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COMMUNICATION

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

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Carbaborane-substituted 1,2-diphosphetane reacts with elemental lithium and hydrogen chloride to give exclusively secondary mono- and bis(phosphino)carbaboranes. The latter reacts with two equivalents of formaldehyde and one equivalent of aniline to give a carbaborane-substituted 1-aza-3,6-diphosphepane.

While the chemistry of 1,2-diphosphetes is well developed, little is known about their saturated relatives, the 1,2-diphosphetanes.¹ The facile high-yield synthesis of carbaborane-substituted 1,2-diphosphetanes by reduction of bis(halophosphino)-dicarbacloso-dodecaborane(12)s now allows their synthetic potential to be studied. Thus, elemental iodine reacts in an oxidative ringopening reaction to give the first chiral 1,2-bis(iodophosphino)-1,2-dicarba-closo-dodecaborane(12)s.² In this preliminary account, we present a new synthetic route to secondary mono- (1) and bis(phosphino)carbaboranes (2) by reductive P-P bond cleavage of carbaborane-substituted 1,2-diphosphetane with elemental lithium and subsequent reaction with hydrogen chloride. Secondary phosphines are very useful starting materials for numerous phosphorus-based compounds.³ However, secondary mono- and bis(phosphino)carbaboranes are rare, as problems such as cleavage of the cluster carbon-phosphorus bond are usually encountered in the reaction of the corresponding mono- and bis(halophosphino)-dicarba-closo-dodecaborane(12)s with LiAlH₄.⁴ Thus, this reaction seemed to be limited to phenylphosphino⁵ and ferrocenylphosphino⁶ derivatives, but using 1,2-diphosphetanes as starting material offers access to secondary mono- and bis(phosphino)carbaboranes that were inaccessible before.

Alkali metals, lithium alkyls and platinum(0) complexes were reported to cleave the P–P bond of phosphorus heterocycles, *e.g.*, 1,2-dihydro-1,2-diphosphetes.⁷ With lithium, the resulting dianionic lithium salts offered access to new, openchain diphosphaethene derivatives. Similarly, the P–P bond of

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Scheme 1 Synthesis of *tert*-butyl-substituted secondary phosphino-carbaboranes 1 and 2.

tert-butyl-substituted 1,2-diphosphetane is cleaved by elemental lithium to give a deep red solution of the lithium diphosphanediide species in THF. Addition of hydrogen chloride in diethyl ether gave equal amounts of *rac*- and *meso*-1,2-bis(*tert*-butylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**2**) in moderate yield (56%). Furthermore, cleavage of one P–C bond is observed with formation of the corresponding 1-*tert*-butylphosphino-1,2-dicarba-*closo*-dodecaborane (**1**) (10% yield) and primary phosphine (Scheme 1). A ³¹P NMR spectrum of the reaction mixture already shows the presence of both species, but the products **1** and **2** can be separated by fractional sublimation and are obtained as air- and water-sensitive colourless solids.§

The ³¹P NMR spectrum of **1** in C₆D₆ exhibits a doublet at 26.2 ppm with a P–H coupling constant (¹*J*_{PH}) of 220 Hz. In the ¹³C{¹H} NMR spectrum, two doublets are observed for the carbon cluster atoms of the mono-substituted carbaborane at 65.8 and 67.6 ppm with ²*J*_{CP} and ¹*J*_{CP} of 22.2 and 66.9 Hz, respectively. The ³¹P NMR spectrum of **2** is more complex and exhibits two multiplets at 9.5 and 10.3 ppm (ratio *ca.* 1 : 0.8) for the *HPC*–*CPH* fragments of the two diastereomers (AA'XX' spin system). The coupling constants were obtained from a simulated ¹H NMR spectrum of one species (¹*J*_{PH} = 222, ³*J*_{PP} = 112 Hz).⁸ The ¹³C{¹H} NMR spectrum shows a complex coupling pattern for the ABX spin system of the PCCP moiety at 78.5 ppm, as reported earlier.⁹ P–H stretching modes for both compounds were observed in the IR spectra (2316 cm⁻¹ for **1** and 2311 cm⁻¹ for **2**).

