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Rhenium Hydride/Boron Lewis Acid Cocatalysis of Alkene Hydrogenations: Activities Comparable to Those of Precious Metal Systems

Yanfeng Jiang, Jeannine Hess, Thomas Fox, and Heinz Berke*

Anorganisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190,
CH-8037 Zürich, Switzerland

Received August 10, 2010; E-mail: hberke@aci.uzh.ch

Abstract: Dibromonitrosyl(dihydrogen)rhenium(I) complexes $[ReBr_2(NO)(PR_3)_2(\eta^2\text{-}H_2)]$ (**1**; R = *i*Pr, **a**; Cy, **b**) and $Me_2NH\cdot BH_3$ (DMAB) catalyze at either 90 °C or ambient temperature under 10 bar of H_2 the hydrogenation of various terminal and cyclic alkenes (1-hexene, 1-octene, cyclooctene, styrene, 1,5-cyclooctadiene, 1,7-octadiene, α-methylstyrene). Maximum turnover frequency (TOF) values of 3.6×10^4 h^{-1} at 90 °C and 1.7×10^4 h^{-1} at 23 °C were achieved in the hydrogenation of 1-hexene. The extraordinary catalytic performance of the **1**/DMAB system is attributed to the formation of five-coordinate rhenium(I) hydride complexes $[Re(Br)(H)(NO)(PR_3)_2]$ (**2**; R = *i*Pr, **a**; Cy, **b**) and the action of the Lewis acid BH_3 originating from DMAB. The related **2**/$BH_3\cdot THF$ catalytic system also exhibits under the same conditions high activity in the hydrogenation of various alkenes with a maximum turnover number (TON) of 1.2×10^4 and a maximum TOF of 4.0×10^4 h^{-1}. For the hydrogenations of 1-hexene with **2a** and **2b**, the effect of the strength of the boron Lewis acid was studied, the acidity being in the following order: $BCl_3 > BH_3 > BEt_3 \approx BF_3 > B(C_6F_5)_3 > BPh_3 \gg B(OMe)_3$. The order in catalytic activity was found to be $B(C_6F_5)_3 > BEt_3 \approx BH_3\cdot THF > BPh_3 \gg BF_3\cdot OEt_2 > B(OMe)_3 \gg BCl_3$. The stability of the catalytic systems was checked via TON vs time plots, which revealed the boron Lewis acids to cause an approximate inverse order with the Lewis acid strength: $BPh_3 > BEt_3 \approx BH_3\cdot THF > B(C_6F_5)_3$. For the **2a**/$BPh_3$ system a maximum TON of 3.1×10^4 and for the **2a**/$B(C_6F_5)_3$ system a maximum TOF of 5.6×10^4 h^{-1} were obtained in the hydrogenation of 1-hexene. On the basis of kinetic isotope effect determinations, H_2/D_2 scrambling, halide exchange experiments, Lewis acid variations, and isomerization of terminal alkenes, an Osborn-type catalytic cycle is proposed with olefin before H_2 addition. The active rhenium(I) monohydride species is assumed to be formed via reversible bromide abstraction with the "cocatalytic" Lewis acid. Homogeneity of the hydrogenations was tested with filtration and mercury poisoning experiments. These "rhenium(I) hydride/boron Lewis acid" systems demonstrate catalytic activities comparable to those of Wilkinson- or Schrock−Osborn-type hydrogenations accomplished with precious metal catalysts.

Introduction

Rhenium as a border element to precious metals is expected to display in its chemistry at least some of the features of its precious metal neighbors.[1] For instance, like precious metals, rhenium is able to undergo facile redox changes,[2] which is for many cases an important prerequisite to achieve proper catalytic performance. However, in contrast to precious metals, rhenium tends to obey, like middle transition element compounds in general, the 18 e^- rule, which limits ligand exchange or the adoption of low coordination numbers. This presumably is the main reason for the as yet restricted applicability of low-valent rhenium in homogeneous catalysis.[3] In this context, it is worth mentioning that rhenium compounds in higher oxidation states often possess 16 or 14 e^- counts, and hence, these reveal higher propensity for catalytic transformations.[4] We thus realized that for the exploitation of low-valent rhenium complexes in catalysis a tuning of the coordination sphere for ligand lability would become necessary using ancillary ligand effects, such as the *trans* effect,[5] the *cis* labilization effect,[6] and effects from ligands with variable electron counts,[7] or eventually utilizing the help

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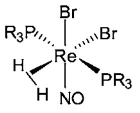
of additional reagents functioning as cocatalysts. In analogy to octahedral ruthenium systems,[8] which possess a priori higher ligand lability and therefore often great catalytic potential, we wanted to approach homogeneous rhenium hydrogenations exploiting among other effects the unique capability of the nitrosyl ligand to exert the *trans* effect.[9] Also by the isoelectronic analogy of Re−NO (NO is a 3 e^- donor; NO^+ is a 2 e^- donor) with the a Ru−L (L = 2 e^- donor) unit, we predicted a respective impact of rhenium compounds on the hydrogenations close to that of ruthenium.[10]

Rhenium(I) complexes containing the nitrosyl and halide ligands have recently been shown to display high affinity to hydrogen and olefins and were found active in hydrogenation (of olefins and imines)[11] and dehydrogenation catalysis (of amine boranes).[12] Related catalyses of hydrosilylations and dehydrogenative silylations could also be established.[13] Therefore, we thought we could "tune" Re(I) complexes for improved performance in hydrogen catalysis by providing assistance in ligand replacements through the cocatalysis with Lewis acids. Thus, novel catalytic systems for highly efficient hydrogenations of alkenes were created consisting of the rhenium(I) bromo hydride complexes **1**−**4** and boron Lewis acids (BR'_3; R′ = H, Et, Ph, C_6F_5). Detailed mechanistic studies were carried out to shed light on the reaction courses of such new catalyses with emphasis on the special role of the boron Lewis acid.



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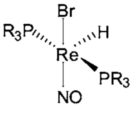

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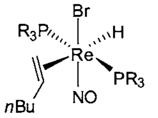

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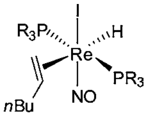

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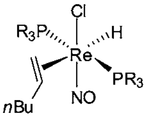

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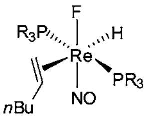

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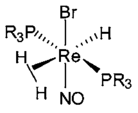

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R = *i*Pr (**a**), Cy (**b**)

Results and Discussion

Exploration of "Re(I)/Boron Lewis Acid" Cocatalyzed Hydrogenations of Alkenes. Rhenium(I) nitrosyl complexes $[ReBr_2(NO)(PR_3)_2(\eta^2\text{-}H_2)]$ (**1**; R = *i*Pr, **a**; Cy, **b**) bearing two *trans*-phosphine ligands were previously reported to catalyze the dehydrogenation of $Me_2NH\cdot BH_3$ (DMAB) and transfer hydrogenations of olefins using DMAB as a hydrogen donor.[12] In extension of this work we realized that the combination of **1** with DMAB led to an efficient catalytic system for hydrogenations of alkenes. For instance, **1a** alone showed only moderate activity in hydrogenations. When a mixture of 5 mL of 1-hexene and 0.03 mol % **1a** was treated with 10 bar of H_2, a 60% conversion was achieved within 3 h at 90 °C, giving a turnover frequency (TOF) value of 803 h^{-1} (Table 1). In comparison, when 0.15 mol % DMAB was added as a cocatalyst, 82% conversion was achieved within only 5 min, giving a turnover number (TON) of 2987 and a TOF of 3.5×10^4 h^{-1}, which means a 43 times acceleration compared to the reaction of **1a** alone. Similar results were obtained using the **1b**/DMAB (1:5) system under the same conditions, where a TON of 3014 and a TOF of 3.6×10^4 h^{-1} were obtained within 5 min. The active species stayed "alive" after catalysis, since readdition of 5 mL of 1-hexene to the resultant solution still afforded a TON of 3213 and TOF of 1.3×10^4 within 15 min. With other alkenes, such as 1-octene, cyclooctene, styrene, and also dienes, such as 1,5-cyclooctadiene and 1,7-octadiene, the **1**/DMAB (1:5) system showed excellent performance in the hydrogenations, leading to satisfactory TONs and TOFs under the condition of full conversions. Only in the case of 1,1-disubstituted alkenes, such as α-methylstyrene, did the hydrogenations proceed slower. Generally, the pursuit of high TONs worked at the expense of the performance in TOFs. For instance, despite the fact that a high TON (8291) was achieved in the hydrogenation of styrene when **1a** was loaded at 0.011 mol % into the catalytic system, the TOF was 2 times less than that with 0.02 mol % **1a**/DMAB. This was even more pronounced in the case of 1,7-octadiene, where the reaction with 0.06 mol % **1a** was nearly 8 times faster than that with 0.03 mol % **1b**. It is also important to note that not only were full conversions accomplished in all cases, but also the catalyses could be carried out under solvent-free conditions. Thus, the hydrogenated products could be easily isolated by distillation.

Previously, we demonstrated that the reactions of **1a,b** with DMAB could generate the five-coordinate rhenium(I) hydrides

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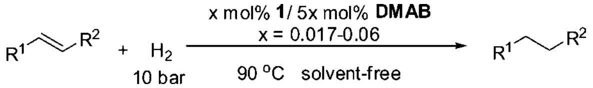
Table 1. Hydrogenations of Alkenes Catalyzed by the **1**/DMAB System at 90 °C under 10 bar of H_2[a]



entry	alkene (vol, mL)	catalyst (amt, mmol)	*T* (h)	conversion (%)	TON	TOF (h^{-1})	isolated (%)
1[b]	1-hexene (0.01)	**1a**/DMAB (0.010)	1/12	30	3		
2	1-hexene (5)	**1a** (0.010)	3	60	2410	803	
3	1-hexene (5)	**1a**/DMAB (0.011)	1/12	82	2987	3.5×10^4	
4	1-hexene (5)	**1b**/DMAB (0.011)	1/12	83	3014	3.6×10^4	
5[c]	1-hexene (5)	**1b**/DMAB (0.011)	0.25	88	3213	1.3×10^4	
6	1-hexene (10)	**1a**/DMAB (0.020)	0.5	100	4005	8010	93
7	1-hexene (10)	**1b**/DMAB (0.020)	1.0	100	4005	4005	92
8	1-octene (10)	**1a**/DMAB (0.011)	0.5	89	5178	1.1×10^4	
9	1-octene (10)	**1a**/DMAB (0.011)	1.5	100	5818	3879	87
10	1-octene (10)	**1b**/DMAB (0.011)	1.2	100	5818	4848	93
11	cyclooctene (10)	**1a**/DMAB (0.011)	6	97	6769	1128	86
12	cyclooctene (10)	**1b**/DMAB (0.015)	1.5	100	5117	3411	95
13	styrene (10)	**1a**/DMAB (0.010)	24	95	8291	345	
14	styrene (10)	**1a**/DMAB (0.020)	6	100	4365	727	78
15	styrene (10)	**1b**/DMAB (0.020)	3	100	4365	1455	88
16	α-methylstyrene (5)	**1a**/DMAB (0.020)	6.5	100	1933	297	89
17	α-methylstyrene (5)	**1b**/DMAB (0.020)	3	100	1933	644	86
18[d]	cyclooctadiene (5)	**1a**/DMAB (0.020)	1.0	100	2041	2041	93
19[d]	cyclooctadiene (5)	**1b**/DMAB (0.020)	2.5	100	2041	816	93
20[e]	1,7-octadiene (5)	**1a**/DMAB (0.020)	0.2	100	1680	8400	88
21[e]	1,7-octadiene (10)	**1b**/DMAB (0.020)	3.0	100	3360	1120	85

[a] Reactions were performed using 10 or 5 mL of alkene, 0.01−0.02 mmol of **1**, and 3.0−6.0 mg of DMAB and monitored with a Buechi Pressflow controller under 10 bar of H_2 at 90 °C. [b] The reaction was carried out in toluene-d_8 without H_2. [c] Second run of entry 3 with 5 mL of 1-hexene. [d] Hydrogenated to cyclooctane (2 equiv of H_2 was consumed). [e] Hydrogenated to octane (2 equiv of H_2 was consumed).

[Re(Br)(H)(NO)(PR_3)$_2$] (**2**; R = *i*Pr, **a**; Cy, **b**) via heterolytic cleavage of the H−H bond.[14] The catalytic activity of **2a** in the hydrogenation of 1-hexene was referenced to the activity of **1a**. **2a** proved to be 2 times as active as **1a**, but both catalysts were much less active than the **1a**/DMAB system. Furthermore, addition of DMAB to **2a** resulted in the same catalytic activity as found for the **1a**/DMAB system in the hydrogenation of 1-hexene and 1-octene. Not only was a high TOF of 3.1×10^4 h^{-1} obtained in the case of 1-hexene (5 mL) using a 0.025 mol % **2a**/DMAB (1:5) mixture, but also the catalytic species was revealed to be "living", affording a TOF of 1.5×10^4 h^{-1} within 15 min after readdition of 5 mL of 1-hexene. Replacement of DMAB with $BH_3 \cdot THF$ resulted in a slightly higher activity. When 5 mL of 1-hexene was treated with 0.03 mol % **2a** and 0.15 mol % $BH_3 \cdot THF$, a 92% conversion was achieved at 90 °C within 5 min corresponding to a TON of 3083 and a TOF of 3.7×10^4 h^{-1}. The active species of the **2a**/$BH_3 \cdot THF$ system has a longer lifetime than that of the **2a**/DMAB system since readdition of 5 mL of 1-hexene results in a 98% conversion within 10 min corresponding to a TON of 3350 and TOF of 2.0×10^4 h^{-1}. This procedure was repeated twice, leading to some decrease in activity, but in absolute terms still high TOFs of 1.3×10^4 h^{-1} (third run) and 7558 h^{-1} (fourth run) were determined (Figure 1). The rate of the catalysis seemed to correlate with the alkene concentration. Due to the living character of the **2**/$BH_3 \cdot THF$ system, the loading of **2a,b** could be decreased to a value of 0.006 mol % (60 ppm), affording a TON of 1.2×10^4 and a TOF of 4.0×10^4 h^{-1} within 18 min (**2a**/$BH_3 \cdot THF$) or a TON of 9942 and a TOF of 2.5×10^4 h^{-1} within 24 min (**2b**/$BH_3 \cdot THF$). With other substrates such as 1-octene, cyclooctene, α-methylstyrene, 1,5-cyclooctadiene, and 3,3-dimethylbutene, the **2**/$BH_3 \cdot THF$ system performed also extremely well, resulting in both high TONs and high TOFs, as depicted in Table 2. Strangely enough, the hydrogenations of allyl derivatives, such as allylbenzene and allyltrimethylsilane, were slow, which may point to the formation of allyl complexes which block the catalyses. It should be noted that under a H_2 atmosphere at 90 °C, only trace amounts of isomerization products of the terminal alkenes could be observed after catalysis using ^1H NMR spectroscopy.

