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Application of β-Diketiminato Arene-Substituted Ru(II) Complexes in Highly Efficient H_2 Dehydrocoupling of Amine Boranes

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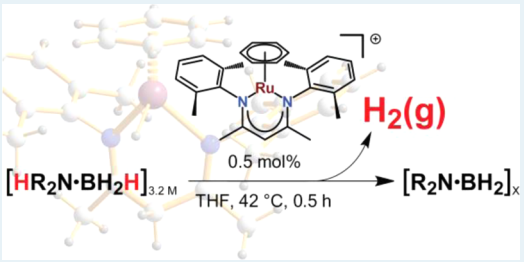
Supporting Information

ABSTRACT: Amine borane type substrates show significant potential as safe and effective chemical hydrogen storage materials. β-Diketiminato(η^6-arene)-Ru(II) complexes have shown the ability to rapidly perform the heterolytic cleavage of H_2 under mild conditions through bifunctional metal-ligand interaction. The presented work explores the applicability of such complexes toward the catalytic dehydrogenation of different substituted amine boranes, in particular, ammonia borane (AB) and *N*,*N*-dimethylamine borane (DMAB). Complex [(η^6-C_6H_6)-Ru(2,6-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH$]OTf (**1**) showed excellent activity in the catalytic release of a single equivalent of H_2 within 0.5 h from a concentrated DMAB solution in THF (3.2 M) at near ambient temperatures. Studies involving structural analogues of **1** allowed insight into the operational dehydrocoupling mechanism. It is concluded from this preliminary work that in solution, **1** forms a homogeneous bifunctional active species that does not undergo deactivation, even after prolonged exposure to H_2 at elevated pressures.



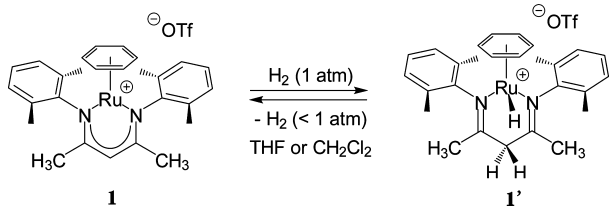
KEYWORDS: *ammonia borane, N,N-dimethylamine borane, dehydrocoupling, ruthenium(II) β-diketiminato complexes, hydrogen generation*

INTRODUCTION

Chemical hydrogen storage, in which H_2 is covalently bound and stored within a carrier molecule, offers a number of key advantages, including high hydrogen per weight content and reduced risk of explosion and volatile dissipation. Hence, this molecular-based technology has the possibility to provide a practical solution for H_2 storage in mobile applications.[1] Low-molecular-weight hydrogen-substituted nitrogen-boron compounds, such as ammonia borane (AB), show significant potential as hydrogen storage materials, with a hydrogen-to-weight ratio up to 19.6%.[2,3] The release of H_2 from AB and related substrates can involve different methods, including thermal decomposition in the solid (i)[4] and solution state (ii);[5] hydrolysis (iii),[6,7] and homogeneous (iv)[8−10] or heterogeneous catalytic dehydrogenation in solution (v).[11,12] In our view, the fourth approach is the most promising because it allows for high selectivity through intimate substrate-catalyst interaction, which could ultimately allow for a controllable and reversible process. Since the first reports on homogeneous transition metal catalyzed dehydrogenation of amine boranes appeared, a number of highly potent systems have been developed.[13−15] In recent years, continuous research in transition metal AB dehydrogenation catalysis examined the performance and mechanisms of different systems in organic solvents and ionic liquids.[16−18] Importantly, studies involving the *N*-methyl[15] and, in particular, *N*,*N*-dimethyl (DMAB)[19−22] derivatives enable a more enhanced understanding of the interaction between the substrate and metal complex because the resulting dehydrocoupling products are less prone to polymerization compared with AB. The propensity of ruthenium-based complexes to react and coordinate dihydrogen is well established, and consequently, a great number of highly active organoruthenium catalysts have been applied to dehydrocoupling reactions of AB and related BN substrates.[23−28]

In 2007, Phillips and co-workers reported the bifunctional [(η^6-C_6H_6)-Ru(II)-β-diketiminato]OTf complex **1**, which cleaves H_2 heterolytically under very mild conditions.[29] The resulting β-diimine-Ru(II)-hydride complex **1′** (Scheme 1) readily reverts back to the dehydrogenated β-diketiminato

Scheme 1. Reversible Formation of Complex 1′ via Heterolytic Cleavage of H_2 by 1



1 **1′**

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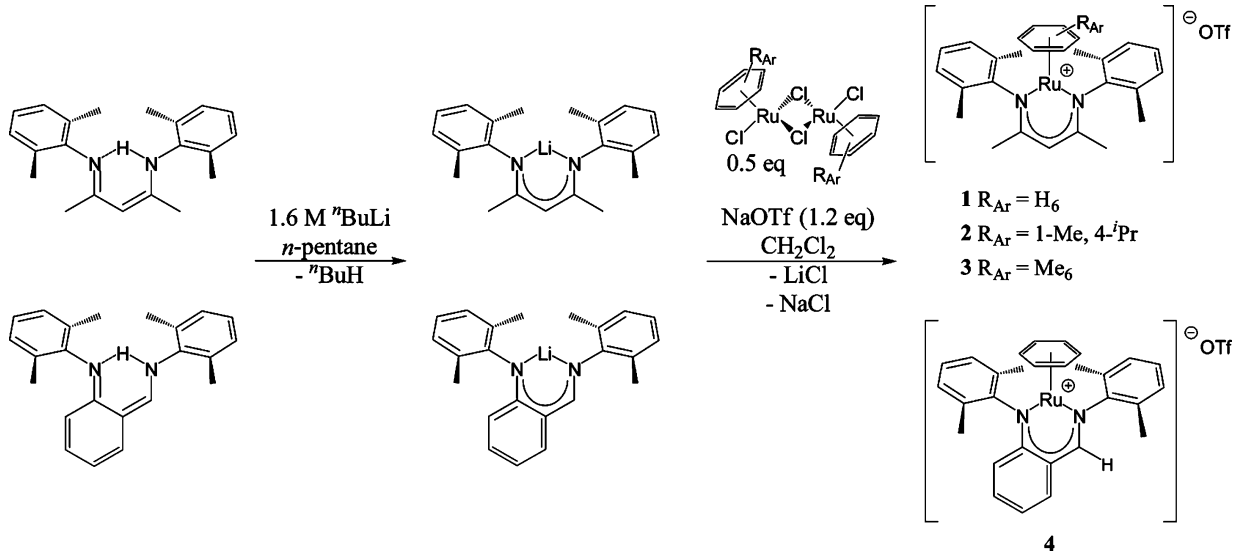
Scheme 2. Synthesis of the Cationic β-Diketiminato-(η^6-arene)-Ru(II) Complexes 1−4 via Deprotonation and Lithiation of the β-Diketiminate Ligands



