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Homogeneous Catalytic Dehydrogenation/Dehydrocoupling of Amine-Borane Adducts by the Rh(I) Wilkinson's Complex Analogue $RhCl(PHCy_2)_3$ (Cy = cyclohexyl)

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The Rh(I) complex $RhCl(PHCy_2)_3$ (**1**) (Cy = cyclohexyl, C_6H_{11}) has been investigated as a catalyst for the dehydrogenation/dehydrocoupling of dimethylamine-borane adduct $Me_2NH \cdot BH_3$ (**3**) at 20 °C to afford the cyclic dimer $[Me_2N-BH_2]_2$ (**4**). Unlike previously studied neutral and cationic Rh(I) precatalysts such as $[\{Rh(\mu\text{-}Cl)(1,5\text{-cod})\}_2]$ and $[Rh(1,5\text{-cod})_2]OTf$ (1,5-cod = 1,5-cyclooctadiene, C_8H_{12}, OTf = OSO_2CF_3) with weakly electron-donating ligands at the metal center, which are reduced to catalytically active Rh(0) species, catalytic dehydrogenation of **3** using **1** was found to occur in a homogeneous manner according to nanofiltration experiments, Hg(0) poisoning and kinetic studies. Moreover, the presence of the sterically bulky ligand $PHCy_2$ in complex **1** has been found to significantly increase the rate of reaction previously reported for Wilkinson's catalyst $RhCl(PPh_3)_3$. The catalytic activity of **1** toward a range of other amine-borane adducts $RR'NH \cdot BH_3$ (e.g., RR′ = $^i Pr_2$, MeBz, MeH) at 20 °C was also investigated. The third row transition metal analogue of **1**, the Ir(I) complex $IrCl(PHCy_2)_3$ (**2**), was also explored as a catalyst for the dehydrocoupling of **3** and was found to exhibit much reduced catalytic activity compared to **1** but proved significantly more active for sterically encumbered substrates. Addition of the strong Lewis acid $B(C_6F_5)_3$ as a co-catalyst to both **1** and **2** has been found to significantly increase the rate of the dehydrocoupling reactions in all cases. The Rh(I) complex **1** (but not the Ir(I) analogue **2**) was also found to be active for the catalytic dehydrocoupling of the phosphine-borane adduct $Ph_2PH \cdot BH_3$ (**14**) at 60−90 °C to afford linear dimer $Ph_2PH-BH_2-PPh_2-BH_3$ (**15**).

Introduction

The use of transition metal catalysts to effect organic transformations is a thoroughly developed and important area of research; however, the development of catalytic processes for inorganic substrates is still in its relative infancy. Catalytic dehydrogenation/dehydrocoupling of main group species with E−H (E = B, N, P, Si etc) bonds is a promising process and has attracted recent attention as a route to new molecules and materials.[1−7] For example, a variety of rings, chains, and high molecular weight polymers based on Group 13-Group 15 skeletons have been accessed via the catalytic dehydrocoupling of amine-borane and phosphine-borane adducts.[8−10] Furthermore, with the current interest in amine-borane adducts, such as $NH_3 \cdot BH_3$ (**11**),[11−17] and phosphine-borane adducts[18] as hydrogen-storage and hydrogen-transfer materials,[19,20] this area has attracted intense recent attention, and many new catalysts based on other metals have been

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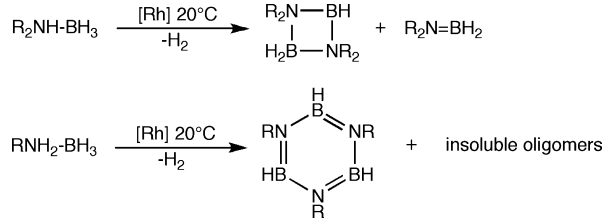
reported.[14,15,21−23] For example, Heinekey, Goldberg et al. identified an Ir-pincer complex which efficiently dehydrocouples **11** in a homogeneous manner and is also active for primary amine-borane adducts such as $MeNH_2 \cdot BH_3$ at room temperature.[10,15,24] In addition, Chirik et al. recently described a highly efficient Group 4 complex with N_2 ligands, $[((\eta^5\text{-}1,2\text{-}(SiMe_3)_2\text{-}C_5H_3)_2Ti)_2N_2]$ for the catalytic dehydrocoupling of $Me_2NH \cdot BH_3$ (**3**), and a mechanism involving initial B−H oxidative addition was proposed.[14] Several other systems have been calculated computationally providing useful insight into possible mechanisms.[25,26] Although many catalysts are now available for the dehydrocoupling of Group 13−15 Lewis acid−base adducts, most are relatively substrate specific, and many exhibit only moderate tunability and activity.

