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Palladium-Borane Cooperation: Evidence for an Anionic Pathway and its Application to Catalytic Hydro- / Deutero-dechlorination

Hajime Kameo,*[a] Jun Yamamoto,[a] Ayaka Asada,[a] Hiroshi Nakazawa,[b] Hiroyuki Matsuzaka,[a] and Didier Bourissou*[c]

Dedicated to Prof. Pablo Espinet on the occasion of his 70th birthday

***Abstract:** Metal-Lewis acid cooperation provides new opportunities in catalysis. In this work, we report a new type of palladium-borane cooperation involving anionic Pd(0) species. The air-stable DPB palladium complex **1** (DPB = diphosphine-borane) was prepared and reacted with KH to give the Pd(0) borohydride **2**, the first monomeric anionic Pd(0) species to be structurally characterized. The boron moiety acts as an acceptor towards Pd in **1** via Pd→B interaction, but as a donor in **2** thanks to B–H–Pd bridging. This enables the activation of C–Cl bonds and the system is amenable to catalysis, as demonstrated by the hydro- / deutero-dehalogenation of a variety of (hetero)aryl chlorides (20 examples, average yield 85%).*

Over the past 15 years, polyfunctional ligands featuring Lewis acid moieties, so-called ambiphilic ligands, have garnered huge interest.[1] Most noticeable is the ability of Lewis acids to behave as σ-acceptor ligands towards transition metals and engage into rare TM→LA interactions.[1] The presence of a Lewis acid at or nearby the metal strongly influences its reactivity[2] and opens new avenues in catalysis.[3] Accordingly, different types of transition metal-Lewis acid cooperation have been progressively authenticated and applications in catalysis have started to emerge (Fig. 1). Typically, Lewis acids have been used to generate electrophilic metals (Fig. 1A), either by abstracting intramolecularly an X-type ligand (i),[4] or directly by withdrawing electron density *via* TM→LA interactions (ii).[5] In addition, cooperative activation of σ-bonds by addition across TM→LA interactions has been shown feasible under stoichiometric and even catalytic conditions (Fig. 1B).[6] This represents a conceptually new approach in metal-ligand cooperation which usually involves electron-rich or redox-active ligands. As a further extension, we reasoned that hydride insertion into TM→LA interactions may give access to anionic complexes in which the TM is electronically enriched by LA–H–M bridging (Fig. 1C).[7,8]

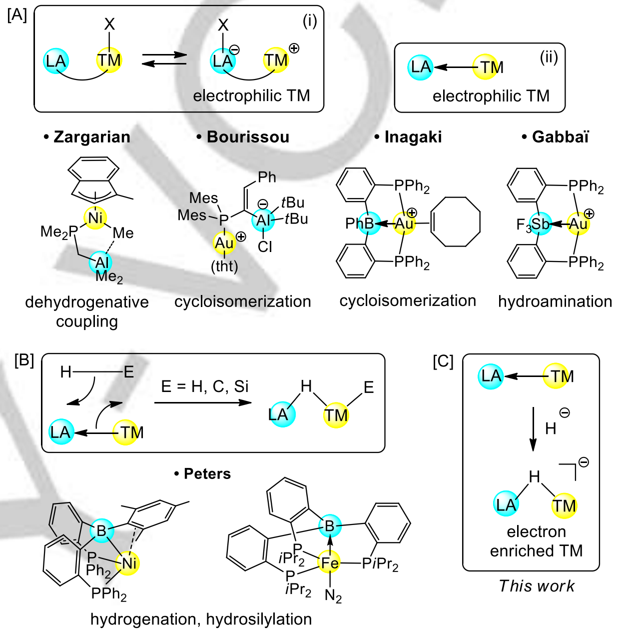

Figure 1. Schematic representation of the different modes of transition metal-Lewis acid cooperation, with selected examples of complexes applied in catalysis.