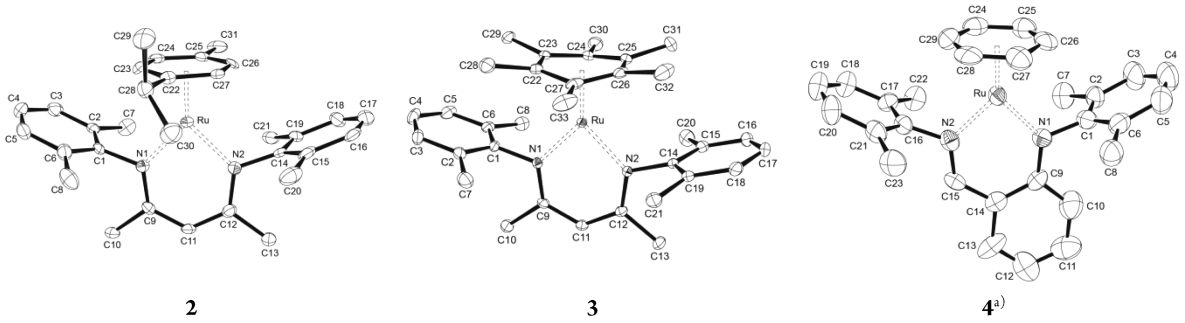


Figure 1. ORTEP representation of complexes **2**−**4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, anions, solvates, and internal atomic disorder were omitted for clarity. Relevant average bond distances (Å) and angles (°): (**2**) Ru−N, 2.017(6); Ru−C^{cent}, 1.713(3); N−Ru−N, 89.1(2); C^{cent}−Ru−N^{cent}, 178.1(2); Ru−N^{cent}−C11, 173.3(3). (**3**) Ru−N, 2.023(1); Ru−C^{cent}, 1.776(1); N−Ru−N, 88.4(1); C^{cent}−Ru−N^{cent}, 180.0(1); Ru−N^{cent}−C11, 179.9(1). (**4**)[a)] Ru−N, 2.011(5); Ru−C^{cent}, 1.719(4); N−Ru−N, 88.4(2); C^{cent}−Ru−N^{cent}, 177.9(2); Ru−N^{cent}−C14, 174.6(3). (a) Unit cell contains two crystallographically independent molecules, and values shown represent an average.

complex **1** when the H_2 atmosphere is removed. This is in stark contrast to the β-diketiminato calcium and magnesium complexes presented by the groups of Harder and Hill, which, albeit active in the dehydrocoupling of AB, do not display bifunctional heterolytic activation of H_2.[30−33] The structure of **1′**, in the presence of H_2 was established by solution NMR and in the solid state through X-ray diffraction studies.[29]

More recently, it has been demonstrated that **1** and related species are potent catalyst precursors in the homogeneous hydrogenation of styrene.[34] From these initial results, the application of **1** toward catalytic dehydrocoupling of ammonia borane (AB) and dimethylamine borane (DMAB) seemed promising. Aside from **1**, there are only very few known dehydrocoupling catalysts that afford the possibility of a bifunctional mechanism.[27,35−39] Importantly, complexes such as **1** that show cooperative activation of H_2 potentially allow for a pressure- or temperature-limited, reversible dehydrocoupling process, as evidenced by the forward and backward reactions depicted in Scheme 1.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes. Scheme 2 outlines the cationic (η^6-arene)-Ru(II)-β-diketiminato complex **1**,[29] and the previously unreported complexes **2**−**4**. These compounds provide the basis for a first insight into the general activity of this class of organoruthenium complexes in the dehydrocoupling of AB and DMAB. The corresponding β-diketiminate ligands were prepared according to literature procedures (Scheme 2).[40−44] Transmetalation of the ligands required deprotonation by ^{n}BuLi at 0 °C to quantitatively yield the air- and moisture-sensitive organolithium salts.[45−48] The subsequent reaction with [(η^6-arene)-RuCl]$_2$-μ_2-Cl$_2$, in the presence of an excess of NaOTf, afforded the organometallic salts **1**−**4** in good to excellent yields.[29]

Characterization of **1**−**3** by ^{1}H NMR in $CDCl_3$ shows the diagnostic β-H ^{1}H signal in **1** (δ = 6.64 ppm) slightly more deshielded than for **2** (δ = 6.55 ppm) and **3** (δ = 6.39 ppm), indicative of the enhanced electron-donating character and increased steric bulk of the η^6-$C_{10}H_{14}$ *p*-cymene and η^6-C_6Me_6 hexamethylbenzene groups, respectively. All complexes were characterized in the solid state by single crystal X-ray diffraction, in which **2**−**4** reveal a well-defined vacant coordination site around the Ru(II) metal center (Figure 1).

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This is a direct consequence of the sterically demanding 2,6-dimethyl substituents of the flanking aryl groups associated with the β-diketiminate ligand. Complex **3** shows increased internal ligand-metal steric repulsion, as evidenced by an elongated bond distance between the $(\eta^6\text{-}C_6Me_6)^{cent}$ and Ru(II) of 1.776(1) Å, as compared with 1.705(3) Å in **1**.[29] Similarly, the $(\eta^6\text{-}C_6H_6)^{cent}$–Ru(II) distance in **4** is within 1.719(4) Å, slightly longer than in **1**, possibly due to the enhanced electron releasing properties of the anilido-imine ligand. The out-of-plane folding of the η^6-coordinated arene group along the median C–C plane in half-sandwich complexes is quite a common feature. In **3**, however, this is with 15° particularly marked due to the steric repulsion between $\eta^6\text{-}C_6Me_6$ and the flanking aryl substituents of the β-diketiminate ligand (Figure 1).