Scheme 1. General Scheme for the Dehydrocoupling of Primary and Secondary Amine-Borane Adducts



We have previously reported the catalytic dehydrocoupling of amine-borane adducts by neutral and cationic Rh(I) complexes with relatively weak electron-donating ligands, such as $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ and $[Rh(1,5\text{-}cod)_2]OTf$ (Scheme 1).[9] In each case, addition of the yellow Rh(I) precatalyst to the substrate solution was found to result in the formation of a black reaction mixture after an induction period. We have provided evidence that this process is associated with the reduction of Rh(I) to form Rh(0) nanoclusters and colloids. The dehydrocoupling of **3** using the precatalyst $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ has been studied in particular detail. Reduced catalytic activity was observed upon filtration through nanoporous filters, treatment with Hg(0), and ligation by substoichiometric amounts of phosphines, which all provided support for a heterogeneous mechanism.[27−29]

The presence of more strongly electron donating ligands at the Rh(I) center in the precatalyst, such as phosphines, would be expected to hinder the reduction process and might therefore provide access to active homogeneous catalysts.[30] However, we have previously found that Wilkinson's catalyst $RhCl(PPh_3)_3$ shows relatively poor activity for the dehydrocoupling of amine-borane adducts, with complete conversion of **3** to **4** requiring about 2 days at 25 °C (with 0.5 mol % precatalyst in toluene).[9] The probable need for ligand loss at the metal center for efficient catalysis led us to explore the use of the more sterically demanding ligand $PHCy_2$ in place of PPh_3. In the paper, we report an investigation of the use of the secondary phosphine analogue of Wilkinson's catalyst, $RhCl(PHCy_2)_3$ (**1**), as a precatalyst for the dehydrocoupling of amine-borane adducts.[31]

Results and Discussion

Synthesis and Characterization of the Wilkinson's Catalyst Analogue, $RhCl(PHCy_2)_3$ (1). The Rh(I) complex $RhCl(PHCy_2)_3$ was prepared as a bright yellow powder by treatment of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ with excess $PHCy_2$ according to the literature method (Scheme 2).[32] Previous characterization was limited to ^1H NMR spectroscopy and elemental analysis. We used ^{31}P NMR spectroscopy to provide additional data. The ^1H-coupled ^{31}P NMR spectrum of **1** exhibited two signals: a doublet of doublets of triplets at $\delta = 50$ and a multiplet (overlapped doublet of doublet of doublets) at $\delta = 33$. This indicated the presence of two different phosphorus environments, corresponding to phosphine ligands *cis* and *trans* to chloride. The signal at $\delta = 50$ split into a doublet due to P−H coupling ($^1J_{P-H} = 300$ Hz), a second doublet by coupling to Rh ($^1J_{P-Rh} = 172$ Hz), and a triplet by coupling to two equivalent phosphorus centers ($^2J_{P-P} = 42$ Hz), and on this basis was assigned to the $PHCy_2$ ligand *trans* to chloride. By similar reasoning the multiplet at $\delta = 33$ that consisted of a doublet ($^1J_{P-H}$ was not resolved due to the second order spectrum), a doublet

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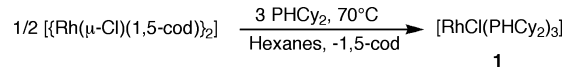
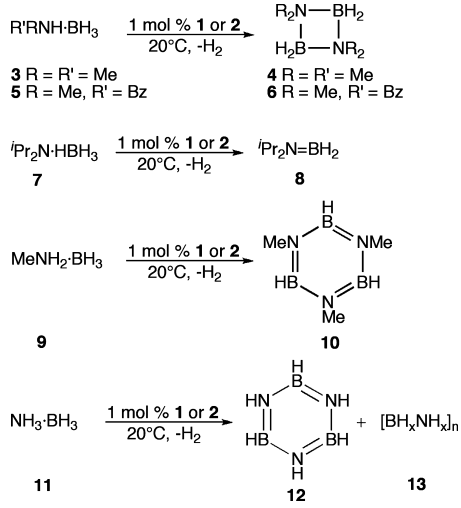
by coupling to Rh ($^1J_{P-Rh}$ = 125 Hz), and a doublet by coupling to another phosphorus center ($^2J_{P-P}$ = 41 Hz), and on this basis is assigned to the two $PHCy_2$ ligands *cis* to chloride (Supporting Information, Figure S-1 and S-2).

Scheme 2. Synthesis of **1**



Catalytic Dehydrocoupling Studies with 1. To investigate the activity of **1** toward secondary amine-borane adducts, a catalytic amount (1 mol %) was added to a toluene solution of **3** and the reaction was monitored by ^{11}B NMR spectroscopy. This showed 65% conversion of **3** to **4** ($^B\delta$ = 4.75, $^1J_{B-H}$ = 110 Hz) in 10 h, with 100% conversion noted after 19 h (Scheme 3). In contrast to the reactions catalyzed by the Rh(I) complexes [{Rh(μ-Cl)(1,5-cod)}$_2$] and [Rh(1,5-cod)$_2$]OTf which turn black because of reduction to Rh(0) species, the reaction mixture remained clear bright yellow. This suggested that the catalysis using **1** might be homogeneous. To determine whether the reaction was homogeneous or heterogeneous further detailed studies were performed.

