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Ester Hydrogenation Catalyzed by CNN-Pincer Complexes of Ruthenium

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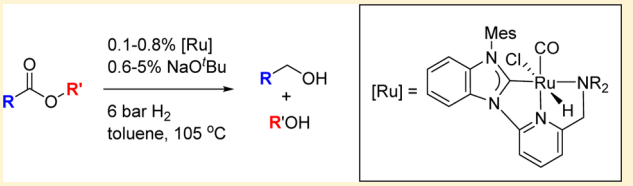
Supporting Information

ABSTRACT: Ruthenium complexes supported by two new CNN-pincer ligands were synthesized. Both were tested as catalysts for the hydrogenation of esters under mild conditions (105 °C, 6 bar H_2). A striking dependence on ligand structure was observed, as a dimethylamino-substituted ligand gave a nearly inactive catalyst, while a diethylamino-substituted variant gave up to 980 catalytic turnovers for the hydrogenation of benzyl benzoate. This system catalyzes the hydrogenation of various substrates including ethyl, benzyl, and hexyl esters, but is surprisingly unreactive toward methyl esters. Experiments demonstrate that base-catalyzed transesterification is rapid under the reaction conditions and that methyl esters are effectively hydrogenated when benzyl alcohol is added to the reaction mixture. The reverse reaction, dehydrogenation of primary alcohols to give esters, was tested as well; up to 920 catalytic turnovers were observed for the dehydrogenation of 1-hexanol to hexyl hexanoate.



INTRODUCTION

The reduction of esters to alcohols is an essential transformation in organic synthesis. Classical methods for laboratory-scale ester reduction with stoichiometric reagents such as $LiAlH_4$ are efficient and predictable, but suffer from low atom economy.[1] On the industrial scale, fatty acid esters are reduced to alcohols by heterogeneous hydrogenation catalysis, typically employing high temperature and pressure.[2] The development of efficient homogeneous catalysts for ester hydrogenation that operate under milder conditions is therefore of great interest, for both economic and environmental purposes.

Although homogeneous catalysts for ester hydrogenation, based primarily on ruthenium, have been known since the early 1980s,[3] progress in the development of highly efficient catalysts has greatly accelerated over the past decade.[4] In 2006, Milstein and co-workers reported a highly active ruthenium PNN-pincer catalyst for ester hydrogenation, which is capable of reversible protonation and deprotonation at the methylene carbon linking the pyridine ring to the di-*tert*-butylphosphino moiety (Figure 1).[5] This acid/base reactivity at a ligand site has become an important design principle for catalytic hydrogenation of polar bonds via the heterolytic activation of H_2.[6] Several structural variations have since been reported as highly active ester-hydrogenation catalysts, including Gusev's Ru-PNN[7a] and SNS[7b] pincer complexes, Kuriyama's Ru-MACHO complex,[7c] and Clarke's Ru-PNN complex.[7d]

N-Heterocyclic carbenes (NHCs) are now firmly established as robust spectator ligands in transition-metal catalysis, due to their exceptional σ-donating capability.[8] Recently, several ruthenium-pincer complexes containing NHC fragments[9] have been developed as bifunctional catalysts for ester hydrogenation or the reverse reaction, dehydrogenative coupling of primary alcohols to esters (Figure 1). Many of these catalysts feature an imidazole ring linked to a pyridine ring by a CH_2 group, which has the potential for reversible deprotonation during catalysis. In each case,[9a−d] stoichiometric reaction of the precatalyst with strong base led to a dearomatized species where a methylene proton adjacent to the NHC was removed, analogous to Milstein's PNN-Ru system.

In the CNN-pincer systems developed by Sánchez and Song, as well as Milstein's PNN-Ru system, an alternative site of deprotonation is the methylene group linking the pyridine ring to the dialkylamine arm. DFT studies of Milstein's complex showed that the tautomer formed by deprotonation at the amine side is less stable than the tautomer shown in Figure 1 by 6.6 kcal/mol, but is still a likely intermediate in photocatalytic water splitting.[10] Song and co-workers showed, also by DFT, that the tautomer of their Ru-CNN complex deprotonated at the amine side is less stable than the tautomer deprotonated at the NHC side by 9.5 kcal/mol.[9c] Experimentally, they observed complete deprotonation at the NHC side upon reaction with strong bases, but exchange of the CH_2 linker hydrogens with deuterium from D_2 indicated that deprotonation at the amine side was kinetically accessible.

In an effort to probe the catalytic relevance of reversible deprotonation at the different positions in cooperative pincer ligands of this nature, we have synthesized two new Ru-CNN pincer complexes that lack CH_2 linkers on the NHC side, contrasting the ligands developed by Song and Sánchez (Figure

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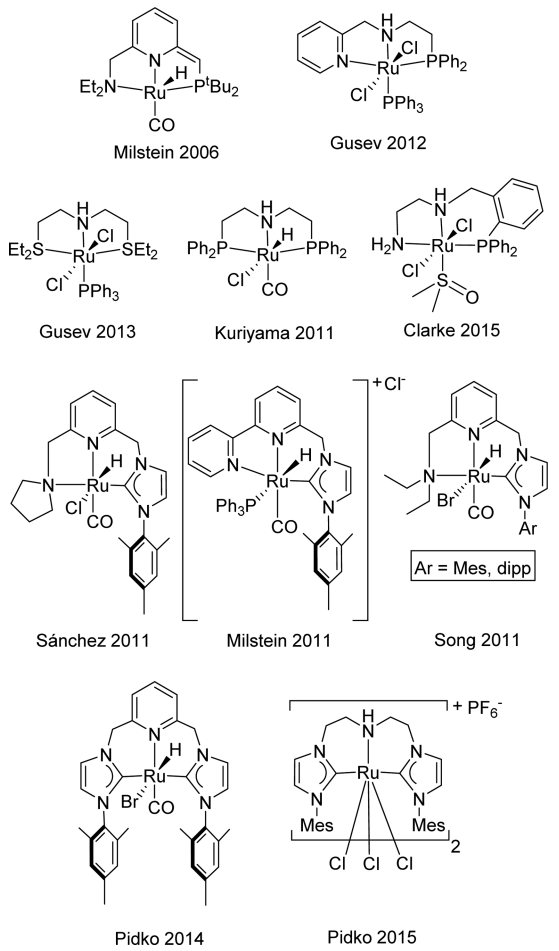


Figure 1. Ruthenium-pincer complexes for ester hydrogenation.

