Stabilization of Acyclic Phosphazides Using

The ortho-closo-Dicarbadodecaboranyl Residue

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Electronic Supplementary Information

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1. Experimental

General: THF and diethyl ether were dried over sodium benzophenone ketyl and distilled under dry argon. n-hexane, benzene, dichloromethane and chloroform were dried over molecular sieves (4 Å). Reactions were carried out under dry argon and subsequent manipulations were carried out quickly in air. Reagents were obtained commercially and used as supplied. Silica gel (standard grade, 60 Å porosity, 230 × 400 mesh) was purchased from Sorbent Technologies. 1-Me-closo-1,2-C2B10H11 was synthesized following a published procedure.1 Tosyl azide2 and 1-Ph-closo-1,2-C2B10H113 were synthesized and purified following modifications of published procedures. NMR spectra were measured using Bruker ARX 400 (31P) and ARX 500 (1H, 13C, 11B) spectrometers. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. 1H spectra were referenced to residual protio-chloroform in the chloroform-d (7.26 ppm). 13C NMR spectra were referenced to the solvent resonance (CDCl3, 77.0 ppm). 11B NMR spectra were referenced externally to BF3·OEt2 (δ = 0 ppm). JHH coupling constants for the 1H NMR spectra are reported to one decimal place and have an error of ± 0.4 Hz. Larger errors are associated with broad multiplets. IR spectra were recorded on a Jasco FT/IR-420 spectrometer. Only the signal with the highest intensity of the boron isotopic envelope is listed. Criteria of identity and purity for the new compounds consisted of clean multinuclear NMR spectra (1H, 11B, 13C and 31P, where appropriate) and single crystal X-ray diffraction analysis in the cases of compounds 2a, 2b, 3a and 3b, backed up with high resolution mass spectrometry (including the pattern of the isotope envelope) and IR spectroscopy where possible.

Tosyl azide: NaN3 (5g, 76.9 mmol) was suspended in 95:5 ethanol/water (100 mL). With stirring, at 0 °C, tosyl chloride (10.0 g, 52.5 mmol) was added in portions over 5 minutes. The mixture was then stirred at room temperature for 38 h. The
volume of the mixture was reduced to 50 ml (rotary evaporator, < 40 °C) and deionized H₂O (20 mL) was added. The remaining ethanol was removed (rotary evaporator, < 40 °C), and another portion of H₂O (20 mL) was added. The two-phase mixture was extracted with diethyl ether (3 × 50 mL) and the combined organic extracts were washed sequentially with H₂O (50 mL), saturated aqueous NaHCO₃ (2 × 50 mL) and H₂O (2 × 50 mL). The washed organic phase was then filtered through a silica plug (2.5 cm × 5 cm φ) and washed through with diethyl ether (160 mL). The solution was dried over Na₂SO₄. Removal of the solvent (rotary evaporator < 40 °C, followed by high vacuum) gave tosyl azide (abbreviated below as TsN₃) as a yellow-tinged liquid (10.1 g, 98%) which was stored at -15 °C.

1-Ph-closo-1,2-C₂B₁₀H₁₁: B₁₀H₁₄ (0.500 g, 4.09 mmol) and phenylacetylene (0.50 mL, 465 mg, 4.55 mmol) were dissolved in a mixture of acetonitrile (0.50 mL) and benzene (5 mL). The mixture was then heated at reflux temperature for 72 hours. The solvent was removed under reduced pressure and the residue was extracted with hot hexanes (5 × 10 mL). The solvent was removed under reduced pressure to leave a pale yellow crystallizing oil, which was purified using column chromatography on silica gel (10 cm × 5 cm φ) eluting with neat hexanes. The solvent was removed (rotary evaporator) to give 698 mg (77 %) of 1-Ph-closo-1,2-C₂B₁₀H₁₁ as a white crystalline solid.