Scheme 3. Dehydrocoupling Reactions of Primary and Secondary Amine-Borane Adducts Investigated



To convincingly distinguish between a homogeneous and a heterogeneous catalytic process it is important to investigate a reaction using a range of methods. Finke and co-workers have recently reviewed the most significant of these techniques.[33] Of these nanofiltration, Hg(0) poisoning, ligation studies, and kinetic analysis can provide particularly useful insight. Thus, strong evidence for a heterogeneous reaction is provided if the rate of reaction is reduced by (i) filtration through nanoporous media by removing insoluble catalytic material, (ii) Hg(0) poisoning through the formation of an amalgam or coating on the catalyst surface, and (iii) ligation by <1 equiv. of a donor ligand by blocking of active sites on the catalyst surface. The presence of an induction period can also provide evidence for the formation of a heterogeneous catalyst by reduction of the precatalyst. In the absence of stabilizing ligation, subsequent agglomeration of catalyst particles via Ostwald ripening leads to a decrease in the reaction rate. Combined with an induction period, an overall sigmoidal kinetic profile results, and this is also characteristic of a heterogeneous catalytic process. If the reaction rate is not affected by any of the aforementioned techniques, and no induction period or sigmoidal kinetic profile is observed, a homogeneous mechanism is indicated.

We used most of these methods to explore the nature of the catalytic dehydrocoupling of **3** by precatalyst **1** (1 mol %, 20 °C).[34] Filtration of the reaction mixture at about 40% conversion of **3** through a small pore (e.g. 200 nm) membrane led to no change in color, and analysis by ^{11}B NMR spectroscopy showed no suppression of the catalytic activity (Figure 1). Furthermore, addition of an excess of mercury (70 equiv.) to the reaction mixture derived from **1** and **3** after about 20% conversion of the latter also led to no significant reduction in the catalytic activity (Figure 2). Both results strongly suggest the presence of a homogeneous catalyst.

In the kinetic profiles in Figures 1 and 2 no induction period was detected before dehydrocoupling commenced. In a typical heterogeneous reaction, for example that of **3** with [{Rh(μ-Cl)(1,5-cod)}$_2$], a sigmoidal plot of reaction progress versus time is observed. Here, the induction period represents the reduction of Rh(I) to colloidal Rh(0), and the lowering in catalytic activity at higher conversion arises from nanoparticle aggregation and a consequential reduction in active surface area.[27] The lack of an induction period and nonsigmoidal kinetic profile further supports the conclusion that the catalytic dehydrocoupling of **3** using **1** as a precatalyst is predominantly homogeneous in nature.

To further probe the catalytic activity of **1**, a range of other amine-borane adducts were also investigated as substrates (Scheme 3, Table 1). We have previously reported the effect of the relative steric bulk of ligands at nitrogen on the rate of reaction with [{Rh(μ-Cl)(1,5-cod)}$_2$] as a precatalyst.[9] In common with these previous results, the rate of catalytic dehydrocoupling of $^iPr_2NH\cdot BH_3$ (**7**) was significantly reduced relative to that for **3**, with no conversion to $^iPr_2N{=}BH_2$ (**8**) after 10 h. Similar treatment of $MeBzNH\cdot BH_3$ (**5**) (Bz = $CH_2C_6H_5$) also led to no conversion after 10 h. Catalyst **1** showed relatively high activity toward the primary amine-borane adduct $MeNH_2\cdot BH_3$ (**9**), with 100% conversion to the borazine $[MeN{-}BH]_3$ (**10**) after 10 h.

Intense recent interest in the development of a suitable portable source of hydrogen has highlighted **11** as a potential candidate because of its high weight percent content (19 %) of hydrogen.[13] We therefore investigated the activity of **1** toward **11** as a substrate. Addition of a catalytic (1 mol %) amount of **1** to a diglyme solution of **11** at 45 °C resulted in the formation of a light yellow solution. However, after 10 h negligible conversion of **11** had occurred.

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(34) We did not perform ligation experiments involving the addition of phosphine as our subsequent studies suggest that the degree of phosphine dissociation from **1** to form an active catalyst is low. Thus small amounts of additional phosphine might therefore lead to significant rate decrease by affecting the dissociation equilibrium rather than heterogeneous catalyst poisoning confusing the interpretation of the results.

