC(CH₃)₂), 51.9 (CAAC-CH2), 29.6 (CAAC-NC(CH3)2), 29.3 (iPr-CH(CH3)2), 28.3 (CAAC-C(CH3)2), 26.6 $(iPr-CH(CH_3)_2)$, 23.5 $(iPr-CH(CH_3)_2)$ ppm. ¹¹B NMR (193 MHz, C₆D₆, 297 K): $\delta = -17.5$ (br t, ${}^{1}J_{\text{HB}} = 104 \text{ Hz}, BH_2$) ppm. ${}^{31}P$ NMR (243 MHz, C₆D₆, 297 K): $\delta = -41.2$ (s, SCP) ppm. HRMS LIFDI for $[C_{21}H_{33}BNPS]^+ = [M]^+$: calcd. 373.2159; found 373.2155.

Synthesis of 3-Ph^{CF3}

2-SIMes (20.0 mg, 50.7 µmol) was suspended in benzene (0.5 mL) and *p*-trifluoromethylphenyl azide (13.0 mg, 66.8 µmol) was added at room temperature. After stirring the reaction mixture for 16 h, all volatile components were removed *in vacuo*. The residual orange solid was washed with hexane (4 x 0.5 mL) and dried *in vacuo*. Yellow single crystals of **3-Ph^{CF3}** suitable for XRD analysis were obtained by evaporation of a saturated benzene solution at room temperature. The crystals were washed with pentane (3 x 0.5 mL) and dried *in vacuo* yielding **3-Ph^{CF3}** as a yellow solid (16.0 mg, 27.5 µmol, 54%). ¹H{¹¹B} NMR (500 MHz, C₆D₆, 297 K): $\delta = 7.44$ (d, ³J_{HH} = 8.7 Hz, 2H, Ph^{CF3}-o-H), 7.14 (d, ³J_{HH} = 8.7 Hz,

2H, Ph^{CF3}-*m*-H), 6.67-6.65 (m, 4H, Mes-*m*-H), 3.03 (s, 4H, NHC-CH₂), 2.61 (s, 2H, BH₂), 2.22 (s, 12H, Mes-*o*-CH₃), 1.95 (s, 6H, Mes-*p*-CH₃) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 297 K): $\delta = 194.5$ (d, ¹J_{PC} = 68 Hz, CPN₃), 190.2 (br s, C_{carbene}, identified by HMBC), 144.7-144.5 (m, CCF₃), 138.9 (Mes-*p*-CCH₃), 135.8 (Mes-*o*-CCH₃), 134.6 (Mes-*ipso*-C), 129.9 (Mes-*m*-C), 128.6 (Ph-*ipso*-C), 126.5 (q, ³J_{FC} = 3.8 Hz, Ph-*m*-C), 124.7 (q, ¹J_{FC} = 271 Hz, CF₃), 121.2 (d, ³J_{PC} = 8.7 Hz, Ph-*o*-C), 49.6 (NHC-CH₂), 20.9 (Mes-*p*-CCH₃), 18.1 (Mes-*o*-CCH₃) ppm. ¹¹B NMR (160 MHz, C₆D₆, 297 K): $\delta = -21.7$ (br, $\omega_{1/2} \approx 600$ Hz, BH₂) ppm. ¹⁹F NMR (471 MHz, C₆D₆, 297 K): $\delta = -62.1$ (s, CF₃) ppm. ³¹P NMR (202 MHz, C₆D₆, 297 K): $\delta = 170.9$ (s, CPN₃) ppm. HRMS LIFDI for [C₂₉H₃₂BF₃N₅PS]⁺ = [M]⁺: calcd. 581.2156; found 581.2138. FT-IR (solid-state): $\tilde{\nu}$ (B–H) = 2407, 2396 cm⁻¹.

Synthesis of 3-Mes

2-SIMes (28.0 mg, 71.0 μmol) was suspended in benzene (0.5 mL) and mesityl azide (11.0 mg, 71.0 μmol) was added at room temperature. After stirring the reaction mixture for 2 days, all volatile components were removed *in vacuo* and the residual orange solid was washed with hexane (4 x 0.5 mL) and benzene (0.5 mL). Final drying *in vacuo* yielded **3-Mes** as an orange solid (23.0 mg, 41.4 μmol, 58%). ¹H{¹¹B} NMR (400 MHz, CD₂Cl₂, 297 K): δ = 6.97 (s, 4H, Mes-*m*-*H*-_{NHC}), 6.94 (s, 2H, Mes-*m*-*H*), 4.04 (s, 4H, NHC-C*H*₂), 2.34 (s, 12H, Mes-*o*-C*H*₃-_{NHC}), 2.32 (s, 3H, Mes-*p*-C*H*₃), 2.29 (s, 6H, Mes-*p*-C*H*₃-_{NHC}), 1.97 (s, 2H, B*H*₂), 1.86 (s, 6H, Mes-*o*-C*H*₃) ppm. ¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 297 K): δ = 193.3 (d, ¹*J*_{PC} = 72 Hz, CPN₃), 189.1 (br s, *C*_{carbene}, identified by HMBC), 139.3 (Mes-*p*-CCH₃-_{NHC}), 139.1 (Mes-*p*-CCH₃), 136.8 (d, ²*J*_{PC} = 8 Hz, Mes-*ipso*-*C*), 136.2 (Mes-*m*-CH-_{-NHC}), 129.2 (Mes-*m*-CH), 50.6 (NHC-CH₂), 21.2 (Mes-*p*-CCH₃-_{NHC}), 129.9 (Mes-*m*-CH-_{-NHC}), 17.6 (d, ⁴*J*_{PC} = 2 Hz, Mes-*o*-CCH₃) ppm. ¹¹B NMR (128 MHz, CD₂Cl₂, 297 K): δ = -22.4 (br t, ¹*J*_{HB} = 94 Hz, *B*H₂) ppm. ³¹P NMR (162 MHz, CD₂Cl₂, 297 K): δ = 173.6 (s, CPN₃) ppm. HRMS LIFDI for [C₃₁H₃₉BN₅PS]⁺ = [M]⁺: calcd. 555.2751; found 555.2742.

Synthesis of 4

2-SIMes (80.0 mg, 202 μ mol) was dissolved in benzene (3 mL) and a freshly prepared solution of [CpCo(C₂H₄)₂] (18.0 mg, 101 μ mol) in benzene (1.5 mL) was added dropwise at room temperature, resulting in a dark red solution. After stirring the reaction mixture for 30 min, all volatile components were removed *in vacuo*. The resulting solid was washed with hexane (4 x 4 mL), redissolved in benzene (4 mL), and precipitated with hexane (4 mL). Final washing with

hexane (3 mL) and drying *in vacuo* yielded complex **4** as a brown solid (28.6 mg, 31.3 μmol, 31%). ¹H{¹¹B} NMR (500 MHz, C₆D₆, 297 K): $\delta = 6.76$ (s, 8H, Mes-*m*-*H*), 4.82 (s, 5H, Cp), 2.96 (s, 8H, NHC-CH₂), 2.20 (s, 24H, Mes-*o*-CH₃), 2.12 (s, 12H, Mes-*p*-CH₃), 1.85 (s, 4H, BH₂) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 297 K): $\delta = 192.4$ (br s, *C*_{Carben}, identified by HMBC), 138.6 (Mes-*p*-CCH₃), 135.9 (Mes-*o*-CCH₃), 134.9 (Mes-*ipso*-*C*), 129.9 (Mes-*m*-*C*), 83.9 (Cp), 49.4 (NHC-CH₂), 21.1 (Mes-*p*-CCH₃), 18.4 (Mes-*o*-CCH₃) ppm. *Note: the* ¹³*C NMR resonance of the* C₂P₂ *four-membered ring could not be detected*. ¹¹B NMR (160 MHz, C₆D₆, 297 K): $\delta = -23.3$ (br, $\omega_{1/2} \approx 800$ Hz, *B*H₂) ppm. ³¹P NMR (202 MHz, C₆D₆, 297 K): $\delta = 56.2$ (s, C₂P₂) ppm. HRMS LIFDI for [C₄₉H₆₁B₂CoN₄P₂S₂]⁺ = [M]⁺: calcd. 912.3326; found 912.3313. FT-IR (solid-state): \tilde{v} (B–H) = 2394, 2380 cm⁻¹.

Synthesis of 5

PPB (23.0 mg, 50.7 µmol) was dissolved in benzene (0.5 mL) and a freshly prepared solution of 2-SIMes (20.0 mg, 50.7 µmol) in benzene (0.5 mL) was added dropwise at room temperature, resulting in an orange solution. After stirring the reaction mixture for 5 min, all volatile components were removed *in vacuo*, yielding **5** as an orange solid (41 mg, 48.9 µmol, 96%). Yellow single crystals of 5 suitable for XRD analysis were obtained by layering a saturated toluene solution with pentane at room temperature. ${}^{1}H{}^{11}B{}$ NMR (500 MHz, C₆D₆, 297 K): $\delta = 7.38$ (d, $J_{\text{HH}} = 7.4$ Hz, 2H, Ph), 7.32-7.28 (m, 2H, Ph), 7.20-7.15 (m, 2H, Ph) 7.03-6.79 (m, 16H, Ph), 6.77-6.71 (m, 3H, Ph), 6.71-6.67 (m, 4H, Mes-m-H), 3.03 (s, 4H, NHC-CH₂), 3.01-2.94 (m, 1H, BH), 2.80-2.70 (m, 1H, BH), 2.22 (s, 6H, Mes-o-CH₃), 2.16 (s, 6H, Mes-*o*-CH₃), 2.06 (s, 6H, Mes-*p*-CH₃) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 297 K): $\delta = 190.0$ (br s, C_{carbene}), 143.3 (br s, $C_{q-\text{phosphole}}$), 141.1 (d, ${}^{2}J_{C-P} = 13.6$ Hz, Ph- C_{q}), 140.7 (d, ${}^{1}J_{C-P} =$ 11.4 Hz, $C_{q-phosphole}$), 140.2 (C_q), 139.3 (C_q), 139.0 (C_q), 138.6 (*p*-Mes- C_q), 135.8 (*i*-Mes- C_q), 135.6 (i-Mes-Cq), 134.4 (Cq), 134.1 (Ph-CH), 134.0 (Ph-CH), 131.6 (Ph-CH), 130.0 (Mes-m-C), 129.9 (Mes-*m*-CH), 129.7 (Ph-CH), 129.3 (d, ${}^{4}J_{C-P} = 13.6$ Hz, Ph-CH), 128.6 (d, {}^{4}J_{C-P} = 13.6 Hz, Ph-CH), 128. 12.3 Hz, Ph-CH), 127.6 (Ph-CH), 127.4 (Ph-CH), 127.1 (Ph-CH), 126.9 (Ph-CH), 126.6 (Ph-*C*H), 125.9 (d, *J* = 2.6 Hz, Ph-*C*H), 125.5 (Ph-*C*H), 124.5 (Ph-*C*H), 89.1 (SP*C*_q), 73.1 (B₂*C*_q), 49.8 (NHC-CH₂), 21.1 (Mes-*p*-CH₃), 18.2 (Mes-*o*-CH₃), 18.1 (Mes-*o*-CH₃) ppm. ¹¹B NMR (160 MHz, C₆D₆, 297 K): $\delta = -20.2$ (br, $\omega_{1/2} \approx 500$ Hz, BH₂) ppm. ³¹P NMR (202 MHz, C₆D₆, 297 K): $\delta = 101.2$ (s, *PC*₄) ppm. HRMS LIFDI for $[C_{56}H_{53}B_2N_2PS]^+ = [M]^+$: calcd. 838.3848; found 838.3822. FT-IR (solid-state): \tilde{v} (B–H) = 2396 cm⁻¹.