Catalytic Dehydrocoupling. To evaluate the ability of **1** to catalytically release H_2 from ammonia borane (AB), an in situ ^{1}H NMR study in THF-d_8 was performed. At room temperature, a THF solution of AB (0.26 mmol) in the presence of **1** (10 mol %) showed initially a gradual increase in dissolved H_2 and the formation of **1′**. After completion, solution ^{11}B NMR analysis of the soluble dehydrocoupling products indicated the formation of B-(cyclodiborazanyl)-aminoborohydride (BCDB) with traces of cyclotriborazane (CTB) and borazine (see the Supporting Information for further details).[49] When the reaction was repeated using 0.65 mmol of AB, the final dehydrocoupling product observed was a colorless, insoluble solid, which readily underwent hydrolysis when exposed to wet solvents, liberating additional quantities of H_2. Infrared spectroscopy and thermogravimetric analysis of the resulting solid were consistent with the previously reported polyaminoborane PAB $(NH_2BH_2)_5$ (see the Supporting Information).[14,50−53] From these initial findings, a more relevant test series examining the dehydrogenation of AB in THF (3.2 M) in presence of **1** (0.5 mol %) was undertaken, employing a sealable stainless steel pressure reactor. Unfortunately, even in the absence of catalyst, the rate of H_2 release from a solution of AB (3.2 M) in THF at 42 °C is not negligible (see the Supporting Information). The thermal stability of AB in various solvents has been studied in detail by Shaw et al.[49]

Given the above findings, it is difficult to evaluate directly the performance of **1** and elucidate a possible mechanism. Furthermore, it is questionable to refer to such a process as being purely under catalytic control, given the modest effect of the complex on the H_2 release. More importantly, in contrast to previous reports, kinetic data require correction with respect to the uncatalyzed thermal AB dehydrogenation process, especially in organic solvents such as THF.[27] Contrary to AB, DMAB is significantly more stable under noncatalytic conditions, showing only marginal H_2 release (Figure 2). Hence, DMAB was chosen to test the activity of **1** and related complexes. From Figure 2, it is observed that a 3.2 M THF solution of DMAB at 42 °C in the presence of 0.5 mol % of **1** leads to the quantitative release of a single equivalent of H_2 in approximately 30 min. The soluble reaction products were identified by ^{11}B NMR to be predominantly the cyclic dimer $(Me_2N\text{-}BH_2)_2$ (see the Supporting Information for details).[13]

To investigate the efficiency and mechanistic properties of **1** in the dehydrocoupling process, the electron-donating $\eta^6\text{-}C_{10}H_{14}$ *p*-cymene analogue **2** was evaluated, which showed a significant decrease in activity as compared with **1** (Figure 2). The latter may be explained by the reduced stability of the Ru–H bond in **2** due to the increase in electron density at the metal center. For complex **3**, the loss in activity is even more pronounced. Not only is the electron density at the metal center the highest within the series, but also the considerable steric bulk of the $\eta^6\text{-}C_6Me_6$ arene ligand interferes strongly with the approach of the DMAB substrate. Moreover, it is important to note that a concentrated THF solution of **3** in the presence of H_2 does not allow for the facile formation of a species analogous to **1′**. Despite the reduced activity, complex **3** still mediates the complete release of 1 equiv of H_2 from DMAB after a prolonged period of 102 h without any indication of deactivation. The latter observation underlines the robustness of the here-presented catalysts under the tested reaction conditions. From the above observations, in particular, the reaction of **1** with H_2 (Scheme 1), the catalytic dehydrocoupling of DMAB can be assumed to proceed initially via the abstraction of the hydride from the BH_3 component by the Ru(II) center. The acidic proton of the NMe_2H group then protonates the β-carbon position of the β-diketiminato ligand, resulting in the formation of the saturated β-diimine complex **1′** (Scheme 3).

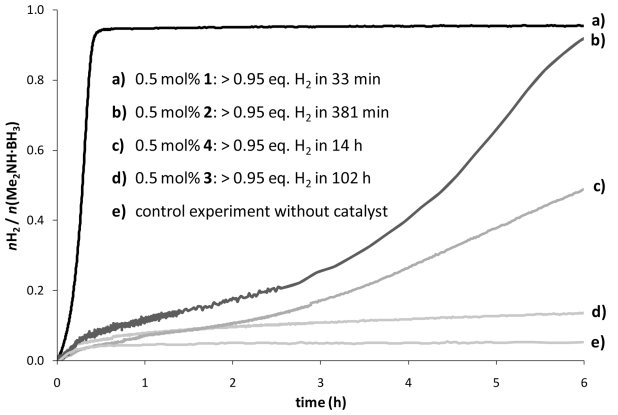

Figure 2. Time dependent H_2 gas evolution (pressure derived DMAB equivalents) in dehydrocoupling reactions of DMAB (3.2 M) in anhydrous THF (10 mL) catalyzed by complexes **1**–**4** (0.5 mol %) at 42 °C and constant volume (details provided in the Supporting Information).

It is important to note that H_2 can be released from **1′** simultaneously via recombination of the metal hydride and one of the β-protons from the diimine ligand. Alternatively, a stepwise mechanism that involves hydride abstraction from **1′** by recombination with the acidic proton of an additional DMAB molecule could be envisaged. To test which of the above mechanisms is active, the substituted β-diketiminate complex **4** was prepared. Here, the protonation of the β-carbon in the aniliodo-imine ligand is considerably hindered because the aromaticity of the incorporated phenyl group is disrupted. As seen in Figure 2, complex **4** retains moderate activity in the catalytic DMAB dehydrocoupling, suggesting that the stepwise mechanism is operational for this complex. However, because **4** is less active than **1**, the formation of **1′** appears to be crucial for an efficient dehydrocoupling process.

Importantly, for each complex tested, Figure 2 reveals an initially slow kinetic regime prior to the offset of the catalytic activity. Therefore, it is crucial to establish whether **1** and related derivatives are, indeed, the actual homogeneous catalysts responsible for the dehydrocoupling of DMAB. The addition of excess Hg(0) is a widely known method to inhibit heterogeneous catalysts;[54,55] however, the required control

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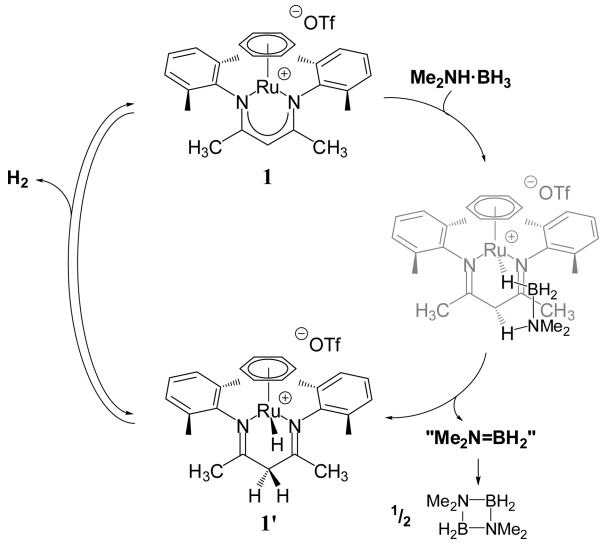
Scheme 3. Formation of 1′ via Catalytic Dehydrocoupling of DMAB by 1



experiment involves the use of a known heterogeneous Ru active species, structurally similar to **1**.

