Donor–Acceptor Systems

Evaluation of Pd—B Interactions in Diphosphinoborane Complexes and Impact on Inner-Sphere Reductive Elimination

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**Abstract:** The dative Pd—B interaction in a series of RPDB'R complexes (RPDB' = (o-PR₂C₆H₄)₂BR', diphosphinoborane) was analyzed using XRD, ¹¹B NMR spectroscopy and NBO/NLMO calculations. The borane acceptor discriminates between the oxidation state Pd⁰ and Pd²⁺, stabilizing the latter. Reaction of lithium amides with [RPDB'Pd(4-NO₂C₆H₄)I] chemoselectively yields the C–N coupling product. DFT modelling indicates no significant impact of Pd²⁺—B coordination on the inner-sphere reductive elimination rate.

**Introduction**

Z-type acceptor ligands have attracted considerable attention over the past decade.[¹][²] Their coordination to transition metals grants access to complexes with unusual coordination geometries[²] and electronic properties by formation of dative M—Z bonds. Group 13 acceptor ligands, with a special focus on boranes, have been particularly well studied. M—Z bonds can stabilize low oxidation states at the coordinated transition metal.[³] Thus, facile access to complexes featuring transition metals with formally negative oxidation states is realized (Figure 1a).[³] This stabilization of low oxidation states appears to inhibit oxidative addition reactions.[³b,e, 5] However, we demonstrated that this obstacle can be overcome for complex 1 by addition of catalytic amounts of acetate, which competes with Pd⁰ for the free coordination site at the borane, thus reversibly breaking the Pd²⁺—B interaction (Figure 1b).[³b] This concept allowed for the application of 1 in catalytic allylic amination, and most recently of 2 in the catalytic hydro-/deutero-dechlorination of aryl chlorides.[³a,5] Alternatively, bifunctional substrate activation across the M—Z interaction has been described.[³a,9] The aptitude of hydride,[³] halide[⁸] and carbon group[⁹] migration between the Z-type ligand and the coordinated transition metal has initiated further applications. Catalytic processes have concentrated on transformations in which the catalyst is not required to change its oxidation state quickly, but rather profits from an electronic fine-tuning by electron-withdrawing Z-ligand coordination.[¹⁰] Successful applications include CO₂ hydrogenation[¹¹] and hydroisilylation,[¹²,13] enyne cyclosomerization[¹⁵] and alkene hydroamination.[¹⁴] Michaelis used the heterobimetallic Ti⁴/Pd⁰ complex (Figure 1c), developed by Nagashima,[¹⁵] for allylic amination of allyl chlorides with hindered secondary amines.[³b,16]

Combined experimental and computational investigations indicated a rate enhancement of 10⁴–10⁶ of the outer-sphere reductive C–N bond elimination, due to the electron-withdraw-
ing Pd$^4$→Ti$^V$ interaction.\cite{Sh17} This result agrees with previous investigations performed with Pd $\eta^1$-allyl and Ni $\eta^1$-allyl complexes, which showed favored reductive outer-sphere reductive elimination in the presence of less electron-donating spectator ligands.\cite{Sh16}

We speculated that the electron-withdrawing properties of the borane functionality in diphosphinoborane (DPB) ligands enhances the rate of inner-sphere reductive elimination from Pd complexes due to 1) overall reduced electron density at the Pd$^4$ center and 2) increasing of the Pd→B interaction strength during reductive elimination. We determine how the oxidation state of Pd and co-ligands affect the strength of the Pd→B interaction in DPB complexes. NBO/NLMO calculations and solid-state structures are used to assess the strength of Pd→B interactions. The value of the $^1$B NMR chemical shift as a probe is discussed. The reductive elimination of $N,N$-dimethyl-4-nitroaniline from ($^{10}$DBP$^{9m}$)Pd(4-NO$_2$C$_6$H$_4$)NMe$_2$) (5) was studied and modelled with DFT calculations to investigate the assumed influence of the borane acceptor.

**Results and Discussion**

**Syntheses and reactivity of ([DPB]Pd) complexes**

A series of ($^{10}$DBP$^{9m}$)Pd$^4$ complexes was synthesized to examine a possible correlation between the nature of ligands at Pd and the strength of the Pd$^4$→B interaction (Scheme 1).

Complex ($^{10}$DBP$^{9m}$)Pd(Cl) (7) was produced by reaction of ($^{10}$DBP$^{9m}$)Pd ligand with [(cod)PdCl]$^+$ in DCM and was isolated in 74% yield (Scheme 1). Single crystals were grown from CH$_2$Cl$_2$/benzene and analyzed by X-ray diffraction (Figure 2). A typical square-pyramidal coordination around the palladium was observed around the Pd$^4$ center. The chloride ligands are located in cis-configuration at the basal position, and the borane adopts the apical position. The Pd→B distance of 2.762(3) Å is shorter than the sum of the van der Waals radii (3.28 Å), but elongated compared to the sum of the covalent radii (2.23 Å).\cite{Sh18} A long Pd,C51 distance of 3.405(3) Å seems to rule out a $\eta^1$-(B,C) type coordination to the Pd$^4$ center. A slightly increased pyramidalization at the boron atom is observed ($\Sigma_B = 355.4\degree$) compared to complex ($^{10}$DBP$^{9m}$)PdCl$_2$ ($\Sigma_B = 359.9\degree$).\cite{Sh21}

