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Dehydrocoupling Reactions of Dimethylamine-Borane by Pt(II) Complexes: A New Mechanism Involving Deprotonation of Boronium Cations

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Ⓢ *Supporting Information*

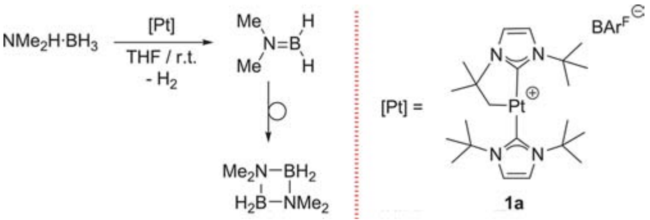
ABSTRACT: Coordinatively unsaturated Pt(II) complex $[Pt(I^tBu')(I^tBu)]^+$ stabilized by N-heterocyclic carbene (NHC) ligands dehydrogenates *N,N*-dimethylamineborane through a mechanism that involves hydride abstraction, assisted by an amine, to yield a platinum-hydride complex $[PtH(I^tBu')(I^tBu)]$ with concomitant formation of the boronium cation $[(NHMe_2)_2BH_2]^+$. This latter species is very likely in equilibrium with the THF stabilized borenium cation $[(NHMe_2)(THF)BH_2]^+$, bearing an acidic NH group that is able to protonate the platinum hydride $[PtH(I^tBu')(I^tBu)]$ releasing H_2, the amino borane $H_2B\text{-}NMe_2$ and regenerating the catalytic $[Pt]^+$ species.

During the past decade a burgeoning research effort has been dedicated to the dehydrocoupling reactions of amine-boranes catalyzed by metal centers.[1] The main reasons for this lay on the high hydrogen content in amine-boranes (particularly ammonia-borane), that makes them very attractive for hydrogen storage purposes,[2] and also for the formation of B−N bonds to produce oligomeric and polymeric materials based on boron and nitrogen.[3] Although at first glance the catalytic dehydrocoupling of amine-boranes seems a simple process, it has been shown that it is actually quite complex, and characterization of intermediates is often challenging.[1c,4] Several scenarios have been brought to light to explain the mechanism for this process that, on the other hand, is highly dependent on the metal center.[1c] When early transition metals and main group elements are used as catalysts, with a few exceptions, the first step is activation of a N−H bond of the amine-borane $R_3N{\cdot}BH_3$,[5] whereas for mid- and late transition metals B−H bond coordination to the metal center followed by a variety of subsequent steps (B−H bond activation, concerted transfer, or N−H transfer to a ligand) is prevalent.[4,6,7] Among the amine-boranes studied dimethylamine-borane, $H_3B{\cdot}NMe_2H$ (DMAB), has been frequently used because its dehydrogenated products are very soluble, and thus mechanistic studies are straightforward. Unveiling the possible mechanistic pathways operating in this complex catalytic process is essential to understand the distribution of the dehydrogenated products. In this contribution we have identified a new mechanistic scenario that involves the initial formation of boronium cations $(NMe_2H)_2BH_2^+$ through hydride abstraction from $H_3B{\cdot}NMe_2H$ by highly electrophilic Pt(II) complexes with concomitant formation of a platinum(II) hydride. Although boronium cations have been recently invoked to be intermediates,[8] we provide a different mechanistic proposal for the generation of H_2 and the dehydrocoupling products based on the deprotonation of such species.

We have very recently prepared a series of coordinatively unsaturated Pt(II) complexes with T-shaped structures stabilized by N-heterocyclic carbene ligands.[9] Encouraged by the fact that B−H sigma complexes of Pt(II) are unknown[10] and that this metal has not been tested in the dehydrocoupling of amine-boranes, we decided to investigate the reactivity of the cationic complex $[Pt(I^tBu')(I^tBu)][BAr^F]$ (**1a**) (where I^tBu is the N-heterocyclic carbene ligand 1,3-di-*tert*-butylimidazol-2-ylidene, and I^tBu' denotes the cyclometalated I^tBu ligand) toward *N,N*-dimethylamine-borane.