1-N₃-2-Me-closo-1,2-C₂B₁₀H₁₀ (1a): 1-Me-closo-1,2-C₂B₁₀H₁₁ (5.01 g, 31.7 mmol) was dissolved in diethyl ether (50 mL) in a 250 mL round-bottomed flask fitted with an argon inlet, a rubber septum, and an empty pressure-compensated addition funnel also fitted with a rubber septum, and cooled to 0 °C. n-BuLi (20 mL, 2.0 M in hexanes, 40 mmol) was then added batchwise over 25 minutes with stirring, at 0 °C. The solution became pale yellow and slightly cloudy during the addition. The mixture was stirred at room temperature for 2.5 hours. The mixture was cooled to -78 °C and a solution of TsN₃ (7.49 g, 38.0 mmol) in Et₂O (40 mL) was transferred to the addition funnel, and then added dropwise to the mixture over 75 minutes. After the first few drops were added, the mixture became orange. The mixture was stirred at -78 °C for a further 60 minutes. The mixture was warmed slowly to 0 °C and stirred at this temperature for 30 minutes, until effervescence ceased. At this point the mixture was clear and dark brown. The mixture was allowed to warm to room temperature, at which point a heavy precipitate formed. The mixture was stirred for a further 2 hours, after which it was filtered. The filtrate was poured into ice-water (ca. 100 mL) and stirred until the ice melted. The mixture was extracted with diethyl ether (3 × 50 mL) and the combined organic extracts were dried over Na₂SO₄. Column chromatography on silica gel (20 cm × 5 cm φ, eluting with neat hexanes) yielded 4.11 g (65%) of compound 1a as a volatile white crystalline solid. Mp: 113-115 °C; ¹H{¹¹B} NMR (500.1 MHz, CDCl₃) δ (ppm) 2.08 (s, 3H, C₃H₃), 2.11 (br s, ca. 2H, BH), 2.19 (br s, ca. 2H, BH), 2.22 (br s, ca. 2H, BH), 2.28 (br s, ca. 2H, BH), 2.49 (br s, ca. 2H, BH); ¹³C{¹H} NMR (125.8 MHz) δ (ppm) 22.17 (CH₃), 76.69, 86.64; ¹¹B{¹H} NMR (160.5 MHz) δ (ppm) -11.3, -10.5, -10.2, -6.9, -6.3; FT-IR (KBr, cm⁻¹) 2589 (vs), 2131 (s), 1441 (w), 1385 (w), 1271 (s), 1009 (m), 725 (m).

1-N₃PPh₃-2-Me-closo-1,2-C₂B₁₀H₁₀ (2a): Compound 1a (300 mg, 1.505 mmol) and triphenylphosphine (395 mg, 1.506 mmol) were dissolved in dry diethyl ether (10 mL) and the solution was heated at reflux with stirring for 2 hours. During this time, a white crystalline solid precipitated. The mixture was allowed to cool to room temperature and filtered. The retentate was washed with a small volume (ca. 2 mL) of cold diethyl ether and dried in vacuo. The volume of the filtrant was reduced (rotary evaporator, < 30 °C) and cooled to -15 °C, resulting in the precipitation of a white crystalline solid,
which was removed by filtration, washed with a small volume of cold diethyl ether, and dried in vacuo. The combined crops yielded 556 mg (80%) of compound 2a as a white, microcrystalline solid. Crystals suitable for single-crystal X-ray diffraction analysis were grown by layering n-hexane over a concentrated solution of 2a in CH₂Cl₂ in a 5mm NMR tube, followed by slow diffusion at room temperature in the dark. Mp: 88 °C (decomp.); ¹H NMR (500.1 MHz, CDCl₃) δ (ppm) 1.3-3.1 (vbr m, 10H, B₃H); ¹³C{¹H} NMR (125.8 MHz) δ (ppm) 22.21 (C–H₃), 74.51 (C–Me), 96.30 (C–N₃), 125.64 (d, 1³JPH = 30.5 Hz, 6H, m-CH); ¹³B{¹H} NMR (160.5 MHz) δ (ppm) 6.83; ¹¹B{¹H} NMR (160.5 MHz) δ (ppm) -13.3, -11.6, -10.7, -7.9; FT-IR (KBr, cm⁻¹) 3055 (w), 2925 (w), 2565 (vs), 1358 (vs), 1113 (s), 717 (s), 694 (s), 524 (s); HR-MS (ESI, +, m/z) calcd. for C₁₂H₂₉¹⁰B₂¹¹B₃NiP: 462.3097 [MH⁺]⁺; observed: 462.3108.