In general Pd-catalyzed coupling reactions proceeds *via* oxidative addition, transmetalation and reductive elimination (Fig. 2, top). With palladium-borane cooperation, the reaction sequence may be reversed, as follows (Fig. 2, bottom): addition of the nucleophilic partner (formal insertion of the Y group into the Pd→B bond), oxidative addition and reductive elimination. Several advantages may be envisioned for such an anionic pathway: (i) stabilized active species (the electron-rich metal center is engaged into Pd→B interaction), (ii) oxidative addition to an activated anionic Pd(0) complex, and (iii) B to Pd transfer of the nucleophilic group assisting the R–Y bond formation.[8]

Herein, we disclose a diphosphine-borane Pd complex displaying this unprecedented mode of reactivity and substantiate its catalytic relevance in hydro- and deutero-dechlorination reactions.

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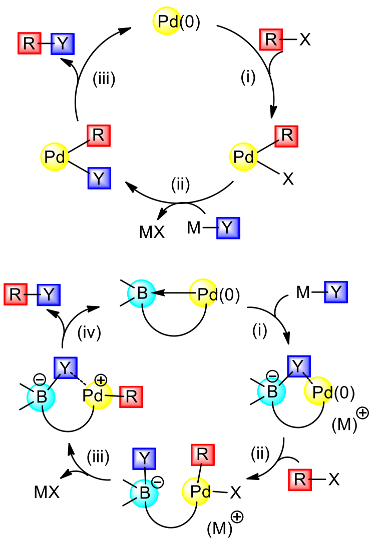
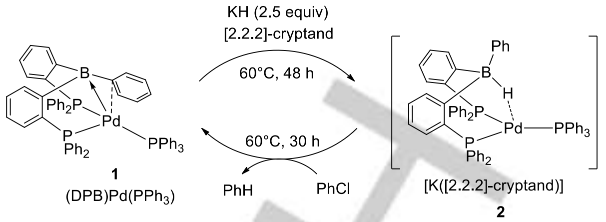


Figure 2. Classical pathway for Pd-catalyzed cross-couplings (top) and envisioned anionic pathway involving Pd-borane cooperation (bottom, this work).

The neutral Pd(0) complex **1** (Scheme 1) was readily prepared by phosphine exchange between $Pd(PPh_3)_4$ and the diphosphine-borane (DPB) ligand.[9] It was isolated in 92% yield as an air-stable yellow powder (no sign of decomposition detected after 3 days standing in air).[10] The molecular structure of **1** was unambiguously established by multi-nuclear NMR spectroscopy and X-ray diffraction analysis (Fig. 3, left). It resembles those of the (DPB)Pd(L) complexes (L = Py, ∅) recently reported by Tauchert[11,12] and is also reminiscent of DPB Ni(0)[6a] and Cu(I)[13] complexes. The Pd−B (2.294(2) Å) distance is only slightly longer than the sum of the covalent radii (2.23 Å).[14] A relatively short $Pd\cdots C_{ipso}$ contact is also observed (2.638(2) Å), in line with η^2-BC coordination of the BPh moiety.[15,16] Complex **1** shows no sign of reaction with substrates such as chlorobenzene, bromobenzene, phenylsilane and dihydrogen even upon heating at 60°C, in line with the depletion of electron density at Pd by the Lewis acid moiety.

