

Endocyclic P–P bond cleavage in carbaborane-substituted 1,2-diphosphetane: A new route to secondary phosphinocarbaboranes

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Supporting Information

†[All reactions were carried out under dry high-purity nitrogen using standard Schlenk techniques. Solvents were purified and degassed with an MBRAUN Solvent Purification System SPS-800. The NMR spectra were recorded with a BRUKER Avance DRX 400 spectrometer (¹H NMR 400.13 MHz, ¹¹B NMR 128.38 MHz, ¹³C NMR 100.63 MHz, ³¹P NMR 161.98 MHz). TMS was used as the internal standard in the ¹H NMR spectra and all other nuclei spectra were referenced to TMS on the Ξ scale. ¹³C{¹H} spectra were recorded as APT spectra. Mass spectra were recorded with a Finnigan MAT MAT8200 (EI). FTIR spectra were recorded with a Perkin-Elmer Spectrum 2000 FTIR spectrometer in the range of 400 – 4000 cm⁻¹ in KBr. Elemental analyses were performed with a Heraeus VARIO EL instrument CHN-O-S Analyzer. The melting points were determined in glass capillaries sealed under nitrogen using a Gallenkamp apparatus and are uncorrected.

The X-ray data for **1** were collected on an Agilent Technologies CCD Xcalibur-S diffractometer (CrysAlis Pro: Data collection and data reduction software package, Varian, Inc.) including the program SCALE3 ABSPACK (SCALE3 ABSPACK: Empirical absorption correction using spherical harmonics) for empirical absorption correction. Structure solution with SIR92.² Anisotropic refinement of all non-hydrogen atoms with SHELXL-97.³ Structure figures were generated with ORTEP.⁴

‡ *Synthesis of 1 and 2:* 2.0 g (6.3 mmol) *tert*-Butyl-substituted 1,2-diphosphetane⁵ was added to 0.1 g (14.5 mmol) of lithium suspended in THF (40 mL). The reaction mixture was stirred overnight and HCl in diethyl ether (9.4 mL of a 2 M solution, 18.8 mmol) was added over a period of 1 h at 0°C. After warming to r.t., THF was removed in vacuo and the residue was extracted with toluene (3×20 mL) to remove LiCl. The solvent was removed in vacuo. **1** (0.14 g, 10 %) was obtained by sublimation at 50 °C (4×10⁻³ mbar) and **2** (1.10 g, 56 %) at 95 °C (4×10⁻³ mbar).

1: M.p.: 92-95 °C. Found: C, 31.20; H, 9.08. Calc.: C, 31.02; H, 9.11. IR (KBr): $\tilde{\nu}$ = 3044 (w), 2955 (m), 2863 (m); 2615 (s), 2580 (s) (B–H); 2337 (m), 2316 (m) (P–H); 1458 (m), 1366 (m), 1262 (w), 1167 (m), 1070 (s), 1025 (s), 946 (m), 922 (m), 801 (m), 721 (m) cm⁻¹. MS (EI, pos, 14 eV): m/z (%) = 232 (20) [M⁺], C₆H₂₁B₁₀P; 173 (40), C₂H₁₀B₁₀P; 142 (40), C₂H₁₀B₁₀.

2: M.p.: 107-108 °C. Found: C, 37.50; H, 9.42. Calc.: C, 37.49; H, 9.44. IR (KBr): $\tilde{\nu}$ = 2980 (m), 2954 (s), 2896 (m), 2862 (m); 2618 (s), 2573 (s) (B–H); 2336 (w), 2311 (m) (P–H); 1459 (s), 1366 (s), 1262 (w), 1202 (m), 1171 (s), 1074 (s), 1031 (m), 949 (m), 934 (m), 798 (m), 729 (m), 666 (w), 623 (w), 422 (w) cm⁻¹. MS (EI, pos, 14 eV): m/z (%) = 320 (10) [M⁺], C₁₀H₃₀B₁₀P₂; 263 (90), C₆H₂₁B₁₀P₂.

Synthesis of 3:

0.74 g (2.3 mmol) of **2** was dissolved in 50 ml DMF and 0.44 g (4.6 mmol) formaldehyde and 0.21 g (2.3 mmol) aniline were added. The reaction mixture was heated to 60 °C over a period of 3 h. DMF was removed in vacuo and the residue extracted with diethylether (3 x 15 ml). The solvent was removed in vacuo and the residue was washed with *n*-hexane to give 0.72 g (67 %) of *rac/meso* **3**. Both diastereomers give the same group of signals in the ¹H, ¹¹B, ¹³C spectra. M.p.: 162-164 °C. Found: C, 49.04; H, 8.25, N, 2.92. Calc.: C, 49.41; H, 8.52, N, 3.20. IR (KBr): $\tilde{\nu}$ = 3057 (w), 2995 (w), 2954 (s), 2927 (s), 2867 (w); 2659 (m), 2582 (s), 2559 (s) (B–H); 1665 (w), 1601 (s), 1494 (s), 1460 (m), 1371 (m), 1319 (m), 1185 (s), 1069 (s), 1032

(w), 840 (w), 804 (w), 751 (s), 693 (m) cm^{-1} . MS (EI, pos, 14 eV): m/z (%) = 438 (10) [M^+], $\text{C}_{18}\text{H}_{37}\text{B}_{10}\text{P}_2\text{N}$; 205 (40), $\text{C}_{11}\text{H}_{16}\text{PN}$; 143 (50), $\text{C}_2\text{H}_{10}\text{B}_{10}$.

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