We first performed a catalytic reaction using 5% of catalyst loading and THF as solvent at room temperature, monitoring the reaction either by $^{11}B\{^1H\}$ NMR or by measuring the hydrogen pressure generated during the process in a closed system (see Supporting Information). Under these conditions we observed rapid gas evolution and the formation of dimethylamino-borane $H_2B{=}NMe_2$ that immediately starts converting into the cyclic dimer $[H_2BNMe_2]_2$ (Scheme 1). The reaction is completed within a few minutes and exhibits a first-order profile dependence on the concentration of the amine-borane (see Supporting Information).

Scheme 1. Catalytic Dehydrogenation of DMAB by 1a



To get insight into the mechanism of this process, stoichiometric experiments at low temperatures using deuterated THF as a solvent were monitored via NMR spectroscopy. When approximately 1 equiv of DMAB was added to complex **1a** the formation of a new complex which was stable at temperatures below 0 °C was observed. This new compound is, with little doubt, the sigma B−H complex **2a** (see Scheme 2). Coordination of DMAB to the platinum center is supported by

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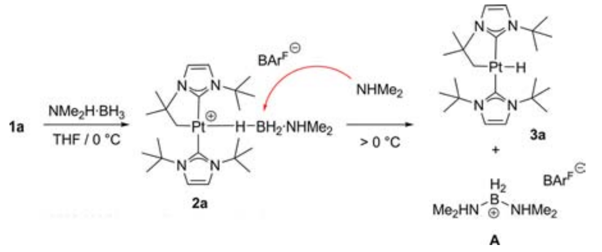
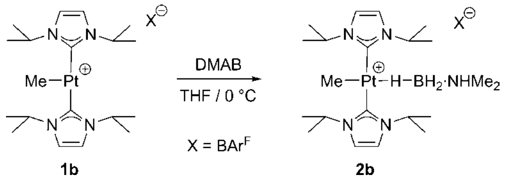
Scheme 2. Reactivity of Complex 1a with DMAB



two facts. First, the ^{1}H NMR signal of the BH_3 fragment of DMAB appears at higher field (0.03 ppm) compared to free DMAB (1.48 ppm), in agreement with previous reports on coordination of amine-boranes to late transition metal centers.[11] In addition, this signal sharpens on ^{11}B decoupling. No satellites due to coupling to ^{195}Pt were observed, but this is probably due to the weak nature of this interaction. Further evidence of DMAB coordination to Pt is the fact that the $^{1}H-^{195}Pt$ coupling constant of the protons of the $Pt-CH_2$ moiety diminishes by about 20 Hz, indicative of coordination of a weak ligand *trans* to it.[9,12] In support of all the above, we have synthesized the related complex $[PtMe(IiPr_2)_2(HBH_2{\cdot}NHMe_2)][BAr^F]$, **2b**, ($IiPr_2$ = 1,3-di-isopropyl-imidazol-2-ylidene ligand) by addition of DMAB to the cationic complex $[PtMe(IiPr_2)_2][BAr^F]$, **1b**, in THF at low temperature (Scheme 3). The smaller size of the $IiPr_2$ ligand facilitates the interaction of the hydrogen atoms of the BH_3 group with the metal center. Thus, at 0 °C the $^{1}H\{^{11}B\}$ NMR spectrum exhibits a signal centered at −0.38 ppm for BH_3 with satellites due to coupling to ^{195}Pt with a $J_{Pt,H}$ value of 107 Hz. The methyl group *trans* to coordinated DMAB shows a $J_{Pt,H}$ of 90 Hz, that is, 15 Hz less than in the starting material (105 Hz).

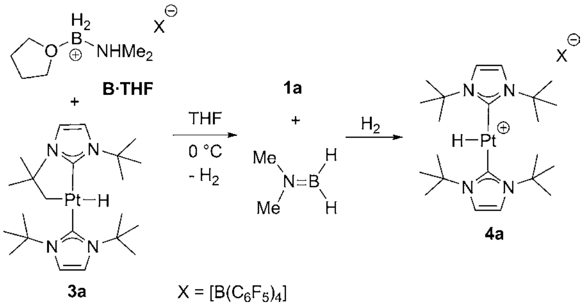
Scheme 3. Formation of the σ-B−H Complex 2b



