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Electron-Rich PNP- and PNN-Type Ruthenium(II) Hydrido Borohydride Pincer Complexes. Synthesis, Structure, and Catalytic Dehydrogenation of Alcohols and Hydrogenation of Esters

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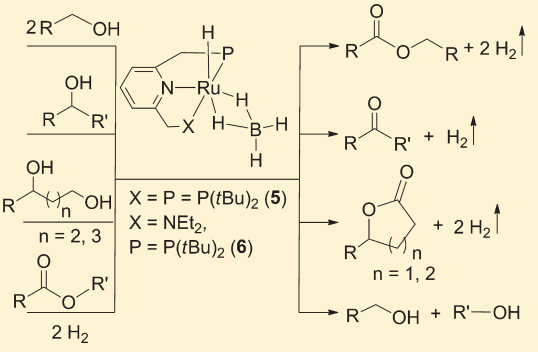
Supporting Information

ABSTRACT: Electron-rich PNP- and PNN-type ruthenium(II) hydrido borohydride pincer complexes, [RuH(BH_4)(^{t}Bu-PNP)] (tBu-PNP = (2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) (**5**) and [RuH(BH_4)(^{t}Bu-PNN)] (^{t}Bu-PNN = 2-di-*tert*-butylphosphinomethyl-6-diethylaminomethylpyridine) (**6**), were prepared from their corresponding N_2-bridged dinuclear Ru(II) complexes [(^{t}Bu-PNP)$RuCl_2$]$_2$(μ-N_2) (**3**) and [(^{t}Bu-PNN)$RuCl_2$]$_2$(μ-N_2) (**4**), respectively. The X-ray structure of **5** reveals a BH_4^- anion η^2 coordinated to ruthenium through two bridging hydrides. A variable-temperature ^{1}H NMR study of **6** exhibits interesting fluxional behavior of the BH_4^- ligand. Similarly, the Ru(II) hydrido borohydride complex **9**, in which the BH_4^- moiety is coordinated in a η^1 bonding mode, was obtained by reaction of [$RuCl_2(PPh_3)$(^{i}Pr-PNP)] (^{i}Pr-PNP = 2,6-bis(diisopropylphosphinomethyl)pyridine) (**8**) with two equivalents of $NaBH_4$ at room temperature. The hydrido borohydride pincer complexes **5**, **6**, and **9** catalyze the acceptorless dehydrogenative coupling of primary alcohols to esters and the dehydrogenation of secondary alcohols to the corresponding ketones, accompanied by evolution of hydrogen gas. The reactivity follows the order **6** > **9** > **5**. With the hydrido borohydride complex **6** as catalyst, high yields (up to 98%) and high turnover numbers (TON ~1000) were obtained in the dehydrogenation of primary alcohols under mild and neutral conditions. In addition, **6** effectively catalyzes the hydrogenation of nonactivated aromatic and aliphatic esters to the corresponding alcohols with TON ~200 under a relatively mild pressure of dihydrogen and neutral and homogeneous conditions. Thus, an efficient homogeneous catalytic system for the dehydrogenation−hydrogenation reactions of alcohols is developed, which is relevant to the current interest in hydrogen storage.



INTRODUCTION

Transition metal borohydride complexes display extensive reactivity with organic substrates and are useful starting materials for the preparation of transition metal hydrides and borides.[1] They have found uses in catalytic hydroboration,[2] polymerization of olefins,[3] and cyclic esters.[4] Ruthenium hydrido borohydride complexes based on bidentate phosphorus ligands and diamines, reported by Noyori[5] and Morris,[6] are effective catalysts in asymmetric transfer hydrogenation of ketones,[5,6] hydrogenation of esters to the corresponding alcohols,[7] and enantioselective Michael addition.[6] Whittlesey et al. recently reported four ruthenium hydrido borohydride complexes bearing series of N-heterocyclic carbene ligands, which are active catalysts for hydrogenation of aromatic ketones.[8] Synthesis of ruthenaborane clusters using ruthenium borohydride complex as precursor has also been reported recently.[9] In addition, borohydride complexes may represent plausible models for CH_4 coordination in the transition state for C−H activation.[10]

Transition metal complexes of bulky, electron-rich tridentate ligands have found useful applications in synthesis, bond activation, and catalysis.[11] The highly electron-donating ^{t}Bu-PNP (2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) and its group 8 metal complexes have been explored by several groups,[12−14] including ours.[15,16a]

Dehydrogenation of alcohols to carbonyl compounds in the absence of a hydrogen acceptor or oxidant, with the evolution of molecular hydrogen, is attractive economically and environmentally (Scheme 1), but homogeneous systems capable of thermally catalyzing dehydrogenation of alcohols are relatively rare.[15c,16a,17−25] Recently, we have reported that electron-rich, bulky ^{t}Bu-PNP-ruthenium complexes catalyze acceptorless dehydrogenation of secondary alcohols to ketones.[15c] When primary alcohols were used, a facile reaction to produce esters with the evolution of molecular hydrogen took place.[16a] The catalytic efficiency of the latter reaction was enhanced with Ru(II) complexes of an analogous ligand having a potentially "hemilabile" amine "arm", ^{t}Bu-PNN

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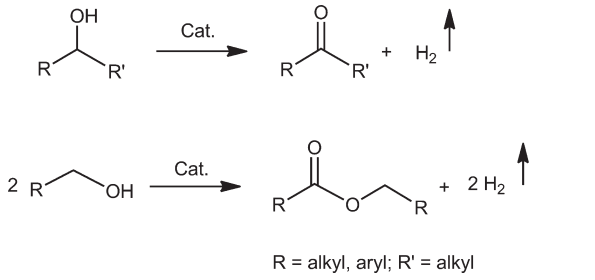
(2-(di-*tert*-butylphosphinomethyl)-6-diethylaminomethyl)-pyridine). (^{t}Bu-PNN)Ru(II) complexes effectively catalyze the acceptorless dehydrogenative coupling of primary alcohols to the corresponding esters and molecular hydrogen in high yields and turnover numbers, in the presence of a catalytic amount of base.[16a,17] Mechanistic studies of this reaction have led to the discovery of a dearomatized PNN Ru hydrido carbonyl complex, which does not require the presence of base, the catalytic reaction proceeding very effectively under neutral, mild conditions.[16a] Following this finding, it was discovered that complex **1** is an efficient catalyst for hydrogenation of esters to alcohols,[15f] the novel coupling of alcohols and amines to yield amides with liberation of H_2,[16b] unique light-induced splitting of water to hydrogen and oxygen,[16c] hydrogenation of amides to alcohols and amines,[16d] transesterfication of esters,[16e] amidation of amines by esters with extrusion of H_2,[16f] and the novel hydrogenation of organic carbonates, carbamates, and formates under very mild conditions.[16g] Complex **2** is an excellent catalyst for the synthesis of imines from alcohols and amines, with liberation of water and H_2[15h] and N−H activation of ammonia.[15i] We now report that dehydrogenation of alcohols to the corresponding carbonyl compound such as esters (from primary alcohols) or ketones (from secondary alcohols) with extrusion of dihydrogen can also be effectively accomplished under very mild conditions with stable, readily synthesized electron-rich PNN- and PNP-Ru borohydride complexes, in the absence of base, under neutral conditions, and in the absence of a hydrogen acceptor.

