### Introduction

Catalytic processes occurring under the action of “frustrated Lewis pairs” (FLPs) have been intensively sought after during the past decade.\(^1,2\) Heterolytic cleavage of H\(_2\) by main group intermolecular FLPs has been proposed to occur through an ‘encounter complex’ where the Lewis acid and Lewis base are in close proximity, but non-bonding, and H\(_2\) is accommodated between the two centers prior to heterolysis. DFT metadynamics studies for the prototypical FLP system P(Mes)\(_3\)/B(C\(_6\)F\(_5\))\(_3\) gave evidence for the H\(_2\) polarization followed by the rate-determining hydride transfer to B and proton transfer to P.\(^1\)

The heterolytic cleavage of H\(_2\) into a proton and a hydride is a crucial step in many chemical and biochemical processes such as, e.g., hydrogen oxidation by hydrogenases, transition metal-catalyzed hydrogenation of C=O bonds, or metal-catalyzed hydrogen oxidation in energy conversion reactions. From this point of view, the nomenclature of FLPs has many parallels in metal–ligand cooperation (bifunctional) catalysis, where the two sites of cooperation are typically metal- and ligand-based.\(^1,4,5\) Closely related to this concept is also an area of bimetallic catalysis, wherein two metal sites demonstrate cooperativity in fundamental catalytic reactions.\(^6\)

The reaction between basic [(PCP)Pd(H)] (PCP = 2,6-(CH\(_3\))\(_2\)C\(_6\)H\(_4\)) and acidic [LWH(CO)\(_3\)] (L = Cp (1a), Tp (1b); Cp = \(\eta^2\)-cyclopentadienyl, Tp = \(\eta^3\)-hydrido(tris(pyrazolyl)borate) leads to the formation of bimolecular complexes [LWH(CO)\(_2\)-(µ-CO)···Pd(PCP)] (4a, 4b), which catalyze amine-borane (Me\(_2\)NHBH\(_3\), \(\text{BuNH}_2\cdot\text{BH}_3\)) dehydrogenation. The combination of variable-temperature (\(\text{H}, \text{H}^1\text{P}(\text{H}), \text{H}^1\text{B}\) NMR and IR) spectroscopies and computational (\(\text{H}97X/D/\text{def}2\text{-TZVP}\)) studies reveal the formation of an \(\eta^2\)-borane complex [(PCP)Pd(Me\(_2\)NHBH\(_3\))]\(^+\)\(\text{LWH(CO)}_3\)^\(-\) (5) in the first step, where a BH bond strongly binds palladium and an amine group is hydrogen-bonded to tungsten. The subsequent intracomplex proton transfer is the rate-determining step, followed by an almost barrierless hydride transfer. Bimetallic species 4 are easily regenerated through hydrogen evolution in the reaction between two hydrides.

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Bifunctional activation of amine-boranes by the W/Pd bimetallic analogs of “frustrated Lewis pairs”\(^\dagger\)


The reaction between basic [(PCP)Pd(H)] (PCP = 2,6-(CH\(_3\))\(_2\)C\(_6\)H\(_4\)) and acidic [LWH(CO)\(_3\)] (L = Cp (1a), Tp (1b); Cp = \(\eta^2\)-cyclopentadienyl, Tp = \(\eta^3\)-hydrido(tris(pyrazolyl)borate) leads to the formation of bimolecular complexes [LWH(CO)\(_2\)-(µ-CO)···Pd(PCP)] (4a, 4b), which catalyze amine-borane (Me\(_2\)NHBH\(_3\), \(\text{BuNH}_2\cdot\text{BH}_3\)) dehydrogenation. The combination of variable-temperature (\(\text{H}, \text{H}^1\text{P}(\text{H}), \text{H}^1\text{B}\) NMR and IR) spectroscopies and computational (\(\text{H}97X/D/\text{def}2\text{-TZVP}\)) studies reveal the formation of an \(\eta^2\)-borane complex [(PCP)Pd(Me\(_2\)NHBH\(_3\))]\(^+\)\(\text{LWH(CO)}_3\)^\(-\) (5) in the first step, where a BH bond strongly binds palladium and an amine group is hydrogen-bonded to tungsten. The subsequent intracomplex proton transfer is the rate-determining step, followed by an almost barrierless hydride transfer. Bimetallic species 4 are easily regenerated through hydrogen evolution in the reaction between two hydrides.