The ligand backbone is twisted (dihedral angle C62-C61-C71-C72: 35.6(3) $\degree$) to allow for a P-Pd-P angle of 95.49(3) $\degree$. This twist renders the two phosphine groups diastereotopic. The $^3$P NMR spectrum of 7 in CD$_2$Cl$_2$ displays two broad resonances of equal integral at $\delta = 39.0$ and 48.2 ppm. A series of $^3$P VT NMR spectra was recorded (Figure 3), covering a temperature range from $-29.8$ to $35.1$ $\degree$C. The two singlet resonances coalesced into a single resonance ($\delta = 48.2$ ppm) at elevated temperatures. The rate constants of the dynamic process were determined by line-shape analysis using Bruker's TopSpin software. An Arrhenius plot analysis gave an activation energy of

\[ E_a = 21.5 \text{ kcal mol}^{-1} \]

**Figure 2.** Left: thermal ellipsoid plot of the solid-state structure of 7 at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C1 = 2.3355(7), Pd1–C2 = 2.3628(7), Pd1–P1 = 2.2558(8), Pd1–P2 = 2.2932(8), Pd1–B1 = 2.762(3), Pd1–C51 = 3.405(3), P1–Pd1–P2 = 95.49(3), C51–B1–C61 = 118.3(3), C51–B1–C71 = 118.2(3), C71–B1–C61 = 118.8(3)\cite{Sh22}. Middle: Ball and stick display of ($^{10}$DBP$^{9m}$)PdCl$_2$-dimer (9) generated by symmetry. Right: thermal ellipsoid plot of the asymmetric unit of 9 at the 50% probability level. Hydrogen atoms and crystal CH$_2$Cl$_2$ are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C11 = 2.3781(11), Pd1–C11$^\ddagger$ = 2.3928(13), Pd1–P1 = 2.2783(13), Pd1–P2 = 2.3084(11), Pd1–B1 = 2.722(5), Pd1–C11 = 3.338(4), P1–Pd1–P2 = 95.38(5), C11–B1–C41 = 117.5(4), C11–B1–C11 = 119.4(4), C1–B1–C41 = 118.9(4).\cite{Sh23}

**Figure 3.** $^3$P VT NMR analysis of 7 in CD$_2$Cl$_2$. Left: recorded $^3$P NMR spectra. Middle: simulated $^3$P NMR spectra. Right: Arrhenius plot.

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\[ E_a = 21.5 \text{ kcal mol}^{-1} \]
$E_g = 9.3 \pm 0.5 \text{ kcal mol}^{-1}$ with a pre-exponential factor of $A = (14 \pm 7) \times 10^9$.

We suggest that the observed dynamic process in the $^{31}$P NMR spectrum of 7 is caused by an interconversion of 7 with its enantiomer ent-7 (Scheme 2).

Scheme 2. Proposed interconversion between 7 and ent-7 by twisting of the DPB ligand.

In order to accommodate for the small P-Pd-P angle of 95.49(3), the α-symmetric DPBP ligand is twisted. As a result, its B–Ph group points towards one of the two phosphine groups, rendering them chemically inequivalent. This assumption is in line with the observed $^{31}$P NMR resonances at low temperatures. Twisting of the C62-C61-C71-C72 dihedral angle converts 7 into its enantiomer ent-7, presumably via a σ-symmetric transition in which the B–Ph group is orientated between the two chloro ligands.

Complex 8 was synthesized in the same fashion as 7 from [(cod)PdBr2] and was isolated in 67% yield. The $^{31}$P NMR spectrum displays two broad resonances of equal intensity at $\delta = 45.2$ and 38.1 ppm (CDCl3), suggesting a similar dynamic process as in 7. Due to the poor solubility of both 7 and 8, no $^{11}$B NMR spectra could be obtained.

Cationic complex [(^{10}DPBP)PdCl]2SbF6 (9) was produced in 51% isolated yield by halide abstraction from 7 with AgSbF6 (Scheme 1). Single crystals were grown from CH2Cl2/hexane and analyzed by X-ray diffraction (Figure 2). In the solid state a chloro-bridged dimer [(^{10}DPBP)PdCl]2SbF6 is observed with an inversion center between the two Pd2+ centers. Within the dimer, the Pd2+ center is coordinated in a square-pyramidal fashion with the borane located in the apical position. The Pd–B distance in complex 9 is 2.721(5) Å, which is slightly shorter than in [(^{10}DPBP)PdCl]2 (2.762(3) Å). However, pyramidalization of the borane is almost identical (2B = 355.8°). The absence of a relevant η1(B,C)–Pd4 interaction is suggested by the long Pd1,C1 distance of 3.38(4) Å. The Pd,B distance and lack of significant pyramidalization at the borane suggest a weak Pd4–B interaction, which is in line with a broad resonance in the $^{11}$B NMR spectrum at $\delta = 65$ ppm ($\omega_{1/2} = 1900 \pm 500$ Hz).

