

A Highly Active PBP-Iridium Catalyst for Dehydrogenation of Dimethylamine-Borane: Catalytic Performance and Mechanism

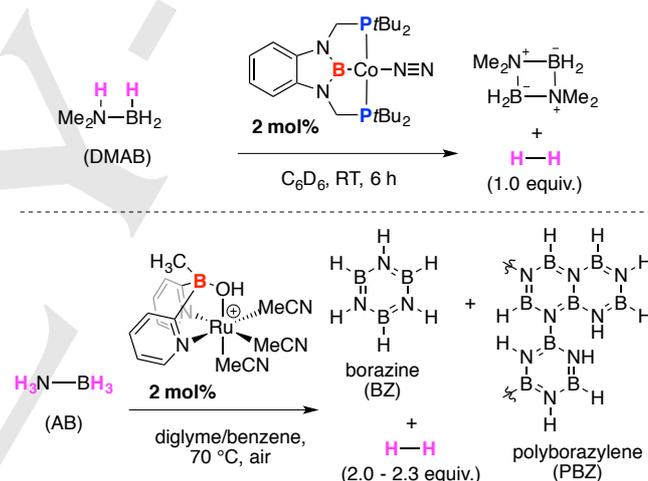
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Dedicated to Professor Takayuki Kawashima on the occasion of his 70th birthday

Abstract: A long-tethered boron-containing (P-B-P)-pincer ligand with aliphatic backbone was synthesized. Oxidative addition of the B-H bond in the ligand to $[\text{Ir}(\text{coe})_2\text{Cl}]_2$ (coe = cyclooctene) afforded (P-B-P)Ir(H)Cl complex. Catalyst consisting of the iridium complex with KO^tBu showed an excellent performance in the dehydrocoupling of *N,N*-dimethylamine-borane (DMAB), releasing one equivalent of dihydrogen gas from a concentrated solution of DMAB at low catalyst loading down to 0.05 mol% and with an initial turnover frequency (TOF) of $\sim 3400 \text{ h}^{-1}$. Dihydride complex (P-B-P)Ir(H)₂ could also catalyze the dehydrogenation of DMAB and was postulated as one of the intermediates in the catalytic cycle.

Low-molecular-weight nitrogen-boron compounds such as ammonia-borane ($\text{NH}_3\text{-BH}_3$, AB) have attracted much attention as a potential hydrogen carrier in the emerging hydrogen economy.^[1] Thermal decomposition of AB (hydrogen-to-weight ratio: 19.6%) produces H₂ with ultrahigh purity, but is poorly controlled and time consuming. An alternative H₂-releasing route from AB and the related substrates is the homogeneous metal-catalyzed dehydrogenation, which allows the dehydrogenation process to be operated at a milder condition with faster reaction rates in a controlled manner. However, to achieve the ultimate goal of utilizing AB as a hydrogen source, re-hydrogenation of the dehydrogenated BN-containing products to regenerate the spent fuel should also be feasible.^[2] Numerous examples of transition metal complexes have been examined for their catalytic performances and mechanisms.^[3-15] Apart from AB, *N,N*-dimethylamine-borane ($\text{Me}_2\text{NH-BH}_3$, DMAB) is the most extensively studied derivative since (i) only one equivalent of hydrogen molecule can be formed per DMAB unit, and (ii) the dehydrogenated product ($\text{Me}_2\text{N}^+=\text{B}^-\text{H}_2$) could coordinate to the metal centre, which facilitates the isolation, and structural and spectroscopic characterization of the catalytically active species.

Among all the reported metal-catalyzed dehydrogenation of amine-borane derivatives,^[2a,3] only two examples were catalyzed by using transition metal complexes supported with boron-containing ligand (Scheme 1). Williams *et al.* in 2011 reported the catalytic dehydrogenation of AB with various bis(pyridyl)(hydroxy)borate ruthenium complexes under aerial condition and released more than two equivalents of H₂ from AB (Scheme 1).^[8d,f] Peters *et al.* demonstrated in 2013 that (PBP)Co(N₂) complex could dehydrogenate DMAB at room temperature in 6 h.^[10a] The complex could further facilitate the transfer hydrogenation of styrene.



Scheme 1. Previously reported examples of catalytic dehydrogenation of ammonia-borane (AB) and amine-borane by using transition metal complexes supporting with boron-containing ligands.

