



A T-shape diphosfinoborane palladium(0) complex

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Letter

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Abstract

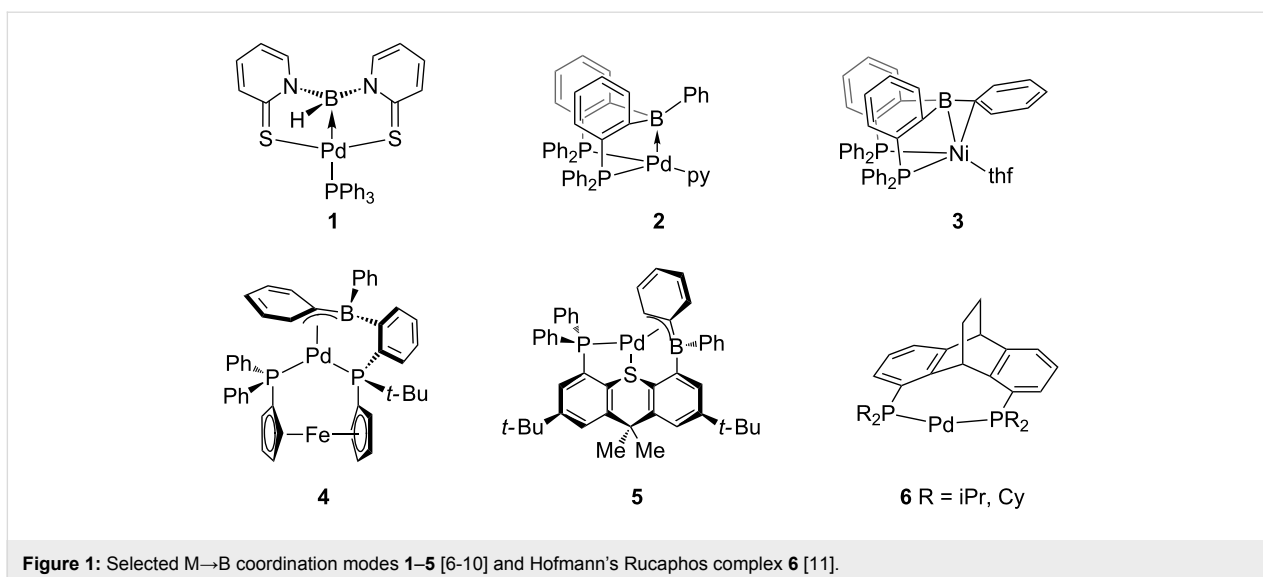
The reaction of $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ with the new diphosfinoborane ligand derivative $(o\text{-PCy}_2\text{-C}_6\text{H}_4)_2\text{BPh}^{\text{CyDPB}^{\text{Ph}}}$ affords the T-shape complex $(\text{CyDPB}^{\text{Ph}})\text{Pd}(0)$ **9**, which was characterized by X-ray analysis.

Introduction

The amplification of traditional bidentate chelating L_2 -type ligands with a tethered borane functionality (e.g., Bourissou's diphosfinoborane $(o\text{-PR}_2\text{-C}_6\text{H}_4)_2\text{BR}'$ ligand $\text{R}^{\text{DPB}^{\text{R}'}}$) has received considerable attention [1-3], with first catalytic applications emerging [4]. The acyclic boron group in these ligands can adopt a variety of coordination modes (Figure 1) [5].

The borane can act as a σ -acceptor ligand in case of $\eta^1\text{-B}$ coordination (e.g., **1** [6] and **2** [7]), or as a boron containing π -ligand adopting $\eta^2\text{-B,C}$ (**3**) [8] or $\eta^3\text{-B,C,C}$ coordination (**4** and **5**) [5,9,10]. Changes of the hapticity appear to have significant influence onto the reactivity of the coordinated transition metal towards substrates [8]. For zerovalent palladium complexes only few examples featuring a η^1 -type $\text{Pd}\rightarrow\text{B}$ interaction have been reported [6,7]. However, these complexes require phos-