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as an energy source but also B–N-containing materials.\textsuperscript{16,17} The metal-free catalysts including FLPs are also known but far less numerous.\textsuperscript{18} Although direct comparison between different catalysts is somewhat ambiguous due to the difference in the reaction conditions, RuH(PMe\textsubscript{3})\textsubscript{2}[N(CH\textsubscript{2}CH\textsubscript{2}PiPr\textsubscript{2})\textsubscript{2}]\textsubscript{2} can be considered as the best catalyst for BH\textsubscript{3}NH\textsubscript{3} dehydrogenation (TOF\textsubscript{max} 72 000 h\textsuperscript{-1})\textsuperscript{19} and (POCOP)IrH\textsubscript{2} (TOF 2400 h\textsuperscript{-1})\textsuperscript{12} and Rh(Xantphos-Pr)H (1500 h\textsuperscript{-1})\textsuperscript{20} for BH\textsubscript{3}NMe\textsubscript{2}H dehydrogenation, whereas a cationic zirconocene–phosphinoaryloxide complex [Cp\textsubscript{2}ZrOC\textsubscript{6}H\textsubscript{4}P\textsubscript{t}Bu\textsubscript{2}]\textsuperscript{+} which can be described as an early transition-metal-containing FLP gives TOF 600 h\textsuperscript{-1} for BH\textsubscript{3}NMe\textsubscript{2}H dehydrogenation.\textsuperscript{21}

The simultaneous presence of protic and hydridic H atoms within the same amine-borane molecule makes them

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Table 1 \(v_{\text{CO}}\) vibrations (cm\(^{-1}\)) of the metal complexes in THF and toluene at 298 K

<table>
<thead>
<tr>
<th>Complex</th>
<th>(v_{\text{CO}}) cm(^{-1}) in THF</th>
<th>(v_{\text{CO}}) cm(^{-1}) in toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a CpWH(CO)(_3)</td>
<td>2018, 1924</td>
<td>2020, 1926</td>
</tr>
<tr>
<td>1b TpWH(CO)(_3)</td>
<td>2003, 1910, 1888</td>
<td>2006, 1914, 1891</td>
</tr>
<tr>
<td>3a, 5a [CpW(CO)(_2)(μ-CO)]</td>
<td>1891, 1775</td>
<td>1887, 1782</td>
</tr>
<tr>
<td>3b, 5b [TpW(CO)(_2)(μ-CO)]</td>
<td>1884, 1754</td>
<td>1862, 1767</td>
</tr>
<tr>
<td>4a [CpW(CO)(_2)(μ-CO)⋅Pd(PCP)]</td>
<td>1910, 1819, 1660 1907, 1814, 1656</td>
<td></td>
</tr>
<tr>
<td>4b [TpW(CO)(_2)(μ-CO)⋅Pd(PCP)]</td>
<td>1901, 1796, 1650 1904, 1798, 1644</td>
<td></td>
</tr>
</tbody>
</table>

alternative reagents in transfer hydrogenation which attracts increased research interest.\(^{22}\) It also triggers an extended dihydrogen bonding (DHB) throughout their solid-state structure.\(^{23}\) DHB is preliminary to \(H_2\) evolution occurring after a simple thermal treatment or in a catalytic fashion.\(^{5,24}\) Given the analogy between protic and hydridic \(H\) atom co-existence and heterolytic \(H_2\) cleavage, the latter is intimately related to \(B/N\) inorganic hydride activation. Herein, we show for the first time that the bimetallic systems reported above act as homogeneous amine-borane dehydrogenation catalysts and explore the impact of hydride and proton transfer steps in the reaction mechanism using 1a in comparison with its more acidic analog TpWH(CO)\(_3\) 1b; Tp = \(κ^3\)-hydridotris(pyrazolyl)borate) as proton donating hydrides (Scheme 1).

Results and discussion

Pairwise interaction of two metal hydrides

The reaction of TpWH(CO)\(_3\) 1b with [PCP]PdH follows the same mechanism (Scheme 1) as that of CpWH(CO)\(_3\) 1a. The IR spectra obtained for the mixture of 1b with a 1.5-fold excess of [PCP]PdH in pure THF at 200 K show two new \(v_{\text{CO}}\) bands of the intermediate 3b at 1884 and 1754 cm\(^{-1}\), which disappear gradually upon temperature increase (Scheme 1 and Fig. S1†). At the same time, the bands at 1650, 1796, and 1901 cm\(^{-1}\) gradually upon temperature increase (Scheme 1 and Fig. S1†).

Interaction with dimethylamine-borane (DMAB)

Since the bifunctional ionic pairs \([LW(CO)\(_2\)(μ-CO)⋅M(PCP)]\) (4) reversibly bind hydrogen, we hypothesised that they could interact with amine-boranes which are typical bifunctional molecules (R'R''NBH\(_3\); R = H, Me; R' = H, Me, \(\text{Bu}\)). We used substituted amine-boranes for these studies because they produce boron-containing reaction products and intermediates soluble in organic solvents.\(^{26}\) Besides, Me\(_2\)NHBH\(_3\) usually reacts slower than ammonia borane (NH\(_3\)BH\(_3\)).\(^{27}\)

