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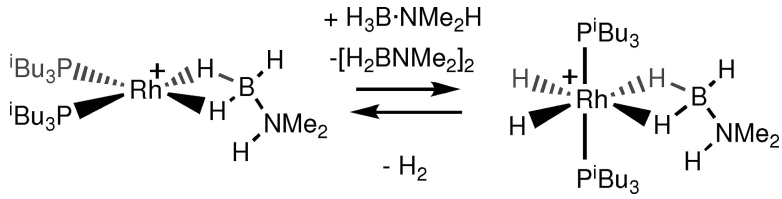

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Amine-Borane σ-Complexes of Rhodium. Relevance to the Catalytic Dehydrogenation of Amine-Boranes

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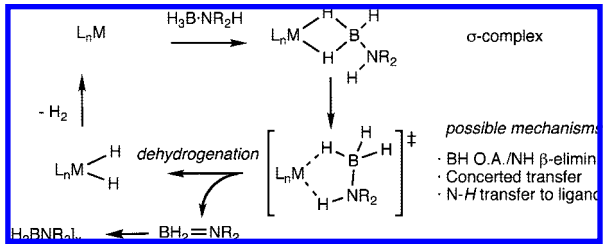
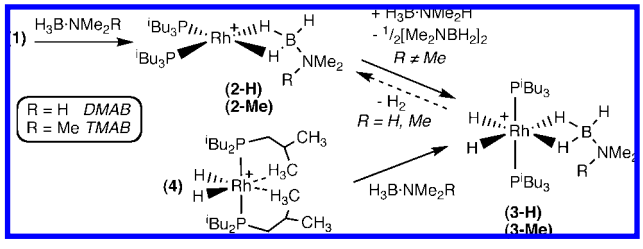
Chemical hydrogen storage in amine-boranes (e.g., $H_3B{\cdot}NH_3$, 19.6 wt% H) is a possible solution to the transport of hydrogen for future energy requirements due to their high hydrogen content.[1] Although solution and solid-state dehydrogenations have been reported, there is much interest in transition-metal-catalyzed dehydrogenation or hydrolytic[2] reactions due to favorable kinetics and lower reaction temperatures. Catalysts for dehydrogenation include Cp_2Ti derivatives,[3,4] Re-nitrosyls,[5] Ir-pincer complexes,[6,7] and Ni-NHC complexes;[8] colloidal-Rh has also been shown to be an active catalyst,[9,10] for which in situ EXAFS suggests that the active species might actually be smaller Rh_4 and Rh_6 "clusters".[11]

Scheme 1. Amine−Borane Dehydrogenation



Scheme 1 illustrates the accepted reaction course for homogeneous systems. Computational studies indicate a number of mechanistic scenarios for the dehydrogenation step: NH proton transfer to a coordinated ligand followed by transfer to the metal (Ni-NHC),[12] intermolecular stepwise transfer of NH then BH (Cp_2Ti-derivatives),[13] and concerted NH/BH activation at the metal center (Ir-pincer complexes).[14] Oxidative addition of the BH bond followed by NH β-elimination has also been suggested.[8] All routes implicate σ-complexes of amine-borane in the reaction, and while details of intermediate species remain scarce,[4,7] materials that represent catalyst deactivation products have been isolated.[4,6,7] We report here η^2-amine-borane σ-complexes of rhodium that are models for such intermediate complexes, and also catalysts for the dehydrogenation of $H_3B{\cdot}NHMe_2$ (DMAB), a close analogue of $H_3B{\cdot}NH_3$. Borane σ-complexes have been reported previously[15] as have σ-amine-borane complexes,[16] but as far as we are aware, there is only a brief report of such species' involvement in catalytic dehydrogenation.[17] No examples involving Rh have been reported.

Scheme 2. Synthesis of New Amine−Borane σ-Complexes



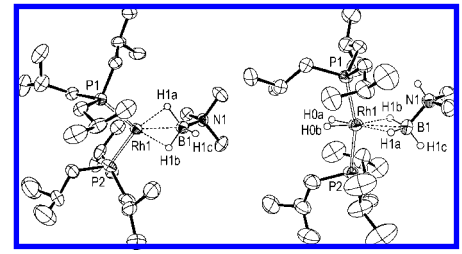


Figure 1. Cationic portion of **2-Me** (left) and **3-H** (right). Selected distances (Å) and angles (deg): **(2-Me)**: Rh1−B1, 2.180(4); P1−Rh1−P2, 97.35(4). **(3-H)**: Rh1−B1, 2.318(8); P1−Rh1−P2, 163.65(7).