The ligand backbone is more similar in the $^{13}$C NMR (4.5 h, all resonances in the spectrum removed) than in the $^{11}$B NMR spectrum, indicating the formation of the expected reductive elimination product in 38% yield. As depicted in Figure 4, complex 10 is located in a trigonal-pyramidal environment in which the borane occupies the pseudo-apical position and the C6H4-ligand. For the trigonal-planar positions, a weak Pd4–B interaction is indicated by a Pd,B distance of 2.676(5) Å, which is in line with a minor pyramidalization at the boron center (2B = 354.7°) and a broad $^{11}$B NMR resonance at $\delta = 62$ ppm ($\omega_{1/2} = 1200 \pm 100$ Hz). A large Pd,C22 distance of 3.066(6) Å eliminates the possibility of a strong η1(β,C)–Pd4 interaction. The η1-coordinated C6H4-ligand is disordered. Using the borane as a reference point, a 39:61 mixture of the exo- and endo-isomers is observed. A wider P-Pd-P angle of 102.86(5)° is realized by a decrease in the twisting of the ligand backbone (dihedral angle C18-C17-C28-C33 of 24.04°). The observed disorder of the C6H4-ligand is in good agreement with the observed NMR spectra. In the $^{13}$P NMR spectrum (CDCl3), two singlet resonances are observed in a 40:60 ratio (δ = 28.1 and 26.9 ppm) and two sets of C6H4-units are detected in the $^1$H NMR spectrum. DFT calculations (B86/def-SVP) based on the solid-state structures of 10-end and 10-exo indicate a small Gibbs free energy preference of $\Delta G = 0.74$ kcal mol$^{-1}$ for 10-endo, predicting a 29:71 ratio at 298 K.

To explore the potential influence of the Pd4–B interaction on reductive elimination proceeding via an inner-sphere mechanism, complex [(^{10}DPBP)Pd(4-NO2-C6H4)] (5) was reacted with lithium amides. Complex 5 was reacted with LiNMe2 (1.1 equiv) at room temperature in [D6]THF (Scheme 3). A conversion of 84% was observed $^{31}$P NMR spectroscopically after 1 h. Two complexes were formed with singlet resonances at $\delta = 31.1$ (70%) and 38.3 ppm (14%). After a total of 4.5 h, all resonances in the $^{31}$P NMR spectrum disappeared in favor of the singlet at $\delta = 31.1$ ppm. $^{11}$B NMR spectroscopy suggested formation of a zero-valent palladium complex by a broad resonance at $\delta = 19$ ppm ($\omega_{1/2} = 400 \pm 100$ Hz). The concurrent formation of the expected reductive elimination prod-
uct N,N-dimethyl-4-nitroaniline was confirmed by GC/MS analysis, using an independently prepared sample as a reference. The absence of an intermediate complex cis-[(DPB)\(_2\)]Pd(4-NO\(_2\)-C\(_6\)H\(_4\))Me\(_2\) suggests that transmetalation is rate-limiting in this transformation. The intermediate occurrence of the \(^{31}\)P NMR resonance at \(\delta = 38.3\) ppm is possibly due to a reversible reaction of LiNMe\(_2\) with complex 6. In a control experiment complex [(DPB)\(_2\)]Pd(pyridine)] \((1)\) was reacted with LiNCy and LiNMe\(_2\) in [D\(_2\)]THF. In both cases ca. 7% of a new complex at \(\delta = 38.5\) (s) and 37.7 ppm (s) were observed.

Complex 6 decomposed within hours with simultaneous precipitation of palladium black. Addition of PMe\(_3\) as a stabilizing co-ligand led to the formation of complex [(DPB)\(_2\)]Pd(PMe\(_3\)) \((1)\). The \(^{31}\)P NMR spectrum of 11 showed a doublet at \(\delta = 35.3\) and a triplet at \(\delta = 40.1\) ppm \((J = 15.1\) Hz) in a 2:1 ratio, which is consistent with the expected \(\kappa^2\)P-coordination.

The broad resonance in the \(^{11}B\) NMR spectrum at \(\delta = 25\) ppm \((\omega_{1,2} = 400 \pm 100\) Hz) suggested a strong Pd\(\rightarrow\)B interaction. Complex 11 could also be synthesized independently by reaction of PBP pincer 12 with PhLi and PMe\(_3\), or reaction of 1 with PMe\(_3\) thus confirming unambiguously the identity of 11 (Scheme 3).

Complex 5 reacted in a similar fashion with LiNCy\(_2\), \(26\%\) after 3 h and LiNHtBu \(14\%\) after 5.5 h. However, the reaction proceeded slower with these sterically more demanding substrates. The reaction of complex 5 with LiNHtBu was monitored for 96 h by \(^{31}P\) NMR spectroscopy (46% conversion towards 6) without any side products being observed (cf. Table S1). This is in line with the assumption of a rate-determining transmetalation followed by a quick reductive elimination.