Synthesis of 6

CBBF (8.0 mg, 25 µmol) was dissolved in benzene (0.3 mL) and a freshly prepared solution of 2-SIMes (10 mg, 25 µmol) in benzene (0.3 mL) was added dropwise at room temperature, resulting in an orange solution. After stirring the reaction mixture for 3 days, yellow crystals formed. The supernatant was removed, and the crystals were washed with hexane (3 x 0.5 mL) and benzene (3 x 0.5 mL). Final drying in vacuo yielded 6 as a yellow solid (9.0 mg, 13 µmol, 50%). ¹H{¹¹B} NMR (500 MHz, CD₂Cl₂, 297 K): 7.60 (t, ³ J_{HH} = 7.1 Hz, 2H, Ph₂-CH), 7.30 (d, ${}^{3}J_{\text{HH}} = 7.6 \text{ Hz}, 1\text{H}, \text{Ph}_2\text{-CH}), 7.25 \text{ (td, } {}^{3}J_{\text{HH}} = 7.1 \text{ Hz}, {}^{3}J_{\text{HH}} = 1.7 \text{ Hz}, 1\text{H}, \text{Ph}_2\text{-CH}), 7.21\text{-}7.14 \text{ (m,}$ 3H, Ph₂-CH), 7.08 (s, 2H, Mes-*m*-CH), 6.98 (s, 2H, Mes-*m*-CH), 6.96 (td, ${}^{3}J_{HH} = 7.6$ Hz, ${}^{3}J_{HH} =$ 1.1 Hz, 1H, Ph₂-CH), 4.33-4.28 (m, 4H, NHC-CH₂), 2.77 (dd, ${}^{3}J_{HH} = 6$ Hz, ${}^{2}J_{PH} = 11$ Hz, 1H, BH), 2.44 (s, 6H, Mes-*o*-CCH₃), 2.36 (s, 6H, Mes-*p*-CCH₃), 2.34 (dd, ${}^{1}J_{HP} = 205$ Hz, ${}^{3}J_{HH} =$ 6 Hz, 1H, PH), 2.34 (s, 6H, Mes-*o*-CCH₃), 1.87 (d, ${}^{3}J_{BH} = 40.6$ Hz, 2H, C₂B₁₀-BH), 1.80-1.68 (m, 4H, C₂B₁₀-BH), 1.54 (s, 3H, C₂B₁₀-CH₃), 1.37 (d, ${}^{3}J_{BH} = 30.6$ Hz, 2H, C₂B₁₀-BH), 0.92 (br s, 1H, C₂B₁₀-BH), 0.54 (br s, 1H, C₂B₁₀-BH) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 297 K): $\delta = 179.8$ (br s, $C_{carbene}$), 153.0 (Ph₂-C(q)), 153.0 (Ph₂-C(q)), 152.6 (Ph₂-C(q)), 141.2 (Ph₂-C(q)), 141.0 (Mes-p-CCH₃), 139.9 (Ph₂-C(q)), 136.4 (Mes-o-CCH₃), 136.0 (Mes-o-CCH₃), 131.7 (Mes-ipso-C), 130.2 (Mes-m-C), 130.1 (Mes-m-C), 126.9 (Ph₂-CH), 126.8 (Ph₂-CH), 126.7 (Ph₂-CH), 126.6 (Ph₂-CH), 126.5 (Ph₂-CH), 126.5 (Ph₂-CH), 119.4 (Ph₂-CH), 119.3 (Ph₂-CH), 84.2 (br s, C₂B₁₀-CB), 77.4 (br s, C₂B₁₀-CCH₃), 51.9 (NHC-CH₂), 24.5 (C₂B₁₀-CH₃), 21.3 (Mes-*p*-CCH₃), 18.7 (Mes-*o*-CCH₃), 18.7 (Mes-*o*-CCH₃), 18.4 (Mes-*o*-CCH₃) ppm. ¹¹B NMR (160 MHz, CD₂Cl₂, 297 K): $\delta = 70.9$ (br s, $\omega_{1/2} \approx 1000$ Hz, 1B, (SIMes)B), -3.7 (br d, ${}^{1}J_{\text{HB}} =$ 130 Hz, B), -6.5 (br d, ${}^{1}J_{\text{HB}} = 137$ Hz, B), -7.2 (s, B), -10.1 (br d, ${}^{1}J_{\text{HB}} = 130$ Hz, B) ppm. ${}^{31}P$ NMR (202 MHz, CD₂Cl₂, 297 K): $\delta = 105.8$ (br d, ${}^{1}J_{HP} = 205$ Hz, BPHB) ppm. HRMS LIFDI for $[C_{37}H_{49}B_{12}N_2PS]^+ = [M]^+$: calcd. 714.4538; found 714.4517. Elemental analysis for $[C_{37}H_{49}B_{12}N_2PS]$ (M_w = 714.5668): calcd. C 62.19, H 6.91, N 3.92, S 4.49%; found C 62.16, H 7.04, N 3.95, S 4.37%. FT-IR (solid-state): \tilde{v} (B–H) = 2401, 2309 cm⁻¹.

In-situ synthesis of 7

1-SIMes (10 mg, 22 µmol) was dissolved in benzene (0.5 mL) and a freshly prepared solution of Na(diox)_{2.0}[AsCO] (6.5 mg, 22 µmol) in THF (0.1 mL) was added at room temperature, resulting in an orange suspension. ¹¹B NMR (128.5 MHz, C₆D₆/d₈-THF, 297 K): δ = -32.9 (br t, ¹J_{HB} = 115 Hz, *B*H₂) ppm.

Synthesis of 8

PPB (47.0 mg, 107 µmol) was suspended in benzene (0.5 mL) and a freshly prepared suspension of 2-SIMes (50 mg, 107 µmol) and Na(diox)_{2.0}[AsCO] (32.0 mg, 107 µmol) in benzene (1.5 mL) and THF (0.3) was added dropwise at room temperature, resulting in a red solution. After stirring the reaction mixture for 1 h, all volatile components were removed in vacuo. The resulting solid was extracted with benzene (3 x 1 mL) and washed with hexane (5 x 2 mL). Red single crystals of 8 suitable for XRD analysis were obtained by layering a saturated benzene solution (2 mL) with pentane (3 mL) at room temperature. Washing the crystals with pentane (3x 0.5 mL) and final drying yielded 8 as an orange solid (12.0 mg, 14.3 µmol, 13%). ¹H NMR $(400 \text{ MHz}, C_6D_6, 297 \text{ K}): \delta = 7.57 \text{ (dd, } {}^3J_{\text{HH}} = 8.1 \text{ Hz}, {}^3J_{\text{HH}} = 1.3 \text{ Hz}, 2\text{H}, \text{Ph-}H), 7.29 \text{ (tt, } {}^3J_{\text{HH}} = 1.3 \text{ Hz}, 2\text{H}, \text{Ph-}H)$ 8.1 Hz, ${}^{3}J_{HH} = 1.3$ Hz, 1H, Ph-*H*), 7.23-7.18 (m, 2H, Ph-*H*), 7.15-7.13 (m, 2H, Ph-*H*), 6.98-6.78 (m, 18H, Ph-H), 6.69 (s, 4H, Mes-m-H), 3.09 (s, 4H, NHC-CH₂), 2.39 (br q, 2H, BH₂), 2.24 (s, 12H, Mes-*o*-CH₃), 2.06 (s, 6H, Mes-*p*-CH₃) ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆, 297 K): $\delta =$ 194.3 (br s, C_{carbene}, identified by HMBC), 141.5 (C_{q-borole}, identified by HMBC), 140.1 (Ph- C_a , 138.7 (Mes-*p*- C_a), 138.6 (Ph- C_a), 135.9 (Ph-*C*H), 135.6 (Mes-*o*- C_a), 134.8 (Mes-*i*- C_a), 132.3 (Ph-CH), 132.1 (Ph-CH), 130.2 (Mes-m-CH), 127.4 (Ph-CH), 127.4 (Ph-CH), 127.3 (Ph-CH), 127.2 (Ph-CH), 126.0 (Ph-CH), 125.0 (Ph-CH), 115.4 (AsCborole, identified by HMBC), 49.4 (NHC-CH₂), 21.1 (Mes-p-CCH₃), 18.8 (Mes-o-CCH₃) ppm. Note: not all borole carbon nuclei could be detected by HMBC owing to line-broadening caused by the adjacent quadrupolar boron and arsenic nuclei. ¹¹B NMR (129 MHz, C₆D₆, 297 K): $\delta = -21.5$ (br, $\omega_{1/2} \approx 750$ Hz, BH₂) ppm. Note: the borole boron nucleus could not be detected due to excessive *line broadening*. HRMS LIFDI for $[C_{55}H_{53}A_{5}B_{2}N_{2}]^{+} = [M]^{+}$: calcd. 838.3605; found 838.3588. Elemental analysis for [C₅₅H₅₃AsB₂N₂] (M_w = 838.5846): calcd. C 78.78, H 6.37, N 3.34%; found C 78.92, H 6.41, N 3.22%. FT-IR (solid-state): \tilde{v} (B–H) = 2435, 2390 cm⁻¹.

NMR spectra of isolated compounds



Figure S1. ${}^{1}H{}^{11}B{}$ NMR spectrum of 1-SIMes in CD₂Cl₂.



Figure S2. ${}^{13}C{}^{1}H$ NMR spectrum of 1-SIMes in CD₂Cl₂.



Figure S3. ¹¹B NMR spectrum of 1-SIMes in CD₂Cl₂.



Figure S4. ¹⁹F NMR spectrum of 1-SIMes in CD₂Cl₂.



Figure S5. ${}^{1}H{}^{11}B{}$ NMR spectrum of 2-SIMes in C₆D₆.



Figure S6. ${}^{13}C{}^{1}H$ NMR spectrum of 2-SIMes in C₆D₆.



Figure S7. ¹¹B NMR spectrum of **2-SIMes** in C_6D_6 .





Figure S9. ${}^{1}H{}^{11}B{}$ NMR spectrum of **2-CAAC**^{Me} in C₆D₆.



Figure S10. ${}^{13}C{}^{1}H$ NMR spectrum of 2-CAAC^{Me} in C₆D₆.



Figure S11. ¹¹B NMR spectrum of 2-CAAC^{Me} in C₆D₆.



Figure S12. ³¹P NMR spectrum of 2-CAAC^{Me} in C₆D₆.



Figure S13. ${}^{1}H{}^{11}B{}$ NMR spectrum of 3-Ph^{CF3} in C₆D₆.



Figure S14. ¹³C{¹H} NMR spectrum of $3-Ph^{CF3}$ in C₆D₆.





Figure S16. ³¹P NMR spectrum of $3-Ph^{CF3}$ in C₆D₆.



Figure S17. ¹⁹F NMR spectrum of $3-Ph^{CF3}$ in C₆D₆.



Figure S18. ${}^{1}H{}^{11}B{}$ NMR spectrum of 3-Mes in CD₂Cl₂.



Figure S19. ¹³C{¹H} NMR spectrum of 3-Mes in CD₂Cl₂.



Figure S20. ¹¹B NMR spectrum of 3-Mes in CD₂Cl₂.



Figure S21. ³¹P NMR spectrum of 3-Mes in CD₂Cl₂.



Figure S22. ${}^{1}H{}^{11}B{}$ NMR spectrum of 4 in C₆D₆.



Figure S23. ${}^{13}C{}^{1}H$ NMR spectrum of 4 in C₆D₆.



Figure S24. ¹¹B NMR spectrum of **4** in C_6D_6 .





Figure S26. ${}^{1}H{}^{11}B{}$ NMR spectrum of the reaction of 5 in C₆D₆.



Figure S27. ${}^{13}C{}^{1}H$ NMR spectrum of 5 in C₆D₆.



Figure S28. ¹¹B NMR spectrum of the reaction of 5 in C_6D_6 .


Figure S29. ³¹P NMR spectrum of the reaction of **5** in C_6D_6 .



Figure S30. ${}^{1}H{}^{11}B{}$ NMR spectrum of the reaction of **6** in CD₂Cl₂.



Figure S31. ${}^{13}C{}^{1}H$ NMR spectrum of the reaction of **6** in CD₂Cl₂.



Figure S32. ¹¹B NMR spectrum of the reaction of 6 in CD₂Cl₂.



Figure S33. ³¹P NMR spectrum of the reaction of **6** in CD₂Cl₂.



Figure 34. In situ ¹¹B NMR spectrum of the reaction of 7 in C₆H₆/THF.



Figure S35. ¹H NMR spectrum of the reaction of **8** in C_6D_6 .



Figure S36. ${}^{13}C{}^{1}H$ NMR spectrum of the reaction of **8** in C₆D₆.



Figure S37. ¹¹B NMR spectrum of the reaction of **8** in C_6D_6 .

IR spectra



Figure S38. Solid-state IR spectrum of 1-SIMes.



Figure S39. Solid-state IR spectrum of 2-SIMes.



Figure S40. Solid-state IR spectrum of 3-Ph^{CF3}.



Figure S41. Solid-state IR spectrum of 4.



Figure S42. Solid-state IR spectrum of 5.



Figure S43. Solid-state IR spectrum of 6.



Figure S44. Solid-state IR spectrum of 8.

UV-vis spectra



Figure S45. UV-vis absorption spectrum of **2-SIMes** (orange) in benzene at 23 °C. $\lambda_{max} = 312$ nm, $\lambda_2 = 344$ nm (shoulder).



Figure S46. UV-vis absorption spectrum of **3-Ph**^{CF3} (yellow) in benzene at 23 °C. $\lambda_{max} = 379$ nm.



Figure S47. UV-vis absorption spectrum of **4** (yellow) in benzene at 23 °C. $\lambda_{max} = 369$ nm.



Figure S48. UV-vis absorption spectrum of **5** (orange) in benzene at 23 °C. $\lambda_{max} = 337$ nm, $\lambda_2 = 418$ nm (shoulder).



Figure S49. UV-vis absorption spectrum of the product of **6** (yellow) in DCM at 23 °C. $\lambda_{max} = 336$ nm.



Figure S50. UV-vis absorption spectrum of the product of **8** (yellow) in benzene at 23 °C. λ_{max} = 319 nm, λ_2 = 397 nm (shoulder).

X-ray crystallographic data

All crystal data were collected on a *XtaLAB Synergy Dualflex HyPix* diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,⁹ refined with the ShelXL program¹⁰ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 2428369 (7), 2428370 (6), 2428371 (5), 2428372 (8), 2428373 (3-Ph^{CF3}), 2428374 (1-SIMes), and 2428375 (2-SIMes). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



Figure S51. Solid-state structures of **1-SIMes**. Atomic displacement ellipsoids set at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity except for B-bound protons. Selected atomic distances (Å) and angles (°): C1–B1 1.608(3), B1–O1 1.554(3), C1–B1–O1 108.90(18).



Figure S52. Solid-state structures of **7**. Atomic displacement ellipsoids set at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity except for B-bound protons.