Addition of DMAB (2 equiv) to $[Rh(P^tBu_3)_2][BAr^F_4]$ **1**[18] (Ar^F_4 = 3,5-$C_6H_3(CF_3)_2$) in 1,2-difluorobenzene results in the immediate formation of a purple Rh(I) species $[Rh(P^tBu_3)_2(\eta^2\text{-}H_3B{\cdot}NHMe_2)][BAr^F_4]$ **2-H**. **2-H** is short-lived ($t_{1/2}$ ~1 min) and evolves to give yellow Rh(III) $[Rh(H)_2(P^tBu_3)_2(\eta^2\text{-}H_3B{\cdot}NHMe_2)][BAr^F_4]$ **3-H** and the cyclic dimer $[BH_2NMe_2]_2$.[10] Addition of smaller amounts of DMAB to **1** resulted in the formation of mixtures of **2-H**, **3H**, and **1** in varying proportions, meaning that **2-H** could not be isolated free of **3-H**. **2-H** was longer-lived under these conditions allowing for its full characterization. Both complexes have been characterized by NMR spectroscopy, ESI-MS/MS, and, for **3-H**, also in the solid state (Figure 1).

^{1}H NMR spectra show the coordinated borane group as a broad 3H signal, relative to ^{t}Bu and NH groups, at δ −2.13 (**2-H**) and δ −0.77 (**3-H**), which sharpen on ^{11}B decoupling. This suggests rapid exchange of terminal and bound hydrides. Cooling **3-H** to 190 K arrests this process (δ −3.15, 2H, Rh−H−B). **2-H** was not stable in suitable low-temperature solvents (CD_2Cl_2). The two hydrido ligands in **3-H** are observed as a 2H dt, δ −17.42 [J(PH) 20, J(RhH) 17], while the NH signals appear at δ 4.67 (**2-H**) and δ 3.87 (**3-H**). ^{31}P{^{1}H} NMR spectra indicate a Rh(I) species **2-H** δ 35.9 [J(RhP) 174] and a Rh(III) species **3-H** δ 22.3 [J(RhP) 105]. ^{11}B{^{1}H} NMR spectroscopy shows broad signals at δ 19.3 (**2-H**) and δ 2.23 (**3-H**), shifted significantly downfield from DMAB (δ −13.4). The solid-state structure of **3-H** shows a pseudo-octahedral Rh(III) center with *trans* phosphines, *cis* hydrides, and an η^2-$H_3B{\cdot}NMe_2H$ ligand [Rh1−B1 2.318(8) Å] (Figure 1). NMR data and structural metrics indicate a Rh(III) center ligated with a σ-borane rather than an alternative Rh(V) tetrahydridoboryl structure;[19] a bond-indices analysis on calculated structures confirms this (see SI). **3-H** probably forms *via* dehydrogenation of the bound DMAB in **2-H** to give $[Rh(H)_2(P^tBu_3)_2][BAr^F_4]$ **4**,[18] which combines with a further equivalent of DMAB. Consistent with this, **3-H** can be formed by addition of DMAB to **4**. **3-H** slowly loses H_2 under vacuum to reform (unstable) **2-H**, establishing a plausible dehydrogenation cycle for DMAB mediated by **1**.

As complex **2-H** is short-lived and undergoes dehydrogenation to give **3-H** by NH/BH scission, blocking this route should afford

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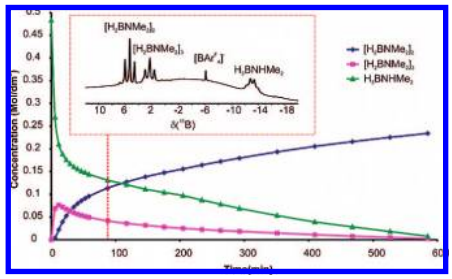

Figure 2. DMAB dehydrogenation by **1** (5 mol%, $C_6H_4F_2$) in a sealed NMR tube. Inset: ^{11}B NMR spectrum after 90 min.

a stable complex. This is the case, with $H_3B{\cdot}NMe_3$ (TMAB) affording a stable (under Ar) analogue **2-Me**. The resulting complex **2-Me** has a solid-state structure that shows a coordinated TMAB ligand with a pseudo square-planar Rh(I) center (Figure 1) and is structurally similar to related hydridoborate complexes of Rh(I).[20] **3-Me** can be prepared by adding H_2 to **2-Me** or addition of TMAB to **4**. Spectroscopic and ESI-MS/MS data are in full accord with these structures and are also similar to **2-H/3-H** underscoring their own structural assignment. Interestingly **3-Me** loses H_2 much more rapidly than **3-H** (simply by flushing with Ar), and we speculate that this is a steric effect arising from the additional *N*-methyl group, forcing the Rh center to adopt a less crowded Rh(I) square-plane configuration.