Zahmakiran et al. recently published their work on the transformation of Ru(cod)(cot) into a heterogeneous active species under AB dehydrogenation conditions.[56] Upon the addition of excess Hg(0), the catalytic activity was completely quenched. In a similar experiment, 50 equiv of Hg(0) was added to a 3.2 M THF solution of DMAB in the presence of **1** (0.5 mol %) at 25 °C. Within the error of the measurement, no change in dehydrogenation activity was observed. Alternatively, a poisoning experiment was envisaged in which the open metal coordination site of **1** is blocked by a nonlabile group. To this end, the coordinatively saturated Ru(II)-Me complex **5** was synthesized (Figure 3). Under conditions identical to the ones

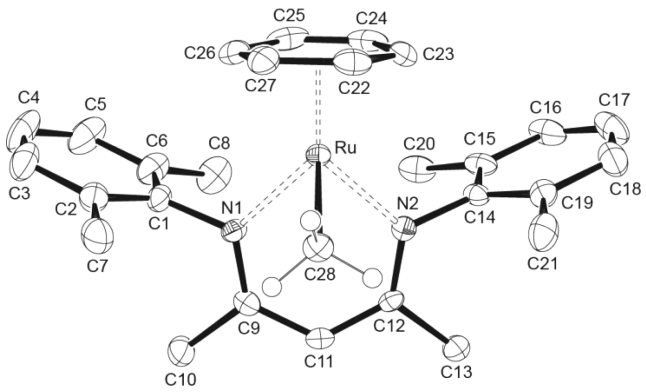


Figure 3. ORTEP representation of complex **5**. Ellipsoids are drawn with 50% probability. Only H atoms associated with C28 are shown. Relevant average bond distances (Å) and angles (°): Ru−C28, 2.124(2); Ru−N, 2.115(2); Ru−C^{cent}, 1.722(1); N−Ru−N, 86.5(1); C^{cent}−Ru−N^{cent}, 152.9(1); Ru−N^{cent}−C11, 155.2(1).

employed for **1**−**4**, complex **5** shows no catalytic activity in the dehydrocoupling of DMAB (see the Supporting Information for details). In addition, Figure 2 reveals distinct characteristic reaction profiles for each of the structurally related complexes tested. It is therefore reasonable to assume that **1** represents a homogeneous active species.

In contrast to the results obtained at 42 °C (Figure 2), similar room temperature experiments involving a THF solution of DMAB in the presence of **1** showed a prolonged induction period of ∼80 min. It is interesting to place these results into context with similar bifunctional Ru(II) catalysts. Friedrich et al. reported the Ru-amido pincer complex $[Ru(H)(PMe_3)(N(CH_2CH_2P^iPr_2)_2)]$ to be highly active in the catalytic dehydrogenation of DMAB;[35,36] however, according to the authors, the complete release of a single equivalent of H_2 could not be achieved because of catalyst deactivation. Whittlesey et al. recently investigated the mixed-metal mono-NHC complex [Ru(1,1′-bis(diphenylphosphino)-ferrocene)(1,3-dicyclohexylimidazol-2-ylidene)HCl], which showed rapid release of 1 equiv of H_2 within 50 min after an initial short induction period.[38] However, the reported induction period is much shorter than the one observed for **1** and is hypothesized to be associated with the formation of a vacant coordination site via ligand loss.

In contrast, complex **1** already features a vacant coordination site, and hence, the observed delay in activity cannot be explained by this process. It is important to note that all the above reactions were performed in N_2-flushed THF, which does not induce the rapid formation of **1**′ via the equilibrium process described in Scheme 1. In a separate experiment, a H_2 saturated solution of THF containing 0.5 mol % of **1** was prepared prior to the addition of DMAB which then resulted in an accelerated dehydrogenation and a considerably shorter induction period (Figure 4). The latter findings clearly suggest that the activity of **1** strongly depends on the rate of formation of H_2 adduct **1**′.

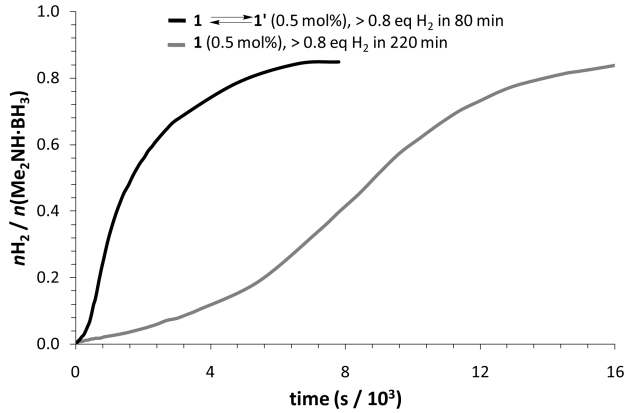


Figure 4. Time-dependent H_2 gas evolution over time (pressure derived DMAB equivalents), measured by volume displacement at 25 °C using a water gas buret. DMAB (3.2 M), 0.5 mol % of **1**, 2 mL of H_2 saturated THF (black) or 2 mL of N_2 saturated THF (gray).

CONCLUSIONS

The fast and controlled release of H_2 from chemical hydrogen storage materials such as amine boranes is crucial to meet the requirements for mobile applications. The here-presented organoruthenium(II) β-diketiminato complexes, in particular, **1**, allow for the catalytic dehydrocoupling of a single equivalent of H_2 from a concentrated solution of DMAB in THF at 42 °C in 0.5 h. As established above, the ability of **1** to heterolytically activate H_2 in an equilibrium process under mild conditions is of key importance in the dehydrocoupling mechanism. The presented findings strongly suggest that **1** transforms into a

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truly homogeneous catalyst **1′** that is a key element in mediating selectivity and activity. Further, complexes **1**−**4** are very robust and do not show deactivation, even after a prolonged exposure to H_2 at elevated pressure in solution. A more comprehensive analysis of the mechanism involved in the dehydrocoupling of DMAB by **1**, including computational studies, is currently in progress and will be reported in due course.