Anionic Pd(0) species are generally formed by addition of nucleophiles, typically halides, to Pd(0) centers.[17] In the case of complex **1**, the borane moiety present in the coordination sphere of Pd can serve as an acceptor to give access to anionic Pd(0) borate species. This chemical behavior was realized by reacting **1** with KH at 60 °C in the presence of [2.2.2]-cryptand. The Pd(0) borohydride complex **2** was thereby obtained in 43% isolated yield after workup.[10] Upon hydride addition, the ^{11}B NMR signal shifts to high field (from δ 27 ppm for **1** to δ −7.2 ppm for **2**) and splits into a doublet due to $^1J_{B\text{-}H}$ coupling (70.2 Hz).[18] Single crystals suitable for X-ray diffraction analysis were grown by slow diffusion of Et_2O into a THF solution of **2** (Fig. 3, right). The complex adopts a separate ion pair structure. The additional hydrogen atom (which was located in the difference Fourier map and refined isotropically) bridges the B and Pd centers (B−H, 1.21(4) Å and Pd−H, 1.889(X) Å).[19,20] The boron center is in tetrahedral environment (the sum of the three C−B−C bond angles reduce to 335.3(5)°), while the Pd center adopts a rare trigonal pyramidal geometry (Σ(P−Pd−P) = 358.3(7)°) with the hydride in the apical position. To our knowledge, this is the first monomeric anionic Pd(0) complex to be structurally characterized.[21]



Scheme 1. Synthesis of the anionic palladium(0) complex **2** and its reaction with chlorobenzene.

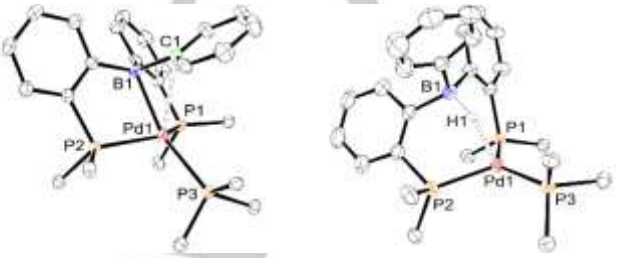


Figure 3. Molecular structures of complexes **1** (left) and **2** (right) (thermal ellipsoids at 40% probability). For clarity, the [K([2.2.2]-cryptand)] cation and hydrogen atoms (except the hydride bonded to B and Pd) are omitted, and only the C_{ipso} carbon atoms of the Ph groups at P are shown.

Unlike the neutral (Pd→B) complex **1**, **2** reacts with chlorobenzene (1 equiv.) at 60°C to give benzene (73% yield) with quantitative regeneration of **1** (Scheme 1).[22] This transformation prompted us to test the catalytic dehalogenation of chlorobenzene (Table 1). Using 5 mol% of complex **1**, 1.5 equiv. of KH and 10 mol% of [2.2.2]-cryptand or 18-crown-6, the transformation indeed proceeded, affording benzene in 68-76% yield (entries 1 and 2). Control experiments with $Pd(PPh_3)_4$ alone or combined with BPh_3 as external Lewis acid led to much lower yields (< 30%), substantiating the role of the (DPB)Pd complex.[10] Of note, NMR analysis of a catalytic run performed with [2.2.2]-cryptand revealed the presence of both complexes **1** and **2** in about 3/1 ratio during catalysis. The anionic pathway disclosed in Fig. 4 is proposed to account for the catalytic hydrodechlorination of PhCl *via* complexes **1** and **2**.

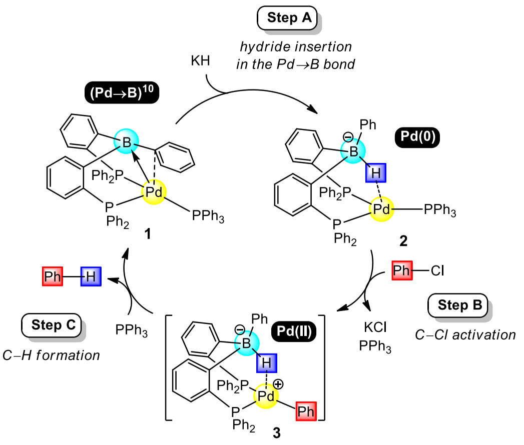


Figure 4. Anionic pathway proposed to account for the catalytic hydrodechlorination of PhCl *via* complexes **1** and **2**.

