Supporting information

Unexpected Direct Dilithiation of a Prochiral Phosphine Borane[**]

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Index

Experimental Details

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried over sodium and distilled prior to use. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was obtained from Aldrich. (*R,R*)-TMCDA was synthesised according to reference 1 via Eschweiler-Clarke reaction of the corresponding amine and enantiomerically pure tartaric salt; enantiomeric purity was determined according to 2. H_2O is distilled water. *tert*-Butyllithium was titrated against diphenylacetic acid.

^{1}H-, ^{13}C-, ^{11}B-, ^{31}P-NMR spectra were recorded on Avance-500 or Avance-400 *Bruker* spectrometers at 22 °C if not stated otherwise. Assignment of the signals was supported by additional DEPT-135 and C,H-COSY experiments. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (*J*) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singulet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. GC/MS analysis were performed on a ThermoQuest TRIO-1000 (EI = 70 eV); Column; Zebron, Capillary GC Column, ZB-1.

Synthesis of dimethylphenylphosphine borane (1)

4.20 g (30.4 mmol) Dimethylphenylphosphane were dissolved in 20 ml diethyl ether and $BH_3{\cdot}SMe_2$ was added at –30 °C. After stirring for 15 min at this temperature the reaction mixture was warmed to room temperature and stirred for a further hour. The solvent was then removed and the residue purified by distillation ($5{\cdot}10^{-3}$ bar, 85-95 °C), giving the product as colourles oil (4.20 g, 27.6 mmol; 91 %). ^{1}H-NMR: (400.1 MHz, C_6D_6, C_6D_6): δ = 1.10 [(d, 6H, $^{2}J_{HP}$ = 10.2 Hz; P(CH_3)$_2$], 1.71 (dq, 3H, $^{1}J_{HB}$ = 96.9 Hz, $^{2}J_{HP}$ = 14.6 Hz; BH_3), 7.15-7.18 (m, 3H; C$H_{meta/para}$), 7.59-7.63 (m, 2H; CH_{ortho}). {^{1}H}^{13}C-NMR (100.6 MHz, C_6D_6, C_6D_6): δ = 12.6 [d, $^{1}J_{CP}$ = 37.9 Hz; P(*C*H$_3$)], 128.8 (d, $^{3}J_{CP}$ = 9.7 Hz; C_{meta}), 131.03 (d, $^{4}J_{CP}$ = 2.4Hz; C_{para}), 131.5 (d, $^{2}J_{CP}$ = 9.5 Hz; C_{ortho}), 131.9 (d, $^{1}J_{CP}$ = 53.2 Hz; C_{ipao}). ^{31}P-NMR: (162.0 MHz, C_6D_6, C_6D_6): δ = 3.0 (q, $^{1}J_{PB}$ = 56.7 Hz). ^{11}B{^{1}H}-NMR (160.5 MHz, C_6D_6, C_6D_6): δ = –38.3 (d, $^{1}J_{PB}$ = 57.2 Hz).

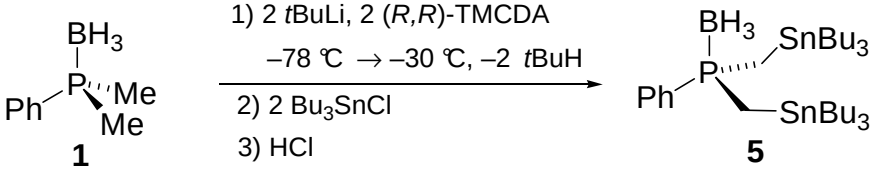
Crystallization of dilithiated phosphine borane 1 to 4

330 mg (1.94 mmol) (*R,R*)-TMCDA were dissolved in 4 ml diethyl ether and 100 mg (0.66 mmol) phosphine borane **1** were added. At –78 °C 0.9 ml (1.35 mmol) *t*BuLi (1.5 M solution in *n*-pentane) were carefully added and the mixture was allowed to warm to –30 °C over a period of 9 h, giving the dilithiated phosphine borane **4** as colourless neadles. Removal of the remaining solution and washing with pentane afforded the dilithiated compound in 81 %

Supplementary Material (ESI) for Chemical Communications

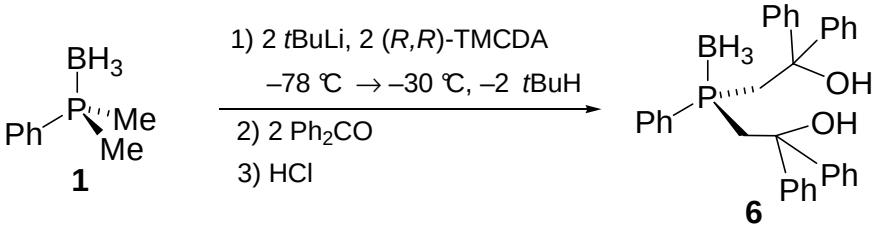
isolated yield. The dilithiated compound is hardly soluable in common solvents (pentane, diethyl ether, toluene).

Trapping of dilithiated phosphine borane 1 with tributyltinchloride to 5



250 mg (1.64 mmol) Dimethylphenylphosphine borane were dissolved in 6 ml diethyl ether and 560 mg (3.29 mmol) (*R,R*)-TMCDA were added. 2 ml (3.40 mmol) *t*-BuLi (1.70 M solution in pentane) were added at –78 °C and warmed to –30 °C over a period of 6 h, giving crystals of the dilithiated compound. After 24 h at this temperature the solution was removed via a syrenge, 20 ml diethyl ether added and the crystaline solid trapped with 1.20 g (3.69 mmol) tributyltinchloride. The mixture was then slowly warmed to room temperature and stirred for 2 h. 10 ml 2.5 M hydrochloric acid were added, the solution exctracted with diethyl ether (3 x 10 ml) and the combined organic layers washed with 2.5 M hydrochloric acid. After drying over Na_2SO_4 the solvent was removed in vacuo giving the product as colourless oil (1.01 g, 1.38 mmol; 74%). ^{1}H-NMR: (500.1 MHz, C_6D_6, C_6D_6): δ = 1.05 (t, $^3J_{CH}$ = 7.3 Hz, 18H; C*H*$_3$), 1.06 – 1.16 (m, 12H; SnC*H*$_2$); 1.13 – 2.10 (m, 3H; BH_3) 1.29 – 1.32 (m, 4H; PC*H*$_2$Sn), 1.44 (sextett, $^3J_{CH}$ = 7.2 Hz, 12 H; C*H*$_2$CH$_3$), 1.53 – 1.70 (m, 12H; SnCH$_2$C*H*$_2$), 7.24-7.25 (m, 3H, C*H*$_{meta,para}$), 7.81-7.85 (m, 2H, C*H*$_{ortho}$). {^{1}H}^{13}C-NMR (125.8 MHz, C_6D_6, C_6D_6): δ = 10.4 (d, $^1J_{CP}$ = 20.9 Hz; P*C*H$_2$Sn), 11.1 [d, $^3J_{CP}$ = 1.7 Hz, ^1J(^{117}SnC) = 161.4 Hz, ^1J(^{119}SnC) = 168.9 Hz; PCH$_2$Sn*C*H$_2$], 13.9 (*C*H$_3$), 27.7 [^3J(^{117}SnC) = 30.1 Hz, ^3J(^{119}SnC) = 31.5 Hz; SnCH$_2$CH$_2$*C*H$_2$], 29.3 [^2J(^{117}SnC) = 8.8 Hz, ^2J(^{119}SnC) = 9.9 Hz; SnCH$_2$*C*H$_2$], 128.7 (d, $^3J_{CP}$ = 9.4 Hz, *C*H$_{meta}$), 130,7 (d, $^4J_{CP}$ = 2.2 Hz, *C*H$_{para}$), 131.5 (d, $^2J_{CP}$ = 9.1 Hz, *C*H$_{ortho}$), 136.2 (d, $^1J_{CP}$ = 52.4 Hz, $^3J_{SnC}$ = 8.7 Hz; *C*$_{ipso}$). ^{119}Sn-NMR: (186.5 MHz, C_6D_6, C_6D_6): δ = –12.5 (d, $^2J_{SnP}$ = 21.1 Hz); ^{31}P-NMR (162.0 MHz, C_6D_6, C_6D_6): δ = 18.1 (d, $^1J_{PB}$ = 67.1 Hz); ^{11}B{^{1}H}-NMR (160.5 MHz, C_6D_6, C_6D_6): δ = –37.3 (d, $^1J_{PB}$ = 57.2 Hz).

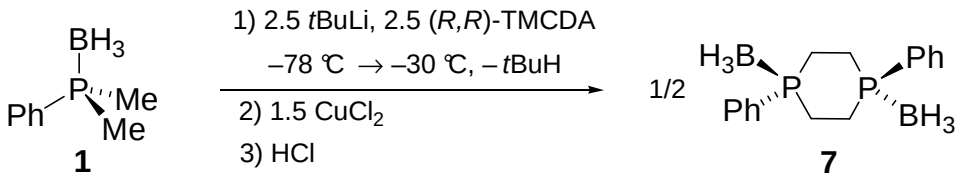
Preparation of dialcohol 6



1.00 g (6.58 mmol) Phosphine borane **1** and 2.64 g (15.5 mmol) (*R,R*)-TMCDA were dissolved in 30 ml diethyl ether and the solution cooled to –78 °C. At this temperature 20 ml

(15.0 mmol) *t*-BuLi (1.5 M in pentane) were added and slowly warmed to –30 °C. After storage at –30 °C for 3 days the reaction mixture was trapped with 3.64 g (20.0 mmol) benzophenone, warmed to room temperature and stirred for additional 3 h. Subsequently 30 ml of 2.5 M hydrochloric acid were added and the mixture afterwards extracted with diethyl ether (3 x 30 ml). The combined organic layers were washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure a crude solid was obtained, which was purified by column chromatography on silica gel (pentane/EtOAc, 4:1) to give dialcohol **5** as colourless crystals (non-optimized yield: 1.73 g, 3.35 mmol; 51 %). ^{1}H-NMR: (400.1 MHz, C_6D_6, C_6D_6): δ = 1.10-2.30 (m, 3H; B*H*$_3$), 2.93 + 3.03 (AB-System, $^2J_{HP}$ = 10.1 Hz, J_{AB} = 12.8 Hz; 4 H; PC*H*$_2$), 4.34 (s, 2H; OH), 6.90-7.00 (m, 8H, C*H*$_{meta}$), 7.04 (dt, $^3J_{HH}$ = 7.50 Hz, $^5J_{PH}$ = 1.5 Hz, 1H; PPh, C*H*$_{para}$), 7.10-7.14 (m, 2H; P*Ph*), 7.20 (t, $^3J_{HH}$ = 7.45 Hz, 4 H; C*H*$_{para}$), 7.25-7.32 (m, 4H; C*H*$_{ortho}$), 7.34-7.39 (m, 2H; P*Ph*), 7.48-7.50 (m, 4 H; C*H*$_{ortho}$). {^{1}H}^{13}C-NMR (75.5 MHz, C_6D_6, C_6D_6): δ = 41.6 (d, $^1J_{CP}$ = 32.7 Hz; P*C*H$_2$), 78.3 (d, $^2J_{CP}$ = 1.35 Hz; *C*OH), 126.5 + 126.7 (*C*H$_{meta}$), 127.4 + 127.6 (*C*H$_{para}$), 128.4 + 128.8 (*C*H$_{ortho}$) 128.7 (d, $^2J_{CP}$ = 9.05 Hz, *C*H$_{ortho}$), 130.4 (d, $^1J_{CP}$ = 56.0 Hz; P*C*$_{ipso}$ PPh), 131.0 (d, $^4J_{CP}$ = 2.90 Hz, *C*H$_{para}$ PPh), 132.7 (d, $^3J_{CP}$ = 10.4 Hz; *C*H$_{meta}$ PPh), 146.3 (d, $^3J_{CP}$ = 4.4 Hz, *C*$_{ipso}$), 148.0 (d, $^3J_{CP}$ = 7.2 Hz; *C*$_{ipso}$). ^{31}P-NMR (162.0 MHz, C_6D_6, C_6D_6): δ = 5.2 (br). ^{11}B{^{1}H}-NMR (160.5 MHz, C_6D_6, C_6D_6): δ = –38.2 (br). CH analysis: observed: C 79.10, H 6.80; calculated: C 79.08, H 6.64.