According to their structures, we can divide the boron-based pincer ligand systems into two classes. One class is based on *m*- or *o*-carborane core, onto which two coordination tethers are attached.^[16a-e] The other class, which is the focus of our research group, is based on the boron-containing five-membered ring diazaborole, onto which two coordinating phosphorus moieties are tethered.^[16f-i] In 2009, we synthesized the hydroboranes that serve as precursors for boron-containing pincer ligands.^[16f,g] Introduction of precursors to different transition metal centres could be easily achieved by oxidative addition of the B-H bonds.^[16h-r] A comprehensive overview, also focusing on the applications of these systems in homogeneous catalysis, was reported in 2015.^[16s] Recently, we prepared the (P-B-P)Ir complexes with propylene sidearms and demonstrated their catalytic performance toward the transfer dehydrogenation of alkanes.^[16i] In this report, the (P-B-P)-pincer ligand is modified by

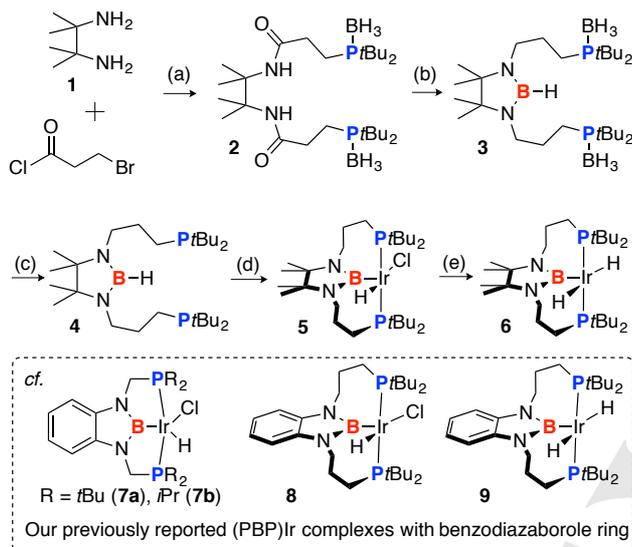
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replacing the benzene ring of the benzodiazaborole backbone with an aliphatic tetramethylethylene moiety, thus decreasing the Lewis acidity on boron centre.

By applying similar synthetic route that we developed previously,^[16] a new (P-B-P)-pincer ligand **4** was synthesized in four steps (Scheme 2), and was then ligated to the iridium to afford (hydrido)chloroiridium complex (P-B-P)Ir(H)Cl **5**. Treatment of **5** with *n*BuLi at room temperature resulted the dihydride complex (P-B-P)Ir(H)₂ **6** in good yield.^[16]



Scheme 2. Synthesis of long-tethered (P-B-P)-pincer ligand precursor **4** with aliphatic tetramethylethylene backbone, its complexation with iridium, and derivatization to dihydride complex. Reaction conditions: (a) *n*BuLi, *t*Bu₂PH-BH₃; (b) BH₃·THF; (c) *N*-acetylene diamine; (d) [Ir(cod)₂Cl]₂; (e) *n*BuLi.

Both complexes **5** and **6** were fully characterized by solution multinuclear NMR analysis and high resolution mass spectrometry (HRMS). Broadening of the methylene protons of the propylene tethers was observed in both complexes, implying that an equilibrium due to flipping of the diazaborolane ring existed in solution.^[16] The structural assignments of both complexes were furthermore supported by single-crystal X-ray diffraction analysis (Figures 1 and 2). Both complexes adopted a distorted trigonal bipyramidal structure (Y-shaped),^[17] consisting of two apical phosphine ligands and equatorial boryl, hydride and/or chloride ligands. Selected bond lengths (Å) and angles (°) of **5** and **6** are summarized in Table S2 in the ESI with those of reference complexes **7a**, **8** and **9** in Scheme 2.

