

A Succession of Isomers of Ruthenium Dihydride Complexes. Which One Is the Ketone Hydrogenation Catalyst?

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Abstract: Reaction of $\text{RuHCl}(\text{PPh}_3)_2(\text{diamine})$ (**1a**, diamine = (*R,R*)-1,2-diaminocyclohexane, (*R,R*)-dach; **1b**, diamine = ethylenediamine, en) with KO^tBu in benzene quickly generates solutions of the amido–amine complexes $\text{RuH}(\text{PPh}_3)_2(\text{NHC}_6\text{H}_{10}\text{NH}_2)$, (**2a'**), and $\text{RuH}(\text{PPh}_3)_2(\text{NHCH}_2\text{CH}_2\text{NH}_2)$, (**2b'**), respectively. These solutions react with dihydrogen to first produce the *trans*-dihydrides $(\text{OC-6-22})\text{-Ru}(\text{H})_2(\text{PPh}_3)_2(\text{diamine})$ (*t,c*-**3a**, *t,c*-**3b**). Cold solutions (-20°C) containing *trans*-dihydride *t,c*-**3a** react with acetophenone under Ar to give (*S*)-1-phenylethanol (63% ee). Complexes *t,c*-**3** have lifetimes of less than 10 min at 20° and then isomerize to the *cis*-dihydride, *cis*-bisphosphine isomers $(\text{OC-6-32})\text{-Ru}(\text{H})_2(\text{PPh}_3)_2(\text{diamine})$ (Δ/Λ -*c,c*-**3a**, *c,c*-**3b**). A solution containing mainly Δ/Λ -*c,c*-**3a** reacts with acetophenone under Ar to give (*S*)-1-phenylethanol in 20% ee, whereas it is an active precatalyst for its hydrogenation under 5 atm H_2 to give 1-phenylethanol with an ee of 50–60%. Complexes *c,c*-**3** isomerize to the *cis*-dihydride, *trans*-bisphosphine complexes $(\text{OC-6-13})\text{-Ru}(\text{H})_2(\text{PPh}_3)_2(\text{diamine})$ (*c,t*-**3a**, *c,t*-**3b**) with half-lives of 40 min and 1 h, respectively. A mixture of Δ/Λ -*c,c*-**3a** and *c,t*-**3a** can also be obtained by reaction of **1a** with $\text{KBH}(\text{Bu}^{\text{sec}})_3$. A solution of complex *c,t*-**3a** in benzene under Ar reacts very slowly with acetophenone. These results indicate that the *trans*-dihydrides *t,c*-**3a** or *t,c*-**3b** along with the corresponding amido–amine complexes **2a'** or **2b'** are the active hydrogenation catalysts in benzene, while the *cis*-dihydrides *c,c*-**3a** or *c,c*-**3b** serve as precatalysts. The complexes $\text{RuCl}_2(\text{PPh}_3)_2((R,R)\text{-dach})$ or **1a**, when activated by KO^tBu , are also sources of the active catalysts. A study of the kinetics of the hydrogenation of acetophenone in benzene catalyzed by **3a** indicates a rate law: $\text{rate} = k[\text{c},\text{c}\text{-}\mathbf{3a}]_{\text{initial}}[\text{H}_2]$ with $k = 7.5 \text{ M}^{-1} \text{ s}^{-1}$. The turnover-limiting step appears to be the reaction of **2a'** with dihydrogen as it is for $\text{RuH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ (**2c'**). The catalysts are more active in 2-propanol, even without added base, and the kinetic behavior is complicated. The basic *cis*-dihydride *c,t*-**3a** reacts with $[\text{NEt}_3\text{H}]\text{BPh}_4$ to produce the dihydrogen complex $(\text{OC-14})\text{-[Ru}(\eta^2\text{-H}_2)(\text{H})(\text{PPh}_3)_2\text{-}((R,R)\text{-dach})]\text{BPh}_4$ (**4**) and with diphenylphosphinic acid to give the complex $\text{RuH}(\text{O}_2\text{PPh}_2)(\text{PPh}_3)_2((R,R)\text{-dach})$ (**5**). The structure of **5** models aspects of the transition state structure for the ketone hydrogenation step. Complex **2b'** decomposes rapidly under Ar to give dihydrides **3b** along with a dinuclear complex $(\text{PPh}_3)_2\text{HRu}(\mu\text{-}\eta^2,\eta^4\text{-NHCHCHNH})\text{RuH}(\text{PPh}_3)_2$ (**6**) containing a rare, bridging 1,4-diazabutadiene group. The formation of an imine by β -hydride elimination from the amido–amine ligand of **2a'** under Ar might explain some loss of enantioselectivity of the catalyst. The structures of complexes **1a**, **5**, and **6** have been determined by single-crystal X-ray diffraction.