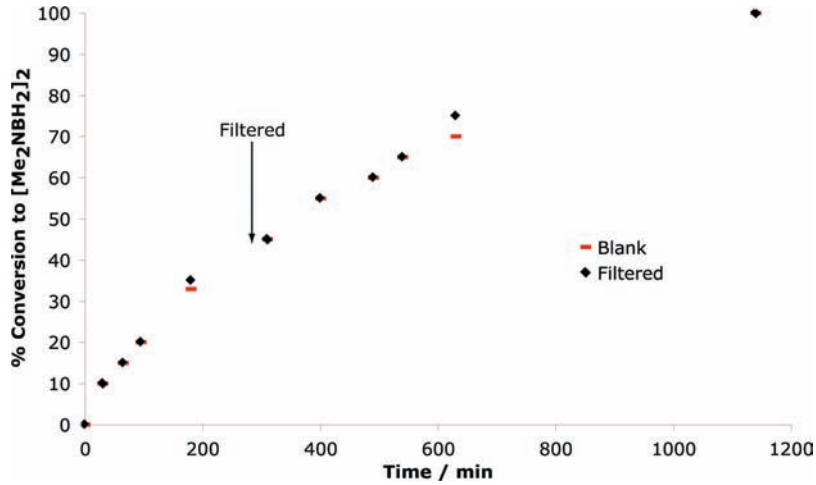


Figure 1. Graph showing blank (unfiltered) and filtered (through a 0.2 μm PTFE membrane after 320 min) dehydrocoupling reactions of **3** catalyzed by 1 mol % **1** (in toluene).

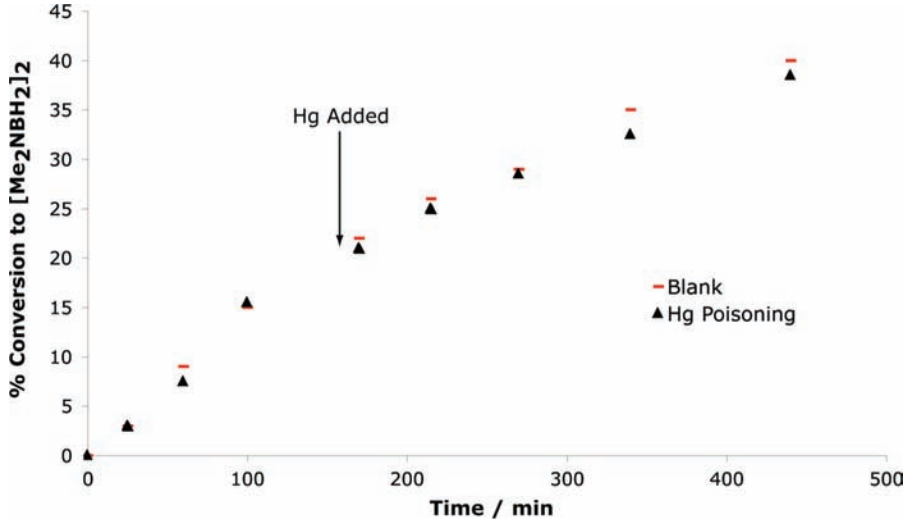


Figure 2. Graph showing blank and Hg poisoned (70 equiv added after 180 min) dehydrocoupling reactions of **3** catalyzed by 1 mol % **1** (in toluene).

Table 1. Catalytic Dehydrocoupling Data for Various Group 13/15 Adducts with Rh(I) Complex **1** and Ir(I) Complex **2**

substrate	*T*/ °C	mol % catalyst	% conversion by **1**[d]	% conversion by **2**[d]	product
$Me_2NH{\cdot}BH_3$ (**3**)[a]	20	1	65	0	**4**
$Me_2NH{\cdot}BH_3$ (**3**)[a]	20	1 + $B(C_6F_5)_3$	100	20	**4**
$^iPr_2NH{\cdot}BH_3$ (**7**)[a]	20	1	0	5	**8**
$^iPr_2NH{\cdot}BH_3$ (**7**)[a]	20	1 + $B(C_6F_5)_3$	20	15	**8**
$MeBzNH{\cdot}BH_3$ (**5**)[a]	20	1	0	20	**6**
$MeBzNH{\cdot}BH_3$ (**5**)[a]	20	1 + $B(C_6F_5)_3$	10	45	**6**
$MeNH_2{\cdot}BH_3$ (**9**)[a]	20	1	100[e]	25	**10**
$MeNH_2{\cdot}BH_3$ (**9**)[a]	20	1 + $B(C_6F_5)_3$	100[e]	45	**10**
$NH_3{\cdot}BH_3$ (**11**)[b]	45	1	0	0	**12, 13**
$NH_3{\cdot}BH_3$ (**11**)[b]	45	1 + $B(C_6F_5)_3$	5	5	**12, 13**
$Ph_2PH{\cdot}BH_3$ (**14**)[c]	90	1	100	0	**15**
$Ph_2PH{\cdot}BH_3$ (**14**)[c]	60	1	80	0	**15**

[a] Reaction carried out in 2 mL toluene with 1 mmol adduct. [b] Reaction carried out in 2 mL diglyme with 1 mmol adduct. [c] Reaction carried out in the melt. [d] % conversion to products calculated by integration of products against starting material by ^{11}B NMR spectroscopy after 10 h at 20 °C. [e] Reaction complete in <10 h.