Complexes **1**, **4**, and **3-H** are active catalysts for the dehydrogenation of DMAB. In an open system under Ar a modest[4,7,8] overall turnover frequency (34 h^{-1}, 298 K, 5 mol%, 100% conversion) is achieved to ultimately afford the cyclic dimer $[H_2BNMe_2]_2$ {$\delta(^{11}B)$ 5.4 [t, *J*(BH) 113]}.[10] Repeating this reaction in a sealed NMR tube resulted in a lower TOF (2 h^{-1}) indicating inhibition by H_2 released during catalysis. Under these attenuated conditions a time/concentration plot (Figure 2) showed no evidence of sigmoidal kinetics. Addition of Hg did not inhibit catalysis. Both observations suggest nanoparticle formation is not occurring in catalysis.[9] A species that shows characteristic intermediate time/concentration dependence is also observed by ^{11}B NMR spectroscopy in both the open and closed systems, δ 2.4 [t, *J*(BH) 112], tentatively identified as $[H_2BNMe_2]_3$. This species has also been identified during the dehydrogenation of DMAB by "Cp_2Ti".[3] A small amount of $H_2B{=}NMe_2$, δ 38 [d, *J*(BH) 123], following a similar concentration/time profile, was also observed.[11]

Monitoring the "closed" system during catalysis by NMR spectroscopy identified a number of metal containing species, including **3-H** (*ca.* 20%). Other species currently elude definitive identification. At the end of catalysis only two compounds are observed in a *ca.* 1:1 ratio: **3-H** and another that is currently only partially characterized. $^{31}P\{^1H\}$ NMR spectroscopy suggests a Rh(III) center, while ^1H NMR data indicate 2 Rh−H, 2 Rh−H−B groups and no NH. These data fit an empirical formula $[Rh(H)_2(P^tBu_3)_2(\eta^2\text{-}H_2B{=}NMe_2)]^+$.[15] In support of this assignment, addition of $H_2B{=}NCy_2$ to **4** results in a complex with similar NMR spectroscopic characteristics (see Supporting Information). We discount assignment as a $[H_2BNMe_2]_2$ adduct, as addition of this fragment[10] to **4** is followed by immediate H_2 loss and the isolation of a different complex in quantitative yield: $[Rh(P^tBu_3)_2\{\eta^2\text{-}(H_2BNMe_2)_2\}][BAr^F{}_4]$ **5** (Figure 3), a σ-complex of a cyclic aminoborane. Addition of excess DMAB to **5** or the postcatalysis mixture gives **3-H** and the resumption of catalysis. Addition of H_2 (1 atm) to **5** gives a mixture of **5**, **4**, and $[H_2BNMe_2]_2$.

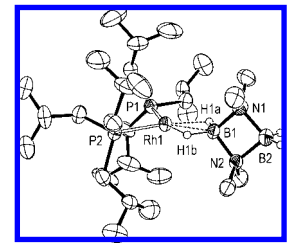

Figure 3. Cationic portion of **5** from asymmetric cell. Selected distance (Å) and angle (deg): Rh1−B1, 2.161(6); P1−Rh1−P2, 98.31(6).

In conclusion we have isolated Rh(I) and Rh(III) σ-amine-borane complexes of $H_3B{\cdot}NMe_2R$, and although the details of the dehydrogenation mechanism currently remain unresolved, these complexes provide useful insight into the likely intermediates. Given the isoelectronic relationship between alkane and amine-boranes, complexes **2** and **3** are also analogues of σ-alkane complexes of late-transition metals.[16] **5** is thus an analogue of a transition metal bound to a cyclic alkane, complexes that have previously been observed in solution at low temperatures by NMR spectroscopy or by time-resolved IR spectroscopy.[21]

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Supporting Information Available: Full experimental details, kinetic and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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