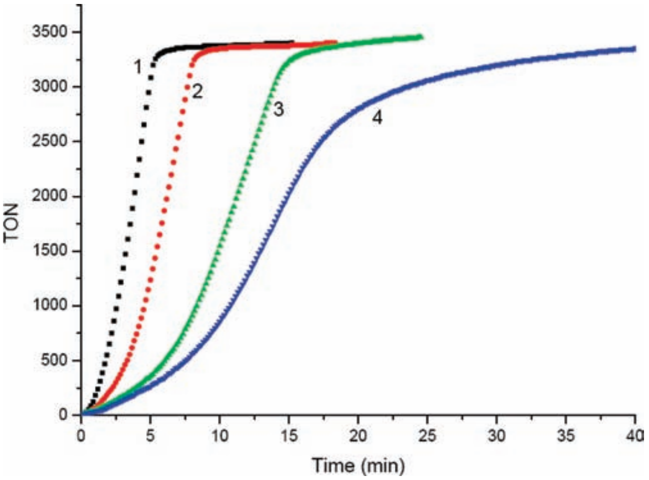


Figure 1. Repeated hydrogenations of 1-hexene (5 mL × 4) catalyzed by the **2a**/$BH_3 \cdot THF$ (7 mg/50 μL) system at 90 °C under 10 bar of H_2: ■, first run, 5 min, 92%, TON = 3083, TOF = 3.7×10^4 h^{-1}; ●, second run, 10 min, 98%, TON = 3350, TOF = 2.0×10^4 h^{-1}; ▲, third run, 15 min, 95%, TON = 3240, TOF = 1.3×10^4 h^{-1}; ▼, fourth run, 24 min, 89%, TON = 3023, TOF = 7558 h^{-1}.

1. Influence of the Type of Boron Lewis Acid. Under the same conditions other boron Lewis acids were tested as cocatalysts in the hydrogenations with **2a,b** as well. The Lewis acidity of the employed boron Lewis acid was initially tested by the

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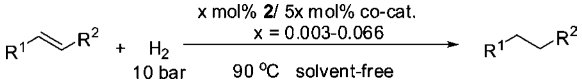
Table 2. Hydrogenations of Alkenes Catalyzed by **2** and Various Boron Lewis Acids at 90 °C[a]



entry	alkene (vol, mL)	catalyst (*x*; amt, mmol)	*T* (h)	conversion (%)	TON	TOF (h^{-1})
1	1-hexene (5)	**2a** (0.030; 0.012)	1.0	56	1860	1860
2	1-hexene (5)	**2a**/DMAB (0.025; 0.010)	0.11	86	3455	3.1×10^4
3	1-octene (5)	**2a**/DMAB (0.016; 0.005)	0.5	94	5897	1.2×10^4
4	1-hexene (5)	**2a**/BH_3 THF (0.030; 0.012)	1/12	92	3083	3.7×10^4
5	1-hexene (10)	**2a**/BH_3 THF (0.006; 0.005)	0.3	73	1.2×10^4	4.0×10^4
6	1-hexene (10)	**2b**/BH_3THF (0.006; 0.005)	0.4	62	9942	2.5×10^4
7	cyclooctene (5)	**2a**/BH_3 THF (0.026; 0.010)	0.4	75	2866	7165
8	cyclooctene (5)	**2b**/BH_3THF (0.026; 0.010)	1/3	90	3468	1.0×10^4
9[b]	1-octene (10)	**2a**/BH_3 THF (0.015; 0.010)	0.4	83	5525	1.4×10^4
10	1-octene (1 0)	**2b**/BH_3THF (0.015; 0.010)	1/3	81	5401	1.6×10^4
11	cyclooctadiene (5)	**2a**/BH_3 THF (0.024; 0.010)	6.0	96	4000	667
12	α -methylstyrene (5)	**2b**/BH_3THF (0.025; 0.010)	7.0	68	2700	385
13	1-hexene (5)	**2a**/BF_3OEt_2 (0.030; 0.012)	0.5	99	3331	6662
14	1-hexene (5)	**2a**/BCl_3 (0.030; 0.012)	2.0	0	0	0
15	1-hexene (5)	**2a**/$B(OMe)_3$ (0.030; 0.012)	0.6	50	1659	2765
16	1-hexene (5)	**2a**/B(hexyl)$_3$[c] (0.030; 0.012)	0.1	97	3227	3.2×10^4
17	1-hexene (5)	**2a**/BEt_3 (0.015; 0.006)	0.1	47	3777	3.8×10^4
18	1-hexene (5)	**2a**/BPh_3 (0.025; 0.010)	0.1	88	3517	3.5×10^4
19	1-hexene (20)	**2a**/BPh_3 (0.003; 0.005)	1.0	87	2.9×10^4	2.9×10^4
20	1-hexene (20)	**2b**/BPh_3 (0.003; 0.005)	1.5	93	3.1×10^4	2.1×10^4
21	1-octene (10)	**2a**/BPh_3 (0.008; 0.005)	0.3	88	1.1×10^4	3.7×10^4
22	1-octene (20)	**2b**/BPh_3 (0.004; 0.005)	1.0	56	1.4×10^4	1.4×10^4
23	cyclohexene (5)	**2a**/BPh_3 (0.020; 0.010)	0.25	65	3260	1.3×10^4
24	cyclohexene (5)	**2b**/BPh_3 (0.020; 0.010)	0.3	51	2544	8480
25	1-hexene (5)	**2a**/$B(C_6F_5)_3$ (0.025; 0.010)	0.06	84	3343	5.6×10^4
26	3,3-dimethylbutene (5)	**2a**/BH_3 THF (0.026; 0.010)	1/12	35	1348	1.6×10^4
27	3,3-dimethylbutene (5)	**2a**/BPh_3 (0.026; 0.010)	1/12	52	2000	2.4×10^4
28	allylbenzene (2)	**2a**/BPh_3 (0.066; 0.010)	4.0	62	946	237
29	allyltrimethylsilane (2)	**2a**/$B(C_6F_5)_3$ (0.04; 0.005)	8.0	100	2500	312
30	1-methyl- 1-cyclohexene (1)	**2a**/$B(C_6F_5)_3$ (0.14; 0.012)	1/3	72	517	1551
31	2,3-dimethyl-2-butene (2)	**2a**/$B(C_6F_5)_3$ (0.03; 0.005)	8.0			
32[d]	1-hexene (5)	**2a**/$B(C_6F_5)_3$ (0.025; 0.01)	1.0	50	2013	2013
33[d]	cyclohexene (5)	**2a**/$B(C_6F_5)_3$ (0.020; 0.01)	1.0	7	384	384
34[d]	1-methyl-1-cyclohexene (1)	**2a**/$B(C_6F_5)_3$ (0.19; 0.016)	1.25	36	190	152

[a] Reactions were performed using 1−20 mL of the alkene, *x* mol % **2** (0.005−0.016 mmol), and 5*x* mol % cocatalyst and monitored by a Buechi Pressflow controller under 10 bar of H_2 at 90 °C. [b] With 10 equiv of BH_3THF relative to **2b**. [c] In situ prepared. [d] Under 1 bar of H_2 at 90 °C.

Gutmann−Beckett method[15] and was found to follow the order BCl_3 (129.2%) > BH_3 (124.8%) > BEt_3 (104.4%) ≈ BF_3 (104.4%) > $B(C_6F_5)_3$ (100%) > BPh_3 (77.8%) ≫ $B(OMe)_3$ (4.2%) (in parentheses is the Gutmann−Beckett value (%) with reference to $B(C_6F_5)_3$). Weaker Lewis acids such as $B(OMe)_3$ did not reveal any rate enhancement with respect to the catalyses of the rhenium complexes alone. Strong Lewis acids, such as $BF_3 \cdot OEt_2$, did show an effect but were found less active than $BH_3 \cdot THF$. In the case of the stronger Lewis acid BCl_3, hydrogenations even failed. The weak Lewis acid BPh_3 turned out to be the most efficient cocatalyst, also demonstrating the longest lifetime of the active species. When 5 mL of 1-hexene was treated with 0.025 mol % **2a** and 0.125 mol % BPh_3 under 10 bar of H_2, a TON of 3517 and a TOF of 3.5×10^4 h^{-1} were obtained at 90 °C within 6 min. Repeated addition of 10 mL of 1-hexene (three times) to the resultant solution still afforded TONs of 6849, 7085, and 6652 corresponding to TOFs of 2.3×10^4, 2.1×10^4, and 1.3×10^4 h^{-1}, respectively. Thus, the loading of **2** could be further decreased to 0.003 mol % in the hydrogenation of 1-hexene. In the case of 1-octene, a low catalyst loading of 0.004−0.008 mol % resulted in both high TONs and high TOFs (Table 2). The relatively bulky Lewis acid $B(C_6F_5)_3$ of medium strength afforded the highest TOF (3.6 min, 84%, 5.6×10^4 h^{-1}) in the hydrogenation of 1-hexene at 90 °C. However, readdition of 1-hexene resulted in a much slower reaction rate, meaning that the catalytic system had a limited stability. The hydrogenation of the more sterically hindered alkenes, such as 1-methyl-1-cyclohexene, proceeded fast with the "**2a**/$B(C_6F_5)_3$" system (0.14 mol %, 1:5), affording a relatively good TOF of 1551 h^{-1} within 20 min corresponding to 72% conversion (Table 2, entry 30). In the case of the most hindered alkene 2,3-dimethyl-2-butene, unfortunately no reaction occurred at all. The **2a**/$B(C_6F_5)_3$ system is so active that the catalysis could even be carried out under 1 bar of H_2. For example, a TON of 2013 and a TOF of 2013 h^{-1} were achieved within a reaction time of 1 h in the hydrogenation of 1-hexene under 1 bar of H_2 at 90 °C (Table 2, entry 32), and a TON of 384 and a TOF of 384 h^{-1} within 1 h were obtained in the case of cyclohexene under the same conditions (Table 2, entry 33). Even the trisubstituted olefin 1-methyl-1-cyclohexene furnished an acceptable TON of 190 and TOF of 152 h^{-1} within 75 min under 1 bar of H_2 at 90 °C (Table 2, entry 34). No catalytic activity was observed in the hydrogenation of tetrasubstituted olefin 2,3-dimethyl-2-butene under the same conditions.

2. Ambient Temperature Hydrogenations. We next compared the catalytic activities of different systems for the hydrogenation of 1-hexene (5 mL) at ambient temperature (23 °C). With a

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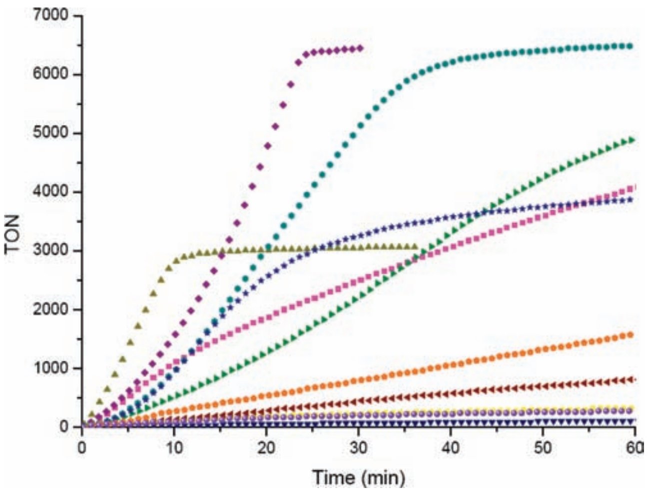

Figure 2. Ambient temperature hydrogenation of 1-hexene (5 mL) catalyzed by 0.012 mol % **2a/**boron Lewis acid: pink solid squares, **2a**/$BH_3\cdot THF$; yellow solid circles, **2a**/DMAB; green solid triangles, **1a**/DMAB; blue inverted solid triangles, **2a**/$BF_3\cdot OEt_2$; purple solid tilted squares, **2a**/$B(C_6F_5)_3$ (1:5); brown left-pointing solid triangles, **2a**/BPh_3; green right-pointing solid triangles, **2a**/BEt_3; aqua solid circles, **2a**/$B(C_6F_5)_3$ (1:4); blue solid stars, **2a**/$B(C_6F_5)_3$ (1:3); orange solid circles, **2a**/$B(C_6F_5)_3$ (1:2); purple solid circles, **2a**/$B(C_6F_5)_3$ (1:1).

catalyst loading of 0.025 mol % **1a** or **2a**, the hydrogenation did not occur at all at 23 °C, but could be initiated at high temperature, probably inducing phosphine dissociation or an isomerization to a geometry with *cis* alignment of the alkene and the hydride.[16] In the presence of 0.06 mol % boron Lewis acid, the hydrogenations catalyzed by **2a** (0.012 mol %) occurred with reaction rates in the order of $B(C_6F_5)_3 > BEt_3 \approx BH_3\cdot THF > BPh_3 > DMAB > BF_3\cdot OEt_2$, as depicted in Figure 2. The **2a**/DMAB system operated at an extremely slow rate, giving a TOF of 321 h^{-1} within 1 h. In contrast, the **2a**/$BH_3\cdot THF$ system showed a satisfying activity with a TOF of 4066 h^{-1} (61%) within 1 h. This can be interpreted in terms of the fact that $BH_3\cdot THF$ is a better Lewis acid than DMAB and that the BH_3 group dissociates more easily from the Me_2NH Lewis base than from THF. The **1a**/DMAB (0.012 mol %) system worked even better than **2a**/$BH_3\cdot THF$ at 23 °C, giving a TON of 2803 and a TOF of 1.7×10^4 h^{-1} within 10 min, as BH_3 can be freed in the process from **1a** to **2a**.[14] The disadvantage of the **1a**/DMAB system is its drop-off in catalysis, with a tremendously slowed reaction after 35% conversion. The weak Lewis acid BPh_3 performed not as efficiently at 23 °C as at 90 °C, giving a TOF of 812 h^{-1}. The better Lewis acid BEt_3 showed an improved activity with a TOF of 4901 h^{-1} within 1 h. The most active cocatalyst for the hydrogenation of 1-hexene at 23 °C proved to be the medium Lewis acid $B(C_6F_5)_3$, which afforded a TON of 6321 and a TOF of 1.6×10^4 h^{-1} within 24 min, corresponding to 79% conversion. In contrast, the stronger Lewis acid $BF_3\cdot OEt_2$ afforded at this temperature the lowest TOF of 107 h^{-1} within 1 h, which might be due to complex irreversible reactions with **2a** or halide exchange with fluoride, among others.