### Analytical data

#### Table 1. Experimental and computational analysis of the Pd\(\rightarrow\)B interactions

| Compound | d(Pd,B) [Å] | (PMe\(_3\)) | Δ(B) [Å] | 11B NMR (δ, J\(\Delta\)) | occ. PMe\(_3\) | occ. PMe\(_3\) | NBMO %B/Pd
|----------|-------------|-------------|----------|------------------------|----------------|----------------|----------------|
| 11       | 2.762(3)    | –           | 2.721(5) | 2.676(5)               | 2.740(4)       | 2.194(3)       | 2.278(3)       |
|          | 2.740(4)    | –           | 2.194(3) | 2.278(3)               | 2.193(3)       | 2.360(2)       | 2.260(2)       |
|          | –           | 2.360(2)    | 2.264(2) | –                      | –              | –              | –              |
|          | 2.253(2)    | 1900 Hz     | 1400 Hz  | 3000 Hz                | 400 Hz         | 500 Hz         | 800 Hz         |
|          | –           | 1400 Hz     | 3000 Hz  | 400 Hz                 | 500 Hz         | 800 Hz         | 400 Hz         |
|          | 11.46       | 10.42       | 11.41    | 8.04                   | 8.72           | 23.46          | 19.53          |
|          | 8.72        | 23.46       | 19.53    | 46.83                  | 42.12          |                |                |
|          | 6.6/91.9    | 6.3/92.2    | 5.4/92.9 | 3.7/93.9               | 4.7/93.4       | 16.0/78.7      | 15.0/81.5      |
|          | 4.7/93.4    | 16.0/78.7   | 15.0/81.5| 15.5/81.5              | 14.3/83.0      |                |                |
|          | 0.390       | 0.387       | 0.400    | 0.360                  | 0.353          | 0.618          | 0.621          |
|          | 0.353       | 0.618       | 0.621    | 0.498                  | 0.519          |                |                |
|          | 1.859       | 1.865       | 1.870    | 1.877                  | 1.887          | 1.866          | 1.702          |
|          | 1.865       | 1.887       | 1.877    | 1.702                  | 1.686          | 1.704          |                |
|          | 7.6/92.4    | 7.2/92.7    | 7.2/92.7 | 6.7/93.3               | 6.4/93.6       | 11.6/88.4      | 13.9/86.1      |
|          | 7.2/92.7    | 7.2/92.7    | 7.2/92.7 | 6.7/93.3               | 6.4/93.6       | 11.6/88.4      | 13.9/86.1      |
|          | 0.2164      | 0.2063      | 0.2117   | 0.1378                 | 0.1810         | 0.4207         | 0.3634         |
|          | 0.2117      | 0.1378      | 0.1810   | 0.4207                 | 0.3634         | 0.5032         | 0.4604         |
|          | 0.0079      | 0.0079      | 0.0208   | 0.0093                 | 0.0062         | 0.0697         | 0.0171         |
|          | 0.0079      | 0.0079      | 0.0208   | 0.0093                 | 0.0062         | 0.0697         | 0.0171         |

[a] Structure optimization: Turbomole 7.0.1, BP86/def-SV(P); NBO analysis: Gaussian 09/NBO 6.0, BP86/6-31G(d), MWB10 (P,C); MWB28 (Pd, Br), MBW46 (I). B-hybrid energy \(E_B\) associated with the Pd-B interaction. [c] Contribution of the donor/acceptor NBO to the NLMO. [d] Occupation of the donor/acceptor NBO. [e] Calculated structure parameters of 9 are based on the monomer.
structure of complexes 1 and 7. The Pd—B interactions were further analyzed using NBO/NLMO calculations. In all cases, an NBO donor/acceptor interaction was found between an occupied d-orbital at Pd and an unoccupied p-orbital at B (Figure 5). For all examined complexes no relevant η(B,C)-coordination was found in the NBO calculations. The Wiberg bond index for Pd,C_{ps} was below 0.02, with the exception of Pd^6 complexes 1 (0.0697) and 6 (0.0325). Reactivity studies of ([DPB]Pd)-complexes presented in this paper thus appear to be unaffected from significant η(B,C)-coordination.

The NBO stabilizing energy of this Pd—B interaction varied depending on the Pd oxidation state. For Pd^6—B interactions, a narrow range of NBO stabilizing energies between 8.04 and 11.46 kcal mol\(^{-1}\) was observed. Surprisingly, generation of cat-ionic complexes (9, 10-endo), exchange of chloro-ligands by bromide (8) or iodide/aryl (5) had very little effect. In the case of Pd^4—B interactions, significantly higher NBO stabilizing energies of 19.53–46.83 kcal mol\(^{-1}\) were found. Regardless of the oxidation state at Pd an approximately linear correlation between the Pd-B distance and the NBO stabilizing energy (E\(_J\)) associated with the Pd,B interaction was observed (Figure 6) for 16 valence electron (VE) complexes 1, 5, 7, 8, 10 and 13. The Pd,B distance appears to be dictated by the Pd,B bond strength, and not by constraints imposed by the chelating ligand. Substitution of PPh\(_3\)-groups (6) by PCy\(_2\)-groups (3) had only a minor effect. The E\(_J\) values for the Pd^6—B interaction in the 14 VE complexes 3 (46.83 kcal mol\(^{-1}\)) and 6 (42.12 kcal mol\(^{-1}\)) significantly deviate from this correlation and are almost twice as much as for 16 VE complexes 1 (23.46 kcal mol\(^{-1}\)) and 13 (19.53 kcal mol\(^{-1}\)). Neither the \(^{11}\)B NMR chemical shift, Pd,B distance or pyramidalization at B indicate a change of the Pd^6—B interaction strength in this magnitude between the 14 VE and the 16 VE complexes (Table 1). This discrepancy might be explained by the difficulty to compare the 2\(^{nd}\) order perturbation interaction energies from NBO analysis from 14 VE with 16 VE complexes.