Catalytic Dehydrocoupling with $IrCl(PHCy_2)_3$ (2). To provide comparative data, we also studied the catalytic activity of the third row Ir(I) analogue of **1**. The synthesis

Scheme 4. Synthesis of **2**

$$1/2\ [\{Ir(\mu\text{-}Cl)(1,5\text{-}cod)\}_2] \xrightarrow[\text{Hexanes, -1,5-cod}]{\text{3 } PHCy_2,\ 70°C} [IrCl(PHCy_2)_3]$$

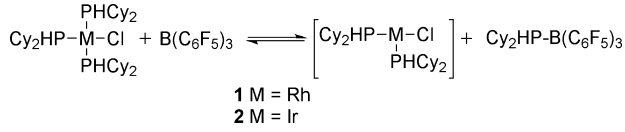
2

of $IrCl(PHCy_2)_3$ (**2**) was achieved in an analogous manner to that of **1**, with the product also isolated as a bright yellow powder (Scheme 4). Key characterization was provided by the ^1H coupled ^{31}P NMR spectrum, which exhibited two signals: a doublet of doublets at $\delta = 26.5$ and a doublet of triplets at $\delta = 19.7$. As in the case of **1**, this indicated the presence of two different phosphorus environments, corresponding to phosphines *cis* and *trans* to a chloride. The signal at $\delta = 26.5$ was split into a doublet by P−H coupling ($^1J_{P-H} = 218$ Hz), a second doublet by coupling to one inequivalent phosphorus nucleus ($^2J_{P-P} = 18$ Hz), and on this basis assigned to two $PHCy_2$ ligands *cis* to chloride. By similar reasoning, the signal at $\delta = 19.7$ was split into a doublet by P−H coupling ($^1J_{P-H} = 327$ Hz), and a triplet by coupling to two equivalent phosphorus centers ($^2J_{P-P} = 24$ Hz), was assigned to one $PHCy_2$ ligand *trans* to chloride (Supporting Information, Figure S-3 and S-4).

Addition of a catalytic amount (1 mol %) of the Ir-complex **2** to a solution of **3** in toluene resulted in the formation of a clear yellow solution. No significant conversion of **3** to **4** was observed after 10 h by ^{11}B NMR spectroscopy. Surprisingly, in contrast to the case of **1** as precatalyst, the use of the more sterically encumbered amine-borane adducts **5** and **7** led to conversion of 5% and 20% to **6** and **8**, respectively. The primary amine-borane adduct **9** was found to proceed to 25% conversion to **10** after the same time period under the same conditions as **2**, whereas no reaction of **11** was observed by ^{11}B NMR spectroscopy after 10 h.

Enhancement of the Catalytic Activity of 1 and 2 Using $B(C_6F_5)_3$ as a Co-catalyst. On the basis of the tentative but reasonable postulate that the catalytic dehydrocoupling mechanism with **1** initially proceeds in a manner similar to that of hydrogenation of alkenes, via the loss of a phosphine ligand and formation of a 14-electron Rh(I) species, we attempted to increase the rate of reaction by addition of a strong Lewis acid to aid dissociation of a Cy_2PH ligand (Scheme 5).[35]

Scheme 5. Proposed Action of $B(C_6F_5)_3$ on Tris-Phosphine Complexes



In a typical reaction, a toluene solution of $B(C_6F_5)_3$ and an equimolar amount of the desired precatalyst were stirred for 5 min prior to the addition of the amine-borane adduct in the same solvent. The reaction was then monitored periodically by ^{11}B NMR spectroscopy. Importantly a significant increase in the rate of reaction was observed for all amine-borane/catalyst combinations (Table 1). The most significant acceleration involved the use of precatalyst **1** with **3**, where addition of a catalytic amount (1 mol %) of $B(C_6F_5)_3$ resulted in 100% conversion to **4** in less than 10 h, compared to only 65% conversion in the absence of the borane. Over the course of the catalytic reactions, $Cy_2PH\cdot B(C_6F_5)_3$ was not detectable in solution. However, on addition of 1 equiv. of $B(C_6F_5)_3$ to **1**, $Cy_2PH\cdot B(C_6F_5)_3$ was formed, along with several unidentified species, according to ^{11}B and ^{31}P NMR spectroscopic analysis (Supporting Information, Figures S-5 and S-6).[36]

The slower rate of reaction observed in the absence of a co-catalyst suggests that a low percentage of the precatalyst is converted into the active species, whereas addition of a co-catalyst shifts this equilibrium in favor of the active species (Scheme 5). In an attempt to access improved catalytic activity without the need for a co-catalyst the *bis*-phosphine dimer, $[RhCl(PHCy_2)_2]_2$ was targeted; however, synthesis by a variety of methods failed.[37] A series of blank reactions were also performed, where $B(C_6F_5)_3$ alone was added to toluene solutions of **3**, **5**, **7**, **9** at 25 °C, or a diglyme solution of **11** at 45 °C, followed by stirring for 2 days. In all cases no evidence for a reaction was apparent by ^{11}B NMR spectroscopy, indicating that $B(C_6F_5)_3$ does not catalyze dehydrocoupling, in contrast to the case of phosphine-borane adducts[38] and **11** under different conditions (glyme and tetraglyme at 60 °C).[39]

