Supporting Information for

A T-shape diphosphinoborane palladium(0) complex

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Experimental procedures and characterization data; crystallographic

information for 9; ¹H, ¹¹B, ¹³C and ³¹P NMR spectra

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General information

All manipulations were carried out under an inert argon atmosphere using either standard Schlenk technique or a MBraun Glovebox. Et₂O, pentane, toluene, DCM and THF were taken from a solvent purification system (M. Braun, SPS 800). Benzene, 1,4-dioxane and *n*-hexane were dried over sodium and distilled under an argon atmosphere. Deuterated solvents were degassed using the freeze pump thaw technique and stored over molecular sieves (4 Å). Cyclopentadienyl allyl palladium [1] and (2-bromophenyl)dicyclohexylphosphine **7** [2] were synthesized following published procedures. NMR spectra were recorded with a Bruker Avance II 400.13 MHz spectrometer at room temperature in a Wilmad[®] quick pressure valve NMR tube. The ¹H and ¹³C NMR spectra were referenced to residual solvent resonances [3] ¹¹B, ¹³C, ¹⁹F and ³¹P NMR-spectra were recorded broadband decoupled. If purchased, all chemicals were used as delivered with no further purification.

Single crystal X-ray diffraction

Mo K α radiation ($\lambda = 0.71073$ Å) was produced from an Incoatec I- μ S microsource equipped with multilayer optics. Data were collected at 100(2) K on a Bruker D8 goniometer equipped with an Apex CCD detector. Temperature stability during data collection was realized by an Oxford Cryosystems 700 controller. Integration was performed by the SAINT software [4]. The SADABS software [5] was used for multi-scan absorption correction. Using Olex2 [6], the structure was solved with the ShelXS [7] structure solution program employing direct methods. Refinement was performed with the XL [8] refinement package using least squares minimization. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

| Identification code | CCDC 1471929 (complex 9) |
|---|--|
| Empirical formula | $C_{48}H_{71}BP_2Pd$ |
| Formula weight | 827.20 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | P2 ₁ /c |
| a/Å | 11.3000(10) |
| b/Å | 14.4355(13) |
| c/Å | 26.239(2) |
| $\alpha/^{\circ}$ | 90.00 |
| β/° | 94.704(2) |
| γ/° | 90.00 |
| Volume/Å ³ | 4265.7(7) |
| Z | 4 |
| $\rho_{calc}g/cm^3$ | 1.288 |
| μ/mm^{-1} | 0.542 |
| F(000) | 1760.0 |
| Crystal size/mm ³ | $0.61 \times 0.36 \times 0.28$ |
| Radiation | MoK α ($\lambda = 0.71073$) |
| 2Θ range for data collection/° | 3.22 to 53.1 |
| Index ranges | -14 \leq h \leq 14, -18 \leq k \leq 18, -32 \leq l \leq 32 |
| Reflections collected | 51374 |
| Independent reflections | 8861 [$R_{int} = 0.0625$, $R_{sigma} = 0.0421$] |
| Data/restraints/parameters | 8861/0/471 |
| Goodness-of-fit on F ² | 1.042 |
| Final R indexes [I>= 2σ (I)] | $R_1 = 0.0323, wR_2 = 0.0742$ |
| Final R indexes [all data] | $R_1 = 0.0408, wR_2 = 0.0784$ |
| Largest diff. peak/hole / e Å ⁻³ | 0.62/-0.38 |

DFT calculation

Geometry optimization of complex **9** was carried out without any symmetry restrictions. The calculation was performed using Turbomole 6.5 [9]. RI-DFT calculation was carried out using BP86/def-SV(P).

| Bond | distance or angle | distance or angle |
|------------|-------------------|-------------------|
| | (XRD) | (DFT) |
| Pd1-P1 | 2.2766(6) Å | 2.277 Å |
| Pd1–P2 | 2.3082(6) Å | 2.308 Å |
| Pd1-B1 | 2.244(2) Å | 2.243 Å |
| С20-В1 | 1.614(3) Å | 1.615 Å |
| C35–B1 | 1.621(3) Å | 1.621 Å |
| C15–B1 | 1.610(3) Å | 1.611 Å |
| P1-Pd1-P2 | 157.73(2)° | 157.7° |
| C15-B1-C35 | 116.64(18)° | 116.7° |
| C15-B1-C20 | 110.86(18)° | 110.8° |
| C20-B1-C35 | 112.70(17)° | 112.7° |

Syntheses

(2-(Dicyclohexylphosphino)phenyl)lithium·Et₂O (8). n-BuLi (7.5 mL; 1.6 M; 12 mmol; 1.3

PCy₂ equiv.) was added to a solution of (2-bromophenyl)dicyclohexylphosphine 7 (3.253 g; 9.239 mmol; 1 equiv) in ether (15 mL) at -78 °C. After stirring the solution at -78 °C (1.5 h) and then at room temperature (0.5 h), a white precipitate was formed. The product was isolated by filtration and washing of the residue with Et₂O. Yield: 2.395 g (6.760 mmol; 73%).