The \(^{11}\)B NMR resonances are shifted linearly towards higher field with an increasing Pd,B distance for Pd^6 complexes, regardless of the valence electron count at the Pd center (Figure 6). Complex ([DPB]Pd(PPh\(_3\)) (2) reported by Kameo and Bourissou\([1e]\) also fits perfectly into this correlation (d(Pd,B) = 2.294(2) Å, δ(\(^{11}\)B) 27 ppm). In contrast, the \(^{11}\)B NMR resonance shifts linearly towards lower field with an increasing Pd,B distance in case of Pd^4 complexes. \(^{11}\)B NMR spectroscopy therefore can be used as a tool to assess the strength of Pd—B interactions within a given ligand system, provided that the oxidation state at the Pd center is taken into account. However, given the difficulty to determine the precise δ(\(^{11}\)B) of ([DPB]Pd^4) complexes (poor solubility and ω_{1/2} > 1000 Hz), a certain error for weak Pd^4—B interactions needs to be factored in.\([2e]\)

Quantum chemical calculations (DFT) were used to model the inner-sphere reductive elimination of N,N-dimethyl-4-nitroaniline from complex 14-B (Scheme 4). C—N bond formation is predicted to proceed via an inner sphere reductive elimination with a low activation barrier of ΔG* = +7.90 kcal mol\(^{-1}\) (transition state 15-B), yielding Pd^0 complex 6 and N,N-dimethyl-4-nitroaniline (overall ΔG = −58.75 kcal mol\(^{-1}\)). In order to understand how the Pd—B interaction affects the reductive elimination, the reaction was also modeled for bis-[2-diphenylphosphino]phenyl]ether (DPEphos) complex 14-O and diphosphinoamine complex 14-N. DPEphos is well established as an effective ligand in palladium catalyzed Buchwald–Hartwig-type coupling reactions.\([2f]\) and commands very similar structural features to \(^{14}\)DPB\(^{16}\) (Table 2). However, DPEphos cannot mimic

**Figure 5.** Graphical representation of the NLMOs associated with the Pd—B interactions in [([DPB]Pd)(0/II)] complexes.

**Figure 6.** Left: correlation between solid state Pd,B distances and δ(\(^{11}\)B). Right: correlation between calculated Pd,B distances and NBO stabilizing energies.
the potential steric effect of the B-Ph group on the coordinate-reactive ligands. For this reason, the diphosphinoamine ligand (o-PPh₂(C₆H₄)₉)NH₂ [28] has also been included in the theoretical considerations, as its N-Ph bridgehead gives a good model of the B-Ph group in 14-B. Elimination of N,N-dimethyl-4-nitroaniline from complexes 14-O and 14-N gave very similar Gibbs free reaction energies of \( \Delta G = -38.52 \, \text{kcal mol}^{-1} \) and \( \Delta G = -38.63 \, \text{kcal mol}^{-1} \), respectively. No Pd⁻⁻E interactions were observed in complexes featuring DPEphos and the diphosphinoamine ligand (Table 2, WBI(Pd,E)). When switching from DBP to DPEphos, a small decrease of \( \Delta G^* = 0.41 \, \text{kcal mol}^{-1} \) was found for the reductive elimination barrier (Scheme 4). This was surprising, as a more facile reductive elimination was expected from 14-B than from 14-O, due to 1) an electronic effect by Pd⁻⁻B coordination and 2) increased steric bulk of the DBP ligand imposed by the B-Ph group. In case of diphosphinoamine complex 14-N the reductive elimination barrier decreased to \( \Delta G^* = 5.54 \, \text{kcal mol}^{-1} \) (\( \Delta G^* = 2.46 \, \text{kcal mol}^{-1} \)), possibly as a result of the increased steric pressure imposed by the N-Ph group (Table 2). Reductive elimination from 14-E (E = B, O, N) proceeds via structurally early transition-state 15-E (Figure 7).