Special refinement details for 1-SIMes: The data was refined as a two-component inversion twin, with BASF 0.51. All Hydrogen atoms except boron-bound H1_1 and H2_1 were assigned to idealised positions. The coordinates of H1_1 and H2_1 were refined freely. Crystal data for 1-SIMes: C₂₂H₂₈BF₃N₂O₃S·(C₆H₆)_{1.5}, $M_r = 585.49$, colourless plate, 0.434×0.149×0.028 mm³, monoclinic space group C2, a = 16.5510(2) Å, b = 8.99420(10) Å, c = 20.2775(2) Å, $\beta = 93.5500(10)^{\circ}$, V = 3012.78(6) Å³, Z = 4, $\rho_{calcd} = 1.291$ g·cm⁻³, $\mu = 1.404$ mm⁻¹, F(000) = 1236, T = 100.00(12) K, $R_I = 0.0326$, $wR_2 = 0.0881$, Flack parameter = 0.513(17), 5588 independent reflections [2 $\theta \le 140.12^{\circ}$] and 382 parameters.

Special refinement details for 2-SIMes: All Hydrogen atoms except boron-bound H1_1 and H2_1 were assigned to idealised positions. The coordinates of H1_1 and H2_1 were refined freely. The asymmetric unit contains half a benzene molecule positioned on an inversion centre and modelled as twofold disordered (RESI 51 and 52 BENZ) in a 58:42 ratio, with PARTs -1 and -2. One Mes substituent was modelled as twofold disordered (RESI 3 and 13 MES) in an 85:15 ratio. The benzene rings in both disorders were idealised with AFIX 66, and the ADPs within the disorders were restrained to similarity with SIMU 0.003 and 0.005, respectively. Crystal data for 2-SIMes: $C_{22}H_{28}BN_2PS \cdot (C_6H_6)_{0.5}$, $M_r = 433.36$, colourless block, 0.220×0.168×0.031 mm³, monoclinic space group $P2_{1}/n$, a = 7.51490(10) Å, b = 19.1431(2) Å, c = 17.13230(10) Å, $\beta = 90.5620(10)^{\circ}, \quad V = 2464.51(4) \text{ Å}^3, \quad Z = 4,$

 $\rho_{calcd} = 1.168 \text{ g} \cdot \text{cm}^{-3}, \quad \mu = 1.867 \text{ mm}^{-1}, \quad F(000) = 924, \quad T = 99.99(10) \text{ K}, \quad R_1 = 0.0538,$ $wR_2 = 0.1378, 4681 \text{ independent reflections } [2\theta \le 140.104^\circ] \text{ and } 359 \text{ parameters.}$

Special refinement details for 3-Ph^{CF3}: The data was refined as a two-component inversion twin. The BASF parameter was refined to 22.6%. All Hydrogen atoms except boron-bound H1 1 and H2 1 were assigned to idealised positions. The coordinates of H1 1 and H2 1 were refined freely. The asymmetric unit contains two crystallographically independent borane compounds and four benzene molecules, one of which was modelled as twofold disordered (RESI 101/102 BENZ) in a 58:42 ratio. All solvent benzene rings were idealised with AFIX 66 and ADPs within the disordered benzene restrained with SIMU 0.005. One CF₃ unit was modelled as threefold rotationally disordered in the three fluorine atoms (RESI 111/112/113 F3), with three FVAR summed up to 1.0 and refined to a 56:20:24 ratio. ADPs within the disordered CF₃ group were restrained with SIMU 0.005, and 1,2- and 1,3-distances restrained to similarity with SAME. Crystal data for 3-Ph^{CF3}: C₂₉H₃₂BF₃N₅PS·(C₆H₆)₂, $M_r = 737.65$, yellow block, $0.430 \times 0.150 \times 0.090 \text{ mm}^3$, monoclinic space group $P2_1$, a = 19.0260(2) Å, b = 24.25870(10) Å, c = 9.71050(10) Å, $\beta = 121.3370(10)^{\circ}$, V = 3828.04(7) Å³, Z = 4, $\rho_{calcd} = 1.280 \text{ g} \cdot \text{cm}^{-3}, \quad \mu = 1.564 \text{ mm}^{-1}, \quad F(000) = 1552, \quad T = 100(2) \text{ K}, \quad R_l = 0.0401,$ $wR_2 = 0.1037$, Flack parameter = 0.226(15), 14270 independent reflections [2 $\theta \le 150.75^\circ$] and 1014 parameters.

Special refinement details for 5: All Hydrogen atoms except boron-bound H1_1 and H2_1 were assigned to idealised positions. The coordinates of H1_1 and H2_1 were refined freely. The asymmetric unit contains a toluene molecule, which was modelled as twofold disordered in a 48:52 ratio. The benzene rings within the disorder were idealised with AFIX 66 and the ADPs restrained to similarity with SIMU 0.005. Crystal data for 5: C₅₆H₅₃B₂N₂PS·C₇H₈, $M_r = 930.78$, yellow block, $0.210 \times 0.150 \times 0.040$ mm³, orthorhombic space group $P2_12_12_1$, a = 9.44370(10) Å, b = 20.19870(10) Å, c = 26.63090(10) Å, V = 5079.86(6) Å³, Z = 4, $\rho_{calcd} = 1.217$ g·cm⁻³, $\mu = 1.180$ mm⁻¹, F(000) = 1976, T = 100(2) K, $R_I = 0.0296$, $wR_2 = 0.0803$, Flack parameter = -0.003(2), 9613 independent reflections [$2\theta \le 140.144^\circ$] and 670 parameters.

Special refinement details for 6: All Hydrogen atoms except boron-bound H1_1 and H2_1 were assigned to idealised positions. The coordinates of H1_1 and H2_1 were refined freely. Crystal data for 6: $C_{37}H_{49}B_{12}N_2PS$, $M_r = 714.53$, yellow plate, $0.200 \times 0.090 \times 0.020$ mm³,

monoclinic space group $P2_1/c$, a = 20.8665(2) Å, b = 8.27010(10) Å, c = 23.3283(2) Å, $\beta = 90.2580(10)^\circ$, V = 4025.68(7) Å³, Z = 4, $\rho_{calcd} = 1.179$ g·cm⁻³, $\mu = 1.297$ mm⁻¹, F(000) = 1504, T = 100(2) K, $R_1 = 0.0523$, $wR_2 = 0.1081$, 8197 independent reflections $[2\theta \le 150.774^\circ]$ and 493 parameters.

Special refinement details for 7: The crystals decomposed rapidly during selection and were extremely poorly diffracting. The data is only sufficient for proof of connectivity and may not be discussed further. The asymmetric unit contains one toluene molecule positioned on an inversion center, the benzene ring of which was idealised with AFIX 66. The H₂BAsCO moiety was modelled as twofold disordered (RESI 11/12 AsCO) in a 17:83 ratio. One mesityl substituent was modelled as twofold disordered (RESI 41/42 MES) in a 70:30 ratio. The benzene rings within this disorder were idealised with AFIX 66. 1,2- and 1,3-distances within these disorders were restrained to similarity with SAME 0.005. All ADPs were restrained to similarity with SIMU 0.005. **Crystal data for 7**: C₂₂H₂₈AsBN₂O·(C₇H₈)_{0.5}, $M_r = 936.52$, colourless plate, 0.085×0.032×0.017 mm³, monoclinic space group $P2_1/n$, a = 7.5069(4) Å, b = 18.7077(16) Å, c = 17.6728(7) Å, $\beta = 90.683(5)^\circ$, V = 2481.7(3) Å³, Z = 4, $\rho_{calcd} = 1.253$ g·cm⁻³, $\mu = 1.982$ mm⁻¹, F(000) = 980, T = 100(2) K, $R_I = 0.1611$, $wR_2 = 0.3669$, 4222 independent reflections [$2\theta \le 130.178^\circ$] and 370 parameters.

Special refinement details for 8: All Hydrogen atoms except H1 1 and H2 1 were assigned to idealised positions. The coordinates of H1_1 and H2_1 were refined freely. The data was twinned but solved and refined as a single crystal as the twinning was < 7%. The structure contains multiple twofold disorders, one in a mesityl substituents (RESI 31/32 MES), refined to a 44:56 ratio, and four in the C-bound phenyl substituents of the borole ring (RESI 71/72, 81/82, 91/92 and 101/102), all refined with the same 71:29 ratio, as refinement with four different variables provided very similar ratios between 69:31 and 72:28. Benzene rings in all five disorders were idealised with AFIX 66. 1,2- and 1,3-distances in RESI 31/32 MES were restrained to similarity with SAME applied to the entire residues. For all disorders ADPs were restrained to similarity using SIMU 0.003 or 0.005. Crystal data for 8: C55H51AsB2N2, vellow block, $0.189 \times 0.094 \times 0.051 \text{ mm}^3$, triclinic group $P\overline{1}$, $M_{\rm r} = 836.51$, space a = 13.8895(2) Å, b = 14.0251(2) Å, c = 14.5748(2) Å, $\alpha = 61.329(2)^{\circ}$, $\beta = 73.8450(10)^{\circ}$, $\gamma = 0.094^{\circ}$, V = 2247.48(8) Å³, Z = 2, $\rho_{calcd} = 1.236$ g·cm⁻³, $\mu = 1.308$ mm⁻¹, F(000) = 876, T = 100(2) K, $R_1 = 0.0472$, $wR_2 = 0.1264$, 8445 independent reflections $[2\theta \le 140.142^\circ]$ and 738 parameters.

Computational details

All density functional theory (DFT) calculations were carried out using either the Gaussian 16, Rev. C.01 quantum chemistry program packages (OCP versus PCO linkage, and postulated mechanism of formation of **5**) or Turbomole 7.8.1¹¹ (postulated mechanism of formation of **6**), as implemented in the user interface TmoleX2024.¹² Optimisations were carried out at the B3LYP¹³⁻¹⁸/D3(BJ)^{19,20}/def2-SVP^{21,22} level of theory, using the X-ray structural data as starting points for the starting materials and products. True minima were confirmed by frequency calculations, which provided no imaginary frequencies.

Wiberg bond indices (WBIs),²³ population analyses based on occupation numbers (PABOON) yielding shared number of electrons (SNE) and multicentre contributions,²⁴ and intrinsic bond orbitals (IBOs)²⁵ were calculated in the interactive property program (proper) implemented in Turbomole 7.8.

Table S1. SCF energies (E_{SCF} , Ha), Gibbs free energies (G, Ha), and relative Gibbs free energies (ΔG , kcal mol⁻¹) of the boron phosphathioketenes **2'-SIMes** and **2'-CAAC**^{Me} versus their boron phosphaalkyne isomers **2-SIMes** and **2-CAAC**^{Me} calculated at the B3LYP/D3(BJ)/def2-SVP level of theory.

	2-SIMes	2'-SIMes	2-CAAC ^{Me}	2'-CAAC ^{Me}
	SIMes SIMes S−C≡P	SIMes P=C=S	CAAC ^{Me} S−C≡P	CAAC ^{Me} P=C=S
$E_{\rm SCF}$	-1728.34344	-1728.34132	-1520.67415	-1520.67352
G	-1727.95459	-1727.95349	-1520.31451	-1520.31400
ΔE	0	0.69	0	0.32

Table S2. SCF energies (E_{SCF} , Ha), Gibbs free energies (G, Ha), and relative Gibbs free energies (ΔG , kcal mol⁻¹) of the reaction intermediates **IntnA** and product versus the starting materials {**2-SIMes** + PPB} in the postulated mechanism of formation of **5** calculated at the B3LYP/D3(BJ)/def2-SVP level of theory using Gaussian 16.

		$E_{\rm SCF}$	G	ΔG
2-SIMes	SIMes S−C≡P	-1728.34344	-1727.95349	
PPB	Ph Ph Ph Ph Ph	-1334.73074	-1334.30608	
$\{2-SIMes + PPB\}$		-3063.07417	-3062.25960	0.0
Int1A	SIMes H H Ph Ph Ph Ph Ph Ph Ph Ph	-3063.14243	-3062.29995	-25.3
Int2A	H-B SIMes Ph-B Ph Ph Ph Ph Ph Ph	-3063.13301	-3062.28992	-19.0
Int3A	SIMes $\rightarrow B \oplus Ph$ $Ph-B \oplus Ph$ $Ph-B \oplus Ph$ Ph Ph	-3063.13481	-3062.28710	-17.3
5	$\begin{array}{c} Ph & Ph \\ Ph & S \\ H & B \\ H & P \\ H & Ph \\ H & Ph \\ H & Ph \end{array}$	-3063.16873	-3062.32120	-38.7

Table S3. SCF energies (E_{SCF} , Ha), Gibbs free energies (G, Ha), and relative Gibbs free energies (ΔG , kcal mol⁻¹) of the reaction intermediates **Int1-3B** and product versus the starting materials {**2-SIMes** + CBBF} in the postulated mechanism of formation of **6** calculated at the B3LYP/D3(BJ)/def2-SVP level of theory using Turbomole 7.8.1.

		$E_{ m SCF}$	G	ΔG
2-SIMes	SIMes <mark>S</mark> −C≡P	-1727.56757	-1727.17774	
	н			
CBBF	Cb	H ^{-856.70044}	-856.38814	
	Me			
$\{\textbf{2-SIMes} + CBBF\}$		-2584.26801	-2583.56588	0
Int1B	SIMes ⊥	-2584.29434	-2583.58179	-10.0
	H~B~H			
	Cb B-P C S			
Int2B	HSIMes	-2584.34796	-2583.61528	-31.0
	H _{///P} B Cb B-C D B-C D			
Int3B	H H SurSIMes	-2584.35844	-2583.62759	-38.7
	CP			
6	H, ⊕, SIMes	-2584.36431	-2583.63201	-41.5
	B = B H_{λ_1} H_{λ_2} H_{λ_3} H_{λ_3}			



Figure S53. Truncated ball-and-stick representations of **6** optimised at the B3LYP/D3(BJ)/def2-SVP level of theory with relevant WBIs (left, in blue) and SNEs (right, in red) obtained from a PABOON analysis. Element colours: hydrogen = white, boron = green, carbon = grey, nitrogen = sky blue, phosphorus = blue.