Introduction

Noyori and co-workers have developed extremely efficient ruthenium catalysts for the hydrogenation of ketones to alcohols and for the asymmetric hydrogenation of prochiral ketones to valuable optically active alcohols.^{1–10} These alcohols find uses

in the pharmaceutical, agrochemical, flavor, fragrance, and material industries. A key discovery in catalyst development was the beneficial effect of certain diamines with at least one NH_2 group, such as ethylenediamine (en) or 1,2-(*R,R*)-diaminocyclohexane ((*R,R*)-dach), on the catalytic activity of ruthenium phosphine complexes toward ketone hydrogenation.⁷ Thus, precatalysts are generated in situ or are isolated as complexes

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of the type $\text{RuCl}_2(\text{PR}_3)_2(\text{diamine})$ or $\text{RuCl}_2(\text{diphosphine})$ -(diamine), including compounds containing enantiomerically pure diamines and diphosphines. These complexes become active when dissolved in basic 2-propanol solutions under H_2 -(g). Attractive features of these catalysts include the use of low pressures of hydrogen gas, high substrate-to-catalyst ratios, high turnover numbers, functional group tolerance, high enantioselectivity, and a high selectivity for the hydrogenation of $\text{C}=\text{O}$ over $\text{C}=\text{C}$ bonds. Another more recently discovered feature is their use in the hydrogenation and asymmetric hydrogenation of $\text{C}=\text{N}$ bonds.^{11–14}

The source of the diamine effect was proposed to be the easy transfer of a proton from the amine to the carbonyl oxygen and a hydride from ruthenium to the carbonyl carbon of the ketone in a unique second coordination sphere reaction.^{7,8,11,15–18} Experimental and theoretical studies of the mechanism of the transfer hydrogenation catalysts of the type $\text{RuH}(\text{alkoxy-amine})(\eta^6\text{-arene})$,^{6,19} $\text{RuH}(\text{Tosyl-amido-amine})(\eta^6\text{-arene})$,^{20–22} and $\text{RuH}(\eta^5\text{-C}_5\text{Ar}_4\text{OH})(\text{CO})_2$ ²³ have shown that this hydride–protonic transfer to the $\text{C}=\text{O}$ group of the ketone is likely to be a concerted process. Noyori and co-workers have called this metal–ligand bifunctional catalysis.^{6–9} These catalysts are regenerated by transfer of hydride to ruthenium from basic 2-propanol or ammonium formate but not from dihydrogen gas. In contrast, ruthenium diamine complexes such as $\text{RuCl}_2(\text{en})$ -(PPh_3)₂^{4,7,24,25} are precatalysts that lead to much more active catalysts for the hydrogenation of ketones than to catalysts for the transfer hydrogenation of ketones.

The structures of the active ruthenium hydride catalysts in the diamine systems are only now emerging. It was expected that the dichloride precursors would be converted into hydride species^{3,7,26,27} under the reducing catalytic conditions of hydrogen gas, 2-propanol, and strong base. Some of us found that the monohydride complexes $\text{RuHCl}(\text{PPh}_3)_2(\text{diamine})$ and $\text{RuHCl}(\text{diphosphine})(\text{diamine})$ were inactive as ketone or imine hydrogenation catalysts but could be converted into active dihydride catalysts by reaction with a strong base and dihydrogen.^{11,12,17,18} Therefore, the catalytic species were proposed^{7–9,11,12,15–18,28} to be the dihydride diamine and hydrido amido–amine complexes as shown in Scheme 1. For example,

Scheme 1. Proposed Roles of the Diamine and the Ruthenium Hydride of a Ruthenium Complex in the Catalytic Hydrogenation of Ketones: Metal–Ligand Bifunctional Catalysis (the [Ru] Notation Represents the Phosphine and Other Ligands)

