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# A Constrained Geometry Fluorenyl Amido Magnesium Catalyst for Amine-Borane Dehydrocoupling

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*Dedicated to Prof. Dr. Dr. h.c. Michael Veith on the occasion of his 80th birthday.*

A fluorenyl amido constrained geometry magnesium complex is described, which was obtained by deprotonation of the corresponding neutral ligand system with dibutyl magnesium. Its structure was determined by SC-XRD and it was shown to be a potent catalyst for amine-borane dehydrogenation/dehydrocoupling.

## Introduction

*ansa*-Metallocenes, complexes with two interlinked cyclopentadienyl moieties, have gained much attention for their application in catalysis and polymer synthesis.[1–3] Related half-sandwich complexes, in which one cyclopentadienyl ring is substituted by an amido moiety are commonly referred to as constrained geometry complexes (CGCs). Such complexes have been reported for a variety of transition metals and are–among other things–of interest as catalysts for olefin polymerization.[4–6] We had previously reported that related complexes of magnesium are accessible by deprotonation of the corresponding neutral ligand system by dibutyl magnesium and that these complexes are versatile catalysts for a variety of dehydrocoupling and hydroelementation reactions.[7]

It is well established in transition metal chemistry that the catalytic activity of cyclopentadienyl complexes can be substantially increased by replacing the cyclopentadienyl group by indenyl or fluorenyl, the benzannulated derivatives. This phenomenon is sometimes referred to as the indenyl effect,[8] and constrained geometry fluorenyl complexes of this sort have been reported for different transition metals (Figure 1).[9–12]

Herein, we report the synthesis and structural characterization of a fluorenyl constrained geometry magnesium complex and its application in amine-borane dehydrogenation/dehydrocoupling. This follows our ongoing interest in these compounds and complements previous work in which we explored different substitution patterns at the silicon atom, the nitrogen atom and the cyclopentadienyl ring.

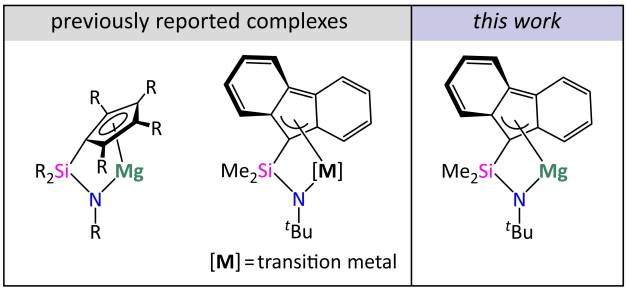
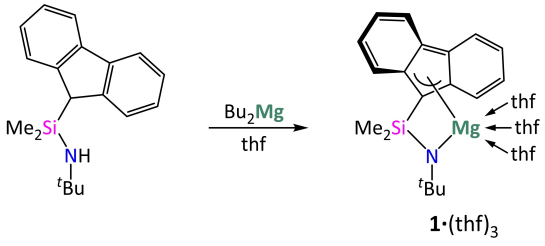



**Figure 1.** Selected examples of constrained geometry complexes.

## Results and Discussion

In analogy to the previously reported cyclopentadienyl constrained geometry magnesium complexes,[7] treatment of the protonated ligand with dibutyl magnesium yields **1**. Owned to the Lewis acidic nature of the magnesium center in these complexes, the product is obtained as a solvent adduct, if the reaction is performed in the presence of a donor solvent, such as thf or dme (Scheme 1).

Crystals of a tris(thf) complex, **1**·(thf)$_3$, and a bis(dme) complex, **1**·(dme)$_2$, suitable for single crystal XRD, could be obtained and allowed for structural characterization of these compounds (Figure 2 a and b). The most apparent characteristic