EXPERIMENTAL SECTION

General Procedures. The complexes were synthesized using standard Schlenk techniques, whereas subsequent syntheses and manipulations of all products and reagents were performed in an Innovative Technologies glovebox with a N_2 atmosphere containing less than 1 ppm of O_2 and H_2O. All glassware was dried at 130 °C for at least 12 h, and the flasks underwent three N_2 purge/refill cycles prior to the introduction of solvents or reagents. All solvents were dried according to literature procedures involving distillation over the appropriate drying agents and stored in Schlenk flasks equipped with a Teflon stopcock. Extra-dry THF was purchased from Acros Organics (Fisher Scientific). Celite for filtration was kept in an oven at 130 °C and degassed prior to use. All other reagents were purchased from commercial sources and were used as received if not specified otherwise.

NMR spectra were recorded using Varian VNMRS 300, 400, and Varian INOVA 500 instruments. CD_2Cl_2 was distilled over CaH_2 and stored under inert conditions. Chemical shifts for ^1H and $^{13}C\{^1H\}$ spectra were referenced to the relevant solvent peaks, observed as residual signals. ^{19}F NMR spectra were referenced to the relevant residual solvent peak and CCl_3F. Infrared spectra were recorded on a Varian 3100FT-IR Excalibur spectrometer. Samples were prepared as nujol mulls on KBr discs. Elemental microanalyses were obtained using an Exeter Analytical EA-1110 elemental analyzer. Mass spectra were recorded using either a solution or a nanoelectrospray ionization (ESI) technique on a Waters alliance HT Micromass Quattro LCT (MeOH/H_2O, 60/40) TOF instrument with a cone voltage of 35 V and a capillary voltage of 2800 V (+ mode) and 2500 V (− mode).

Starting materials and reagents were purchased from Sigma-Aldrich, Acros Organics (Fisher Scientific), and Precious Metals Online ($RuCl_3$). Ammonia borane and *N*,*N*-dimethylamine borane were synthesized according to literature procedures.[58,59] The syntheses of the bis(dichloro(η^6-arene)Ru(II)) dimer (arene = benzene or *p*-cymene) was carried out by a slightly modified procedure according to Bennett et al.[60] The bis(dichloro(η^6-C_6Me_6)Ru(II)) dimer was synthesized according to Vriamont et al.[61] (2,6-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH_2$, (2,6-$(CH_3)_2$-$C_6H_3NH)C_6H_4C(H)$=NC_6H_3-2,6-$(CH_3)_2$, and the corresponding lithium salts were synthesized according to literature procedures.[62,63] [(η^6-C_6H_6)-Ru(2,6-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH$]OTf (**1**) was synthesized according to the procedures published by Phillips et al.[29]

[(η^6-$C_{10}H_{14}$)-Ru(2,6-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH$]OTf (**2**). A 312 mg (1.0 mmol) portion of (2,6-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH_2$, 306 mg (0.5 mmol) of bis(dichloro(η^6-$C_{10}H_{14}$)Ru(II)) dimer, and 190 mg (1.1 mmol) of sodium trifluoromethanesulfonate were dissolved in 20 mL of dried and degassed CH_2Cl_2 in a N_2-flushed 50 mL Schlenk flask. The reaction was stirred under N_2 for 12 h and filtered over Celite to remove LiCl and NaCl. The filtrate was reduced in volume to about 2 mL, and *n*-pentane was added to precipitate the product, which was then dried under vacuum for 24 h to yield a light brown solid (560 mg, 81%). Elemental analysis: found [calculated] C, 55.43 [55.72]; H, 5.48 [5.70]; N, 3.81 [4.06]. TOF MS-ES (25 °C, MeCN), positive mode (*m*/*z*): 541.2162 [parent M^+, 100%, calcd. 541.2157]. ^1H NMR (300 MHz, 25 °C, CD_2Cl_2) δ (ppm): 1.15 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-cymene ^{i}Pr-$(CH_3)_2$), 1.90 (s, 3H, *p*-cymene CH_3), 2.15 (s, 12H, *o*-CCH_3), 2.18 (s, 6H, α-CH_3), 2.50 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-cymene ^{i}Pr-C*H*), 4.41 (d, $^3J_{HH}$ = 6.6 Hz, 2H, *p*-cymene Ar C*H*), 4.79 (d, $^3J_{HH}$ = 6.6 Hz, 2H, *p*-cymene Ar C*H*′), 6.55 (s, 1H, β-C*H*), 7.31−7.36 (m, 2H, *p*-C*H*), 7.40−7.42 (m, 4H, *m*-C*H*). $^{13}C\{^1H\}$ NMR (101 MHz, 25 °C, CD_2Cl_2) δ (ppm): 19.1 (s, *o*-CCH_3), 19.5 (s, *p*-cymene CH_3), 23.3 (s, α-CH_3), 23.6 (s, *p*-cymene ^{i}Pr-$(CH_3)_2$), 32.7 (s, *p*-cymene ^{i}Pr-CH), 84.1 (s, *p*-cymene Ar *C*′H), 87.3 (s, *p*-cymene Ar CH), 93.0 (s, *p*-cymene Ar *C*-Me), 104.3 (s, *p*-cymene Ar *C*-^{i}Pr), 104.8 (s, β-CH), 127.9 (s, *p*-CH), 129.5 (s, *m*-CH), 130.0 (s, *o*-CCH_3), 158.5 (s, *i*-*C*), 164.1 (s, C=N). ^{19}F NMR (282 MHz, 25 °C, CD_2Cl_2) δ(ppm): −78.87 (s, $^1J_{FC}$ = 321.1 Hz, $CF_3SO_3^-$). FT-IR (25 °C, nujol mull, KBr discs) υ (cm^{-1}): 2997(b, m), 2829(w), 1562(vw), 1552(m), 1479(m), 1434(w), 1384(w), 1346(m), 1270(vs), 1224(m), 1147(m), 1032(m), 775(w), 637(m).