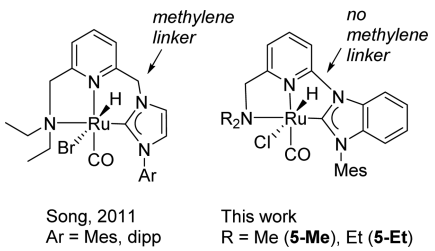


Figure 2. Comparison of Song's CNN-Ru complexes and the newly reported complexes in this work.

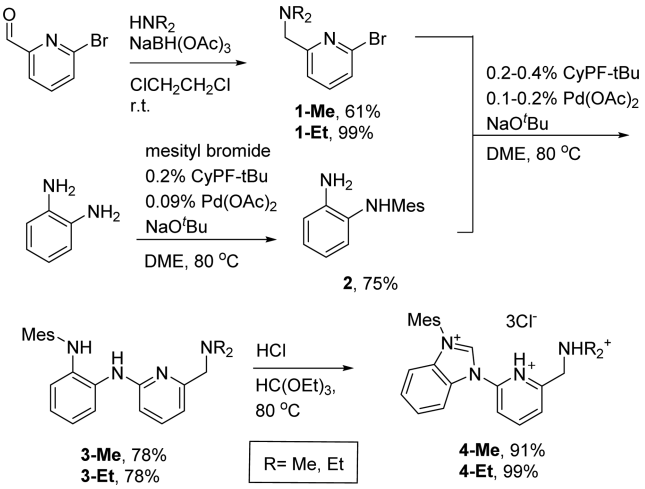
2). In addition to removing the possibility of deprotonation at this position, an increase in the structural rigidity of the ligand backbone is expected. Subtle ligand modifications of this nature have previously been shown to have substantial effects on reactivity in the context of alkane-dehydrogenation catalysis.[11,12]

Complexes **5-Me** and **5-Et** were tested as catalysts for ester hydrogenation, showing turnover numbers up to 980 under mild conditions (105 °C, 6 bar H_2). Surprisingly, a subtle change from NMe_2 to NEt_2 is associated with a drastic increase in catalytic activity. Although **5-Et** is unreactive toward methyl esters, it is highly active for the hydrogenation of other esters such as benzyl, ethyl, and hexyl, as well as lactones. The dehydrogenation of primary alcohols—the microscopic reverse of ester hydrogenation—was briefly explored, and **5-Et** showed promise as a catalyst for this reaction as well.

RESULTS AND DISCUSSION

Ligand Synthesis and Metalation. We have previously reported the synthesis of CCC-pincer ligands bearing two benzimidazole groups, employing successive palladium-catalyzed aminations to construct the ligand backbone followed by cyclization with triethylorthoformate to give dicationic bis-benzimidazolium salts.[11,13] The two novel ligands **4-Me** and **4-Et** were synthesized in a similar fashion, as shown in Scheme 1.

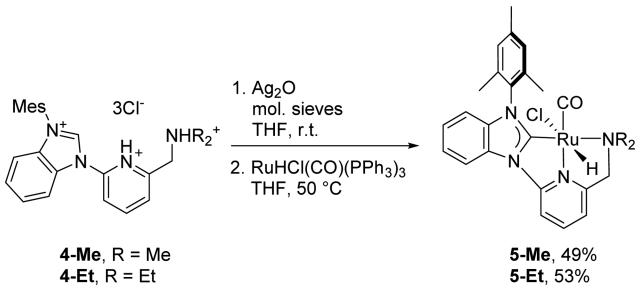
Scheme 1. Synthesis of CNN-Pincer Ligands 4-Me and 4-Et



The reductive amination of 6-bromopyridine-2-carboxaldehyde with the appropriate secondary amines gave compounds **1-Me** and **1-Et**. The known diamine **2**, synthesized previously in two steps,[14] was prepared in one step via the palladium-catalyzed coupling of 1,2-diaminobenzene and mesityl bromide.[15] Compounds **1-Me** and **1-Et** were then coupled[15] with diamine **2** to give the corresponding ligand precursors **3-Me** and **3-Et**. Finally, the ligands **4-Me** and **4-Et** were obtained as trihydrochloride salts via cyclization using HCl and triethylorthoformate.

As NHC complexes, especially those of multidentate NHC ligands, are often challenging to synthesize,[16] a wide variety of methods for their metalation have been developed.[17] Transmetalation from the silver-NHC complex[18] was employed in the synthesis of Sánchez's CNN-Ru complex,[9a] while complexation of free carbenes generated by the reaction of the imidazolium salt with strong base was successful in the synthesis of Song's CNN-Ru complex.[9c] For our CNN-pincer ligands **4-Me** and **4-Et**, transmetalation from silver proved to be the more reliable route (Scheme 2). For the formation of the

Scheme 2. Synthesis of Ruthenium-Pincer Complexes via Transmetalation



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silver NHC complex, the presence of molecular sieves to absorb the byproduct water was crucial, as the silver complex did not form cleanly when they were omitted. Transmetalation to ruthenium to give **5-Me** and **5-Et** occurred smoothly as monitored by ^{1}H NMR spectroscopy, but the isolation of the pure product was challenging. Although silver halide often precipitates upon transmetalation of NHCs from silver, in this case the silver-containing byproduct showed a similar solubility profile to the desired products and was identified by crystallography as the known tetramer $Ag_4Cl_4(PPh_3)_4$.[19] While the desired products **5-Me** and **5-Et** are moderately air stable in solution, they decompose during column chromatography in air, giving irreproducible yields. The ultimately successful isolation strategy involved collecting the crude precipitate from the THF reaction solution, performing air-free column chromatography on neutral alumina, and finally recrystallizing from CH_2Cl_2/toluene/pentane.