**Scheme 1.** Synthesis of constrained geometry magnesium complex **1**·(thf)$_3$.

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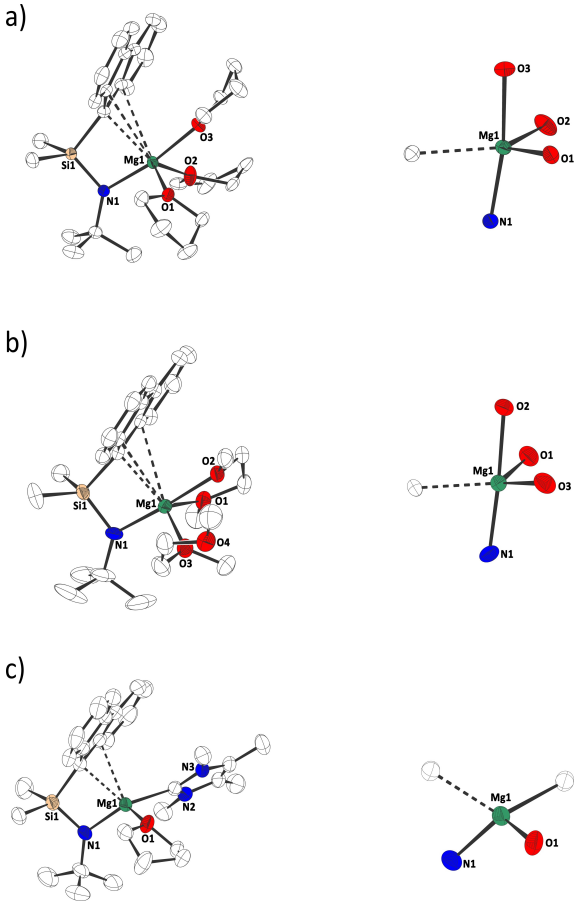


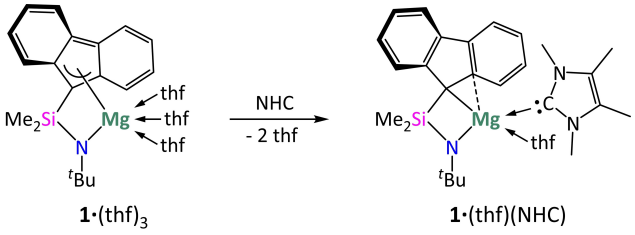

**Figure 2.** Molecular structures and coordination environment around magnesium of a) **1**·(thf)$_3$, b) **1**·(dme)$_2$, and c) **1**·(NHC)(thf) in the crystal (thermal ellipsoids for 50% probability level, hydrogen atoms omitted for clarity). Selected bond lengths: a) Mg1–N1: 200.63(14) pm; Mg1–C$^{Flu}$: 241.49(15)/300.70(16)/320.99(15) pm; Mg1–O$^{thf}$: 207.80(12)/206.24(13)/213.08(12) pm; b) Mg1–N1: 200.92(23) pm; Mg1–C$^{Flu}$: 233.39(23)/296.06(25)/304.25(24) pm; Mg1–O$^{dme}$: 207.02(19)/208.25(21)/212.99(19) pm; c) Mg1–N1: 197.46(18) pm; Mg1–C$^{Flu}$: 231.60(19)/267.24(19) pm; Mg1–O$^{thf}$: 202.80(16) pm; Mg1–C$^{NHC}$: 217.43(21) pm.

is the fact that in both cases the magnesium atom is coordinated by three oxygen atoms as opposed to two in the previously reported cyclopentadienyl derivatives, with one dme molecule coordinated monodentately in case of **1**·(dme)$_2$. This is a result of the different electronic properties of the fluorenyl ligand compared to cyclopentadienyl. While cyclopentadienyl often favors an $\eta^5$ coordination, due to the negative charge being fully delocalized, the fluorenyl ligand is known for its very flexible bonding properties. Originating from the more localized negative charge in fluorenyl, it exhibits $\eta^{1-3}$ coordination in many cases, as well as $\eta^6$.[7,13–16] Thus, an additional thf or dme molecule is bound to the magnesium center to compensate for the electron deficiency. To investigate the impact of more strongly coordinating ligands, and since related fluorenyl NHC complexes are known to the literature,[17–21] we reacted **1**·(thf)$_3$ with an NHC (NHC = tetramethyl-imidazolin-2-ylidene; Scheme 2). However, NMR investigations of the reaction mixture were inconclusive, presumably due to the fact that the formed magnesium NHC complex was not stable in solution and decomposed quickly into a complex mixture of products, which eluded further characterization. Fortunately, on one occasion, serendipitous crystals of the resulting complex, **1**·(thf)(NHC), could be obtained and allowed for its structure to be determined by single crystal XRD. In this complex, two thf molecules are replaced by the carbene, while the fluorenyl ligand is bound in an $\eta^2$ coordination mode (Figure 2c).