Scheme 1. Dehydrogenation of Alcohols with Extrusion of Dihydrogen



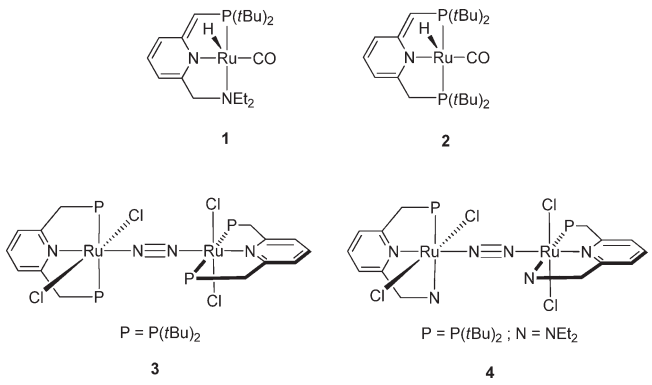


Figure 1. Electron-rich PNN- and PNP-type Ru(II) pincer complexes.

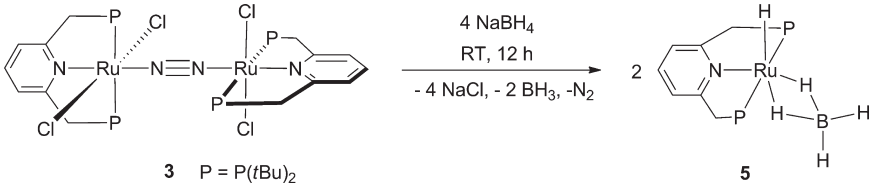
RESULTS AND DISCUSSION

Synthesis and Characterization of [RuH(η^2-BH$_4$)(^{t}Bu-PNP] 5. The N_2-bridged binuclear Ru(II) complex [(^{t}Bu-PNP)-$RuCl_2$]$_2$(μ-N_2) (**3**) was prepared by the reaction of $RuCl_2$-$(PPh_3)_3$ with one equivalent of the ligand 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine (^{t}Bu-PNP) according to a previously reported procedure from our group.[15c] Treatment of **3** with an excess (5 equiv) of $NaBH_4$ in 2-propanol for 12 h resulted in the formation of the Ru(II) hydrido borohydride complex **5** in almost quantitative yield by $^{31}P\{^1H\}$ NMR (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibits a singlet peak at δ 86.3 ppm, representing a downfield shift of δ 21 ppm relative to parent complex **3** (δ 65.0 ppm). In the ^1H NMR spectrum, the hydride ligand gives rise to a triplet peak at δ −16.09 ppm with J_{PH} = 18.0 Hz. In addition, two broad signals are observed for the two bridging hydrides at δ −16.01 and −4.48 ppm, and another broad feature is also observed at δ 5.49 ppm belonging to the terminal boron hydrides. The IR spectrum of **5** indicates two strong bands in the terminal B−H region at 2395 and 2327 cm^{-1} and two bands in the bridging M−H−B region at 2104 and 2024 cm^{-1}, consistent with the bidentate η^2-BH_4 bonding mode.[3c]

Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of a pentane solution of **5** at −32 °C (~3 days). The crystal structure of **5** (Figure 2) displays a distorted octahedral geometry around the ruthenium center, including the pincer ligand (^{t}Bu-PNP), hydride, and the BH_4 units. The hydride ligand is bound to the Ru center *cis* to the pyridine nitrogen (N1−Ru1−HRu, 80(2)°), while the BH_4 unit is coordinated to the Ru(II) center in a η^2 bonding mode. The two Ru−H bonds to the chelating BH_4 unit are not equal (1.67(4) and 1.85(5) Å, respectively), while the corresponding Ru−H bonds in the reported structure of RuH(BH_4)-$(PMe_3)_3$[26a] are of equal length. The difference in the case of **5** is likely a result of the larger *trans* effect of hydride relative to that of the pyridinic nitrogen atom. Because of the meridional coordination geometry of the ^{t}Bu-PNP framework and lack of a plane of symmetry involving the P, N, and P atoms, the protons of the four *tert*-butyl and two methylene groups are magnetically nonequivalent.

Synthesis and Characterization of [RuH(η^2-BH$_4$)(^{t}Bu-PNN)], 6. The N_2-bridged binuclear Ru(II) complex [($RuCl_2$-$(PNN))_2$](μ-N_2) (**4**) was prepared by the reaction of

Scheme 2. Synthesis of Complex 5



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$RuCl_2(PPh_3)_3$ with one equivalent of the ^{t}Bu-PNN pincer ligand, using a similar method to the one used for the preparation of **3**.[17] Treatment of **4** with an excess (5 equiv) of $NaBH_4$ in 2-propanol for 12 h resulted in the formation of the ruthenium(II) hydrido borohydride complex **6** in excellent yield, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of **6** shows a singlet peak at δ 116.7 ppm, representing a downfield shift of δ 29 ppm relative to the starting complex **4**. The hydride ligand of complex **6** gives rise to a doublet at δ −16.24 ppm with J_{PH} = 28.0 Hz in the ^{1}H NMR spectrum. The IR spectrum of **6** exhibits two strong bands in the terminal B−H region at 2378 and 2311 cm^{-1} and two bands in the bridging Ru−H−B region at 2096 and 1956 cm^{-1}, similar to the IR spectrum of complex **5**, consistent with the bidentate η^2-BH_4 bonding mode.[3c]

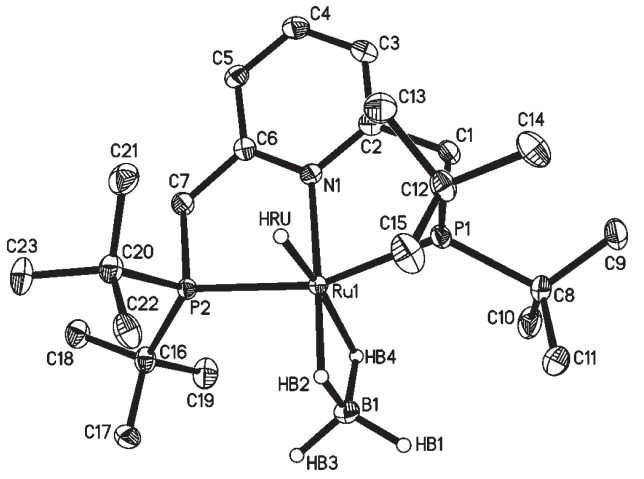


Figure 2. ORTEP diagram of complex **5** with thermal ellipsoids at the 50% probability level. All hydrogen atoms except the hydrides are omitted for clarity.

