Supporting Information for

Adaption of a Ph₂P(BH₃)CHP(BH₃)Ph₂ ligand *via* formal 1,2-Borane migration

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Experimental Section

General data

All manipulations were carried out using modified Schlenk techniques under an atmosphere of argon. Prior to use, thf, diethyl ether, benzene, toluene and tetramethylethylendiamine (tmeda) were dried according to common procedures and distilled in an argon atmosphere. Deuterated solvents were dried over sodium, degassed, and saturated with argon. The yields given are not optimized. ¹H, ¹¹B{¹H}, ¹³C{¹H} and ³¹P{1H} NMR spectra were recorded on Bruker AC 200 MHz or AC 400 spectrometers. ¹H and ¹³C chemical shifts are reported in parts per million relative to Me₄Si as external standard. The reported ³¹P and ¹¹B shifts are relative to 85% H₃PO₄ and BF₃·Et₂O as external references, respectively. Coupling constants are given in hertz. The following abbreviations are used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet. Elemental analyses were performed utilizing a Leco CHNS-932 Elemental Analyzer at the Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich-Schiller-University Jena.

Synthesis of [K{Ph₂P(BH₃)CHP(BH₃)Ph₂}]_∞ (1)

According to literature,^{S1} solid KOtBu (0.19 g, 1.70 mmol) was added to a stirred solution of $[(Et_2O)_2Li{Ph_2P(BH_3)CHP(BH_3)Ph_2}],$ freshly prepared from 0.71 g (1.72 mmol) dppm(BH₃)₂ and 1.1 mL of *n*-buthyllithium (1.6M in Hexane) in diethylether (35 mL). The resulting suspension was stirred for additional two hours and the precipitate formed was isolated by filtration afterwards. The pale yellow solid was thereafter washed with cold diethylether $(2 \times 10 \text{ mL})$ and dried in a vacuum. Yield: 0.74 g of 1 (1.64 mmol, 97%); elemental analysis: C₂₅H₂₇B₂KP₂ (450.16), calcd.: C 66.70, H 6.05; found: C 66.82, H 6.50; ¹H NMR (400 MHz, d₈-THF, 25°C): δ 0.4-1.4 (br, 6H, BH₃), 0.61 (t, ²J_{H,P} = 7.2 Hz, 1H, PCHP), 7.09-7.16 (m, 12H, Ph), 7.66 (m, 8H, Ph). ¹¹B{¹H} NMR (128.4 MHz, d₈-THF, 25°C): δ –34.0 (br). ¹³C{¹H} NMR (100.6 MHz, d₈-THF, 25°C): δ 6.9 (t, ¹J_{C,P} = 76.8 Hz, 1C, PCP), 127.6 (pseudo-t, 8C, CH Ph), 128.3 (s, 4C, p-CH Ph), 132.8 (pseudo-t, 8C, CH Ph), 143.7 (d, ${}^{1}J_{C,P} = 60.0$ Hz, 4C, *i*-C Ph). ${}^{31}P{}^{1}H{}$ NMR (161.95 MHz, d₈-THF, 25°C): δ 14.3 (br).





Figure S1. $^{13}C{^{1}H}$ NMR spectrum of **1** in d₈-THF.