Coupling of dilithiated phosphine borane 1 to *trans*-1,4-diphenyl-1,4-diphosphacyclo-hexane-diborane 7



982 mg (6.46 mmol) Dimethylphenylphosphine borane **1** and 3.10 g (18.2 mmol) (*R*,*R*)-TMCDA were dissolved in 20 ml diethyl ether and at –45 °C 9 ml (15.3 mmol) *t*-BuLi (1.70 M in pentane) were added. The reaction mixture was warmed to –30 °C over a period of 6 h, giving crystals of the dilithiated compound. After 24 h at this temperature 3.68 g (27.4 mmol) dried copper(II)-chloride were added and stirred for additional 2 h at room temperature. After trapping with 2.5 M hydrochloric acid, the mixture was extracted with diethyl ether (3 x 20 ml) and dried over Na_2SO_4. The solvent was removed and the crude residue was dissolved in ethyl acetate and stored at –30 °C giving the product as colourless crystals (321 mg, 1.07 mmol; 33 %). ^{1}H-NMR: (500.1 MHz, C_6D_6, C_6D_6): δ = 0.85 (br q, $^1J_{BH}$ = 92.5 Hz, 6H; B*H*$_3$), 2.17 (AB-System, J_{AB} = 11.0 Hz, $^2J_{HP}$ = 21.5 Hz, 4 H; PC*H*$_2$), 2.78 (AB-System, J_{AB} = 11.7 Hz, $^2J_{HP}$ = 10.3 Hz, 4 H; PC*H*$_2$), 7.49-7.58 (m, 6H, C*H*$_{meta,para}$), 7.84-7.89 (m, 4H, C*H*$_{ortho}$). {^{1}H}^{13}C-NMR (125.8 MHz, C_6D_6, C_6D_6): δ = 19.7 (d, $^1J_{CP}$ = 33.4 Hz; P*C*H$_2$), 127.6 (d, $^1J_{CP}$ =

56.0 Hz; PC_{ipso}), 129.2 (d, $^{2}J_{CP}$ = 10.1 Hz, *C*H$_{ortho}$), 131.8 (d, $^{3}J_{CP}$ = 9.48 Hz, *C*H$_{meta}$), 132.3 (t, $^{4}J_{CP}$ = 1.2 Hz, *C*H$_{para}$). ^{31}P-NMR (162.0 MHz, C_6D_6, C_6D_6): δ = 7.09 (br d, $^{3}J_{PP}$ = 69.5 Hz). ^{11}B{^{1}H}-NMR (160.5 MHz, C_6D_6, C_6D_6): δ = –43.4 (d, $^{1}J_{PB}$ = 54.3 Hz). GC-MS: t_R = 10.621 min [80 °C (2 min) – 10 °C·min^{-1} – 280 °C (5min)]; *m/z* (%): 272 (100) [(M – 2 BH_3)$^+$], 183 (52) [($C_9H_{13}P_2$)$^+$], 138 (25) [$PhPMe_2$], 107 (78) {[$CH_2PH(CH_2)_2PH_2$]$^+$}, 77 (41) [(C_6H_5)$^+$]. X-ray crystallography see below.

Crystal Structure Determination of Compounds 4, 6 and 7

Data collection of compounds **4** and **7** were conducted with a Bruker APEX-CCD (D8 three-circle goniometer) (Bruker AXS), cell determination and –refinement with Smart version 5.622 (Bruker AXS, 2001), integration with SaintPlus version 6.02 (Bruker AXS, 1999); empirical absorption correction with Sadabs version 2.01 (Bruker AXS, 1999). Data collection of compound **6** was conducted with CrysAlis CCD, Oxford Diffraction Ltd. CCD (D8 three-circle goniometer), cell determination, refinement and integration with CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.32.37. The crystals of all three compounds were mounted in an inert oil (perfluoropolyalkylether) at –60 °C (N_2 stream), using the X-TEMP 2 device (Kottke, T.; Stalke, D. *J. Appl. Cryst.* **1993**, *26*, 615. Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Cryst.* **1996**, *29*, 615. Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.), the crystal structure determinations were effected at –100 °C (**4**, **5, 7**) (type of radiation: Mo-Kα, α = 0.71073 Å). The structures were solved applying direct and fourier methods, using SHELXS-90 (G. M. Sheldrick, University of Göttingen 1990) and SHELXL-97 (G. M. Sheldrick, SHELXL97, University of Göttingen 1997). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-746595 (**4**) and CCDC-746596 (**6**). Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk). The crystal structure of the coupling product has already been reported by *Y. Morisaki* et al [see ref. 12].

Table 1. Data collection and structure refinement details for compound **4**, **6** and **7**.

Compound	Dilithiated Phosphine borane (**4**)	Dialcohol (**6**)	Cyclic product (**7**)
Empirical Formula	$C_{46}H_{90}B_2Li_4N_6P_2$	$C_{34}H_{34}BO_2P$	$C_{16}H_{24}B_2P_2$
Formula Wight	838.56	516.39	299.91
Temperature	173(2) K	173(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å

Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*1 (1)	$P2_1/c$ (14)	$P\bar{1}$ (2)
Cell dimensions	a = 13.792(4) Å	11.9867(15) Å	a = 6.811(2) Å
	b = 14.275(5) Å	13.8915(11) Å	b = 7.639(3) Å
	c = 16.271(4) Å	17.6964(16) Å	c = 9.182(3) Å
	α = 76.327(7)°	α = 90°	α = 99.298(5)°
	β = 66.351(7)°	β = 109.362(12)°	β = 109.621(5)°
	γ = 65.941(5)	γ = 90°	γ = 100.283(5)
Volume	2669.3(15) $Å^3$	2780.0(5) $Å^3$	429.9(2) $Å^3$
Z	Z = 2	Z = 4	Z = 1
Calculated density	1.043 Mg/m^3	1.234 Mg/m^3	1.159 Mg/m^3
Absorption coefficient	0.116 mm^{-1}	0.129 mm^{-1}	0.240 mm^{-1}
F(000)	920	1096	160
Crystal size	0.50 x 0.20 x 0.20 mm^3	0.50 x 0.30 x 0.10 mm^3	0.20 x 0.20 x 0.20 mm^3
Theta for data collection	1.37 to 25.00°	2.32 to 26.00°	2.43 to 26.99°
Index ranges	–16<h<16	–14<=h<=14,	–8<h<8
	–16<k<16	–17<=k<=16,	–9<k<9
	–19<l<19	–20<=l<=21	–11<l<11
Collected reflections	56322	17640	6210
Independent reflections	18625 [R_{int} = 0.0522]	5408 [R(int) = 0.0358]	1877 [R_{int} = 0.0275]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameter	18625 /3 / 1217	5408 / 0 / 367	1877 / 0 /92
Goodness-of-fit on F^2	1.035	1.003	1.018
Final *R*-Indices	*R*1 = 0.0603	*R*1 = 0.0371	*R*1 = 0.0347
[I > 2σ (I)]	w*R*2 = 0.1407	w*R*2 = 0.0704	w*R*2 = 0.0924
R-Indices (all Data)	*R*1 = 0.0794	*R*1 = 0.0616	*R*1 = 0.0365
	w*R*2 = 0.1555	w*R*2 = 0.0727	w*R*2 = 0.0948
Absolute structure parameter	–0.01(7)	-	-
Largest diff. peak and hole	0.416 and –0.203 e·$Å^{-3}$	0.313 and –0.289 e.$Å^{-3}$	0.360 and –0.200 e.$Å^{-3}$

2.1 Crystallographic data for compound 4

Refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; All H atoms were refined on a riding model in their ideal geometric positions, except of H(1A), H(1B), H(1C), H(2A), H(2B), H(2C), H(3A), H(3B), H(3C), H(4A), H(4B) H(4C), H(54B), H(53A), H(62A), H(8B), H(54A), H(8A), H(15A), H(7A), H(53B), H(7B), H(15B), H(62B), H(61A), H(16A), H(161) and H(16B), which were refined independently.

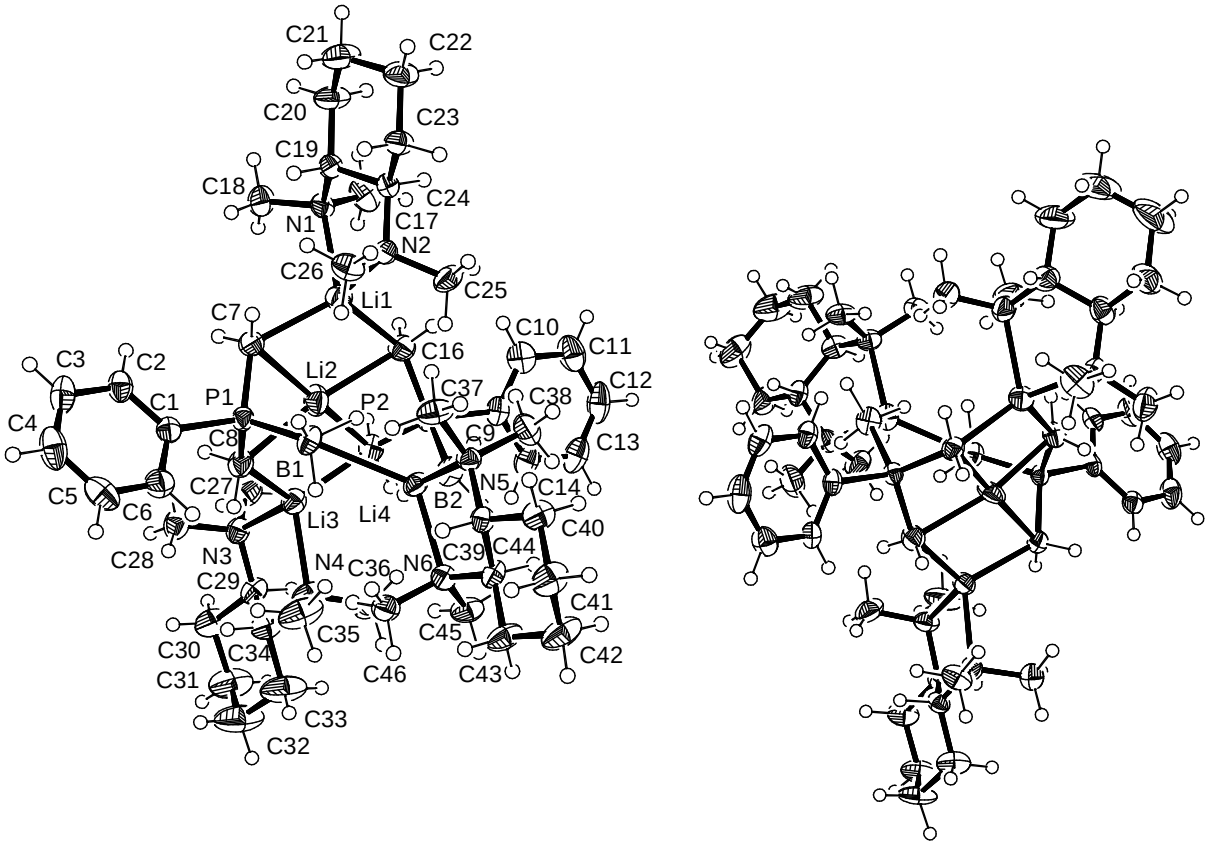


Figure 1. ORTEP plot of **4** at 50 % probability level.

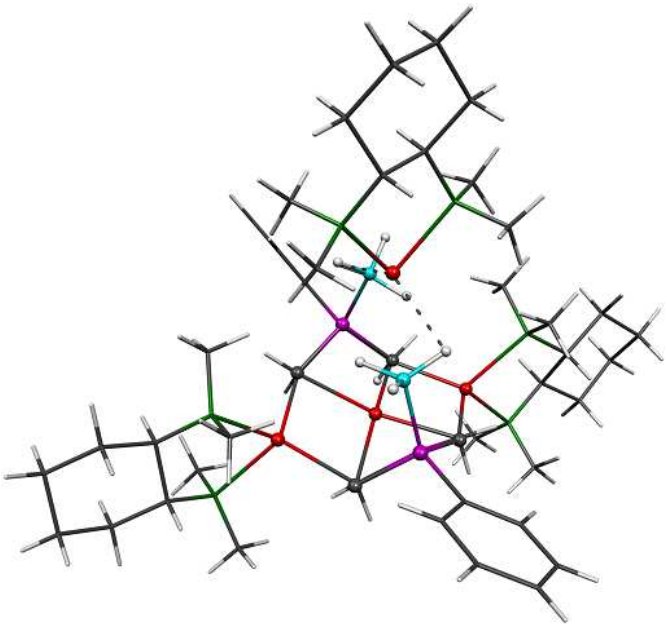


Figure 2. Schematic drawing of **4**.