The hydride ligand of **5** showed a triplet signal at $\delta_{\text{H}} -21.4$ ppm ($^2J_{\text{PH}} = 15$ Hz) with no broadening due to the interaction with quadrupolar boron, consistent with a terminal iridium hydride. It is also similar to that of our previously reported **8** ($\delta_{\text{H}} -20.0$ ppm), and is lower-field shifted in comparison to those (ca. -40 ppm) of previously reported (PCP)Ir(H)Cl and (POCOP)Ir(H)Cl complexes.^[18] The existence of hydride ligand in **5** was further confirmed by an IR spectrum (2259 cm^{-1}), and supported by frequency

calculations using DFT methods (see Figure S30 in the ESI). The two phosphorus atoms in **5** resonated as two doublets at $\delta_{\text{P}} 36.7$ ($^2J_{\text{PP}} = 321$ Hz) and 41.4 ($^2J_{\text{PP}} = 321$ Hz) ppm at room temperature. It is similar to that of **8** ($\delta_{\text{P}} 41.2$ ppm, singlet), but more upfield than those of **7a-b** (ca. 80 ppm, singlet). The splitting of the signal into two doublets should be the result of the magnetic inequivalency below and above the (P-B-P)Ir plane and the twisted structure. The boron nucleus showed a broad singlet at $\delta_{\text{B}} 17.1$ ppm, which is more upfield than those reported for **7a-b** (ca. 30 ppm), but similar to that of **8** ($\delta_{\text{B}} 12.3$ ppm). The Ir-B bond [2.035(4) Å], Ir-P bonds [2.3557(9) and 2.3300(9) Å] and Ir-Cl bond [2.4676(9) Å] in **5** are slightly longer than those of **8**, while the B-N bond lengths [1.431(5) and 1.432(5) Å] in **5** are similar to those of **8**. The acute angle of P-Ir-P in **5** [165.06(3)°] is slightly smaller than that of **8** [167.59(5)°], implying that the iridium centre in **5** is more congested. In complex **5**, both the bond angles of B-Ir-Cl [107.84(11)°] and N-B-N [107.3(3)°] are slightly larger when compared with those of **8**.

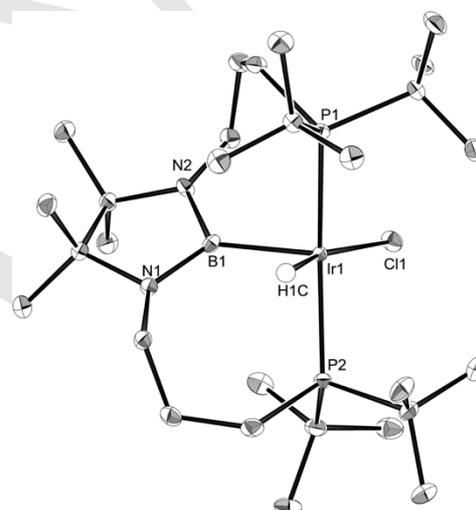


Figure 1. ORTEP drawing of **5** (thermal ellipsoids at 50% probability; all hydrogens but the hydride H1C are excluded for clarity).

The two hydride ligands in **6** resonated as a triplet at $\delta_{\text{H}} -1.39$ ppm ($^2J_{\text{PH}} = 15$ Hz), with no evidence of broadening from coupling with boron. The presence of hydride ligands was confirmed by an IR spectrum (1861 and 1765 cm^{-1}), and DFT calculations (see Figures S29 and S31 in the ESI). The ^{31}P NMR signal of **6** ($\delta_{\text{P}} 58.6$ ppm) was significantly shifted to lower field than that of **5**. The singlet of **6** at $\delta_{\text{B}} 19.1$ ppm is of similar value to **5**, suggesting that the (P-B-P)-ligand should be a boryl ligand to iridium. Dihydride **6** possesses a twisted geometry similar to that of **5**. In the crystal structure of **6**, the P-Ir-P bond angle of $177.32(4)^\circ$ is larger than that in **5**. The Ir-B bond length in **6** of $2.138(5)$ Å is the longest among those of our previously reported (PBP)Ir complexes. It is also longer than a typical Ir-B single bond (**A**) [$1.991(6)$ to $2.12(2)$ Å],^[19b,c] but shorter than a dative bond from Ir to B atom (**D**) [$2.326(11)$ Å] (Figure 3).^[19d] Ozerov recently reported a series of iridium complexes possessing a σ -borane/dihydride (**B**) and borate/dihydride (with some degree of $\text{Ir}\cdots\text{B}$ interaction) (**C**) formulation.^[19a,e] The Ir-B bond length in **6** is similar to those in **B**

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and **C**, although the ^1H and ^{11}B NMR spectroscopy indicated no evidence for the existence of σ -borane and/or borate species. Other structural features of **6** are similar to those of **5**.