phines or pyridines as a stabilizing co-ligand, which can act as an inhibitor in catalytic transformations [7]. Similarly, monometallic 14 VE palladium complexes featuring a chelating diphosphine, such as in Hofmann's Rucaphos complexes **6**, are very scarce [11]. While the dative $\text{Pd}\rightarrow\text{B}$ bond is strong in zerovalent $\text{Pd}(0)$ **DPB** complexes such as **2**, only weak $\text{Pd}\rightarrow\text{B}$ interactions have been observed for the respective $\text{Pd}(\text{II})$ complexes [7,12]. Discrimination by the borane functionality between the oxidation states $\text{Pd}(0)/\text{Pd}(\text{II})$ is of potential interest for organometallic transformations involved in homogeneous catalysis, such as the reductive elimination. Here we report the synthesis of the diphosfinoborane $(o\text{-PCy}_2\text{-C}_6\text{H}_4)_2\text{BPh}$ ligand CyDPB^{Ph} . CyDPB^{Ph} reacts with $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ yielding monometallic zerovalent palladium complex **9** featuring a distinct $\eta^1\text{-B}$ coordination mode, without the need of a stabilizing co-ligand.



Findings

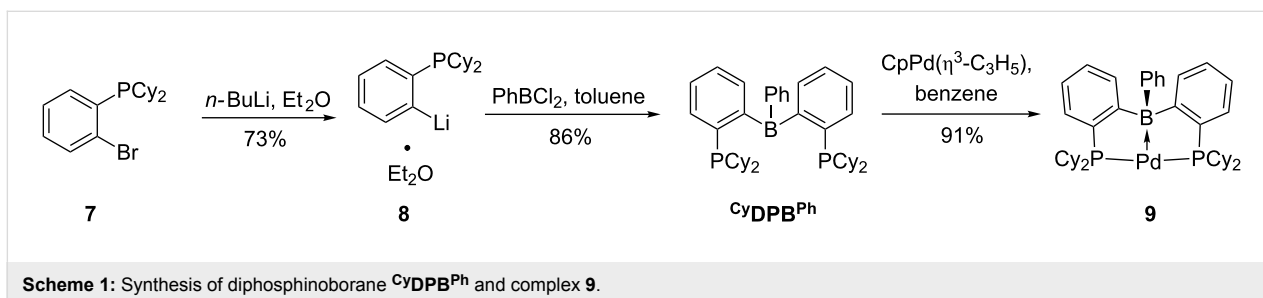
For the synthesis of **CyDPB^{Ph}** we adapted the known reaction sequence for the production of Bourissou's (*o*-PPh₂-C₆H₄)₂BPh ligand **PhDPB^{Ph}** (Scheme 1) [13,14].

Starting material (2-bromophenyl)dicyclohexylphosphine (**7**) was produced by palladium catalyzed coupling of dicyclohexylphosphine with 1-iodo-2-bromobenzene [15]. Phosphine **7** was lithiated in diethyl ether with *n*-BuLi [16,17], affording the diethyl ether adduct **8**. Reaction of **8** with 0.5 equiv of PhBCl₂ in toluene at –78 °C produced the desired ligand **CyDBP^{Ph}** in 86% isolated yield. Typical resonances for a DPB ligand were observed in the ³¹P NMR spectrum at δ 1.70 and in the ¹¹B NMR spectrum at δ 41 (*w*_{1/2} = 1300 ± 120 Hz), which are indicative for a dynamic P→B bond in solution [18].

CyDPB^{Ph} was reacted with 1 equiv of CpPd(η³-C₃H₅) in benzene. Complete conversion towards complex **9** with equimolar formation of 5-allylcyclopenta-1,3-diene was reached within 18 h at 50 °C. Complex **9** showed a singlet resonance at δ 41.0 in the ³¹P NMR spectrum and a broad resonance at δ 22 (*w*_{1/2} = 800 ± 50 Hz) in the ¹¹B NMR spectrum. High field shift and narrowing of the ¹¹B NMR with respect to the free