Both **5-Me** and **5-Et** were characterized by X-ray crystallography, NMR spectroscopy, and elemental analysis. Crystal structures of **5-Me** (Figure 3) and **5-Et** (Figure 4) show

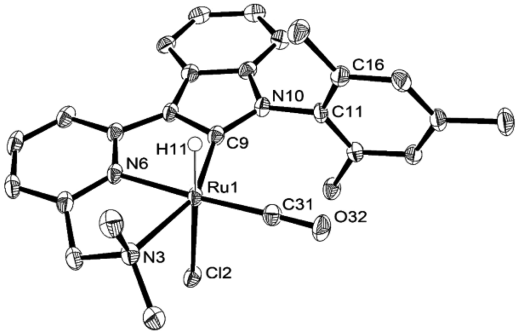


Figure 3. Crystal structure of **5-Me** showing 50% probability ellipsoids. Hydrogen atoms, except for the ruthenium-bound hydride, are omitted for clarity. Selected metric data (bond lengths in Å and angles in deg): Ru(1)−C(31), 1.848(2); Ru(1)−Cl(2), 2.5365(6); Ru(1)−N(6), 2.0540(19); Ru(1)−N(3), 2.245(2); Ru(1)−C(9), 1.932(2); Ru(1)−H(11), 1.601; C(31)−O(32), 1.154(3); C(9) − N(10), 1.351(3); N(10)−C(11), 1.441(3); N(3)−Ru(1)−N(6), 78.09(8); N(6)−Ru(1)−C(9), 78.40(9); N(6)−Ru(1)−C(31), 176.75(9); Cl(2)−Ru(1)−C(31), 95.26(8); C(9)−N(10)−C(11)−C(16), 88.19.

that both are octahedral complexes with the chloride and hydride ligands trans to each other. A correlation is observed via NOESY between the ruthenium-hydride and an ortho-methyl group on the mesityl ring for both **5-Me** and **5-Et**, which is consistent with this geometry being retained in solution. The ruthenium-containing bonds and angles, except for the Ru−N_{amine} bond length and N_{pyr}−Ru-N_{amine} angle, do not differ significantly between **5-Me** and **5-Et**, indicating that the additional steric bulk from the diethylamine group in **5-Et** does not result in a drastically different coordination environment around the metal compared with **5-Me**. It is noteworthy that the Ru−N_{amine} bond length of **5-Et** is longer than that of **5-Me** by 0.07 Å; this is likely due to the greater steric bulk of the diethylamino group.

When compared with Song's Ru-CNN complexes[9c] shown in Figure 2, the immediate coordination environment around ruthenium in **5-Me** and **5-Et** is similar but shows a clear effect of the lack of a methylene linker between the pyridine and NHC rings. Most strikingly, the N_{pyr}−Ru-C_{NHC} bite angle is 88−89° in Song's complexes and is approximately 78.5° in **5-Me** and **5-Et**. The hydrides of **5-Me** and **5-Et** were observed by ^{1}H NMR at −14.62 and −14.73 ppm, respectively, in CD_2Cl_2, while the hydride ligands in Song's Ru-CNN complexes appear at −15.34 ppm (Ar = 2,6-diisopropylphenyl) and −15.35 ppm (Ar = mesityl) in CD_2Cl_2.[9c]

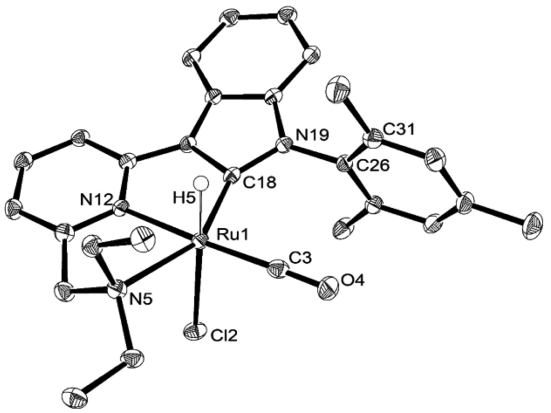
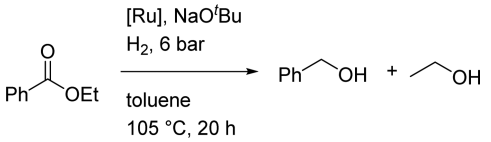


Figure 4. Crystal structure of **5-Et** showing 50% probability ellipsoids. Hydrogen atoms, except for the ruthenium-bound hydride, are omitted for clarity. Selected metric data (bond lengths in Å and angles in deg): Ru(1)−C(3), 1.854(3); Ru(1)−Cl(2), 2.5289(6); Ru(1)−N(12), 2.057(2); Ru(1)−N(5), 2.315(2); Ru(1)−C(18), 1.933(2); Ru(1)−H(5), 1.591; C(3)−O(4), 1.152(3); C(18)−N(19), 1.359(3); N(19)−C(26), 1.438(3); N(5)−Ru(1)−N(12), 75.99(8); N(12)−Ru(1)−C(18), 78.65(9); N(12)−Ru(1)−C(3), 175.63(10); Cl(2)−Ru(1)−C(3), 90.92(8); C(18)−N(19)−C(26)−C(31), 95.17.

Ester Hydrogenation. Both **5-Me** and **5-Et** were tested as catalysts for the hydrogenation of ethyl benzoate under mild conditions (105 °C, 6 bar H_2) in the presence of catalytic amounts of NaO^{t}Bu. Yields were more reproducible when several equivalents of base were used, relative to the ruthenium complexes. As shown in Table 1, the substrate-to-catalyst ratio was altered, while keeping the ratio of base to ruthenium constant at 6:1. Interestingly, **5-Et** is highly active, producing benzyl alcohol with a turnover number (TON) of up to 420, while **5-Me** is significantly less active, giving a maximum TON of 33. Although we have limited evidence at this point, such a stark difference in activity for such a subtle steric modification suggests that dissociation of the amine arm during catalysis may be important.[20] In their seminal 2006 paper, Milstein and co-

Table 1. Comparison of the Catalytic Activity of 5-Me and 5-Et[a]



Substrate: [Ru]	[Substrate] (M)	[Ru] (mM)	yield, [Ru] = **5-Me**	yield, [Ru] = **5-Et**
125:1	0.25	2.0	20%	>99%
250:1	0.25	1.0	13%	>99%
250:1	0.50	2.0	3%	>99%
500:1	0.50	1.0	2%	84%

[a]Reactions performed in toluene, with a total solution volume of 2.0 mL. In each case, the ratio of NaO^{t}Bu to [Ru] was 6:1. Yields were measured by ^{1}H NMR.