Synthesis of $[(tmeda)_2K{Ph_2P(BH_3)CHP(BH_3)Ph_2}]_{\infty}(2)$

Compound **1** (265 mg, 0.59 mmol) was taken up in tmeda (10 mL) and the resulting suspension was stirred for 30 minutes. The tiny colorless needles formed were collected on a Schlenk frit and dried in a vacuum. Yield: 350 mg (0.51 mmol, 87%). ¹H NMR (400 MHz, d₈-THF, 25°C): δ 0.4-1.4 (br, 6H, BH₃), 0.61 (t, ²J_{H,P} = 7.1 Hz, 1H, PCHP), 2.16 (s, 12H, CH₃ tmeda), 2.31 (s, 4H, CH₂ tmeda), 7.09-7.16 (m, 12H, Ph), 7.66 (m, 8H, Ph). ¹¹B{¹H} NMR (128.4 MHz, d₈-THF, 25°C): δ –34.0 (br). ¹³C{¹H} NMR (100.6 MHz, d₈-THF, 25°C): δ 6.9 (t, ¹J_{C,P} = 76.8 Hz, 1C, PCP), 46.3 (s, 4C, CH₃ tmeda), 59.0 (s, 2C, CH₂ tmeda), 127.6 (pseudo-t, 8C, CH Ph), 128.3 (s, 4C, *p*-CH Ph), 132.8 (pseudo-t, 8C, CH Ph), 143.7 (d, ¹J_{C,P} = 60.0 Hz, 4C, *i*-C Ph). ³¹P{¹H} NMR (161.95 MHz, d₈-THF, 25°C): δ 14.3 (br).

Suitable crystals for X-ray diffraction experiments were obtained at ambient temperature by layering a saturated solution of 2 in a THF/tmeda mixture with *n*-heptane.



Figure S2. ${}^{13}C{}^{1}H$ NMR spectrum of **2** in d₈-THF.

Synthesis of $[(solv)_2Ba{Ph_2P(BH_3)CHP(BH_3)Ph_2}_2]$ (solv = Et₂O, THF) and [Ba₄O{Ph₂P(BH₃)CHP(BH₃)Ph₂}₃{Ph₂P(BH₃)CHP(BH₃)Ph₂}₃]·benzene (3)

Solid 1 (1.04 g, 2.31 mmol) was added to a stirred solution of [(thf)₅BaI₂] (0.77 g, 1.02 mmol) in THF (20 mL), leading to the precipitation of colorless potassium iodide. The reaction mixture was stirred for an additional hour and reduced to dryness afterwards. The remaining colorless residue was dried in vacuo and suspended in toluene (15 mL) thereafter. The formed suspension was stirred for 30 minutes and then filtered. The insoluble residue was discarded. The colorless solution was reduced to dryness, resulting in the formation of colorless foam. Addition of diethyl ether (10 mL) led to precipitation of a colorless solid of the composition $[(solv)_2Ba{Ph_2P(BH_3)CHP(BH_3)Ph_2}_2]$ (solv = mixture of Et₂O and thf, ratio four to one) which was collected on a Schlenk frit and gently dried in a vacuum. Prolonged drying in vacuum led to a partial loss of incorporated diethyl ether. Yield: 1.01 g white powder (0.91 mmol, 89%). ¹H NMR (200 MHz, C_6D_6 , 25°C): δ 0.6-2.8 (br, 12H, BH₃), 1.10 (t, ³J_{H,H} = 7.0 Hz, CH₃ Et₂O), 1.20 (m, CH₂ thf), 1.51 (t, ${}^{2}J_{H,P} = 13.1$ Hz, 2H, PCHP), 3.27 (q, OCH₂ Et₂O), 3.48 (m, OCH₂ thf), 6.9-7.1 (m, 24H, Ph), 7.77 (m, 16H, Ph). $^{11}B{^{1}H}$ NMR (128.4 MHz, C₆D₆, 25°C): δ -29.6 (br). ¹³C{¹H} NMR (50.3 MHz, C₆D₆, 25°C): δ 7.9 (t, ¹J_{C,P} = 49.8 Hz, 2C, PCP), 15.5 (s, CH₃ Et₂O), 25.3 (s, CH₂, thf), 65.9 (OCH₂, Et₂O), 68.8 (OCH₂, thf), 128.4 (m, 16C, CH Ph), 129.4 (br, 8C, *p*-CH Ph), 130.1 (m, 16C, CH Ph), 138.6 (d, ¹J_{C,P} = 65.1 Hz, 8C, *i*-C Ph). ${}^{31}P{}^{1}H{}$ NMR (81.0 MHz, C₆D₆, 25°C): δ 8.4 (br).