The addition of excess Me\(_2\)NHBH\(_3\) (DMAB, 3.3 equiv.) to the bimetallic complexes 4 in THF at 270 K disrupts the inter-ion interaction due to the simultaneous coordination of DMAB molecules between the two metals. The decrease of \(v_{\text{CO}}\) bands of 4 and the appearance of two new \(v_{\text{CO}}\) bands of a new ionic complex 5 (Table 1) are observed in the IR spectra (Fig. S3†). These changes are reversible; the equilibrium shifts toward 5 upon cooling. Changing the solvent to less polar toluene allows the reaction to move one step forward: the bands of LWH(CO)\(_3\) (1) and [PCP]PdH (\(v_{\text{PdH}}\) 1717 cm\(^{-1}\)) appear in the IR spectrum (Fig. S4†), confirming the occurrence of proton and hydride transfer and the formation of neutral molecules. The hydride transfer from the boron atom to palladium is confirmed by the synchronous decrease of the DMAB band intensity (\(v_{\text{DMAB}}\) 2364 cm\(^{-1}\)) and the \(v_{\text{PdH}}\) growth on going from 260 K to 190 K (Fig. S5†). Warming the mixture from 190 to 260 K restores the
original spectral picture, further confirming the existence of the equilibrium shown in Scheme 2. Definitely, the neutral trimo-
lecule complex should be unfavorable due to the high entropy effect (see DFT calculations below), but it is conserved at low temperatures when $\Delta S$ contribution to the Gibbs energy is diminished.

The behavior of two ionic complexes 4a and 4b is qualita-
tively the same. However, the proton transfer from DMAB to 4a is easier; the tungsten hydride 1a is formed in a larger quantity, in agreement with the higher basicity of the [CpW(CO)$_3$]$^-$ anion: pK$_a$ of the conjugated acid LWH(CO)$_3$ in CH$_3$CN is 16.1 (ref. 28) and 14.4 (ref. 29) for 1a and 1b, respectively.

Thus, at low temperature (below 270 K), the DMAB molecule becomes “arrested” between the two metal ions of 4. The bifunctional nature of 4 allows the proton transfer from the N–H moiety to the Lewis base center on tungsten and the hydride transfer from the B–H moiety to the Lewis acid center on palladium. The position of the equilibrium (Scheme 2) depends on the solvent, temperature, and basicity of the [LW(CO)$_3$]$^-$ anion. Interestingly, neither (PCP)PdH, LWH(CO)$_3$, [LW(CO)$_3$]$^-$ (obtained by the reaction of LWH(CO)$_3$ with NaHMDS) or [(PCP)Pd]$^+$ (ref. 27) taken individually shows any activity in DMAB dehydrogenation. This confirms the crucial role played by the bimetallic complex in the process.

Catalytic DMAB dehydrogenation

At ambient temperature in the presence of up to 50-fold excess of DMAB over 4, the catalytic dehydrogenation reaction occurs. To deeper understand the mechanism, the reaction was followed spectrosopically and volumetrically. IR monitoring shows the progressive decrease of $v_{BH}$ (2360–2260 cm$^{-1}$) and $v_{NH}$ (3200 cm$^{-1}$) bands of DMAB in the presence of 4a or 4b until their complete disappearance (Fig. S6†). This observation provides strong confirmatory evidence for the cleavage of B–H and N–H bonds. A decrease of the typical DMAB signal ($\delta_B$ −15.3) and the accumulation of the dehydrogenation product – i.e. the cyclic dimer (Me$_2$NBH$_2$)$_2$ ($\delta_B$ 3.4), as well as the appearance of the steady-state intermediate – aminoborane Me$_2$N=BH$_2$ ($\delta_B$ 35.8, Fig. 3) – was observed in the $^{11}$B{$^1$H} NMR spectra, evidencing the off-metal dimerization mechanism. 30

Under these conditions, $^1$H NMR spectroscopy shows the initial appearance of metal hydride resonances ($\delta_{WH}$ and $\delta_{PdH}$, Fig. S7 and S8†). Then, the tungsten hydride singlet ($\delta_{WH}$ −7.4 and −2.3 for 1a and 1b, respectively) disappears, but the palladium hydride triplet ($\delta_{PdH}$ −4.2) still accumulates. $^{31}$P{$^1$H} NMR spectra show the corresponding growth of the (PCP)PdH

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**Fig. 3** $^{11}$B{$^1$H} NMR spectra (128.3 MHz, THF-$d_8$) of DMAB (5 equiv.) in the presence of 4a (top) and the corresponding changes in molar fractions in time (bottom).

**Fig. 4** Kinetic curves obtained from the IR spectra of DMAB (1 equiv. (top) and 5 equiv. (bottom)) dehydrogenation catalyzed by 4b (c = 0.003 M), 298 K, THF.
concentration from 0.003 M to 0.006 M leads to the doubling of substrate concentration constant, the increase of the catalyst (PCP)PdH restore their initial intensity when the concentration of both the catalyst and reaction intermediates is nearly constant (Fig. 4, bottom). An increase in DMAB loading increases the length of the quasi-stationary stage of the reaction conversion of DMAB (Fig. 4, top). An increase in DMAB loading consumes and then restored (Fig. S9 and S10).