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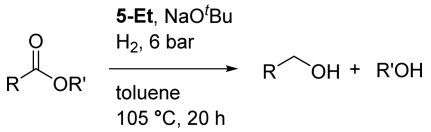
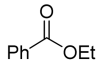
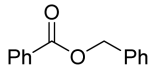
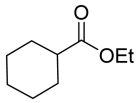
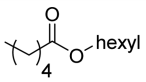
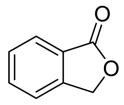
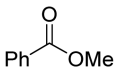
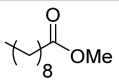
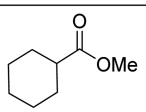
workers proposed that dissociation of the NEt_2 arm might be important for the high activity of their PNN-Ru catalysts compared to the lower activity seen with PNP ligands.[5] For the related hydrogenation of carbonate esters with this catalyst, Wang and co-workers showed via DFT that a pathway involving NEt_2 dissociation is slightly less favorable than a pathway not involving dechelation, with an energy difference of 2.4 kcal/mol.[21]

As catalyst **5-Et** was highly active for the hydrogenation of ethyl benzoate, its activity was tested for a range of ester substrates (Table 2). A range of catalyst loadings was tested for each substrate; Table 2 shows the lowest loading that gave full or nearly full conversion. The catalyst tolerates a variety of aromatic and aliphatic esters, including ethyl, benzyl, and hexyl esters. A hydrogen pressure of 30 bar was required to fully hydrogenate phthalide, as only 36% conversion was observed under 6 bar. Because high H_2 pressures have been necessary for this substrate in every example we are aware of, the necessity is likely of thermodynamic origin.[9e,22]

Table 2. Substrate Scope of Ester Hydrogenation Catalyzed by 5-Et[a]



Substrate	S/C	Yield
	250:1	>99%
	1000:1	98%
	125:1	96%
	250:1	97%
	500:1	36% (6 bar H_2) 99% (30 bar H_2)
	125:1	8%
	125:1	5%
	125:1	6%

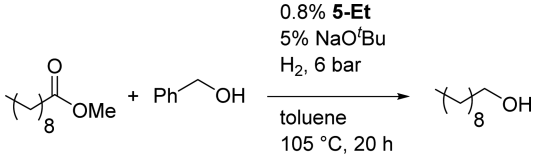
[a]Reactions performed in toluene, with a total solution volume of 2.0 mL. In each case, the ratio of NaO^{t}Bu to [Ru] was 6:1. For substrate:ruthenium ratios of 500 or 1000, the substrate concentration was 0.50 M. For substrate:ruthenium ratios of 125 or 250, the substrate concentration was 0.25 M. Yields were measured by ^{1}H NMR.

While **5-Et** is a highly active catalyst, it is strikingly inactive for the hydrogenation of a variety of methyl esters. For example, ethyl benzoate and ethyl cyclohexanecarboxylate are smoothly hydrogenated, while very low yields are obtained for the corresponding methyl esters. To our knowledge, this unique selectivity has not been reported to date for related ester-hydrogenation catalysts. Compound **5-Et** is generally inactive in alcohol solvents, indicating that the product alcohols may have an inhibiting effect on catalysis. A plausible explanation for the lack of reactivity of methyl esters in our system is that the byproduct methanol is a uniquely strong catalyst poison. Alternatively, methyl esters may display an intrinsically lower reactivity in our catalytic system.

To distinguish between these alternative hypotheses, we aimed to compare catalytic productivity in the presence of different amounts of methanol and to compare the rates of conversion of different esters (e.g., benzyl vs methyl) in the same pot. Our initial efforts to conduct these experiments were hampered by the observation that base-catalyzed transesterification occurs rapidly under our hydrogenation conditions. While our hydrogenation experiments are conducted at 105 °C, we observed that NaO^{t}Bu-catalyzed transesterification reaches equilibrium within minutes at room temperature.[23] Therefore, an experiment examining the effect of added methanol might show inhibition of catalysis because methanol is a poison or because transesterification produces the less-reactive methyl ester.

To cleanly distinguish between these hypotheses given that transesterification occurs rapidly during hydrogenation, we conducted an experiment where methyl decanoate was hydrogenated in the presence of increasing amounts of benzyl alcohol (Table 3). Due to rapid transesterification, an increase in added benzyl alcohol will have two effects: (1) the concentration of methanol will increase and (2) the methyl decanoate reactant will be increasingly converted to benzyl decanoate. If the primary cause of the low reactivity of methyl esters is inhibition by methanol, we should observe slower hydrogenation when more benzyl alcohol is added. If methyl

Table 3. Effect of Added Benzyl Alcohol on the Hydrogenation of Methyl Decanoate[a]



equiv BnOH added	yield 1-decanol
0	5%
0.2	25%
0.5	98%
1.0	99%

[a]Reactions performed in toluene, with a total solution volume of 2.0 mL and 0.25 M methyl decanoate. Yields were measured by ^{1}H NMR.

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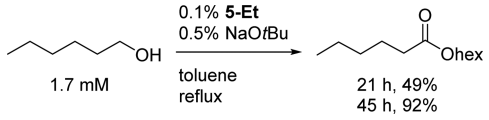
esters are intrinsically less reactive than benzyl esters, we should observe faster hydrogenation when more benzyl alcohol is added. As the data in Table 3 show, we observed a greater yield of 1-decanol as the amount of added benzyl alcohol was increased, with 0.5 equiv leading to nearly full conversion. This result is inconsistent with strong inhibition by methanol and supports the alternative hypothesis that methyl esters are intrinsically less reactive in our system. This result is particularly surprising, and we do not have a clear explanation for it at this stage. Stoichiometric reactions between **5-Et** and NaO^{t}Bu—in the presence or absence of ester substrates—produced mixtures of ruthenium complexes that we have not as yet been able to characterize.

Dehydrogenation of 1-Hexanol. Many of the ruthenium-based catalysts for ester hydrogenation have been shown to be effective catalysts for the reverse reaction, dehydrogenative coupling of primary alcohols to esters, under conditions where hydrogen gas is removed from the system to shift the position of equilibrium.[7a,9a,24] An initial test for the dehydrogenation of 1-hexanol was conducted using **5-Et**/NaO^{t}Bu, and good activity was observed (Scheme 3). At a substrate-to-catalyst ratio of

Scheme 3. Alcohol Dehydrogenation Catalyzed by 5-Et



1000:1, 1-hexanol was converted to hexyl hexanoate in 92% yield in 45 h. A more detailed study of the dehydrogenative coupling activity of our catalyst system is in progress.