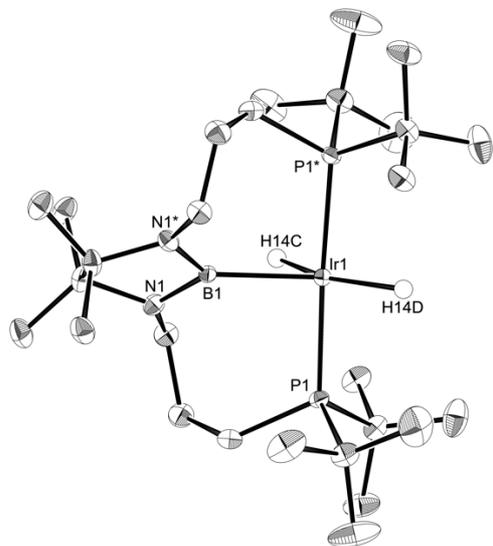


Figure 2. ORTEP drawing of **6** (thermal ellipsoids at 50% probability; all hydrogens but the hydrides H14C and H14D in **6** are excluded for clarity).

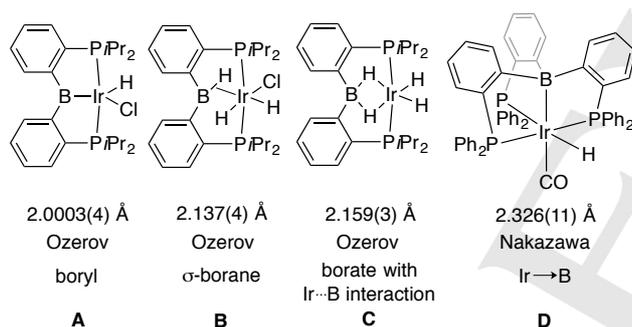
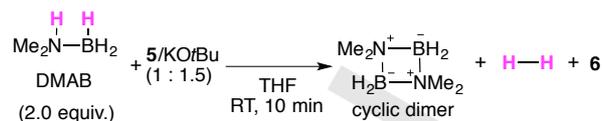


Figure 3. The reported Ir-B bond length (Å) in some of the structurally characterized iridium boryl complexes.

Prior to study of catalytic dehydrogenation, **5** was treated with KOtBu in the presence of stoichiometric amount of DMAB at room temperature to lead to rapid effervescence (Scheme 3). As evidenced by ^{11}B NMR spectroscopy, all DMAB was consumed and converted into cyclic dimer $(\text{Me}_2\text{N}^+-\text{B}^-\text{H}_2)_2$, with a trace amount of $\text{BH}(\text{NMe}_2)_2$ detected.^[20] After working up the reaction mixture, yellow crystals together with an orange oil were obtained. The yellow crystals were confirmed as dihydride complex (P-B-P)Ir(H)₂ **6** by solution multinuclear NMR analysis and single-crystal X-ray diffraction analysis. The intractable orange oil (δ_{P} 35.9 ppm) could not be recrystallized after numerous attempts. Complex **6** isolated from the above stoichiometric reaction mixture was then introduced into a fresh batch of DMAB (in THF) at 23 °C to give a similar result as using **5**/KOtBu, implying that **6** should be involved in the catalytic cycle of the dehydrogenation.



Scheme 3. Reaction of **5**/KOtBu with DMAB in a 1:2 stoichiometry resulted in (i) the quantitative formation of cyclic dimer $(\text{Me}_2\text{N}^+-\text{B}^-\text{H}_2)_2$ and dihydrogen gas, and (ii) the isolation of dihydride complex **6**.

Table 1. Optimization of reaction conditions for the dehydrogenation of DMAB catalyzed by (P-B-P)Ir complexes

Entry ^[a]	Catalyst	Catalyst loading (mol%)	Temp (°C)	Yield ^[b] (%)		
				5 min	30 min	180 min
1		2.0	23	>95	>99	-
2		0.5	23	33	47	65
3		0.5	45	43	56	73
4		0.5	60	59	73	83
5 ^[c]	5 /KOtBu	0.5	60	77	88	97
6 ^[f]		0.5	60	38	49	62
7 ^{[c][d]}		0.1	60	-	-	88 (11 h)
8 ^{[c][e]}		0.05	60	-	-	87 (18 h)
9 ^[c]	8 /KOtBu	2.0	23	trace	trace	trace
10 ^[c]	9	2.0	23	-	-	trace