Very interestingly, complex **2a** is unstable at temperatures above 0 °C, rearranging into the neutral Pt(II) hydride **3a** within a few minutes. Complex **3a** has been prepared and fully characterized independently by reaction of derivative **1a** with NaH in THF (see Supporting Information). Remarkably, the ^{1}H NMR spectrum of the reaction of **1a** and DMAB above 0 °C reveals the formation of another species whose NMR signals grow at the same rate as those for the platinum hydride **3a**. This new compound has been identified as the boronium cation $(NHMe_2)_2BH_2^+$ (**A**), which shows ^{1}H resonances for the NH, CH_3 and BH_2 protons at 6.44, 2.57, and 1.87 ppm, respectively. In the $^{11}B\{^{1}H\}$ NMR spectrum this compound exhibits a signal at −2.8 ppm that becomes a triplet in the ^{11}B spectrum with a B−H coupling constant of 113 Hz. These chemical shifts match those of an authentic sample of the boronium cation $[(NHMe_2)_2BH_2][BAr^F]$ prepared by an adapted literature method (see Supporting Information). Formation of boronium cations is known to be favored in more polar environments, and in fact they are believed to be formed as intermediates during thermolysis of ammonia borane.[13]

During the catalytic cycle the concentration of both the complex **3a** and the boronium cation remains constant until almost all DMAB is consumed. At the end of the reaction the only observable platinum complex is the 14-electron Pt(II) species $[PtH(I^tBu)_2][BAr^F]$, **4a** (Scheme 4), that is formed by hydrogenation of complex **1a**. With respect to the dehydrocoupling products of DMAB, besides the formation of $H_2B{=}NMe_2$ (that rearranges into dimer $[H_2BNMe_2]_2$), only $HB(NMe_2)_2$ was detected as a minor species. No traces of the linear dimer $BH_3-NMe_2-BH_2-NMe_2$ have been observed in the ^{11}B NMR at any point in the reaction.[4,6c]

Scheme 4. Protonation of Hydride 3a by Boronium B·THF



When considering the mechanism of this transformation, it seems very likely that platinum complex **1a** is acting as a Lewis acid abstracting a hydride atom from the BH_3 unit of DMAB in a similar way to the reaction of $B(C_6F_5)_3$ with $NH_3{\cdot}BH_3$ to yield $HB(C_6F_5)_3^-$ and $[H_3N{\cdot}BH_2]^+$.[8c] However, the observation of the boronium cation $[(NHMe_2)_2BH_2]^+$, **A**, suggests that the transfer of the H atom from boron to platinum is assisted by dimethylamine (originated from dissociation of DMAB[14,15]) (Scheme 2), in a somehow related manner to the nucleophilic addition of alcohols and ethers to cationic silane-sigma complexes of iridium.[16]

In addition to the above, DFT calculations[17] reveal that coordination of one molecule of AB (used as the model for DMAB) to **1a** is exothermic by 14.6 kcal·mol^{-1} in THF and yields a Shimoi-type complex[6h] ($\mathbf{2_C}$) that maps onto experimental **2a**. The optimized geometry of $\mathbf{2_C}$ (Figure 1) is in agreement with predominant σ-B−H electron donation to the

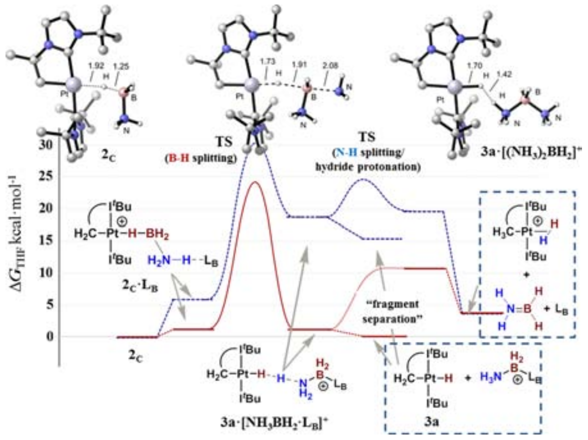


Figure 1. Simplified DFT-optimized geometries of key species and calculated free energy profile in THF of the AB dehydrogenation reaction assisted by NH_3 (red solid trace) and Me_2O (blue dashed trace).