CyDPB^{Ph} ligand indicated the presence of a strong dative Pd(0)→B bond [7]. Despite the absence of a stabilizing co-ligand, we found complex **9** to be very stable in solution. The coordinating properties of **CyDPB^{Ph}** deviate from those observed for its aryl derivatives (**PhDPB^{Ph}** ((*o*-PPh₂-C₆H₄)₂BPh) and **PhDPB^{Mes}** ((*o*-PPh₂-C₆H₄)₂B(Mes))). For these ligands the reaction with one equivalent of CpPd(η³-C₃H₅) leads to 50% consumption of CpPd(η³-C₃H₅) with simultaneous formation of 5-allylcyclopenta-1,3-diene, but complete conversion of the ligand pointing towards the formation of a bisligand complex (DPB)₂Pd [7]. Unlike complex **2** we were unable to form a pyridine adduct complex by treatment of **9** with 10 equiv of pyridine. Single crystals of complex **9** suitable for X-ray diffraction analysis were grown from hexane (Figure 2).

The solid-state structure of **9** displayed a slightly distorted T-shape geometry around the palladium center. A short Pd1–B1 distance of 2.243(2) Å (cf. complex **2**: 2.194(3) Å) and a significant pyramidalization at the boron center (Σ*B*_α = 341°) is observed, indicating a strong Pd(0)→B bond. The distance between C20 and Pd1 was found to be 3.0805(22) Å. The η¹-B coordination mode was well reproduced by DFT calculations (Supporting Information File 1). DFT calculations predict



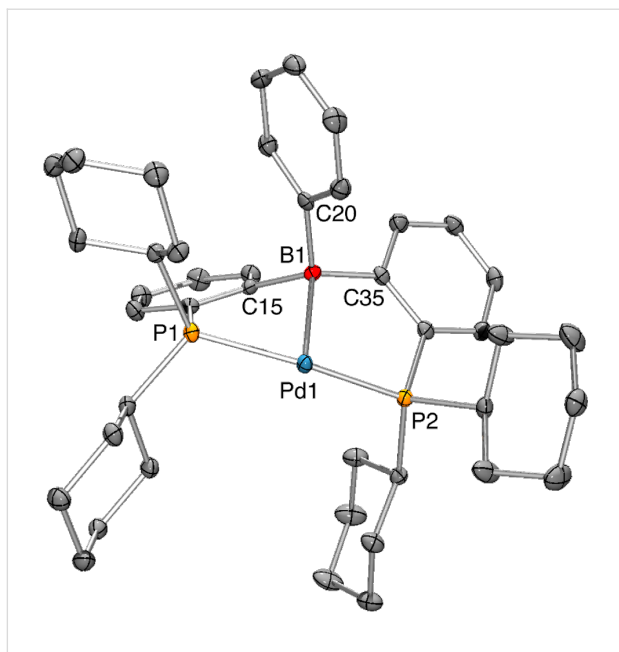


Figure 2: Thermal ellipsoid plots of complex **9** at the 50% probability level. H atoms and one molecule of hexane have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Pd1–B1 2.243(2), Pd1–P1 2.2761(6), Pd1–P2 2.3084(6), B1–Pd1–P1 85.82(6), B1–Pd1–P2 82.49(6), P1–Pd1–P2 157.72(2), C15–B1–C20 110.94(18), C15–B1–C35 116.58(18), C20–B1–C35 112.56(18).

T-shape complexes with an almost linear P–Pd–P angle for model complexes $(\text{PMe}_3)_2\text{Pd} \rightarrow \text{EX}_3$ (E = B; X = H, F, Cl, Br, I) [17]. In complex **9** the *trans*-coordinated palladium center featured an obtuse P1–Pd1–P2 angle of 157.72(2)°.

Conclusion

In conclusion we synthesized the zerovalent palladium complex $[(o\text{-PCy}_2\text{-C}_6\text{H}_4)_2\text{BPh}\{\text{Pd}(0)\}]$ **9**. Complex **9** supplements the few known examples (e.g., **6** [11]) of 14 VE palladium complexes bearing a chelating diphosphine ligand by introduction of a borane acceptor functionality.

Supporting Information

Supporting Information File 1

Experimental procedures and characterization data; crystallographic information for **9**; ^1H , ^{11}B , ^{13}C and ^{31}P NMR spectra.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-12-152-S1.pdf>]

Supporting Information File 2

CIF file of **9**, CCDC 1471929.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-12-152-S2.cif>]

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