Figure S54. Truncated ball-and-stick representations of **8** optimised at the B3LYP/D3(BJ)/def2-SVP level of theory with relevant WBIs (left, in blue) and SNEs (right, in red) obtained from a PABOON analysis. Element colours: hydrogen = white, boron = green, carbon = grey, nitrogen = sky blue, arsenic = purple.



Figure S55. IBOs of **8** involved in As bonding. Stick representation with hydrogen atoms omitted for clarity. Isovalues = 0.06. Element colours: boron = pink, carbon = dark green, nitrogen = blue, arsenic = purple.

	Atom con	ntribution	Main at	omic orbital o	contributions		
IBO1	As1	97%	4s	71%	4p _x	24%	
IBO2	As1	53%	4p _x	66%			
	B1	41%	$2p_x$	49%			
	C1	5%	$2p_x$	83%			
IBO3	As1	39%	4py	85%			
	C3	51%	2py	27%	2pz	61%	
	C4	4%	$2p_y$	38%	2pz	57%	
IBO4	As1	41%	4pz	84%			
	C2	55%	2py	36%	2pz	56%	
	B2	9%	2py	25%	2pz	73%	

Table S4. Atom and orbital contributions in IBOs 1-4.

Cartesian coordinates of optimised compounds

1) <u>B-PSC versus B-SCP linkage (calculated using Gaussian 16, Rev. C.01)</u>

2-SIMes

 $E_{SCF} = -1728.343437 \text{ Ha}$ $v_{min} = 14.29 \text{ cm}^{-1}$

В	0.20240	0.40480	-1.2646
С	0.30420	-0.45360	0.09060
S	0.03680	2.29750	-0.70880
С	-1.59660	2.64500	-0.82040
Р	-3.10790	3.03870	-0.94240
Ν	-0.72170	-0.98260	0.76940
Ν	1.45020	-0.73710	0.72890
С	-2.10600	-0.90470	0.41380
С	-0.29180	-1.69210	1.98450
С	1.23990	-1.55060	1.93640
С	2.77040	-0.39450	0.29540
С	-2.92930	0.02230	1.07390
С	-2.60820	-1.78550	-0.55980
С	-4.28330	0.05760	0.72700
С	-2.37290	0.96500	2.10760
С	-4.81920	-0.78930	-0.24990
С	-3.96770	-1.70690	-0.87790
С	-6.26980	-0.67970	-0.64280
С	-1.70020	-2.75860	-1.26420
С	3.40860	-1.21560	-0.65100
С	3.40680	0.72600	0.85510
С	4.71270	-0.88870	-1.03420
С	2.68430	-2.38290	-1.26690
С	5.38080	0.22210	-0.50220
С	4.71310	1.01280	0.44040
С	6.77210	0.57500	-0.96250
С	2.69740	1.60640	1.85070
Н	-0.77300	0.10670	-1.91240
Н	1.25430	0.34910	-1.86660
Н	-0.63100	-2.73880	1.94770
Н	-0.73420	-1.22460	2.87650
Η	1.65210	-1.04200	2.82050

Н	1.75860	-2.51680	1.83270
Н	-4.93150	0.78870	1.21670
Н	-4.37100	-2.37730	-1.64180
Н	-2.23750	0.46470	3.08280
Н	-3.05110	1.81440	2.26020
Н	-1.40040	1.36990	1.79240
Н	-6.61490	-1.57570	-1.17930
Н	-6.42470	0.18730	-1.30780
Н	-6.91620	-0.53260	0.23640
Н	-2.27990	-3.49760	-1.83450
Н	-1.05150	-3.30220	-0.55890
Н	-1.03760	-2.22770	-1.96710
Н	5.21900	-1.51630	-1.77290
Н	5.21920	1.88480	0.86350
Н	2.20980	-3.02460	-0.50750
Н	3.36840	-3.00550	-1.85970
Н	1.88150	-2.02640	-1.93330
Н	7.30820	1.17240	-0.21030
Н	6.73680	1.17010	-1.89140
Н	7.36730	-0.32590	-1.17630
Н	2.43010	1.05720	2.76890
Н	1.76300	2.00880	1.42730
Н	3.33190	2.45360	2.14520

2'-SIMes

 $E_{\rm SCF} = -1728.341324$ Ha $v_{\rm min} = 18.37$ cm⁻¹



В	0.18680	0.36860	-1.2727
С	0.29730	-0.42610	0.10760
С	-1.47280	2.63210	-0.83610
Ν	-0.73210	-0.92280	0.81120
Ν	1.44150	-0.67920	0.76790
С	-2.11120	-0.88160	0.43380
С	-0.30840	-1.55820	2.06750
С	1.22450	-1.43490	2.01010
С	2.76340	-0.38420	0.30840
С	-2.96390	0.05230	1.04520
С	-2.58290	-1.80890	-0.51320
С	-4.31140	0.05360	0.66950
С	-2.45220	1.03440	2.06550

С	-4.81510	-0.83820	-0.28330
С	-3.93710	-1.76660	-0.85760
С	-6.25920	-0.77030	-0.70910
С	-1.64840	-2.79600	-1.16100
С	3.36040	-1.23660	-0.63840
С	3.44710	0.72030	0.84450
С	4.66450	-0.95140	-1.05300
С	2.59890	-2.40060	-1.21450
С	5.37500	0.14690	-0.55080
С	4.75160	0.96530	0.39800
С	6.76480	0.45470	-1.04680
С	2.79830	1.61890	1.86480
Н	-0.82000	0.08270	-1.87710
Н	1.21560	0.27530	-1.91020
Н	-0.65730	-2.60190	2.09850
Н	-0.74380	-1.03050	2.92920
Н	1.64220	-0.89340	2.87160
Н	1.73220	-2.41110	1.94840
Н	-4.98030	0.79130	1.12030
Н	-4.31550	-2.47490	-1.59970
Н	-2.40490	0.58380	3.07260
Н	-3.11400	1.90860	2.12240
Н	-1.44800	1.39570	1.80200
Н	-6.59590	-1.71710	-1.15670
Н	-6.40300	0.02230	-1.46370
Н	-6.92020	-0.53430	0.13900
Н	-2.20750	-3.57110	-1.70350
Н	-0.99930	-3.29380	-0.42330
Н	-0.98620	-2.28540	-1.87900
Н	5.13790	-1.60400	-1.79200
Н	5.29190	1.82600	0.80120
Н	2.10830	-3.00130	-0.43250
Н	3.26250	-3.06260	-1.78780
Н	1.80460	-2.04230	-1.88950
Н	7.32850	1.06100	-0.32250
Н	6.72510	1.02300	-1.99220
Н	7.33550	-0.46550	-1.24520
Н	2.67320	1.10990	2.83590
Н	1.80160	1.94760	1.53120
Н	3.40900	2.51510	2.04080
S	-3.00120	2.99290	-0.96570
Р	0.14320	2.35880	-0.71880

2-CAAC^{Me} $E_{\rm SCF} = -1520.674146$ Ha $v_{\rm min} = 25.73 \ {\rm cm}^{-1}$ В 0.76000 1.53300 -1.3996 С 1.51000 0.46380 -0.47320 S 0.12590 2.93430 -0.13260 С -1.53120 2.73000 -0.08300 Р -3.09260 2.60280 -0.02090 Ν 0.96040 -0.56600 0.12280 С -0.44370 -0.89150 0.02450 С 1.92700 -1.48160 0.85010 С 3.18160 -0.59040 0.90190 С -1.31040 -0.48670 1.05700 С -0.92000 -1.57200 -1.11350 С -2.65940-0.841400.95690 С -0.87910 0.35690 2.22890 С -3.16530 -1.55000 -0.13600 С -2.28060 -1.89580 -1.16160 С -4.63590 -1.86270 -0.23080 С -0.05060 -1.93010 -2.29300 Η -0.20320 1.08290 -1.97280 Η 1.56310 2.09260 -2.12230 Η 3.24020 -0.10390 1.88670 Η 4.10200 -1.17620 0.76980 Η -3.34150 -0.51630 1.74670 Η -2.66230 -2.41550 -2.04480 Η -0.88310 -0.22460 3.16450 Η -1.58660 1.18990 2.34640 Η 0.11350 0.79800 2.08920 Η -5.02520 -2.257600.72070 Η -4.84580 -2.59790-1.02110 Η -5.20910 -0.94860 -0.46110 Η -0.59370 -3.22820 -1.73090 Η 0.21550 -2.99970-2.29000 Η 0.87780 -1.35000 -2.32740 С 3.00260 0.48630 -0.19550 С 3.74910 0.12630 -1.49810 Η 3.53190 0.86230 -2.28390 Η 4.83370 0.12350 -1.30760 Η 3.46830 -0.86800 -1.87500 С 3.45620 1.87400 0.28320

Н	3.32090	2.62760	-0.50500
Н	2.88440	2.19920	1.16500
Н	4.52410	1.84000	0.55170
С	2.12600	-2.75870	0.02360
Н	2.85660	-3.40540	0.53140
Н	1.18310	-3.31640	-0.06580
Н	2.50100	-2.54420	-0.98460
С	1.42890	-1.86510	2.24230
Н	1.31930	-0.98850	2.89080
Н	0.46680	-2.39480	2.19530
Н	2.16660	-2.53890	2.70340

2'-CAAC^{Me}



В	0.77790	1.49640	-1.4214
С	1.50990	0.44840	-0.48090
С	-1.37300	2.75350	-0.09070
Ν	0.94460	-0.56530	0.13940
С	-0.46050	-0.87880	0.03240
С	1.89650	-1.48230	0.87990
С	3.16810	-0.61480	0.90610
С	-1.33710	-0.46290	1.05300
С	-0.93200	-1.56290	-1.10610
С	-2.68870	-0.80430	0.93800
С	-0.91420	0.37280	2.23380
С	-3.18860	-1.51500	-0.15610
С	-2.29450	-1.87640	-1.16790
С	-4.66030	-1.81820	-0.26500
С	-0.05380	-1.94110	-2.27290
Н	-0.21210	1.06130	-1.96090
Н	1.57440	2.03710	-2.16770
Н	3.23790	-0.10390	1.87790
Н	4.07710	-1.22120	0.78800
Н	-3.37650	-0.46940	1.71870
Н	-2.66970	-2.40110	-2.05090
Η	-0.93290	-0.21480	3.16570
Н	-1.61910	1.20800	2.35200
Н	0.08310	0.80690	2.10850

Н	-5.06230	-2.20650	0.68400
Н	-4.86660	-2.55590	-1.05410
Н	-5.22610	-0.90220	-0.50580
Н	-0.58280	-1.74030	-3.21570
Н	0.19570	-3.01460	-2.25900
Н	0.88280	-1.37450	-2.30010
С	3.00820	0.43730	-0.21750
С	3.72630	0.01540	-1.51820
Н	3.53390	0.74310	-2.31800
Н	4.81150	-0.03210	-1.33680
Н	3.39830	-0.97270	-1.87200
С	3.52350	1.81720	0.21570
Н	3.38890	2.55860	-0.58400
Н	2.99320	2.18060	1.10840
Н	4.59780	1.75140	0.45120
С	2.06820	-2.78370	0.08510
Н	2.78560	-3.43310	0.60800
Н	1.11350	-3.32340	0.01030
Н	2.44620	-2.60310	-0.92840
С	1.40110	-1.82510	2.28400
Н	1.31230	-0.93240	2.91360
Н	0.42900	-2.33780	2.25500
Н	2.12870	-2.50250	2.75580
S	-2.93930	2.58730	-0.02930
Р	0.24600	3.02660	-0.11730

2) <u>Mechanism of the formation of 5 (calculated using Gaussian 16, Rev. C.01)</u>

PPB

 $E_{\rm SCF} = -1334.730737$ Ha $v_{\rm min} = 20.32 \text{ cm}^{-1}$



С	0.76380	0.87950	-0.01000
С	1.25820	-0.39260	-0.01820
В	-0.00090	-1.35660	0.00010
С	-0.00200	-2.90180	0.00020
С	1.01880	-3.63520	0.64840
С	-1.02380	-3.63360	-0.64800
С	1.00880	-5.02960	0.66560
Н	1.82450	-3.10090	1.15430
С	-1.01590	-5.02810	-0.66550
Н	-1.82890	-3.09810	-1.15380
С	-0.00400	-5.72850	0.00000
Н	1.79870	-5.57540	1.18750
Н	-1.80650	-5.57260	-1.18750
Н	-0.00480	-6.82170	-0.00010
С	2.68340	-0.76700	0.00590
С	3.58360	-0.19180	0.92420
С	3.17890	-1.73570	-0.88840
С	4.92750	-0.56380	0.93990
Н	3.21600	0.55150	1.63380
С	4.52610	-2.10120	-0.87870
Н	2.49480	-2.19980	-1.60140
С	5.40710	-1.51750	0.03580
Н	5.60640	-0.10690	1.66440
Н	4.88870	-2.84960	-1.58790
Н	6.46070	-1.80690	0.04780
С	1.55250	2.12630	-0.01260
С	1.28920	3.15390	0.91220
С	2.59530	2.30730	-0.94010
С	2.05670	4.31920	0.91870
Н	0.48290	3.03200	1.63680
С	3.35080	3.47900	-0.94220
Н	2.80540	1.51840	-1.66380
С	3.08710	4.48820	-0.01010
Н	1.84390	5.10250	1.65020
Н	4.15210	3.60520	-1.67430
Н	3.68190	5.40480	-0.01000
С	-1.54950	2.12850	0.01260
С	-2.59230	2.31090	0.94000
С	-1.28470	3.15580	-0.91200
С	-3.34610	3.48360	0.94210
Н	-2.80350	1.52210	1.66360
С	-2.05050	4.32220	-0.91850
Н	-0.47840	3.03290	-1.63650
С	-3.08090	4.49250	0.01020
Н	-4.14730	3.61080	1.67410
Н	-1.83660	5.10530	-1.64980
Н	-3.67430	5.41000	0.01010
С	-2.68450	-0.76330	-0.00590
С	-3.18140	-1.73120	0.88840