[a] Standard conditions: [P-B-P]Ir cat (3.0 mg, 1.0 equiv.) and KOtBu (0.7 mg, 1.5 equiv.) were dissolved in 1.00 mL THF, and was then transferred to a NMR tube containing 48.7 mg of DMAB and 0.5 mL of THF ([DMAB] = 0.551 M). The catalytic reaction was performed under an open system. The reaction mixture was monitored by ^{11}B NMR spectroscopy at preset temperature. [b] The amount of cyclic dimer $(\text{Me}_2\text{N}^+-\text{B}^-\text{H}_2)_2$ was estimated by ^{11}B NMR spectroscopy. [c] 0.75 mL THF in total was used ([DMAB] = 1.10 M). [d] 9.0 mg of **5**, 2.1 mg of KOtBu, and 730 mg of DMAB were used ([DMAB] = 16.5 M). [e] 9.0 mg of **5**, 2.1 mg of KOtBu, and 1460 mg of DMAB were used ([DMAB] = 33.0 M). [f] Closed system.

Encouraged by this result, reaction condition for the catalytic dehydrogenation of DMAB was optimized (Table 1). Stirring 2 mol% of **5**/KOtBu (1/1.5) in THF under Ar at room temperature gave an almost quantitative yield within 10 min (entry 1). The induction period was negligibly short (< 5 s) as H₂ was evolved immediately upon mixing the substrate and catalyst. Reducing the catalyst loading to 0.5 mol% resulted in an incomplete dehydrocoupling of DMAB even after 3 h at 23 °C (entry 2). Warming the reaction mixture at 45 °C improved the conversion (entry 3). Further increasing the reaction temperature to 60 °C slightly boosted the yield of cyclic dimer to 83 % (entry 4). A concentrated reaction medium (by reducing the volume of THF used) resulted in the almost quantitative conversion (97 %) of DMAB to cyclic product at 60 °C after 3 h (entry 5). In a closed system, catalysis was significantly slow (entry 6, and Figure S33 in the ESI) and a very similar induction period to the open system

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was observed. The catalyst loading could be as low as 0.05 mol% to give high yield of the cyclic dimer, but with a longer reaction time (entries 7-8). The catalytic activities of the previously reported PBP-pincer Ir complexes **8**/KOtBu and **9** toward dehydrogenation of DMAB were also explored (entries 9-10). In both systems, only trace amount of DMAB was dehydrogenated to give the linear dimer and cyclic product. Prolonged reaction time (16 h) led to no improvement in the conversion of DMAB to dimeric products (see Figures S34 and S35 in the ESI).