CONCLUSION

New ruthenium-CNN pincer complexes (**5-Me** and **5-Et**) were synthesized and tested as catalysts for ester hydrogenation. The more active **5-Et** catalyzes the hydrogenation of a variety of substrates including ethyl, benzyl, and hexyl esters as well as lactones. However, **5-Et** is weakly active for the hydrogenation methyl esters. Experiments were inconsistent with catalyst poisoning by methanol and supported the hypothesis that methyl esters are intrinsically less reactive than other esters tested in our catalytic system. An initial screen of our catalyst system for the acceptorless dehydrogenative coupling of primary alcohols showed promising activity. Several extensions to this work are currently under way, including mechanistic characterization of the current system, modulation of the ligand structure, and the application of first-row transition-metal analogues.

EXPERIMENTAL SECTION

General Methods. Unless stated otherwise, all reactions were carried out either on a Schlenk line under argon or in an argon-filled MBraun Labmaster 130 glovebox. Solvents were purified by sparging with argon and passing through columns of activated alumina, using an MBraun solvent purification system. All reagents and materials were commercially available and were used as received, unless otherwise noted. For the ruthenium precursor RuHCl(CO)(PPh$_3$)$_3$, both commercially purchased samples (Alfa Aesar) and synthesized material, prepared according to a literature method,[25] were used. Flash chromatography employing solvent gradients was performed by using a Teledyne Isco Combiflash RF system. NMR spectra were recorded at room temperature on a Bruker spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) and referenced to the residual solvent resonance (δ in parts per million, J in Hz). Elemental analyses were performed by Robertson Microlit, Madison, NJ, USA. High-resolution mass spectroscopic analysis was performed at the University of Illinois Mass Spectroscopic Laboratory, Urbana, IL, USA. Detailed NMR assignments for complexes **5-Me** and **5-Et** are given in the Supporting Information.

Synthesis of (6-Bromopyridin-2-ylmethyl)dimethylamine (1-Me). A Schlenk flask was flame-dried, and 6-bromopyridine-2-carboxaldehyde (1.65 g, 8.87 mmol) was added. The flask was purged and filled with argon. Dichloroethane (30 mL) and dimethylamine (22.2 mL of a 2 M solution in THF, 44.4 mmol) were added, and the mixture was stirred for 5 min. Then, sodium triacetoxyborohydride (2.63 g, 12.4 mmol) was added, and the mixture was stirred overnight. An additional portion of sodium triacetoxyborohydride (0.94 g, 4.4 mmol) was added the next day. After 1 h, saturated aqueous sodium bicarbonate (15 mL) was added. The mixture was extracted twice with 30 mL of diethyl ether. The organic portions were combined and dried over MgSO$_4$. The solvent was evaporated, and the residue was purified by column chromatography on silica gel, using a gradient of 0 to 30% 2-propanol in hexane. Yield: 1.16 g, 61%. ^{1}H NMR ($CDCl_3$): δ 7.50 (t, 1H, $^3J_{HH}$ = 7.7 Hz, C$H_{pyridine}$), 7.38 (d, 1H, $^3J_{HH}$ = 7.4 Hz, C$H_{pyridine}$), 7.34 (d, 1H, $^3J_{HH}$ = 7.8 Hz, C$H_{pyridine}$), 3.55 (s, 2H, CH_2NMe$_2$), 2.27 (s, 6H, N(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): δ 161.2, 141.4, 138.9, 126.4, 121.8, 65.2, 45.8. HRMS (ESI+): calcd for $C_8H_{12}N_2Br$ 215.0184, found 215.0181.

Synthesis of (6-Bromopyridin-2-ylmethyl)diethylamine (1-Et). This compound was synthesized by a slight modification of a known method.[26] A Schlenk flask was flame-dried, and 6-bromopyridine-2-carboxaldehyde (3.83 g, 20.6 mmol) was added. The flask was purged and filled with argon. Dichloroethane (50 mL) and diethylamine (7.5 mL, 106 mmol) were added, and the mixture was stirred for a minute. Then, sodium triacetoxyborohydride (6.10 g, 28.8 mmol) was added, and the mixture was stirred. The reaction was monitored for completion by TLC, using 30% ethyl acetate in hexanes. After 1.5 h, 10% aqueous sodium hydroxide (40 mL) was added. The mixture was extracted with 100 mL of diethyl ether, and this organic fraction was washed with 2 × 50 mL of aqueous sodium hydroxide. The organic portion was dried over MgSO$_4$, the solvent was evaporated, and a yellow oil (4.935 g, 99%) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.50 (d, 2H, J_{HH} = 4.7 Hz, C$H_{pyridine}$), 7.32 (t, 1H, $^3J_{HH}$ = 4.4 Hz, C$H_{pyridine}$), 3.70 (s, 2H, CH_2NEt$_2$), 2.57 (q, 4H, $^3J_{HH}$ = 7.1 Hz, N(CH_2CH$_3$)$_2$), 1.04 (t, 6H, $^3J_{HH}$ = 7.1 Hz, N(CH$_2$CH_3)$_2$). ^{13}C NMR ($CDCl_3$): δ 163.2, 141.1, 138.8, 125.9, 121.4, 59.2, 47.6, 12.2.