3. Influence of the Cocatalyst Loading. The influence of the cocatalyst loading was examined exemplarily for the **2a**/$B(C_6F_5)_3$ system. In the range of 1:1 to 1:5 ratios of **2a** and $B(C_6F_5)_3$, the reaction proceeded with increasing rates with TOFs of 507 h^{-1} (1:1, 20 min), 1571 h^{-1} (1:2, 1 h), 5807 h^{-1} (1:3, 18 min), 7978 h^{-1} (1:4, 48 min), and 1.6×10^4 h^{-1} (1:5, 24 min), respectively. There is a sharp increase in the performance from the 1:3 ratio (46%) to the 1:4 ratio (over 80%). The presence of a Re−H bond proved to be crucial to the catalyses, since the hydrogenation of 1-hexene at 23 °C catalyzed by the **1a**/BEt_3 system is much slower (TOF of 200 h^{-1}, 30 min) than with the **2a**/BEt_3 system. The **1a**/$B(C_6F_5)_3$ combination showed no reaction at room temperature at all. Other alkenes, such as 1-octene, cyclohexene, cyclooctene, 1,5-cyclooctadiene, styrene, and 3,3-dimethylbutene, could also be hydrogenated at ambient temperature, affording satisfactory TOFs using **1a**/DMAB, **2a**/$B(C_6F_5)_3$, or **2a**/$BH_3\cdot THF$ as the catalyst system, as depicted in Table 3. It should be noted that isomerization of alkenes was not observed in all these cases when the reaction was performed under a H_2 atmosphere and at ambient temperature. Similarly, applying the most active catalytic system of our series, **2a**/$B(C_6F_5)_3$, we found hydrogenations to perform surprisingly good at ambient temperature under 1 bar of H_2. A TON of 2875 and a TOF of 1725 h^{-1} were achieved within 100 min in the hydrogenation of 1-hexene, and a TON of 230 and a TOF of 230 h^{-1} were obtained within 1 h in the case of cyclohexene.

Mechanistic Studies. 1. Deuterium Isotope Studies. Deuterium isotope kinetics were pursued with 10 bar of H_2 or D_2 in the hydrogenation of 1-hexene with **2a**/$BH_3\cdot THF$ (0.030 mol %, 1:5) at different temperatures. At 23 °C, a kinetic isotope effect (KIE) value of 1.11 was determined with initial TOFs of 6107 h^{-1} (H_2) and 5521 h^{-1} (D_2) within 18 min. The reactions at 60 and 90 °C proceeded much faster ($1.5{-}1.6 \times 10^4$ h^{-1} within 9−10 min at 60 °C and $3.1{-}3.7 \times 10^4$ h^{-1} within 5−6 min at 90 °C), giving similar but on an absolute scale small KIE values of 1.07 (60 °C) and 1.19 (90 °C). In general, very small kinetic isotope effects were seen, which might imply that hydrogen-related transformations such as H−H splitting, β hydride shift (olefin insertion), and reductive elimination are not rate-determining steps, since KIEs with rate-determining H_2 splitting are generally high,[17] and those of reductive eliminations of alkanes are often inverse.[18] The KIEs of β hydride shifts

$$L_nM(H)(CH_2=CHR^1) \rightarrow L_nM(CH_2-CH_2R^1)$$

are in most cases small,[19] which leaves some ambiguity of whether the olefin insertion is rate-determining in the catalyses or other steps which do not involve X−H bond breakages. Ligand replacements, for instance, are in hydrogenations not expected to be associated with any primary KIE_1, but since the

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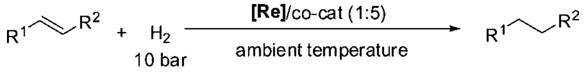
Table 3. Hydrogenation of Alkenes Catalyzed by Re/Boron Lewis Acid at Ambient Temperature[a]



entry	alkene (vol, mmol)	catalyst (amt, mmol)	*T* (min)	TON	TOF (h^{-1})
1	1-hexene (40)	**1a** (0.010)	60	0	0
2	1-hexene (40)	**2a** (0.010)	60	0	0
3	1-hexene (40)	**2a**/DMAB (0.005)	60	321	321
4	1-hexene (40)	**2a**/BH_3THF (0.005)	60	4066	4066
5	1-hexene (40)	**2a**/BEt_3 (0.005)	60	4901	4901
6	1-hexene (40)	**2a**/BPh_3 (0.005)	60	812	812
7	1-hexene (40)	**1a**/DMAB (0.005)	10	2803	1.7×10^4
8	1-hexene (40)	**1b**/DMAB (0.005)	3	357	7140
9	1-hexene (40)	**2a**/$B(C_6F_5)_3$ (0.005)	24	6321	1.6×10^4
10	1-hexene (40)	**2b**/$B(C_6F_5)_3$ (0.005)	3	1026	2.0×10^4
11	1-octene (10)	**1a**/DMAB (0.005)	5	1750	2.1×10^4
12	1-octene (10)	**2a**/$B(C_6F_5)_3$ (0.005)	15	1964	7856
13	cyclohexene (10)	**1a**/DMAB (0.005)	10	464	2784
14	cyclohexene (5)	**2a**/BH_3THF (0.010)	5	200	2400
15	cyclohexene (10)	**2a**/$B(C_6F_5)_3$ (0.005)	5	1196	1.4×10^4
16	1,5-cyclooctadiene (3)	**2a**/BH_3THF (0.005)	20	491[b]	1473
17	cyclooctene (10)	**1a**/DMAB (0.005)	30	1200	2400
18	cyclooctene (10)	**2a**/$B(C_6F_5)_3$ (0.005)	5	161	1932
19	styrene (10)	**1a**/DMAB (0.005)	12	200	1000
20	3,3-dimethylbutene (10)	**2a**/$B(C_6F_5)_3$ (0.005)	5	1339	1.6×10^4
21[c]	1-hexene (5)	**2a**/$B(C_6F_5)_3$ (0.012)	100	2875	1725
22[c]	cyclohexene (5)	**2a**/$B(C_6F_5)_3$ (0.012)	60	230	230

[a] Reactions were performed using 3−40 mmol of alkene, *x* mmol of Re, and 5*x* mmol of cocatalyst under 10 bar of H_2 at ambient temperature. [b] A 2 equiv amount of H_2 was consumed to produce cyclooctane. [c] Under 1 bar of H_2 at 23 °C.

determined KIEs are slightly greater than 1.0, we might be inclined to state that the olefin insertion into Re−H could to a very small extent participate in the rate-determining step(s) of the described catalyses and cause a small KIE_1.

2. Filtration and Mercury Poisoning Experiments. To exclude any heterogeneous reaction course in the hydrogenation catalyses, filtration experiments were carried out.[20] At 50% conversion (TON of 2000) of the hydrogenation of 1-hexene (5 mL) catalyzed by the **2a**/$BH_3 \cdot$THF system at 90 °C under 10 bar of H_2, the reaction solution was found to be of a light brown color and clear without any visible precipitate. Repeated trials showed no black precipitate or dark solutions expected for metallic or colloidal rhenium. The ^{31}P NMR spectrum of the filtrate indicated that **3a** remained in solution as the major rhenium-containing species (66% by integration) along with 10% free P*i*Pr_3 and a 24% concentration of one yet unknown organometallic species showing a singlet at δ 55.4 ppm. The solution was filtered through Celite into a new vessel with a new stirring bar, and 2 mL of additional 1-hexene was added. The catalysis was conducted again at 90 °C under 10 bar of H_2, revealing a high TOF value of 1.2×10^4 h^{-1} within 10 min, which indeed implies a homogeneous reaction course. The slight reduction of the originally higher activity is most probably due to the loss of the active rhenium species via yet unidentified side reactions during the filtration process. The catalytic potential of the Celite after the filtration step was examined in the hydrogenation of 1-hexene at 90 °C under 10 bar of H_2. It proved to be catalytically inactive, implying the absence of catalytically active rhenium deposits. Similar results were obtained under the same conditions in the hydrogenation of 1-hexene using the **2a**/BPh_3 system. At 53% conversion within 3 min, the reaction solution was filtered through Celite, and 2 mL of 1-hexene was added. The filtrate still showed quite acceptable catalytic performance, affording a TOF of 1.5×10^4 h^{-1} within 5 min and full conversion within 12 min, which further supported the hypothesis of a homogeneous reaction course.

Mercury poisoning tests were also carried out on the "**2a**/BPh_3" and "**2a**/$B(C_6F_5)_3$" catalytic systems. In the presence of 50 equiv of Hg (per Re atom), the hydrogenation of 1-hexene using the **2a**/$B(C_6F_5)_3$ cocatalytic system proceeded at 23 °C under either 1 or 10 bar of H_2 as fast as the reference system with no mercury added. No reduction of the activity was noticed in the catalytic hydrogenation with the **2a**/BPh_3 system at 90 °C under 10 bar of H_2 in the presence of excess mercury. The filtration and mercury poisoning tests were thus all negative, ruling out colloid and amalgam formation. This is consistent with the fact that rhenium metal has a very high atom binding energy (second largest in the Periodic Table of Elements) with low propensity for colloid and amalgam formation.[21]

3. Boron Lewis Acids as Halide Abstractors. In this context the function of the boron Lewis acid is more closely examined. A few respective observations are summarized in the following: (1) The stoichiometric reaction between **2a,b** and $BH_3 \cdot$THF in 1-hexene immediately afforded the 18 e^- rhenium(I) hydride complex $[Re(Br)(H)(NO)(PR_3)_2(\eta^2\text{-}CH_2{=}CHBu)]$ (**3**; R = *i*Pr, **a**; Cy, **b**). (2) Formation of P−B adducts, such as *i*$Pr_3P \cdot BH_3$ and *i*$Pr_3P \cdot BCy_3$, was not observed within the NMR detection limits.[22] (3) After the autoclave was filled with 10 bar of H_2, hydrogenation took place at ambient temperature without any induction period. The courses of the reactions were examined by ^{31}P NMR spectroscopy at 50% conversion, providing evidence that **3a** and **3b** are the major organometallic species stable in solution. (4) The ^{11}B NMR spectra indicated that the cocatalyst $BH_3 \cdot$THF underwent hydroboration during catalysis and that this species was completely transformed into trihexy-

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lborane (s, 92 ppm). A mixture of **3a** and B(hexyl)$_3$ was then separately prepared and tested for hydrogenation of 1-hexene, showing activities similar to those of the **2a**/BH$_3$·THF and **2a**/BEt$_3$ systems (entry 16, Table 2). Similarly, the hydrogenation of cyclohexene catalyzed by the **2a**/BH$_3$·THF system also furnished initial hydroboration and formation of Cy$_3$B (s, 81.5 ppm, in the ^{11}B NMR spectrum). The hydroboration of cyclohexene is thus faster than the hydrogenation reaction. Using BPh$_3$ as a cocatalyst provided no evidence that phosphine abstraction from rhenium could have taken place either at 23 °C or at 90 °C. In separate experiments it was also confirmed that BPh$_3$ does not form adducts with P*i*Pr$_3$, also not in the presence of H$_2$ or alkene. All these results point to primary generation of alkylboranes, when possible phosphine abstraction could however not be induced by action of the cocatalyst and is therefore not the activation process. It should be mentioned at this point that the most active cocatalyst B(C$_6$F$_5$)$_3$ caused during catalysis insoluble precipitates of yet unidentified structures. This precipitate turned out to be inactive in catalytic hydrogenations of 1-hexene in THF solutions. However, yet unknown homogeneous deactivation pathways may be another cause for the shorter lifetimes of the B(C$_6$F$_5$)$_3$ cocatalytic systems.