Catalytic Dehydrocoupling of $Ph_2PH\cdot BH_3$. We also explored the catalytic dehydrocoupling activity of **1** and **2** toward the secondary phosphine-borane adduct $Ph_2PH\cdot BH_3$ (**14**). In contrast to the case of amine-borane adducts such as **3**, previous studies have indicated that the dehydrocoupling of **14** by Rh precatalysts such as $[\{Rh(\mu\text{-Cl})(1,5\text{-cod})\}_2]$ and $[Rh(1,5\text{-cod})_2]OTf$ are homogeneous processes.[27] The adduct **14** has been shown to form the linear dimer, $Ph_2PH-BH_2-Ph_2P-BH_3$ (**15**), at 90 °C or cyclic trimer and tetramer, $[Ph_2P-BH_2]_3$ (**16**) and $[Ph_2P-BH_2]_4$ (**17**) respectively, at 120 °C when catalyzed by $[\{Rh(\mu\text{-Cl})(1,5\text{-cod})\}_2]$ in the melt (Scheme 6).[8]

Addition of a catalytic amount of **1** (1 mol %) to solid **14** and heating in the melt at 90 °C resulted in complete conversion to **15** after 10 h by ^{11}B and ^{31}P NMR spectroscopy. By comparison, treatment of **14** with **2** resulted in no detectable reaction by ^{11}B NMR spectroscopy under the same conditions. To investigate the activity of **1** at a lower temperature, **14** was heated to 60 °C in the presence of a catalytic amount of **1** for 10 h. Analysis by ^{11}B and ^{31}P NMR spectroscopy showed resonances corresponding to **15** (80%) and starting material **14** (20%). Formation of a small amount (ca. 1%) of $Cy_2PH\cdot BH_3$ was also noted, when **1** and **2** were used as catalysts, which suggested that some dissociation of the phosphine-borane adduct **14** and subsequent combination of the borane with the more basic phosphine $PHCy_2$ dissociated from the precatalyst.

Conclusion

The Rh(I) complex $RhCl(PHCy_2)_3$ (**1**) has been found to catalyze the dehydrocoupling of amine-borane adduct **3** under ambient conditions. Moreover, unlike the cases of previously studied Rh(I) precatalysts with 1,5-cod ligands, the catalytic reaction of **1** with **3** has been shown to be *homogeneous* by a variety of methods. The third row transition metal analogue of **1**, $IrCl(PHCy_2)_3$ (**2**), showed significantly reduced catalytic dehydrocoupling activity toward **3** but was more active than **1** toward more sterically encumbered substrates. Addition of the strong Lewis-acid $B(C_6F_5)_3$ has been found to significantly increase the rate of the dehydrocoupling reactions catalyzed by **1** and **2**, presumably by acting as a phosphine abstraction reagent.

Complex **1** is a member of the extensive class of neutral Rh(I) complexes $[RhX(PR_3)_3]$ (X = halogen), and this

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(37) Synthesis of $[RhCl(PHCy_2)_2]_2$ was attempted in a manner similar to the method used for $[RhCl(PPh_3)_2]_2$, by refluxing in benzene or by addition of 4 equiv of $PHCy_2$ to $[\{RhCl(cod)\}_2]$. This resulted in no reaction in the former case, the formation of RhCl(cod)$(PHCy_2)$ and $RhCl(PHCy_2)_3$ in the latter. An attempted synthesis by the addition of 4 equiv of $PHCy_2$ to $[\{RhCl(coe)_2\}_2]$ or $[\{RhCl(CH_2CH_2)_2\}_2]$ also failed with partial conversion to $RhCl(PHCy_2)_3$ in both cases.
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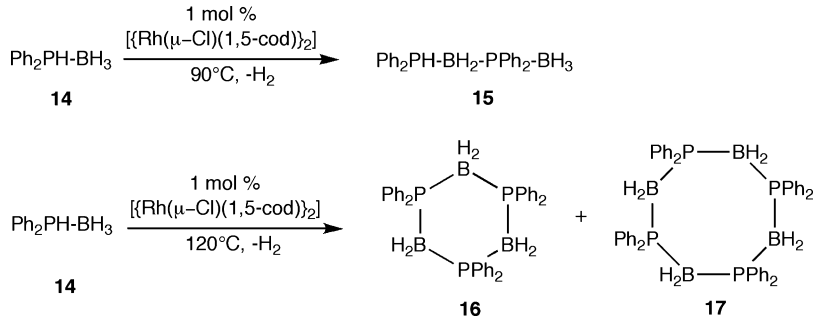
Scheme 6. Catalytic Dehydrocoupling of **14**



suggests that fruitful tuning of catalytic activity should be possible in the future by means of controlling ligand steric bulk and electronic character.[40] We are currently performing in-depth kinetic experiments and theoretical studies to provide detailed mechanistic information on the dehydrocoupling chemistry.