1-N₃PPh₂-2-Me-closo-1,2-C₂B₁₀H₁₀ (3a): Compound 2a (100 mg, 0.217 mmol) was dissolved in benzene (5 mL) and the mixture was heated at reflux for 3 hours. The solvent was removed (rotary evaporator) to give 94 mg (100%) of compound 3 as a white crystalline solid. Crystals suitable for single-crystal X-ray diffraction analysis were grown by layering n-hexane over a concentrated solution of 2b in CH₂Cl₂ in a 5mm NMR tube, followed by slow diffusion and then slow evaporation at room temperature in the dark. Mp: 157 °C; ¹H{¹¹B} NMR (500.1 MHz, CDCl₃) δ (ppm) 1.2 (d, 3H, C–H₃), 7.49 (td, 3³JHH = 7.4 Hz, 4³JPH = 3.13 Hz, 6H, m-CH); ¹³C{¹H} NMR (125.8 MHz) δ (ppm) 21.75 (C–H₃), 80.66 (C–Me), 101.58 (br, C–N), 128.65 (d, 3³JPH = 12.5 Hz), 129.38 (br d, 4³JPC = 103 Hz), 132.34 (d, 4³JPC = 2.1 Hz), 132.78 (d, 2³JPC = 10.3 Hz); ¹³B{¹H} NMR (160.5 MHz) δ (ppm) -13.3, -11.6, -10.7, -7.9; FT-IR (KBr, cm⁻¹) 3055 (w), 2925 (w), 2565 (vs), 1358 (vs), 1113 (s), 717 (s), 694 (s), 524 (s); HR-MS (ESI, +, m/z) calcd. for C₁₂H₂₉¹⁰B₁²¹¹B₃NP: 434.3035 [MH⁺]⁺; observed: 434.3052.

1-N₃PPh₂-closo-1,2-C₂B₁₀H₁₁ (1b): 1-Ph-closo-1,2-C₂B₁₀H₁₁ (300 mg, 1.362 mmol) was dissolved in diethyl ether (5 mL). The mixture was cooled to 0 °C and n-BuLi (0.94 mL, 1.6 M in hexanes, 1.504 mmol) was added over 5 minutes. The colorless solution was allowed to warm to room temperature and stirred for 100 minutes. The solution was then cooled to -78 °C and TsN₃ (311 mg, 1.577 mmol) in diethyl ether (2 mL) was added over 10 minutes. The pale yellow solution was stirred for a further 90 minutes at -78 °C and then allowed to warm to 0 °C. The mixture was stirred for 40 minutes at 0 °C, during which time the solution cleared, effervesced slightly, and a small amount of solid precipitated which then dissolved. The mixture was then allowed to warm to room temperature and stirred for a further 2 hours. TLC at this point showed partial conversion to product 1b. The mixture was poured into ice-water (30 mL) and the resulting mixture was washed into a separating funnel with diethyl ether (20 mL). Saturated aqueous NaCl (6 mL) was added to induce phase separation. The phases were separated, and the aqueous layer was washed with ether (2 × 20 mL). The combined organic extracts were dried over Na₂SO₄, and the solvent was removed (rotary evaporator < 35 °C) to give a colorless oily residue. Purification via column chromatography on silica gel (250 mL, 15 cm × 5 cm ϕ, eluting with neat hexanes) yielded 273 mg (77%) of compound 1b as a white, crystalline, low-melting solid. Mp: ca. 25-30 °C; ¹H{¹¹B} NMR (500.1 MHz, CDCl₃) δ (ppm) 2.24 (br s, ca. 2H, BH); 2.37 (br s, ca. 2H, BH); 2.43 (br s, ca. 1H, BH); 2.47 (br s, ca. 2H, BH); 2.59 (br s, ca. 2H, BH); 2.86 (br s, ca. 2H, BH); 7.43 (t, 3³JHH = 7.9 Hz, 2H, m-CH); 7.51 (tt, 3³JHH = 7.4 Hz, 4³JPH = 2.1 Hz, 1H, p-H); 7.70 (d, 3³JHH = 7.4 Hz, 2H, o-H); ¹³C{¹H} NMR (125.8 MHz) δ (ppm) 85.37, 89.89, 128.89, 129.67, 131.01, 131.04; ¹¹B{¹H} NMR (160.5
\(1\text{-N}3\text{PPh}_3\text{-2-Ph-}\text{closo}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10} (2b)\): A solution of triphenylphosphine (99.8 mg, 0.380 mmol) in diethyl ether (2 mL) was added to a solution of compound 1b (73.6 mg, 0.282 mmol) in diethyl ether (2 mL) at room temperature. The solution became slightly yellow, and a white solid precipitated within a few seconds. The mixture was stirred at room temperature under argon for 60 minutes. The mixture was cooled to -15 °C for 2 hours, then allowed to warm to room temperature and filtered. The retentate was washed with hexanes (1 mL) and dried in vacuo to give 130.8 mg (89%) of compound 2b as a white microcrystalline solid. Compound 2b was stored in the dark at -15 °C. Crystals suitable for single-crystal X-ray diffraction analysis were grown by layering diethyl ether over a concentrated solution of 2b in chloroform in a 5mm NMR tube, and allowing slow diffusion to occur over 24 hours at -15 °C in the dark. Mp: 131 °C (decomp.); \(^1\text{H} \text{NMR} (500.1 \text{ MHz, CDCl}_3) \delta (\text{ppm}) 1.7-3.4 (\text{vbr m}, 10\text{H}, \text{B} \text{H}), 7.16 (\text{t}, 2\text{H}, J_{\text{HH}} = 7.8 \text{ Hz}), 7.27 (\text{t}, 1\text{H}, J_{\text{HH}} = 7.3 \text{ Hz}), 7.49 (\text{m}, 14\text{H}), 7.62 (\text{br t}, J_{\text{HH}} = 7 \text{ Hz}); \quad ^{13}\text{C} \{^1\text{H}\} \text{NMR} (125.8 \text{ MHz, CDCl}_3) \delta (\text{ppm}) 83.09, 100.18, 125.45 (\text{d}, J_{\text{PC}} = 95 \text{ Hz}), 127.97, 128.92 (\text{d}, J_{\text{PC}} = 12.1 \text{ Hz}), 129.39, 131.09, 131.31, 133.05 (\text{d}, J_{\text{PC}} = 2.3 \text{ Hz}), 133.40 (\text{d}, J_{\text{PC}} = 9.5 \text{ Hz}); \quad ^{31}\text{P} \{^1\text{H}\} \text{NMR} (162.0 \text{ MHz, CDCl}_3) \delta (\text{ppm}) 24.54; \quad ^{11}\text{B} \{^1\text{H}\} \text{NMR} (160.5 \text{ MHz, CDCl}_3) \delta (\text{ppm}) -12.9, -11.6, -7.5 (1\text{B}), -5.5 (1\text{B}); \quad \text{FT-IR (KBr, cm}^{-1}) 3064 (\text{w}), 2925 (\text{w}), 2596 (\text{vs}), 2368 (\text{m}), 1495 (\text{m}), 1448 (\text{m}), 1269 (\text{s}).