Synthesis of 2-(Mesitylamino)aniline (2). Pd(OAc)$_2$ (5 mg, 0.02 mmol), (*R*)-(−)-1-[(*S*)-2-(dicyclohexylphosphino)ferrocenyl]-ethyldi-*tert*-butylphosphine (CyPF-^{t}Bu) (24.5 mg, 0.0442 mmol), a stir bar, and 1,2-dimethoxyethane (40 mL) were added to a 100 mL oven-dried round-bottom flask in the glovebox. After the mixture became homogeneous, mesityl bromide (3.38 mL, 4.40 g, 22.1 mmol), *o*-phenylenediamine (4.78 g, 44.2 mmol), and NaO^{t}Bu (6.37 g, 66.3 mmol) were added. The flask was sealed with a rubber septum and heated at 80 °C overnight while stirring. The flask was brought out of the glovebox and opened, and the mixture was filtered through a plug of silica with 200 mL of ethyl acetate. The solvent was evaporated, and the residue was isolated as a white solid by column chromatography on silica gel, using a gradient of 0 to 25% ethyl acetate in hexanes. Yield: 3.75 g, 75%. NMR spectroscopic data were in agreement with those reported in the literature.[14]

Synthesis of (6-((2-Mesitylamino)phenylamino)pyridin-2-ylmethyl)dimethylamine (3-Me). A stir bar, (6-bromopyridin-2-ylmethyl)dimethylamine (**1-Me**, 0.914 g, 4.25 mmol), 2-(mesitylamino)aniline (**2**, 0.962 g, 4.25 mmol), NaO^{t}Bu (1.23 g, 12.7 mmol), and 1,2-dimethoxyethane (25 mL) were added to a 40 mL vial in the glovebox. Then, a solution of Pd(OAc)$_2$ (1.91 mg, 8.50 μmol) and CyPF-^{t}Bu (9.43 mg, 17.0 μmol) in dimethoxyethane (1.5 mL) was made by stirring for 5 min and was added to the reaction vial. The reaction mixture was heated at 80 °C overnight. The vial was removed from the glovebox, and the mixture was filtered through a plug of silica gel, eluting with 125 mL of ethyl acetate and 300 mL of methanol. The volatiles were removed, and the residue was purified by

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column chromatography, using a gradient of 0 to 25% methanol in dichloromethane. Yield: 1.19 g, 78%. ^{1}H NMR ($CDCl_3$): δ 7.43 (t, 1H, $^3J_{HH}$ = 7.8 Hz, CH_{arom}), 7.24 (dd, 1H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, CH_{arom}), 7.00 (td, 1H, $^3J_{HH}$ = 7.9 Hz, J_{HH} = 1.4 Hz, CH_{arom}), 6.91 (s, 2H, CH_{arom}), 6.77 (d, 1H, $^3J_{HH}$ = 7.2 Hz, CH_{arom}), 6.71 (td, 1H $^3J_{HH}$ = 7.5 Hz, J_{HH} = 1.4 Hz, CH_{arom}), 6.42 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 6.41 (br s, 1H, N*H*) 6.23 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, J_{HH} = 1.2 Hz, CH_{arom}), 5.59 (br s, 1H, N*H*), 3.54 (s, 2H, CH_2NMe_2), 2.39 (s, 6H, $CH_2N(CH_3)_2$), 2.28 (s, 3H, $CH_{3\text{-mesityl}}$), 2.10 (s, 6H, $CH_{3\text{-mesityl}}$). ^{13}C NMR ($CDCl_3$): δ 158.0, 156.2, 143.1, 138.4, 136.0, 135.6, 135.2, 129.3, 127.5, 127.1, 125.4, 117.8, 114.4, 112.3, 106.2, 65.3, 45.5, 21.0, 18.3. HRMS (ESI+): calcd for $C_{23}H_{29}N_4$ 361.2397, found 361.2392.

Synthesis of (6-((2-Mesitylamino)phenylamino)pyridin-2-ylmethyl)diethylamine (3-Et). $Pd(OAc)_2$ (2.11 mg, 9.39 μmol) and CyPF-^{t}Bu (10.4 mg, 18.8 μmol) were combined in a 20 mL vial in the glovebox with 1,2-dimethoxyethane (5 mL) and stirred for 5 min. Then, (6-bromopyridin-2-ylmethyl)diethylamine (**1-Et**, 2.28 g, 9.39 mmol) and 2-(mesitylamino)aniline (**2**, 2.13 g, 9.39 mmol) were added followed by the addition of NaO^{t}Bu (2.71 g, 28.2 mmol). After adding more dimethoxyethane to nearly fill the vial, the reaction mixture was heated at 80 °C overnight. The vial was removed from the glovebox, and the mixture was filtered through a plug of silica gel, eluting with 200 mL of ethyl acetate. The volatiles were removed, and the residue was purified by column chromatography, using a gradient of 0 to 20% methanol in dichloromethane. Yield: 2.84 g, 78%. ^{1}H NMR ($CDCl_3$): δ 7.42 (t, 1H, $^3J_{HH}$ = 7.7 Hz, CH_{arom}), 7.25 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, J_{HH} = 1.4 Hz, CH_{arom}), 7.00 (t, 1H, $^3J_{HH}$ = 7.9 Hz, CH_{arom}), 6.91 (s, 2H, CH_{arom}), 6.86 (d, 1H, $^3J_{HH}$ = 7.3 Hz, CH_{arom}), 6.72 (td, 1H, $^3J_{HH}$ = 7.5 Hz, J_{HH} = 1.4 Hz, CH_{arom}), 6.39 (d, 1H, $^3J_{HH}$ = 8.3 Hz, CH_{arom}), 6.33 (br s, 1H, N*H*), 6.23 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, J_{HH} = 1.3 Hz, CH_{arom}), 5.59 (s, 1H N*H*), 3.63 (s, 2H, CH_2NEt_2), 2.65 (q, 4H, $^3J_{HH}$ = 7.1 Hz, $N(CH_2CH_3)_2$), 2.29 (s, 3H, $CH_{3\text{-mesityl}}$), 2.11 (s, 6H, $CH_{3\text{-mesityl}}$), 1.10 (t, 6H, $^3J_{HH}$ = 7.1 Hz, $N(CH_2CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 158.7 (br) 157.8, 143.1, 138.3, 136.0, 135.5, 135.3, 129.3, 127.3, 127.0, 125.7, 117.8, 114.0, 112.3, 105.6, 59.3 (br), 47.4, 21.0, 18.3, 11.7. HRMS (ESI+): calcd for $C_{25}H_{33}N_4$ 389.2705, found 398.2711.