If only the *ipso* carbon atom of the fluorenyl group is considered, the coordination environment around the magnesium atom can be described as distorted trigonal bipyramidal in case of **1**·(thf)$_3$ and **1**·(dme)$_2$, and distorted tetrahedral in case of **1**·(thf)(NHC) (Figure 2). The different binding modes of the fluorenyl group observed in the solid state highlight its ability to adopt to different steric and electronic situations at the metal center. The Mg–O bond length in **1**·(thf)$_3$ and **1**·(dme)$_2$ are similar to what has been observed in the related cyclopentadienyl complexes, and the Mg–C$^{NHC}$ bond in **1**·(thf)(NHC) is similar to those in other Mg-NHC complexes.[7,22]

As mentioned in the introduction, the constrained geometry cyclopentadienyl magnesium complexes, which we reported in 2022 and which have an obvious structural resemblance to **1**, were found to be versatile *s*-block catalyst for different transformations, with a particularly good performance in amine-borane and amine silane (cross-)dehydrocoupling/dehydrogenation. Therefore, as *s*-block metal catalyzed amine-borane dehydrogenation/dehydrocoupling is a vibrant research field,[23,24] we investigated the catalytic activity of **1** in dehydrocoupling/dehydrogenation of different amine-boranes (Scheme 3).

A dme solution of the corresponding amine-borane and 5 mol% of [**Mg**] (**1**·(dme)$_2$)[25] showed quick and selective conversion to the corresponding dehydrocoupling/dehydrogenation products over the course of a few hours (Table 1).[26]




**Scheme 2.** Synthesis of constrained geometry magnesium NHC complex **1**·(thf)(NHC) (NHC = tetramethyl-imidazolin-2-ylidene).


**Scheme 3.** Amine-borane dehydrogenation/dehydrocoupling, catalyzed by **1** ($R_2NH$: $Me_2NH$; $^iPr_2NH$; Piperidine).

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**Table 1.** Catalytic dehydrogenation/dehydrocoupling of amine-boranes.[a]

| Substrate | Product | Catalyst loading | Reaction time | Conversion |
|---|---|---|---|---|
| $Me_2NH{\cdot}BH_3$ | $[Me_2NBH_2]_2$ | 5 mol% | 4 h | 62% |
| $Me_2NH{\cdot}BH_3$ | $[Me_2NBH_2]_2$ | 5 mol% | 8 h | 84% |
| $Me_2NH{\cdot}BH_3$ | $[Me_2NBH_2]_2$ | 5 mol% | 16 h | >99% |
| $^iPr_2NH{\cdot}BH_3$ | $^iPr_2N{=}BH_2$ | 5 mol% | 4 h | >99% |
| $PipNH{\cdot}BH_3$[b] | $[Pip_2NBH_2]_2$ | 5 mol% | 4 h | 90% |

[a] dme, r.t. [b] PipNH: piperidine.

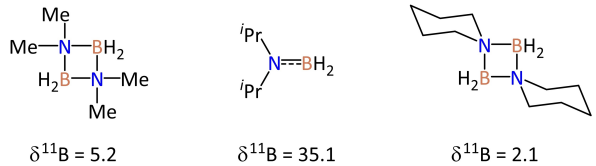
The products were identified by their characteristic $^{11}B$ NMR chemical shifts, with the cyclic diborazanes exhibiting more upfield shifted signals and the diisopropylamino borane a more deshielded resonance (Figure 3).

The overall catalytic performance of **1** is similar to its cyclopentadienyl derivatives, although it is worth mentioning that our previous studies focused on 8 h reactions, while we now found that **1** is cable of achieving full conversion after only 4 h in some cases. With this, **1** is one of the most potent magnesium catalysts in the field, as other magnesium-based catalysts for dimethylamine-borane dehydrogenation/dehydrocoupling do not only require longer reactions times, but also higher catalyst loadings and elevated reaction temperatures of 333 K.[27,28] Based on our previous work about magnesocenophane-catalyzed amine-borane dehydrogenation/dehydrocoupling reactions and the literature,[27,29] we propose a mechanism in which the ligand system is directly involved in the deprotonation of the amine-borane (Scheme 4).

This may involve either protonation of the fluorenyl group or of the amido functionality. Both routes appear to be viable, although DFT calculations suggest the amine intermediate (amide protonation) to be lower in energy. Subsequent hydrogen elimination by B–H bond activation at the magnesium center in proximity to the acidic N–H or Flu–H moieties will produce dihydrogen along with the aminoborane, possibly via a transient magnesium hydride species. The aminoborane has been observed by $^{11}B$ NMR spectroscopy ($\delta^{11}B(Me_2NBH_2) = 37.7$ (t, $^1J_{BH} = 128$ Hz)).