Unexpectedly, the Pd⁻⁻B interaction is slightly weakened in transition-state 15-B, compared to starting complex 14-B, as indicated by a slightly elongated Pd-B distance (2.947 Å) in 15-B compared to 14-B (2.906 Å). Similarly, the Wiberg bond index for the Pd⁻⁻B interaction is reduced to 0.162 in 15-B (14-B: 0.176), and the NPA charge at the borane remains unchanged (14-B: +0.737 vs. 15-B: +0.735). The increase of the Pd⁻⁻B interaction strength occurs after the reductive elimination, explaining why the inner-sphere reductive elimination of the C-N bond does not kinetically profit from the substantial increase of the Pd⁻⁻B strength in the course of the reaction. To rule out effects originating from restraints imposed by a chelating ligand frame work, the reductive elimination of N,N-dimethyl-4-nitroaniline was also modeled using cis-[(PMe₃)₉Pd(4-NO₂C₆H₄)₂NMe₂] (17, \( \Delta G = 37.47 \, \text{kcal mol}^{-1} \)) and its

![Scheme 4. Reductive elimination of N,N-dimethyl-4-nitroaniline from PEP complexes 14-B, 14-O and 14-N.](image)

![Figure 7. Calculated intermediates of reductive elimination from 14-B (top), 14-O (middle) and 14-N (bottom). For clarity the H atoms are omitted, and only the C atoms of the Ph-groups at B and P are shown. Red: NPA charges, blue: bond distances.](image)

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Table 2. Computational analysis of C-N bond formation from complexes 14-B, 14-O and 14-N.

| E | B, O, N | 14-B | 15-B | 6 | 14-O | 15-O | 16-O | 14-N | 15-N | 16-N |
|---|---|---|---|---|---|---|---|---|---|---|
| d(Pd,E) [Å] | 2.845 | 2.947 | 2.253 | 2.343 | 3.349 | 2.955 | 3.360 | 3.381 | 3.023 |
| d(C,N) [Å] | 2.904 | 2.084 | – | 2.816 | 2.077 | – | 2.801 | 2.068 | – |
| d(Pd,C) [Å] | 2.042 | 2.059 | – | 2.036 | 2.051 | – | 2.033 | 2.051 | – |
| d(Pd,N) [Å] | 2.102 | 2.108 | – | 2.091 | 2.102 | – | 2.089 | 2.100 | – |
| q(Pd) [e] | 101.2 | 101.0 | 147.1 | 100.4 | 102.0 | 136.4 | 97.5 | 98.8 | 132.9 |
| q(B,O) [e] | +0.376 | –0.330 | +0.055 | +0.318 | +0.275 | –0.162 | +0.320 | +0.276 | –0.123 |
| q(P,B) [e] | +0.722 | +0.735 | +0.527 | –0.498 | –0.496 | –0.485 | –0.448 | –0.448 | –0.444 |
| WBI(Pd,E) | 0.193 | 0.162 | 0.460 | 0.005 | 0.005 | 0.005 | 0.005 | 0.005 | 0.005 |
| \( \Omega_B \) | 355.4 | 354.6 | 348.8 | – | – | – | – | – | – |

[a] Structure optimization: Turbomole 7.0.1, BP86/def-SV(P); NBO analysis: Gaussian 09/NBO 6.0, BP86/6-31G(d), MWB10 (P), MWB28 (Pd). [b] Natural population analysis (NPA) charge. [c] Wiberg bond index.
BH₃ adduct [(PMMe₂)₂(BH)Pd[(4-NO₂C₆H₄)NMe₂] (17B, ΔG = 49.19 kcal mol⁻¹) as substrates (cf. Scheme S1). Again, a more favorable transition state was found for the acceptor free complex 17 (ΔG° = + 7.35 kcal mol⁻¹), than for the borane adduct 17-8 (ΔG° = + 8.55 kcal mol⁻¹).

Conclusions

The strength of Pd—B interactions in [(DPB)Pd] complexes depends primarily on the oxidation state of Pd. In contrast, modifications of the DPB ligand or co-ligands have only a minor effect. ¹³B NMR spectroscopy has been established as a useful tool to assess the strength of Pd—B interactions in solution. Reaction of lithium amides with [(³⁰PDPh)Pd(4-NO₂C₆H₄)H] (5) chemoselectively yields the C-N coupling product and [(³⁰PDPh)Pd] (6). Inner-sphere reductive C–N bond elimination was modelled with DFT methods for the [(³⁰PDPh)Pd] ligand. In contrast to reports on acceptor promoted outer-sphere reductive C–N bond elimination,¹⁴ no significant effect of the borane acceptor on the inner-sphere reductive elimination rate was found. This is explained by the fact that the strengthening of the Pd—B bond occurs after the reductive elimination.

Experimental Section

General

All manipulations were performed under an argon atmosphere using standard Schlenk line and glovebox techniques. Glassware was oven dried at 120 °C overnight and dried with a heat gun under vacuum prior to use. Tetrahydrofuran was dried by an MBraun solvent purification system. Benzene and n-hexane were dried over sodium, distilled under argon prior to use and stored over activated molecular sieves (4 Å).

CDCl₃ and C₂D₅ were degassed employing the freeze-pump-thaw technique and stored over activated molecular sieves (4 Å). D₂O/THF was dried over activated molecular sieves (3 Å), distilled under an argon atmosphere and degassed employing the freeze-pump-thaw technique. [(³⁰PDPh)Pd], [(³⁰PDPh)OAcPd(C₂H₅)] (4), [(³⁰PDPh)Pd(4-NO₂C₆H₄)H] (5) and [(³⁰PF₆P(C₆H₅)Pd(4-NO₂C₆H₄)] (12) were synthesized according to published procedures.¹⁵⁻¹⁷

NMR-experiments were performed in Wilmad™ quick pressure valve NMR tubes. ¹¹B, ¹³C[H], ¹⁷F[H], and ³¹P[H] NMR spectra were recorded on a Bruker Avance II (400.1 MHz, probe: BBO) or a Bruker Avance (400.3 MHz, probe: ATM BBFO) spectrometer. ¹³C and ¹⁷F NMR spectra were referenced to residual solvent resonances as implemented in MesReNova 10.0.2. Infrared spectra were recorded on an Avatar 360 FT-IR E.S.P. device by Nicolet. CHRN combustion analysis was carried out on an Elemental EL device by Elementar Analyseysysteme GmbH.