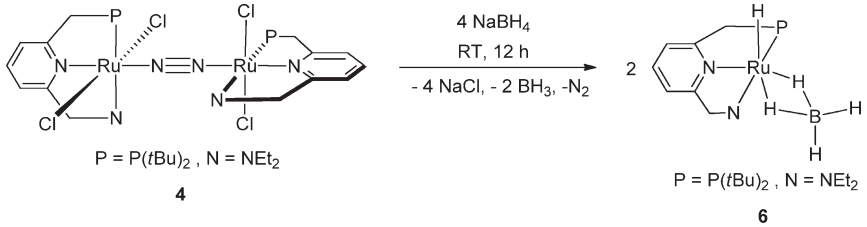
Table 1. Selected Bond Distances (Å) and Angles (deg) of Complex 5

Ru1−N1	2.123(3)	Ru1−P1	2.312(1)
Ru1−P2	2.322(1)	Ru1−HRu	1.57(4)
Ru1−HB2	1.67(4)	Ru1−HB4	1.85(5)
N1−Ru1−HRu	80(2)	HRu−Ru1−HB4	167(2)
P1−Ru1−P2	159.6(0.3)	HB2−Ru1−N1	177(2)
N1−Ru1−P2	82.9(1)	P1−Ru1−N1	82.5(1)
P2−Ru1−HRu	79(1)	HRu−Ru1−P1	84(2)
HB2−Ru1−HB4	69(2)	HB3−B1−HB1	111(3)
HB2−B1−HB4	103(3)		

At room temperature, one broad singlet peak at δ −13.01 ppm is observed in the ^{1}H NMR spectrum of complex **6** for one proton of BH_4^-. A variable-temperature ^{1}H NMR (in 400 MHz) study of **6** in toluene-d_8 is shown in Figure 3, revealing interesting fluxional behavior of the BH_4^- ligand. At 213 K, two singlets are observed at −δ 13.21 and −4.33 ppm for the bridging hydrides and two broad singlets at δ 4.70 and 5.13 ppm for the two terminal hydrides of the BH_4^- ligand, respectively. Upon raising the temperature to 248 K, the signals for the two terminal hydrides are coalesced, while the signal at δ −4.33 ppm collapses. At 263 K, the signal (δ ∼5 ppm) for the two terminal hydrides and the signal at δ −4.33 ppm for one bridging hydride disappear in the baseline and the signal (δ −13.21 ppm) of the other bridging hydride also collapses. Upon increasing the temperature to 323 K, the resonance at δ −13.21 ppm disappears into the baseline of the spectrum. At 353 K, a very broad singlet peak appears around δ −2 ppm, indicating that the four hydrides of the BH_4^- moiety start to coalesce. The signal of the terminal Ru−H ligand appears as a doublet peak throughout the 213−373 K temperature range, indicating that it does not participate in the fluxional process of the BH_4^- ligand. These variable-temperature ^{1}H NMR spectra of complex **6** are similar to those reported for the (bidentate η^2 bonding mode) complexes $RuH(BH_4)(PMe)_3$[26a] and $RuH(BH_4)(ttp)$ (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$).[26b] The bridging hydride (δ −4.33 ppm) *trans* to the terminal Ru−H exchanges positions with the two terminal hydrides on the boron at 263 K. These hydrogen atoms further exchange with the bridging hydride (δ −13.21 ppm) *trans* to pyridinic nitrogen above 323 K, and the calculated coalescence frequency at δ −2.0 ppm was observed at 353 K.

Synthesis and Characterization of $[RuCl_2(PPh_3)(^i$Pr-PNP$)]$ (8) and $[RuH(\eta^1\text{-}BH_4)(PPh_3)(^i$Pr-PNP$)]$ (9). Heating a suspension of $RuCl_2(PPh_3)_3$ with one equivalent of 2,6-bis(diisopropylphosphinomethyl)pyridine (^{i}Pr-PNP) **7** in THF at 65 °C for 6 h resulted in formation of the complex **8** in 75% yield (Scheme 4). The $^{31}P\{^1H\}$ NMR spectrum of **8** exhibits one doublet at δ 46.4 ppm and one triplet peak at δ 43.2 ppm, indicating that triphenylphosphine is coordinated to the Ru(II) center, as observed also with the reported Ph-PNP-Ru(II) dichloride complex (Ph-PNP = 2,6-bis(diphenylphosphinomethyl)pyridine).[27] In contrast, the ^{t}Bu complexes **3** and **5** do not contain coordinated PPh_3, under similar preparation conditions, probably because of the steric bulk of the *tert*-butyl group of the ^{t}Bu-PNP and the ^{t}Bu-PNN ligands. The two methylene groups of the ^{i}Pr-PNP give rise to one triplet peak at δ 3.92 ppm with J_{PH} = 4.0 Hz, indicating the existence of a symmetric plane involving the P, N, and P atoms. The PPh_3 ligand is coordinated to the Ru(II) center *trans* to the nitrogen atom of the ^{i}Pr-PNP, and the chloride ligands are coordinated to the metal center *trans* to each other.

Scheme 3. Synthesis of Complex 6



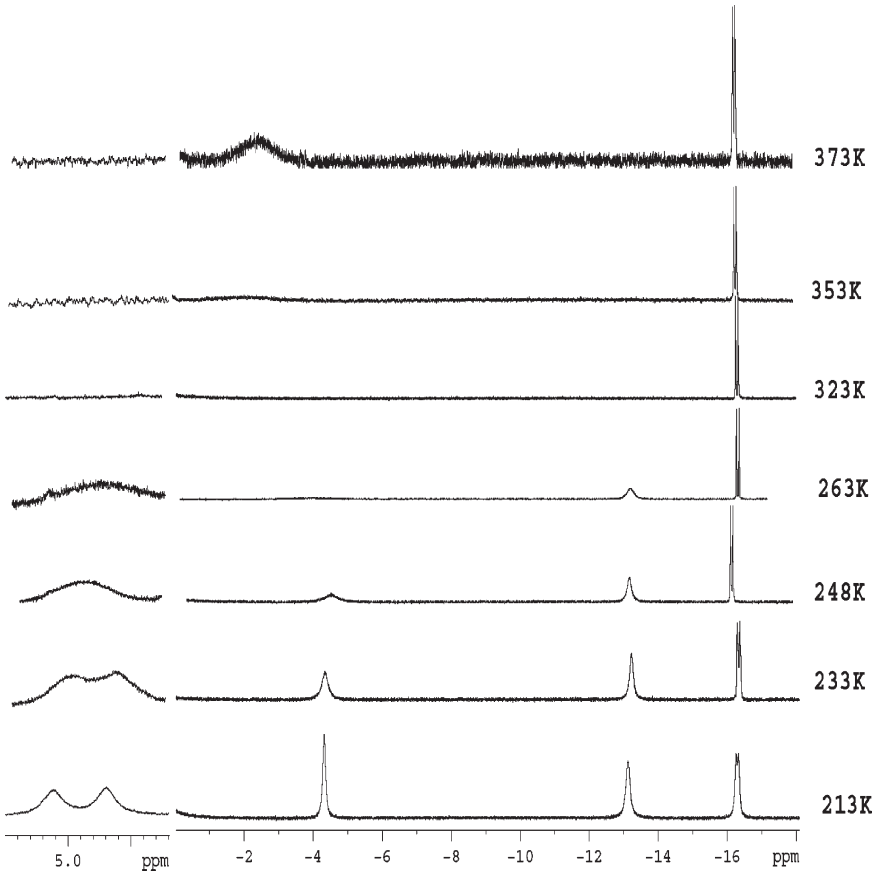
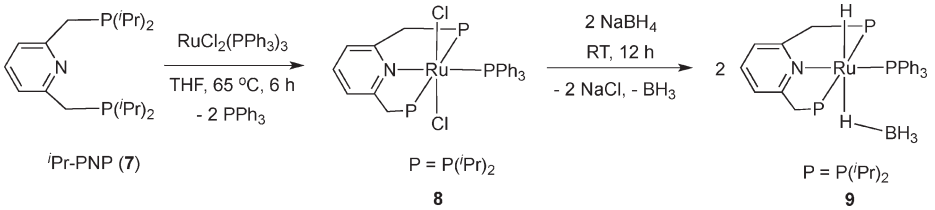