4. Halide Abstraction as the Crucial Mechanistic Step. We next examine whether the dissociation of the bromide ligand might get crucially involved in the catalytic pathway. In the presence of 5 equiv of *n*Bu$_4$NBr, the hydrogenation of 1-hexene catalyzed by the **2a**/BH$_3$·THF (1:10) system proceeded rapidly, showing an initial TOF value of 1.6 × 10^4 h^{-1} within 8 min. However, the reaction decelerated after a TOF of 8235 h^{-1} was reached within 20 min. A similar rate drop was observed in the presence of an excess of various other halide salts *n*Bu$_4$NX (X = I, Cl, F). In general, the extent of the inhibitation was found to correlate with increasing electronegativity of the halide in the order F > Cl > Br ≈ I. For example, the rate inhibitation was minor in the presence of excess *n*Bu$_4$NI so that a TOF of 2.3 × 10^4 h^{-1} was reached within 5 min and a TOF of 7698 h^{-1} was reached within 20 min. In the case of *n*Bu$_4$NCl, the reaction rate was diminished to a great extent, showing TOFs of 1.8 × 10^4 h^{-1} within 4 min and 2866 h^{-1} within 1 h. The catalysis in the presence of excess *n*Bu$_4$NF turned out to be very sluggish, showing a TOF of 539 h^{-1} within 6 h, which is even slower than the hydrogenation catalyzed by "plain" **1a** or **2a.**

This led us to investigate stoichiometric transformations of the rhenium catalyst in the presence of halide salts *n*Bu$_4$NX. The reaction of **2a** with *n*Bu$_4$NCl (5 equiv) and 1-hexene (5 equiv) in benzene afforded at 85 °C within 5 min the 18 e$^-$ rhenium(I) monochloro hydride complex [Re(Cl)(H)(NO)(P*i*Pr$_3$)$_2$(η^2-CH$_2$=CHBu)] (**3a-Cl**) in over 99% in situ yield. The reverse reaction from **3a-Cl** to **3a** by chloride replacement with bromide failed even with a large excess of *n*Bu$_4$NBr and prolonged reaction times. Addition of *n*Bu$_4$NF to the solution of **3a-Cl** or **3a** in benzene instantaneously afforded at room temperature the corresponding 18 e$^-$ fluoride derivative [Re(F)(H)(NO)(P*i*Pr$_3$)$_2$(η^2-CH$_2$=CHBu)] (**3a-F**) in over 99% in situ yield. Although the direct substitution of bromide with iodide via the reaction of **3a** with *n*Bu$_4$NI failed, the iodide analogue [Re(I)(H)(NO)(P*i*Pr$_3$)$_2$(η^2-CH$_2$=CHBu)] (**3a-I**) could be accessed by treatment of **3a** with a small excess of AgSbF$_6$ followed by reaction with *n*Bu$_4$NI, although this product was contaminated by a small amount of **3a-F** formed through substitution of iodide with fluoride from the AgSbF$_6$ reagent. The halide substitution proceeds in the order I → Br → Cl → F, which is interpreted in terms of thermodynamics with an increasing Re−X bond strength in this order. In the ^{31}P NMR spectra the chemical shifts of the phosphine ligands were found shifted to low field in the sequence of I, Br, Cl, and F, for example, from δ 10.7 ppm (d, $^2J_{PP}$ = 122 Hz) and 4.2 ppm (d, $^2J_{PP}$ = 122 Hz) in **3a-I** to 26.1 (dd, $^2J_{PP}$ = 145 Hz, $^2J_{FP}$ = 31 Hz) and 19.3 (dd, $^2J_{PP}$ = 145 Hz, $^2J_{FP}$ = 31 Hz) in **3a-F** (Figure 3). This trend looks reasonable, since the electronegativity of the halide increases from I to F, resulting in a decrease of the electron density at the phosphorus atom.

The in situ prepared halide derivatives including **3a-I**, **3a-Cl**, and **3a-F** were tested as catalysts in combination with 5 equiv of BH$_3$·THF as a cocatalyst to hydrogenate 1-hexene at 90 °C under 10 bar of H$_2$. Their activities were indeed found to increase with decreasing electronegativity of the halide X. For example, a TON of 2982 and TOF of 1.8 × 10^4 h^{-1} were achieved with the **3a-Cl**/BH$_3$·THF (1:5) system within 10 min, corresponding to a 78% conversion, which is merely half as active as the **2a**/BH$_3$·THF system. The iodide case in the form of the **3a-I**/BH$_3$·THF (1:5) system digressed from the given trend of the halide order. A TON of 4600 and a TOF of 2.8 × 10^4 h^{-1} were achieved within 10 min. Although the **3a-I**/BH$_3$·THF system was expected to be superior to the **3a**/BH$_3$·THF system, a lower activity was observed for the earlier. This observation could not be attributed to the presence of small amounts of a **3a-F** contaminant; rather it is assumed that the relatively hard Lewis acids BH$_3$ and BR′$_3$ are only moderate abstractors for the soft iodide ion. The **3a-F**/BH$_3$·THF (1:5) system constitutes the worst case within this halide catalysis series. A TOF of 2937 h^{-1} was accomplished within 1 h. The Lewis acid is anticipated to be an effective fluoride abstractor. However, the Re−F bond is very strong, as we derived from the thermodynamically determined exchange experiments. The superior role of the bromide as the "best" halide in this series of "Re(I) complex/boron Lewis acid" systems is interpreted in terms of a proper balance between the Re−Br bond strength and the still relatively high affinity of BH$_3$ or BR′$_3$ species for the Br$^-$ ion. These results suggest that the reversible abstraction of the bromide ligand by the boron Lewis acid is most probably the initiation step in these hydrogenation processes to generate the catalytic species driving the cycle. The cocatalyst determines the initiation process of the catalyses. In many types of organometallic catalyses the initiation processes are kinetically relevant. For the actual case, we can state that the initiation rate is high when the Lewis affinity of the cocatalyst is high. However, for the benefit of high TON values or the longevity of real catalytic species, the halide affinity of the boron Lewis acid should be intermediate. Strong Lewis acids, such as BCl$_3$ and BF$_3$, were also suspected to interact with the substrate (alkene) or with the hydride ligand.[23] For our systems these interactions seemed kinetically not relevant, since the halide interactions were expected to dominate. The interaction between the boron Lewis acid and the bromide ligand in **3** could however not be traced. Variable temperature (VT) NMR measurements in the temperature range of −80 to +23 °C of **3a** with B(C$_6$F$_5$)$_3$, BH$_3$·THF, BEt$_3$, or BPh$_3$ in excess 1-hexene did not provide any evidence for the formation of a new species in concentrations above the NMR detection limit.

5. H$_2$/D$_2$ Scrambling Catalyzed by 2a. To gain some insight into the interaction between the rhenium complex and hydrogen,

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(23) Kawata, N.; Maruya, K.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 413.

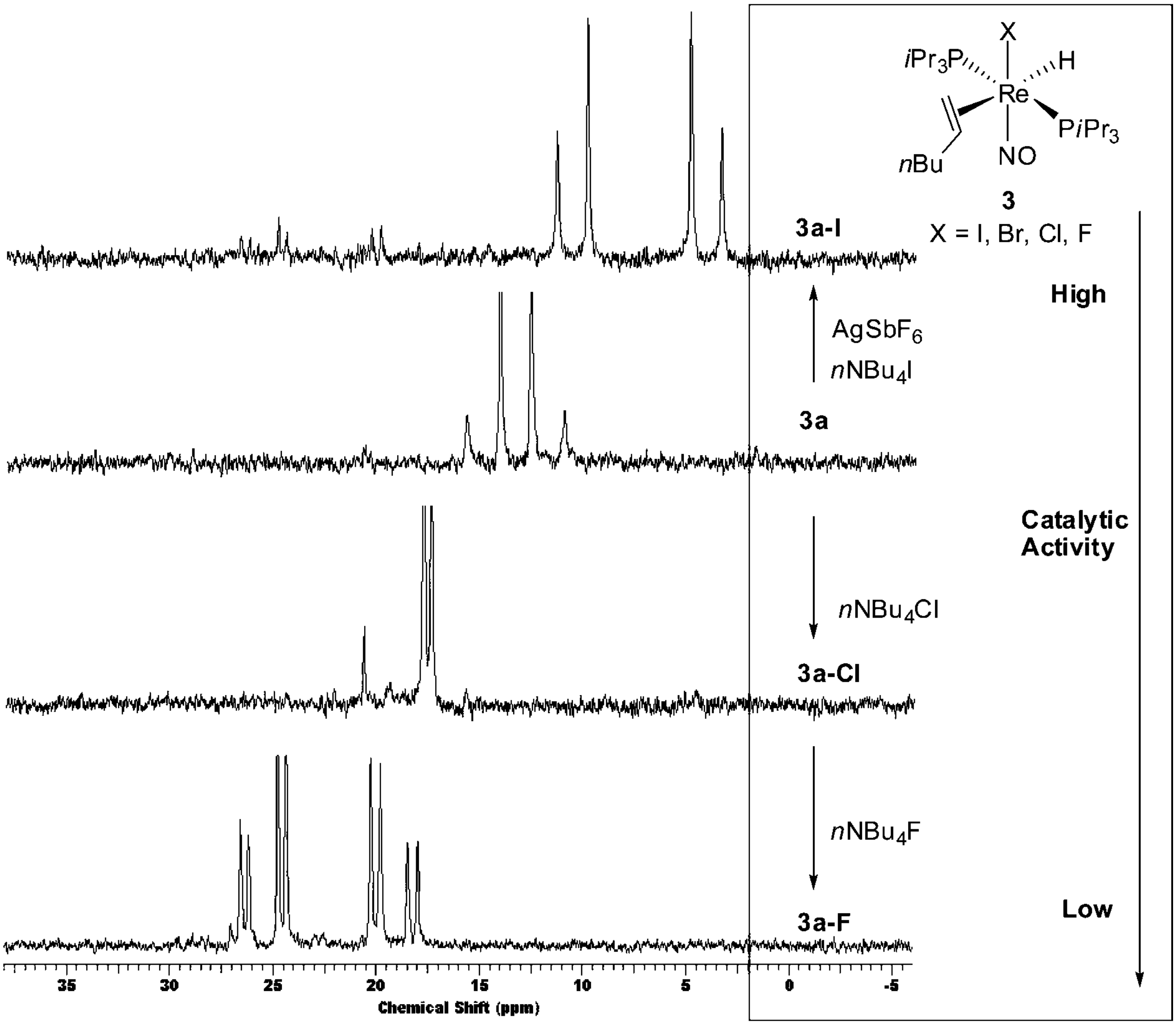

Figure 3. Halide exchange experiments based on **3a** monitored by ^{31}P NMR spectroscopy at room temperature or 85 °C in benzene. The AB coupling pattern of the ^{31}P NMR spectrum presumably originates from chemically different phosphorus ligands caused by binding of 1-hexene with parallel alignment with the P−Re−P axis and hindered rotation.[13b]

H_2/D_2 isotope scrambling experiments were carried out. Previously we reported that addition of H_2 to **2** instantaneously afforded the unstable rhenium(I) dihydrogen hydride complexes [Re(Br)(H)(NO)$(PR_3)_2(\eta^2\text{-}H_2)$] (**4**; R = *i*Pr, **a**; Cy, **b**).[14] When a solution of **2a** and 5 equiv of $B(C_6F_5)_3$ in toluene in an NMR tube was purged with a 1:1 mixture of H_2 and D_2 (each 600 mbar, 23 °C), an instantaneous H_2/D_2 scrambling was observed using VT ^1H NMR measurements in the temperature range of +23 to −50 °C. At room temperature, the ^1H NMR spectrum showed coalescence of the free H_2 and the rhenium-bound H_2 signal merging into a broad singlet at 3.83 ppm, indicative of fast exchange between free H_2 and coordinated H_2 in **4**. When the temperature was decreased to −50 °C, not only was the free hydrogen signal observed as a singlet at 4.50 ppm, but also the hydrogen scrambling product HD was detected, displaying the well-known triplet resonance at 4.46 ppm ($J_{HD} = 43$ Hz, $T_1 = 827$ ms). The ^1H NMR spectrum (500.25 MHz) showed two Re−H triplets at 3.44 ppm ($J_{HP} = 26$ Hz, $T_1 = 264$ ms) and 3.42 ppm ($J_{HP} = 25$ Hz, $T_1 = 260$ ms). Rhenium-coordinated H−H and H−D moieties were observed as a broadened multiplet at 3.07 ppm (H_2, $T_1 = 116$ ms) and a broad (>80 Hz) signal at 2.73 ppm (HD, $T_1 = 501$ ms), respectively. The ^{31}P NMR spectrum revealed the formation of four H,D isotopomers, displaying singlets at 41.72, 41.66, 41.53, and 41.44 ppm. With the aid of a 2D $^1H,^{31}P$ correlation spectrum, the downfield signals at 41.72 and 41.66 ppm could be assigned to Re−*H*/H_2, Re−*H*/HD or Re−*H*/D_2 species, whereas the signals at 41.53 and 41.44 ppm were attributed to the Re−*D*/H_2 and Re−*D*/HD species, showing no $^{31}P,^1H$ cross-peak.