Experimental Section

General Procedures and Materials. All reactions and product manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a MBraun glovebox filled with dry argon. NMR spectra were collected on a Jeol Lambda 300 or Jeol ECP 300. Chemical shifts were referenced to solvent peaks or internal TMS (^{1}H, ^{13}C), external $BF_3 \cdot OEt_2$ (^{11}B) or H_3PO_4 (^{31}P). Toluene and hexanes were purified using a Grubbs solvent system. ^{i}PrOH and MeOH were degassed prior to use by three freeze−pump−thaw cycles. Mercury (99.9995%), [{Rh(μ-Cl)(1,5-cod)}$_2$], $MeNH_2$ and $NH_3 \cdot BH_3$ were purchased from Aldrich and used as received. $PHCy_2$, $RhCl_3 \cdot 3H_2O$ and [{Ir(μ-Cl)(1,5-cod)}$_2$] were purchased from Strem and used as received. Cyclooctene was purchased from Acros and used as received. Ethylene was purchased from BOC and used as received. $Me_2NH \cdot BH_3$ (Strem) was sublimed twice prior to use, $^i Pr_2NH$ (Aldrich) and BzMeNH (Aldrich) were distilled from CaH_2, $BH_3 \cdot THF$ (Acros) was distilled prior to use, and $B(C_6F_5)_3$ (Boulder Scientific) was dried with Me_3SiCl and sublimed prior to use. Filters (Millex-FG, 0.2 μm hydrophobic fluoropore PTFE) were purchased from Fischer. Ph_2PH,[41] $RhCl(PHCy_2)_3$,[32] $^i Pr_2NH \cdot BH_3$,[9] $BzMeNH \cdot BH_3$,[9] $MeNH_2 \cdot BH_3$,[9] $Ph_2PH \cdot BH_3$,[8] $[RhCl(coe)_2]_2$,[42] and $[RhCl(CH_2CH_2)_2]_2$[43] were synthesized by literature methods. All dehydrocoupling experiments were performed at lease twice to ensure reproducibility.

Synthesis of $RhCl(PHCy_2)_3$ (1).[32] To a solution of [{Rh(μ-Cl)-(1,5-cod)}$_2$] (0.246 g, 0.5 mmol) in hexanes (40 mL) $PHCy_2$ (0.793 g, 4.0 mmol) was added. The resulting suspension was stirred overnight at 70 °C, giving a yellow precipitate. The precipitate was collected, washed with hexanes (3 × 20 mL) and dried. Yield 0.55 g (75%). ^{1}H{^{31}P} NMR (300 MHz, C_6D_6, 20 °C) δ = 4.3−3.9 (m, 3H, 3 × PH), 2.8−1.1 (m, 66H, 3 × Cy); ^{31}P NMR (300 MHz, C_6D_6, 20 °C) δ = 50 (m (overlapped doublet of doublet of triplets), $^1J_{P-H}$ = 300 Hz, $^1J_{P-Rh}$ = 172 Hz, $^2J_{P-P}$ = 42 Hz, 1 × $PHCy_2$ *trans* to Cl), δ = 33 (m (overlapped doublet of doublet of doublets), $^1J_{P-H}$ was not resolved, $^1J_{P-Rh}$ = 125 Hz, $^2J_{P-P}$ = 41 Hz, 2 × $PHCy_2$ *cis* to Cl) (Supporting Information, Figure S-1 and S-2).

Synthesis of $IrCl(PHCy_2)_3$ (2). To a solution of [{Ir(μ-Cl)-(1,5-cod)}$_2$] (0.335 g, 0.5 mmol) in hexanes (40 mL) was added $PHCy_2$ (0.793 g, 4.0 mmol). The resulting suspension was stirred at 70 °C overnight giving a yellow precipitate. The precipitate was collected, washed with hexanes (3 × 20 mL), and dried. Yield 0.78 g (95%). ^{1}H{^{31}P} NMR (300 MHz, C_6D_6, 20 °C): δ = 4.5−3.5 (m, 3H, 3 × PH), 2.79−1.17 (m, 66H, 6 × Cy); ^{13}C NMR (300 MHz, C_6D_6, 20 °C): δ = 33.2−30.9 (m), 27.4−26.7 (m); ^{31}P NMR (300 MHz, C_6D_6, 20 °C): δ = 26.5 (dd, $^1J_{P-H}$ = 208 Hz, $^2J_{P-P}$ = 18.2 Hz, $PHCy_2$ *cis* to Cl), 19.7 (dt, $^1J_{P-H}$ = 327 Hz, $^2J_{P-P}$ = 24 Hz, $PHCy_2$ *trans* to Cl) (Supporting Information, Figure S-3 and S-4). EA calculated (%) for $IrClP_3C_{36}H_{69}$: C 52.57, H 8.46; found C 53.20, H 8.49.