-3.58370	-0.18710	-0.92460
-4.52910	-2.09480	0.87860
-2.49810	-2.19600	1.60170
-4.92810	-0.55720	-0.94040
-3.21500	0.55550	-1.63430
-5.40920	-1.51000	-0.03610
-4.89290	-2.84250	1.58790
-5.60630	-0.09950	-1.66510
-6.46310	-1.79800	-0.04820
	-3.58370 -4.52910 -2.49810 -4.92810 -3.21500 -5.40920 -4.89290 -5.60630 -6.46310	-3.58370-0.18710-4.52910-2.09480-2.49810-2.19600-4.92810-0.55720-3.215000.55550-5.40920-1.51000-4.89290-2.84250-5.60630-0.09950-6.46310-1.79800

Int1A

 $E_{\rm SCF} = -3063.142434$ Ha $v_{\rm min} = 11.04$ cm⁻¹

С	2.46080	0.18970	0.9314
С	1.33990	-0.80700	1.23730
С	2.38800	-1.29640	-0.92150
С	3.02450	-0.09070	-0.27320
С	0.17600	-0.50180	0.28180
Р	0.54650	-0.87300	-1.38740
В	1.63350	-2.05510	0.22990
С	1.34140	-3.57200	0.42610
С	1.71210	-4.21630	1.62340
С	0.78470	-4.36430	-0.59710
С	1.53620	-5.59260	1.78950
Н	2.14630	-3.63470	2.43830
С	0.59700	-5.73660	-0.43250
Н	0.48760	-3.88800	-1.53480
С	0.97460	-6.35670	0.76350
Н	1.83390	-6.06810	2.72770
Н	0.15620	-6.32700	-1.24010
Н	0.83030	-7.43250	0.89440
С	1.07830	-1.18710	2.67260
С	2.08910	-1.02380	3.63690
С	-0.08570	-1.87220	3.06240
С	1.93030	-1.49350	4.94220
Н	3.02240	-0.53390	3.36200
---	----------	----------	----------
С	-0.24830	-2.33850	4.36760
Н	-0.86770	-2.06590	2.33080
С	0.75540	-2.14750	5.32010
Н	2.73570	-1.34770	5.66660
Н	-1.16480	-2.87060	4.63560
Н	0.62860	-2.51430	6.34160
С	2.69810	1.38540	1.75680
С	1.65570	1.95140	2.51660
С	3.97760	1.97160	1.85290
С	1.88670	3.05030	3.34390
Н	0.65510	1.52410	2.45270
С	4.20160	3.07980	2.66890
Н	4.80640	1.53820	1.29310
С	3.15760	3.62530	3.42410
Н	1.06310	3.46050	3.93410
Н	5.20340	3.51300	2.72600
Н	3.33650	4.48480	4.07460
С	3.93620	0.77390	-1.05490
С	3.47920	2.02090	-1.51190
С	5.22470	0.35120	-1.41830
С	4.29670	2.83240	-2.30030
Н	2.47120	2.33930	-1.24410
С	6.04470	1.16660	-2.20050
Н	5.57960	-0.62630	-1.08690
С	5.58410	2.40990	-2.64410
Н	3.92720	3.80010	-2.64960
Н	7.04690	0.82560	-2.47160
Н	6.22520	3.04530	-3.26010
С	3.12520	-1.98120	-2.03560
С	3.14590	-1.44790	-3.33430
С	3.87320	-3.14160	-1.78080
С	3.88850	-2.05390	-4.34910
Н	2.58130	-0.53650	-3.54290
С	4.61810	-3.75090	-2.79350
Н	3.86740	-3.56940	-0.77690
С	4.62820	-3.20930	-4.08180
Н	3.89360	-1.61910	-5.35180
Н	5.19180	-4.65500	-2.57420
Н	5.21050	-3.68580	-4.87450
S	-1.35790	0.04970	0.84900
В	-2.42630	0.11800	-0.76950
Н	-1.68670	0.38770	-1.69570
Н	-3.00910	-0.93160	-0.93560
С	-4.32480	3.50060	-0.70320
С	-5.48410	2.49710	-0.61290
С	-3.45770	1.33500	-0.65350
N	-3.14270	2.63440	-0.56390
Ν	-4.78990	1.20440	-0.73260

Н	-4.28510	4.01870	-1.67610
Н	-4.34690	4.26520	0.08550
Н	-6.22730	2.61800	-1.41360
Н	-6.01560	2.54310	0.35230
С	-1.82710	3.19550	-0.47910
С	-1.03460	3.33490	-1.62830
С	-1.38780	3.65050	0.78190
С	0.23100	3.92660	-1.48540
С	-0.13480	4.25240	0.86590
С	0.69970	4.38780	-0.25340
Н	0.86170	4.03100	-2.37250
Н	0.22000	4.60360	1.83530
С	-5.51730	-0.02780	-0.68710
С	-6.03870	-0.54860	-1.88370
С	-5.70590	-0.66980	0.54700
С	-6.78350	-1.72900	-1.81890
С	-6.45930	-1.85030	0.56290
С	-7.00680	-2.39350	-0.60450
Н	-7.19110	-2.14840	-2.74290
Н	-6.61460	-2.36280	1.51610
С	-5.74820	0.12470	-3.19930
Н	-6.12460	1.16060	-3.22900
Н	-4.66180	0.17050	-3.37940
Н	-6.21000	-0.42190	-4.03300
С	-5.06670	-0.14540	1.80610
Н	-5.13630	0.95000	1.88890
Н	-5.53360	-0.58480	2.69850
Н	-3.99370	-0.40100	1.83070
С	-7.78850	-3.68190	-0.57100
Н	-8.68600	-3.62460	-1.20660
Н	-7.17740	-4.51980	-0.94800
Н	-8.10590	-3.93680	0.45050
С	-1.48320	2.86200	-2.98660
Н	-0.99680	1.90660	-3.23950
Н	-2.56720	2.69250	-3.03630
Н	-1.21010	3.59280	-3.76290
С	-2.22260	3.44000	2.01730
Н	-1.72750	3.86910	2.89920
Н	-3.22180	3.89870	1.93930
Н	-2.36640	2.36320	2.20120
С	2.07370	4.98220	-0.09650
Н	2.73610	4.28100	0.43640
Н	2.53370	5.20860	-1.06860
Н	2.04170	5.90900	0.49730

Int2A

 $E_{\rm SCF} = -3063.133010 \text{ Ha}$ $v_{\rm min} = 12.03 \text{ cm}^{-1}$



S	1.06870	-0.26190	1.10320
В	2.33500	0.32430	-0.26740
Н	2.49800	-0.52650	-1.12190
Н	2.02260	1.40160	-0.70490
С	5.71800	0.05760	1.63510
С	5.33030	1.52840	1.88690
С	3.67660	0.50670	0.58640
Ν	4.60170	-0.43490	0.81180
Ν	4.03380	1.64240	1.20160
Н	6.66800	-0.05050	1.08900
Н	5.79580	-0.52960	2.56300
Н	6.04820	2.24290	1.45360
Н	5.22440	1.76570	2.95610
С	4.61020	-1.75420	0.25330
С	5.12360	-1.92760	-1.04550
С	4.13580	-2.83510	1.01290
С	5.16390	-3.22110	-1.57200
С	4.20030	-4.11320	0.44340
С	4.70750	-4.32680	-0.84100
Н	5.55620	-3.36880	-2.58220
Н	3.81810	-4.96130	1.01620
С	3.33030	2.88790	1.11660
С	3.51280	3.69290	-0.02100
С	2.48090	3.27300	2.16850
С	2.82050	4.90580	-0.08820
С	1.80270	4.49130	2.05030
С	1.95290	5.31660	0.92930
Н	2.94660	5.53440	-0.97310
Н	1.12850	4.79700	2.85510
С	4.35780	3.23020	-1.17660
Н	5.29090	2.74590	-0.85040
Η	3.79460	2.49060	-1.77010
Н	4.61660	4.06860	-1.83800

С	2.26190	2.38120	3.36110
Н	3.20830	2.08760	3.84310
Н	1.64240	2.88370	4.11720
Н	1.74760	1.45790	3.04570
С	1.15660	6.58900	0.79680
Н	0.97990	7.06260	1.77450
Н	1.66150	7.31790	0.14540
Н	0.16730	6.38140	0.35230
С	5.56760	-0.74050	-1.85850
Н	4.70130	-0.10980	-2.11740
Н	6.27740	-0.10160	-1.30880
Н	6.05150	-1.05890	-2.79230
С	3.51380	-2.63040	2.36720
Н	3.38350	-3.58910	2.88810
Н	4.11480	-1.96940	3.01080
Н	2.52240	-2.16000	2.25150
С	4.72210	-5.70430	-1.45200
Н	4.54170	-6.48350	-0.69760
Н	3.93660	-5.79900	-2.22140
Н	5.68350	-5.91780	-1.94540
С	-0.59410	-0.28840	0.38260
С	-1.27030	-1.63970	0.26310
С	-2.67010	0.82710	-0.42580
С	-2.61910	-1.59490	0.37970
С	-3.15780	-0.18740	0.58530
В	-1.15700	0.74580	-0.69590
Р	-1.76650	0.86980	1.35520
С	-0.47780	-2.83700	-0.08430
С	-0.72890	-4.07720	0.52720
С	0.55160	-2.75720	-1.03940
С	0.01530	-5.20630	0.18140
Н	-1.51130	-4.15030	1.28380
С	1.29050	-3.88630	-1.38780
Н	0.78430	-1.79870	-1.50200
С	1.02540	-5.11720	-0.78050
Н	-0.19480	-6.16160	0.66930
Н	2.09140	-3.79590	-2.12440
Н	1.61070	-6.00050	-1.04750
С	-3.55230	-2.71190	0.09650
С	-3.52780	-3.34260	-1.15990
С	-4.48400	-3.15770	1.05000
С	-4.40250	-4.38970	-1.45270
Н	-2.80670	-3.00430	-1.90630
С	-5.35800	-4.20610	0.75820
Н	-4.51860	-2.67970	2.02970
С	-5.32180	-4.82570	-0.49420
Н	-4.36630	-4.86730	-2.43510
Н	-6.07250	-4.54020	1.51460
Н	-6.00780	-5.64520	-0.72240

С	-4.55960	-0.05320	1.10410
С	-5.63980	-0.18530	0.21850
С	-4.82400	0.15230	2.46400
С	-6.95250	-0.11080	0.68180
Н	-5.44240	-0.35070	-0.84170
С	-6.13950	0.23070	2.93160
Н	-3.98940	0.24620	3.16270
С	-7.20710	0.09880	2.04090
Н	-7.78190	-0.21710	-0.02130
Н	-6.32860	0.39320	3.99550
Н	-8.23600	0.15860	2.40410
С	-3.54060	1.89430	-0.97900
С	-4.26020	2.79220	-0.17450
С	-3.64700	2.00790	-2.37450
С	-5.07220	3.77000	-0.74970
Н	-4.17960	2.72580	0.91190
С	-4.46600	2.98060	-2.95060
Н	-3.07340	1.32860	-3.00770
С	-5.18280	3.86490	-2.14020
Н	-5.62280	4.46160	-0.10720
Н	-4.53690	3.05290	-4.03860
Н	-5.82090	4.62950	-2.59000
С	-0.39900	1.75240	-1.62030
С	-0.33680	3.12660	-1.33780
С	0.22270	1.29130	-2.79330
С	0.34290	4.00610	-2.18210
Н	-0.81430	3.51170	-0.43340
С	0.89680	2.16630	-3.64680
Н	0.20030	0.22440	-3.03150
С	0.96510	3.52880	-3.33910
Н	0.38640	5.06980	-1.93720
Н	1.37860	1.78410	-4.55070
Н	1.49780	4.21650	-4.00130

Int3A

 $E_{\rm SCF} = -3063.134809$ Ha $v_{\rm min} = 13.51$ cm⁻¹



С	-1.31750	2.57980	0.09430
С	-0.02830	2.94710	-0.27300
С	0.84150	1.83110	-0.66900
С	0.19180	0.61910	-0.50090
Р	-1.39020	0.78550	0.28440
С	-2.37050	-0.30470	-0.78350
S	0.35210	-0.91610	-1.34760
В	-1.54420	-1.35750	-1.39570
С	-3.83190	-0.19320	-0.74040
С	-4.50940	0.40050	0.34840
С	-4.63480	-0.65240	-1.81020
С	-5.89990	0.48880	0.39270
Н	-3.93030	0.79860	1.18270
С	-6.02550	-0.57610	-1.76220
Н	-4.14710	-1.06230	-2.69510
С	-6.67460	-0.01150	-0.65750
Н	-6.37990	0.95830	1.25550
Н	-6.61090	-0.94680	-2.60820
Н	-7.76450	0.05790	-0.62800
С	-1.83210	-2.70870	-2.13320
С	-3.01640	-3.44310	-1.90750
С	-0.90040	-3.27670	-3.02910
С	-3.25010	-4.67200	-2.52250
Н	-3.76750	-3.04000	-1.23040
С	-1.12540	-4.50760	-3.65140
Н	0.02550	-2.74190	-3.25490
С	-2.30170	-5.21590	-3.39680
Н	-4.17880	-5.21200	-2.31860
Н	-0.37830	-4.91310	-4.33880
Н	-2.48290	-6.17980	-3.87930
С	-2.39620	3.48970	0.51130
С	-3.07280	3.31280	1.73280