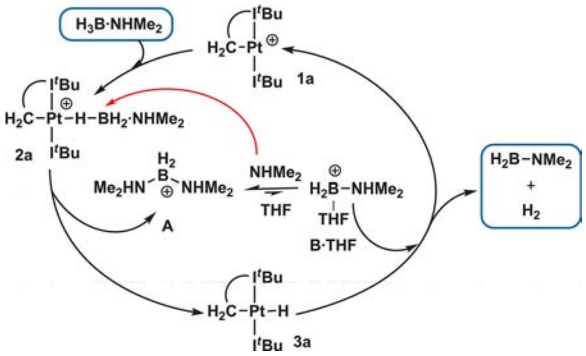
electrophilic Pt(II) center. When routes for activation of the B−H linkage at the Pt center were explored, the calculations showed that AB dehydrogenation occurs in a single elemental step, with B−H and N−H splitting to give transient $[Pt(H_2)(I^tBu')(I^tBu)]^+$ and $H_2B{=}NH_2$. However, the energy barrier for this step is 42.5 $kcal{\cdot}mol^{-1}$ (see the Supporting Information).[18] Inclusion of a Lewis base (L_B) such as Me_2O or NH_3 (models for THF and $NHMe_2$, respectively) lowers the energy barrier associated to B−H splitting by more than 18 $kcal{\cdot}mol^{-1}$ ($\Delta E^{\neq}_{THF}$ = 24.1 and 24.3 $kcal{\cdot}mol^{-1}$ for the Me_2O- and the NH_3-assisted reactions, respectively). In addition, these Lewis bases stabilize the resulting borenium cations, and minima were located for the corresponding adducts $\mathbf{3a}{\cdot}[NH_3BH_2{\cdot}L_B]^+$ (L_B = OMe_2, NH_3). The Me_2O adduct is 13.1 $kcal{\cdot}mol^{-1}$ above $\mathbf{2_C}{\cdot}OMe_2$, whereas the NH_3 adduct has nearly the same energy as $\mathbf{2_C}{\cdot}NH_3$. Both adducts of **3a** feature dihydrogen bonds[19] between the metal hydride and one acidic N−H of the boronium.

At this point two diverging routes were evaluated: (a) fragment separation leading to **3a** and the stabilized borenium cation and (b) metal hydride protonation[20] to yield $[Pt(H_2)(I^tBu')(I^tBu)]^+$, $H_2B{=}NH_2$ and the base (and eventually H_2 and regeneration of **1a**). While both processes are faster than B−H splitting (Figure 1), which remains rate limiting, fragment separation (a) is kinetically and thermodynamically favored in THF for **3a·A** ($\Delta G_{THF} = -1.3$ $kcal{\cdot}mol^{-1}$ for fragment separation vs 2.5 $kcal{\cdot}mol^{-1}$ for metal hydride protonation; see Figure S21 for the kinetic preference). This agrees with the observation of **3a** and boronium **A** during catalysis. Conversely hydride protonation (b), which accounts for catalytic ammoniaborane dehydrogenation is thermodynamically preferred in the OMe_2-stabilized system (ΔG_{THF} = −3.7 $kcal{\cdot}mol^{-1}$ for fragment separation vs −15.1 $kcal{\cdot}mol^{-1}$ for metal hydride protonation). The overall reaction from $\mathbf{2_C}$ to $[Pt(H_2)(I^tBu')(I^tBu)]^+$ and $H_2B{=}NH_2$ is predicted to be slightly endergonic (ΔG_{THF} = 3.7 $kcal{\cdot}mol^{-1}$), and H_2 substitution by a molecule of AB turns the catalytic cycle over.