An X-ray structure analysis was carried out for **1** (Fig. 1).¹⁰ The P1–C2 bond length (1.864(2) Å) is similar to those in the *tert*-butyl-substituted 1,2-diphosphetane (1.883(6) Å), the C1_{carb}–C2_{carb} bond (1.696(2) Å) is slightly longer (*cf.* 1.645(4) Å).² The P1–H1p bond length (1.31(2) Å) compares well with

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Fig. 1 Molecular structure of 1-*tert*-butylphosphino-1,2-dicarba-*closo*-dodecaborane (1) with selected bond distances (Å) and angles (°): C1–C2 1.696(2), C1–H1 1.03(2), C2–P1 1.864(2), P1–H1p 1.31(2), P1–C3 1.863(2), B–B 1.767–1.789, B–C 1.715–1.739, C1–C2–P1 112.6(1), C2–P1–C3 109.90(7), C2–P1–H1p 106(1) (ellipsoids are shown at 50% probability).

similar bonds found in secondary phosphinocarbaboranes⁴ or phosphonium salts.¹¹ As expected, the C_{Carb} – C_{Carb} –P bond angle (112.6(1)°) in **1** is much larger than in the 1,2-diphosphetane (97.9(7)°).²

Aminomethylation of secondary phosphines is well known and allows easy access to tertiary phosphino amino derivatives.¹² Formaldehyde and secondary amines give linear condensation products,¹³ whereas the reaction with primary amines results in P,N-heterocyclic compounds.¹⁴ Accordingly, **2** reacts with two equivalents of formaldehyde and one equivalent of aniline in DMF at 60 °C (3 h) to give the seven-membered air- and waterstable 4,5-(dicarba-*closo*-dodecaboranyl)-3,6-di-*tert*-butyl-1phenyl-1-aza-3,6-diphosphepane (**3**) in 67% yield (Scheme 2).§

The ${}^{31}P{}^{1}H$ NMR spectrum of **3** shows two singlets at 30.2 and 36.7 ppm (ratio 30 : 1 for *rac* : *meso*) for the two expected diastereomers, while the ${}^{1}H$, ${}^{13}C$ and ${}^{11}B$ NMR spectra show identical signals for both diastereomers.

The P–CH₂–N protons appear as two multiplets (${}^{2}J_{\text{HH}} = 15 \text{ Hz}$, ${}^{2}J_{\text{PH}} = 7-11 \text{ Hz}$). The ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR spectrum shows a complex coupling pattern for the ABX spin system of the PCCP moiety at 84.6 ppm and a multiplet at 52.6 ppm for the CH₂–P moiety (${}^{1}J_{\text{CP}} = 16 \text{ Hz}$). Compound *rac*-3 crystallizes from *n*-hexane and was structurally characterized (Fig. 2).¹⁰

In summary, a potentially versatile route to secondary *tert*butyl-substituted mono- and bis(phosphino)carbaboranes was developed by reductive P–P bond cleavage of 1,2-diphosphetanes with lithium and subsequent reaction with hydrogen chloride. The phosphorus-containing heterocycle **3** was synthesized by a



Scheme 2 Condensation reaction of 2 with formaldehyde and aniline.



Fig. 2 (a) Molecular structure of $(R_{P'}R_P/S_{P'}S_P)$ -4,5-(*ortho*-dicarba*closo*-dodecaboranyl)-3,6-di-*tert*-butyl-1-phenyl-1-aza-3,6-diphosphepane; (b) central 7-membered heterocycle with selected bond lengths (Å) and angles (°): C1–C2 1.750(7), C1–P1 1.915(6), C3–P1 1.860(6), C3–N1 1.472(7), N1–C4 1.447(7), C4–P2 1.869(6), P2–C2 1.895(6), C2–C1–P1 121.1(4), C2–P1–C4 101.1(3), P2–C4–N1 113.1(4), C4–N1–C3 111.3(5) (ellipsoids are shown at 50% probability).

Mannich-type reaction of 2 with formaldehyde and a primary amine. The secondary bis(phosphino)carbaborane 2 and the P,N-heterocycle 3 will now be employed as a chelating ligand in transition metal complexes.