The reaction kinetics was measured following the decrease of νBH bond intensity of DMAB. The observed initial rate of reaction and can be reused for the next substrate loading with the Cp-ligand: the initial reaction rate is 2.1 × 10⁻⁶ M s⁻¹ for 4a at 20 mol% catalyst loading. Keeping the initial reaction rate is 2.1 × 10⁻⁶ M s⁻¹ for 4a at 20 mol% catalyst loading. Keeping the concentration of both the catalyst and reaction intermediates is nearly constant (Fig. 4, bottom).

The reaction kinetics was measured following the decrease of νBH bond intensity of DMAB. The observed initial rate corresponds to the substrate disappearance (Fig. S6†). In the presence of excess DMAB, the kinetic curves (c(DMAB) vs. t) are linear (Fig. S12†). DMAB dehydrogenation occurs faster in the presence of the bimetallic complex 4a with the Cp-ligand: the initial reaction rate ν0 is 5.8 × 10⁻⁶ M s⁻¹ for 4a and 1.7 × 10⁻⁶ M s⁻¹ for 4b at 20 mol% catalyst loading. Keeping the substrate concentration constant, the increase of the catalytic 4a concentration from 0.003 M to 0.006 M leads to the doubling of the initial reaction rate. It should be noted that the kinetic curves obtained by the integration of proton NMR spectra have very similar behavior to the IR curves (Fig. S13†). According to the spectral data obtained, the bimetallic species [LW(CO)₂(μ−CO)···Pd(PCP)] (4) are regenerated at the end of the catalytic reaction and can be reused for the next substrate loading (Fig. 5). The initial reaction rates ν0 are similar when DMAB is added to the mixture of two neutral hydrides or to the pre-generated bimetallic complex 4, revealing that the reagents' mixing sequence does not affect the reaction rate (Fig. S11 and S12†).

The H₂ production in the reaction of DMAB with [CpW(CO)₂(μ−CO)···Pd(PCP)] (4a) in THF was monitored using the Man on the Moon X103 kit at ambient temperature and 313 K (Fig. 5 and S14†). At 313 K and 1 : 5 catalyst : DMAB ratio, complete DMAB conversion is achieved in 4 h (Fig. 7 and Table S3†) with an initial reaction rate of 2.5 × 10⁻⁶ M s⁻¹. The increase of substrate loading to 50 equivalents at the same concentration of 4a (c = 0.003 M, 2 mol%; T = 313 K) leads to complete DMAB conversion in less than 3 hours (Fig. 7), and the initial reaction rate is 2.1 × 10⁻⁵ M s⁻¹. Under these conditions, the TOF value reaches 26 h⁻¹ at a half-conversion time (Table S3†). The initial reaction rate at a catalyst : DMAB ratio of 1 : 50 is higher than that at 1 : 5, since the increase of DMAB amount at a constant catalyst concentration shifts the equilibrium of complex 5 formation (Scheme 2 and Fig. 6).

**Mechanism of R’RNHBH₃ dehydrogenation by bimetallic ion pairs**

According to the experimental data, we suggest the reaction mechanism shown in Scheme 3 involving three important steps: (1) amine-borane molecule insertion between the two units of the bimetallic complex, (2) proton and hydride transfer, yielding aminoborane (Me₂N=BH₃) and neutral metal hydrides, (3) dihydrogen release as a result of the reaction between palladium and tungsten hydrides via the DHB complex. The insertion of the amine-borane molecule into the bimetallic complex 4 yields the η¹-borane complex 5 (Scheme 3).
The latter is also an ionic pair with the tungsten anion [LW(CO)3]−, which could explain the accumulation of LW(CO)3 in the reaction mixture (Fig. 4). In the next stage, the proton transfer from the NH group of coordinated amine-borane to tungsten atom gives the neutral hydride 1 and the zwitterionic complex 6. The hydride transfer from the BH group to the palladium atom inside complex 6 leads to Me3N–BH2 elimination and the formation of (PCP)PdH. To close the catalytic cycle, the two neutral metal hydrides react with each other, regenerating the catalytically active complex 4.