Synthesis of Benzimidazolium Chloride 4-Me. To a flame-dried 250 mL round-bottomed flask, **3-Me** (1.19 g, 3.31 mmol), a stir bar, triethylorthoformate (65 mL), and concentrated hydrochloric acid (3.3 g, 33 mmol) were added. The reaction mixture was heated at 80 °C for 1 h, and then additional triethylorthoformate (10 mL) and concentrated hydrochloric acid (2 mL) were added. The solvent was evaporated under a stream of nitrogen while heating at 70 °C, and a hygroscopic solid was obtained. The solid was washed with diethyl ether and dried under vacuum. Yield: 1.44 g, 91%. ^{1}H NMR ($CDCl_3$): δ 12.13 (br, 1H, $CH_{benzomidazolium}$), 8.64 (br, 1H, CH_{arom} or N*H*), 8.50 (br, 1H, CH_{arom} or N*H*), 8.22 (br, 1H, CH_{arom} or N*H*), 8.07 (br, 1H, CH_{arom} or N*H*), 7.83 (br, 1H, CH_{arom} or N*H*), 7.65 (br t, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.26 (br d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.04 (br, 2H, CH_{arom}), 4.81 (br, 2H, CH_2NMe_2), 2.92 (br, 6H, $CH_2N(CH_3)_2$), 2.31 (s, 3H, $CH_{3\text{-mesityl}}$), 2.03 (s, 6H, $CH_{3\text{-mesityl}}$). ^{13}C NMR ($CDCl_3$): δ 152.5, 146.4, 143.6, 142.4, 141.9, 134.9, 132.2, 130.3, 129.4, 129.0, 128.7, 127.6, 127.0, 117.0, 116.4, 113.5, 60.8, 43.8, 21.2, 17.8. HRMS (ESI+): calcd. for $C_{24}H_{27}N_4$ (M − 2H − 3Cl) 371.2236, found 371.2231.

Synthesis of Benzimidazolium Chloride 4-Et. The synthesis was performed in an analogous fashion to that of **4-Me**, starting with **3-Et** (2.85 g, 7.3 mmol). Yield: 3.70 g, 99%. ^{1}H NMR ($CDCl_3$): δ 12.38 (s, 1H, $CH_{benzomidazolium}$), 11.54 (br s, 1H, N*H*), 8.61 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 8.51 (br s, 1H, N*H*), 8.26 (br m, 2H, CH_{arom}), 7.84 (t, 1H, $^3J_{HH}$ = 8.1 Hz, CH_{arom}), 7.68 (t, 1H, $^3J_{HH}$ = 7.8 Hz, CH_{arom}), 7.30 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 7.08 (s, 2H, CH_{arom}), 4.86 (br, 2H, CH_2NEt_2), 3.29 (br, 4H, $N(CH_2CH_3)_2$), 2.35 (s, 3H, $CH_{3\text{-mesityl}}$), 2.07 (s, 6H, $CH_{3\text{-mesityl}}$), 1.41 (br, 6H, $N(CH_2CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 152.6 (br), 146.3, 144.0, 142.3, 142.0, 134.9, 132.4, 130.4, 129.3, 129.2, 128.7, 127.7, 127.3 (br) 117.1, 116.1 (br), 113.7, 56.0 (br), 48.3, 21.3, 17.9, 9.6 (br). HRMS (ESI+): calcd for $C_{26}H_{31}N_4$ (M − 2H − 3Cl) 399.2549, found 399.2551.

Synthesis of RuClH(CO)(CNN^{Me}), 5-Me. In the glovebox, the trihydrochloride salt **4-Me** (200 mg, 0.417 mmol), a stir bar, molecular sieves (ca. 700 mg), Ag_2O (483 mg, 2.08 mmol), and THF (16 mL) were added to a vial and stirred for 1.5 h in the dark. The mixture was filtered through a PTFE filter disk into a vial with $RuHCl(CO)(PPh_3)_3$ (397 mg, 0.417 mmol). The reaction mixture was stirred and heated at 50 °C overnight. The reaction was then brought outside the glovebox, and half of the solvent was evaporated. The mixture was filtered through a medium frit and washed with THF (5 mL). The yellow solid obtained was brought into the glovebox, and a short column was performed on neutral alumina (10 mL) using a 20 mL plastic syringe and a PTFE filter disk. The crude product was loaded with dichloromethane, and impurities were washed away with dichloromethane (20 mL). The product was then eluted with 2:1 CH_2Cl_2/THF (30 mL). Material purified in this manner was pure by NMR spectroscopy, but catalytic trials were conducted using samples that were further purified by recrystallization: a solution in dichloromethane was first layered with a small amount of toluene, then an excess of pentane. Yield after recrystallization: 123 mg, 49% (corrected for solvent impurities shown below). ^{1}H NMR (CD_2Cl_2): δ 8.02 (t, 1H, $^3J_{HH}$ = 7.8 Hz, CH_{arom}), 7.91 (d, 1H, $^3J_{HH}$ = 8.3 Hz, CH_{arom}), 7.83 (d, 1H, $^3J_{HH}$ = 8.1 Hz, CH_{arom}), 7.29 (m, 2H, CH_{arom}), 7.21 (t, 1H, $^3J_{HH}$ = 7.8 Hz, CH_{arom}), 7.14 (s, 1H, CH_{arom}), 7.07 (s, 1H, CH_{arom}), 6.73 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 4.86 (d, 1H, $^2J_{HH}$ = 14.6 Hz, CH_2NMe_2), 3.57 (d, 1H, $^2J_{HH}$ = 14.8 Hz, CH_2NMe_2), 2.98 (s, 3H, $CH_2N(CH_3)_2$), 2.76 (s, 3H, $CH_2N(CH_3)_2$), 2.41 (s, 3H, $CH_{3\text{-mesityl}}$), 2.17 (s, 3H, $CH_{3\text{-mesityl}}$), 1.92 (s, 3H, $CH_{3\text{-mesityl}}$), −14.62 (s, 1H, Ru*H*). ^{13}C NMR (CD_2Cl_2): δ 215.4, 205.0, 159.6, 151.2, 140.0, 139.0, 138.1, 136.8, 136.8, 133.1, 131.8, 129.9, 129.4, 124.0, 123.0, 116.9, 110.2, 109.8, 109.4, 69.4, 58.7, 51.9, 21.4, 18.4, 17.8. Recrystallized samples contained disordered dichloromethane, pentane, and toluene that was retained upon prolonged storage under vacuum at 50 °C and was quantified by ^{1}H NMR spectroscopy. Anal. Calcd for $C_{25}H_{27}ClN_4ORu{\cdot}0.51CH_2Cl_2{\cdot}0.09CH_3C_6H_5{\cdot}0.14C_5H_{12}$: C, 53.92; H, 5.12; N, 9.38. Found: C, 53.82; H, 5.11; N, 9.24.