General Procedure for the Catalytic Dehydrogenation of Amine-Borane Adducts. To a solution of amine-borane (1 mmol) in toluene (2 mL) was added catalyst (1 mol %). The toluene solution was stirred and an aliquot subsequently removed for analysis by ^{11}B NMR spectroscopy after 10 h (see Table 1). Product structures were assigned based on previous literature.[9]

General Procedure of the $B(C_6F_5)_3$ Co-catalyzed Dehydrogenation of Amine-Borane Adducts. A solution of catalyst (1 mol %) and $B(C_6F_5)_3$ (1 mol %) in toluene (1 mL) was stirred for 5 min. To this a solution of the desired amine-borane adduct (1 mmol) in toluene (1 mL) was added. The solution was stirred and an aliquot subsequently removed for analysis by ^{11}B NMR spectroscopy after 10 h (see Table 1). Product structures were assigned based on previous literature.[9]

General Procedure for $B(C_6F_5)_3$ Blank Reaction. In a typical reaction, a catalytic amount of $B(C_6F_5)_3$ was added to a toluene solution of the desired amine-borane adduct (**3**, **7**, **5**, or **9**) at 20 °C, or a diglyme solution of **11** at 45 °C, and the solution stirred for 2 days. An aliquot was then removed for analysis by ^{11}B NMR spectroscopy, and no reaction was observed in any case.

General Procedure for Filtration Reactions. To a solution of $Me_2NH \cdot BH_3$ (0.1 g, 1.7 mmol) in toluene (2 mL) was added **1** (11 mg, 0.015 mmol, 1 mol %) with vigorous stirring. The reaction was monitored by ^{11}B NMR spectroscopy at regular intervals until 40% conversion to products was achieved. The reaction was then filtered through a 0.2 μm filter into a new vial with a new stir bar and septum. Monitoring at regular intervals was continued by ^{11}B NMR spectroscopy. No change in the rate of reaction was observed, with the reaction going to completion in 19 h.

General Procedure for Hg Poisoning Reactions. A toluene solution of catalyst (1 mol %) and **3** was monitored by ^{11}B NMR spectroscopy, and after 20% conversion to **4**, Hg (70 equiv.) was added with vigorous stirring. ^{11}B NMR monitoring was continued, and the % conversion compared to a blank reaction. Important: Good stirring is known to be needed to ensure contact of the catalyst with Hg(0), a condition required to avoid false negatives in this experiment.[33]

Catalytic Dehydrocoupling of $NH_3 \cdot BH_3$(11). To a suspension of catalyst (0.014 mmol, 1 mol %) in diglyme (2 ml) **11** (0.043 g,

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1.4 mmol) was added and heated to 40 °C, resulting in complete dissolution. An aliquot was removed for analysis by ^{11}B NMR spectroscopy after 10 h (see Table 1). Product structures were assigned based on previous literature.[9]

$B(C_6F_5)_3$ Co-catalyzed Dehydrocoupling of NH_3BH_3(11). To a suspension of catalyst (0.014 mmol, 1 mol %) and $B(C_6F_5)_3$ (7.0 mg, 0.014 mmol, 1 mol %) in diglyme (2 ml) **11** (0.043 g, 1.4 mmol) was added and heated to 40 °C, resulting in complete dissolution. An aliquot was removed for analysis by ^{11}B NMR spectroscopy after 10 h (see Table 1). Product structures were assigned based on previous literature.[9]

Catalytic Dehydrocoupling of $Ph_2PH \cdot BH_3$. $Ph_2PH \cdot BH_3$ (0.2 g, 1.0 mmol) and the desired catalyst (1 mol %) were heated in the melt at 60 or 90 °C for 10 h. On cooling, the material was dissolved and analyzed by ^{11}B NMR spectroscopy (see Table 1). Product structures were assigned based on previous literature.[8]

Stoichiometric Reaction of 1 with $B(C_6F_5)_3$. To a solution of **1** (0.04 g, 0.055 mmol) in toluene (1 mL) was added $B(C_6F_5)_3$ (28 mg, 0.055 mmol), and the resulting mixture stirred for 12 h. Analysis was achieved by NMR. ^{11}B NMR (300 MHz, d_8-toluene) $\delta = -16.1$ ($J_{B-P} = 58$ Hz), lit. (96.29 MHz, C_6D_6, 20 °C) $\delta = -13.5$ ($J_{B-P} = 64$ Hz); ^{31}P (300 MHz, d_8-toluene) $\delta = 7.9$ ($J_{B-P} = 56$ Hz), lit. (121.5 MHz, C_6D_6, 20 °C) $\delta = 9.29$ ($J_{B-P} = 76$ Hz)[36] (Supporting Information, Figure S-5 and S-6).

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Supporting Information Available: Relevant ^{31}P and ^{11}B NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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