DFT calculations

This mechanism was supported by DFT calculations at the ωB97XD/def2-TZVP theory level taking the real system for the structure optimization in toluene, which was introduced within the SMD model. Complex 5 is 7.7 kcal mol−1 above 4 on the Gibbs free energy scale (Fig. 8); however, its formation is possible (electronic energy difference ΔE(4-5) = −7.5 kcal mol−1). The formation of 5 from 1 + Pd + DMAB is nearly ergoneutral (∆G(1-5) = +1.9 kcal mol−1) and thus this equilibrium can be effectively shifted toward 5 in the presence of excess DMAB. The key bonds in complex 5 (Fig. 9) are elongated (r(Pd–Hn) = 1.89 Å and r(B–Hn) = 1.28 Å) relative to the B–H bond in free DMAB (1.21 Å) and Pd–H in (PCP)PdH (1.64 Å). The amine group of the dimethylamine fragment is hydrogen-bonded to the tungsten anion (H5–W 3.09 Å, N–H–W 162.6°). Despite the B–Hn bond elongation, the relaxed potential energy surface (PES) scan for BH bond distance in the complex 5 did not lead to any TS, continuously going up to 50 kcal mol−1. Hydride transfer does not occur at this step, due to the instability of NR3BH2+, in agreement with the rather low hydride-donating ability of amine-boranes. This is consistent with the suggested hydride transfer from DMAB to the cationic Pt-catalyst where additional stabilization of [Me2NH2BH3]+ by a strong nucleophile was required. For the DMAB molecule, the proton transfer from nitrogen to tungsten occurs with a barrier ∆G‡ = 21.8 kcal mol−1 and the formation of the zwitterionic complex 6 and LW(CO)3H (13.0 kcal mol−1 above complex 5). B–H bond cleavage in complex 6 is almost barrierless (<2 kcal mol−1) (Fig. S15†). As a result, the hydride transfer goes faster than the proton transfer (k1 ≫ k2); therefore, complex 6 could not be observed experimentally. The ensemble of the reaction products ([PCP]PdH, LW(CO)3H and H3B–NR3) is only slightly higher in free energy than the starting adduct 5 (+1.0 kcal mol−1), and the reaction is still reversible. However, since H2 evolution from the two hydrides (k1, Scheme 3) and the off-metal B–N dimerization are featured with a comparable barrier, the overall reaction of dehydrogenative DMAB coupling becomes irreversible.

Catalytic TBAB dehydrogenation

Dehydrogenation of mono-substituted tert-butylamine-borane ([BuNH]BH3, TBAB) was also studied using complex 4a as a catalyst. However, in this case, the IR spectroscopic picture and kinetic curves are not similar to those with DMAB (Fig. S16†). On the quasi-stationary stage, the concentration of neutral tungsten hydride 1a is higher, and that of the η1-borate complex 5a is lower than in DMAB dehydrogenation. Measured 60 min after TBAB addition (δH = 21.8), the 11B NMR spectrum shows the formation of the intermediate [BuNH=BH2 (δB 36.1, t) and cycloborazane [BuNH=BH3] (δB = 3.7, t) – the product of the evolution of the first H2 equivalent (Fig. S17†). At the end of the reaction, there is no initial TBAB, and the single product of the evolution of the second H2 equivalent – borazine [BuN–BH3] (δB 28.1, d) – is observed. The formation of two equiv. H2...
per 'BuNH2BH3 molecule was also confirmed by volumetric measurements (Fig. S18†).

To explain the different ratios of ionic and molecular forms of catalyst units in the reaction with DMAB and TBAB, we considered the behavior of the first dehydrogenation product that accumulates in an unexpectedly high amount in the case of TBAB. Monomeric aminoborane H2B=NR2 is potentially basic36 and appears to be able to deprotonate the tungsten hydride (eqn (1)).

$$\text{LW(CO)}_3 \text{H} + \text{H}_2\text{B} = \text{NR}_2 \rightleftharpoons [\text{H}_2\text{B} - \text{NHR}_2]^{-} + \text{LW(CO)}_3 \text{H}$$

(1)

The isolated [H2B=NR2]− cation is not stable, but it can be stabilized by interacting with nucleophilic atoms like the carbonyl or the THF’s oxygen atoms. Indeed, the neutral CpWH(CO)3/H2B=NMMe2 complex appears to be almost ergo-neutral relative to the ion pair CpWH(CO)3−/H2B=NMMe2H+ (ΔE = −1.3 kcal mol−1 in favor of the neutral form, Fig. S19†) stabilized by B···OCH3 interactions. Introducing a THF molecule into the system also allows stabilizing the ion pair via B···O THF interactions (ΔE = +0.2 kcal mol−1; Fig. S19†), whereas CO groups of the CpW(CO)3− anion appear unbounded, having a geometry similar to that of the CpW(CO)3−/R3NH+ ion pair.37 It should be noted that H2B=NH4Bu appears to be a weaker base than H2B=NMMe2; its neutral form is preferred by 3.8 kcal mol−1. That suggests a further deprotonation extent of LWH(CO)3 when H2B=NH4Bu is formed (Fig. S19 and S20†).

Based on these computational data, we could expect the equilibrium side process of LW(CO)3H deprotonation, yielding the ion pair CpW(CO)3−/H2B=NMMe2H+ with CO···B interaction for DMAB dehydrogenation in toluene. When THF is used as a solvent, this ion pair is likely converted into the THF stabilized one. Consequently, the IR spectra in the νCO range in THF resemble those of the tungsten anion, while the IR spectra in toluene would rather resemble those of the ion pair CpW(CO)3−/H2B=[CpW(CO)3]−/H2B=nBu.38 Such high KIE values suggest proton tunneling that is likely to occur when there is hydrogen bonding between both metals in hydridic forms in the reaction mixture (Fig. S16†).