The reaction of the **2a**/$B(C_6F_5)_3$ system with D_2 in toluene led to the spontaneous formation of a D_{Re} signal. Similarly, VT ^2H NMR spectroscopy showed a broad coalescence signal at 3.40 ppm at room temperature, which was resolved by decoalescence in the temperature range of −40 to −60 °C into a singlet of free H_2 at 4.50 ppm, a small HD doublet at 4.55 ppm, and two broad signals at 3.56 and 3.13 ppm, which are assigned to various Re−D ($T_1 = 22$ ms) and Re−D_2 ($T_1 = 24$ ms) isotopomers. The quadrupolar deuterium relaxation of Re−D_2 is obviously reduced by rotation and, therefore, is slightly less efficient than in the case of Re−D.[24] The Re−H, Re−H_2, and Re−HD assignments of the ^1H NMR spectrum at −50 °C could also be confirmed by ^1H T_1 relaxation time measurements. Here the ^1H relaxation in Re−H_2 is very efficient ($T_1 = 116$ ms),

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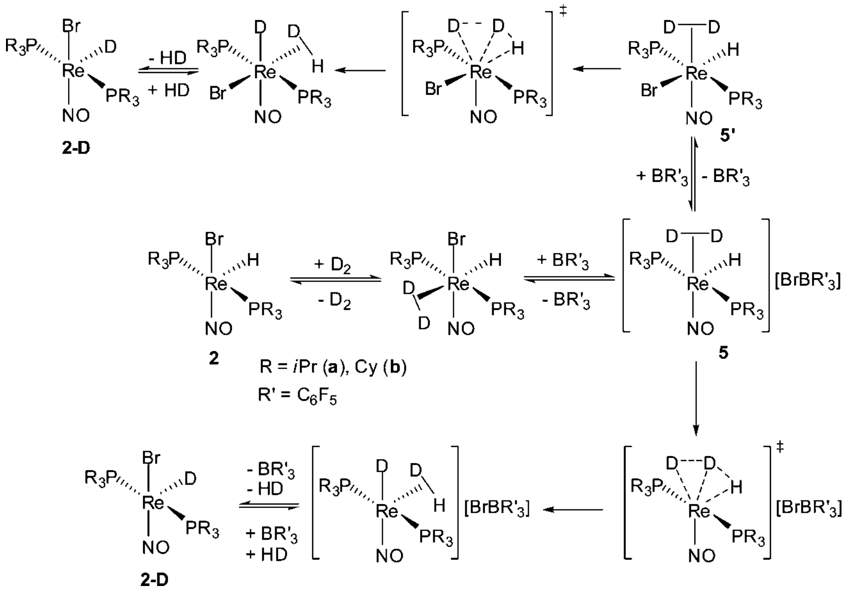
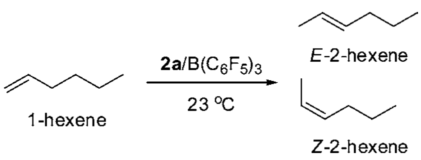
(24) Facey, G. A.; Fong, T. P.; Gusev, D.; Macdonald, P. M.; Morris, R. H.; Schlaf, M.; Xu, W. *Can. J. Chem.* **1999**, *77*, 1899.

Scheme 1. Proposed Reaction Path for the H_2/D_2 Scrambling with the **2a**/$B(C_6F_5)_3$ System



because it is rotation accelerated and based on mutual $^1H-^1H$ dipolar interaction. In contrast, the ^1H relaxation in the Re−HD unit is slow ($T_1 = 501$ ms) due to a weak proton−deuterium dipolar interaction, whereas the relaxation time of Re−H is in the range of about 260 ms, which is typical for M−H bonds. Under a D_2 atmosphere, ^{31}P NMR shows a prominent singlet of the Re−D/D_2 unit at 41.40 ppm, which corresponds to the high-field signal at 41.44 ppm under a H_2/D_2 atmosphere. Besides the given one, at least two more isotopomers are present in solution, displaying weak resonances at 41.47 and 41.63 ppm. In total, these NMR studies support a rhenium trihydride exchange mechanism[25] induced by bromide abstraction assisted by the boron Lewis acid, as depicted in Scheme 1.[26] **2a** alone is also a catalyst in the H_2/D_2 scrambling at room temperature, although it is less efficient than the **2a**/$B(C_6F_5)_3$ system, furnishing a much slower H_2/D_2 conversion to HD in the ^1H NMR spectrum. This can be interpreted in terms of an only slow intramolecular rearrangement from the *trans*-Re(H)(H_2) to the *cis*-Re(H_3) transition state, in which the scrambling can take place. Exactly this geometrical rearrangement is anticipated to be promoted by Br^- abstraction with the Lewis acid.

6. Catalysis of the Terminal Alkene Isomerization. Besides H_2/D_2 scrambling, the **2a**/$B(C_6F_5)_3$ system was also found to be active in the isomerization of terminal alkenes to internal ones, the so-called one-carbon migration process:[27]



When 10 equiv of 1-hexene was added to a solution of **2a**/$B(C_6F_5)_3$ (1:5) in toluene, the purple solution instantaneously turned light yellow, forming **3a** as the only organometallic species (NMR monitoring). After being allowed to stand at room temperature for 24 h, the solution turned deep brown with formation of the internal alkene isomer (*E*/*Z*)-2-hexene in over 90% yield, showing a characteristic multiplet signal at 5.3 ppm in the ^1H NMR spectrum. Unfortunately, the 2-hexene isomer could not be distinguished as either (*E*)-2-hexene or (*Z*)-2-hexene due to the overlap of the C−H protons in the region of 5.3 ppm. However, in a ^{13}C, ^1H correlation spectrum the scalar couplings between the multiplet H_{alkene} signals and the three C_{alkene} atoms (δ = 132.0, 130.6, 124.7 ppm) were observable, which indicated the presence of both the (*E*)- and (*Z*)-2-hexene isomers. It should also be added that 2-hexene coordinates rather weakly to the rhenium center in comparison with 1-hexene; therefore, the five-coordinate Re(I) species **2a** was partially recovered in solution, as indicated by ^{31}P NMR spectroscopy. In contrast, isomerization of 1-hexene did not take place at all with **2a** alone at room temperature, even at prolonged reaction times. Nevertheless, a nearly complete conversion to the 2-hexenes could be achieved by **2a** alone at 85 °C within 5 min, which implied that the required *trans*/*cis* rearrangement of the Re(H)(olefin) unit could also be thermally induced. These results all point to a reversible alkene migratory insertion of the alkenes into the Re−H bond involved in catalyses, as depicted in Scheme 2. The key species are **6** and **6′** containing a *cis*-aligned alkene and hydride ligand. The complex salt **6** is formed via the boron Lewis acid induced bromide abstraction, while its neutral congener **6′** is formed by a Br^- abstraction−*trans*/*cis* rearrangement−Br^- recoordination sequence supported by the Lewis acid. Then the migratory insertion of the olefin into the Re−H bond takes place with different orientations of the olefinic ligand. The formed primary or secondary alkyl species undergo β-hydride shift, leading to the 1-alkene or to the 2-alkene.

Besides the boron Lewis acid promoted activation of the rhenium catalysts, another standard protocol was applied to activate these complexes, replacing the halide ligand with a

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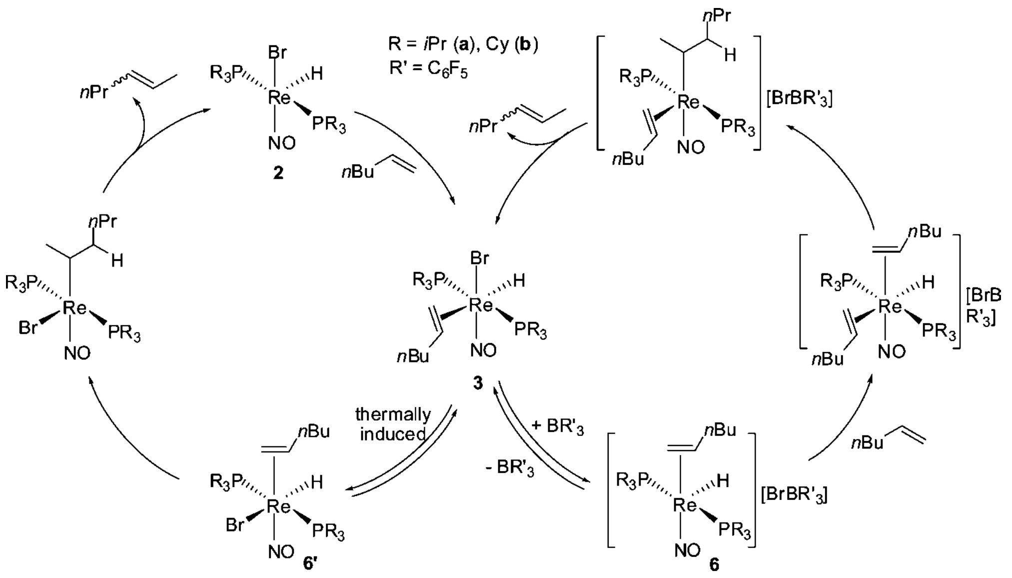
(25) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Luo, X.; Crabtree, R. *J. Am. Chem. Soc.* **1990**, *112*, 6912.

(26) (a) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305. (b) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(27) (a) Gauthier, D.; Lindhardt, A. T.; Olsen, E. P. K.; Overgaard, J.; Skrydstrup, T. *J. Am. Chem. Soc.* **2010**, *132*, 7998. (b) Donohoe, T. J.; O'Riordan, T. J. C.; Rosa, C. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 1014.

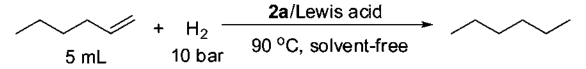
Scheme 2. Proposed Reaction Pathway for the Isomerization of 1-Hexene to (*E*)- and (*Z*)-2-Hexene Catalyzed by the **2a**/$B(C_6F_5)_3$ System or **2a** Alone



weakly coordinating anion.[28] When the hydrogenation of 1-hexene was carried out at 90 °C under 10 bar of H_2 with a mixture of **2a** and a slight excess of $AgSbF_6$, no reaction occurred at all. In contrast, the in situ filtered solution of **2a** and $AgSbF_6$ (2 equiv) in 1-hexene exhibited excellent catalytic activity, affording a satisfactory TON of 3446 and a TOF of 1.4×10^4 h^{-1} within 15 min, which is 16 times faster than that with **2a** alone. This not only suggests that a "catalytic" vacant site is created via bromide release, but also implies that even a slight excess of silver ions could completely block the catalysis. This is most probably due to the loss of Re(I) active species via the oxidation of Re(I) to Re(II) by Ag(I) ions. Repeated addition of 5 mL of 1-hexene to the resultant solution afforded only moderate TONs and TOFs, indicating degradation of the catalyst. The stoichiometric reaction of **2a** with 2 equiv of 1-hexene and 1 equiv of $AgSbF_6$ was carried out in benzene-d_6 at room temperature. The reaction yielded a mixture of rhenium species as indicated by ^{31}P NMR spectroscopy, which could not be identified. The formation of a small amount of (*E*)- and (*Z*)-2-hexene was also observed in the ^1H NMR spectrum.

7. Non-Boron Lewis Acids as Cocatalysts. Besides boron Lewis acids, we also tested other types of Lewis acids as cocatalysts in **2a** catalyzed hydrogenations of 1-hexene under 10 bar of H_2 at 90 °C, as listed in Table 4. In general, most of these performed not comparable to boron Lewis acids with respect to high conversions, good activities, and longevity of the catalytic system, except for AlF_3, $AlBr_3$, and $Yb(OTf)_3$. Again the appropriate balance between the Re−Br bond strength and the Lewis affinity for Br of the Lewis acid is expected to determine the performance of the catalyses. For example, $InCl_3$ was even found to inhibit the hydrogenation, which can be interpreted in terms of $InCl_3$ being such a soft Lewis acid that replacement of the bromide ligand at rhenium by chloride could take place, resulting in poorer activity. The slightly better catalytic performance with AlF_3 with respect to $AlBr_3$ may be related to the higher Lewis affinity of AlF_3 over $AlBr_3$.[29]

Table 4. Hydrogenation of 1-Hexene at 90 °C Using Catalyst **2a** with Various Non-Boron Lewis Acids[a]



entry	Lewis acid (amt, equiv)	*T* (min)	conversion (%)	TON	TOF (h^{-1})
1	$AlBr_3$ (5)	4	26	919	1.4×10^4
2	$AlBr_3$ (3)	10	53	1861	1.1×10^4
3	$AlBr_3$ (1)	8	89	3102	2.3×10^4
4	$AlCl_3$ (5)	2	29	1000	3.0×10^4
5	$AlCl_3$ (1)	60	1	50	50
6	AlF_3 (5)	10	83	2910	1.7×10^4
7	AlF_3 (1)	7	95	3308	2.8×10^4
8	$InCl_3$ (1)	40	19	665	998
9	$InCl_3$ (5)	40	27	946	1419
10	$Yb(OTf)_3$ (5)	7	76	2647	2.3×10^4
11	$Yb(OTf)_3$ (1)	7	89	3116	2.7×10^4
12	$Zn(OTf)_2$ (5)	14	58	2022	8665

[a] Reactions were performed using 5 mL of 1-hexene (40 mmol), 7 mg of **2a** (0.0113 mmol), and an appropriate amount of non-boron Lewis acid under 10 bar of H_2 at 90 °C.