\(1\text{-N}3\text{PPh}_3\text{-2-Ph-}\text{closo}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10} (3b)\): A solution of compound 2b (30.0 mg, 0.0573 mmol) in benzene (3 mL) was heated at the reflux temperature for 3 hours under argon. The solvent was removed (rotary evaporator) to give 29.0 mg (99%) of compound 3b as a white crystalline solid. Crystals suitable for single-crystal X-ray diffraction analysis were grown by layering n-hexane over a concentrated solution of 3b in chloroform in a 5mm NMR tube, and allowing slow diffusion to occur at room temperature in the dark. Mp: 184 °C; \(^1\text{H} \text{NMR} (500.1 \text{ MHz, CDCl}_3) \delta (\text{ppm}) 1.89 (\text{br s}, \text{ca. 3H}, \text{B} \text{H}), 2.20 (\text{br s, ca. 1H}, \text{B} \text{H}), 2.27 (\text{br s, ca. 2H}, \text{B} \text{H}), 2.48 (\text{br s, ca. 2H}, \text{B} \text{H}), 2.51 (\text{br s, ca. 2H}, \text{B} \text{H}), 7.32 (\text{t}, J_{\text{HH}} = 7.7 \text{ Hz}, 2\text{H}, \text{C}_{\text{cage}}\text{-Ph }o\text{-H}, m\text{-H}), 7.38 (\text{m}, 12\text{H}, \text{PPh}_3 o\text{-H}, m\text{-H}), 7.42 (\text{t}, J_{\text{HH}} = 7.8, 1\text{H}, \text{C}_{\text{cage}}\text{-Ph }p\text{-H}), 7.53 (\text{m}, 3\text{H}, \text{PPh}_3 p\text{-H}), 7.62 (\text{d}, J_{\text{HH}} = 7.8 \text{ Hz}, 2\text{H}, \text{C}_{\text{cage}}\text{-Ph }o\text{-H}); \quad ^{13}\text{C} \{^1\text{H}\} \text{NMR} (125.8 \text{ MHz, CDCl}_3) \delta (\text{ppm}) 89.89, 108.95, 127.94, 128.43 (\text{d}, J_{\text{PC}} = 12.5 \text{ Hz}), 128.70 (\text{br d}, J_{\text{PC}} = 103.1 \text{ Hz}), 129.49, 132.18, 132.30 (\text{br}), 132.84 (\text{d}, J_{\text{PC}} = 10.5 \text{ Hz}), 133.22; \quad ^{31}\text{P} \{^1\text{H}\} \text{NMR} (162.0 \text{ MHz, CDCl}_3) \delta (\text{ppm}) 7.14; \quad ^{11}\text{B} \{^1\text{H}\} \text{NMR} (160.5 \text{ MHz, CDCl}_3) \delta (\text{ppm}) -14.7, -12.4, -11.1, -6.3; \quad \text{FT-IR (KBr, cm}^{-1}) 3059 (\text{w}), 2571 (\text{s}), 1432 (\text{vs}), 1109 (\text{s}), 717 (\text{s}), 692 (\text{s}), 525(\text{s}); \quad \text{HR-MS (ESI, +, m/z) calcd. for } C_{26}H_{31}^{10}\text{B}_2^{11}\text{B}_8\text{N}_3\text{P}: 524.3253 [\text{MH}]^+; \quad \text{observed: 524.3265.}
2. Spectroscopic data