Synthesis of RuClH(CO)(CNN^{Et}), 5-Et. The synthesis, chromatographic purification, and recrystallization of **5-Et** was performed in an identical fashion to those of **5-Me**, starting with **4-Et**. Yield after recrystallization: 116 mg, 53% (corrected for solvent impurities shown below). ^{1}H NMR (CD_2Cl_2): δ 7.90 (t, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.85 (d, 1H, $^3J_{HH}$ = 8.3 Hz, CH_{arom}), 7.79 (d, 1H, $^3J_{HH}$ = 8.1 Hz, CH_{arom}), 7.27 (t, 1H, $^3J_{HH}$ = 8.3 Hz, CH_{arom}), 7.19 (t, 1H, $^3J_{HH}$ = 8.2 Hz, CH_{arom}), 7.15 (s, 1H, CH_{arom}), 7.09 (m, 2H, CH_{arom}), 6.73 (d, 1H, $^3J_{HH}$ = 7.9 Hz, CH_{arom}), 4.73 (d, 1H, $^2J_{HH}$ = 15.1 Hz, CH_2NEt_2), 3.96 (d, 1H, $^2J_{HH}$ = 15.0 Hz, CH_2NEt_2), 3.37 (m, 2H, $N(CH_2CH_3)_2$), 2.87 (m, 2H, $N(CH_2CH_3)_2$), 2.41 (s, 3H, $CH_{3\text{-mesityl}}$), 2.24 (s, 3H, $CH_{3\text{-mesityl}}$), 1.92 (s, 3H, $CH_{3\text{-mesityl}}$), 1.12 (t, 3H, $^3J_{HH}$ = 7.0 Hz, $N(CH_2CH_3)_2$), 1.09 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $N(CH_2CH_3)_2$), −14.76 (s, 1H, Ru*H*). ^{13}C NMR (CD_2Cl_2): δ 215.3, 205.7, 160.3, 151.2, 140.2, 139.2, 138.3, 137.1, 136.9, 133.3, 131.9, 130.1, 129.6, 124.2, 123.2, 117.1, 110.4, 109.9, 109.3, 64.4, 55.0, 50.4, 21.6, 18.6, 18.0, 11.1, 9.9. Recrystallized samples contained disordered pentane and toluene that was retained upon prolonged storage under vacuum at 50 °C and were quantified by ^{1}H NMR spectroscopy. Anal. Calcd for $C_{27}H_{31}ClN_4ORu{\cdot}0.24CH_3C_6H_5{\cdot}0.19C_5H_{12}$: C, 59.32; H, 5.91; N, 9.33. Found: C, 59.22; H, 5.88; N, 9.24.

General Procedure for Ester Hydrogenation. In an argon-filled glovebox, the appropriate ruthenium complex and NaO^{t}Bu were dissolved in toluene. This mixture was stirred at 50 °C for 1 h, and a homogeneous, orange solution formed. The appropriate ester substrate was added as a solution in toluene, and this solution was transferred to a glass-lined, stainless steel pressure reactor. The reactor was sealed and brought out of the box. The reactor was pressurized with 6 bar of hydrogen gas and vented three times. Next, the reactor was pressurized with 6 bar of hydrogen gas and heated to an internal temperature of 105 °C while stirring for 20 h. After this time, the reactor was cooled for at least 30 min, vented carefully, and opened to the atmosphere. An aliquot was analyzed by ^{1}H NMR spectroscopy.

Dehydrogenation of 1-Hexanol. In an argon-filled glovebox, **5-Et** (2.8 mg, 5.0 μmol) and NaO^{t}Bu (2.4 mg, 25 μmol) were dissolved

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in 2.5 mL of toluene, and the solution was stirred at 50 °C for 1 h. Then, 1-hexanol (5.0 mmol, 0.63 mL) was added, and the solution was transferred to a flame-dried Schlenk flask. The flask was brought out of the glovebox, and the system was refluxed using a J-Kem Scientific aluminum heating/cooling block while stirring under a slight argon flow. Aliquots were removed via cannula and analyzed by ^{1}H NMR spectroscopy.

X-ray Crystallography, General Methods. Structure determinations were performed on an Oxford Diffraction Gemini-R diffractometer, using Mo Kα radiation. Single crystals were mounted on Hampton Research Cryoloops using Paratone-N oil. Unit cell determination, data collection and reduction, and empirical absorption correction were performed using the CrysAlisPro software package.[27] Direct methods structure solution was accomplished using SIR92,[28] and full-matrix least-squares refinement was carried out using CRYSTALS.[29] All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, hydrogen atoms were placed in calculated positions, and their positions were initially refined using distance and angle restraints. All hydrogen positions were fixed in place for the final refinement cycles.

X-ray Structure Determination of 5-Me. X-ray quality crystals of **5-Me** (yellow blocks) were grown by layering pentane over a CH_2Cl_2 solution of **5-Me**. The ruthenium-bound hydride was located in the difference map, and its position was refined freely before being fixed in place for the final refinement cycles. Highly disordered solvent was present; correction for this residual density was performed using the option SQUEEZE in the program package PLATON.[30] A total of 113 electrons were removed from a total potential solvent-accessible void of 499.4 Å^3.

X-ray Structure Determination of 5-Et. X-ray quality crystals of **5-Et** (yellow rods) were grown by layering pentane over a CH_2Cl_2 solution of **5-Et**. The ruthenium-bound hydride was located in the difference map, and its position was refined freely before being fixed in place for the final refinement cycles. A disordered pentane molecule was present close to a center of inversion, such that one of two possible inversion-related orientations is adopted in each asymmetric unit. The occupancy of all atoms in the pentane molecule was set to 0.5, the atoms (including carbon) were refined isotropically, and the structure was refined using SAME restraints for the pentane molecule.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00009.

Images of NMR spectra and detailed NMR assignments for complexes **5-Me** and **5-Et** (PDF)

CIF file giving crystallographic data for complexes **5-Me** and **5-Et** (CIF)

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Notes

The authors declare no competing financial interest.

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