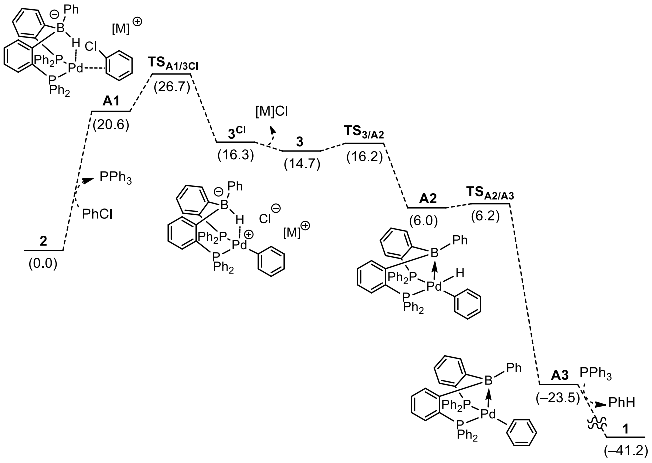
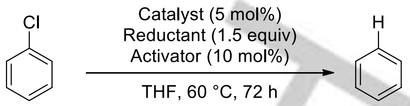


Figure 5. Reaction profile computed for the hydrodechlorination of PhCl mediated by the anionic Pd(0) complex **2** (G in kcal/mol, [M]=K[2.2.2]-cryptand).

DFT calculations performed on the real system support this mechanism and shed light into the interplay between Pd and B.[10] Fig. 5 shows the most favorable reaction profile. Following the endergonic displacement of PPh_3 by PhCl at Pd, leading to complex **A1**, C–Cl activation takes places (the overall energy barrier amounts to 26.7 kcal/mol) to afford the Pd(II) complex $\mathbf{3^{Cl}}$. After KCl elimination, B to Pd hydride transfer[8] and reductive elimination are very exergonic and proceed with very low activation barriers to give complex **A3**. Displacement of benzene by PPh_3 is further downhill in energy and affords **1**.

The catalytic performance of complex **1** was then assessed further.[10] First, different hydrides were surveyed. While LiH, NaH, and HCOONa proved inefficient (Table 1, entries 3-5) probably due to unfavourable trapping of the Li/Na cations, the use of HCOOK with [2.2.2]-cryptand improved the selectivity of the reaction and afforded benzene in 89% yield (entry 6).[23] The borohydride complex **2** exhibited comparable catalytic activity (entry 8). The scope of chloroarenes was then explored (Table 2). The transformation displays high functional group tolerance (ether, CF_3, NO_2, CN, ester, amide, F, OH, and ketone). It proceeds well with chloronaphthalenes and chloroheteroarenes including thiophene, isoquinoline, and quinolone frameworks. However, significantly lower yields were obtained with chlorobenzenes featuring methyl and methoxy groups in the *para* position, indicating that the reaction is very sensitive to the electron density of the aromatic ring. This feature enabled the selective mono-dechlorination of dichloroquinolines. The broad interest of deuterium-labelled compounds, in particular in pharmacology and drug discovery,[24] prompted us to investigate catalytic deutero-dechlorination with the Pd→B complex **1**. Gratifyingly, the use of DCOOK provided straightforward access to a variety of deuterium-labelled compounds with high deuterium incorporation (>95%). Mono and selective deutero-dechlorination of polychloro heteroarenes, as achieved here for the first time, is particularly noteworthy.