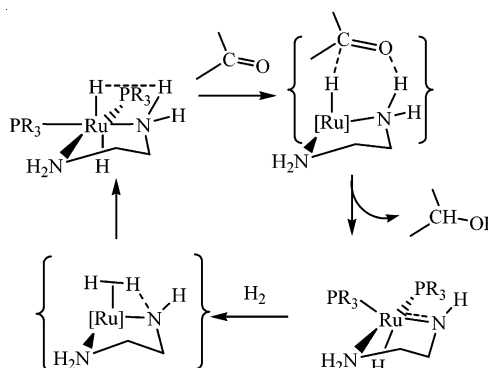
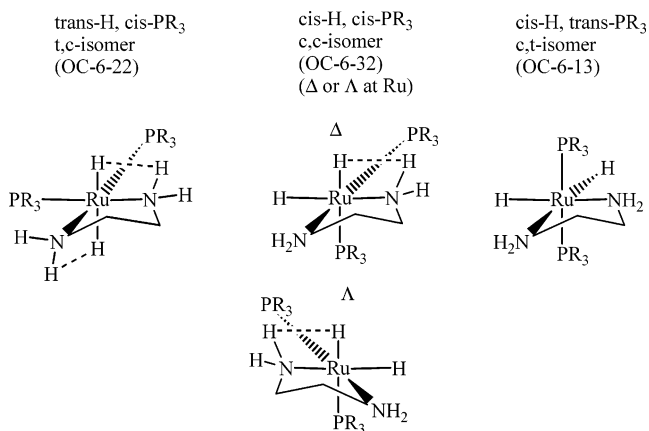


Chart 1. Isomers of Dihydride Complexes



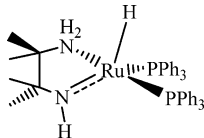
well-characterized ruthenium complexes with *trans*-dihydride and *cis*-phosphine ligands, *t,c*- $\text{Ru}(\text{H})_2(\text{tmen})(\text{PPh}_3)_2$, *tmen* = $\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2$, and *trans*- $\text{Ru}(\text{H})_2(\text{tmen})((R)\text{-binap})$, are active ketone hydrogenation catalysts without the need for activation by a base.^{17,18} The dihydrides react directly with ketones to produce alcohols and are regenerated by the reaction of the hydrido amido–amine complexes $\text{RuH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ and $\text{RuH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)((R)\text{-binap})$ with hydrogen gas (Scheme 1). The heterolytic splitting across a ruthenium–amido bond of an η^2 -dihydrogen ligand that is weakly coordinated to ruthenium is the turnover limiting step of the catalytic cycle. The complex *trans*- $\text{RuH}(\text{HBH}_3)((R)\text{-tolbinap})((R,R)\text{-dpn})$, *tolbinap* = 2,2′-bis(ditolylphosphino)-1,1′-binaphthyl, *dpn* = 1,2-diphenylethylenediamine, is also an active catalyst without the need of added base;¹⁰ this precatalyst was used in a kinetic study that supported the mechanism of Scheme 1 for basic conditions in 2-propanol.²⁸ Hartmann and Chen have proposed an alternate mechanism where potassium is located on a hydridoamido intermediate and serves to activate the ketone and promotes the heterolytic splitting of dihydrogen by positioning an alkoxide ion for an efficient deprotonation reaction.^{29,30} Similarly, a dihydride complex $\text{RuH}_2(\text{P-NH-NH-P})$ and amido–amine complex $\text{RuH}(\text{P-N-NH-P})$ were proposed to be the active hydrogenation

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Table 1. Compound Numbering

diamines		amido–amine ligands	
a	<i>trans</i> -(1 <i>R</i> ,2 <i>R</i>)-diaminocyclohexane ((<i>R,R</i>)-dach)	a'	(<i>R,R</i>)-NHC ₆ H ₁₀ NH ₂ [−]
b	1,2-diaminoethane (en)	b'	NHCH ₂ CH ₂ NH ₂ [−]
c	2,3-diamino-2,3-dimethylbutane (tmen)	c'	NHCMe ₂ CMe ₂ NH ₂ [−]

complexes	
1a, 1b, 1c 2a', 2b', 2c'	(OC-6-43)-RuHCl(PPh ₃) ₂ (diamine) (<i>trans</i> -H···Cl, <i>cis</i> -P···P) RuH(PPh ₃) ₂ (amido–amine)
	