Figure 3. Variable-temperature (213−373 K) ^{1}H NMR (400 MHz) spectra of complex **6** in the region of Ru−H and BH_4^- ligands (toluene-d_8 as solvent).

Scheme 4. Synthesis of Complexes 8 and 9



In analogy with the preparation of complexes **5** and **6**, treatment of complex **8** with an excess (2.5 equiv) of $NaBH_4$ in 2-propanol for 12 h at room temperature resulted in the precipitation of the Ru(II) hydrido borohydride complex **9** as a yellow solid in 85% yield (Scheme 4). The $^{31}P\{^{1}H\}$ NMR spectrum of **9** exhibits a doublet signal at δ 61.6 ppm and a triplet signal at δ 67.9 ppm, corresponding to the two phosphorus atoms of the ^{i}Pr-PNP and one phosphorus atom of the PPh_3, respectively. It is noted that the signal of the PPh_3 ligand of **9** is downfield shifted relative to that of the ^{i}Pr-PNP, unlike the corresponding signals of complex **8**. The Ru−H gives rise in the ^{1}H NMR of **9** to a quartet signal at δ −14.0 ppm with $J_{PH} = J_{P'H} =$ 28.0 Hz. A broad peak at δ −0.84 ppm is assigned for the four protons of the BH_4 ligand, which is probably coordinated to the Ru(II) center in a η^1 bonding mode, similar to the reported bonding of ruthenium borohydride complexes by Noyori[5] and Morris.[6] The IR spectrum of **9** exhibits strong absorption bands at 2361 and 2292 cm^{-1} and a strong broad peak at 1884 cm^{-1}, consistent with the monodentate η^1-BH_4 bonding mode,[3c] and variable-temperature ^{1}H NMR studies on complex **9** were not performed.

Catalytic Activities of Hydrido Borohydride Ru(II) Pincer Complexes. Dehydrogenation of Alcohols Catalyzed by Complexes 5, 6, and 9. The ruthenium hydrido borohydride complexes **5**, **6**, and **9** catalyze the dehydrogenation of alcohols with extrusion of molecular hydrogen under base-free conditions. 1-Phenylethanol was selected as test substrate for optimizing the dehydrogenation of alcohols to the corresponding carbonyl compounds. Initial experiments revealed that the reaction could be achieved without the need for base and hydrogen acceptors. Thus, refluxing a toluene solution containing 1-phenylethanol and a catalytic amount (0.1 mol %) of **5** under an

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Table 2. Dehydrogenation of Secondary Alcohols to the Corresponding Ketones Catalyzed by Complexes 5, 6, and 9[a]

entry	cat.	alcohol	temp (°C)	time (h)	conv (%)[b]	yield (%)[b]
1	**5**	1-phenylethanol	115	24	27	27
2	**6**	1-phenylethanol	115	24	87	87
3	**9**	1-phenylethanol	115	24	77	77
4	**6**	1-phenylethanol	115	48	93	93 (81)[c]
5	**6**	2-hexanol	115	48	83	83
6	**6**	2-butanol	110	48	89	89
7	**6**	cyclohexanol	115	48	57	56
8[d]	**6**	2-propanol	83	48	13	13
9	**6**	2-propanol	105	48	90	90

[a] Reaction conditions: catalyst (0.01 mmol), alcohol (10 mmol), and 2 mL of toluene were refluxed in an open system under argon. [b] Conversion and yields of the products were analyzed by GC. [c] Isolated yield. [d] Refluxed in absence of solvent in an open system under argon.

Table 3. Dehydrogenation of Primary Alcohols to Esters and Aldehydes Catalyzed by Complexes 5, 6, and 9[a]

entry	cat.	alcohol	temp (°C)	conv (%)[b]	yield of aldehyde (%)[b]	yield of ester (%)[b]
1	**5**	benzyl alcohol	115	75	4	70
2	**5**	1-hexanol	115	72	3	69
3[c]	**5**	1-hexanol	157	70	10	59
4	**6**	benzyl alcohol	115	99	0	99 (88)[d]
5	**6**	1-hexanol	115	94	0	94 (77)[d]
6	**6**	1-butanol	110	96		96
7	**9**	benzyl alcohol	115	62	3	59
8[c]	**9**	1-hexanol	157	57.5	10	47

[a] Reaction conditions: catalyst (0.01 mmol), alcohol (10 mmol), and toluene (2 mL) were heated under reflux for 24 h in an system under argon. [b] Conversion and yields of the products were analyzed by GC. [c] Reflux under (solvent-free) neat condition in an open argon atm. [d] Isolated yields.

argon atmosphere for 24 h resulted in 29% conversion of the alcohol to acetophenone, accompanied by the evolution of hydrogen gas, as determined by GC and GC-MS analysis (Table 2, entry 1). Notably, under similar conditions (1000 equiv of alcohol/cat.; reflux at 24 h) employing **6** or **9** as catalysts, acetophenone was formed in 87% and 77% yield, respectively (Table 2, entries 2 and 3). The catalytic activity of the PNN-derived complex **6** is significantly higher than that of the PNP-derived complex **5** or **9**, probably as a result of the potentially "hemilabile" amine arm of **6**, which can play an important role in the catalytic cycle.[16] Similar kinds of reactivity were also observed for their corresponding dearomatized complexes **1** and **2**. As expected, a longer reaction time (48 h) resulted in a higher yield of the ketone (Table 2, entry 4). Other secondary alcohols can also be dehydrogenated to the corresponding ketones using complex **6** as catalyst in good yields (Table 2, entries 5−9). The catalysis by **6** was quite sensitive to the reaction temperature (and/or solvent), and when 2-propanol was heated at 80 °C with 0.1 mol % of complex **5** under solvent-free conditions, acetone was formed in only 13% yield with TON 126 after 48 h (Table 2, entry 8), while when heated in toluene at 105 °C, 90% of acetone was formed during the same reaction period with a higher TON of 900 (Table 2, entry 9).