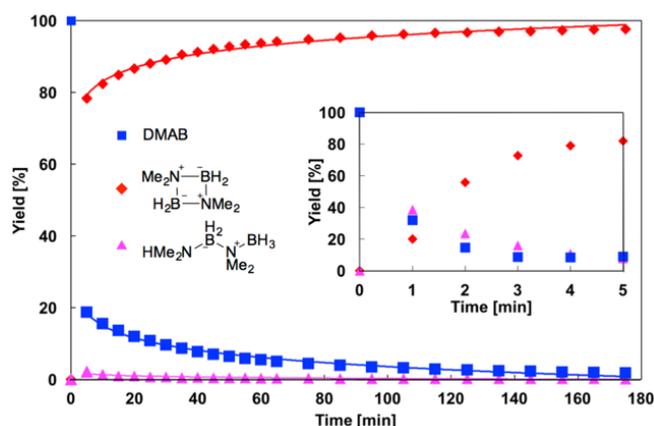


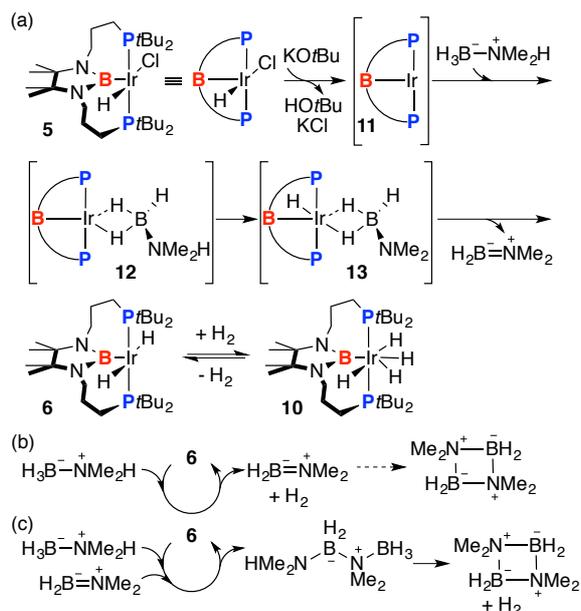
Figure 4. Time course for concentrations of each component estimated by ^{11}B NMR spectroscopy during the catalytic dehydrogenation of DMAB under the conditions of entry 5 in Table 1 for 5-180 min. (inset: for 0-5 min. in a separate experiment), Components: DMAB (blue), cyclic dimer (red) and linear product (purple). Curve fittings were based on simple exponential decay.

In order to estimate the reaction mechanism, the catalytic reaction was monitored by NMR spectroscopy. The ^{11}B NMR spectra of the reaction mixture under the condition of entry 5 (0.5 mol% catalyst loading) in Table 1 was monitored at 1- or 5-minute intervals (Figure 4). During the time course of the reaction, DMAB, dehydrogenated cyclic dimer, linear dimer ($\text{HMe}_2\text{N}-\text{B}^-\text{H}_2-\text{N}^+\text{Me}_2-\text{BH}_3$),^[20] dehydrogenated monomer ($\text{Me}_2\text{N}^+=\text{B}^-\text{H}_2$), and a small amount of $\text{BH}(\text{NMe}_2)_2$ were detected (see Figure S36 in the ESI). The reaction was rapid during the first 5 min, with 77% of cyclic dimer formed and almost full conversion was achieved after 3 h. In the first 5 min, conversion of DMAB to the linear dimer and subsequent cyclization to the cyclic dimer were observed (Figure 4, inset). The concentration of the linear dimer became untraceable only when the concentration of DMAB was significantly low. At the end of catalysis, most of ^{11}B -containing compounds were converged to the cyclic dimer (Figure 4). To provide a more detailed insight into the plausible mechanism, the initial 5 min of the catalysis was monitored under slightly diluted condition with 0.2 mol% of catalyst (see Figure S37 and S38 in the ESI). Considerable growth of the linear dimer until two minutes was detected. After the saturation of the linear dimer, the concentration of the cyclic dimer increased with time, while the signals of the linear dimer and DMAB dropped simultaneously as the catalysis proceeded. The dehydrogenated monomer ($\text{Me}_2\text{N}^+=\text{B}^-\text{H}_2$) was perceived at very low concentration during the course of catalysis.

To investigate the fate of the iridium complex in the catalysis, the reaction mixture was also monitored by using ^{31}P NMR spectroscopy. Signals for complex **5** disappeared immediately upon addition of KOtBu and DMAB. Only one sharp singlet at δ_{P} 35.9 ppm was detected during the course of the catalysis (see Figure S39 in the ESI). In the ^1H NMR spectrum of the reaction mixture, a triplet signal with a coupling constant of 13 Hz and an integral ratio of 4H was observed at δ_{H} -11.1 ppm (see Figure S40 in the ESI). This observed iridium species is tentatively assigned as a tetrahydride complex (P-B-P)Ir(H)₄ **10**. The high concentration of H_2 in the solution during catalysis would promote the oxidative addition of H_2 to the active catalyst and result in the formation of the tetrahydride complex **10**. Signal for the dihydride **6**, which could be generated by reductive elimination of H_2 from **10**, at δ_{P} 68.6 ppm could not be detected even after prolonged reaction time.

Turnover frequency (TOF) was reviewed to compare the catalytic performance of our (P-B-P)-iridium catalysts with those of previously reported examples. In 2009, Schneider reported the use of 2 mol% of a bifunctional complex $[(\text{PNP})\text{Ru}(\text{H})(\text{PMe}_3)]$ ($\text{PNP} = \text{HN}(\text{CH}_2\text{CH}_2\text{P}/\text{Pr}_2)_2$) for the same catalytic reaction, releasing 70% H_2 in 28 h.^[8h] The catalyst exhibited a relatively high initial rate with a $\text{TOF}_{\text{initial}}$ of $\sim 3600 \text{ h}^{-1}$ in ~ 0.5 min; after which, a much slower regime operated ($\text{TOF} \sim 1.5 \text{ h}^{-1}$), suggesting two catalytic regimes owing to catalyst deactivation in the course of the reaction. In our (P-B-P)Ir catalytic system, an initial TOF of $\sim 3400 \text{ h}^{-1}$ was achieved in 2 min. using 0.5 mol% catalyst (see Figure S41 in the ESI). Thus, regarding the catalytic performance of dehydrogenation of DMAB, our system should be ranked second and with a shorter reaction time and lower catalyst loading.