2c' <i>t,c</i> - 3a, 3b, 3c Δ - <i>c,c</i> - 3a Λ - <i>c,c</i> - 3a <i>c,c</i> - 3b <i>c,t</i> - 3a, 3b, 3c 4 5 6	(OC-6-22)-RuH ₂ (PPh ₃) ₂ (diamine) (with <i>trans</i> -H···H, <i>cis</i> -P···P) Δ -(OC-6-32)-RuH ₂ (PPh ₃) ₂ ((<i>R,R</i>)-dach) (with <i>cis</i> -H···H, <i>cis</i> -P···P) Λ -(OC-6-32)-RuH ₂ (PPh ₃) ₂ ((<i>R,R</i>)-dach) (with <i>cis</i> -H···H, <i>cis</i> -P···P) (OC-6-32)-RuH ₂ (PPh ₃) ₂ (en) (with <i>cis</i> -H···H, <i>cis</i> -P···P) (OC-6-13)-Ru(PPh ₃) ₂ (H) ₂ (diamine) (with <i>cis</i> -H···H, <i>trans</i> -P···P) (OC-6-14)-[Ru(η^2 -H ₂)H(PPh ₃) ₂ ((<i>R,R</i>)-dach)]BPh ₄ (OC-6-22)-RuH(O ₂ PPh ₂)(PPh ₃) ₂ ((<i>R,R</i>)-dach) Ru ₂ H ₂ (PPh ₃) ₄ (μ - η^2 : η^4 -HN=CHCH=NH)

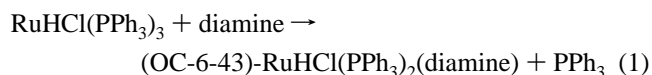
tion catalysts for a tetradentate ligand system (*R,R*)-cyclo-C₆H₁₀-{NHCH₂C₆H₄PPh₂}₂.³¹

Dihydrido diamine complexes of ruthenium with monodentate phosphine ligands can potentially exist as four geometric isomers, two of which are enantiomers (Chart 1). The *fac*-stereochemistry of the hydride and diamine at ruthenium has been proposed to be a requirement for catalytic activity.⁷ The *t,c* and *c,c* isomers have this stereochemistry and potentially have hydridic–protonic interactions^{32–34} between a ruthenium hydride and an amino hydrogen that is axial with respect to the diamine–Ru ring. However, the *cis*-dihydride complex *c,t*-Ru-(H)₂(PPh₃)₂((*R,R*)-dach) has a *mer*-diamine–hydride stereochemistry and yet was also reported to be an active hydrogenation catalyst.¹¹ Noyori and co-workers have provided evidence for two dihydride isomers of the corresponding ethylenediamine (en) system *c,t*-Ru(H)₂(PPh₃)₂(en) and *c,c*-Ru(H)₂(PPh₃)₂(en).²⁶ In this article, we address the questions: which of these isomers are competent catalysts or precatalysts for ketone hydrogenation and what is the effect of the structure of each catalyst isomer on the reactivity and obtained ee values? Although the ee of the alcohol produced by the (*R,R*)-dach catalyst under study here is lower than that observed for Noyori's synthetically valuable RuCl₂(binap)(diamine) precatalysts, it is high enough to answer some of these questions for the first time.

Results and Discussion

Starting Complexes. The starting complexes for this work are the known yellow hydrido chloro complexes RuHCl(PPh₃)₂-(diamine)^{11,35} that have hydride trans to chloride (OC-6-43) (**1a**, diamine= (*R,R*)-dach, **1b**, en; see Table 1 for the numbering

scheme). They are prepared here by the reaction of RuHCl-(PPh₃)₃ with the appropriate diamine (eq 1).



Occasionally, a second, purple, insoluble diastereomer of **1a** is produced in small amount in eq 1. It is thought to be the (OC-6-32) isomer with *trans*-PPh₃ ligands. The structure of **1a** has been confirmed by X-ray crystallography (see Supporting Information).