Mechanism of the Re(I)/Boron Lewis Acid Cocatalyzed Hydrogenations of Alkenes. A mechanism including reversible bromide abstraction by the Lewis acid is proposed for the **1**/DMAB and **2**/BR'_3 (R′ = Et, Ph, C_6F_5, "H") catalyzed hydrogenations of alkenes, as depicted in Scheme 3. Two catalytic cycles are proposed depending on whether the Lewis acid promoted reversible bromide abstraction is involved as an initiation step (A) and the cycle is turning over "bromide-free" or whether the bromide is coming back during the course of the cycle (B). Invariably the alkene-coordinated 18 e^- rhenium(I) hydride **7** is first generated either directly from **2** or indirectly from **1** with DMAB and the alkene. Then the Lewis acidic BR'_3 component reversibly abstracts the bromide ligand, affording Re(I) species **8** bearing one vacant site and the bromo borate counteranion $[BBrR'_3]^-$. This step serves as the initial step for

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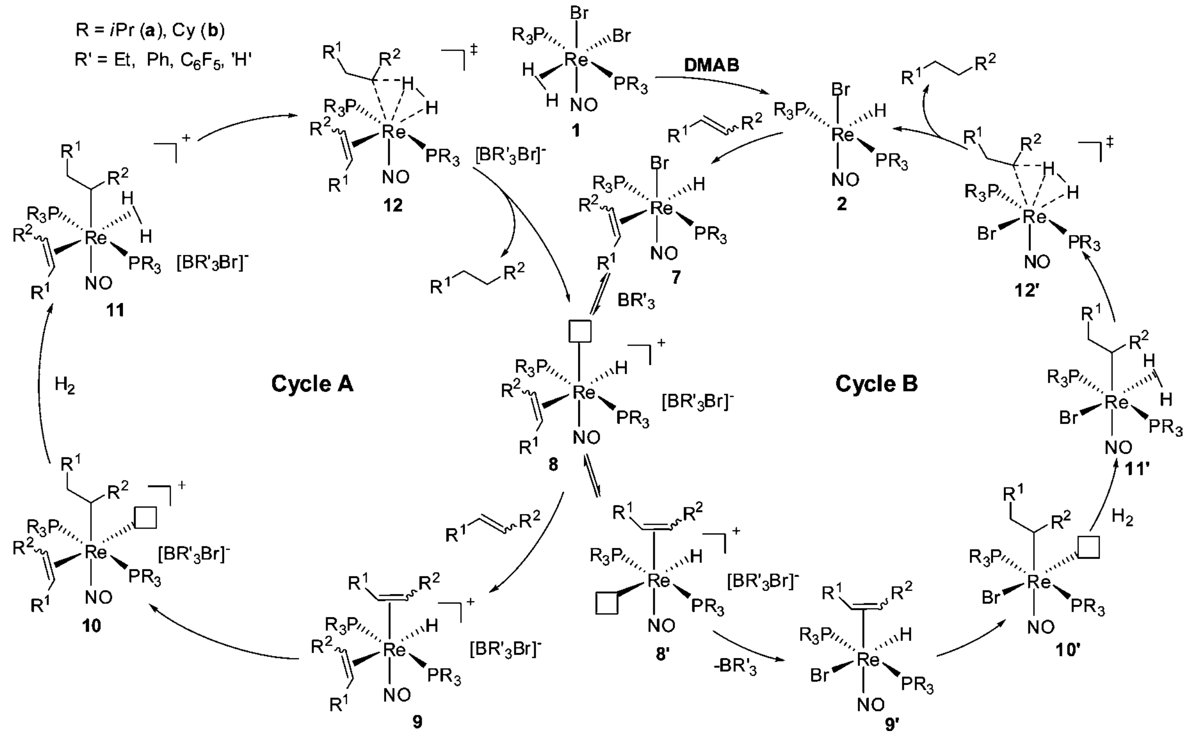
(28) (a) Strauss, S. H.; Shriver, D. F. *Inorg. Chem.* **1978**, *17*, 3069. (b) Beck, W.; Sunkel, K. *Chem. Rev.* **1988**, *88*, 1405. (c) Lassauque, N.; Francio, G.; Leitner, W. *Eur. J. Org. Chem.* **2009**, 3199.

(29) (a) Branchadell, V.; Sbai, A.; Oliva, A. *J. Phys. Chem.* **1995**, *99*, 6472. (b) Wilson, M.; Coolidge, M. B.; Mains, G. J. *J. Phys. Chem.* **1992**, *96*, 4851. (c) Ogawa, A.; Fujimoto, H. *Inorg. Chem.* **2002**, *41*, 4888.

Scheme 3. Alternative Rhenium Hydrogenation Cycles: (A) Lewis Acid Promoted Bromide-Free Catalysis, (B) Lewis Acid Promoted Bromide On−Off Catalysis



catalytic cycle A. The Osborn-type cycle begins operation with the alkene before H_2 addition, reaching transition state **12**, through which the alkane is eventually released by reductive elimination, re-forming **8** to close the catalytic cycle. The bromide may coordinate back to form the resting state **7**. In this mechanism, the initial step from **7** to **8** would be rate-determining.[30]

An alternative catalytic cycle (cycle B) can be formulated. Different from cycle A, the Lewis acid promoted reversible bromide dissociation and association are involved as steps in the catalytic cycle. Otherwise, the sequence of an Osborn-type hydrogenation cycle is followed again with the alkene before H_2 addition. Then alkane reductive elimination occurs from transition state **12′**, being distinguished from **12** of cycle A by a bromide in the coordination sphere. Cycle B is presumably slower than cycle A, because the bromide on−off process would in principle retard the reaction rate. It should be noted that the H_2 uptake from **10** (**10′**) to **11** (**11′**) could be to some extent rate-determining, as the equilibria are dependent on the concentration of H_2. In this step, the alkene could in principle occupy the vacant site rather than H_2, yielding the bisalkene-coordinated rhenium(I) alkyl species as a resting state. As discussed before, the migratory insertion of the alkene into Re−H from **9** (**9′**) to **10** (**10′**) could also contribute to the overall rate.

Another possible Lewis basic site where the Lewis acid could dock on is the O_{NO} atom.[31] Nitrosyl ligands may be either linear or bent at a metal center. The bending of a nitrosyl ligand would create a vacant site.[32] Interaction of the O_{NO} atom with Lewis acids would in principle increase metal to nitrosyl π-back-donation, enforcing the tendency for NO bending. However, no experimental evidence for NO bending in any species of the catalytic cycle and eventual take-up of alkenes or H_2 was obtained. This possibility is currently still under investigation by density functional theory (DFT) calculation.

Conclusions

In conclusion, **1**/DMAB was discovered in the course of dehydrocoupling of DMAB to be a very efficient catalytic system for homogeneous hydrogenation of alkenes at both high temperature and ambient temperature. Mechanistic studies revealed that the high activity is derived from cooperation of the five-coordinate rhenium(I) hydride **2** with Lewis acids, in the best cases with boron Lewis acids as cocatalysts. The influence of the boron Lewis acid on the total catalytic activity was found to be in the qualitative order $B(C_6F_5)_3 > BEt_3 \approx BH_3 \cdot THF > BPh_3$, but the longevity of the catalytic system was found to be of the reverse order, $BPh_3 > BEt_3 \approx BH_3 \cdot THF > B(C_6F_5)_3$, so that activity and longevity have to be compromised for the best choice of systems. Detailed mechanistic studies were carried out. The boron Lewis acids assisted reversible bromide abstraction, which is anticipated to contribute to the rate-limiting step. It is the initiating step of the catalyses and influences the catalytic performance. From the point of view of catalytic activity and longevity of the catalysts, these rhenium hydrogena-

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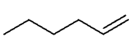
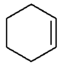
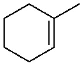
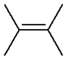
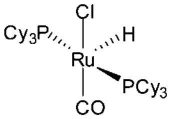
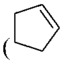
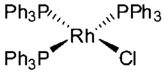
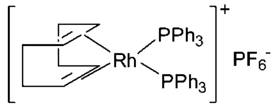
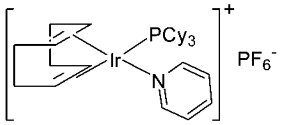
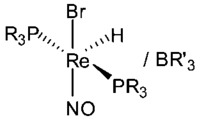
Table 5. Comparison of the Catalytic Performance of Classic Precious Metal Catalysts with the “Rhenium(I) Hydride/Boron Lewis Acid” System[1a]

		TOF (h^{-1})			
	Conditions				
 [8c]	23 °C, 1 bar H_2, benzene	1200	960 ()	---	---
 Wilkinson catalyst [1h]	25 °C, 1 bar H_2, C_6H_6/EtOH	650	700	13	---
 Schrock-Osborn catalyst [1i, 1k]	25 °C, 1 bar H_2, CH_2Cl_2	4000	10	---	---
 Crabtree catalyst [1a]	0 °C, 1 bar H_2, CH_2Cl_2	6400	4500	3800	4000
 Jiang/Berke catalytic system	23 °C, 1 bar H_2 solvent-free	1725	230	---	---
	90 °C, 1 bar H_2 solvent-free	2013	384	152	---
	23 °C, 10 bar H_2 solvent-free	17000	14000	---	---
	90 °C, 10 bar H_2 solvent-free	56000	13000	1551	---

tion systems belong to the best transition-metal catalysts for hydrogenations and are comparable in performance to most of the reported hydrogenation catalyses involving precious metals, e.g., $RuHCl(CO)(PCy_3)_2$ (TOF of 1200 h^{-1} for 1-hexene at 25 °C and 1 bar of H_2)[8c] and its derivatives,[8] $RhCl(PPh_3)_3$ (Wilkinson catalyst, TOF of 650 h^{-1} for 1-hexene at 25 °C and 1 bar of H_2),[1h] $[Rh(cod)(PPh_3)_2]PF_6$ (Schrock−Osborn catalyst, TOF of 4000 h^{-1} for 1-hexene at 25 °C and 1 bar of H_2),[1i,k] and $[Ir(cod)(py)(PCy_3)][PF_6]$ (Crabtree catalyst, TOF of 6400 h^{-1} for 1-hexene at 0 °C and 1 bar of H_2).[1a] Further details concerning substrate selectivities of these catalysts are depicted in Table 5. It is worth mentioning that the Crabtree catalyst is remarkably active at room temperature, but is thermally less stable and susceptible to deactivation through formation of an inactive hydride-bridged trimer. This work provides great potential for the application of rhenium in fine-chemical production, showing hydrogenation activities of the same order of magnitude as those of precious metals. Despite the fact that the current cost of rhenium is comparable to that of ruthenium, it is still much cheaper than rhodium or iridium. We are very optimistic that in the future rhenium will attain a more important role in industrial processes. Studies of the scope of functional group tolerance and of enantioselective hydrogenations are in progress.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze−thaw cycles prior to use. The deuterated solvents were dried with sodium/benzophenone (benzene-d_6) and vacuum transferred for storage in Schlenk flasks fitted with Teflon valves. ^1H NMR, $^{13}C\{^1H\}$ NMR, $^{31}P\{^1H\}$ NMR, and ^{11}B NMR data were recorded on a Varian Gemini-300, Varian

Mercury 200, or Bruker DRX 500 spectrometer using 5 mm diameter NMR tubes equipped with Teflon valves, which allow degassing and further introduction of gases into the probe. Chemical shifts are expressed in parts per million. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual proton or ^{13}C resonances of the deuterated solvent. All chemical shifts for the $^{31}P\{^1H\}$ NMR data are reported downfield in parts per million relative to external 85% H_3PO_4 at 0.0 ppm. Signal patterns are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were obtained by using ATR methods with a Bio-Rad FTS-45 FTIR spectrometer. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zurich. ESI-MS spectroscopic data were obtained from an HCT Esquire Bruker Daltonics instrument. Rhenium(I) complexes **1**[31b] and **2**[13b] were prepared according to reported procedures. DMAB, $BH_3\cdot THF$, BPh_3, BEt_3, BCl_3, $BF_3\cdot OEt_2$, $B(OMe)_3$, $AlBr_3$, $AlCl_3$, AlF_3, $InCl_3$, $Yb(OTf)_3$, $Zn(OTf)_2$, and diverse alkenes were purchased from Aldrich and Fluka and used without further purification. 1-Hexene, 1-octene, cyclooctene, allylbenzene, and 1,5-cyclooctadiene were purified by distillation.

General Procedure for Hydrogenation of Alkenes Cocatalyzed by Rhenium Complexes and Lewis Acids. In a 30 mL steel autoclave equipped with a stirring bar, a certain amount of substrate alkene (e.g., 1-hexene, 5 mL, 40 mmol; 1-octene, 10 mL, 64 mmol; cyclooctene, 10 mL, 77 mmol; 1,5-cyclooctadiene, 5 mL, 41 mmol; cyclohexene, 5 mL, 49 mmol; α-methylstyrene, 5 mL, 38 mmol; 3,3-dimethylbutene, 5 mL, 39 mmol; styrene, 10 mL, 87 mmol; 1,7-octadiene, 5 mL, 34 mmol; allylbenzene, 2 mL, 15 mmol; allyltrimethylsilane, 2 mL, 12 mmol; 1-methyl-1-cyclohexene, 1 mL, 8.5 mmol; 2,3-dimethyl-2-butene, 2 mL, 17 mmol), the appropriate amount of rhenium catalyst (e.g., **1a**, 6.7 mg, 0.01 mmol; **1b**, 9.6 mg, 0.01 mmol; **2a**, 7.0 mg, 0.0113 mmol; **2b**, 8.6 mg, 0.01 mmol), and 5 equiv of Lewis acid (e.g., DMAB, 3.0 mg, 0.05 mmol; $BH_3\cdot THF$, 50 μL, 0.05 mmol; BPh_3, 12.2 mg, 0.05 mmol; BEt_3 in hexane, 50 μL, 0.05 mmol; $B(C_6F_5)_3$, 12.8 mg, 0.025 mmol; BCl_3 in hexane, 50 μL, 0.05 mmol; $BF_3\cdot OEt_2$, 8 μL, 0.05 mmol; $AlBr_3$, 2.68 mg, 0.01 mmol; $AlCl_3$, 6.6 mg, 0.05 mmol; AlF_3, 4.2 mg, 0.05 mmol; $InCl_3$, 11 mg, 0.05 mmol; $Yb(OTf)_3$, 31 mg, 0.05 mmol; $Zn(OTf)_2$, 18.2 mg, 0.05 mmol) were mixed. After being flushed with 10 bar (or 1 bar) of H_2 one time, the system was charged with 10 bar (or 1 bar) of H_2 and was heated in an oil bath with stirring at either ambient temperature or 90 °C. The progress of the reactions was monitored by a Buechi Pressflow gas controller, and the conversion of the hydrogenations was calculated on the basis of the consumption of H_2 in the system. At the end of the catalyses, the autoclave was cooled to ambient temperature and vented carefully. The hydrogenation products were characterized by ^1H NMR spectroscopy in $CDCl_3$. Some of the products were also characterized by GC−MS analyses. The TONs and TOFs were determined on the basis of the consumption of H_2. These data were found to be quite comparable to the results determined according to the integrations in the ^1H NMR spectra. In the reactions, where full conversions were obtained, the hydrogenated products were isolated via reduced pressure distillation. The boiling points were comparable to the reported values.

KIE Studies of 2a/$BH_3\cdot$THF Catalyzed Hydrogenation of 1-Hexene at Different Temperatures. In a 20 mL vial in a glovebox, 62 mg (0.10 mmol) of [Re(Br)(H)(NO)(P*i*Pr$_3$)$_2$] (**2a**) was dissolved in 2 mL of 1-hexene. The resultant solution was divided into 10 portions ready for catalysis. In a 30 mL steel autoclave equipped with a stirring bar, 1-hexene (5 mL) was mixed with one portion of the prepared 1-hexene solution of **2a** and 50 μL (0.05 mmol) of $BH_3\cdot THF$. After being flushed with 10 bar of H_2 or D_2 once, the system was charged with 10 bar of H_2 or D_2 and was heated in an oil bath with stirring at the required temperature (23, 60, and 90 °C). The reaction process was monitored by a Buechi Pressflow gas controller. At the end of the catalyses, the autoclave was cooled to ambient temperature and vented carefully. The hydrogenation products from the reaction with H_2 were characterized by ^1H NMR spectroscopy in $CDCl_3$.