In contrast to the dehydrogenation of secondary alcohols to the corresponding ketones, homogeneous systems capable of dehydrogenation of primary alcohols to the corresponding aldehydes or esters are very rare,[16a,b,17,18,24,25] probably because of decarbonylation of the product (or intermediate) aldehyde to form an inactive carbonyl complex.[28]

When a toluene solution of benzyl alcohol and 0.1 mol % complex **5** was refluxed for 24 h in an open system under argon, benzyl benzoate was formed in 70% yield, accompanied by 4% of benzaldehyde (Table 3, entry 1). Refluxing 1-hexanol with 0.1 mol % **5** in toluene (115 °C) or neat (157 °C) for 24 h resulted in formation of 59% and 69% of hexyl hexanoate, accompanied by 3% and 10% of hexanal, respectively (Table 3, entries 2 and 3). Complex **9** was slightly less catalytically active than **5** under these conditions (Table 3, entries 7 and 8). The PNN complex **6** exhibited significantly higher catalytic activity than that of the PNP complexes **5** and **9**. Thus, benzyl alcohol, 1-hexanol, and 1-butanol were dehydrogenated to the corresponding esters in over 95% yield (Table 3, entries 4−6) with extrusion of H_2 using a catalytic amount of **6** (0.1 mol %).

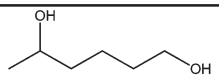
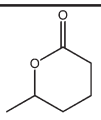
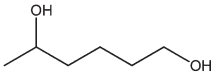
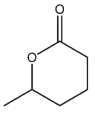
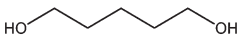
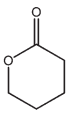
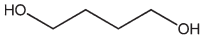
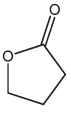
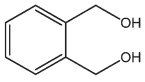
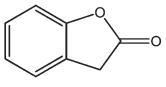
Dehydrogenation of Diols to Lactones Catalyzed by Complexes 5 and 6. Next we examined the catalytic activity of complexes **5** and **6** for the dehydrogenative cyclization of diols to the corresponding lactones[22,29] under very mild, acceptorless conditions with liberation of dihyrogen as the only byproduct. Thus, refluxing a toluene solution containing 3 mmol of 1,5-hexanediol (bearing both secondary and primary alcohol groups) and a catalytic amount of **5** (0.0 L mmol) under an argon atmosphere for 48 h resulted in a 33% yield of 6-methyltetrahydro-2*H*-pyran-2-one, as observed by ^{1}H NMR spectroscopy of the crude reaction mixture (Table 4, entry 1). Significantly, under similar conditions (300 equiv of diol/cat.; 48 h reflux) using **6** as catalyst, the lactone was formed in 72% yield (Table 4, entry 2) by ^{1}H NMR. The reaction is general, and various diols were dehydrogenated to the corresponding lactones (Table 4).

Hydrogenation of Esters Catalyzed by Complexes 5 and 6. Catalytic dehydrogenation and hydrogenation reactions of organic molecules are fundamental and important processes in organic transformations.[30] Moreover, these reactions have recently attracted considerable attention from the viewpoint of hydrogen storage. This phenomenon is common and well studied in the case of nitrogen heterocycles.[31] To the best of our knowledge, no reports deal with reversible dehydrogenation−hydrogenation of an alcohol−ester couple under very mild, neutral conditions using a well-defined soluble catalyst except for complex **1** as reported by us.[15k,16a]

While the ruthenium hydrido borohydride complexes **5**, **6**, and **9** catalyze the dehydrogenative coupling reaction of alcohols to form esters and dihydrogen, we expected that it is possible to reverse the reaction by the application of mild hydrogen pressure.[15f,k] Thus, complexes **5** and **6** were employed as catalyst for the hydrogenation of nonactivated esters using dihydrogen under base-free and relatively very mild conditions. Thus, when a THF solution of butyl butyrate (2 mmol) and complex **5** (0.01 mmol) was heated at 110 °C (bath temperature) for 12 h under 10 atm of H_2, only 9% yield of 1-butanol was determined by GC

(Table 5, entry 1). Remarkably, under similar conditions complex **6** was very efficient, and almost quantitative conversion to 1-butanol was observed. Thus, heating a THF solution of butyl butyrate (2 mmol) and complex **6** (0.01 mmol) at 110 °C (bath temperature) for 12 h under 10 atm of H_2 yielded 97% of 1-butanol as observed by GC, with the corresponding consumption of dihydrogen (Table 5, entry 4). Hydrogenation of methyl benzoate resulted in formation of 96% of benzyl alcohol and 93% of methanol after 12 h (Table 5, entry 6). The reaction is general and does not require activated esters (Table 5). The high efficiency of complex **6** in the hydrogenation reaction may be a result of hemilability of the amine arm.

Table 4. Dehydrogenation of Diols to the Corresponding Lactones Catalyzed by Complexes 5 and 6[a,b,c]

entry	cat.	diol	temp. (°C)	time (h)	yield of lactone (%)[b]
1	**5**		115	48	 (33)
2	**6**		115	48	 (72)
3	**6**		115	48	 (81)
4	**6**		115	48	 (86)
5	**6**		115	48	 (90) and 76[c]

[a] Reaction conditions: catalyst (0.01 mmol), diol (3 mmol) and 2 mL of toluene were refluxed in an open system under argon. [b] Yields of the lactones were analyzed by ^{1}H NMR of the reaction mixture. [c] Isolated yield.

The reaction provides an attractive method for "green", mild synthesis of primary alcohols from nonactivated esters without the need for the traditionally used stoichiometric amounts of metal hydride reagents, which generate stoichiometric amounts of waste.[7,15k,15f,32,33]

SUMMARY

New electron-rich PNP (complexes **5**, **9**) and PNN (complex **6**) ruthenium(II) hydrido borohydride pincer complexes were prepared and were found to catalyze the acceptorless dehydrogenative coupling of primary alcohols to esters, the dehydrogenation of secondary alcohols to the corresponding ketones, and dehydrogenative cyclization of diols to lactones, accompanied by evolution of hydrogen gas. The PNN complex **6** is the most effective, and it also catalyzes the hydrogenation of nonactivated esters to the corresponding alcohols with TON ≈ 200 under relatively mild pressure of H_2, neutral and homogeneous conditions. These dehydrogenation−hydrogenation reactions of alcohols−esters are of interest synthetically, as well as in the context of hydrogen storage.