A portion of $[(solv)_2Ba{Ph_2P(BH_3)CHP(BH_3)Ph_2}_2]$ (236 mg, 0.21 mmol) was dissolved in benzene (4 mL) and heated to 65 °C (bath temperature) for 24 hours. Afterwards the solution was cooled to ambient temperature and filtered to remove a small amount of a colorless precipitate. Thereafter, pentane (4 mL) was added to the benzene solution *via* vapor diffusion. The resulting well shaped colorless crystals were isolated by decantation, washed with *n*pentane (3 mL) and dried in a vacuum. Yield: 67 mg of **3** (0.022 mmol, 40%); racemic mixture of the (*R*,*R*,*R*)- and (*S*,*S*,*S*)-enatiomer. Elemental analysis: C₁₅₆H₁₆₈Ba₄B₁₂P₁₂O (3109.787), calcd.: C 60.25, H 5.45; found: C 60.05, H 5.57.



Figure S3. ¹³C{¹H} NMR spectrum of $[(solv)_2Ba{Ph_2P(BH_3)CHP(BH_3)Ph_2}_2]$ in C₆D₆ (* denotes the signals of Ph_2P(BH_3)CH_2P(BH_3)Ph_2, present as an impurity due to partial hydrolysis of the product during sample preparation).

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X-ray structure determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_{α} radiation. Data was corrected for Lorentz and polarization effects but not for absorption effects.^{S2,S3} The structures were solved by direct methods (SHELXS^{S4}) and refined by full-matrix least squares techniques against F_o² (SHELXL-97^{S4}). All non-disordered, non-hydrogen atoms were refined anisotropically.^{S4} Hydrogen atoms were introduced in calculated positions and refined with a riding model. The crystals of **1** were extremely thin and of low quality, resulting in a substandard data set; however, the structure is sufficient to show connectivity and geometry despite the high final *R* value. We will only publish the conformation of the molecule and the crystallographic data. We will not deposit the data in the Cambridge Crystallographic Data Centre. The crystal structure of **3** contains solvent accessible voids (5308 Å³/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the Squeeze routine of Platon resulting in 918 electrons/unit cell.^{S5} Crystallographic data as well as structure solution and refinement details are summarized in Table S1. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Compound	1	2	3
formula	$C_{25}H_{27}B_2KP_2$	$C_{37}H_{59}B_2KN_4P_2$	C ₁₅₀ H ₁₆₂ B ₁₂ Ba ₄ OP ₁₂ + disordered solvent
fw/ g·mol ⁻¹	450.13	682.54	3031.52
T/ °C	-140(2)	-140(2)	-90(2)
crystal system	triclinic	triclinic	hexagonal
space group	Pī	Pī	P -3 c 1
<i>a</i> / Å	8.0894(4)	10.1261(2)	24.6465(8)
<i>b</i> / Å	13.9878(5)	11.4604(4)	24.6465(9)
<i>c</i> / Å	22.2741(9)	18.7902(8)	35.3753(10)
α/\deg	72.917(3)	87.101(2)	90
β / deg	89.712(2)	89.417(2)	90
γ/ deg	87.486(3)	70.312(2)	120
$V/ \text{\AA}^3$	2406.78(18)	2050.43(12)	18609.8(11)
Ζ	4	2	4
ρ / g·cm ⁻³	1.242	1.106	1.082
μ/ cm^{-1}	3.64	2.36	9.77
measured data	11424	12653	33241
data with $I > 2\sigma(I)$	7339	7613	6031
unique data (R _{int})	9020/0.0501	9136/0.0302	12177/0.0594
wR_2 (all data, on F^2) ^{a)}	0.5678	0.1762	0.2311
$R_1 \left(I > 2\sigma(I) \right)^{a}$	0.2251	0.0836	0.0746
S ^{b)}	2.483	1.178	1.056
Res. dens./e·Å ⁻³	4.468/-1.312	0.370/-0.372	2.292/-1.330
absorpt method	none	none	none
CCDC No.	motif	900418	900419

Table S1. Crystal data and refinement details for the X-ray structure determination	ons of 1-3 .