[(η^6-C_6Me_6)-Ru(2,6-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH$]OTf (**3**). A 374 mg (1.2 mmol) portion of (2,6-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH_2$, 400 mg (0.6 mmol) of bis(dichloro(η^6-C_6Me_6)Ru(II)) dimer, and 275 mg (1.6 mmol) of sodium trifluoromethanesulfonate were dissolved in 20 mL of dried and degassed CH_2Cl_2 in a N_2-flushed 50 mL Schlenk flask. The reaction was carried out using a method identical to that for **2**. The product was obtained as a light brown solid (630 mg, 73%). Elemental analysis: found [calculated + 3/4 CH_2Cl_2] C, 53.62 [53.40]; H, 5.74 [5.74]; N, 3.55 [3.58]. TOF MS-ES (25 °C, MeCN), positive mode (*m*/*z*): 569.2447 [parent M^+, 100%, calcd. 569.2470]. ^1H NMR (500 MHz, 30 °C, CD_2Cl_2) δ (ppm): 1.52 (s, 18H, $C_6(CH_3)_6$, 1.94 (s, 6H, α-CH_3), 2.07 (s, 12H, *o*-CH_3), 6.40 (s, 1H, β-C*H*), 7.30−7.33 (m, 2H, *p*-C*H*), 7.41−7.42 (m, 4H, *m*-C*H*). $^{13}C\{^1H\}$ NMR (126 MHz, 30 °C, CD_2Cl_2) δ (ppm): 16.2 (s, $C_6(CH_3)_6$), 19.2 (s, *o*-CH_3), 24.5 (s, α-CH_3), 96.1 (s, $C_6(CH_3)_6$), 103.7 (s, β-CH), 127.5 (s, *p*-CH), 130.4 (s, *m*-CH), 131.2 (s, *o*-CCH_3), 156.0 (s, *i*-*C*), 163.2 (s, C=N). ^{19}F NMR (282 MHz, 25 °C, CD_2Cl_2) δ (ppm): −78.88 (s, $^1J_{FC}$ = 319.9 Hz, $CF_3SO_3^-$). FT-IR (25 °C, nujol mull, KBr discs) υ (cm^{-1}): 2938(vs), 2861(vs), 2360(w), 2340(w), 1624(w), 1560(m), 1467(s), 1382(m), 1362(w), 1267(vs), 1222(m), 1183(m), 1149(s), 1061(w), 1032(s), 1010(m), 857(vw), 778(m), 638(s).

[(η^6-C_6H_6)-Ru(2,6-$(CH_3)_2$-$C_6H_3N)C_6H_4C(H)$=NC_6H_3-2,6-$(CH_3)_2$]OTf (**4**). A 334 mg (1.0 mmol) portion of (2,6-$(CH_3)_2$-$C_6H_3NH)C_6H_4C(H)$=NC_6H_3-2,6-$(CH_3)_2$, 250 mg (0.5 mmol) of bis(dichloro(η^6-C_6H_6)Ru(II)) dimer, and 222 mg (1.3 mmol) of sodium trifluoromethanesulfonate were added to an oven-dried and N_2-flushed 50 mL Schlenk tube and dissolved in 20 mL of dried and degassed CH_2Cl_2. The reaction was carried out using the same method as for **2**. The title compound was obtained as a dark, microcrystalline brown solid (492 mg, 75%). Elemental analysis: found [calculated + 1.1 CH_2Cl_2] C, 49.83 [49.86]; H, 4.20 [4.20]; N, 3.49 [3.74]. TOF MS-ES (25 °C, MeCN), positive mode (*m*/*z*): 507.1362 [parent M^+, 100%, calcd. 507.1374]. ^1H NMR (400 MHz, 25 °C, CD_2Cl_2) δ (ppm): 2.09 (s, 6H, *o*-CH_3), 2.21 (s, 6H, *o*-CH_3*), 5.27 (s, 6H, C_6H_6), 7.16−7.19 (m, 1H, Ph *o*-C*H*), 7.40−7.41 (m, 1H, Ar *p*-C*H*), 7.43−7.45 (m, 4H, Ar *m*-C*H*), 7.43−7.45 (m, 1H, Ar *p*-C*H**), 7.55−7.60 (m, 1H, Ph *m*-C*H*),

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7.63−7.67 (m, 1H, Ph *p*-C*H*), 7.72−7.74 (m, 1H, Ph *m*-C*H**), 8.75 (s, 1H, N=C*H**). $^{13}C\{^1H\}$ NMR (101 MHz, 25 °C, CD_2Cl_2) δ (ppm): 18.5 (s, Ar *o*-CH_3), 18.8 (s, *o*-C*H_3), 85.0 (s, C_6H_6), 114.0 (s, Ph *o*-CH), 115.9 (s, *β*-*C*), 120.3 (q, $^1J_{CF}$ = 318.6 Hz, $CF_3SO_3^-$), 123.9 (s, Ph *p*-CH), 128.2 (s, Ar *p*-CH), 128.9 (s, Ar *p*-C*H), 129.5 (s, Ar *m*-C*H), 129.7 (s, Ar *m*-CH), 130.2 (s, Ar *o*-C*CH_3), 131.2 (s, Ar *o*-CCH_3), 137.0 (s, Ph *m*-C*H), 137.3 (s, Ph *m*-CH), 150.4 (s, Ph *C*=N), 158.8 (s, *i*-C*), 159.2 (s, *i*-*C*), 164.7 (s, N=C*H). ^{19}F NMR (376 MHz, 25 °C, CD_2Cl_2) δ (ppm): −78.68 (s, $^1J_{FC}$ = 318.6 Hz, $CF_3SO_3^-$). * = imine side. FT-IR (25 °C, CH_2Cl_2, KBr cell) υ (cm^{-1}): 3090(b, m), 2685(m), 2522(m), 2411(m), 2337(m), 2304(m), 2155(w), 2126(w), 2055(w), 1793(wv), 1772(vw), 1748(vw), 1633(m), 1607(m), 1574(w), 1531(m), 1185(m), 1031(vs), 840(vw), 636(vw).