Observation of Amido–Amine Complexes. The reaction of RuHCl(PPh₃)₂(tmen) **1c** in THF under Ar with the strong base potassium *tert*-butoxide produced the red amido–amine complex RuH(PPh₃)₂(HNCMe₂CMe₂NH₂)₂ **2c'**, as described elsewhere.¹⁸ This complex is stable and completely characterized. By contrast, the red solutions of complexes RuH(PPh₃)₂-(HNC₆H₁₀NH₂) **2a'** and RuH(PPh₃)₂(NHCH₂CH₂NH₂) **2b'**, when prepared in a similar fashion (eq 2 shows the reaction for **2a'**), are stable only for short periods of time. The neutral phosphazene base 'BuNP(NP(NMe₂)₃)₃³⁶ (pK_a^{THF} ≈ 40^{37,38}) can be used in place of KO^tBu in eq 2, although an excess is required to drive the reaction to completion. The low-temperature NMR spectra of **2a'** in toluene-*d*₈ are complex, probably because of a monomer–dimer dynamic equilibrium (see Supporting Information). NMR spectra of C₆D₆ solutions of **2a'** under Ar for 1 h start to show the presence of uncharacterized products of its decomposition as well as the dihydride *c,t*-**3a**. The latter compound likely forms from the abstraction by **2a'** of H₂ from other species in solution. The amido complex **2b'** has not been produced in a pure state because decomposition starts im-

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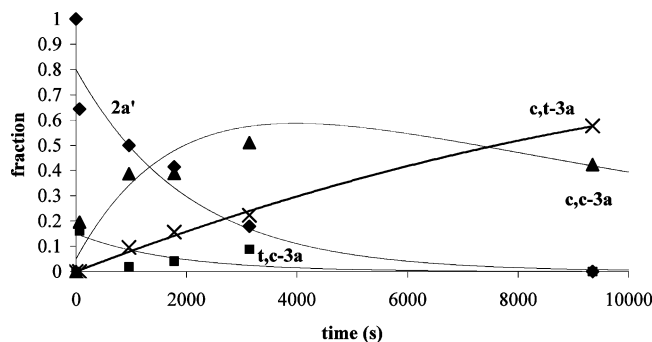
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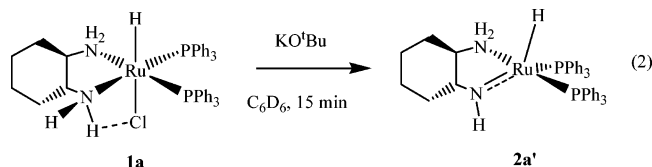
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Table 2. NMR Properties of the RuH(PPh₃)₂(amido–amine) Complexes **2** in C₆D₆

	2a'	2b'	2c' ¹⁸
δ_{H} (ppm)	−20.7 (br t)	−20.9 (t)	−21.1 (t)
$^2J_{\text{HP}}$ (Hz)	33	34	36
δ_{P} (ppm)	72.5 (A of AB) 73.0 (B of AB)	72.0 (m)	71.1 (s)
$^2J_{\text{PP}}$ (Hz)	25	73.2 (br)	

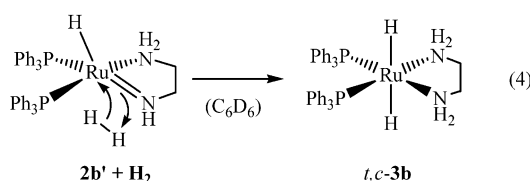
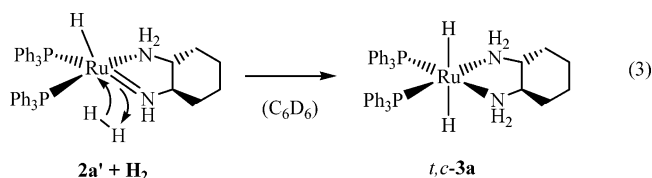
**Figure 1.** Plot of the fraction of the dihydride species *t,c*-**3a** (■), Δ/Λ -*c,c*-**3a** (▲), and *c,t*-**3a** (×) produced in the reaction of complex **2a'** (◆) (0.08 M) in toluene-*d*₈ with dihydrogen (1 atm) as monitored by ¹H NMR.

mediately. An interesting dimeric product of the decomposition of **2b'** is discussed below. The spectra and chemical properties of **2a'** and **2b'** in solution are similar to those of **2c'** (Table 2).