## Conclusions

In this work, we report the synthesis and SC-XRD determined solid-state structure of a fluorenyl amido constrained geometry complex of magnesium, **1**. The complex has been demonstrated to be a potent catalyst for amine-borane dehydrocoupling/dehydrogenation that can operate at room temperature.




$\delta^{11}B = 5.2$ $\delta^{11}B = 35.1$ $\delta^{11}B = 2.1$

**Figure 3.** Dehydrogenation/dehydrocoupling products and their $^{11}B$ NMR chemical shifts.

## Experimental Section

All manipulations were carried out under an inert gas atmosphere (argon 5.0, using either Schlenk line techniques or a glovebox. NMR spectra were recorded on Bruker Avance III 300 and Bruker Avance III 400 spectrometers. $^1H$ and $^{13}C$ NMR spectra were referenced using the solvent signals.[30] $^{11}B$ and $^{29}Si$ NMR spectra were referenced using external standards ($\delta^{11}B$ ($BF_3{\cdot}OEt_2$) = 0, $\delta^{29}Si$ ($SiMe_4$) = 0). Single crystal X-ray diffraction analysis were carried out on a Bruker D8 Venture diffractometer with a microfocus sealed tube and a Photon II detector and using monochromated $MoK_\alpha$ radiation ($\lambda = 0.71073$ Å). Correction for absorption effects was performed with the multi-scan method. The structure was solved by direct methods using SHELXT and was refined by full matrix least squares calculations on $F^2$ (SHELXL 2019) in the graphical user interface Shelxle.[31–33] Crystal structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and are available free of charge from the Cambridge Structural Database (reference numbers: 2367014, 2367015, 2367016). The ligand system was synthesized according to a previously described procedure.[34,35]

### *Synthesis of 1·(thf)$_3$*

To a solution of 6.57 g (22.2 mmol) of the neutral ligand in hexane (~100 mL) and thf (~5 mL) was added 31.7 mL (22.2 mmol) of an *n*-butyl-*sec*-butylmagnesium solution (0.7 M in hexane) at 273 K. The mixture was allowed to warm to room temperature and stirred over night at 333 K. The product precipitated as a yellow solid, which was isolated by filtration and dried in vacuum to obtain **1**·$(thf)_3$.

Yield: 4.35 g (9.42 mmol; 42%).

**$^1H$ NMR** (400 MHz, dmso-d6, 293 K): $\delta = 0.40$ (s, 6H, Si($C\underline{H}_3$)$_2$); 1.10 (s, 9H, C($C\underline{H}_3$)$_3$); 1.76 (m, thf); 3.60 (m, thf); 6.46 (t, $^3J = 7$ Hz, 2H, Flu-H); 6.80 (t, $^3J = 8$ Hz, 2H, Flu-H); 7.58 (d, $^3J = 8$ Hz, 2H, Flu-H); 7.83 (d, $^3J = 8$ Hz, 2H, Flu-H). **$^{13}C\{^1H\}$ NMR** (101 MHz, dmso-d6, 293 K): $\delta = 5.5$ (Si($C\underline{H}_3$)$_2$); 25.2 (thf); 33.7 (C($C\underline{H}_3$)$_3$); 48.8 (C($CH_3$)$_3$); 67.1 (thf); 85.7 (Flu); 109.0 (Flu); 117.8 (Flu); 118.2 (Flu); 119.2 (Flu); 125.4 (Flu); 143.1 (Flu). **$^{29}Si\{^1H\}$ NMR** (79 MHz, dmso-d6, 293 K): $\delta = -15.8$. **$^1H$ NMR** (400 MHz, $C_6D_6$, 294 K): $\delta = 0.95$ (m, 8H, thf); 1.01 (s, 6H, Si($C\underline{H}_3$)$_2$); 1.54 (s, 9H, C($C\underline{H}_3$)$_3$); 2.72 (m, 8H, thf); 7.23 (m, 2H, Flu-H); 7.39 (m, 2H, Flu-H); 8.17–8.19 (m, 2H, Flu-H); 8.45–8.47 (m, 2H, Flu-H). **$^{13}C\{^1H\}$ NMR** (101 MHz, $C_6D_6$, 294 K) $\delta = 7.4$ (Si($C\underline{H}_3$)$_2$); 25.1 (thf); 38.3 (C($C\underline{H}_3$)$_3$); 51.2 (C($CH_3$)$_3$); 69.4 (thf); 75.5 (Flu); 114.5 (Flu); 119.2 (Flu); 120.2 (Flu); 122.8 (Flu); 129.8 (Flu); 145.5 (Flu). **$^{29}Si\{^1H\}$ INEPT NMR** (79 MHz, $C_6D_6$, 294 K): $\delta = -19.9$. **$^1H$ NMR** (400 MHz, thf-d8, 299 K): $\delta = 0.36$ (s, 6H, Si($C\underline{H}_3$)$_2$); 1.24 (s, 9H, C($C\underline{H}_3$)$_3$); 1.69 (thf); 3.54 (thf); 6.67–6.72 (m, 2H, Flu-H); 6.92–6.97 (m, 2H, Flu-H); 7.78 (d, $^3J =$