Table 2 Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for compound **4**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	8020(4)	8785(4)	7711(3)	35(1)
B(2)	7192(4)	6673(4)	7061(4)	38(1)
B(3)	2367(4)	337(4)	3372(3)	32(1)
B(4)	3063(4)	2510(4)	4029(3)	36(1)
C(1)	7724(3)	9482(3)	9433(3)	29(1)
C(2)	7078(4)	10281(3)	9985(3)	36(1)
C(3)	7574(4)	10699(4)	10328(3)	46(1)
C(4)	8723(5)	10323(4)	10119(3)	52(1)
C(5)	9392(4)	9521(4)	9568(3)	49(1)
C(6)	8890(4)	9112(3)	9227(3)	40(1)
C(7)	5661(3)	9687(3)	9085(3)	33(1)
C(8)	6986(4)	7745(3)	9609(3)	37(1)
C(9)	5063(3)	6336(3)	7348(3)	32(1)
C(10)	4100(4)	6885(4)	7126(3)	44(1)
C(11)	3685(4)	6433(4)	6742(3)	54(1)
C(12)	4238(4)	5403(4)	6571(3)	55(1)
C(13)	5192(4)	4848(4)	6787(3)	49(1)
C(14)	5598(4)	5302(3)	7167(3)	41(1)
C(15)	5560(4)	6389(3)	8974(3)	35(1)
C(16)	4813(4)	8252(3)	7976(3)	36(1)
C(17)	2326(4)	10484(4)	8494(3)	48(1)
C(18)	2691(4)	11072(4)	9545(3)	43(1)
C(19)	3179(3)	11842(3)	7992(2)	29(1)
C(20)	2049(4)	12710(3)	8030(3)	49(1)
C(21)	2207(4)	13667(3)	7400(3)	59(1)
C(22)	2853(4)	13375(3)	6444(3)	47(1)
C(23)	4003(3)	12560(3)	6381(3)	36(1)
C(24)	3903(3)	11585(3)	7016(2)	28(1)
C(25)	5485(4)	10185(3)	6191(3)	41(1)
C(26)	5846(3)	11163(3)	6969(3)	40(1)
C(27)	5167(4)	5530(4)	11389(3)	48(1)
C(28)	6458(4)	6073(3)	11596(3)	44(1)
C(29)	7152(3)	4415(3)	10963(2)	35(1)
C(30)	7234(4)	3812(3)	11860(3)	48(1)
C(31)	8070(4)	2708(4)	11749(3)	71(2)
C(32)	9229(5)	2716(5)	11130(4)	85(2)
C(33)	9162(4)	3268(4)	10227(4)	71(2)
C(34)	8327(3)	4379(3)	10305(3)	39(1)
C(35)	9209(4)	5343(4)	8968(4)	63(1)
C(36)	8221(5)	4375(4)	8828(3)	64(2)
C(37)	8853(4)	9520(3)	5335(3)	42(1)
C(38)	8467(4)	8362(4)	4765(3)	43(1)
C(39)	10365(3)	7879(3)	4850(2)	28(1)
C(40)	10836(4)	8123(3)	3826(3)	39(1)
C(41)	12110(4)	7580(3)	3430(3)	49(1)
C(42)	12411(4)	6418(3)	3663(3)	57(1)

C(43)	11976(4)	6186(3)	4679(3)	44(1)
C(44)	10689(3)	6723(3)	5083(2)	31(1)
C(45)	10127(4)	5414(3)	6233(3)	39(1)
C(46)	10844(3)	6504(3)	6574(3)	37(1)
C(47)	2660(3)	-408(3)	1672(2)	27(1)
C(48)	1501(3)	-18(3)	1858(3)	34(1)
C(49)	994(4)	-426(4)	1525(3)	46(1)
C(50)	1638(4)	-1238(4)	1000(3)	49(1)
C(51)	2794(4)	-1634(3)	787(3)	47(1)
C(52)	3314(4)	-1227(3)	1124(3)	32(1)
C(53)	4733(3)	-602(3)	2009(3)	32(1)
C(54)	3382(4)	1348(3)	1505(3)	33(1)
C(55)	5233(3)	2759(3)	3793(2)	28(1)
C(56)	4704(3)	3798(3)	3957(2)	32(1)
C(57)	5143(4)	4248(3)	4330(3)	42(1)
C(58)	6097(4)	3668(4)	4545(3)	49(1)
C(59)	6631(4)	2651(4)	4377(3)	42(1)
C(60)	6200(3)	2195(3)	4005(2)	31(1)
C(61)	4784(4)	2693(3)	2165(3)	31(1)
C(62)	5412(4)	849(3)	3217(3)	38(1)
C(63)	4840(4)	3950(4)	-79(3)	53(1)
C(64)	4542(4)	2716(4)	-608(3)	57(1)
C(65)	2927(3)	4245(3)	-21(2)	41(1)
C(66)	3039(4)	4954(4)	-913(3)	65(1)
C(67)	1880(5)	5716(6)	-942(4)	110(3)
C(68)	1278(7)	6354(6)	-165(4)	131(4)
C(69)	1119(5)	5655(5)	726(4)	93(2)
C(70)	2266(4)	4908(3)	787(3)	47(1)
C(71)	1266(4)	3834(4)	1965(4)	60(1)
C(72)	2045(5)	4805(4)	2357(3)	60(1)
C(73)	8131(3)	-1088(3)	2413(3)	40(1)
C(74)	7587(4)	-2050(3)	1767(3)	44(1)
C(75)	7470(3)	-2462(3)	3362(2)	30(1)
C(76)	8556(3)	-3403(3)	3133(3)	47(1)
C(77)	8638(3)	-4192(3)	3940(3)	55(1)
C(78)	7606(4)	-4517(3)	4343(3)	50(1)
C(79)	6551(4)	-3591(3)	4590(3)	43(1)
C(80)	6423(3)	-2788(3)	3792(2)	30(1)
C(81)	4406(4)	-2173(4)	4110(4)	57(1)
C(82)	5139(4)	-1402(3)	4777(3)	55(1)
C(83)	-511(4)	2631(4)	4331(3)	47(1)
C(84)	155(3)	3428(3)	5036(3)	39(1)
C(85)	-528(3)	2005(3)	5876(3)	36(1)
C(86)	-1645(4)	2780(4)	6420(3)	60(1)
C(87)	-2200(4)	2261(4)	7332(3)	73(2)
C(88)	-1397(4)	1781(4)	7862(3)	66(1)
C(89)	-305(4)	983(4)	7331(3)	49(1)
C(90)	277(3)	1469(3)	6408(2)	33(1)
C(91)	2241(4)	469(5)	6234(3)	65(2)
C(92)	1263(4)	-200(3)	5742(3)	48(1)

Li(1)	4761(6)	9755(5)	8199(4)	35(2)
Li(2)	5720(7)	8021(6)	8941(5)	44(2)
Li(3)	6707(6)	6279(5)	9675(4)	33(2)
Li(4)	8558(5)	7604(5)	6578(4)	30(1)
Li(5)	3661(6)	2819(5)	1437(5)	37(2)
Li(6)	4613(6)	1061(5)	2199(5)	41(2)
Li(7)	5580(6)	-676(5)	2921(4)	33(2)
Li(8)	1791(6)	1484(5)	4508(4)	35(2)
N(1)	3069(3)	10901(2)	8593(2)	29(1)
N(2)	5003(2)	10771(2)	6977(2)	29(1)
N(3)	6339(3)	5485(2)	11034(2)	32(1)
N(4)	8267(3)	4970(3)	9431(2)	44(1)
N(5)	9120(2)	8427(2)	5271(2)	28(1)
N(6)	10200(3)	6451(2)	6068(2)	29(1)
N(7)	4008(3)	3487(2)	48(2)	32(1)
N(8)	2193(3)	4244(3)	1642(2)	40(1)
N(9)	7369(3)	-1647(2)	2604(2)	31(1)
N(10)	5363(3)	-1887(2)	3986(2)	35(1)
N(11)	55(3)	2457(2)	4981(2)	33(1)
N(12)	1360(3)	746(2)	5852(2)	32(1)
P(1)	7073(1)	8918(1)	8970(1)	28(1)
P(2)	5633(1)	6939(1)	7859(1)	30(1)
P(3)	3320(1)	162(1)	2124(1)	25(1)
P(4)	4642(1)	2177(1)	3285(1)	26(1)

Table 3 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **4**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	37(3)	38(3)	27(2)	-10(2)	-3(2)	-13(2)
B(2)	31(3)	44(3)	39(3)	-10(2)	-3(2)	-19(2)
B(3)	39(3)	33(3)	30(2)	-7(2)	-11(2)	-15(2)
B(4)	39(3)	40(3)	34(3)	-2(2)	-7(2)	-24(2)
C(1)	40(2)	23(2)	28(2)	4(2)	-15(2)	-14(2)
C(2)	47(3)	39(2)	27(2)	0(2)	-13(2)	-21(2)
C(3)	71(4)	48(3)	30(2)	-2(2)	-16(2)	-33(3)
C(4)	81(4)	62(3)	41(3)	8(2)	-28(3)	-51(3)
C(5)	47(3)	57(3)	53(3)	13(2)	-28(2)	-28(2)
C(6)	42(3)	37(2)	42(3)	-2(2)	-16(2)	-13(2)
C(7)	35(2)	30(2)	28(2)	-2(2)	-10(2)	-9(2)
C(8)	45(3)	30(2)	38(3)	-4(2)	-16(2)	-15(2)
C(9)	35(2)	39(2)	24(2)	-2(2)	-3(2)	-23(2)
C(10)	44(3)	51(3)	41(3)	-1(2)	-10(2)	-26(2)
C(11)	49(3)	80(4)	47(3)	-3(3)	-19(2)	-36(3)
C(12)	68(4)	82(4)	38(3)	-15(3)	-9(3)	-53(3)
C(13)	59(3)	51(3)	41(3)	-15(2)	-3(2)	-32(3)
C(14)	44(3)	43(3)	39(2)	-11(2)	-7(2)	-23(2)

C(15)	41(3)	34(2)	31(2)	-1(2)	-10(2)	-18(2)
C(16)	41(3)	29(2)	43(3)	-2(2)	-17(2)	-14(2)
C(17)	49(3)	59(3)	40(2)	9(2)	-18(2)	-29(2)
C(18)	48(3)	49(3)	24(2)	-2(2)	-7(2)	-16(2)
C(19)	34(2)	28(2)	22(2)	1(1)	-8(2)	-10(2)
C(20)	39(2)	40(2)	29(2)	6(2)	1(2)	5(2)
C(21)	56(3)	37(2)	43(2)	3(2)	-5(2)	7(2)
C(22)	45(2)	37(2)	37(2)	8(2)	-11(2)	-4(2)
C(23)	29(2)	37(2)	25(2)	1(2)	-4(2)	-3(2)
C(24)	31(2)	30(2)	26(2)	-2(1)	-12(2)	-10(2)
C(25)	46(2)	30(2)	28(2)	-6(2)	-2(2)	-5(2)
C(26)	36(2)	39(2)	44(2)	5(2)	-16(2)	-14(2)
C(27)	39(2)	47(3)	49(3)	-11(2)	-3(2)	-15(2)
C(28)	61(3)	37(2)	37(2)	-3(2)	-16(2)	-21(2)
C(29)	41(2)	26(2)	33(2)	-1(2)	-6(2)	-15(2)
C(30)	49(3)	38(2)	34(2)	6(2)	0(2)	-13(2)
C(31)	66(3)	50(3)	53(3)	21(2)	-3(3)	-8(2)
C(32)	58(3)	62(4)	74(4)	21(3)	-4(3)	6(3)
C(33)	46(3)	58(3)	53(3)	16(2)	6(2)	2(2)
C(34)	37(2)	32(2)	34(2)	4(2)	-4(2)	-10(2)
C(35)	45(3)	45(3)	60(3)	1(2)	14(2)	-14(2)
C(36)	69(4)	50(3)	45(3)	-16(2)	-9(3)	3(3)
C(37)	35(2)	27(2)	50(3)	1(2)	-8(2)	-6(2)
C(38)	41(2)	58(3)	35(2)	-1(2)	-18(2)	-18(2)
C(39)	30(2)	29(2)	26(2)	-2(1)	-8(2)	-12(2)
C(40)	43(2)	32(2)	31(2)	7(2)	-6(2)	-15(2)
C(41)	50(3)	43(2)	33(2)	3(2)	3(2)	-18(2)
C(42)	57(3)	37(2)	44(3)	-4(2)	7(2)	-8(2)
C(43)	39(2)	30(2)	36(2)	-2(2)	5(2)	-5(2)
C(44)	37(2)	27(2)	24(2)	-6(1)	-5(2)	-12(2)
C(45)	41(2)	22(2)	41(2)	6(2)	-10(2)	-9(2)
C(46)	32(2)	40(2)	30(2)	-2(2)	-9(2)	-7(2)
C(47)	38(2)	27(2)	19(2)	7(2)	-12(2)	-18(2)
C(48)	42(2)	37(2)	28(2)	4(2)	-18(2)	-17(2)
C(49)	42(3)	64(3)	42(3)	2(2)	-16(2)	-28(2)
C(50)	67(3)	60(3)	47(3)	5(2)	-32(3)	-41(3)
C(51)	75(4)	40(3)	41(3)	-5(2)	-24(3)	-28(3)
C(52)	43(2)	27(2)	27(2)	2(2)	-13(2)	-14(2)
C(53)	36(2)	30(2)	30(2)	-6(2)	-12(2)	-9(2)
C(54)	47(3)	28(2)	31(2)	5(2)	-16(2)	-20(2)
C(55)	34(2)	34(2)	19(2)	-1(2)	-5(2)	-20(2)
C(56)	41(2)	31(2)	25(2)	-3(2)	-6(2)	-19(2)
C(57)	52(3)	40(3)	36(2)	-12(2)	-3(2)	-24(2)
C(58)	62(3)	65(3)	37(3)	-10(2)	-9(2)	-46(3)
C(59)	38(2)	55(3)	41(3)	-3(2)	-15(2)	-23(2)
C(60)	35(2)	39(2)	25(2)	-6(2)	-9(2)	-17(2)
C(61)	35(2)	27(2)	32(2)	-5(2)	-10(2)	-11(2)
C(62)	48(3)	32(2)	41(3)	-4(2)	-22(2)	-15(2)
C(63)	53(3)	60(3)	58(3)	8(2)	-23(2)	-32(2)
C(64)	79(3)	50(3)	33(2)	-7(2)	-11(2)	-22(3)