Deposition Number(s) 1987620 (7), 1987625 (9) and 1987626 (10) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

 Reactivity studies

A solution of the respective lithium amide (5.7 µmol, 1.1 equiv) in D₂O/THF (0.25 mL) was added dropwise over a period of 4 min to a stirred solution of nitroarene complex 5 (5.0 mg, 5.2 µmol, 1.0 equiv) in D₂O/THF (0.25 mL). The resulting mixture was stirred for another 5 min and then transferred into an NMR tube. Reductive elimination was monitored by ¹³B NMR spectroscopy.

Synthesis of [³⁰PDPhCl] (7)

CH₂Cl₂ (8 mL) was added to a mixture of ³⁰PDPh (400 mg, 0.665 mmol, 1.0 equiv) and [(cod)PdCl₂] (187 mg, 0.665 mmol, 1.0 equiv). The mixture was stirred for 30 min at room temperature. Yellow crystals (380 mg, 0.482 mmol, 74%) were formed by overlaying the solution n-pentane (16 mL). Single crystals suitable for X-ray diffraction were grown from a solution of [(cod)PdCl₂] (9 mg, 34 µmol, 1.0 equiv) and ³⁰PDPh (21.2 mg, 34.7 µmol, 1.0 equiv) in CDCl₃ (0.7 mL) overlaid with benzene (0.3 mL). ¹³B and ¹⁵C NMR data have not been collected due to poor solubility. ¹³B NMR (400.13 MHz, CDCl₃, 25 °C): δ 7.81–7.76 (m, 2H), 7.55 (tdd, J = 7.3, 3.0, 1.1 Hz, 3H), 7.50–7.46 (m, 3H), 7.46–7.38 (m, 6H), 7.35–7.14 (m, 13H), 6.97–6.78 (m, 5H), 5.32 (s, 2H, CH₂Cl₂). ³¹P[H] NMR (161.98 MHz, CDCl₃, 26 °C): δ 45.4 (s, w₁₂ = 75.0 Hz). IR (KBr): ν = 3643–3284 (w), 3049 (w), 1587 (w), 1497 (m), 1433 (vs., sh), 1223 (s), 1158 (vw), 1128 (vw), 1093 (vs), 987 (w), 889 (vw), 864 (vw), 754 (s), 744 (s), 733 (m), 688 (vs), 667 (w), 611 (m), 600 (s), 542 (m), 523 (vs), 505 (m) cm⁻¹. Elemental analysis calc. (%) for C₂H₃B₃Cl₃PdCD₃Cl₆: C 59.18, H 0.40, found: C 59.61, H 4.33.

Synthesis of [³⁰PDPhBr₂] (8)

The ³⁰PDPh ligand (200 mg, 0.328 mmol, 1.0 equiv) and [(cod)PdBr₂] (122.7 mg, 0.328 mmol, 1.0 equiv) were solved in DCM (10 mL) and stirred at rt. for 30 min. The solution was overlayered with n-hexane (20 mL) yielding title compound 8 as orange crystals (192.0 mg, 0.219 mmol, 67%). ¹³B and ¹⁵C NMR data have not been collected due to poor solubility. ¹³B NMR (400.30 MHz, CDCl₃, 25 °C): δ 8.55–7.76 (m, 3H), 7.59–7.19 (m, 30H). ³¹P[H] NMR (162.04 MHz, CDCl₃): δ 45.2 (bs, 1P, w₁₂ = 450 Hz), 38.1 (bs, 1P, w₁₂ = 450 Hz). IR (KBr): ν = 3424 (s), 3048 (m), 1621 (w), 1587 (w), 1478 (m), 1455 (w), 1432 (s), 1311 (w), 1237 (w), 1220 (s), 1205 (m), 1187 (m), 1153 (w), 1126 (w), 1092 (s), 1027 (w), 1000 (m), 887 (w), 863 (w), 753 (s), 741 (s), 713 (m), 699 (s), 690 (s), 667 (m), 610 (s), 600 (s), 539 (s), 522 (s), 505 (s), 465 (m) cm⁻¹. Elemental analysis calc. (%) for C₅H₃Br₂P₃Cl₃Pd: C 56.51, H 3.76, found: C 56.72, H 3.83.
Synthesis of \([\text{P}^6\text{DPB}^6\text{P}^\text{d}](\text{C}_6\text{H}_{12})\text{SbF}_5\) (10)

Allyl complex 4 (120 mg, 143 µmol, 1.0 equiv) and AgSbF₅ (49.0 mg, 143 µmol, 1.0 equiv) were solved in CH₂Cl₂ (7 mL) and stirred at rt for 20 min. The suspension was filtered through a syringe filter (0.2 µm, PTFE membrane). The clear solution was overlaid with n-hexane (10 mL). The obtained crystals showed insufficient purity and were crystallized again under the same conditions yielding 10 as slightly yellow crystals (50.2 mg, 33.8 µmol, 38%).