С	-2.79140	4.55470	-0.31970
С	-4.11490	4.16230	2.10610
Н	-2.75850	2.50570	2.39850
С	-3.83060	5.40500	0.05630
Н	-2.27980	4.70270	-1.27190
С	-4.49990	5.21310	1.26910
Н	-4.62500	4.00610	3.06010
Н	-4.12500	6.22200	-0.60720
Н	-5.31570	5.87910	1.55990
С	0.40850	4.36780	-0.28450
С	0.88620	4.95900	-1.46640
С	0.32310	5.15620	0.87450
С	1.27500	6.29880	-1.48590
Н	0.95080	4.35720	-2.37500
С	0.71430	6.49620	0.85610
Н	-0.05860	4.70840	1.79380
С	1.19320	7.07230	-0.32390
Н	1.64250	6.74260	-2.41450
Н	0.64130	7.09460	1.76770
Н	1.49760	8.12170	-0.33940
С	2.23120	2.00360	-1.16040
С	2.71860	1.24990	-2.24420
С	3.10830	2.91930	-0.54620
С	4.02510	1.41680	-2.70600
Н	2.06220	0.53290	-2.73730
С	4.41230	3.08800	-1.01100
Н	2.76330	3.50580	0.30480
С	4.87690	2.34120	-2.09710
Н	4.37600	0.82180	-3.55250
Н	5.06940	3.81040	-0.52000
Н	5.89620	2.47950	-2.46620
В	1.66650	-2.11850	-0.57330
Н	1.40010	-3.19130	-1.07710
Н	2.71000	-1.67420	-0.98510
С	1.49210	-3.18220	3.17180
С	2.95890	-2.77260	2.99240
C	1.78040	-2.34920	1.01230
Ν	2.99890	-2.35960	1.58210
Ν	0.86920	-2.73820	1.91110
Н	3.25340	-1.93080	3.63890
Н	3.66450	-3.59700	3.17080
Н	1.00960	-2.70530	4.03410
Н	1.36090	-4.27230	3.26880
С	4.18410	-1.76380	1.03980
С	4.36780	-0.37890	1.20340
С	5.12200	-2.56840	0.37930
С	5.53350	0.19070	0.68690
С	6.27360	-1.95250	-0.12570
С	6.49450	-0.57760	0.01580

Н	5.68290	1.26690	0.79020
Н	7.01060	-2.56320	-0.65410
С	-0.55720	-2.79020	1.78520
С	-1.30630	-1.80070	2.45670
С	-1.17610	-3.86630	1.12780
С	-2.69860	-1.87600	2.39410
С	-2.57470	-3.91110	1.12640
С	-3.35360	-2.91660	1.72350
Н	-3.29110	-1.09470	2.87530
Н	-3.06550	-4.74300	0.61840
С	-0.39720	-4.93830	0.41530
Н	-0.89630	-5.91290	0.51770
Н	-0.33910	-4.71080	-0.66090
Н	0.63220	-5.03040	0.78840
С	-0.63870	-0.71010	3.25610
Н	-1.30460	0.15570	3.35900
Н	-0.38700	-1.05820	4.27440
Н	0.28610	-0.35770	2.77980
С	-4.85310	-2.93810	1.60300
Н	-5.33920	-2.48060	2.47720
Н	-5.17100	-2.35500	0.72240
Н	-5.23400	-3.96360	1.48540
С	4.85510	-4.03460	0.16590
Н	4.62600	-4.55540	1.10970
Н	3.98580	-4.17500	-0.49770
Н	5.72000	-4.53240	-0.29400
С	3.31260	0.46640	1.86690
Н	3.05320	0.09770	2.87230
Н	3.64860	1.50590	1.96500
Н	2.38450	0.47680	1.27350
С	7.71700	0.08170	-0.56800
Н	8.21320	0.73270	0.16910
Н	8.44980	-0.65790	-0.92160
Н	7.43830	0.71880	-1.42400

5 $E_{SCF} = -3063.168728$ Ha $v_{min} = 14.43$ cm⁻¹



-2.24910	0.07280	0.2977
-2.67780	0.29700	-1.22570
-0.71640	0.22690	0.73920
-1.15780	-1.28780	1.10200
-0.28830	1.13120	1.85070
0.46630	0.12940	-0.71010
-1.55020	-1.66390	2.59680
-0.10210	-2.64050	0.21780
1.11460	-1.50740	-0.34820
2.48710	-1.53270	-0.33680
3.27730	-2.73970	-0.03220
3.05040	-0.16640	-0.47840
2.12300	0.85820	-0.49610
4.50760	0.06910	-0.61300
2.40940	2.29100	-0.73130
-2.99190	-0.64210	-2.12650
-2.81990	1.51390	-1.77060
-2.66620	2.76330	-1.08700
-3.29910	1.45090	-3.16020
-3.35530	-0.06220	-3.43100
-3.09820	-2.05120	-1.89130
-3.67320	3.19440	-0.20390
-1.52920	3.55410	-1.35200
-1.37560	4.74220	-0.63410
-0.52100	3.16670	-2.40020
-2.32140	5.16890	0.30690
-3.47300	4.39750	0.48640
-2.07850	6.41340	1.11970
-4.93490	2.40480	0.03090
-2.13250	-2.91650	-2.43080
-4.19210	-2.53190	-1.14510
-4.27880	-3.90760	-0.91730
-5.23120	-1.59420	-0.58690
	-2.24910 -2.67780 -0.71640 -1.15780 -0.28830 0.46630 -1.55020 -0.10210 1.11460 2.48710 3.27730 3.05040 2.12300 4.50760 2.40940 -2.99190 -2.81990 -2.81990 -2.81990 -2.86620 -3.29910 -3.35530 -3.09820 -3.67320 -1.52920 -1.37560 -0.52100 -2.32140 -3.47300 -2.07850 -4.93490 -2.13250 -4.93490 -2.13250 -4.27880 -5.23120	-2.24910 0.07280 -2.67780 0.29700 -0.71640 0.22690 -1.15780 -1.28780 -0.28830 1.13120 0.46630 0.12940 -1.55020 -1.66390 -0.10210 -2.64050 1.11460 -1.50740 2.48710 -1.53270 3.27730 -2.73970 3.05040 -0.16640 2.12300 0.85820 4.50760 0.06910 2.40940 2.29100 -2.99190 -0.64210 -2.81990 1.51390 -2.66620 2.76330 -3.29910 1.45090 -3.35530 -0.06220 -3.09820 -2.05120 -3.67320 3.19440 -1.52920 3.55410 -1.37560 4.74220 -0.52100 3.16670 -2.32140 5.16890 -3.47300 4.39750 -2.07850 6.41340 -4.93490 2.40480 -2.13250 -2.91650 -4.19210 -2.53190 -5.23120 -1.59420

S81

С	-3.32720	-4.80140	-1.42750
С	-2.27640	-4.28790	-2.19220
С	-3.41040	-6.27380	-1.11980
С	-0.96890	-2.40030	-3.23370
С	0.89790	0.85280	2.55680
С	-1.00610	2.28370	2.19750
С	-0.55350	3.13910	3.20730
С	0.62940	2.85570	3.89330
С	1.35200	1.70240	3.56410
С	-2.84060	-1.51030	3.13160
С	-0.54820	-2.14120	3.46370
С	-3.12210	-1.80730	4.46820
С	-2.10790	-2.26620	5.31180
С	-0.81660	-2.43330	4.80180
С	4.39550	-2.70170	0.82440
С	2.88540	-3.98720	-0.55380
С	3.58480	-5.15230	-0.23660
С	4.69480	-5.09760	0.61030
С	5.09390	-3.86640	1.14050
С	5.26940	-0.66430	-1.53920
С	5.15730	1.02990	0.18150
С	6.63850	-0.43320	-1.67750
С	7.27330	0.52700	-0.88410
С	6.52760	1.25540	0.04790
С	1.90580	3.27420	0.13850
С	3.16860	2.70790	-1.84160
С	3.41820	4.06050	-2.07280
С	2.92090	5.02900	-1.19310
С	2.16810	4.62780	-0.08640
Н	-3.06630	0.54790	1.04600
Н	-2.39860	-1.24490	0.45970
Н	-2.60580	1.97750	-3.83010
Η	-4.28360	1.94050	-3.23400
Н	-4.35430	-0.41410	-3.72920
Η	-2.63650	-0.38230	-4.19910
Н	-0.47980	5.34150	-0.80830
Η	-4.23900	4.73200	1.19140
Н	-0.89540	3.41280	-3.40970
Η	-0.29920	2.09020	-2.37630
Н	0.42110	3.70960	-2.25910
Н	-3.00040	6.77560	1.59760
Н	-1.66520	7.22560	0.50200
Η	-1.34550	6.20850	1.91890
Н	-5.17410	1.73930	-0.80960
Н	-5.78830	3.07980	0.19040
Н	-4.84020	1.76820	0.92460
Н	-5.11350	-4.29240	-0.32530
Н	-1.51880	-4.96920	-2.58800
Н	-4.84190	-1.03020	0.27560

Н	-6.11720	-2.14950	-0.25050
Н	-5.55630	-0.85150	-1.33250
Н	-2.96590	-6.88100	-1.92250
Н	-4.45110	-6.59990	-0.97350
Н	-2.86000	-6.50380	-0.19120
Н	-1.23430	-2.29160	-4.30030
Н	-0.12140	-3.09640	-3.17520
Н	-0.62120	-1.42540	-2.86440
Н	-1.91830	2.52430	1.65580
Н	-1.13150	4.03390	3.45410
Н	0.98660	3.52430	4.68050
Н	2.27660	1.46500	4.09650
Н	1.47320	-0.03630	2.29310
Н	-3.64870	-1.14920	2.49100
Н	-4.13810	-1.68000	4.85240
Н	-2.32250	-2.49690	6.35860
Н	-0.01510	-2.79710	5.45040
Н	0.45980	-2.29700	3.07220
Н	2.02500	-4.03350	-1.22390
Н	3.26210	-6.10860	-0.65620
Н	5.24520	-6.00860	0.85800
Н	5.95520	-3.81270	1.81110
Н	4.71070	-1.75160	1.25610
Н	4.77770	-1.42150	-2.15290
Н	7.21440	-1.00980	-2.40570
Н	8.34660	0.70380	-0.98830
Н	7.01680	2.00370	0.67640
Н	4.57580	1.59590	0.91110
Н	3.55980	1.95510	-2.52800
Н	4.00600	4.36180	-2.94370
Н	3.12230	6.08850	-1.37010
Н	1.77790	5.37120	0.61310
Н	1.31130	2.97570	0.99950

3) Mechanism of the formation of 6 (calculated using Turbomole 7.8.1)

2-SIMes

 $E_{\rm SCF} = -1727.5675660$ Ha $v_{\rm min} = 21.72$ cm⁻¹



В	0.20167	0.40377	-1.26501
С	0.30424	-0.45512	0.09052
S	0.03629	2.29742	-0.70886
С	-1.59730	2.64589	-0.82140
Р	-3.10839	3.04123	-0.94413
Ν	-0.72176	-0.98478	0.76925
Ν	1.45065	-0.73847	0.72897
С	-2.10651	-0.90567	0.41389
С	-0.29147	-1.69596	1.98380
С	1.24035	-1.55252	1.93657
С	2.77106	-0.39471	0.29553
С	-2.92903	0.02221	1.07435
С	-2.60973	-1.78600	-0.56006
С	-4.28323	0.05924	0.72699
С	-2.37212	0.96426	2.10902
С	-4.82012	-0.78683	-0.25049
С	-3.96943	-1.70570	-0.87846
С	-6.27105	-0.67573	-0.64363
С	-1.70277	-2.76071	-1.26435
С	3.41047	-1.21608	-0.65033
С	3.40650	0.72706	0.85470
С	4.71455	-0.88805	-1.03368
С	2.68771	-2.38551	-1.26499
С	5.38156	0.22429	-0.50257
С	4.71271	1.01508	0.43960
С	6.77287	0.57843	-0.96338
С	2.69661	1.60691	1.85089
Н	-0.77476	0.10591	-1.91235
Н	1.25348	0.34774	-1.86825
Н	-0.62956	-2.74332	1.94499
Н	-0.73505	-1.23046	2.87659
Н	1.65157	-1.04329	2.82121
Н	1.76041	-2.51849	1.83329
Н	-4.93054	0.79150	1.21683
Н	-4.37338	-2.37575	-1.64270
Н	-2.23667	0.46300	3.08413
Н	-3.05033	1.81388	2.26236
Н	-1.39929	1.36941	1.79437
Н	-6.61751	-1.57230	-1.17911
Н	-6.42487	0.19082	-1.30999
Н	-6.91749	-0.52655	0.23552