*(η^6-C_6H_6)-Ru(Me)(2,6-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH$ (**5**).* A 200 mg (0.39 mmol) portion of (η^6-C_6H_6)-RuCl(2,6-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH$[29] was loaded into an oven-dried and N_2-flushed 50 mL Schlenk tube under inert conditions, and 0.45 mL (0.45 mmol) of a 1.0 M methylmagnesium bromide solution in dibutyl ether was added over 5 min at 0 °C, and the reaction was allowed to stir for 1 h. Dry and degassed *n*-pentane (10 mL) was added at 0 °C, and the reaction was allowed to warm to room temperature and stirred under N_2 for 12 h. The *n*-pentane solution was filtered over Celite under N_2, and the solvent was removed in vacuo to afford 120 mg (62%) of the title compound as a red-purple solid. Elemental analysis: found [calculated] C, 67.20 [67.31]; H, 6.83 [6.86]; N, 5.36 [5.61]. TOF MS-ES (25 °C, MeCN), positive mode (*m*/*z*): 485.20 [(M − Me)$^+$, 75%, calcd. 485.15], 501.00 [(M + H)$^+$, 70%, calcd. 501.18], 515.00 [parent (M −H + O)$^+$, 100%, calcd. 515.16]. ^1H NMR (400 MHz, 25 °C, C_6D_6) δ (ppm): 1.42 (s, 6H, *α*-CH_3), 1.94 (s, 3H, Ru−CH_3), 2.17 (s, 6H, *o*-CH_3), 2.42 (s, 6H, *o*-CH_3'), 3.91 (s, 6H, C_6H_6), 4.69 (s, 1H, *β*-CH), 6.87−6.91 (m, 2H, *p*-CH), 6.94−6.96 (m, 2H, *m*-CH), 7.02−7.04 (m, 2H, *m*-CH′). $^{13}C\{^1H\}$ NMR (101 MHz, 25 °C, C_6D_6) δ (ppm): 4.8 (s, Ru-CH_3), 19.0 (s, *o*-C′H_3), 19.9 (s, *o*-CH_3), 23.2 (s, *α*-CH_3), 86.5 (s, C_6H_6), 99.0 (s, *β*-CH), 124.5 (s, *p*-CH), 128.48 (s, *m*-C′H), 128.53 (s, *m*-CH), 132.1 (s, *o*-CCH_3), 133.4 (s, *o*-C′CH_3), 156.6 (s, *i*-*C*), 159.0 (s, *C*=N). FT-IR (25 °C, nujol mull, KBr discs) υ (cm^{-1}): 2820(vw), 2386(vw), 2349(vw), 1591(vw), 1563(w), 1552(m), 1514(s), 1426(s), 1402(vs), 1263(w), 1185(s), 1100(w), 1022(w), 972(vw), 770(m), 740(w).

Dehydrocoupling Reactions (Constant Volume). A typical procedure involved charging a preheated 50 mL Parr pressure reactor (see Supporting Information) with 954 mg (16.2 mmol) of *N*,*N*-dimethylamine borane and 0.5 mol % of **1** under a stream of N_2. The reactor was closed and placed in an oil bath to maintain the inner temperature at 42 °C. Anhydrous N_2-saturated THF, 5 mL (3.2 M solution of DMAB) was added through the sampling valve via syringe, and the reactor was sealed. The pressure increase was monitored at regular intervals using an automated pressure gauge (Impress Sensors and Systems). The recorded pressure was converted to H_2 equivalents using the ideal gas law with a reactor volume of 84 mL (including head space).

Dehydrocoupling Reactions (Constant Pressure). A custom-built two-way side arm reaction flask was charged on one side with 439 mg (7.5 mmol) of DMAB dissolved in 2.3 mL of anhydrous N_2 saturated THF (3.2 M). To the second side arm of the reaction flask, 24 mg (0.0375 mmol) of **1** was added under inert conditions. The reaction vessel was placed in a 25 °C water bath and connected to a 50 mL gas buret (Chemglass CG-1818) fitted with a 500 mL water reservoir and a thermometer. A bubbler was placed between the reaction vessel and the buret to ensure no contamination of the reaction vessel with water vapor. The system was flushed with N_2 prior to the experiment. To initiate the catalytic release of H_2, the DMAB/THF solution was poured onto the solid catalyst by inverting the reaction vessel. The water displacement in the buret was recorded at regular intervals, and the result was corrected for the given water vapor pressure and temperature of 20 °C.

■ ASSOCIATED CONTENT

Supporting Information

Additional data for the AB/DMAB dehydrogenation reactions and characterization of dehydrocoupling products, detailed information for the dehydrogenation reaction of DMAB with **5**, and crystallographic details for all relevant complexes, including CIF files, are provided. 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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■ REFERENCES

(1) Ahluwalia, R. K.; Hua, T. Q.; Peng, J. K. *Int. J. Hydrogen Energy* **2012**, *37*, 2891−2910.
(2) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613−2626.
(3) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279−293.
(4) Basu, S.; Zheng, Y.; Gore, J. P. *J. Power Sources* **2011**, *196*, 734−740.
(5) Zimmerman, P. M.; Zhang, Z.; Musgrave, C. B. *J. Phys. Chem. Lett.* **2011**, *2*, 276−281.
(6) Brockman, A.; Zheng, Y.; Gore, J. *Int. J. Hydrogen Energy* **2010**, *35*, 7350−7356.
(7) Liu, C.-H.; Wu, Y.-C.; Chou, C.-C.; Chen, B.-H.; Hsueh, C.-L.; Ku, J.-R.; Tsau, F. *Int. J. Hydrogen Energy* **2012**, *37*, 2950−2959.
(8) Sloan, M. E.; Clark, T. J.; Manners, I. *Inorg. Chem.* **2009**, *48*, 2429−2435.
(9) Ciganda, R.; Garralda, M. A.; Ibarlucea, L.; Pinilla, E.; Torres, M. R. *Dalton Trans.* **2010**, *39*, 7226−7229.
(10) Baker, R. T.; Gordon, J. C.; Hamilton, C. W.; Henson, N. J.; Lin, P.-H.; Maguire, S.; Murugesu, M.; Scott, B. L.; Smythe, N. C. *J. Am. Chem. Soc.* **2012**, *134*, 5598−5609.
(11) Robertson, A. P. M.; Suter, R.; Chabanne, L.; Whittell, G. R.; Manners, I. *Inorg. Chem.* **2011**, *50*, 12680−12691.