Lewis Acidity Tests. Gutmann−Beckett Method in Toluene-*d*$_8$ at 23 °C. The boron Lewis acid was coordinated to triethylphosphine oxide ($Et_3P{=}O$ or TPO), and the Lewis acidity was compared by the change of the chemical shift in the $^{31}P\{^1H\}$ NMR spectra (121.47 MHz, ppm): $Et_3P{=}O$, $\delta = 45.9$; $(Et_3P{=}O)(B(C_6F_5)_3)$, $\delta = 75.7$, reference shift $\Delta\delta = 29.8$; $(Et_3P{=}O)(BF_3)$, $\delta = 77.0$, reference shift $\Delta\delta = 31.1$, Lewis acidity relative to $B(C_6F_5)_3$ 104.4%; $(Et_3P{=}O)(BH_3)$, $\delta = 83.1$, reference shift $\Delta\delta = 37.2$, Lewis acidity relative to $B(C_6F_5)_3$ 124.8%; $(Et_3P{=}O)(BPh_3)$, $\delta = 69.1$, reference shift $\Delta\delta = 23.2$, Lewis acidity relative to $B(C_6F_5)_3$ 77.8%; $(Et_3P{=}O)(BEt_3)$, $\delta = 77.0$, reference shift $\Delta\delta = 31.1$, Lewis acidity relative to $B(C_6F_5)_3$ 104.4%; $(Et_3P{=}O)(BCl_3)$, $\delta = 84.4$, reference shift $\Delta\delta = 38.5$, Lewis acidity relative to $B(C_6F_5)_3$ 129.2%; $(Et_3P{=}O)[B(OMe)_3]$, $\delta = 47.1$, reference shift $\Delta\delta = 1.2$, Lewis acidity relative to $B(C_6F_5)_3$ 4.2%.

[Re(Br)(H)(NO)(PiPr$_3$)$_2$(η^2-CH$_2$=CHBu)] (3a). In a 3 mL Young NMR tube, **2a** (31 mg, 0.05 mmol) and 1-hexene (6.3 μL, 0.05 mmol) were mixed in benzene-*d*$_6$ (0.5 mL). Immediately a light brown solution was formed. The NMR spectrum indicated the formation of **3a** in 100% in situ yield. The solvent was evaporated in vacuo for 24 h to give a light brown residue. Yield: 35 mg, 99%. IR (ATR, cm^{-1}): ν(C−H) 2961, 2922, 2873, ν(NO) 1662. ^1H NMR (500.25 MHz, benzene-*d*$_6$, ppm): δ 3.54 (dd, $^2J_{HP}$ = 29.0 Hz, 38.0 Hz, 1H, ReH), 3.44 (br, 1H, CH$_2$=C*H*−), 3.12 (br, 1H, C*H*$_2$=CH−), 3.05 (br, 1H, C*H*$_2$=CH−), 2.83 (m, 3H, PC*H*(CH$_3$)$_2$), 2.69 (m, 3H, PC*H*(CH$_3$)$_2$), 1.81 (m, 2H, CH$_2$), 1.59 (m, 4H, CH$_2$), 1.14−1.24 (m, 36H, PCH(C*H*$_3$)$_2$), 1.00 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, benzene-*d*$_6$, ppm): δ 53.2 (s, CH$_2$=*C*H−), 45.0 (s, *C*H$_2$=CH−), 39.4 (s, CH$_2$), 38.6 (s, CH$_2$), 25.8 (t, P*C*H(CH$_3$)$_2$), 22.7 (s, CH$_2$), 21.7 (s, PCH(*C*H$_3$)$_2$), 20.2 (s, PCH(*C*H$_3$)$_2$), 19.8 (s, PCH(CH$_3$)$_2$),19.5 (s, PCH(CH$_3$)$_2$), 14.5 (s, CH$_3$). $^{31}P\{^1H\}$ NMR (80.94 MHz, benzene-*d*$_6$, ppm): δ 14.9 (d, *J* = 128 Hz, 1P), 12.0 (d, *J* = 128 Hz, 1P). Anal. Calcd for $C_{24}H_{55}BrNOP_2Re$ (701.76): C, 41.08; H, 7.90; N, 2.00. Found: C, 41.26; H, 7.99; N, 1.83.

[Re(Br)(H)(NO)(PCy$_3$)$_2$(η^2-CH$_2$=CHBu)] (3b). In a 3 mL Young NMR tube, [Re(Br)(H)(NO)(PCy$_3$)$_2$] (**2b**; 34 mg, 0.04 mmol) and 1-hexene (5.0 μL, 0.04 mmol) were mixed in benzene-*d*$_6$ (0.5 mL). Immediately a light brown solution was formed. NMR spectroscopy indicated the formation of **3b** in 100% in situ yield. The solvent was evaporated in vacuo for 24 h to give a light brown residue. Yield: 36 mg, 99%. IR (ATR, cm^{-1}): ν(C−H) 2922, 2848, ν(NO) 1661. ^1H NMR (300.08 MHz, benzene-*d*$_6$, ppm): δ 3.82 (dd, $^2J_{HP}$ = 27.0 Hz, 33.0 Hz, 1H, ReH), 3.42 (br, 2H, C*H*$_2$=CH−), 3.12 (br, 1H, CH$_2$=C*H*−), 1.31−2.86 (m, 66H, P(C$_6$H$_{11}$)$_3$), 1.86 (m, 2H, CH$_2$), 1.67 (m, 4H, CH$_2$), 1.02 (br, 3H, CH$_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, benzene-*d*$_6$, ppm): δ 52.7 (s, CH$_2$ dbd=*C*H−), 45.2 (s, *C*H$_2$=CH−), 39.6 (s, CH$_2$), 39.1 (s, CH$_2$), 36.8 (d, *J* = 22 Hz, PC), 35.7 (d, *J* = 19 Hz, PC), 32.0 (s), 30.5 (s), 30.0 (s), 28.0 (s), 26.9 (s), 23.0 (s), 14.5 (s). $^{31}P\{^1H\}$ NMR (121.47 MHz, benzene-*d*$_6$, ppm): δ 4.9 (d, *J* = 126 Hz, 1P), −0.4 (d, *J* = 126 Hz, 1P). Anal. Calcd for $C_{42}H_{79}BrNOP_2Re$ (942.14): C, 53.54; H, 8.45; N, 1.49. Found: C, 53.28; H, 1.44; N, 1.57.

Preparation of the Rhenium(I) Chloro Hydride Complex [Re(Cl)(H)(NO)(PiPr$_3$)$_2$(η^2-CH$_2$=CHBu)] (3a-Cl) and Its Test for Catalytic Activity. In a 3 mL Young NMR tube, **2a** (12.3 mg, 0.02 mmol), 1-hexene (100 μL, 0.80 mmol), and *n*Bu$_4$NCl (10 mg, 0.036 mmol) were mixed in benzene (0.5 mL). The mixture was kept at 80 °C for 5 min. Complete formation of **3a-Cl** was achieved in over 99% yield as indicated by ^{31}P NMR spectroscopy. The solution was dried in vacuo, and the residue was extracted with pentane (3 × 2 mL). The solvent was evaporated in vacuo, affording a purple solid which was identified to be a mixture containing 19% [Re(Cl)(H)(NO)(P*i*Pr$_3$)$_2$] and 81% **3a-Cl** by ^1H NMR and ^{31}P NMR spectroscopy. Yield: 5.8 mg. The following are data for **3a-Cl**. IR (ATR, cm^{-1}): ν(C−H) 2958, 2926, 2870, ν(NO) 1597. ^1H NMR (199.95 MHz, benzene-*d*$_6$, ppm): δ 3.92 (t, $^2J_{HP}$ = 34.0 Hz, 1H, ReH), 3.38 (br, 1H, $CH_2{=}CH-$), 2.76−2.96 (m, 2H, $CH_2{=}CH-$), 2.64 (m, 6H, $PCH(CH_3)_2$), 1.84 (m, 2H, CH_2), 1.50 (m, 4H, CH_2), 1.22 (m, 36H, $PCH(CH_3)_2$), 1.03 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3). $^{31}P\{^1H\}$ NMR (80.94 MHz, benzene-d_6, ppm): δ 19.1 (d, J = 130 Hz, 1P), 17.3 (d, J = 130 Hz, 1P). The following are data for [Re(Cl)(H)(NO)(P*i*Pr$_3$)$_2$]. IR (ATR, cm^{-1}): ν(C−H) 2958, 2926, 2870, ν(NO) 1687. ^1H NMR (199.95 MHz, benzene-d_6, ppm): δ 2.80 (m, 6H, $PCH(CH_3)_2$), 1.19 (m, 36H, $PCH(CH_3)_2$), −17.94 (br, 1H, ReH). $^{31}P\{^1H\}$ NMR (80.94 MHz, benzene-d_6, ppm): δ 46.8 (s, 1P). These data are quite comparable to those of the five-coordinate rhenium(I) bromo hydride compound **2a**. ESI-MS spectroscopy confirmed the composition of fragments of **3a-Cl** bearing a Re−Cl unit. MS (ESI): *m/z* 572.1 [Re(Cl)(NO)(P*i*Pr$_3$)$_2$]$^+$. The obtained solid was dissolved with 5 mL of 1-hexene and transferred to a 30 mL steel vessel. Afterward 50 μL of $BH_3\cdot THF$ (5 equiv relatrive to Re) was added, and the mixture was charged with 10 bar of H_2 and continuously stirred at 90 °C. The reaction process was monitored by a Buechi Pressflow gas controller.

Preparation of the Rhenium(I) Fluoro Hydride Complex [Re(F)(H)(NO)(PiPr$_3$)$_2$(η^2-$CH_2{=}CHBu$)] (3a-F) and Its Test for Catalytic Activity. In a 3 mL Young NMR tube, **2a** (26 mg, 0.04 mmol), 1-hexene (100 μL, 0.80 mmol), and *n*Bu$_4$NF in THF (80 μL, 0.08 mmol) were mixed in benzene (0.5 mL). The mixture was kept at room temperature for 2 min. The formation of **3a-F** was achieved in over 99% in situ yield as indicated by ^{31}P NMR spectroscopy. The solution was dried in vacuo, and the residue was extracted with cold pentane (2 × 2 mL). The solvent was evaporated in vacuo, affording a light brown residue. Yield: 12.8 mg, 0.02 mmol, 50%. IR (ATR, cm^{-1}): ν(C−H) 2955, 2925, 2870, ν(NO) 1647. ^1H NMR (300.08 MHz, benzene-d_6, ppm): δ 4.58 (ddd, $^2J_{HP}$ = 33.0 Hz, $^2J_{HP}$ = 30.0 Hz, $^2J_{HF}$ = 8.0 Hz, $^2J_{HF}$ = 6.0 Hz, 1H, ReH), 3.38 (br, 1H, $CH_2{=}CH-$), 3.14 (m, 2H, $CH_2{=}CH-$), 2.74 (m, 3H, $PCH(CH_3)_2$), 2.57 (m, 3H, $PCH(CH_3)_2$), 1.89 (m, 2H, CH_2), 1.64 (m, 4H, CH_2), 1.19−1.37 (m, 36H, $PCH(CH_3)_2$), 1.07 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, benzene-d_6, ppm): δ 54.3 (s, $CH_2{=}CH-$), 39.9 (s, $CH_2{=}CH-$), 36.7 (s, CH_2), 30.2 (s, CH_2), 28.4 (d, J = 21 Hz, $PCH(CH_3)_2$), 27.8 (d, J = 21 Hz, $PCH(CH_3)_2$), 23.0 (s, CH_2), 19.8 (s, $PCH(CH_3)_2$), 19.5 (s, $PCH(CH_3)_2$),19.0 (s, $PCH(CH_3)_2$), 14.6 (s, CH_3). $^{31}P\{^1H\}$ NMR (121.47 MHz, benzene-d_6, ppm): δ 24.9 (dd, J_{PP} = 146 Hz, J_{FP} = 30 Hz, 1P), 18.7 (dd, J_{PP} = 146 Hz, J_{FP} = 30 Hz, 1P). ^{19}F NMR (282.33 MHz, THF-d_8, ppm): −271.65 (s). Satisfactory elemental analysis data were not obtained due to the presence of a trace amount of free 1-hexene in the residue. ESI-MS spectroscopy confirmed the composition of fragments of **3a-F** bearing a Re−F unit. MS (ESI): *m/z* 556.4 [Re(F)(NO)(P*i*Pr$_3$)$_2$]$^+$. The obtained residue was dissolved with 200 μL of 1-hexene, and half of it was mixed with 50 μL of $BH_3\cdot THF$ and 5 mL of 1-hexene in a steel vessel. The mixture was charged with 10 bar of H_2 and continuously stirred at 90 °C. The reaction process was monitored by a Buechi Pressflow gas controller.