C(65)	41(2)	51(2)	30(2)	3(2)	-12(2)	-20(2)
C(66)	56(3)	78(4)	41(3)	9(2)	-18(2)	-9(3)
C(67)	69(4)	150(6)	46(3)	36(4)	-19(3)	0(4)
C(68)	96(5)	118(6)	59(4)	35(4)	-14(4)	42(4)
C(69)	77(4)	71(4)	58(4)	11(3)	-16(3)	26(3)
C(70)	51(3)	37(2)	38(2)	3(2)	-11(2)	-7(2)
C(71)	42(3)	63(3)	54(3)	-5(2)	-4(2)	-9(2)
C(72)	71(4)	49(3)	46(3)	-15(2)	-23(3)	1(3)
C(73)	37(2)	41(2)	45(2)	12(2)	-18(2)	-20(2)
C(74)	47(3)	46(3)	35(2)	-5(2)	-14(2)	-12(2)
C(75)	34(2)	25(2)	34(2)	2(2)	-18(2)	-11(2)
C(76)	34(2)	35(2)	63(3)	4(2)	-13(2)	-12(2)
C(77)	34(2)	29(2)	83(3)	17(2)	-23(2)	-1(2)
C(78)	43(3)	29(2)	73(3)	16(2)	-23(2)	-13(2)
C(79)	42(2)	30(2)	51(3)	14(2)	-15(2)	-17(2)
C(80)	35(2)	27(2)	33(2)	-2(2)	-15(2)	-12(2)
C(81)	29(2)	55(3)	72(3)	23(2)	-19(2)	-14(2)
C(82)	65(3)	30(2)	38(2)	-4(2)	-8(2)	4(2)
C(83)	38(2)	54(3)	48(3)	-3(2)	-21(2)	-8(2)
C(84)	34(2)	26(2)	44(2)	9(2)	-7(2)	-10(2)
C(85)	33(2)	29(2)	42(2)	-1(2)	-6(2)	-15(2)
C(86)	37(3)	49(3)	56(3)	2(2)	5(2)	-5(2)
C(87)	45(3)	62(3)	59(3)	5(3)	19(2)	-10(3)
C(88)	71(3)	59(3)	36(2)	-5(2)	15(2)	-24(3)
C(89)	55(3)	49(3)	29(2)	-3(2)	-1(2)	-20(2)
C(90)	41(2)	34(2)	28(2)	-5(2)	-8(2)	-20(2)
C(91)	50(3)	104(4)	39(3)	-9(3)	-19(2)	-23(3)
C(92)	63(3)	28(2)	37(2)	-2(2)	-8(2)	-11(2)
Li(1)	40(4)	28(4)	35(4)	0(3)	-13(3)	-10(3)
Li(2)	57(5)	43(4)	42(4)	-6(3)	-22(4)	-22(4)
Li(3)	36(4)	33(4)	29(4)	-2(3)	-8(3)	-13(3)
Li(4)	35(4)	21(3)	28(3)	-4(3)	-8(3)	-6(3)
Li(5)	51(4)	25(3)	36(4)	4(3)	-17(3)	-15(3)
Li(6)	53(4)	26(4)	50(4)	12(3)	-35(4)	-11(3)
Li(7)	39(4)	29(3)	35(4)	-1(3)	-20(3)	-10(3)
Li(8)	33(4)	44(4)	34(4)	-3(3)	-9(3)	-24(3)
N(1)	30(2)	34(2)	20(2)	3(1)	-7(1)	-12(1)
N(2)	27(2)	31(2)	24(2)	-4(1)	-7(1)	-8(1)
N(3)	35(2)	33(2)	27(2)	-3(1)	-7(2)	-14(2)
N(4)	43(2)	35(2)	33(2)	1(2)	1(2)	-8(2)
N(5)	28(2)	25(2)	30(2)	-2(1)	-12(1)	-8(1)
N(6)	35(2)	26(2)	25(2)	3(1)	-10(1)	-13(1)
N(7)	40(2)	28(2)	28(2)	-4(1)	-6(2)	-16(2)
N(8)	44(2)	38(2)	30(2)	-4(2)	-8(2)	-11(2)
N(9)	37(2)	29(2)	29(2)	-1(1)	-14(2)	-12(1)
N(10)	29(2)	30(2)	36(2)	4(1)	-12(1)	-6(1)
N(11)	31(2)	26(2)	37(2)	0(1)	-9(1)	-11(1)
N(12)	29(2)	38(2)	31(2)	-1(1)	-11(1)	-15(2)
P(1)	36(1)	23(1)	28(1)	-2(1)	-13(1)	-11(1)
P(2)	33(1)	31(1)	31(1)	-4(1)	-8(1)	-17(1)

P(3)	33(1)	24(1)	23(1)	-2(1)	-12(1)	-12(1)
P(4)	31(1)	24(1)	27(1)	-2(1)	-11(1)	-13(1)

Table 4 Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 103) for compound **4**.

	x	y	z	U(eq)
H(1A)	8740(30)	8100(30)	7650(30)	35(10)
H(1B)	8280(30)	9480(30)	7420(30)	41(11)
H(1C)	7480(30)	8700(30)	7330(30)	40(11)
H(2A)	7180(30)	7260(30)	6470(20)	25(9)
H(2B)	7550(50)	5930(50)	6800(40)	92(18)
H(2C)	7650(40)	6660(30)	7530(30)	56(13)
H(3A)	2020(40)	-220(30)	3620(30)	48(12)
H(3B)	1570(40)	1170(40)	3420(30)	78(16)
H(3C)	2950(30)	380(30)	3710(20)	22(9)
H(4A)	2620(30)	2360(30)	3680(20)	30(10)
H(4B)	2660(40)	3370(30)	4180(30)	51(12)
H(4C)	3010(40)	1990(30)	4660(30)	51(12)
H(2)	6281	10548	10133	43
H(3)	7115	11246	10707	55
H(4)	9062	10610	10352	63
H(5)	10189	9254	9426	58
H(6)	9351	8567	8846	48
H(10)	3713	7590	7240	53
H(11)	3022	6827	6595	65
H(12)	3957	5088	6307	66
H(13)	5575	4143	6673	58
H(14)	6262	4903	7312	49
H(17A)	2342	9845	8886	71
H(17B)	2581	10341	7866	71
H(17C)	1552	10985	8662	71
H(18A)	1944	11615	9711	64
H(18B)	3230	11280	9639	64
H(18C)	2646	10433	9920	64
H(19)	3596	12115	8201	35
H(20A)	1626	12906	8656	59
H(20B)	1592	12455	7860	59
H(21A)	1460	14203	7439	71
H(21B)	2627	13950	7585	71
H(22A)	2948	13991	6036	56
H(22B)	2423	13106	6255	56
H(23A)	4444	12847	6537	43
H(23B)	4417	12370	5753	43
H(24)	3497	11294	6812	34
H(25A)	4927	9934	6179	62
H(25B)	6162	9597	6228	62
H(25C)	5690	10630	5640	62

H(26A)	6094	11546	6387	61
H(26B)	6498	10583	7063	61
H(26C)	5506	11620	7452	61
H(27A)	5050	5188	10998	72
H(27B)	4659	6251	11408	72
H(27C)	5004	5181	11998	72
H(28A)	5967	6794	11552	66
H(28B)	7246	6031	11386	66
H(28C)	6241	5784	12224	66
H(29)	6882	4044	10700	42
H(30A)	7470	4173	12155	58
H(30B)	6476	3798	12260	58
H(31A)	8105	2356	12344	85
H(31B)	7813	2326	11493	85
H(32A)	9769	2000	11049	102
H(32B)	9502	3070	11398	102
H(33A)	8928	2886	9950	85
H(33B)	9922	3272	9824	85
H(34)	8601	4740	10574	46
H(35A)	9911	4760	8756	94
H(35B)	9272	5692	9385	94
H(35C)	9076	5827	8453	94
H(36A)	8045	4832	8313	97
H(36B)	7633	4071	9158	97
H(36C)	8954	3825	8611	97
H(37A)	9172	9580	5753	63
H(37B)	8031	9869	5556	63
H(37C)	9180	9841	4739	63
H(38A)	7659	8609	5122	64
H(38B)	8705	7645	4647	64
H(38C)	8604	8790	4192	64
H(39)	10748	8120	5121	34
H(40A)	10459	7912	3535	47
H(40B)	10657	8876	3691	47
H(41A)	12499	7836	3676	59
H(41B)	12369	7732	2768	59
H(42A)	12067	6154	3382	69
H(42B)	13241	6070	3425	69
H(43A)	12354	6419	4954	52
H(43B)	12169	5433	4825	52
H(44)	10344	6479	4779	37
H(45A)	9652	5399	5926	59
H(45B)	9795	5252	6882	59
H(45C)	10887	4904	6002	59
H(46A)	11578	5940	6431	55
H(46B)	10423	6441	7220	55
H(46C)	10963	7165	6408	55
H(48)	1045	543	2222	41
H(49)	198	-144	1660	56
H(50)	1285	-1528	783	59

H(51)	3240	-2184	410	56
H(52)	4111	-1506	981	39
H(56)	4039	4201	3814	38
H(57)	4782	4956	4435	51
H(58)	6388	3972	4810	58
H(59)	7299	2254	4516	51
H(60)	6574	1488	3895	38
H(63A)	5058	4269	-697	80
H(63B)	5510	3415	30	80
H(63C)	4506	4476	346	80
H(64A)	4011	2383	-535	85
H(64B)	5224	2196	-508	85
H(64C)	4745	3053	-1220	85
H(65)	2461	3849	6	49
H(66A)	3521	5341	-975	78
H(66B)	3411	4525	-1428	78
H(67A)	1983	6169	-1510	132
H(67B)	1418	5330	-931	132
H(68A)	530	6833	-193	158
H(68B)	1718	6768	-191	158
H(69A)	711	6085	1241	111
H(69B)	656	5259	760	111
H(70)	2711	5334	743	57
H(71A)	539	4394	2168	90
H(71B)	1351	3308	2468	90
H(71C)	1294	3526	1474	90
H(72A)	2695	5022	2184	90
H(72B)	1991	4355	2918	90
H(72C)	1352	5413	2444	90
H(73A)	7977	-799	2961	61
H(73B)	8009	-530	1940	61
H(73C)	8916	-1561	2211	61
H(74A)	7441	-1475	1311	66
H(74B)	7089	-2434	1888	66
H(74C)	8377	-2508	1544	66
H(75)	7487	-2142	3838	36
H(76A)	8588	-3733	2647	56
H(76B)	9214	-3175	2903	56
H(77A)	9330	-4804	3749	66
H(77B)	8694	-3891	4402	66
H(78A)	7588	-4875	3900	60
H(78B)	7651	-5000	4885	60
H(79A)	6554	-3267	5064	52
H(79B)	5889	-3816	4846	52
H(80)	6427	-3145	3330	36
H(81A)	4594	-2562	3611	85
H(81B)	3742	-1549	4123	85
H(81C)	4239	-2600	4680	85
H(82A)	4912	-1844	5324	82
H(82B)	4530	-731	4803	82

H(82C)	5825	-1309	4731	82
H(83A)	-1288	3114	4556	71
H(83B)	-521	1976	4253	71
H(83C)	-99	2920	3751	71
H(84A)	602	3659	4442	59
H(84B)	529	3316	5469	59
H(84C)	-601	3954	5234	59
H(85)	-721	1459	5757	43
H(86A)	-2166	3063	6073	71
H(86B)	-1497	3359	6523	71
H(87A)	-2900	2779	7683	88
H(87B)	-2407	1722	7230	88
H(88A)	-1765	1447	8444	79
H(88B)	-1219	2325	7990	79
H(89A)	-479	415	7241	59
H(89B)	214	690	7680	59
H(90)	464	2018	6532	40
H(91A)	2313	1096	6309	97
H(91B)	2961	45	5828	97
H(91C)	2042	79	6821	97
H(92A)	1018	-566	6334	72
H(92B)	1999	-642	5370	72
H(92C)	707	-23	5448	72
H(54B)	3870(40)	1170(40)	970(30)	55(15)
H(53A)	5220(40)	-630(40)	1310(40)	64(15)
H(62A)	6180(50)	750(40)	2890(40)	66(16)
H(8B)	6560(40)	7890(30)	10230(30)	47(12)
H(54A)	2540(40)	1770(30)	1650(30)	33(11)
H(8A)	7780(40)	7300(30)	9580(30)	34(11)
H(15A)	4720(40)	6520(30)	9310(30)	43(12)
H(7A)	5660(30)	10380(30)	8730(30)	37(11)
H(53B)	4810(30)	-1260(30)	2240(20)	26(10)
H(7B)	5250(30)	9740(30)	9700(30)	20(9)
H(15B)	5990(40)	5590(40)	8880(30)	53(13)
H(62B)	5260(30)	600(30)	3800(30)	40(11)
H(61A)	5550(40)	2560(30)	1850(30)	32(11)
H(16A)	4050(40)	8310(30)	8290(30)	40(12)
H(161)	4310(30)	3370(30)	2200(20)	20(9)
H(16B)	4710(30)	8570(30)	7440(30)	38(11)

2.2 Crystallographic data for dialcohol 6

Refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; All H atoms except of H(11), H(1B), H(2B), H(3B), H(2O) and H(1O)were refined on a riding model in their ideal geometric positions.