^{a)} Definition of the *R* indices: $R_1 = (\Sigma || F_0 - F_c ||) / \Sigma |F_0|$; $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2 (F_0^2) + (aP)^2 + bP$; $P = [2F_c^2 + Max(F_0^2)/3;$ ^{b)} $s = \{\Sigma[w(F_0^2 - F_c^2)^2] / (N_0 - N_p)\}^{1/2}$.





Figure S4. Structural motif and numbering scheme of **1** (top); and coordination polymer formed (bottom).

Theoretical Calculations

Methods

Structural optimizations and transition state calculations were carried out with the Gaussian09 program package.^{S6} The molecular geometries were first optimized with BP86/TZVP,^{S7,S8} and subsequently with B97-D/TZVP in order to consider dispersive interactions,^{S9,S10} both times in combination with the resolution of identity ('RI') density fitting technique,^{S11} as implemented in the Gaussian09 program. Molecular structures were visualized with the GaussView Program.

Comparison of optimized and experimentally determined structures

In Table S2 the structural parameters of $Ph_2P(BH_3)CHP(BH_3)Ph_2$ (L) (see also Figure S5) and its isomer $Ph_2PCH(BH_3)P(BH_3)Ph_2$ (L') (see also Figure S6) are shown. One transition state for the transfer of a boryl group from one phosphorus atom to the central carbon atom (L-TS) (see also Figure S7) was found.

Structural	Type of Structure					
Parameters	0	ptimized Structu	res	X-ray Structures		
	L	L'	L-TS	L ^[a]	L' ^[b]	-
Distances [pm]						
P1-B1	196.0(196.8)	282.1(289.7)	281.8(286.8)	192.9	274.6	
P1-C(Ph1)	186.9(186.3)	189.6(189.1)	187.0(187.7)	183.4	181.4	
P1-C(Ph2)	187.2(186.5)	187.4(187.5)	188.6(189.0)	183.6	181.9	
C-B1	306.7(308.4)	169.9(172.0)	274.3(289.5)	298.1	163.8	
P2-C(Ph3)	187.9(186.6)	186.1(186.4)	187.7(185.9)	183.8	180.9	
P2-C(Ph4)	187.1(187.4)	187.2(185.2)	186.3(187.4)	183.0	181.4	
P2-B2	195.6(196.3)	194.9(195.4)	195.7(196.5)	194.1	191.9	
P1-C	175.1(174.8)	188.0(188.3)	177.7(176.9)	171.4	183.8	
P2-C	175.2(174.6)	184.4(183.8)	178.5(177.6)	171.7	183.0	
Angle [deg]						
P1-C-P2	133.7(130.4)	112.5(111.3)	131.6(131.2)	134.6	109.9	

Table S2. Structural parameters of **L** and **L'** optimized with BP86/TZVP (B97-D optimized values are in parenthesis).

[a] The data of $[(dme)_3Li][Ph_2P(BH_3)CHP(BH_3)Ph_2]$ was used.^{S1} [b] The data of compound **3** was used; P1 corresponds to P4, P2 to P3, B1 to B4 and B2 to B3 in compound **3**.



Figure S5. The BP86/TZVP optimized structure of L.



Figure S6. The BP86/TZVP optimized structure of L'.



Figure S7. The BP86/TZVP transition state structure for the intramolecular isomerization of **L**.

References

- S1 J. Langer, K. Wimmer, H. Görls and M. Westerhausen, *Dalton Trans.*, 2009, 2951–2957.
- S2 COLLECT, Data Collection Software; Nonius B.V., Netherlands, 1998.
- S3 Otwinowski, Z.; Minor, W. Processing of X-Ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: 1997; pp 307-326.
- S4 G. M. Sheldrick, *Acta Cryst.*, 2008, A64, 112-122.
- S5 A. L. Spek, Acta Cryst., 2009, **D65**, 148-155.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.
- S7 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
- S8 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824.
- S9 S. Grimme, J. Comput. Chem., 2004, 25, 1463-1473.
- S10 A. Schäfer, C. Huber and R. Ahlrichs, J. Chem. Phys., 1994, 100, 5829-5835.
- S11 K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, 242, 652-660.