(12) Chen, G.; Desinan, S.; Rosei, R.; Rosei, F.; Ma, D. *Chem. Commun.* **2012**, *48*, 8009−8011.
(13) Clark, T. J.; Russell, C. A.; Manners, I. *J. Am. Chem. Soc.* **2006**, *128*, 9582−9583.
(14) Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 12048−12049.
(15) Staubitz, A.; Sloan, M. E.; Robertson, A. P. M.; Friedrich, A.; Schneider, S.; Gates, P. J.; Schmedt auf der Günne, J.; Manners, I. *J. Am. Chem. Soc.* **2010**, *132*, 13332−13345.
(16) Pons, V.; Baker, R. T.; Szymczak, N. K.; Heldebrant, D. J.; Linehan, J. C.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Chem. Commun.* **2008**, 6597−6599.
(17) Smythe, N. C.; Gordon, J. C. *Eur. J. Inorg. Chem.* **2010**, 509−521.
(18) Wright, W. R. H.; Berkeley, E. R.; Alden, L. R.; Baker, R. T.; Sneddon, L. G. *Chem. Commun.* **2011**, *47*, 3177−3179.
(19) Douglas, T. M.; Chaplin, A. B.; Weller, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 14432−14433.
(20) Douglas, T. M.; Chaplin, A. B.; Weller, A. S.; Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* **2009**, *131*, 15440−15456.
(21) Stevens, C. J.; Dallanegra, R.; Chaplin, A. B.; Weller, A. S.; MacGregor, S. A.; Ward, B.; McKay, D.; Alcaraz, G.; Sabo-Etienne, S. *Chem.—Eur. J.* **2011**, *17*, 3011−3020.
(22) Sewell, L. J.; Lloyd-Jones, G. C.; Weller, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 3598−3610.
(23) Blaquiere, N.; Diallo-Garcia, S.; Gorelsky, S. I.; Black, D. A.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 14034−14035.
(24) Alcaraz, G.; Vendier, L.; Clot, E.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 918−920.
(25) Boulho, C.; Djukic, J.-P. *Dalton Trans.* **2010**, *39*, 8893−8905.
(26) MacInnis, M. C.; McDonald, R.; Ferguson, M. J.; Tobisch, S.; Turculet, L. *J. Am. Chem. Soc.* **2011**, *133*, 13622−13633.
(27) Conley, B. L.; Guess, D.; Williams, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 14212−14215.
(28) Wallis, C. J.; Dyer, H.; Vendier, L.; Alcaraz, G.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 3646−3648.
(29) Phillips, A. D.; Laurenczy, G.; Scopelliti, R.; Dyson, P. J. *Organometallics* **2007**, *26*, 1120−1122.
(30) Spielman, J.; Jansen, G.; Bandmann, H.; Harder, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6290−6295.
(31) Spielmann, J.; Harder, S. *J. Am. Chem. Soc.* **2009**, *131*, 5064−5065.
(32) Spielmann, J.; Bolte, M.; Harder, S. *Chem. Commun.* **2009**, 6934−6936.
(33) Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; MacDougall, D. J. *Chem—Eur. J.* **2010**, *16*, 8508−8515.
(34) Moreno, A.; Pregosin, P. S.; Laurenczy, G.; Phillips, A. D.; Dyson, P. J. *Organometallics* **2009**, *28*, 6432−6441.
(35) Kaess, M.; Friedrich, A.; Drees, M.; Schneider, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 905−907.
(36) Friedrich, A.; Drees, M.; Schneider, S. *Chem.—Eur. J.* **2009**, *15*, 10339−10342.
(37) Conley, B. L.; Williams, T. J. *Chem. Commun.* **2010**, *46*, 4815−4817.
(38) Ledger, A. E. W.; Ellul, C. E.; Mahon, M. F.; Williams, J. M. J.; Whittlesey, M. K. *Chem.—Eur. J.* **2011**, *17*, 8704−8713.
(39) Swinnen, S.; Nguyen, V. S.; Nguyen, M. T. *Chem. Phys. Lett.* **2011**, *513*, 195−200.
(40) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514−1516.
(41) McGeachin, S. G. *Can. J. Chem.* **1968**, *46*, 1903−1912.
(42) Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1968**, *7*, 1408−1416.
(43) Rauchfuss, T. B., *Inorganic Syntheses*; John Wiley & Sons, Inc: New York, 2010; Vol. *35*; p 187.
(44) Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.; Noack, C. L.; Piers, W. E.; Parvez, M. *Organometallics* **2003**, *22*, 1577−1579.
(45) Budzelaar, P. H. M.; Van, O. A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485−1494.
(46) Carey, D. T.; Cope-Eatough, E. K.; Vilaplana-Mafe, E.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Dalton Trans.* **2003**, 1083−1093.
(47) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.* **2001**, *40*, 2794−2799.
(48) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le, P. L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307−6321.
(49) Shaw, W. J.; Linehan, J. C.; Szymczak, N. K.; Heldebrant, D. J.; Yonker, C.; Camaioni, D. M.; Baker, R. T.; Autrey, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7493−7496.
(50) Dietrich, B. L.; Goldberg, K. I.; Heinekey, D. M.; Autrey, T.; Linehan, J. C. *Inorg. Chem.* **2008**, *47*, 8583−8585.
(51) Hebden, T. J.; Goldberg, K. I.; Heinekey, D. M.; Zhang, X.; Emge, T. J.; Goldman, A. S.; Krogh-Jespersen, K. *Inorg. Chem.* **2010**, *49*, 1733−1742.
(52) Paul, A.; Musgrave, C. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 8153−8156.
(53) Demirci, U. B.; Bernard, S.; Chiriac, R.; Toche, F.; Miele, P. *J. Power Sources* **2011**, *196*, 279−286.
(54) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317−341.
(55) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776−9785.
(56) Zahmakiran, M.; Ayvalı, T.; Philippot, K. *Langmuir* **2012**, *28*, 4908−4914.
(57) Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, 2003; p 608.
(58) Ortmann, R.; Schlitzer, M. *Synthesis* **2009**, 1757−1759.
(59) Ramachandran, P. V.; Gagare, P. D. *Inorg. Chem.* **2007**, *46*, 7810−7817.
(60) Bennett, M. A.; Smith, A. K. *Dalton Trans.* **1974**, 233−241.
(61) Vriamont, N.; Govaerts, B.; Grenouillet, P.; de Bellefon, C.; Riant, O. *Chem.—Eur. J.* **2009**, *15*, 6267−6278.
(62) Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P. *Dalton Trans.* **2001**, 3465−3469.
(63) Gao, H.; Guo, W.; Bao, F.; Gui, G.; Zhang, J.; Zhu, F.; Wu, Q. *Organometallics* **2004**, *23*, 6273−6280.