**Reaction kinetics**

Both DFT calculations and experimental data suggest that the NH-bond cleavage is the rate-determining step of the catalytic reaction. Under these conditions, the overall reaction rate is determined by the rate of proton transfer in complex 5 (5 → 6) r2 = k2[5]. As shown by DFT calculations, the activation energy values for stepwise proton and hydride transfer (ΔG‡ff = 21 kcal mol−1 and ΔG‡ff < 2 kcal mol−1) indicate that k1 ≫ k2 (Scheme 3). Thus, the hydride transfer goes much faster than proton transfer and conversion of 5 to products has no influence on the reaction rate. When DMAB is in excess, the reaction is pseudo-zero order in DMAB. Taking into account the pre-kinetic step of DMAB coordination to bimetallic complex 4 in the presence of excess DMAB, the reaction rate is r = k2K5[DMAB]−4 = k5[4], K = [5]/[4][DMAB]. Thus, analysis of the experimental data gives the k5 values of the rate-limiting step equal to 0.17 s−1 and 0.03 s−1 for 4a and 4b, respectively (Table S4†). These values correspond to ΔG‡S8K 18.5 ± 0.1 and 19.5 ± 0.1 kcal mol−1, in reasonable agreement with DFT calculations. For TBAB dehydrogenation by complex 4a, the k5 value is 0.10 s−1 (ΔG‡S8K 18.8 ± 0.1 kcal mol−1), indicating faster proton transfer. The overall activation free energy ΔG‡S8K for the conversion of 4 to 6 is ca. 25 kcal mol−1 that is in good agreement with DFT calculations (Fig. 8).

The use of deuterated amine-boranes NDMe2BH3 and NDMe2BD3 proves that the rate-limiting stage is the N–H bond cleavage, as is often for AB dehydrogenation.39 The rate constant kND for NDMe2BH3 dehydrogenation catalyzed by 4a (Fig. S22 and S23†) is substantially lower (kND = 2.8 × 10−7 M s−1) than that for DMAB (kDMAB = 5.8 × 10−6 M s−1) giving the kinetic isotope effect (KIE = kND/kDMAB) of 20.6 ± 0.3. The use of the fully deuterated analogue NDMe2BD3 does not lead to a further decrease in the reaction rate, giving KIE = kND/kDMAB of 20.6 ± 0.7. The KIE obtained is substantially higher than typical KIEs in metal-catalyzed amine-borate dehydrogenation.40–41 This value also exceeds the KIEs for self-exchange in CpW(CO)3H/[CpW(CO)3]− or for proton transfer of CpW(CO)3H to aniline.42,43 Such high KIE values suggest a proton tunneling that is likely to occur when there is...
a minimal geometry distortion along the reaction coordinate.\textsuperscript{44} Our computations partially reproduce the observed magnitude of the isotope effect predicting increasing of the barrier upon NH to ND substitution by $\Delta G_{398} = 1.5$ kcal mol\textsuperscript{−1} (KIE = $K_{\text{NH}}/K_{\text{ND}} = 13$). One of the reasons for large KIE magnitudes (>10) is long (large acid–base separations) and strong H-bonded complexes.\textsuperscript{47}

Conclusions

In summary, bimetallic complexes [[LW(CO)$_2$(μ-μ-CO)$\cdots$Pd(PCP)] (4) act as “metallic-analogs” of typical main group FLPs. The presence of acidic and basic metal centers in these ionic pairs triggers the cooperative BH/NH bond activation in amine-boranes in the first reaction stage, the $\eta^1$-borane complex ([PCP]Pd(σ-$^3$BHBH$_2$-NR$_2$H)$\cdots$W(CO)$_2$L$_2$) (5) is formed, in which BH is strongly bound to the palladium atom and the amine group is hydrogen-bonded to the tungsten atom. The step-wise proton transfer to W and hydride transfer to Pd yield the unsaturated B=N fragment and neutral metal hydrides. Molecular hydrogen evolution is the result of two metal hydrides interacting, regenerating bimetallic species 4. One equivalent of H$_2$ can be produced from Me$_2$NH-BH$_2$, whereas dehydrogenation of BuNH-BH$_3$ gives two equivalents of hydrogen per monomer at room temperature. The catalytic system can be easily generated through direct mixing of LWH(CO)$_2$, [PCP]PdH and amine-borane, without preliminary synthesis of the ionic catalyst 4. The presence of ionic intermediates during the dehydrogenation cycle requires the use of polar solvents to achieve effective catalysis. The mechanistic study showed that proton transfer is the rate-determining step; therefore, the reaction is accelerated by a more basic anion ([CpW(CO)$_2$]$>^{>}[\text{TpW(CO)}]_2$) while the hydride transfer is almost barrierless. The dehydrogenation process starts only in the presence of excess amine-borane due to the shift of the prekinetic equilibrium (H$_2$BNH$_2$R + 4 = 5) to the right, which in turn causes the increase of the initial reaction rate. Yet another notable observation is that the dimethylaminoborane monomer H$_2$B═NR$_2$ is able to deprotonate tungsten hydride in competition with H$_2$ evolution from two hydrides and H$_2$B═NR$_2$ oligomerization. Different basicities of dehydrogenated DMAB and TBAB monomers lead to a different impact of this side process to the overall catalytic reaction.