1H NMR (400.30 MHz, CDCl₃): δ 7.72–7.59 (m, 4H), 7.55–7.53 (m, 2H), 7.53–7.44 (m, 13H), 7.43–7.29 (m, 6H), 7.23–7.15 (m, 2H), 7.05–6.87 (m, 5.5H), 6.78–6.67 (bs, 2H), 5.88–5.70 (bs, 0.7H), 3.77–3.61 (bs, 1.3H), 3.59–3.33 (bs, 1.3H), 3.03–2.85 (bs, 0.9H), 2.49–2.29 (bs, 1.2H) (fractional integrals are a result from signal splitting caused by a dynamic process).

\[^{11}B\] NMR (128.38 MHz, CDCl₃): δ 64 (bs, w₁₂ = 1550 ± 50 Hz), \[^{13}C\] (H) NMR (100.67 MHz, CDCl₃): δ 141.1, 140.2, 136.1, 135.3, 135.3, 135.0, 134.3, 134.0, 133.2 (t, J = 5.8 Hz), 132.3, 132.2, 132.1, 131.6, 131.5, 131.2, 129.6 (d, J = 5.3 Hz), 129.3, 128.9, 128.1, 80.4, 80.2. \[^{31}P\] (H) NMR (162.04 MHz, CDCl₃): δ 28.1 (s, 0.6P), 26.9 (s, 0.4P). IR (KBr): ν = 3430 (s), 3000 (m), 1588 (m), 1450 (w), 1343 (s), 1268 (m), 1227 (s), 1127 (m), 1095 (m), 1031 (w), 999 (w), 950 (wv), 875 (w), 772 (w), 754 (m), 742 (m), 733 (m), 695 (s), 659 (vs), 537 (m), 521 (s), 478 (w), 430 (w) cm⁻¹. Elemental analysis calcd (%) for C₁₉H₁₂BCIF₅PdSb₂: C 51.22, H 3.74, found: C 51.77, H 3.785.

Synthesis of \([\text{P}^6\text{DPB}^6\text{P}^\text{d}](\text{PMe}_3)(11)

A solution of PhLi (3.2 mg, 38 µmol, 1.2 equiv) in THF (0.25 mL) was added over a period of 3 min to a solution of complex 5 (5.0 mg, 5 µmol, 1 equiv) in D₂O (0.25 mL). The combined solutions were transferred to an NMR tube and NMR spectra were recorded after 1.5 and 4.5 h. \[^{11}B\] (H) NMR (128.38 MHz, D₂O): δ 19 (bs, w₁₂ = 550 Hz ± 50 Hz). \[^{31}P\] (H) NMR (162.04 MHz, D₂O): δ 30.93 (s).

\[^{13}C\] (H) NMR (162.04 MHz, D₂O): δ 74.2 (m), 73.1 (m), 72.7 (m), 70.8 (m), 70.7 (m), 70.0 (m), 69.9 (m), 69.1 (m), 68.8 (m), 68.6 (w, 4H), 7–7.8 (bs, 1.2H), 7.6–7.4 (m, 4H), 7.36–7.26 (m, 4H, Ar-H), 7.12 (t, 2H, J = 6.7 Hz), 7.09–7.05 (m, 13H), 6.85 (m, 2H), 6.68 (pt, 4H, J = 7–8.8 Hz), 6.04 (t, J = 5.0 Hz, 9H, PMe). \[^{11}B\] (H) NMR (128.38 MHz, D₂O): δ 25 (bs, w₁₂ = 740 Hz ± 50 Hz). \[^{13}C\] (H) NMR (100.62 MHz, CDCl₃): δ 168.7 (bs), 143.2 (d, J = 16.3 Hz), 143.0 (d, J = 16.3 Hz), 141.5 (d, J = 15.2, 2.0 Hz), 138.9 (t, J = 13.5 Hz), 135.8 (t, J = 6.4 Hz), 135.7 (t, J = 2.7 Hz), 133.5 (t, J = 7.7 Hz), 133.0 (t, J = 16.7, 5.0 Hz, 132.3 (s), 132.3 (s), 129.5 (s, 129.5 (s), 128.6 (s), 127.2 (s), 126.1 (t, J = 2.8 Hz), 125.2 (s), 18.1 (d, J = 11.8, 2.2 Hz, PMe). \[^{31}P\] (H) NMR (162.04 MHz, CDCl₃): δ 35.44 (d, J = 14.1 Hz, 2P, ArPh₃), −40.13 (t, J = 14.2 Hz, 1P, PMe).

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Conflict of interest

The authors declare no conflict of interest.
will result in a cascade of reactions eventually leading to the formation of [{o-PPh$_2$ChCl$_2$Pd}$_2$] (cf. ref. 9d).

In a control experiment LInMe$_2$ was reacted with 1-iodo-4-nitrobenzene in THF, resulting in an unselective product mixture.

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