In fact, when an isolated sample of the platinum hydride **3a** was reacted with the boronium cation $[(NHMe_2)_2BH_2][BAr^F]$ in a 1:1 ratio (see Supporting Information), a very slow dehydrogenation reaction does take place leading to the formation of insoluble materials of unknown composition, but, most importantly, formation of $H_2B{=}NMe_2$ was *not* observed. Conversely, the boronium cation $[(NMe_2H)(THF)BH_2][B(C_6F_5)_4]$ (see Supporting Information), **B·THF**, bearing a quite acidic N−H proton and a better leaving group (THF), reacts rapidly with complex **3a** in THF at 0 °C generating H_2, the amino-borane $H_2B{=}NMe_2$ and the cationic Pt(II) complex **1a** (Scheme 4), which evolves to the cationic Pt(II) hydride derivative **4a**. This process is reminiscent to that proposed for the hydrolysis and alcoholysis of silanes by electrophilic transition metal complexes, in which silylium cations are believed to be key intermediates.[16c,d]

The borenium cation $[HMe_2N{\cdot}BH_2]^+$ (**B**), stabilized by coordination of a THF molecule (**B·THF**), should be present at some point during the catalytic cycle, but its fast reactivity toward the platinum hydride **3a** precludes its observation via NMR in the course of the reaction. It is reasonable to assume that in THF solution the boronium cation $[(NHMe_2)_2BH_2]^+$ (**A**) is in equilibrium with the boronium ion $[(NHMe_2)(THF)BH_2]^+$ (**B·THF**). This equilibrium must be shifted to the left to be consistent with the observation of the boronium cation and the platinum hydride **3a** by NMR. Protonation of the hydride ligand in **3a** by the acidic NH of the boronium cation $[(NMe_2H)(THF)BH_2]^+$ yields back the cationic complex **1a**, that in the presence of more DMAB and the liberated $NHMe_2$ rapidly regenerates complex **3a** and the boronium cation **A** closing the catalytic cycle (Scheme 5). Interestingly, in a very recent paper by Weller et al., the formation of the boronium cation $[(NHMe_2)_2BH_2][Cl]$ along with the iridium complex $[IrH_2(\eta^2\text{-}H_2BH_2)(PCy_3)_2]$ has also been observed in the reaction of $[IrH_2Cl(PCy_3)_2]$ with DMAB, inducing in this case a deactivation of the catalyst.[21]

Scheme 5. Proposed Catalytic Cycle



An alternative mechanistic pathway involving direct activation of the NH or the BH moieties of DMAB by hydride complex **3a**, followed by β-hydride elimination, might be envisioned.[21] However, although derivative **3a** does dehydrogenate DMAB, the rate of this process is considerably slower than that observed with catalyst **1a** under identical reaction conditions, requiring nearly 90 min to achieve ca. 45% of conversion into amino-borane (see Supporting Information). This alternative mechanism is not kinetically competent.

In summary, the highly electrophilic Pt(II) complex **1a** dehydrogenates DMAB through a mechanism somehow related to that suggested for Frustrated Lewis Pairs[8b] that involves hydrogen transfer from the BH_3 fragment to the platinum center, assisted by $NHMe_2$, leading to a neutral Pt(II) hydride that is protonated by the acidic NH of the boronium cation $[(HMe_2N)(THF)BH_2]^+$ releasing amino-borane $H_2B{\cdot}NMe_2$, H_2 and regenerating complex **1a**. In our opinion, this mechanism might be operative in other catalytic systems where high oxidation states are not readily accessible or in systems where the coligands are mere spectators.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) Dissociation of DMAB should also lead to the release of BH_3. In fact we have observed some degradation of the catalyst leading to the very few amounts of the carbene adduct $I^tBu \cdot BH_3$ and some unidentified Pt species. This degradation was further confirmed by an independent experiment between complex **1a** and THF·BH_3. To exclude catalysis being produced by platinum colloids or nanoparticles, test experiments were performed in the presence of mercury without noticing a diminishing in the catalytic activity.

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(17) Calculations were carried out at the M06/6-31g(d,p)/SDD level, using the Gaussian 09 program. Calculated intermediates that do not match experimental species are indicated with the subscript C. The data reported in the text correspond to potential energy variations in THF (single point calculations with the SMD continuum model from structures freely optimized in the gas phase, unless otherwise stated). Free energy variation in solution were calculated according to the expression $\Delta G_{\mathrm{THF}} = \Delta E_{\mathrm{THF}} + (\Delta G_{\mathrm{gas}} - \Delta E_{\mathrm{gas}})$. Further computational details and the full reference for the Gaussian 09 program can be found in the Supporting Information.

(18) Interestingly the transition state can be described as a fleeting adduct between **3a** and one borenium cation linked by a dihydrogen bond, but no minimum was located for the metal hydride.

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