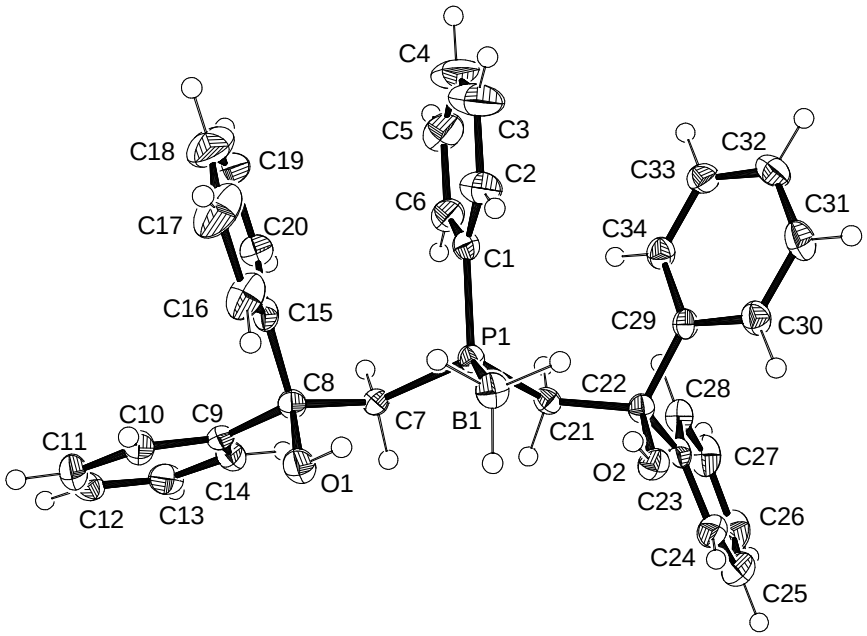


Figure 3 ORTEP plot of **6** at 50 % probability level. Selected bond lengths (Å) and angles (°): B(1)-P(1) 1.9190(19), C(7)-P(1) 1.8228(15), C(21)-P(1) 1.8331(14), C(1)-P(1) 1.8002(16); C(1)-P(1)-C(7) 106.20(7), C(1)-P(1)-C(21) 107.67(7), C(7)-P(1)-C(21) 99.34(7), C(1)-P(1)-B(1) 112.91(8), C(7)-P(1)-B(1) 115.14(8), C(21)-P(1)-B(1) 114.39(8).

Table 5 Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for compound **6**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	7065(2)	3358(2)	5627(1)	25(1)
C(1)	7524(1)	2730(1)	7385(1)	24(1)
C(2)	8499(1)	3324(1)	7554(1)	36(1)
C(3)	9277(2)	3403(2)	8329(1)	57(1)
C(4)	9088(2)	2886(2)	8929(1)	58(1)
C(5)	8115(2)	2290(2)	8776(1)	45(1)
C(6)	7335(1)	2215(1)	8007(1)	31(1)
C(7)	6324(1)	1352(1)	6155(1)	19(1)
C(8)	7238(1)	813(1)	5877(1)	21(1)
C(9)	6957(1)	-259(1)	5760(1)	21(1)
C(10)	7678(1)	-832(1)	5474(1)	30(1)
C(11)	7516(2)	-1813(1)	5405(1)	36(1)
C(12)	6630(1)	-2250(1)	5615(1)	32(1)
C(13)	5891(1)	-1687(1)	5874(1)	31(1)
C(14)	6051(1)	-699(1)	5949(1)	27(1)
C(15)	8488(1)	918(1)	6467(1)	23(1)

C(16)	9408(1)	1253(1)	6233(1)	38(1)
C(17)	10539(2)	1311(2)	6775(1)	54(1)
C(18)	10774(2)	1033(2)	7553(1)	54(1)
C(19)	9875(2)	687(1)	7790(1)	43(1)
C(20)	8741(1)	626(1)	7253(1)	29(1)
C(21)	5050(1)	2950(1)	6364(1)	19(1)
C(22)	4617(1)	4002(1)	6237(1)	20(1)
C(23)	3304(1)	3989(1)	6167(1)	22(1)
C(24)	2428(1)	4205(1)	5455(1)	30(1)
C(25)	1249(1)	4108(1)	5388(1)	40(1)
C(26)	933(2)	3811(1)	6026(1)	42(1)
C(27)	1794(1)	3618(1)	6745(1)	36(1)
C(28)	2973(1)	3713(1)	6815(1)	27(1)
C(29)	5306(1)	4686(1)	6902(1)	19(1)
C(30)	5438(1)	5641(1)	6724(1)	27(1)
C(31)	6024(1)	6279(1)	7323(1)	33(1)
C(32)	6476(1)	5980(1)	8104(1)	30(1)
C(33)	6362(1)	5038(1)	8293(1)	27(1)
C(34)	5780(1)	4398(1)	7696(1)	24(1)
O(2)	4636(1)	4330(1)	5480(1)	24(1)
O(1)	7156(1)	1156(1)	5096(1)	28(1)
P(1)	6538(1)	2636(1)	6369(1)	19(1)

Table 6 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **6**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	29(1)	24(1)	27(1)	3(1)	13(1)	-1(1)
C(1)	24(1)	26(1)	22(1)	-4(1)	7(1)	5(1)
C(2)	31(1)	46(1)	30(1)	-7(1)	8(1)	-5(1)
C(3)	37(1)	88(2)	40(1)	-22(1)	5(1)	-13(1)
C(4)	39(1)	102(2)	26(1)	-19(1)	0(1)	9(1)
C(5)	49(1)	71(2)	20(1)	4(1)	14(1)	21(1)
C(6)	31(1)	38(1)	24(1)	1(1)	11(1)	7(1)
C(7)	21(1)	18(1)	18(1)	1(1)	5(1)	1(1)
C(8)	24(1)	22(1)	18(1)	2(1)	8(1)	2(1)
C(9)	22(1)	21(1)	17(1)	0(1)	1(1)	3(1)
C(10)	26(1)	26(1)	35(1)	-3(1)	8(1)	2(1)
C(11)	34(1)	27(1)	42(1)	-9(1)	7(1)	7(1)
C(12)	40(1)	19(1)	29(1)	-3(1)	0(1)	-2(1)
C(13)	37(1)	25(1)	26(1)	2(1)	6(1)	-5(1)
C(14)	32(1)	23(1)	25(1)	-2(1)	10(1)	-2(1)
C(15)	24(1)	16(1)	30(1)	0(1)	10(1)	2(1)
C(16)	29(1)	35(1)	54(1)	13(1)	18(1)	3(1)
C(17)	24(1)	44(2)	92(2)	20(1)	17(1)	-4(1)
C(18)	27(1)	47(2)	73(2)	4(1)	-5(1)	-4(1)
C(19)	37(1)	43(1)	36(1)	-1(1)	-4(1)	4(1)

C(20)	27(1)	30(1)	29(1)	-1(1)	7(1)	1(1)
C(21)	23(1)	19(1)	18(1)	-1(1)	9(1)	-2(1)
C(22)	25(1)	19(1)	18(1)	3(1)	10(1)	2(1)
C(23)	26(1)	13(1)	27(1)	-2(1)	9(1)	1(1)
C(24)	28(1)	31(1)	30(1)	1(1)	8(1)	7(1)
C(25)	29(1)	41(1)	43(1)	-2(1)	3(1)	9(1)
C(26)	24(1)	39(1)	66(2)	-7(1)	18(1)	1(1)
C(27)	36(1)	30(1)	50(1)	2(1)	24(1)	1(1)
C(28)	29(1)	23(1)	33(1)	2(1)	13(1)	2(1)
C(29)	20(1)	18(1)	22(1)	0(1)	10(1)	2(1)
C(30)	34(1)	21(1)	26(1)	1(1)	12(1)	1(1)
C(31)	45(1)	20(1)	37(1)	-2(1)	18(1)	-2(1)
C(32)	29(1)	31(1)	31(1)	-12(1)	11(1)	-5(1)
C(33)	26(1)	33(1)	21(1)	-2(1)	8(1)	4(1)
C(34)	28(1)	21(1)	24(1)	2(1)	11(1)	2(1)
O(2)	28(1)	26(1)	20(1)	6(1)	11(1)	2(1)
O(1)	41(1)	25(1)	22(1)	3(1)	14(1)	3(1)
P(1)	21(1)	18(1)	19(1)	1(1)	8(1)	0(1)

Table 7 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **6**.

	x	y	z	U(eq)
H(2)	8637	3680	7135	43
H(3)	9943	3817	8443	68
H(4)	9630	2935	9459	70
H(5)	7985	1935	9198	55
H(6)	6662	1808	7899	37
H(7A)	6288	1030	6646	23
H(7B)	5541	1268	5738	23
H(10)	8292	-543	5324	36
H(12)	6534	-2929	5581	39
H(13)	5260	-1977	6004	37
H(14)	5532	-320	6132	32
H(16)	9261	1445	5694	46
H(17)	11161	1548	6605	65
H(18)	11554	1078	7925	65
H(19)	10032	488	8329	51
H(20)	8125	380	7426	35
H(21A)	4483	2559	5940	23
H(21B)	4986	2734	6881	23
H(24)	2634	4419	5009	36
H(25)	652	4251	4893	48
H(26)	122	3738	5971	51
H(27)	1581	3421	7193	43
H(28)	3566	3586	7315	33
H(30)	5123	5859	6185	32
H(31)	6114	6931	7192	39

H(32)	6868	6426	8513	36
H(33)	6682	4826	8832	32
H(34)	5702	3745	7831	29
H(11)	8018(12)	-2206(12)	5199(9)	32(5)
H(1B)	7082(12)	4134(12)	5811(8)	29(4)
H(2B)	7954(12)	3082(11)	5692(8)	28(4)
H(3B)	6410(13)	3235(11)	5036(9)	35(4)
H(2O)	5361(14)	4364(13)	5481(9)	40(5)
H(1O)	7338(16)	1764(15)	5146(11)	61(7)

2.3 Crystallographic data for the coupling product 7

Refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; All H atoms were refined on a riding model in their ideal geometric positions.

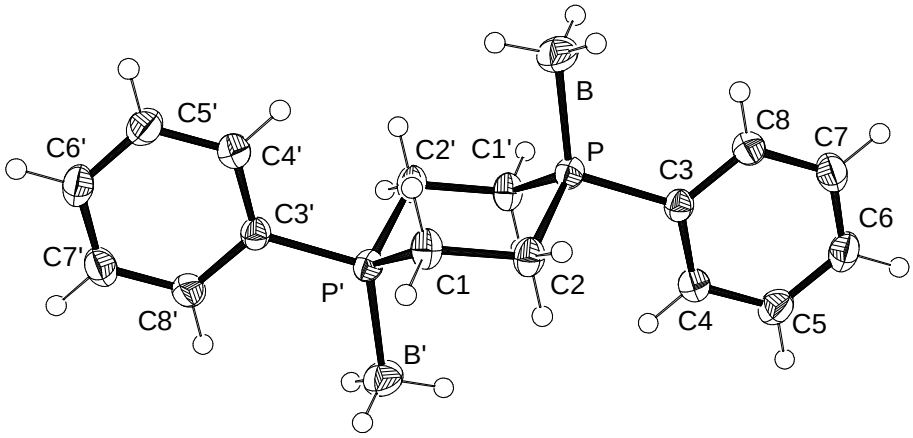


Figure 4 ORTEP plot of **7** at 50 % probability level.

Table 8 Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for compound **7**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B	11609(3)	3635(3)	7566(2)	39(1)
C(1)	12087(2)	5173(2)	11601(2)	28(1)
C(2)	10711(2)	3245(2)	10625(2)	28(1)
C(3)	7602(2)	934(2)	7637(2)	24(1)
C(4)	5912(2)	448(2)	8150(2)	29(1)
C(5)	4431(2)	-1238(2)	7450(2)	34(1)
C(6)	4623(3)	-2451(2)	6243(2)	34(1)
C(7)	6289(3)	-1989(2)	5728(2)	34(1)
C(8)	7776(2)	-301(2)	6417(2)	29(1)
P	9516(1)	3145(1)	8504(1)	24(1)

Table 9 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **7**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B	34(1)	40(1)	47(1)	11(1)	23(1)	6(1)
C(1)	26(1)	23(1)	30(1)	5(1)	4(1)	7(1)
C(2)	29(1)	21(1)	29(1)	6(1)	5(1)	7(1)
C(3)	26(1)	21(1)	25(1)	6(1)	8(1)	6(1)
C(4)	31(1)	27(1)	30(1)	4(1)	12(1)	6(1)
C(5)	31(1)	31(1)	37(1)	9(1)	12(1)	2(1)
C(6)	38(1)	23(1)	31(1)	5(1)	5(1)	1(1)
C(7)	45(1)	26(1)	28(1)	2(1)	11(1)	9(1)
C(8)	34(1)	27(1)	28(1)	6(1)	13(1)	8(1)
P	23(1)	21(1)	28(1)	6(1)	9(1)	5(1)

Table 10 Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 103) for compound **7**.

	x	y	z	U(eq)
H(0A)	12390	2672	7615	58
H(0B)	12625	4824	8151	58
H(0C)	10884	3660	6452	58
H(1A)	13232	5554	11196	33
H(1B)	12790	5137	12727	33
H(2A)	9551	2874	11018	34
H(2B)	11622	2363	10785	34
H(4)	5777	1276	8981	35
H(5)	3283	-1561	7800	41
H(6)	3607	-3606	5767	41
H(7)	6418	-2827	4900	41
H(8)	8916	15	6057	35

Computational Studies

If not otherwise mentioned all calculations were done without symmetry restrictions. Starting coordinates were obtained with Chem3DUltra 10.0. Optimization and additional harmonic vibrational frequency analyses (to establish the nature of stationary points on the potential energy surface) were performed with the software package Gaussian 03 (Revision D.01) on the same level.[3] Table 11 lists the total (SCF) and zero-point energies (ZPE) of all educts and transition states of the deprotonation of phosphine borane **1** with *t*BuLi and TMEDA; figure 5 and figure 6 give an energetic display of both the mono- and the dilithiation. For all compounds the optimisation and vibrational frequency analyses were performed at B3LYP/6-31+G(d) level. The vibrational frequency analyses showed imaginary frequencies for the transition states representing the corresponding vibration for the deprotonation. For the starting systems no imaginary frequencies were obtained. For the dilithiation further conformers were calculated. However, these structures showed higher energies compared to the one given in table 11.