¹**H NMR** (THF-*d*₈, 400 MHz): $\delta = 7.72$ (m, 1H, Ar-*H*); 7.03 (m, 1H, Ar-*H*); 6.63-6.73 (m, 2H, Ar-*H*); 3.39 (q, 4H, (CH₃CH₂)₂O); 1.93 – 1.70 (m, 6H, Cy-*H* and residual THF-*d*₈ signal); 1.71 – 1.58 (m, 4H, Cy-*H*); 1.35 – 0.95 (m, 18H, Cy-*H* and (CH₃CH₂)₂O) ppm. ³¹**P NMR** (THF-*d*₈, 162 MHz): $\delta = 3.96$ (s) ppm. ⁷Li **NMR** (THF-*d*₈, 156 MHz): 1.41 (s) ppm.

((Phenylboranediyl)bis(2,1-phenylene))bis(dicyclohexylphosphine) (^{Cy}DPB^{Ph}). To a



solution of (2-(dicyclohexylphosphino)phenyl)lithium·Et₂O (8) (1.999 g; 5.640 mmol; 1 equiv) in toluene (20 mL) cooled to -78 °C, a standard solution of PhBCl₂ in toluene (5.64 mL; 2.82 mmol; 0.50 M; 0.5 equiv) was added drop wise over a period of 4 h. After stirring for 1 h at -78 °C, all volatiles were removed in vacuo. The solid was solubilized in DCM,

the salts were filtered off, and volatiles were removed under reduced pressure. $^{Cy}DPB^{Ph}$ was obtained as a colorless powder by washing the resulting solid with pentane (3 × 5 mL) and removing all volatiles in vacuo. Yield: 1.547 g (2.44 mmol; 86%).

¹**H** NMR (DCM- d_2 , 400 MHz): $\delta = 8.07$ (d, 2H, J = 7.5 Hz, Ar-*H*); 7.43-7.35 (m, 4H, Ar-*H*); 7.28-7.20 (m, 4H, Ar-*H*); 7.16-7.11 (m, 3H, Ar-*H*); 1.88-1.78 (m, 4H, Cy-*H*); 1.74-1.59 (m, 8H, Cy-*H*); 1.59-1.46 (m, 8H, Cy-*H*); 1.46-1.37 (m, 4H, Cy-*H*); 1.18-0.96 (m, 16H, Cy-*H*); 0.93-0.81 (m, 4H, Cy-*H*) ppm. ¹¹**B** NMR (DCM- d_2 , 128 MHz): $\delta = 41$ (s, w_{1/2} = 1300 ± 120 Hz) ppm. ¹³C NMR (DCM- d_2 , 101 MHz): $\delta = 160.87$ (bs, 1C, C1 or C1'); 160.43 (bs, 1C, C1' or C1); 148.55 (bs, 1C, C7); 136.76-136.57 (m, 3C); 135.257 (pt, 2C, J = 23.7 Hz, C2, C2;); 131.43 (s, 2C); 128.68 (s, 2C); 128.40 (s, 1C, C10); 127.37 (s, 2C); 126.41 (s, 2C); 35.76 (m_c, 4C, C13, C13', C19, C19'); 30.47-30.07 (m, 8C, C14, C14', C18, C18', C20, C20', C24, C24'); 27.88 (m_c, 4C); 27.71 (m_c, 4C); 26.88 (s, 4C, C16, C16', C22, C22') ppm. ³¹P NMR (DCM- d_2 , 162 MHz): $\delta = 1.70$ (s) ppm. MS: EI⁺ m/z = 634.5 (M), 551.4 (M-Cy), 437.3 (M-PCy₂), 361.3 (M-PPhCy₂), 274.3 (PPhCy₂) and 192.2 (PCyPh). HRMS (EI): calculated for C₄₂H₅₇BP₂ (M) 634.40286; found 634.40260. **IR** (KBr): $\mathfrak{P} = 3388$ (vs), 2922 (m), 2848 (w), 1628 (m), 1446 (vw), 1236 (vw), 521 (m) cm⁻¹. **M.P.** = $280 \degree C$ (decomposition).

Synthesis of {[(o-PCy₂C₆H₄)₂BPh]Pd(0)} (9). ^{Cy}DPB^{Ph} (500.2 mg, 788.1 µmol, 1 equiv) and



CpPd-(η^3 -C₃H₅) (167.7 mg, 787.7 µmol, 1 equiv) were solubilized in benzene (2 mL). After stirring for 18 h at 50 °C the volatiles were removed in vacuo. The product was obtained after washing the yellow residue three times with pentane (3 mL) and removing all volatiles in vacuo. Yield: 532.2 mg (718.1 µmol; 91%). Compound

9 may be crystalized from hexane or pentane. Crystals suitable for single crystal X-ray diffraction analysis were obtained by crystallization from hexane at 4 °C.