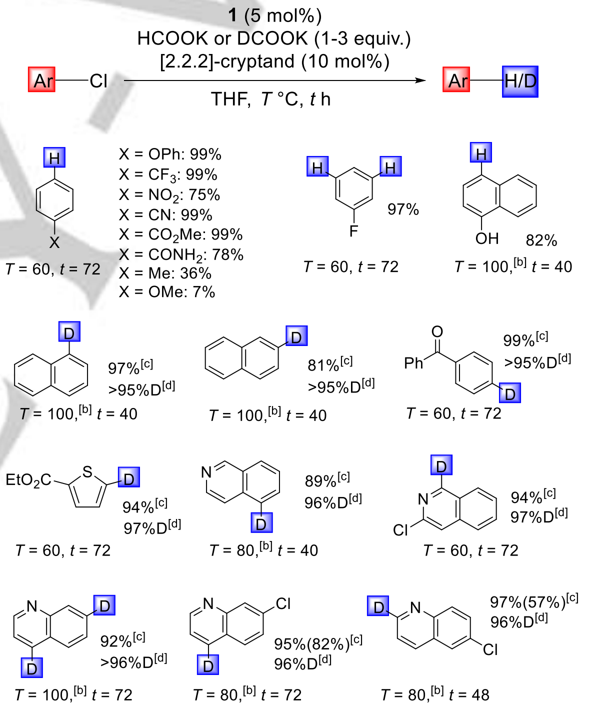
Table 1. Screening of conditions for the catalytic dehalogenation of chlorobenzene.



Entry	Catalyst	Reductant / Activator	Conv.[a]	Yield[a]
1	**1**	KH / [2.2.2]-cryptand	>99	68
2	**1**	KH / 18-crown-6	>99	76
3	**1**	NaH / 15-crown-5	trace	trace
4	**1**	LiH / 12-crown-4	trace	trace
5	**1**	HCOONa / 15-crown-5	trace	trace
6	**1**	HCOOK / [2.2.2]-cryptand	89	89
7	**1**	HCOOK / 18-crown-6	38	38
8	**2**	HCOOK / [2.2.2]-cryptand	88	88

[a] Determined by GC.

Table 2. Catalytic hydro / deutero-dechlorination catalyzed by the Pd→B complex **1**: scope of (hetero)aryl chlorides.[a]



[a] Yields were determined by GC. [b] Reactions were performed in close systems using pressure resistant vessels. [c] Isolated yields of deuterium-labeled products. [d] Determined by ^{1}H NMR.

In summary, the air-stable Pd→B complex **1** was found to react with potassium hydride to give the B–H–Pd bridged complex **2**, the first monomeric anionic Pd(0) complex to be structurally characterized. Insertion of the hydride in the Pd→B bond increases the electron density at Pd and promotes the activation of chlorobenzene. Upon B to Pd hydride transfer and reductive elimination, benzene is obtained. This anionic pathway is amenable to catalysis and accordingly, complex **1** was found to efficiently promote the hydro and deutero-dehalogenation of a range of (hetero)aryl chlorides. Future studies will aim to develop further this new type of palladium-borane cooperation, including towards catalytic carbon-heteroatom coupling reactions.

Acknowledgements

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Keywords: Anionic Complexes • Boranes • Catalysis • Dehalogenation • Deuteration • Palladium

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[23] DFT calculations also suggest an anionic pathway under these conditions: coordination of formate to boron, C–Cl activation, B to Pd formate migration, decarboxylation, reductive elimination (C–H coupling).[10] Attempts to generate the formate analog of **2** failed. Reaction of complex **1** with HCO_2K/[2.2.2]-cryptand was unproductive and the formate adduct of the diphosphine borane [(DPB)OCHO][K([2.2.2]-cryptand)] reacted with $Pd(PPh_3)_4$ to give the Pd→B complex **1**.[10]

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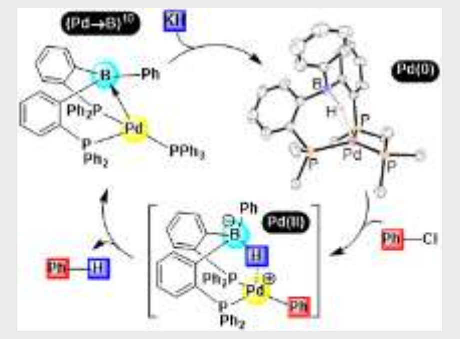
COMMUNICATION

A palladium-borane dance: an anionic reaction pathway involving hydride insertion into Pd→B bond, C–Cl bond activation by an anionic Pd(0) species and B-assisted C–H bond formation has been discovered and leveraged into catalysis.



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