EXPERIMENTAL SECTION

General Procedures. All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Complexes **3**[15c] and **4**[17] were prepared according to a previously reported procedure from our group. The ligand ^{i}Pr-PNP (2,6-bis-(diisopropylphosphinomethyl)pyridine)[34] and $RuCl_2(PPh_3)_3$[35] were prepared according to literature procedures.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 400 or 500, 100 or 126, and 162 or 202 MHz, respectively, using Bruker AMX-400 and AMX-500 NMR spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{31}P NMR chemical shifts are reported in parts per million downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid

Scheme 5. Catalytic Hydrogenation of Esters to the Corresponding Alcohols

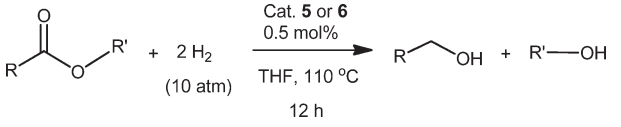


Table 5. Hydrogenation of Esters Catalyzed by Complexes 5 and 6[a]

entry	ester	catalyst	PH_2 (atm)	time (h)	conv (%)[b]	products (yield [%])[b]
1	butyl butyrate	**5**	10	12	10	1-butanol (9)
2	benzyl benzoate	**5**	10	12	17	benzyl alcohol (15)
3	hexyl hexanoate	**6**	10	12	94	1-hexanol (94)
4	butyl butyrate	**6**	10	12	98	1-butanol (97)
5	benzyl benzoate	**6**	10	12	99	benzyl alcohol (99)
6	methyl benzoate	**6**	10	12	97	benzyl alcohol (96), methanol (93)

[a] A solution of complex **5** or **6** (0.01 mmol) and ester (2 mmol) in THF (2 mL) was heated at 110 °C (bath temperature) under H_2 (10 atm) for 12 h. [b] Conversion of esters and percentage of maximum possible amount of each of the product alcohols were determined by GC.

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in D_2O. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, v, virtual. Elemental analyses were performed at Kolbe Laboratorium, Mulheim, Germany. IR spectra were recorded on a Nicolet FT-IR spectrophotometer. GC−MS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. GC analyses were carried out using a Carboxen 1000 column on a HP 690 series GC system or HP-5 cross-linked 5% phenylmethylsilicone column (30 m × 0.32 mm × 0.25 μm film thickness, FID) on a HP 6890 series GC system.

Synthesis of [RuH(η^2-BH_4)(^{t}Bu-PNP)] (5). To a suspension of complex **3** (58 mg, 0.05 mmol) in 2-propanol (10 mL) was added a very fine powder of $NaBH_4$ (9.5 mg, 0.25 mmol), and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was filtered, the orange filtrate was evaporated under vacuum, and the residue was extracted with diethyl ether (3 × 5 mL). The ether solution was evaporated under vacuum to yield complex **5** as an orange solid.

Yield: 50 mg (98%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 86.3 (s). ^1H NMR (C_6D_6): δ −16.09 (t, 1H, J_{PH} = 18.0 Hz, Ru-*H*), −16.01 (br s, 1H, B*H*$_4$), −4.48 (br s, 1H, B*H*$_4$), 1.45 (t, 18H, J_{PH} = 6.0 Hz, P(C(C*H*$_{a3}$)$_3$)), 1.56 (t, 18H, J_{PH} = 6.0 Hz, P(C(C*H*$_{b3}$)$_3$)$_2$), 3.08 (dt, 2H, J_{HH} = 16.0 Hz, J_{PH} = 4.0 Hz, C*H*$_a$HP), 3.19 (dt, 2H, J_{HH} = 16.0 Hz, J_{PH} = 4.0 Hz, CH*H*$_b$P), 5.49 (br s, 2H, B*H*$_4$), 6.52 (d, 2H, J_{HH} = 8.0 Hz, Py-*H*3 and Py-*H*5), 6.76 (t, 1H, J_{HH} = 8.0 Hz, Py-*H*4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 29.7 (s, P(C(*C*$_a$H$_3$)$_2$)$_2$), 30.2 (s, P(C(*C*$_b$H$_3$)$_3$)$_2$), 35.0 (t, J_{PC} = 6.5 Hz, P(*C*$_a$(CH$_3$)$_3$)$_2$), 35.6 (t, J_{PC} = 5.0 Hz, P(*C*$_b$(CH$_3$)$_3$)$_2$), 39.0 (t, J_{PC} = 7.0 Hz, *C*H$_2$P), 118.2 (t, J_{PC} = 4.0 Hz, Py-*C*3 and Py-*C*5), 131.0 (s, Py-*C*4), 165.1 (t, J_{PC} = 4.5 Hz, Py-*C*2 and Py-*C*6). IR (KBr pellets): 2395, 2327, 2104, 2024, 1461, 1184 cm^{-1}. Anal. Calcd for $C_{23}H_{48}BNP_2Ru$: C, 53.90; H, 9.45. Found: C, 53.86; H, 9.49.

Synthesis of [RuH(η^2-BH_4)(^{t}Bu-PNN)] (6). To a suspension of complex **4** (51 mg, 0.05 mmol) in 2-propanol (10 mL) was added a very fine powder of $NaBH_4$ (9.5 mg, 0.25 mmol), and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was filtered, the orange filtrate was evaporated under vacuum, and the orange solid residue was extracted with diethyl ether (3 × 5 mL). The ether solution was evaporated under vacuum to yield complex **6** as a red-orange solid, which was dried under vacuum overnight.