A plausible mechanism is shown in Scheme 4. Complex **5** was activated by KOtBu to generate the three-coordinated “T-shaped”^[21] (P-B-P)iridium(I) species **11** (Scheme 4a). Coordination of a DMAB molecule through its nucleophilic B–H end to **11** generated intermediate **12**, possessing a η^2 coordination of the BH_3 end of DMAB to the iridium centre. The N–H proton in **12** was then transferred to the iridium centre, bent toward boron atom, and formed intermediate **13**. Dissociation of the dehydrogenated monomer $\text{Me}_2\text{N}^+=\text{B}^-\text{H}_2$ from **13** generated the dihydride complex **6**. The dihydride **6** could convert DMAB to the dehydrogenated monomer and H_2 (Scheme 4b). Catalyst **6** could also mediate a coupling reaction of DMAB and the dehydrogenated monomer to produce the linear dimer ($\text{HMe}_2\text{N}-\text{B}^-\text{H}_2-\text{N}^+\text{Me}_2-\text{BH}_3$) (Scheme 4c). The linear dimer was spontaneously transformed into the cyclic dimer by releasing an additional equivalent of H_2 . Judging from the low concentration of the dehydrogenated monomer observed in the time-course study, its dimerization to give the cyclic dimer is unlikely. Under the catalytic condition, dihydride **6** may be in equilibrium with the tetrahydride **10**, which was observed as a resting state. This equilibrium is consistent with the poor catalytic performance under a closed reaction medium (Table 1, entry 6).



Scheme 4. Plausible mechanism for the catalytic dehydrogenation of DMAB by using the (P-B-P)Ir complexes **5** and **6**: (a) Generation of catalytically active **6** and its reaction with H₂ providing the resting state of **10**, (b) catalytic cycle for dehydrogenation of DMAB to form the dehydrogenated monomer, (c) catalytic cycle for a coupling reaction between DMAB and the dehydrogenated monomer followed by a spontaneous cyclization to form the cyclic dimer.

In conclusion, we have prepared a new long-tethered (P-B-P)-pincer ligand **4** having an aliphatic backbone. Complexation of **4** with Ir afforded (P-B-P)Ir(H)Cl complex **5**, which could be further derived to (P-B-P)Ir(H)₂ complex **6**. Both complexes **5** (with KOtBu) and **6** could catalyze dehydrogenation of DMAB to form the cyclic dimer and release one equivalent of H₂, in which **6** was postulated as catalytically active species. A relatively high initial TOF of ~3400 h⁻¹ was observed and the catalyst loading could be as low as 0.05 mol%.

Acknowledgements

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Keywords: iridium • boron • pincer • *N,N*-dimethylamine-borane (DMAB) • dehydrocoupling

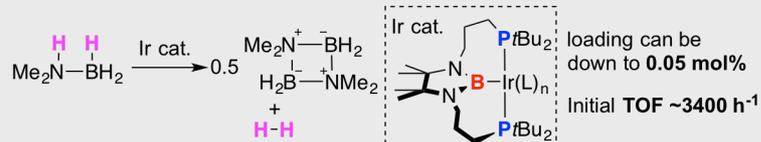
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**A Highly Active PBP-Iridium Catalyst
for Dehydrogenation of
Dimethylamine-Borane: Catalytic
Performance and Mechanism**

Reaction of a newly synthesized boron-containing pincer ligand with aliphatic backbone reacted with $[\text{Ir}(\text{coe})_2\text{Cl}]_2$ resulted in the formation of (P-B-P)Ir(H)Cl complex. Catalyst consisting of the Ir complex with KO^tBu showed an excellent performance in releasing one equivalent of H_2 from N,N-dimethylamine-borane at low catalyst loading down to 0.05 mol% with an initial TOF of $\sim 3400 \text{ h}^{-1}$.