In Situ Preparation of the Rhenium(I) Iodo Hydride Complex [Re(I)(H)(NO)(PiPr$_3$)$_2$(η^2-$CH_2{=}CHBu$)] (3a-I) and Its Test for Catalytic Activity. In a small vial in a glovebox, **2a** (12.4 mg, 0.02 mmol) and 1-hexene (0.1 mL) were mixed in 0.5 mL of benzene. To the light yellow solution was added $AgSbF_6$ (10.3 mg, 0.03 mmol), and a brown precipitate was formed immediately. After being stirred at room temperature for 5 min, the solution was filtered through Celite. The filtrate was checked by ^{31}P NMR spectroscopy, indicating the quantitative formation of a new species which might be assigned to a complex salt, [Re(H)(NO)(P*i*Pr$_3$)$_2$(η^2-$CH_2{=}CHBu$)$_2$][SbF_6]. $^{31}P\{^1H\}$ NMR (80.94 MHz, benzene, ppm): δ 27.5 (d, J = 112 Hz, 1P), 24.3 (d, J = 122 Hz, 1P). To the filtrate was added *n*NBu$_4$I (11.1 mg, 0.03 mmol). The mixture was kept at room temperature for 2 h, and ^{31}P NMR spectroscopy indicated the formation of iodide hydride analogue **3a-I** in 81% in situ yield along with 19% rhenium(I) fluoro hydride byproduct **3a-F**. The following are data for **3a-I**. ^1H NMR (300.08 MHz, benzene-d_6, ppm): δ 3.36−3.59 (t, $^2J_{HP}$ = 30.0 Hz, 2H, ReH and $CH_2{=}CH-$), 3.13 (m, 2H, $CH_2{=}CH-$), 2.87 (m, 6H, $PCH(CH_3)_2$), 1.78 (m, 2H, CH_2), 1.54 (m, 4H, CH_2), 1.24 (m, 36H, $PCH(CH_3)_2$), 1.04 (t, $^3J_{HH}$ = 6.0 Hz, 3H, CH_3). $^{31}P\{^1H\}$ NMR (121.47 MHz, benzene, ppm): δ 10.5 (d, J = 120 Hz, 1P), 3.7 (d, J = 120 Hz, 1P). ESI-MS spectroscopy confirmed the composition of fragments of **3a-I** bearing a Re−I unit. MS (ESI): *m/z* 718.9 {[Re(I)(NO)(P*i*Pr$_3$)$_2$(η^2-$CH_2{=}CHBu$)] − Et}$^+$. The solution was dried in vacuo, and the residue was extracted with pentane (4 × 2 mL). The solvent was evaporated, affording a light brown residue (5.6 mg, 0.006 mmol, of **3a-I**). The obtained residue was dissolved with 5 mL of 1-hexene, to which 30 μL of $BH_3\cdot THF$ was added. The mixture was charged with 10 bar of H_2 and continuously stirred at 90 °C. The reaction process was monitored by a Buechi Pressflow gas controller.

Halide Exchange Experiments As Traced by ^{31}P NMR Spectroscopy. In a 3 mL Young NMR tube, **2a** (6.2 mg, 0.01 mmol), 1-hexene (10.0 μL, 0.08 mmol), and *n*Bu$_4$NCl (14 mg, 0.05 mmol) were mixed in benzene (0.5 mL). The mixture was kept at 85 °C for 5 min. ^{31}P NMR spectra indicated the formation of **3a-Cl** in stoichiometric yield. $^{31}P\{^1H\}$ NMR (80.94 MHz, benzene, ppm): δ 19.1 (d, J = 130 Hz, 1P), 17.3 (d, J = 130 Hz, 1P). Furthermore, to the obtained mixture was added *n*Bu$_4$NF in THF (50 μL, 0.05 mmol). ^{31}P NMR spectra indicated the immediate formation of **3a-F** at room temperature within 1 min. $^{31}P\{^1H\}$ NMR (80.94 MHz, benzene, ppm): δ 26.1 (dd, J_{PP} = 145 Hz, J_{FP} = 31 Hz, 1P), 19.3 (dd, J_{PP} = 145 Hz, J_{FP} = 31 Hz, 1P).

Similarly, in a 3 mL Young NMR tube, **2b** (8.4 mg, 0.01 mmol), 1-hexene (10.0 μL, 0.08 mmol), and *n*Bu$_4$NCl (14 mg, 0.05 mmol) were mixed in benzene (0.5 mL). The mixture was kept at 85 °C for 5 min, and the ^{31}P NMR spectra indicated the formation of [Re(Cl)(H)(NO)(PCy$_3$)$_2$(η^2-$CH_2{=}CHBu$)] (**3b-Cl**) in stoichiometric yield. $^{31}P\{^1H\}$ NMR (80.94 MHz, benzene, ppm): δ 7.9 (d, J = 132 Hz, 1P), 4.8 (d, J = 132 Hz, 1P). Subsequently, *n*Bu$_4$NF in THF (50 μL, 0.05 mmol) was added to the obtained mixture. The ^{31}P NMR spectra indicated the immediate formation of [Re(F)(H)(NO)(PCy$_3$)$_2$(η^2-$CH_2{=}CHBu$)] (**3b-F**). $^{31}P\{^1H\}$ NMR (80.94 MHz, benzene, ppm): δ 13.8 (dd, J_{PP} = 146 Hz, J_{FP} = 34 Hz, 1P), 6.4 (dd, J_{PP} = 146 Hz, J_{FP} = 34 Hz, 1P). Detailed experimental data for **3b-F**, **3b-Cl**, and **3b-I** are given in the Supporting Information.

VT ^{31}P NMR Measurement of the Reaction between 3a and Boron Lewis Acids in 1-Hexene. In a 3 mL Young NMR tube, **2a** (6.2 mg, 0.01 mmol) and 0.05 mmol of each boron Lewis acid ($B(C_6F_5)_3$, 26.0 mg; $BH_3\cdot THF$, 50 μL; BEt_3, 50 μL; BPh_3,12.2 mg) were mixed in 0.5 mL of 1-hexene. The immediate formation of the 18 e$^-$ 1-hexene-coordinated rhenium(I) hydride **3a** was observed in quantitative yield, as checked by the ^{31}P NMR spectra. The mixture was monitored by ^{31}P NMR spectroscopy in the temperature range of +23 to −80 °C in intervals of 20 °C.

H_2/D_2 Scrambling Experiments. In a 3 mL Young NMR tube, **2a** (3.1 mg, 0.005 mmol) and $B(C_6F_5)_3$ (12.8 mg, 0.025 mmol) were dissolved in 0.5 mL of toluene-d_8. The nitrogen atmosphere was replaced with 1100 mbar of H_2 and D_2 in a 1:1 ratio using a freeze−pump−thaw cycle. The solution was immediately investigated by ^1H NMR spectroscopy in a temperature range of +23 to −50 °C in intervals of 20 °C. At 296 K, H_2, HD, and rhenium-coordinated H_2 (or HD) cannot be observed due to a too fast exchange between free H_2 and coordinated H_2. ^1H NMR (199.95 MHz, toluene-d_8, ppm, 296 K): δ 3.82 (br, ReH, free H_2, η^2-H_2), 2.40 (m, 6H, $PCH(CH_3)_2$), 1.18 (m, 36H, $PCH(CH_3)_2$). At 243 K, a broad triplet at around 4.5 ppm could be detected. ^1H NMR (199.95 MHz, toluene-d_8, ppm, 243 K): δ 4.48 (s, free H_2), 4.45 (t, J = 42 Hz, HD), 3.40 (t, J = 26 Hz, 1H, ReH), 3.06 (br, 2H, η^2-H_2), 2.37 (m, 6H, $PCH(CH_3)_2$), 1.16 (m, 36H, $PCH(CH_3)_2$). At 223 K, the formation of HD was observed. ^1H NMR (199.95 MHz, toluene-d_8, ppm, 223 K): δ 4.50 (s, free H_2), 4.46 (t, J = 43 Hz, HD), 3.47 (t, J = 26 Hz, 1H, ReH), 3.08 (br, 2H, η^2-H_2), 2.33 (m, 6H, $PCH(CH_3)_2$), 1.14 (m, 36H, $PCH(CH_3)_2$). From the NMR results, it is concluded that the H_2/D_2 scrambling occurs spontaneously at room temperature with the **2a**/$B(C_6F_5)_3$ system.

The 500 MHz ^{1}H NMR data are as follows. ^{1}H NMR (500.25 MHz, toluene-d_8, 223 K, ppm): 4.46 (t, $J_{HD} = 43$ Hz, HD, $T_1 = 827$ ms), 3.44 (t, $J_{HP} = 26$ Hz, ReH, $T_1 = 264$ ms), 3.42 (t, $J_{HP} = 25$ Hz, ReH, $T_1 = 260$ ms), 3.07 (m, ReH_2, $T_1 = 116$ ms), 2.73 (br, ReHD, $T_1 = 501$ ms). ^{31}P NMR (202.5 MHz, toluene-d_8, 223 K, ppm): 41.72 (s), 41.66 (s), 41.53 (s), 41.44 (s).

Reaction of the 2a/$B(C_6F_5)_3$ System with D_2. In a 3 mL Young NMR tube, **2a** (12.4 mg, 0.02 mmol) and $B(C_6F_5)_3$ (30 mg, 0.06 mmol) were mixed in toluene (0.5 mL). The nitrogen atmosphere was replaced with 995 mbar of D_2 using a freeze−pump−thaw cycle. VT ^{2}H NMR measurements were carried out immediately. At 293 K, a broad signal was observed in the range of 3.00−5.00 ppm. ^{2}H NMR (93.13 MHz, toluene-d_8, ppm, 293 K): δ 3.30 (free D_2, ReD, η^2-D_2). At low temperatures, such as 213 K, the formation of the Re−D/D_2 isotopomer was clearly observed, displaying a broad singlet at 3.56 and 3.13 ppm. ^{2}H NMR (93.13 MHz, toluene-d_8, 213 K, ppm): δ 4.55 (s, HD), 4.50 (s, free D_2), 3.56 (br, ReD, $T_1 = 22$ ms), 3.13 (br, ReD_2, $T_1 = 24$ ms). ^{31}P NMR (202.5 MHz, toluene-d_8, 213 K, ppm): 41.40 (s, ReD/D_2).

Isomerization of 1-Octene to (*E*/*Z*)-2-Octene Induced by the 2a/$B(C_6F_5)_3$ System. In a 3 mL Young NMR tube, **2a** (12.4 mg, 0.02 mmol), $B(C_6F_5)_3$ (30 mg, 0.06 mmol), and 1-octene (15 μL, 0.10 mmol) were dissolved in 0.5 mL of toluene-d_8. The solution was immediately investigated by ^{1}H NMR spectroscopy, and the formation of (*E*)- or (*Z*)-2-octene was observed instantly in 23% in situ yield. ^{1}H NMR (199.95 MHz, toluene-d_8, ppm): δ 5.33 (m, $-CH{=}CH-$). In the case of the isomerization of 1-hexene induced by the **2a**/$B(C_6F_5)_3$ system, the same conditions were applied. In the reaction of 1-hexene with **2a** alone, a high temperature of 80 °C was applied to initiate the isomerization.

Hydrogenation of 1-Hexene Catalyzed by the in Situ Prepared active Complex from 2a with $AgSbF_6$. In a small vial in a glovebox, **2a** (6.3 mg, 0.01 mmol) and 1-hexene (5.0 mL) were mixed. To the light yellow solution was added $AgSbF_6$ (6.9 mg, 0.02 mmol), and a brown precipitate was formed immediately. After being stirred at room temperature for 10 min, the solution was filtrated through Celite, and the filtrate was transferred to a steel vessel. After being flushed with 10 bar of H_2 once, the system was charged with 10 bar of H_2 and was heated in an oil bath with stirring at 90 °C. The progress of the reaction was monitored by a Buechi Pressflow gas controller. At the end of the reaction, the autoclave was cooled to ambient temperature and vented carefully. The hydrogenation products were characterized by ^{1}H NMR spectroscopy in $CDCl_3$, and the conversion of the hydrogenation was calculated on the basis of the consumption of H_2.

Filtration Experiments. In a 30 mL steel autoclave equipped with a stirring bar, 1-hexene (5 mL) and **2a**/$BH_3 \cdot THF$ (0.01 mmol/0.05 mmol) were mixed. After one flush with 10 bar of H_2, the system was charged with 10 bar of H_2 and was heated in an oil bath with stirring at 90 °C. After 5 min, a TON of 2000 was reached, corresponding to a 50% conversion. At this point, the reaction was terminated manually by removing the H_2 atmosphere and cooling the reaction vessel to room temperature. Then the autoclave was transferred to a glovebox, and the solution was found to be light brown and clear without any precipitate or colloids formed. The filtrate was examined by ^{31}P NMR spectroscopy, indicating the presence of **3a** (66%, δ 14.7 (d, $J = 127$ Hz, 1P), 11.6 (d, $J = 127$ Hz, 1P)), free P*i*Pr_3 (10%, δ 20.4 ppm), and an unknown organometallic species (24%, δ 55.4 (s)). The solution was filtered through Celite into a new vessel with a new stirring bar, to which 2 mL of 1-hexene was readded. No residue was visible on the Celite surface. The catalysis batch was repeated at 90 °C under 10 bar of H_2, and it was found that the high activity still remained (TOF of 1.2×10^4 h^{-1}). The Celite was washed with 2 mL of 1-hexene and transferred into a autoclave vessel containing 5 mL of 1-hexene. No catalytic activity was observed at 90 °C under 10 bar of H_2 within 1 h. Similar manipulations were applied to the **2a**/BPh_3 system except that 3 mL of 1-hexene was used and the reaction was terminated at 53% conversion within 3 min.

Mercury Poisoning Experiments. In a 30 mL steel autoclave equipped with a stirring bar, excess mercury (96−112 mg) was added to the 1-hexene (5 mL) solution loaded with **2a**/BPh_3 (0.01 mmol/0.05 mmol) or **2a**/$B(C_6F_5)_3$ (0.01 mmol/0.05 mmol) before the catalysis was carried out. The hydrogenation catalyzed by the **2a**/$B(C_6F_5)_3$ system was carried out at 23 °C under either 1 or 10 bar of H_2. The hydrogenation catalyzed with the **2a**/BPh_3 system was carried out at 90 °C under 10 bar of H_2.

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Supporting Information Available: Various experimental details, figures including the KIE measurements, the filtration and mercury poisoning experiments, catalysis under 1 bar of H_2, and the halide exchange experiments, and NMR spectra including those of the VT ^{1}H NMR and VT ^{2}H NMR measurements for H_2/D_2 scrambling and the isomerization reactions of terminal alkenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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