Prior studies have shown that bimetallic systems featuring a metal–metal bond\textsuperscript{48} can indeed operate in a concerted way activating H$_2$, C–H, B–H, and other bonds.\textsuperscript{49–52} These complexes activate the ONE bond, splitting it between two metals, often in an oxidative addition fashion. In our case, two transition metal-based building units of a bimetallic complex do not interact directly but act cooperatively as a Lewis acid and a Lewis base, splitting the N–H and B–H bond without changing the metals’ oxidation state. So far, such reactivity has been reported only for [Cp$_2$ZrOC$_6$H$_4$PBU$_3$]$^{+}$ which can be described as an early transition-metal-containing linked FLP.\textsuperscript{53} This behavior is similar to that of Stephan’s main group FLPs\textsuperscript{18} and can be exploited for other catalytic conversions; these studies are underway in our laboratories.

**Experimental section**

All reactions were performed using standard Schlenk procedures under a dry argon atmosphere. Commercial reagents (dimethylamine-borane, tert-butylamine-borane) were purchased from Aldrich and used after preliminary sublimation. Tetrahydrofuran (THF) and toluene were dried over Na/benzophenone and distilled under an argon atmosphere. THF-d$_6$ (Aldrich) was stored over 4Å molecular sieves and degassed before use by three freeze–pump–thaw cycles. NDMe$_2$BH$_3$ and NDMe$_2$BD$_3$ were prepared as described in the literature.\textsuperscript{49,51} Variable-temperature (VT) NMR spectra were recorded on Bruker AVANCE II and Varian Inova FT-NMR spectrometers operating at 300 and 400 MHz in the 200–320 K temperature range. $^1$H chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were calibrated against the residual resonance of the deuterated solvent, while $^{31}$P($^1$H) chemical shifts were referenced to 85% H$_3$PO$_4$ with downfield shift taken as positive. $^{1}$B and $^{11}$B ($^1$H) were referenced to BF$_3$–OEt$_2$. IR spectra were recorded at different temperatures (190–293 K) using a home-modified cryostat (Carl Zeiss Jena) with a Nicolet 6700 spectrometer using 0.05–0.2 cm CaF$_2$ cells. The accuracy of the experimental temperature was ±0.5 °C. The cryostat modification allows transferring the reagents (premixed at either low or room temperature) under an inert atmosphere directly into the cells.

Elemental analyses were carried out in the Laboratory of Microanalysis of INEOS RAS. The classic manual technique was used. The sample was burned in a platinum crucible in a stream of oxygen at 950 °C followed by trapping CO$_2$ and water with Ascaris (asbestos impregnated with NaOH) and Anhydrone (anhydrous magnesium perchlorate), respectively, and the analysis of the mass changes.

**Synthesis of [[LW(CO)$_2$(μ-CO)$\cdots$Pd(PCP)] L = Cp (4a), Tp (4b)**

Solid LW(CO)$_3$H (0.03 mmol) was placed in a Schlenk flask filled with argon (10 ml) together with 1 ml of tetrahydrofuran. Then, 1 ml of a (PCP)PdH THF solution (0.03 mmol of hydride in 2 ml of the solvent) was added to this solution. The resulting mixture of two colorless hydrides instantly became yellow colored. After an hour of stirring, the solvent was concentrated to ca. 0.1 ml under vacuum. Then, the Schlenk flask was filled with argon and left for several days standing at ambient temperature until a crystalline precipitate was obtained. The resulting solid (yellow needle-shaped crystals) was washed with a small amount of cold THF (2 × 0.2 ml) and dried in a vacuum. Yield: 90%.

4a. IR (THF, $\nu_{\text{CO}}$, cm$^{-1}$): 1907, 1815, 1656. $^1$H NMR (400 MHz, THF-d$_6$, ppm): δ 6.93–6.85 (m, 3H, ArH); 5.10 (s, 5H, Cp–H); 3.28 (t, $^3$$J$-H$_3$ = 4.12 Hz, 4H, –CH$_2$–); 1.43 (t, $^3$$J$-H$_3$ = 7.0 Hz, 36H, C(CH$_3$)$_3$). $^{31}$P($^1$H) (161.9 MHz, THF-d$_6$, ppm): δ 75.3. Anal. calc. (%) for C$_{32}$H$_{27}$O$_3$PdW (%): C 46.20, H 5.69. Found: C, 46.00; H, 5.78.