Reaction of the Amido–Amine Complexes with Dihydrogen To Produce *trans*-Dihydrides. Understanding the course of the reaction of these amido–amine complexes with dihydrogen is important since this is thought to be a step in the catalytic cycle in the hydrogenation of ketones (Scheme 1)^{7,9,11,17,18} and imines.¹¹ When hydrogen is added to **2a'** or **2b'** in solution, the resulting dihydrides undergo a succession of isomerization reactions, leading from the least stable *trans*-dihydride, *cis*-PPh₃ isomer *t,c*-**3**, via the intermediate *cis*-dihydride, *cis*-PPh₃ isomers Δ/Λ -*c,c*-**3a**, to the most stable *cis*-dihydride, *trans*-PPh₃ isomer *c,t*-**3**. In contrast, the reaction of **2c'** with dihydrogen stops at the isomer *t,c*-**3c**, presumably because the methyl groups on the backbone of the diamine hinder the formation of the other isomers.¹⁸ Figure 1 shows how the concentrations of **2a'** and the dihydride isomers change with time after the addition of hydrogen gas to a solution of **2a'** in toluene-*d*₈. As long as the amido and H₂ are present there is always a small amount of the *trans*-dihydride *t,c*-**3a**.

The species that are formed first from the reaction of dihydrogen at 1 atm pressure with **2a'** and **2b'** are the very reactive *trans*-dihydride complexes *t,c*-**3a** or *t,c*-**3b**, respectively (eqs 3 and 4). Because the formation of this isomer requires the lowest degree of structural reorganization, it is reasonable that it is produced fastest. This has also been observed for **2c'** and calculated for **2b'**.¹⁸ Evidence for the structural assignment of *t,c*-**3a** and *t,c*-**3b** comes from the NMR spectra (see Table 3).



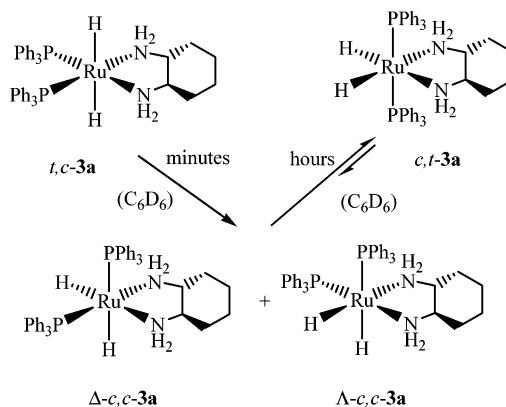
The *trans*-dihydride complexes *t,c*-**3a** and *t,c*-**3b** are not easily detectable because of their short lifetimes. However, *t,c*-**3a** can be observed when a solution of **2a'** in toluene-*d*₈ is prepared, frozen in liquid N₂, and then reacted with 1 atm of dihydrogen at −60 to −20 °C. After 40 min at −20 °C, there is about 40% conversion to *t,c*-**3a**; some Δ/Λ -*c,c*-**3a** also forms by isomerization of *t,c*-**3a**. After 10 min at 20 °C, *t,c*-**3a** has almost disappeared while *c,c*-**3a** continues to grow in and then it, in turn, isomerizes to *c,t*-**3a**.

Isomerization of the Dihydrides. Two different diastereomers (Δ -*c,c*-**3a** and Λ -*c,c*-**3a**) are produced in the isomerization of *t,c*-**3a** (Scheme 2) in a ratio of about 1:2. These result from chirality at Ru (Δ/Λ) and at the enantiopure (*R,R*)-dach ligand. It is not clear which is the major diastereomer, although we argue below that it may be the Λ isomer on the basis of the results of the reaction the diastereomers with the prochiral ketone, acetophenone. The ethylenediamine complex *t,c*-**3b** isomerizes to *c,c*-**3b** (Scheme 3). Complex *c,c*-**3b** exists as a racemate (chirality at Ru only).