-2.28352	-3.49941	-1.83464
-1.05476	-3.30548	-0.55871
-1.03900	-2.23108	-1.96778
5.22189	-1.51612	-1.77173
5.21806	1.88794	0.86247
2.21474	-3.02756	-0.50458
3.37279	-3.00760	-1.85794
1.88365	-2.03093	-1.93135
7.30876	1.17676	-0.21130
6.73681	1.17345	-1.89275
7.36904	-0.32221	-1.17711
2.42970	1.05699	2.76921
1.76161	2.00906	1.42777
3.33071	2.45464	2.14590
	-2.28352 -1.05476 -1.03900 5.22189 5.21806 2.21474 3.37279 1.88365 7.30876 6.73681 7.36904 2.42970 1.76161 3.33071	-2.28352-3.49941-1.05476-3.30548-1.03900-2.231085.22189-1.516125.218061.887942.21474-3.027563.37279-3.007601.88365-2.030937.308761.176766.736811.173457.36904-0.322212.429701.056991.761612.009063.330712.45464

CBBF



С	13.63044	0.33110	20.83820
С	13.56415	-0.66957	19.52152
С	13.74153	-0.04206	18.15069
Н	13.09562	0.83913	18.03588
Н	13.46516	-0.77249	17.37917
Н	14.78457	0.25945	17.98902
В	12.10945	-0.32804	20.35609
Н	11.33122	0.37473	19.79880
В	12.56844	-0.21870	22.05973
Н	12.03738	0.60732	22.74203
В	14.32543	-0.47992	22.17302
Н	14.98045	0.16985	22.93305
В	14.94301	-0.74527	20.54036
Н	15.95260	-0.30412	20.09625
В	12.46104	-1.95520	19.77848
Н	11.85652	-2.34941	18.82480
В	11.82527	-1.70506	21.41789

Н	10.70377	-2.01177	21.70702
В	13.20386	-1.80568	22.55313
Н	13.07478	-2.19483	23.67927
В	14.68310	-2.12781	21.59943
Н	15.62325	-2.74096	22.01873
В	14.21095	-2.20964	19.88647
Н	14.79141	-2.77858	19.00898
В	13.13545	-2.88543	21.13416
Н	12.95631	-4.06786	21.21461
В	13.87926	1.89425	20.67806
С	15.25692	2.63897	20.68350
С	14.99273	4.00148	20.36106
С	13.53235	4.22791	20.21538
С	12.81374	3.01762	20.44039
С	16.57646	2.25423	20.94281
С	11.41544	3.05701	20.43181
С	12.87176	5.42034	19.94663
С	16.02007	4.93159	20.26019
С	17.34023	4.51617	20.50723
Н	15.81390	5.97410	20.00535
С	17.61656	3.19326	20.85628
Н	16.80856	1.22761	21.22653
Н	13.42710	6.34428	19.76719
С	11.46609	5.42936	19.92329
Н	10.83495	2.15776	20.63759
С	10.74297	4.26249	20.17485
Н	18.64461	2.88745	21.06409
Н	10.93619	6.36305	19.71715
Н	9.65074	4.28666	20.17355
Н	18.15583	5.24051	20.43521

Int1B

 $E_{\rm SCF} = -2584.3107550 \text{ Ha}$ $v_{\rm min} = 8.45 \text{ cm}^{-1}$



С	12.71187	2.43689	16.88133
С	13.53128	1.39537	17.88172
С	14.05476	1.92407	19.20415
Н	14.17158	3.01662	19.17288
Н	15.03977	1.48456	19.40747
Н	13.37982	1.65900	20.02825
В	14.31005	1.97164	16.47177
Н	15.17009	2.77594	16.62254
В	13.04849	2.06732	15.24055
Н	13.08087	2.97482	14.46483
В	11.51513	1.59817	16.00005
Н	10.50653	2.18649	15.74272
В	11.83822	1.19301	17.68808
Н	11.12953	1.48392	18.59651
В	14.46265	0.28451	16.97388
Н	15.50443	-0.06468	17.44791
В	14.14704	0.67630	15.27601
Н	14.98601	0.52540	14.43321
В	12.40164	0.43734	14.97989
Н	11.97530	0.11056	13.90765
В	11.65085	-0.10558	16.50918
Н	10.69036	-0.82080	16.55841
В	12.93463	-0.19466	17.73603
Н	12.93845	-0.87249	18.72223
В	13.28255	-0.67576	16.05818
Н	13.50543	-1.82162	15.78291
С	12.73980	6.59760	16.10892
Р	13.70697	5.25465	16.65943
В	12.41645	3.98687	17.17627
С	11.21264	4.47182	18.03853
С	10.27473	5.41766	17.54851
С	10.27288	5.86520	16.13437
С	11.39823	6.43096	15.47768

S	13.33398	8.22036	15.93434
С	11.08752	4.05654	19.38101
С	11.24879	6.86264	14.14179
С	9.06258	5.75752	15.42197
С	9.25919	5.89285	18.39704
С	9.17006	5.47829	19.72492
Н	8.54416	6.62120	18.00784
С	10.09480	4.55660	20.22173
Н	11.80152	3.34190	19.78886
Н	8.20400	5.31226	15.92894
С	8.94220	6.16998	14.09756
Н	12.11344	7.29988	13.64154
С	10.04868	6.72608	13.45119
Н	10.04180	4.22493	21.26180
Н	7.99224	6.04900	13.57132
Н	9.98058	7.04909	12.40941
Н	8.38468	5.87865	20.37099
В	15.18362	8.31481	16.54544
Н	15.23387	9.27702	17.28455
Н	15.51661	7.27248	17.05809
С	16.01712	8.60514	15.19937
Ν	16.12813	9.80784	14.61128
С	16.93559	9.76322	13.38158
С	17.24230	8.26280	13.23697
Ν	16.65361	7.68996	14.45983
Н	18.31965	8.04071	13.19932
Н	16.36799	10.16850	12.53124
Н	17.84131	10.37892	13.50657
Н	16.77252	7.81410	12.34802
С	15.64912	11.05236	15.13267
С	16.39179	11.69699	16.13911
С	15.92580	12.92586	16.61763
С	14.75696	13.51683	16.12018
С	14.05473	12.85260	15.10711
С	14.48098	11.62146	14.59440
С	17.63520	11.06528	16.70742
Н	16.49172	13.43483	17.40312
С	14.25131	14.82072	16.68342
Н	13.14292	13.30199	14.70367
С	13.70785	10.93336	13.49899
С	16.86066	6.30630	14.76692
С	17.89226	5.96431	15.66242
С	18.15770	4.60969	15.87047
С	17.43708	3.60405	15.20808
С	16.40600	3.98388	14.34410
С	16.09293	5.33088	14.11371
С	18.66311	7.03259	16.39265
Н	18.95427	4.32812	16.56556
С	17.76238	2.15295	15.45158

Н	15.80969	3.21282	13.85119
С	14.95906	5.70734	13.19578
Н	14.17852	4.93400	13.21156
Н	15.30030	5.81232	12.15039
Н	14.49663	6.65671	13.50003
Н	17.58910	1.88235	16.50596
Н	18.82187	1.94194	15.23117
Н	17.14075	1.48943	14.83648
Н	19.52322	6.60443	16.92627
Н	19.03876	7.81181	15.70940
Н	18.01974	7.53800	17.13198
Н	17.37384	10.19806	17.33585
Н	18.19330	11.78043	17.32782
Н	18.31031	10.69768	15.91826
Н	12.73864	11.42547	13.33713
Н	14.25298	10.95769	12.53938
Н	13.51596	9.87936	13.75018
Н	13.68840	15.39509	15.93206
Н	15.07627	15.44908	17.05233
Н	13.57148	14.64018	17.53451

Int2B

 $E_{\rm SCF} = -2584.3479602$ Ha $v_{\rm min} = 5.85$ cm⁻¹



С	13.15045	5.30156	15.76451
С	13.84342	3.80020	16.09184
С	14.45017	3.50384	17.44988
Н	15.06478	4.34212	17.80039
Н	15.08734	2.61441	17.36006
Н	13.66597	3.29833	18.18717
В	14.64623	4.87943	15.03990
Н	15.62770	5.41737	15.43945
В	13.37649	5.65971	14.10555
Н	13.50263	6.80362	13.80260
В	11.82818	5.05144	14.68550
Н	10.87212	5.75135	14.75540
В	12.14398	3.90924	15.98105

Н	11.50697	3.81462	16.98109
В	14.58771	3.14164	14.70174
Н	15.58809	2.50516	14.86978
В	14.28014	4.30180	13.40652
Н	15.06808	4.45135	12.51546
В	12.51826	4.40965	13.18221
Н	12.02193	4.67090	12.11962
В	11.74520	3.31315	14.35935
Н	10.69423	2.76859	14.16458
В	13.03201	2.53649	15.28960
Н	12.97375	1.48566	15.86018
В	13.26785	2.84094	13.55606
Н	13.33125	1.93371	12.77261
С	12.71068	7.89577	16.16894
Р	15.02136	6.89569	17.67046
В	13.16906	6.54207	16.92518
С	12.06602	6.26985	18.07561
С	10.72839	6.70828	17.89711
С	10.33346	7.42498	16.66024
С	11.30734	8.05472	15.82960
S	13.76405	9.13357	15.79684
С	12.37634	5.59227	19.26518
С	10.90656	8.75773	14.67360
С	8.98709	7.52308	16.26525
С	9.77250	6.46320	18.90326
С	10.10742	5.77673	20.06749
Н	8.75254	6.83424	18.78995
С	11.42081	5.33648	20.24987
Н	13.40400	5.26802	19.43760
Н	8.21761	7.02671	16.85646
С	8.60916	8.19771	15.10691
Н	11.67610	9.20913	14.04407
С	9.57106	8.82136	14.30117
Н	11.70462	4.81024	21.16542
Н	7.55453	8.22681	14.82132
Н	9.27729	9.33706	13.38423
Н	9.34996	5.60111	20.83554
В	15.33033	8.68179	16.84374
Н	15.28721	9.50074	17.73818
Н	14.60933	7.40835	18.93436
С	16.75002	8.93147	16.13890
Ν	17.85063	9.12412	16.88993
С	19.05831	9.34914	16.08189
С	18.49316	9.43609	14.65791
Ν	17.08396	9.04847	14.84269
Н	18.98917	8.75396	13.95397
Н	19.56430	10.27128	16.40456
Н	19.76440	8.51332	16.21060
Н	18.54036	10.45408	14.23689

С	17.91464	9.14484	18.32126
С	18.29933	7.98286	19.01350
С	18.37265	8.04971	20.41028
С	18.08395	9.22505	21.11396
С	17.73342	10.36933	20.38493
С	17.64841	10.35454	18.98937
С	18.60780	6.70232	18.28381
Н	18.66168	7.15151	20.96301
С	18.12427	9.25348	22.62061
Н	17.52085	11.30088	20.91718
С	17.26622	11.59345	18.22196
С	16.24401	8.85204	13.70035
С	16.32552	7.62353	13.01589
С	15.49248	7.43144	11.91193
С	14.58732	8.41377	11.48974
С	14.57796	9.64320	12.15788
С	15.41320	9.89507	13.25403
С	17.30104	6.55441	13.43530
Н	15.51749	6.47008	11.39539
С	13.62140	8.11920	10.37255
Н	13.89680	10.43085	11.82330
С	15.42972	11.25817	13.89945
Н	16.17180	11.91056	13.40580
Н	15.68764	11.21967	14.96660
Н	14.44975	11.74736	13.80872
Н	12.84844	7.41155	10.71926
Н	14.12772	7.64704	9.51592
Н	13.11461	9.02895	10.01821
Н	16.95616	5.56479	13.11186
Н	18.29126	6.72642	12.97659
Н	17.43628	6.52495	14.52459
Н	17.71715	6.35508	17.73385
Н	18.89724	5.91159	18.98996
Н	19.43369	6.82494	17.56362
Н	16.28372	11.46602	17.73848
Н	17.20712	12.46641	18.88685
Н	17.99183	11.82423	17.42476
Н	18.40283	10.24872	22.99951
Н	18.83907	8.51842	23.02038
Н	17.13301	9.00897	23.04096

Int3B

 $E_{\rm SCF} = -2584.3583734$ Ha $v_{\rm min} = 8.36$ cm⁻¹



С	12.59770	5.15530	15.90791
С	12.23029	3.84403	16.89388
С	12.67115	3.87327	18.34433
Н	13.58923	4.46199	18.46441
Н	12.86581	2.84729	18.68285
Н	11.89148	4.31658	18.97627
В	13.41689	3.64382	15.68325
Н	14.55600	3.55679	16.01316
В	12.85430	4.60678	14.30831
Н	13.66203	5.19371	13.65250
В	11.32842	5.38145	14.76376
Н	11.07017	6.47653	14.39110
В	10.97783	4.93048	16.43381
Н	10.53751	5.64174	17.27557
В	12.23348	2.37852	16.00852
Н	12.60890	1.40029	16.58704
В	12.60999	2.84068	14.33953
Н	13.23741	2.11663	13.61739
В	11.30426	3.91397	13.77143
Н	10.97864	3.96730	12.61793
В	10.13406	4.11875	15.10503
Н	8.96285	4.31337	14.93854
В	10.72498	3.17269	16.48442
Н	10.06597	2.73177	17.38093
В	10.91745	2.53843	14.83200
Н	10.30329	1.57469	14.46690
С	13.05208	7.86161	16.67294
Р	15.31778	6.15881	16.77537
В	13.52853	6.33952	16.46516
С	12.01506	7.86693	17.78260
С	10.78466	8.36839	17.30073
С	10.95595	8.74364	15.89185
С	12.28696	8.46199	15.51306
S	14.48136	8.99420	17.11581