Additionally calculated Gibbs free energies seem in such large systems to be less reliable due to very low frequencies, where the harmonic oscillator model produces significant deviations.[4] Thus, enthalpy values are discussed. Corrections for basis set superposition errors (BSSE) are not included. For polar compounds entropy is crucially influenced by solvent effects and thus – if subsumable – only with high computational costs. With the use of the ligand molecules coordinating to lithium the first coordination sphere/solvation at lithium is already considered. The handling of such compounds in such a way is state of the art. Additional inaccuracies (polar bonds, basis set errors, weak interactions) cancel each other out to a large extent when comparing similar systems with each other (mono- vs. dilithiation, starting system vs. transition state).

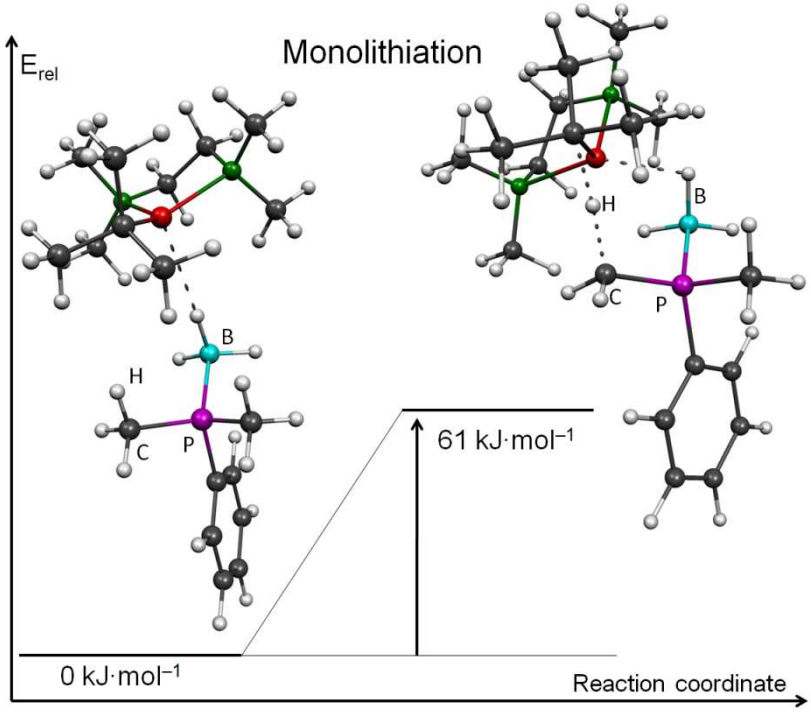


Figure 5. Energies and optimized structures of the monolithiation of **1**.

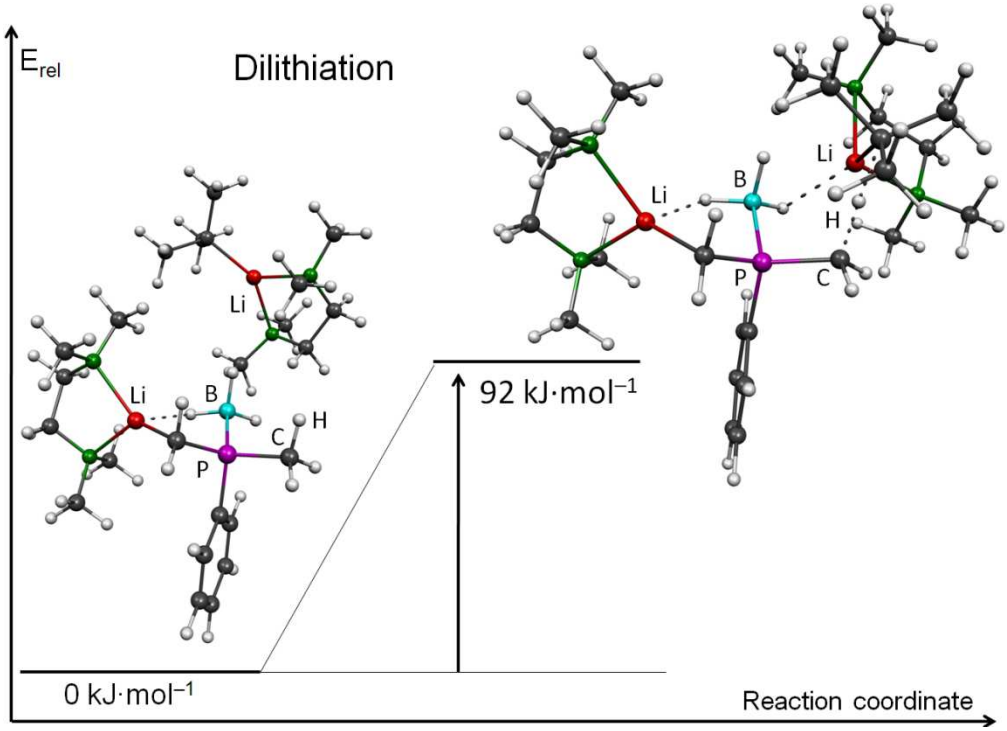


Figure 6. Relative energies and optimized structures of the dilithiation of **1**.

Table 11 Energies of the optimized structures of the mono- and dilithiation of phosphine borane **1**.

Compound	method/basis	Min./TS	SCF (Hartree)	ZPE (Hartree)
Monolithiation	B3LYP/6-31+G(d)	TS.	–1192.637585	–1192.095994
Monolithiation	B3LYP/6-31+G(d)	Global Min.	–1192.664354	–1192.119624
Dilithiation without BH3-Li contact	B3LYP/6-31+G(d)	Global Min.	– 1547.392047	–1546.632848
Dilithiation without BH3-Li contact	B3LYP/6-31+G(d)	TS.	–1547.352673	–1546.596172
Dilithiation with BH3-Li contact	B3LYP/6-31+G(d)	Global Min.	–1547.395194	–1546.635844
Dilithiation with BH3-Li contact	B3LYP/6-31+G(d)	TS	–1547.356733	–1546.600658
*t*BuLi·TMEDA	B3LYP/6-31+G(d)	Global Min.	–513.144619	–512.799849
*t*BuLi·TMEDA	B3LYP/6-31+G(d)	TS	–513.101803	–512.761418

Table 12 Standard orientation of the transition state of the lithiation of phosphine borane **1** with MeLi·TMEDA [TS, B3Lyp/6-31+G(d)].

Atomic symbol	x	y	z
P	-1.314596	-1.525657	0.477971
B	-1.314596	0.416806	0.477971
C	-3.026884	-2.204376	0.477971

C	-0.581021	-2.241447	2.01811
C	-0.531104	-2.080862	-1.025733
C	-0.683684	-1.555867	3.239718
C	-0.144165	-2.102113	4.407724
C	0.508297	-3.337893	4.369013
C	0.622014	-4.024456	3.156333
C	0.083889	-3.476889	1.988728
H	-0.149111	0.743511	0.325424
H	-1.788136	0.8972	1.481266
H	-1.986784	0.706718	-0.50226
H	-3.556495	-1.837385	-0.405448
H	-3.555848	-1.871479	1.376321
H	-3.008898	-3.299103	0.458875
H	0.555336	-1.96194	-0.946635
H	-0.758259	-3.124676	-1.271591
H	-1.179844	-0.589705	3.275224
H	-0.229509	-1.560049	5.346634
H	0.930448	-3.761076	5.277277
H	1.133008	-4.983687	3.118215
H	0.187626	-4.007177	1.044581
Li	-0.497123	0.818479	-1.884834
N	-0.540403	3.211742	-1.860031
N	1.706905	1.161621	-2.033503
C	1.859109	2.553259	-1.558219
C	-0.875072	3.652881	-0.494724
C	0.862472	3.526166	-2.188795
C	-1.442215	3.884892	-2.806251
C	2.486412	0.263342	-1.16345
C	2.192993	1.01548	-3.416244
H	2.884566	2.917744	-1.755303
H	1.731002	2.544366	-0.471287
H	-0.781857	4.749963	-0.396023
H	-0.225626	3.173658	0.238712
H	-1.90058	3.359316	-0.259662
H	1.122964	4.552616	-1.868834
H	0.964956	3.508834	-3.278605
H	-1.24244	3.545965	-3.826227
H	-1.328834	4.983687	-2.76973
H	-2.479417	3.639135	-2.559886
H	3.556495	0.537229	-1.151894
H	2.398713	-0.763727	-1.526658
H	2.098393	0.305166	-0.142631
H	1.619523	1.643308	-4.101688
H	2.070528	-0.022299	-3.734814
H	3.260276	1.288793	-3.501028
C	-1.462107	-0.763544	-3.436778
C	-0.631589	-1.658921	-4.361783
C	-1.61672	0.61619	-4.09546
C	-2.866372	-1.361471	-3.295891
H	-1.116687	-1.812468	-5.346634

H	-0.476174	-2.655956	-3.924523
H	0.364071	-1.237629	-4.564994
H	-0.656684	1.132003	-4.260508
H	-2.26518	1.287405	-3.512947
H	-2.08634	0.543669	-5.099895
H	-3.519283	-0.728611	-2.67609
H	-2.837358	-2.357758	-2.831591
H	-3.370698	-1.48079	-4.275177
H	-0.926997	-1.255783	-2.088426

Table 13 Standard orientation of the reactant of the lithiation of phosphine borane **1** with MeLi·TMEDA [global Minimum, B3Lyp/6-31+G(d)].

Atomic symbol	x	y	z
P	-0.4272840749	0.2345191808	-0.1829182459
B	-1.3253959964	-0.0613133035	1.5107666399
C	1.4059714754	0.1899848843	-0.0449900278
C	-0.8093826861	1.8439559519	-0.9770351199
C	-0.8270159345	-1.0436510479	-1.4415168749
C	-1.6566345222	2.7512096571	-0.3230795521
C	-1.9518885585	3.9874424366	-0.9060013197
C	-1.4058690136	4.3277749726	-2.1454475083
C	-0.5615147365	3.4286503723	-2.8053832964
C	-0.2652767845	2.1948530255	-2.2242035217
Li	-0.6600046482	-3.6152087798	2.8191667476
N	-0.3191914562	-2.9819229	4.8527038412
N	-2.7263778883	-3.7734597426	3.324010286
C	-2.8052802942	-3.0401522067	4.6011836665
C	-0.0472714976	-1.5363347955	4.9053671202
C	-1.6003606299	-3.3153425616	5.5072489214
C	0.7972227541	-3.7200780347	5.4620465926
C	-3.6613445212	-3.2110536566	2.337534904
C	-2.9888117432	-5.2108093309	3.4933030444
C	0.4859231922	-4.7479087432	1.4834635509
C	-0.3527743235	-5.1976076985	0.2800906257
C	0.98790057	-6.0139492887	2.1928437364
C	1.7148380502	-4.0073049786	0.9429365906
H	-2.5179765016	-0.0074907745	1.2911611785
H	-0.9393733807	0.7993969609	2.2741367807
H	-0.9606021668	-1.1741515638	1.8400292122
H	1.70883267	-0.7842887346	0.3515893821
H	1.7323484712	0.9709295267	0.6484801375
H	1.8888831846	0.3476155162	-1.0144983502
H	-1.9050902899	-1.0385669418	-1.6286236991
H	-0.5439151654	-2.0264083701	-1.0511016714
H	-0.2992470053	-0.867816295	-2.3841002837
H	-2.083385622	2.4890996823	0.6403153172
H	-2.609126137	4.6823156557	-0.389665109
H	-1.6360763685	5.2890135987	-2.597800101

H	-0.1344983219	3.6880601642	-3.7707328776
H	0.3933027595	1.5074328127	-2.7500254562
H	-3.7328465811	-3.2888877011	5.1505021346
H	-2.8540752442	-1.9721495407	4.3644752091
H	0.062049522	-1.1829308932	5.9469642577
H	-0.8468874421	-0.9715704106	4.4221177309
H	0.8790670167	-1.3214877238	4.3648153121
H	-1.7242299511	-2.7567212432	6.4528005107
H	-1.5732646267	-4.3763991481	5.7753420844
H	0.6276364851	-4.7967400073	5.372040413
H	0.9276693805	-3.4662612944	6.5296508203
H	1.7222143489	-3.4800711221	4.9303016406
H	-4.7115609919	-3.3007581016	2.6695078954
H	-3.549641531	-3.7477326773	1.3906549474
H	-3.4296298994	-2.1571077567	2.1648732643
H	-2.2580608292	-5.6646032489	4.1677273686
H	-2.8958122123	-5.7094345529	2.5250513148
H	-4.0016418414	-5.3965170506	3.8954560102
H	0.2238924303	-5.8398213261	-0.4313863847
H	-0.731065557	-4.348245011	-0.3128385215
H	-1.232311174	-5.7917821989	0.5781360782
H	0.1639453583	-6.633721824	2.5843036004
H	1.6506335581	-5.7852340578	3.0432466891
H	1.57711699	-6.6800286466	1.5148356621
H	2.3935370381	-3.6741650716	1.7448627441
H	1.4384298745	-3.110992992	0.3634040834
H	2.3317428982	-4.6392128954	0.2559667627

Table 14 Standard orientation of the educt of the deprotonation of lithiated phosphine borane **1** with MeLi·TMEDA without stabilising interaction between the lithium and the borane moiety [global Minimum, B3Lyp/6-31+G(d)].