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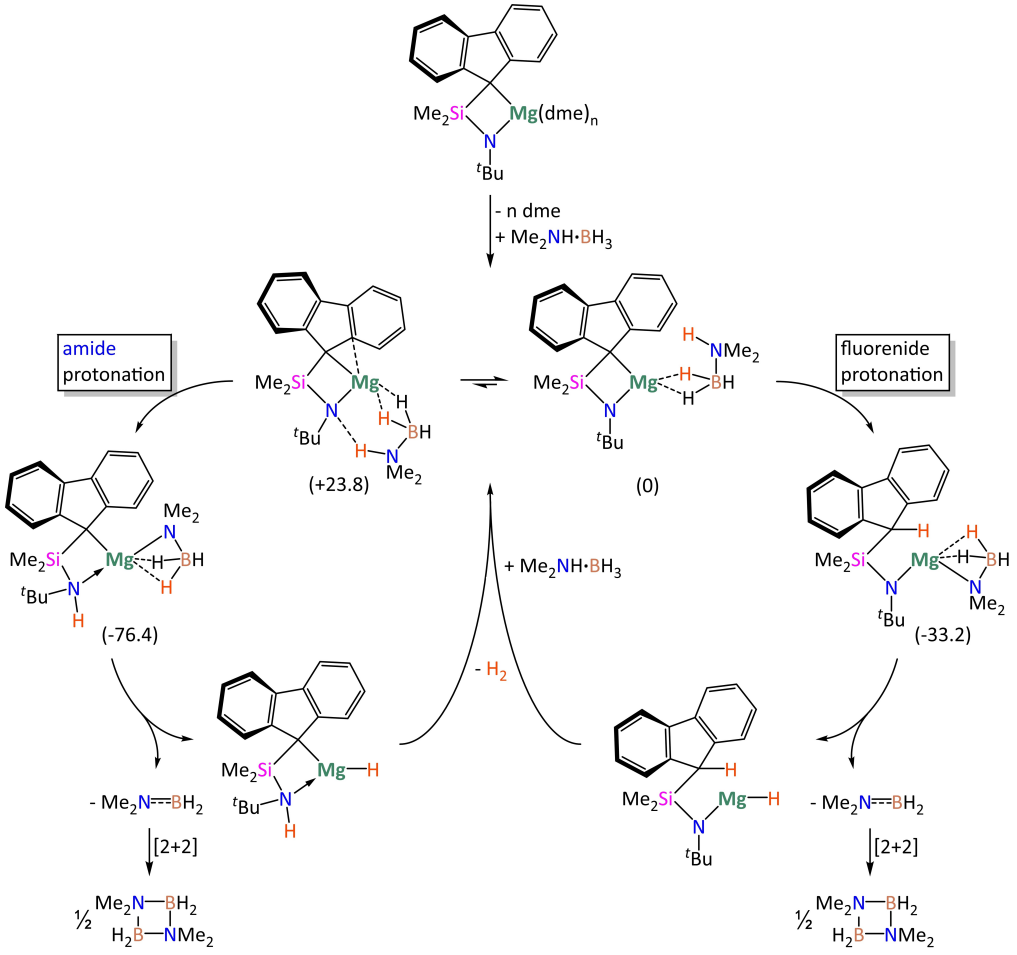


**Scheme 4.** Proposed catalytic cycle for the dehydrogenation of dimethylamine-borane by **1** (relative energies calculated at M06-2X-D3/def2-SVP given in kJ mol$^{-1}$ in brackets).