¹**H NMR** (benzene- d_6 , 400 MHz): $\delta = 7.79$ (d, 2H, J = 7.0 Hz, H3/H3'); 7.63 (dd, 2H, J = 8.1 Hz, J = 1.5 Hz, H6/H6'); 7.27 (pdt, 2H, J = 7.4 Hz, 3.0 Hz, Ar-H); 7.24-7.17 (m, 4H, Ar-*H*); 7.14-7.09 (m, 3H, Ar-*H*); 2.14 (ptt, 2H, J = 12.0 Hz, 2.6 Hz, H13 or H19); 2.09-1.97 (m, 6H, Cy-H); 1.83-1.75 (m, 2H, Cy-H); 1.72-1.47 (m, 14H, Cy-H); 1.46-0.91 (m, 20H, Cy-H) ppm. ¹¹**B** NMR (benzene- d_6 , 128 MHz): $\delta = 22$ (s, $w_{1/2} = 800 \pm 50$ Hz) ppm. ¹³C NMR (benzene- d_6 , 101 MHz): $\delta = 166.33$ (bs, 2C, C1/C1'); 156.00 (bs, 1C, C7); 135.12 (s, 2C, C6/C6'); 134.82 (pt, 2C, J = 16.4 Hz, C2/C2'); 132.28 (pt, 2C, J = 10.8 Hz, C3/C3'); 129.99 (s, 2C); 128.71 (s, 2C); 126.82 (s, 2C); 125.74 (s, 1C, C10); 125.15 (t, 2C, J = 2.6 Hz, C4/C4'); 35.9 (pt, 2C, J = 9.3 Hz, C13'/C13); 35.66 (pt, 2C, J = 9.3 Hz, C13/C13'); 31.75 (pt, 2C, 4.5 Hz, C13/C13' or C19/C19'); 31.33 (pt, 2C, J = 4.0 Hz, C19/C19' or C13/C13'); 29.70 (s, 2C); 29.15 (s, 2C); 27.50 (pt, 2C, J = 6.6 Hz); 27.43 (pt, 2C, J = 5.1 Hz); 27.23 (pt, 2C, J = 5.8 Hz); 27.09 (pt, 2C, J = 6.8 Hz); 26.59 (s, 2C, C16/C16'); 26.29 (s, 2C, C16'/C16) ppm. ³¹**P** NMR (benzene- d_6 , 162 MHz): $\delta = 41.0$ (s) ppm. MS: EI⁺ m/z = 740.3 (M), 663.3 (M-Ph), 580.2 (M-Ph-Cy), 361.3 (M-PdPPhCy₂), 274.3 (PPhCy₂), 192.2 (PCyPh). Combustion analysis (batch crystalized from pentane): calculated for C₄₂H₅₇BP₂Pd•0.5C₅H₁₂ C 68.77%, H 8.17%; found: C 68.91%, H 8.092. M.P. = 126 °C (decomposition).

NMR Spectra



Fig. S1. ¹H NMR (400 MHz, dichloromethane-d²) of ^{Cy}DPB^{Ph}.



Fig. S2. ³¹P NMR (162 MHz, dichloromethane-d²) of ^{Cy}DPB^{Ph}.



Fig. S3. ¹¹B NMR (128 MHz, dichloromethane-d²) of ^{Cy}DPB^{Ph}.



Fig. S4. ¹¹B NMR (128 MHz, dichloromethane-d²) of ^{Cy}DPB^{Ph} after background substraction.



Fig. S5. ¹³C NMR (101 MHz, dichloromethane-d²) of ^{Cy}DPB^{Ph}.

Fig. S6. 1 H NMR (400 MHz, benzene-d⁶) of **8**.

Fig. S7. 31 P NMR (162 MHz, benzene-d⁶) of **8**.

Fig. S8. ¹¹B NMR (128 MHz, benzene- d^6) of **8**.

Fig. S9. ¹¹B NMR (128 MHz, benzene-d⁶) of **8** after background substraction.

Fig. S10. 13 C NMR (101 MHz, benzene-d⁶) of **8**.

References

- 1. Tatsuno, O. S.; Yoshida, T.; Otsuka, S. Inorg. Synth. 1990, 26, 242.
- 2. Murata, M.; Buchwald, S. L., Tetrahedron 2004, 60, 7397-7403.
- Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., *Organometallics* 2010, 29, 2176.
- 4. SAINT, Version 6.45. Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
- 5. SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
- Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. Appl. Cryst., 2009, 42, 339.
- 7. Sheldrick, G. M. Acta Cryst., 2008, A64, 112.
- 8. Sheldrick, G. M. Acta Cryst., 2015, C71, 3.
- **9**. TURBOMOLE V6.5 2013, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007.