Atomic symbol	x	y	z
P	-0.0093033486	0.350472166	-0.2879574513
B	-0.1834390417	0.113233564	1.6426727339
H	1.7325982048	0.4332564105	-1.9506099392
C	1.6652089125	0.4361671652	-0.8538856424
C	-1.091778764	1.7353326924	-0.9085607478
C	-0.7561413619	-1.0998389335	-1.1613135868
C	-0.6801914817	2.5296182112	-1.9887131062
C	-1.4901424604	3.5624468797	-2.4709130229
C	-2.7255733459	3.8217624677	-1.8712223525
C	-3.1423156184	3.0453127231	-0.7853816417
C	-2.3307626965	2.0128708027	-0.3066489781
Li	-1.6253480665	-4.9674516776	0.6811984552
N	4.4456649747	-2.0608233072	-0.6447580105
N	-3.4633603384	-5.2664055189	-0.3375626703
N	3.8162304188	-0.9850140826	2.0207550939
N	-2.7539925027	-4.2938519394	2.3360473247

C	-4.0996525003	-4.8198551397	2.0352704862
C	5.1895392553	-1.3682468687	1.6379539695
C	5.1797622947	-1.0775019274	-1.457099009
C	-3.6048422617	-6.7299502123	-0.4050264774
C	-4.4685558068	-4.6564544295	0.5558657612
C	5.2063385718	-2.4570999217	0.558698087
C	4.1144397958	-3.2345258172	-1.4701692571
C	-3.5294990673	-4.6964917114	-1.6913929886
C	3.7878128212	0.3434192054	2.6565412661
C	-2.2543629384	-4.8231941893	3.6141732249
C	3.2101895289	-1.9773701677	2.9274280199
C	-2.7352072688	-2.8195548978	2.367625065
C	0.282669597	-5.720926022	0.3257937549
C	1.3488021493	-4.8805911027	1.0331914804
C	0.6262332989	-5.7612758161	-1.1674654509
C	0.3807725123	-7.1527616521	0.8691833181
H	0.3865124434	1.0430360718	2.1817264994
H	0.3670422795	-0.9568327125	1.8639593463
Li	2.809998712	-0.9825357329	0.1627707943
H	-1.8231461799	-1.1669505071	-0.9239232788
H	-0.258214447	-2.0167956212	-0.8282866738
H	-0.6412555823	-1.0047663888	-2.2467948885
H	0.2880383939	2.3431246054	-2.4477831639
H	-1.153280364	4.1677554919	-3.3097253888
H	-3.3548244926	4.6281553263	-2.2406644569
H	-4.0962296645	3.2499266624	-0.3040322292
H	-2.65249416	1.4295893851	0.5519410947
H	-4.8715596981	-4.3292819151	2.6560097371
H	5.767476558	-1.7177487982	2.5124047764
H	-4.1099424672	-5.8818997069	2.3044595028
H	5.6966756806	-0.4706223452	1.2682147645
H	6.1340598007	-1.4898782639	-1.8313355421
H	-4.5763500177	-7.0260258487	-0.839894381
H	-3.5235712529	-7.1719742835	0.5918546245
H	5.3960597927	-0.1761143705	-0.8770215404
H	4.5631638143	-0.7827124143	-2.3105049459
H	-2.8006223593	-7.1438019984	-1.019327127
H	-5.473572977	-5.0819067309	0.3827291516
H	6.2542251116	-2.7026605808	0.3069436942
H	4.7522098222	-3.3738131894	0.9482900655
H	-4.5329388579	-3.5924258223	0.3074120737
H	3.5332625277	-3.953468446	-0.8871359923
H	-3.3722536986	-3.6143293556	-1.6484731206
H	-4.501506025	-4.8920118882	-2.1781001759
H	5.0205419309	-3.738021247	-1.8510741667
H	-2.7369474621	-5.1331854252	-2.3058506867
H	3.5107355492	-2.9158299327	-2.3252271999
H	-2.8941925837	-4.5255488597	4.4638029124
H	4.3714601125	0.3629139719	3.5941330727
H	-1.2436957564	-4.445229537	3.7909956755

H	2.7518304081	0.6151670198	2.8748057651
H	4.2016643912	1.0909554216	1.9721268236
H	-2.2087721034	-5.9159747667	3.5736796449
H	3.1847032582	-2.9654190866	2.4606789469
H	-3.0732435115	-2.4068602963	1.4137892301
H	2.1811550125	-1.6806454457	3.1439839098
H	-1.71776819	-2.4593452187	2.5348701465
H	3.7731428945	-2.0499229325	3.8752209333
H	-3.3864003075	-2.4224943524	3.1660838643
H	2.383866596	-5.2870379156	0.8813655528
H	1.1976956442	-4.8381500811	2.1234414152
H	1.3646318993	-3.8386859854	0.6729691792
H	0.6166681918	-4.7612468503	-1.6301387079
H	-0.0753193403	-6.3863120448	-1.7436329795
H	1.6430881307	-6.1875368757	-1.361356965
H	-0.3325872073	-7.8376298522	0.3826710223
H	0.1901241424	-7.2062588914	1.9533712904
H	1.393131867	-7.6008855086	0.7111744258
H	-1.3640084109	0.0670153116	1.9335519325
H	2.1287098265	1.3590671409	-0.4731503395

Table 15 Standard orientation of the transition state of the deprotonation of lithiated phosphine borane **1** with MeLi·TMEDA without stabilising interaction between the lithium and the borane moiety [TS, B3Lyp/6-31+G(d)].

Atomic symbol	x	y	z
P	-1.3451181913	0.5071619454	0.3820703529
B	-1.7945254368	2.4134464211	0.3703829738
H	-2.4955470904	-1.5507066398	0.8365741686
C	-2.7328251668	-0.4791134542	0.9142060901
C	0.135409595	0.2452009067	1.4985609374
C	-0.8108114417	-0.1437626386	-1.2427741468
C	0.6786157788	-1.0404064711	1.671721756
C	1.7692721468	-1.2577613452	2.5148893067
C	2.3429751169	-0.1860693519	3.2111867397
C	1.810203952	1.0956267802	3.0568097267
C	0.7155726174	1.3081455726	2.2089401505
Li	-0.226418943	0.9773773908	-3.1299846044
N	-6.237053511	-0.9598748714	-0.2508591021
N	1.3525033612	0.0545313228	-4.3846650154
N	-5.8299326591	1.8027495734	0.691470035
N	1.1365324139	2.6358570411	-2.8858141526
C	2.1297127066	2.3862441448	-3.948922172
C	-7.0993604697	1.0831806742	0.9038838409
C	-6.2066801447	-1.8758467298	0.9007564763
C	1.0987990614	0.094129711	-5.8349018458
C	2.5115302787	0.9069767173	-4.039004689
C	-7.3467037616	0.0079931039	-0.1588360847
C	-6.3258714181	-1.737583693	-1.4942989002

C	1.5857523516	-1.3400816341	-3.9704608399
C	-5.3758541123	2.4547215933	1.9323889912
C	0.4783480818	3.940965702	-3.0774919668
C	-5.9486044095	2.8089053118	-0.3769189631
C	1.7745977052	2.6137659625	-1.5535690183
C	-2.4161429581	0.5284889013	-3.6130346542
C	-3.7371172536	0.7131718224	-2.8686621795
C	-2.4646495354	-0.7972752804	-4.3758033654
C	-2.2506499658	1.7002642555	-4.5934103535
H	-2.0932750496	2.7275333766	1.510022438
H	-2.7474656898	2.5164081151	-0.3857651104
Li	-4.4738884988	0.2640571786	0.0655566956
H	0.2805212035	0.0084508125	-1.3067709766
H	-1.5782010391	0.2799828104	-2.3849698797
H	-0.9599053518	-1.2330741901	-1.2527748937
H	0.2360138892	-1.8825375255	1.1424661426
H	2.1709289348	-2.2621994973	2.6349774333
H	3.1918074332	-0.3528238305	3.8706182486
H	2.2431240309	1.9341735027	3.5989493919
H	0.3024704044	2.3072260839	2.1019386288
H	3.0422992014	2.9886469773	-3.788342093
H	-7.9584427858	1.7788850064	0.9177358245
H	1.6986140152	2.7179818409	-4.9000921382
H	-7.0596187675	0.6209112573	1.895532902
H	-7.133512726	-2.4745136882	0.969391277
H	1.9587136289	-0.301626201	-6.4043292727
H	0.9090661572	1.1181472837	-6.1668798032
H	-6.0779364631	-1.3230166905	1.8345809723
H	-5.3521498537	-2.5495581959	0.8000208979
H	0.2171599948	-0.5052212646	-6.0728725153
H	3.3270526983	0.7805671096	-4.773159903
H	-8.3054206143	-0.4997684416	0.0578636077
H	-7.4546614555	0.4777757999	-1.1422775804
H	2.9039071799	0.5686120274	-3.0752987811
H	-6.3074948473	-1.0663088345	-2.3573851272
H	1.7404531682	-1.3873073239	-2.8889174452
H	2.465130685	-1.7778338169	-4.475051394
H	-7.2482599294	-2.3447342592	-1.5363842832
H	0.7066841195	-1.9429478096	-4.2152591569
H	-5.4646839752	-2.4084085898	-1.5648072242
H	1.2034731054	4.7730290199	-3.0424148642
H	-6.0976547246	3.214636531	2.2824751362
H	-0.2615347351	4.0874166204	-2.285926948
H	-4.4072208739	2.9281478127	1.7569009397
H	-5.2484945426	1.7034089801	2.717950719
H	-0.0320976657	3.9620603988	-4.0452610979
H	-6.2451997643	2.3397112861	-1.3195429809
H	2.2314477151	1.6414207741	-1.3544623256
H	-4.9769662642	3.2863847281	-0.5258780504
H	1.0168507899	2.7912591131	-0.7889848289

H	-6.695011398	3.5831795542	-0.1219810144
H	2.5563232122	3.390140474	-1.4765846177
H	-4.609780315	0.7085864541	-3.5541284214
H	-3.7538994899	1.6588798481	-2.3123572071
H	-3.8860232333	-0.1078103274	-2.1502506794
H	-2.559781705	-1.650162756	-3.6875372817
H	-1.562086233	-0.9728928077	-4.9783940856
H	-3.3231290799	-0.851751306	-5.0770257665
H	-1.3307967157	1.636404277	-5.1991451145
H	-2.2400877451	2.6702079972	-4.0750377605
H	-3.0817245926	1.7514141874	-5.3298117514
H	-0.8563179781	3.0808776057	-0.0286606115
H	-2.917676163	-0.2516502329	1.9770122385

Table 16 Standard orientation of the educt of the deprotonation of lithiated phosphine borane **1** with MeLi·TMEDA without stabilising interaction between the lithium and the borane moiety [global Minimum, B3Lyp/6-31+G(d)].