8 Hz, Flu-*H*); 7.90 (d, $^{3}J$ = 7.7 Hz, Flu-H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, thf-d8, 300 K): δ = 7.8 (Si($\underline{C}H_3$)$_2$); 16.5 (C($\underline{C}H_3$)$_3$); 38.0 (thf); 52.0 ($\underline{C}$(CH$_3$)); 68.4 (thf); 114.0 (Flu); 119.6 (Flu); 120.0 (Flu); 122.0 (Flu); 130.7 (Flu); 147.8 (Flu). **$^{29}$Si{$^{1}$H} INEPT NMR** (79 MHz, thf-d8, 300 K): δ = −22.8.

### *Synthesis of 1·(dme)$_2$*

To a solution of 7.60 g (25.7 mmol) of the neutral ligand in hexane (~100 mL) and dme (5 mL) was added 36.7 mL (25.7 mmol) of an *n*-butyl-*sec*-butylmagnesium solution (0.7 M in hexane) at 273 K. The mixture was allowed to warm to room temperature and stirred over night at 333 K. The product precipitated as a yellow solid, which was isolated by filtration and recrystallized from dme to obtain **1**·(dme)$_2$ as yellow crystals.

Yield: 6.36 g (12.8 mmol; 50 %).

**$^{1}$H NMR** (400 MHz, dmso-d6, 298 K): δ = 0.41 (s, 6H, Si($\underline{C}H_3$)$_2$); 1.10 (s, 9H, C($\underline{C}H_3$)$_3$); 3.43 (dme); 3.24 (dme); 6.44–6.48 (m, 2H, Flu-H); 6.78–6.83 (m, 2H, Flu-H); 7.56–7.59 (m, 2H, Flu-H); 7.82–7.85 (m, 2H, Flu-H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, dmso-d6, 300 K): δ = 5.4 (Si($\underline{C}H_3$)$_2$); 33.6 (C($\underline{C}H_3$)$_3$); 48.7 ($\underline{C}$(CH$_3$)$_3$); 58.0 (dme); 71.0 (dme); 85.6 (Flu); 108.9 (Flu); 117.7 (Flu); 118.1 (Flu); 119.1 (Flu); 125.3 (Flu); 143.1 (Flu). **$^{29}$Si{$^{1}$H} INEPT NMR** (79 MHz, dmso-d6, 299 K): δ = −15.8. **$^{1}$H NMR** (400 MHz, $C_6D_6$, 297 K): δ = 0.96 (s, 6H, Si($\underline{C}H_3$)$_2$); 1.48 (s, 9 H, C($\underline{C}H_3$)$_3$); 2.32 (dme); 2.62 (dme); 7.19–7.23 (m, 2H, Flu-H); 7.36–7.40 (m, 2H, Flu-H); 8.13–8.16 (m, 2H, Flu-H); 8.38–8.41(m, 2H, Flu-H). **$^{29}$Si{$^{1}$H} INEPT NMR** (79 MHz, $C_6D_6$, 294 K): δ = −20.8.

**CHN**: calculated for $C_{19}H_{23}MgNSi$ + 1.77 dme: C: 65.63 %, H: 8.59 %, N: 2.93 %; found: C: 65.28 %, H: 8.65 %, N: 2.85 %.

### *Synthesis of 1·(thf)(NHC)*

To 500 mg (1.15 mmol) of **1**·(thf)$_3$ and 143 mg (1.15 mmol) of 1,3,4,5-tetramethylimidazol-2-ylidene was added toluene (~50 mL) and the resulting mixture was stirred until all components had completely dissolved. The solution was then stored at 248 K. On one occasion, a small amount of serendipitous crystal of **1**·(thf)(NHC) could be obtained. All attempts to characterize the compound in solution failed.

### *General Procedure for Catalytic Experiments*

1.02 mmol of the corresponding amine-borane (60 mg $Me_2NH{\cdot}BH_3$; 117 mg $^{i}Pr_2NH{\cdot}BH_3$; 101 mg $PipNH{\cdot}BH_3$) along with 5 mol % of **1**·(dme)$_2$ (25 mg; 50.2 µmol) were charged into a vial and dissolved in dme (~1 mL). The mixture was stirred for the indicated time at room temperature and then investigated by $^{1}$H and $^{11}$B NMR spectroscopy. Conversions were determined by integration of the

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$^{11}B\{^{1}H\}$ NMR spectra. Spectroscopy data was identical to the literature.[29,36]

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Constrained geometry complex · Fluorenyl · Magnesium · Amine-borane · Dehydrocoupling

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