$^1$H$^{11}$B 500 MHz NMR Spectrum for compound 1a.
$^{13}$C{$_{1}^1$H} 126 MHz NMR Spectrum for compound 1a.
$^{11}$B{\textsuperscript{1}H} 160 MHz NMR Spectrum for compound 1a.
$^1$H{$_{^1}$B} 500 MHz NMR Spectrum for compound 1b.
$^{13}C$ 126 MHz NMR Spectrum for compound 1b.
$^{11}$B{¹H} 160 MHz NMR Spectrum for compound 1b.
$^1$H 500 MHz NMR Spectrum for compound 2a.
$^{13}$C 126 MHz NMR Spectrum for compound 2a.
$^{11}$B($^{1}$H) 160 MHz NMR Spectrum for compound 2a.
$^1$H 500 MHz NMR Spectrum for compound 2b.
$^{13}$C 126 MHz NMR Spectrum for compound 2b.
$^{11}$B\{$^1$H} 160 MHz NMR Spectrum for compound 2b.
$^1$H$^1$B 500 MHz NMR Spectrum for compound 3a.
$^{13}$C\{$^1$H} 126 MHz NMR Spectrum for compound 3a.
$^{11}$B{\textsuperscript{1}H} 160 MHz NMR Spectrum for compound 3a.
$^1$H/$^1$B 500 MHz NMR Spectrum for compound 3b.
$^{13}$C 126 MHz NMR Spectrum for compound 3b.
$^{11}$B{$_1^1$H} 160 MHz NMR Spectrum for compound 3b.
3. Hi-Res Mass Spectrometry

HR-MS (ESI, +) Compound 2a

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HR-MS (ESI, +) Compound 2b

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Measured Mass: 524.3265
HR-MS (ESI, +) Compound 3a

Measured Mass: 434.3052

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4. **Crystallography**

X-ray intensity data were measured at 100 K on a Bruker SMART APEX2 CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073 \text{ Å}$) operated at 2250 watts power. The detector was placed at a distance of 6.000 cm from the crystal center. A total of 1800 frames were collected using an $\omega/\phi$ scan, with a scan width of 0.5° and an exposure time of 10 seconds per frame. The data frames were collected using the program APEX2 and processed using the SAINT routine within APEX2. The data were corrected for absorption based on the multi-scan technique as implemented in SADABS. Structure solution and refinement were performed using the Bruker SHELXTL (v. 6.12) software package. Diamond (v. 2.1c) and Mercury CSD (v. 2.2 Build RC5) were used to visualize the structures.

5. **Computational Details**

Natural population analyses [Gaussian NBO (version 3.1) as implemented in the Gaussian 03 software package] were performed using density functional theory [B3LYP/6-311+G(2d,p)]. The geometries were obtained from the X-ray diffraction data with partial optimization: The coordinates of the non-hydrogen atoms were frozen, and the positions of hydrogen atoms were optimized [B3LYP/6-31G(d)].

6. **References**

4. APEX2 v2.2-0 and SAINT v7.34A data collection and data processing programs, respectively. Bruker Analytical X-ray Instruments, Inc., Madison, WI.
5. SADABS v2008/1 semi-empirical absorption correction program. G.M. Sheldrick, University of Göttingen, Germany.