Atomic symbol	x	y	z
Li	-4.3189988494	-0.0761007581	0.3408491908
P	2.3913499092	-1.5751366109	-1.2164080578
B	0.7575956424	-1.0266472509	-0.3050375239
C	2.1433433499	-3.2230462906	-2.0521480283
C	-5.0295102112	1.8737982768	0.2171838014
C	3.7458782932	-1.9624644609	-0.0233769749
C	2.9482067662	-0.2398635854	-2.2282515985
C	3.4465584109	-2.2741180758	1.3123678474
C	4.4639298364	-2.5978100366	2.2166230428
C	5.7966446066	-2.6150809726	1.7974741035
C	6.1071228674	-2.3073664164	0.4688552242
C	5.0896595839	-1.9841983638	-0.4325659311
Li	2.3074904838	1.2459152457	-0.8593373025
N	1.2664304381	3.0232190683	-1.341548145
N	3.3233536101	2.3369245495	0.6675084301
C	1.574097579	3.9017115377	-0.1950648352
C	3.0161910502	3.7336262351	0.2948425112
C	-0.189194688	2.8560633823	-1.4973827247
C	1.8433931685	3.5387508256	-2.5934377624
C	4.7745646325	2.0941292435	0.6562883462
C	2.7727221074	1.9959350852	1.9895309289
C	-6.0072620886	2.0569330998	-0.9508920372
C	-3.8891046873	2.8831114662	0.0324653318
C	-5.7713188046	2.2423839457	1.5097410712
N	-3.4417648458	-1.2357278249	1.8745913874
N	-4.348764182	-1.8344037337	-0.8448354618
C	-4.5122866219	-1.4768688735	2.8531372937
C	-2.2965529717	-0.5907861612	2.5358590919
C	-5.6281508116	-2.0691085906	-1.5292696917

C	-4.052567942	-2.9084403966	0.1241860128
C	-3.2710263878	-1.6788539476	-1.8364069309
C	-3.030018937	-2.4726493292	1.1808487231
H	1.3491202605	-3.1141484639	-2.7990538399
H	0.3714940926	-1.8795433072	0.4691906828
H	-0.0460191157	-0.813501374	-1.1948394689
H	1.0238549297	0.0125929968	0.2949339548
H	3.0619347516	-3.5416489771	-2.5570076545
H	1.8443061642	-3.9897971793	-1.3276965956
H	3.9394111631	-0.3843643336	-2.6711074189
H	2.2150390935	-0.0753380536	-3.031694936
H	2.4121546091	-2.2621670413	1.6443451055
H	4.2134677605	-2.8368609705	3.2476301394
H	6.5880348629	-2.867706713	2.4990057492
H	7.1416784725	-2.3202520609	0.1337189289
H	5.3471273072	-1.7439395873	-1.4607448336
H	0.8768586071	3.650526366	0.610657504
H	1.3973881967	4.9638233756	-0.443736303
H	3.7129670553	4.0273617269	-0.4973407802
H	3.1945031892	4.4213127187	1.1412354435
H	-0.6162561934	2.4244326764	-0.5891179478
H	-0.3879037749	2.1695173831	-2.3251276861
H	-0.6960596592	3.8136899982	-1.703594116
H	1.6252920933	2.8401263317	-3.4057149175
H	2.9305818426	3.6243588772	-2.5140501114
H	1.43001795	4.5290175745	-2.8556143837
H	5.1740688282	2.2889700576	-0.3433994618
H	4.9703331809	1.0466009028	0.9007599037
H	5.3060307313	2.7336801738	1.3835586635
H	2.9758069515	0.9438191975	2.2059874169
H	1.6890038201	2.1359233554	2.0031137352
H	3.2190800275	2.6169726071	2.7869564558
H	-6.8836708373	1.3932743468	-0.873242092
H	-5.5363397248	1.8558091674	-1.9270741206
H	-6.4115707148	3.0979757498	-1.011027669
H	-3.3341087801	2.7176657978	-0.9050969154
H	-3.1552740803	2.8432562404	0.8547464277
H	-4.254911946	3.940093188	-0.0054445217
H	-5.1228314095	2.1792725598	2.3996190818
H	-6.6402811415	1.5906734807	1.6974075354
H	-6.167725024	3.2881302693	1.4920399234
H	-5.3901183674	-1.9145091147	2.3686155272
H	-4.8166432062	-0.5257905993	3.2994038868
H	-4.18407769	-2.159358043	3.6581052152
H	-2.6208937771	0.3605424366	2.9685055661
H	-1.5063162187	-0.3958838023	1.8058870827
H	-1.8784043861	-1.2205319321	3.3417302669
H	-5.8399360864	-1.2310081471	-2.1991559345
H	-6.4382450897	-2.1305979012	-0.7957253354
H	-5.6173855967	-3.0015435825	-2.1220236417

H	-3.6811262735	-3.8168557993	-0.3837881672
H	-4.9951364143	-3.1853217726	0.608837882
H	-2.3150529003	-1.4721654785	-1.3488932745
H	-3.5063426324	-0.8364938145	-2.4939154089
H	-3.1551753901	-2.5866564754	-2.4558971844
H	-2.8779503369	-3.3024525601	1.8955155729
H	-2.0605864849	-2.2828814211	0.7105051656

Table 17 Standard orientation of the transition state of the deprotonation of lithiated phosphine borane **1** with MeLi·TMEDA without stabilising interaction between the lithium and the borane moiety [TS, B3Lyp/6-31+G(d)].

Atomic symbol	x	y	z
Li	-0.6910559121	-2.166605223	-0.6488768948
P	-0.7178919635	1.0497344052	-0.6532961362
B	0.9082515772	-0.0245158122	-0.6326342794
C	-2.0739085794	-0.1051792874	-0.9965117214
C	-2.3834084392	-2.2224880515	1.0131174066
C	-0.6420969677	2.320023032	-2.0021540099
C	-0.7925676069	1.9809762232	0.864457784
C	0.355217185	2.2742347494	-2.9905331608
C	0.3782284139	3.2064824243	-4.0348917028
C	-0.596997495	4.2041350543	-4.1082160851
C	-1.597391821	4.2611045662	-3.1300630588
C	-1.6192859965	3.3275216213	-2.0923543884
Li	1.2781872818	2.2005268868	0.9996737868
N	2.4861076949	1.8568417783	2.7253699288
N	2.5898530592	3.8180513479	0.5148550658
C	3.665445514	2.7077110309	2.4776070468
C	3.2939653405	4.0287018452	1.7943319378
C	2.8737497927	0.4519045619	2.9161710001
C	1.7057031882	2.3217157458	3.882566307
C	1.8289352888	5.0156748229	0.1236107892
C	3.5179638575	3.4436406025	-0.5631193887
C	-3.5741542882	-1.4203961083	1.5503866282
C	-1.3245254311	-2.2910630539	2.120805775
C	-2.8819024127	-3.629638881	0.6671806976
N	0.9932253885	-3.8779694058	-0.533556051
N	-0.9612822616	-3.0553898862	-2.7388933745
C	0.640329139	-5.1055631162	0.196076003
C	2.2458211711	-3.34136166	0.0208829306
C	-2.3781810772	-3.3446582768	-3.0149439636
C	-0.181415328	-4.308600711	-2.700928298
C	-0.4431521752	-2.1544216146	-3.7831264257
C	1.1548014162	-4.1509077335	-1.9743394077
H	1.0786711199	-0.6027818082	-1.6910822809

H	0.7156336649	-0.8245140072	0.2717133323
H	1.8911227512	0.6595792837	-0.3632838207
H	-2.1168336008	-1.183069689	-0.09704987
H	-3.0495142947	0.37043508	-0.8371548554
H	-2.0298022833	-0.4475965767	-2.0397507315
H	-1.5519027683	2.7719836576	0.8289981086
H	-1.0587703689	1.2888963782	1.6781114089
H	1.1174848858	1.5006361617	-2.9434947437
H	1.1585054411	3.1508846561	-4.7914463383
H	-0.581867659	4.9283371139	-4.9193286983
H	-2.3627481072	5.0327514946	-3.1787670831
H	-2.4070072611	3.3802471564	-1.3443109362
H	4.3529460461	2.1434703239	1.8387902281
H	4.2102069709	2.9246101615	3.4149352917
H	2.6323867848	4.6084552286	2.4466790487
H	4.2082899682	4.6346184951	1.6548089826
H	3.3926221812	0.0875921125	2.0249973044
H	1.9753031199	-0.1557171644	3.0554432592
H	3.5303934095	0.3191923833	3.7949506079
H	0.8128617029	1.7003565245	3.9891329508
H	1.3734642905	3.3524557329	3.7346843179
H	2.293267928	2.2705160912	4.8173068427
H	1.0910122003	5.2520664854	0.895576449
H	1.2916964128	4.8156106025	-0.8070429573
H	2.4862347119	5.8912509569	-0.0257540724
H	2.95073128	3.2577263125	-1.4788020334
H	4.0537740725	2.5250914293	-0.3100141661
H	4.2575917715	4.2415207336	-0.7582963068
H	-4.3849674659	-1.3509552132	0.8103299831
H	-3.2866551045	-0.3916561994	1.8094558702
H	-4.0048514998	-1.8798576717	2.4623823609
H	-0.9639556975	-1.2885901827	2.3916203337
H	-0.4398799574	-2.883022473	1.8408228842
H	-1.7230207704	-2.7507905416	3.0515227741
H	-2.0913526121	-4.2899531575	0.2793585438
H	-3.6809442206	-3.5993222001	-0.0878620982
H	-3.3082150561	-4.1522593192	1.5513635676
H	-0.2906128592	-5.5330158263	-0.1825851926
H	0.4923038067	-4.8748299619	1.2541470416
H	1.4356713317	-5.8689401189	0.1087177433
H	2.1096384458	-3.1300115366	1.0854845655
H	2.5029185866	-2.4059835128	-0.4800554721
H	3.0800863618	-4.0587079818	-0.0905290316
H	-2.9466857915	-2.4107970335	-3.0151599863
H	-2.7844013894	-3.9905520577	-2.2331111882
H	-2.5107982531	-3.8392902665	-3.9940857111
H	0.0050871979	-4.6844660407	-3.7240984381
H	-0.7896463924	-5.06693552	-2.1978652692
H	0.6003622731	-1.8992049045	-3.5895976984
H	-1.0151314046	-1.223412682	-3.7841477657

H	-0.5203354087	-2.6176536824	-4.7836097923
H	1.7629728135	-5.0612657336	-2.1356410671
H	1.7146911421	-3.3174533693	-2.4096609364

Table 18 Standard orientation of *t*BuLi·TMEDA [minimum, B3Lyp/6-31+G(d)].

Atomic symbol	x	y	z
N	0.016768597	-0.0559089014	0.0085683075
C	0.6600538717	1.2573875756	-0.1895804679
C	1.5026775691	1.3045441624	-1.4708418485
N	2.4883063275	0.2091475724	-1.530271037
C	3.6431387186	0.4546315298	-0.6520376695
C	2.9493677083	-0.0275388196	-2.9067469152
C	-0.3874311594	-0.2487769876	1.4095026123
C	-1.1438146915	-0.2420395343	-0.8768303985
Li	1.47804721	-1.4410854661	-0.6658972828
C	1.8483282528	-3.4700530478	-0.531970407
C	2.3451668117	-3.8454521958	0.8718260758
C	2.9263664753	-3.8980423311	-1.5377492618
C	0.5875732071	-4.298362279	-0.8183408999
H	1.2979251076	1.4476781609	0.6801267665
H	-0.0851549808	2.0732003667	-0.2170955639
H	1.9897838452	2.2939439208	-1.5458574412
H	0.8510231464	1.2116207134	-2.3461244588
H	4.3133030365	-0.4088078197	-0.687584604
H	3.319908502	0.5857476533	0.3846437418
H	4.206510048	1.3545130511	-0.9574734225
H	3.6261367736	-0.8861742576	-2.9181962756
H	3.4771928636	0.8483675383	-3.323842492
H	2.0950033492	-0.2600469053	-3.5499710082
H	-0.8088524194	-1.2506498099	1.5297776036
H	-1.1402591755	0.4929174195	1.7304472021
H	0.4863952911	-0.1667537304	2.0630956958
H	-1.5519048001	-1.2462075293	-0.7315364967
H	-0.8486768619	-0.1491640907	-1.9259550139
H	-1.9381837974	0.4980001361	-0.6725172652
H	1.6084198148	-3.6080775725	1.6566101921
H	3.2796431813	-3.3259266985	1.1403215154
H	2.5600023793	-4.9380377112	0.9699834296
H	3.8852522706	-3.3788013654	-1.3721973791
H	2.6294811295	-3.7034782687	-2.5813764181
H	3.155211935	-4.9905343029	-1.4802160091
H	0.1873406796	-4.1197734874	-1.8296982221
H	-0.2267438389	-4.0835949917	-0.106659227
H	0.7749246226	-5.3980946963	-0.7490176569

Table 19 Standard orientation of the transition state of *t*BuLi·TMEDA [TS, B3Lyp/6-31+G(d)].

Atomic symbol	x	y	z
N	-1.6519726548	1.0091890158	0.5940649587
C	-0.80752	2.227267245	0.6010520488
C	0.0445515649	2.3858384206	-0.6665787955
N	0.7459012774	1.1540351235	-1.0335079199
C	1.7067910463	0.6570940259	0.020143449
C	1.3590501514	1.2717176602	-2.3553851566
C	-2.1983499738	0.7586702571	1.9366636501
C	-2.7473121224	1.111804196	-0.3834181782
Li	-0.2179850819	-0.3227268921	-0.1111659455
C	0.921934889	-2.1638063064	0.28149307
C	1.5498816442	-2.5527923386	1.6202962532
C	1.7060316945	-2.7900457719	-0.8718698779
C	-0.5333554921	-2.6698571127	0.2483573554
H	-0.1521470199	2.157090739	1.4745254794
H	-1.4282759491	3.1318259013	0.7335510069
H	0.7514577763	3.2202293285	-0.4900189308
H	-0.5921645199	2.6791609585	-1.5117393196
H	1.3254709609	-0.7329803628	0.27777187
H	1.8122524434	1.3970347028	0.8273351226
H	2.6973827871	0.5345555102	-0.4346029112
H	1.8194007611	0.3177808021	-2.6286271266
H	2.1428557738	2.0516679317	-2.3791282873
H	0.5968823266	1.5131846683	-3.1076577917
H	-2.7915968259	-0.1611555675	1.926323906
H	-2.8433944888	1.5856500593	2.2816244246
H	-1.3795805849	0.6336372058	2.6516356601
H	-3.3402494454	0.1917280241	-0.3647197888
H	-2.3452265429	1.239675955	-1.3917623205
H	-3.416235036	1.96202236	-0.1608971159
H	1.0018791432	-2.1178847571	2.470664891
H	2.587816339	-2.1964213464	1.6940316443
H	1.5710644906	-3.6489956951	1.7769622086
H	2.7410039483	-2.4186886043	-0.8979460771
H	1.2567116546	-2.5625063225	-1.8507357997
H	1.7642789353	-3.8945571368	-0.7966335902
H	-1.033450913	-2.4747158497	-0.7172083301
H	-1.1576680199	-2.2290445218	1.0453830733
H	-0.6022335191	-3.7680239331	0.3969437569

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