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Notes and references

§ NMR spectroscopic data of 1–3 (in C₆D₆ for 1 and 2): 1: ¹H NMR: $\delta = 0.87$ (d, ³J_{PH} = 14.2 Hz, 9H, C(CH₃)₃), 2.80 (s, 1H, C_{Carb}–H), 3.76 (d, ¹J_{PH} = 220 Hz, 1H, P–H), 1.20–3.60 ppm (m, 10H, B₁₀H₁₀); ¹¹B{¹H} NMR: $\delta = -0.7$ (br s, 1B), -1.4 (br s, 1B), -7.2 (br s, 2B), -8.9 (br s, 1B), -10.3 (br s, 1B), -11.6 (br s, 2B), -12.8 ppm (br s, 2B); ¹³C{¹H} NMR: $\delta = 28.5$ (d, ²J_{CP} = 14.9 Hz, C(CH₃)₃), 31.9 (m, C(CH₃)₃), 65.8 (d, ²J_{CP} = 22.2 Hz, C_{Carb}–H), 67.6 ppm (d, ¹J_{CP} = 66.9 Hz, C_{Carb}–P); ³¹P NMR: $\delta = 26.2$ ppm (d, ¹J_{PH} = 220 Hz). 2: ¹H NMR: $\delta = 1.00$ (m, ³J_{PH} = 8 Hz, 18H, C(CH₃)₃), 3.93 (m, ¹J_{PH} = 222 Hz, ³J_{PP} = 112 Hz, 2H, P–H), 1.50–3.50 ppm (m, 10H, B₁₀H₁₀); ¹¹B{¹H} NMR: $\delta = 0.3$ (br s, 2B), -6.3 (br s, 5B), -9.0 ppm (br s, 3B); ¹³C{¹H} NMR: $\delta = 2.92$ (m, C(CH₃)₃), 32.6 (m, C(CH₃)₃), 78.5 ppm (m, C₂B₁₀H₁₀); ³¹P NMR: $\delta = 9.51$ (m, ¹J_{PH} = 222 Hz, ³J_{PP} = 112 Hz), 10.27 ppm (m, ¹J_{PH} = 222 Hz, ³J_{PP} = 112 Hz). 3: ¹H NMR (CDCl₃): $\delta = 1.16$ (d, ³J_{PH} = 13.4 Hz, 18H, C(CH₃)₃), 3.86 (m, ²J_{HH} = 15 Hz, ²J_{PH} = 7 Hz, 2H, CH₂P), 3.91 (m, ²J_{HH} = 15 Hz, ²J_{PH} = 11 Hz, 2H, CH₂P), 6.82–7.24 (m, 5H, C₆H₅), 1.80–3.20 ppm (m, 10H, B₁₀H₁₀); ¹¹B{¹H} NMR (CDCl₃): $\delta = 0.2$ (br s, 2B), -5.1 (br s, 2B), -9.2 (br s, 6B); ¹³C{¹H} NMR (C₆D₆): $\delta = 26.9$ (d, ²J_{CP} = 14.8 Hz, C(CH₃)₃), 33.5 (d, ¹J_{CP} = 27.6 Hz, C(CH₃)₃), 52.8 (m, ¹J_{CP} = 16.0 Hz, CH₂P), 84.6 (m, ¹J_{CP} + ²J_{CP} = 105 Hz, (2₂B₁₀H₁₀), 118.0, 120.7, 129.2, 149.9 ppm (s, C₆H₅); ³¹P NMR (CDCl₃): $\delta = 30.2$ (s), 36.7 (s) ppm.

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- 10 Structural data of 1: $C_6H_{21}B_{10}P$, M = 232.30, monoclinic, space group $P2_1/c$, a = 10.6520(4) Å, b = 10.6114(3) Å, c = 13.2551(6) Å, $\beta = 112.994(5)^\circ$, V = 1379.22(9) Å³, Z = 4, $\rho_{calc} = 1.119$ Mg m⁻³, $\mu = 0.162$ mm⁻¹, $2\theta_{max} = 30.51^\circ$, R = 0.0541, Rw = 0.1091. T =130(2) K, 4206 independent reflections, 243 parameters, 1 restraint, max. residual electron density 0.288 e Å⁻³. The bond length analysis revealed a disorder of C1 and B5 with a ratio of 0.53(2) : 0.47(2). The PH hydrogen atom is disordered as well (ratio 0.50(2) : 0.50(2)). Structural data of 3: $C_{18}H_{37}B_{10}NP_{2}$, M = 437.53, orthorhombic, space group *Pbca*, a = 11.8524(8) Å, b = 19.298(1) Å, c = 21.565(2) Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$. V =4932.5(6) Å³, Z = 8, $\rho_{calc} = 1.178$ Mg m⁻³, $\mu = 0.184$ mm⁻¹, $2\theta_{max} = 23.26^\circ$, R = 0.0759, Rw = 0.1504. T = 130(2) K, 3533 independent reflections, 286 parameters, 0 restraint, max residual electron density 0.701 e Å⁻³. CCDC 877502 (1) and 891099 (3)‡.
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