Yield: 40 mg (91%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 116.7 (s). ^1H NMR (C_6D_6, 298 K): δ −16.24 (t, 1H, J_{PH} = 28.0 Hz, Ru-*H*), −13.10 (br s, 1H, B*H*$_4$), 0.84 (t, 3H, J_{HH} = 6.0 Hz, N(CH$_2$C*H*$_{a3}$)$_2$), 0.99 (t, 3H, J_{HH} = 6.0 Hz, N(CH$_2$C*H*$_{b3}$)$_2$), 1.28 (d, 9H, J_{PH} = 12.0 Hz, P(C(C*H*$_{a3}$)$_3$)), 1.43 (d, 9H, J_{PH} = 12.0 Hz, P(C(C*H*$_{b3}$)$_3$)$_2$), 2.31 (m, 1H, N(C*H*$_a$HCH$_3$)$_2$), 2.49 (m, 1H, N(CH*H*$_{a'}$CH$_3$)$_2$), 2.71 (dd, 1H, J_{HH} = 16.0 Hz, J_{PH} = 8.0 Hz, C*H*$_a$HP), 2.98 (dd, 1H, J_{HH} = 16.0 Hz, J_{PH} = 12.0 Hz, CH*H*$_b$P), 3.05 (m, 1H, N(C*H*$_b$HCH$_3$)$_2$), 3.41 (d, 1H, J_{HH} = 14.0 Hz, NC*H*$_a$H-Py), 3.54 (d, 1H, J_{HH} = 14.0 Hz, NCH*H*$_b$-Py), 3.73 (m, 1H, N(CH*H*$_{b'}$CH$_3$)$_2$), 6.30 (d, 1H, J_{HH} = 8.0 Hz, Py-*H*5), 6.51 (d, 1H, J_{HH} = 8.0 Hz, Py-*H*3), 6.71 (t, 1H, J_{HH} = 8.0 Hz, Py-*H*4), signals for three other protons of BH_4 collapsed in the baseline (which was detected at low-temperature NMR spectra). ^1H NMR (toluene-d_8, 243 K): δ −16.30 (t, 1H, J_{PH} = 28.0 Hz, Ru-*H*), −13.21 (br s, 1H, B*H*$_4$), −4.33 (br s, 1H, B*H*$_4$), 0.71 (br s, 3H, N(CH$_2$C*H*$_{a3}$)$_2$), 0.92 (br s, 3H, N(CH$_2$C*H*$_{b3}$)$_2$), 1.18 (d, 9H, J_{PH} = 12.0 Hz, P(C(C*H*$_{a3}$)$_3$)), 1.35 (d, 9H, J_{PH} = 12.0 Hz, P(C(C*H*$_{b3}$)$_3$)$_2$), 2.10 (m, 1H, N(C*H*$_a$HCH$_3$)$_2$), 2.31 (m, 1H, N(CH*H*$_b$CH$_3$)$_2$), 2.53 (dd, 1H, J_{HH} = 16.0 Hz, J_{PH} = 8.0 Hz, C*H*$_a$HP), 2.82 (dd, 1H, J_{HH} = 16.0 Hz, J_{PH} = 8.0 Hz, CH*H*$_b$P), 2.93 (br m, 1H, N(C*H*$_{a'}$HCH$_3$)$_2$), 3.15 (d, 1H, J_{HH} = 16.0 Hz, NC*H*$_a$H-Py), 3.33 (d, 1H, J_{HH} = 16.0 Hz, NCH*H*$_b$-Py), 3.37 (m, 1H, N(CH*H*$_{b'}$CH$_3$)$_2$), 4.69 (br s, 1H, B*H*$_4$), 5.00 (br s, 1H, B*H*$_4$), 6.16 (d, 1H, J_{HH} = 8.0 Hz, Py-*H*5), 6.38 (d, 1H, J_{HH} = 8.0 Hz, Py-*H*3), 6.62 (t, 1H, J_{HH} = 8.0 Hz, Py-*H*4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.8 (s, N(CH$_2$*C*$_a$H$_3$)$_2$), 11.0 (s, N(CH$_2$*C*$_b$H$_3$)$_2$), 29.0 (d, J_{PC} = 4.0 Hz, P(C(*C*H$_3$)$_3$)$_2$), 34.2 (d, J_{PC} = 15.1 Hz, P(*C*$_a$(CH$_3$)$_3$)$_2$), 37.0 (d, J_{PC} = 10.0 Hz, P(*C*$_b$(CH$_3$)$_3$)$_2$), 38.9 (d, J_{PC} = 19.1 Hz, *C*H$_2$P), 51.1 (s, N(*C*$_a$H$_2$CH$_3$)$_2$), 51.2 (s, N(*C*$_b$H$_2$CH$_3$)$_2$), 63.7 (s, *C*H$_2$N-Py), 117.5 (s, Py-*C*3), 118.5 (s, Py-*C*5), 128.8 (s, Py-*C*4), 159.9 (s, Py-*C*6), 163.7 (d, J_{PC} = 4.0 Hz, Py-*C*2). IR (KBr pellets): 2378, 2311, 2096, 1956, 1469, 1177 cm^{-1}. Anal. Calcd for $C_{19}H_{40}BN_2PRu$: C, 51.93; H, 9.18. Found: C, 51.86; H, 9.24.

Synthesis of [$RuCl_2$(PPh_3)(^{i}Pr-PNP)] (8). To a suspension of $Ru(PPh_3)_3Cl_2$ (480 mg, 0.5 mmol) in dry THF (20 mL) was added the ligand 2,6-bis(diisopropylphosphinomethyl)pyridine (^{i}Pr-PNP) (**7**) (170 mg, 0.5 mmol), and the reaction mixture was heated at 65 °C for 6 h with constant stirring. The clear, yellow solution was concentrated to ∼4 mL under vacuum, and 20 mL of pentane was added to precipitate a yellow solid. The solid was isolated by filtration, washed with pentane (3 × 2 mL), and dried under vacuum to give 290 mg (75% yield) of **8** as an analytically pure sample.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.4 (d, J_{PP} = 27.5 Hz), 43.2 (t, J_{PP} = 27.5 Hz). ^1H NMR (CD_2Cl_2): δ 0.87 (q, 12H, J_{PH} = J_{HH} = 8.0 Hz, P(CH(C*H*$_{a3}$)$_2$)$_2$), 1.13 (q, 12H, J_{PH} = J_{HH} = 8.0 Hz, P(CH(C*H*$_{b3}$)$_2$)$_2$), 2.43 (m, 4H, P(C*H*$_a$(CH$_3$)$_2$)$_2$), 3.92 (t, 4H, J_{PH} = 4.0 Hz, 2C*H*$_2$P), 7.26 (m, 9H, P(C$_6$*H*$_5$)$_3$), 7.30 (d, 2H, J_{HH} = 8.0 Hz, Py-*H*3 and Py-*H*5), 7.53 (t, 1H, J_{HH} = 8.0 Hz, Py-*H*4), 7.91 (m, 6H, P(C$_6$*H*$_5$)$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 19.6 (s, P(CH(*C*$_a$H$_3$)$_2$)$_2$), 20.7 (s, P(CH(*C*$_b$H$_3$)$_2$)$_2$), 25.1 (t, J_{PC} = 8.0 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 38.9 (t, J_{PC} = 10.1 Hz, *C*H$_2$P), 119.9 (s, Py-C3 and Py-C5), 127.2 (d, J_{PC} = 9.0 Hz, *m*-*C*$_6$H$_5$-P), 128.8 (s, *p*-*C*$_6$H$_5$-P), 135.0 (d, J_{PC} = 9.0 Hz, *o*-*C*$_6$H$_5$-P), 136.7 (s, Py-*C*4), 140.4 (d, J_{PC} = 36.2 Hz, *ipso*-*C*$_6$H$_5$-P), 164.8 (t, J_{PC} = 4.0 Hz, Py-*C*2 and Py-*C*6). Anal. Calcd for $C_{37}H_{50}NP_3Cl_2Ru$: C, 57.44; H, 6.52. Found: C, 57.28; H, 6.53.