С	12.14298	7.42640	19.09701
С	12.72294	8.68970	14.21175
С	10.04958	9.24819	14.95460
С	9.66673	8.40890	18.13857
С	9.79138	7.94805	19.45372
Н	8.70784	8.78399	17.77234
С	11.01928	7.46669	19.93199
Н	13.10539	7.06262	19.46361
Н	9.01327	9.45430	15.23364
С	10.48814	9.47106	13.64547
Н	13.74987	8.45297	13.92938
С	11.81392	9.19676	13.27666
Н	11.09887	7.12233	20.96635
Н	9.78969	9.85878	12.89958
Н	12.13470	9.37217	12.24663
Н	8.92359	7.96712	20.11793
В	15.81194	7.75343	17.79138
Н	15.76964	7.58487	18.99260
Н	15.69120	4.92031	17.34683
С	17.22282	8.45065	17.40388
Ν	17.85986	9.25961	18.26409
С	19.09864	9.82285	17.70198
С	19.08935	9.28415	16.26142
Ν	17.89748	8.41857	16.24400
Н	19.98646	8.69774	16.01130
Н	19.07644	10.92165	17.75242
Н	19.96568	9.47734	18.28782
Н	18.98645	10.08100	15.50881
С	17.51437	9.49222	19.63589
С	17.94776	8.56932	20.60442
С	17.64598	8.82927	21.94480
С	16.93222	9.97197	22.33039
С	16.51928	10.86688	21.33582
С	16.79421	10.64825	19.98028
С	18.66565	7.30875	20.19886
Н	17.97415	8.11805	22.70820
С	16.58633	10.21519	23.77761
Н	15.95834	11.76185	21.61961
С	16.28404	11.59690	18.92776
С	17.58337	7.61607	15.09818
С	18.04674	6.28807	15.06935
С	17.66477	5.47851	13.99650
С	16.84142	5.95948	12.96997
С	16.45198	7.30454	13.00536
С	16.81876	8.15893	14.05251
С	18.87237	5.73580	16.20240
Н	17.99504	4.43634	13.97556
С	16.35849	5.04195	11.87770
Н	15.83458	7.70265	12.19532

С	16.38306	9.60016	14.06654
Н	17.24553	10.28654	14.10657
Н	15.74578	9.79967	14.94302
Н	15.80902	9.84432	13.16190
Н	15.43502	4.52835	12.19668
Н	17.10205	4.26577	11.64103
Н	16.12520	5.59472	10.95541
Н	19.22835	4.72211	15.97187
Н	19.75245	6.36275	16.41960
Н	18.28291	5.67897	17.13296
Н	17.97620	6.62923	19.66962
Н	19.05875	6.77648	21.07626
Н	19.50738	7.50672	19.51609
Н	15.42747	11.14975	18.39516
Н	15.94843	12.54119	19.37914
Н	17.04659	11.83372	18.16959
Н	16.55068	11.29067	24.00927
Н	17.31337	9.73993	24.45340
Н	15.59287	9.79703	24.01692

6

 $E_{\rm SCF} = -2584.3643071 \text{ Ha}$ $v_{\rm min} = 10.31 \text{ cm}^{-1}$



В	14.83371	4.02198	14.51904
Н	14.24472	2.96270	14.61346
С	16.45826	3.67373	14.55372
S	16.76302	2.57685	13.02899
В	15.50764	3.22989	11.96366
Р	14.53287	4.68777	12.62273
Н	13.22427	4.29181	12.22621
С	17.50279	4.77666	14.51256
С	17.64831	5.83424	13.61636
Н	16.94076	5.97300	12.79828
С	18.71339	6.72806	13.78227
Н	18.82347	7.56703	13.09051

С	19.62793	6.56704	14.83226
Н	20.44749	7.28035	14.95308
С	19.49384	5.50349	15.73058
Н	20.20485	5.37812	16.55109
С	18.43394	4.60809	15.56424
С	18.05473	3.42024	16.33833
С	18.62548	2.84528	17.47696
Н	19.51158	3.28614	17.94071
С	18.03888	1.69700	18.01932
Н	18.47101	1.23745	18.91199
С	16.89794	1.13296	17.43156
Н	16.45009	0.23779	17.87076
С	16.31998	1.71328	16.29559
Н	15.42487	1.28461	15.84104
С	16.89797	2.85795	15.75406
С	15.34572	2.61674	10.52252
Ν	14.33975	1.83268	10.13314
С	14.47025	1.45060	8.71444
Н	13.56388	1.72968	8.15821
Н	14.59948	0.35982	8.63255
С	15.72204	2.23933	8.26126
Н	16.50902	1.59267	7.84631
Н	15.49256	3.01663	7.51560
Ν	16.18222	2.86546	9.51461
С	13.24621	1.46818	10.98842
С	13.41851	0.43062	11.92089
С	12.36911	0.17355	12.81203
Н	12.49152	-0.62293	13.55113
С	11.18126	0.91307	12.79140
С	11.03796	1.91848	11.82464
Н	10.11433	2.50297	11.79232
С	12.05518	2.21551	10.91353
С	14.69770	-0.36060	11.99697
Н	15.13220	-0.54306	11.00219
Н	14.52677	-1.33279	12.48050
Н	15.45398	0.18111	12.58934
С	10.09755	0.66394	13.80779
Н	10.10878	-0.37616	14.16623
Н	9.09940	0.88030	13.39815
Н	10.23966	1.31616	14.68674
С	11.88072	3.31545	9.89759
Н	12.79703	3.91255	9.77888
Н	11.07390	3.99880	10.19653
Н	11.61467	2.90959	8.90555
С	17.31776	3.73863	9.64208
С	17.12315	5.12587	9.52920
С	18.21644	5.96026	9.79556
Н	18.07892	7.04294	9.73061
С	19.46455	5.44815	10.16583

С	19.62487	4.05625	10.22624
Н	20.59666	3.64087	10.50687
С	18.56745	3.18116	9.97007
С	15.77551	5.71238	9.19927
Н	15.13976	5.73601	10.10256
Н	15.24190	5.13395	8.42939
Н	15.87674	6.74531	8.83777
С	20.60506	6.36045	10.53200
Н	21.54464	6.04625	10.05040
Н	20.76829	6.33790	11.62283
Н	20.40014	7.40245	10.24614
С	18.74371	1.69279	10.11885
Н	18.25585	1.12808	9.30924
Н	18.30828	1.34969	11.07244
Н	19.80909	1.42325	10.12592
С	14.25774	5.06301	15.64220
С	12.66392	4.83574	16.12287
С	11.85248	3.72355	15.48297
Н	11.95315	3.72870	14.39072
Н	10.79408	3.86930	15.73817
Н	12.17413	2.74185	15.85141
В	13.04242	6.18942	15.16031
Н	12.67872	6.18603	14.02460
В	14.62716	6.73076	15.70720
Н	15.39290	7.15760	14.89601
В	15.16692	5.62907	16.97646
Н	16.30770	5.30940	17.06271
В	13.92353	4.39914	17.19374
Н	14.12846	3.23830	17.36461
В	11.90678	6.31571	16.50970
Н	10.74012	6.41135	16.25416
В	13.15336	7.55370	16.27572
Н	12.87114	8.65887	15.90244
В	14.47770	7.20337	17.41698
Н	15.16829	8.06891	17.88065
В	14.03938	5.73803	18.34362
Н	14.40067	5.53291	19.46918
В	12.44986	5.20062	17.77268
Н	11.65156	4.54406	18.37861
В	12.78854	6.94050	17.91551
Н	12.23202	7.60970	18.74243

8



Н	18.15833	5.608484	7.534793
Н	17.65169	4.527566	6.223835
С	15.51974	9.132417	5.257412
С	14.355	9.919627	5.357252
С	14.47225	11.3003	5.15907
Н	13.58697	11.92752	5.288815
С	15.69667	11.90007	4.841934
С	16.82291	11.07928	4.699797
Н	17.78559	11.52883	4.440645
С	16.76077	9.697154	4.912397
С	13.00034	9.323644	5.646128
Н	12.39507	10.01979	6.241944
Н	13.06284	8.382009	6.206223
Н	12.45365	9.127455	4.706453
С	15.79924	13.39852	4.727973
Н	16.74343	13.70809	4.255705
Н	15.75392	13.85527	5.731278
Н	14.9639	13.8181	4.145873
С	17.99592	8.841453	4.821812
Н	18.82613	9.393128	4.358479
Н	17.81828	7.926567	4.234519
Н	18.31334	8.521767	5.827963
С	15.06169	9.354225	10.77578
В	13.5932	9.190777	11.27643
С	15.03465	10.53315	9.858459
С	13.6962	11.19605	9.988992
С	12.84167	10.47677	10.79919
С	13.02672	7.971038	12.07741
С	12.08987	8.151567	13.11436
Н	11.71802	9.155786	13.33147
С	11.62969	7.074926	13.87891
Н	10.90797	7.246192	14.68245
С	12.08806	5.781865	13.61357
Н	11.72816	4.937194	14.20755
С	13.01246	5.575529	12.58232
Н	13.38278	4.568705	12.3729
С	13.47416	6.655421	11.82946
Н	14.20501	6.478148	11.03604
С	16.29521	8.819478	11.40766
С	16.23133	8.338209	12.73104
Н	15.27555	8.337414	13.25372
С	17.36936	7.870502	13.39059
Н	17.28356	7.505792	14.41781
С	18.60938	7.875142	12.74691
Н	19.50229	7.510145	13.26151
С	18.69373	8.357857	11.43792
Н	19.65621	8.372747	10.91937
С	17.55606	8.822364	10.77785
Н	17.65035	9.18527	9.758328

С	16.23633	11.34973	9.52075
С	16.95911	11.95608	10.56182
Н	16.66289	11.7678	11.59595
С	18.04463	12.78835	10.28364
Н	18.59804	13.25174	11.10457
С	18.42546	13.02481	8.958099
Н	19.27717	13.67419	8.738999
С	17.7136	12.42204	7.917509
Н	18.00272	12.59609	6.878746
С	16.62708	11.59055	8.198399
Н	16.06787	11.12593	7.389478
С	13.31984	12.29873	9.069318
С	12.21092	12.13634	8.217006
Н	11.62	11.22235	8.291274
С	11.86745	13.11962	7.288838
Н	11.00377	12.96972	6.635319
С	12.62468	14.29228	7.194856
Н	12.3578	15.06422	6.468303
С	13.72044	14.47254	8.043435
Н	14.31315	15.38929	7.986194
С	14.06712	13.48576	8.970206
Н	14.92376	13.64009	9.625933
С	11.41879	10.81861	10.99573
С	10.41741	9.843598	10.822
Н	10.70984	8.828308	10.54778
С	9.06823	10.16313	10.98505
Н	8.307983	9.390911	10.83854
С	8.687906	11.46215	11.33666
Н	7.631742	11.71111	11.46877
С	9.671739	12.43873	11.52286
Н	9.386598	13.45654	11.8028
С	11.0199	12.12049	11.35368
Н	11.7848	12.88614	11.50063

<u>References</u>

- 1. S. Ono, T. Watanabe, Y. Nakamura, H. Sato, T. Hashimoto and Y. Yamaguchi, *Polyhedron*, 2017, **137**, 296-305.
- 2. S. Hagspiel, M. Arrowsmith, F. Fantuzzi, A. Hermann, V. Paprocki, R. Drescher, I. Krummenacher and H. Braunschweig, *Chem. Sci.*, 2020, **11**, 551-555.
- F. Tambornino, A. Hinz, R. Köppe and J. M. Goicoechea, *Angew. Chem. Int. Ed*, 2018, 57, 8230-8234.
- 4. A. R. Jupp, M. B. Geeson, J. E. McGrady and J. M. Goicoechea, *Eur. J. Inorg. Chem.*, 2016, 639-648.
- 5. K. Jonas, E. Deffense and D. Habermann, Angew. Chem. Int. Ed, 1983, 22, 716-717.
- H. Braunschweig, I. Fernández, G. Frenking and T. Kupfer, *Angew. Chem. Int. Ed*, 2008, 47, 1951-1954.
- 7. T. Bischof, X. Guo, I. Krummenacher, L. Beßler, Z. Lin, M. Finze and H. Braunschweig, *Chem. Sci.*, 2022, **13**, 7492-7497.
- 8. A. Hinz and J. M. Goicoechea, *Angew. Chem. Int. Ed*, 2016, **55**, 8536-8541.
- 9. G. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.
- 10. G. Sheldrick, Acta Cryst., 2008, A64, 112-122.
- TURBOMOLE V7.8.1, A development of University of Karlsruhe, Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, 2007, http://www.turbomole.com.TmoleX2022.
- 12. TmoleX2024. Dassault Systemes: Versailles.
- 13. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
- 14. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824.
- 15. A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- 16. C. Lee, W. Yang and R. Parr, *Phys. Rev. B: Condens. Matter, Mater Phys*, 1988, **37**, 785-789.
- 17. S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 1980, 58, 1200-1211.
- P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.* 1994, 98, 11623-11627.
- 19. S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem. 2011, 32, 1456-1465.
- 20. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. 2010, **132**, 154104-154118.
- 21. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, 7, 3297-3305.

- 22. F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057-1065.
- 23. K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083-1096.
- 24. C. Ehrhardt and R. Ahlrichs, *Theor. Chim. Acta*, 1985, **68**, 231-245.
- 25. G. Knizia, J. Chem. Theory Comput., 2013, 9, 4834-4843.