4b. IR (THF, $\nu_{\text{CO}}$, cm$^{-1}$): 1901, 1796, 1650. $^1$H NMR (600 MHz, THF-d$_6$, ppm): δ 7.66 (s, 3H, Tp CH); 7.59 (s, 3H, Tp CH), 5.98 (s,


**General procedure for DMAB dehydrogenation by 4**

For **NMR kinetic studies**, (PCP)PdH (c = 0.01 M) and 1a or 1b complexes (c = 0.01 M) and DMAB (5, 10 eq.) were mixed simultaneously at 290 K in THF-d₄.

For **variable temperature IR studies**, Complex 4a or 4b was generated in situ by the reaction of (PCP)PdH (c = 0.003–0.0039 M) with 1a or 1b (c = 0.003 M), respectively. The reagents were dissolved in THF or toluene at 270 K and allowed to react for 30 min. Then, a chosen amount of DMAB was added, and the obtained mixture was monitored in the temperature range 190–290 K.

For **kinetic IR studies**, Reagents were prepared via three methods.

**Method I.** A portion of isolated complex 4a or 4b was dissolved in THF (c = 0.003 M). Then, a chosen amount of DMAB (5 equiv.) was added and the IR spectra were monitored until full catalyst regeneration.

**Method II.** Complex 4a or 4b was generated in situ by the reaction of (PCP)PdH (c = 0.003–0.0036 M) with 1a or 1b (c = 0.003 M), respectively. The reagents were dissolved in THF at 290 K and allowed to react for 20 min. Then, a chosen amount of DMAB (1–5 eq.) was added, and the mixture was monitored until full catalyst regeneration.

**Method III.** (PCP)PdH (c = 0.003–0.0036 M), 1a or 1b complexes (c = 0.003 M) and DMAB (5 eq.) were mixed simultaneously at 290 K in THF. The reaction mixture was monitored until full catalyst regeneration.

**Volumetric studies of amine-borane dehydrogenation.** Hydrogen evolution during dehydrogenation of amine-boranes was monitored using the Man on the Moon X103 kit. The volume of the system is 32 ml (two-necked round-bottom flask – 30 ml, three-way valve – 2 ml). The monitored solutions were prepared via three methods.

**Method I.** A portion of the isolated complex 4a or 4b (0.006 mmol) was dissolved in THF (1 ml) in an argon-filled flask of the device connected to a three-way valve. Then the flask was tightly closed with a septum cap, and the valve was opened to the pressure sensor. The chosen amount of DMAB (5–50 equiv.) in 1 ml of THF was injected with a syringe through a septum cap.

**Method II.** Complex 4a or 4b (c = 0.003–0.01 M) was generated in situ by mixing the solutions of (PCP)PdH (1–1.2 eq.) and 1 (c = 0.003–0.01 M, 1 eq.) in THF in an argon-filled flask of the device connected to a three-way valve. Then the flask was tightly closed with a septum cap, and the valve was opened to the pressure sensor. A chosen amount of DMAB (5–50 eq.) in THF was injected with a syringe through a septum cap.

**Method III.** The solution of (PCP)PdH in THF (1–1.2 eq.) was prepared in an argon-filled flask of the device connected to a three-way valve. Then the flask was tightly closed with a septum cap, and the valve was opened to the pressure sensor. The mixture of 1 (c = 0.003–0.01 M, 1 eq.) and amine-borane (5–50 equiv.) in THF was injected with a syringe.

The resulting mixture was stirred at 295 K. Data from a pressure sensor connected via a wireless network to a computer were recorded as a function of pressure versus time for 3–20 hours. The values accumulated were referenced by the pressure of THF in a blank experiment at 295 K and used for calculations of the H₂ equivalents evolved. The calculations were performed in the ideal gas approximation (pV = nRT).

**Computational details.** Calculations were performed with the Gaussian 09 (ref. 54) package at the DFT/ωB97XD³ level without any ligand simplification. For all atoms, the def2-TZVP basis set was applied, supplemented with an effective core potential in the case of Pd and W. The structures of all complexes and transition states were fully optimized in toluene (ϵ = 2.3741) described by the SMD model, without any symmetry restrictions. The nature of the stationary points was confirmed by vibrational analysis. Transition state (TS) structures showed only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.

**X-ray crystallography.** For crystals of 4a and 4b, X-ray diffraction data were collected at 120 K with a Bruker ApexII DUO diffractometer using graphite monochromatic Cu-Kα radiation, respectively. Using Olex2, the structures were solved with the ShelXT structure solution program using intrinsic phasing and refined with the XD refinement package using least-squares minimization. Hydrogen atom of the BH group in 4b was found in the difference Fourier synthesis while positions of other hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. Crystallographic data and structure refinement parameters are given in Table S1.† CCDC 2020560 and 2020559 contain the supplementary crystallographic data for 4a and 4b, respectively.†

**Conflicts of interest.** There are no conflicts to declare.

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Notes and references