Synthesis of [RuH(η^1-BH_4)(PPh_3)(^{i}Pr-PNP)] (9). To a suspension of complex **8** (77 mg, 0.1 mmol) in 2-propanol (10 mL) was added a fine powder of $NaBH_4$ (9.5 mg, 0.25 mmol), and the reaction mixture was stirred at room temperature for 12 h and then filtered. The resulting yellow solid was washed with 2-propanol (3 × 2 mL) and then dissolved in benzene (10 mL), and the solution was filtered. The yellow filtrate was evaporated to dryness under vacuum, to yield complex **9** as a yellow solid, which was dried under vacuum overnight to give 61 mg (85% yield) of analytically pure compound.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.6 (d, J_{PP} = 29.2 Hz), 67.9 (t, J_{PP} = 29.2 Hz). ^1H NMR (C_6D_6): δ −14.0 (q, 1H, J_{PH} = 28.0 Hz, Ru-*H*), −0.84 (br s, 4H, B*H*$_4$), 0.91 (q, 6H, J_{PH} = J_{HH} = 8.0 Hz, P(CH(C*H*$_3$)$_2$)$_2$), 0.87 (m, 12H, J_{PH} = J_{HH} = 8.0 Hz, P(CH(C*H*$_3$)$_2$)$_2$), 1.18 (q, J_{PH} = J_{HH} = 8.0 Hz, 6H, P(CH(C*H*$_3$)$_2$)$_2$), 1.44 (m, 2H, P(C*H*$_a$(CH$_3$)$_2$)$_2$), 1.77 (m, 2H, P(C*H*$_b$(CH$_3$)$_2$)$_2$), 2.85 (dt, 2H, J_{HH} = 16.0 Hz, J_{PH} = 4.0 Hz, C*H*$_a$HP), 3.92 (dt, 2H, J_{HH} = 16.0 Hz, J_{PH} = 4.0 Hz, CH*H*$_b$P), 6.56 (d, 2H, J_{HH} = 8.0 Hz, Py-*H*3 and Py-*H*5), 6.79 (t, 1H, J_{HH} = 8.0 Hz, Py-*H*4), 7.01 (d, 3H, J_{HH} = 8.0 Hz, P(C$_6$*H*$_5$)$_3$), 7.12 (t, 6H, J_{HH} = 8.0 Hz, P(C$_6$*H*$_5$)$_3$), 8.18 (t, 6H, J_{HH} = 8.0 Hz, P(C$_6$*H*$_5$)$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.0 (s, P(CH(*C*$_a$H$_3$)$_2$)$_2$), 18.5 (s, P(CH(*C*$_b$H$_3$)$_2$)$_2$), 19.6 (s, P(CH(*C*$_{a'}$H$_3$)$_2$)$_2$), 20.8 (s, P(CH(*C*$_{b'}$H$_3$)$_2$)$_2$), 25.6 (t, J_{PC} = 8.0 Hz, P(*C*$_a$H(CH$_3$)$_2$)$_2$), 26.4 (t, J_{PC} = 11.6 Hz, *C*H$_2$P), 39.2 (t, J_{PC} = 6.0 Hz, P(*C*$_b$H(CH$_3$)$_2$)$_2$), 118.4 (t, J_{PC} = 2.5 Hz, Py-*C*3 and Py-*C*5), 127.1 (d, J_{PC} = 9.0 Hz, *m*-*C*$_6$H$_5$−P), 128.8 (s, *p*-*C*$_6$H$_5$−P), 134.2 (s, Py-*C*4), 135.7 (d, J_{PC} = 10.1 Hz, *o*-*C*$_6$H$_5$-P), 142.0 (d, J_{PC} = 36.2 Hz, *ipso*-*C*$_6$H$_5$-P), 163.7 (t, J_{PC} = 4.5 Hz, Py-*C*2 and Py-*C*6). IR (KBr pellet): 2361, 2293, 2246, 1884, 1458, 1060 cm^{-1}. Anal. Calcd for $C_{37}H_{55}BNP_3Ru$: C, 61.84; H, 7.72. Found: C, 61.98; H, 7.66.

General Procedures for Catalytic Dehydrogenation of Alcohols. (a) Complex **5** (0.01 mmol), **6** (0.01 mmol), or **9** (0.01 mmol) was dissolved in the neat primary or secondary alcohol (10 mmol). The flask was equipped with a condenser, and the solution was heated with stirring in an open system under argon at the specified temperature and time (Tables 2 and 3). After cooling to room temperature, the product aldehydes, esters, or ketones were determined

by GC, using mesitylene or benzene (in the case of 1-butanol) as internal standard, employing a Carboxen 1000 column on a HP 6890 series GC system.

(b) A solution containing the catalyst (0.01 mmol) (complex **5**, **6**, or **9**) and the alcohol (10 mmol) in toluene (2 mL) was heated in a flask equipped with a reflux condenser under argon in an open system at the specified temperatures and times (Tables 2 and 3). After cooling to room temperature, the products were determined by GC using mesitylene or benzene (for 1-butanol) as internal standard, employing a Carboxen 1000 column on a HP 6890 series GC system.

General Procedure for the Catalytic Dehydrogenation of Diols to Lactones. Complex **5** or **6** (0.01 mmol), diol (3 mmol), and toluene (2 mL) were taken in a Schlenk flask under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox. The flask was equipped with a condenser, and the solution was refluxed with stirring in an open system under argon for 48 h. After cooling to room temperature, the yield of the lactones was determined by ^{1}H NMR spectroscopy from the reaction mixture.

Isolation of Products (for Table 2, entry4, Table 3, entries 4 and 5, and Table 4, entry 5). The reaction mixture was cooled to room temperature (after the reaction time mentioned in the corresponding tables), and the resulting mixture was concentrated in vacuo for about 3−4 h. The purification was performed on a silica gel column using a hexane−ethylacetate mixture as eluent. The products were analyzed by ^{1}H NMR, and the spectra were identical with the authentic sample.

General Procedure for Catalytic Hydrogenation of Esters. A 100 mL Fischer−Porter tube was charged with the catalyst **5** or **6** (0.01 mmol), the ester (2.0 mmol), and THF (2 mL) under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox. The pressure tube was taken out of the glovebox and subjected to three successive cycles of pressurization/venting with H_2 (2 atm), then pressurized with H_2 (10 atm) and closed. The tube was placed behind a protective shield, and the reaction mixture was heated in an oil bath at 110 °C with constant stirring for 8 h. After cooling to room temperature, excess H_2 was vented off carefully and the products were determined by GC with *m*-xylene (1.0 mmol) as an internal standard.

X-ray Crystal Structure Determination of 5. The crystal was mounted on a nylon loop and flash frozen in a nitrogen stream at 120 K. Data were collected on a Nonius Kappa CCD diffractometer mounted on a FR590 generator equipped with a sealed tube with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The structure was solved using the direct method with SHELXS-97 based on F^2.

Complex ***5****:* $C_{23}H_{48}BNP_2Ru$, yellow plate, 0.40 × 0.40 × 0.30 mm^3, monoclinic, s.g. $P2_1$, a = 12.541(2) Å, b = 15.314(3) Å, c = 15.131(3) Å, β = 111.85(3)°, V = 2697.3(11) Å^3, Z = 4, fw = 512.44, $F(000)$ = 1088, D_c = 1.262 Mg/m^3, μ = 0.709 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.0325 for data with $I > 2\sigma(I)$ and R = 0.0364 for all data (11 912 reflections) with a goodness-of-fit of 1.014. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H−Ru and Hb1−Hb4, which were located in the difference map and refined independently. The X-ray crystal structure of complex **5** is deposited in the CCDC with number 620246.

■ ASSOCIATED CONTENT

Supporting Information. CIF file containing X-ray crystallographic data for complex **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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