The isomers *c,c*-**3a** and *c,c*-**3b** have half-lives of 40 min and about 1 h, respectively, at 20 °C with respect to further

Table 3. NMR Properties of the *trans*-Dihydride Complexes, *t,c*-**3**, in C₆D₆

<i>trans</i> -H, <i>cis</i> -PPh ₃	<i>t,c</i> - 3a	<i>t,c</i> - 3b	<i>t,c</i> - 3c ¹⁸
δ_{H} (ppm)	−5.45 (t)	−5.90 (t)	−5.50 (t)
$^2J_{\text{HP}}$ (Hz)	18	20	18
δ_{P} (ppm)	86.5 (s)	86.0 (s)	87.8 (s)
<i>cis</i> -H, <i>trans</i> -PPh ₃	<i>c,t</i> - 3a	<i>c,t</i> - 3b	
δ_{H} (ppm)	−18.30 (t)	−18.35 (t)	
$^2J_{\text{HP}}$ (Hz)	27	27	
δ_{P} (ppm)	66.0 (s)	66.0 (s)	

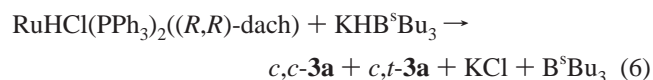
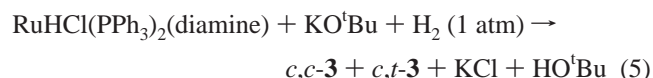
Scheme 2. Isomerization of the Dihydride *t,c*-**3a**

isomerization that allows an approach to equilibrium with a *cis*-dihydride that has *trans*-phosphines (*c,t*-**3a** and *c,t*-**3b**; Schemes 2 and 3). The minor diastereomer of *c,c*-**3a** appears to isomerize at a slightly greater rate than the major diastereomer on the basis of changes in the intensities of the hydride resonances between -5 and -6 ppm. At equilibrium there is about 8% *c,c*-**3a** and 92% *c,t*-**3a**. When a pure sample of crystalline *c,t*-**3a** is dissolved in C_6D_6 , the *c,c*-**3a** isomers can be observed to grow in over a period of a day until equilibrium is established, although there is also some decomposition. An equilibrium mixture of **3b** is richer in the *cis,cis* isomer than **3a** and consists of about 30% *c,c*-**3b** and 70% *c,t*-**3b**.

The NMR experiments showed that the rate of the isomerization of *c,c*-**3a** to *c,t*-**3a** in C_6D_6 is independent of the starting dihydride concentration and therefore appears to be a unimolecular process. The addition of PPh_3 (0.012 M PPh_3 to 0.016 M of complex) did not cause a significant change either. Therefore, the isomerization could involve a trigonal twist of groups on the octahedral metal. However, this result does not rule out a mechanism where isomerization takes place after the rate-limiting dissociation of a phosphine. The rate of isomerization from *c,t*-**3a** to *c,c*-**3a** is about 10 times slower than the reverse process, making *c,t*-**3a** a less active ketone hydrogenation precatalyst in benzene than *c,c*-**3a** (see below).

The isomerization between *cis*- and *trans*-dihydrides has been reported in a few cases. Milstein and co-workers reported a case where the *cis*-dihydride $Ir\{C_6H_3(CH_2P^iPr_2)_2\}(H)_2(CO)$ isomerizes to the more stable *trans*-dihydride.³⁹ Theoretical calculations provide evidence for two consecutive trigonal twists as the mechanism for this reaction; that is, there is no ligand dissociation involved.⁴⁰ The complex $Ru(H)_2(PPh_2CH_2PPh_2)_2$ exists as a mixture of *cis*- and *trans*-isomers in a ratio of 1:4 and in dynamic equilibrium,⁴¹ while other complexes, $M(H)_2$ (diphosphine)₂^{42,43} and $M(H)_2$ (phosphine)₄,⁴⁴ $M = Fe, Ru, Os$, tend to have a more stable *cis*-isomer than a *trans* one.

Preparation of the *cis*-Dihydrides. Two effective procedures to synthesize mixtures of *c,c*-**3** and *c,t*-**3** in high yield are given by eqs 5 and 6.



In either case, the ratio of *c,c*-**3** to *c,t*-**3** depends on the reaction time and the time until precipitation of the product. Shorter reaction times produce the mixtures enriched up to 85% in the *c,c*-**3** isomers. The same 1:2 ratio of diastereomers of Δ/Λ -*c,c*-**3a** is produced by both methods. The ratio of the isomers remains unchanged after storage in the solid state. The *cis*-dihydrides *c,c*-**3b** and *c,t*-**3b** have been mentioned in a patent.²⁶

Scheme 3. Isomerization of the Dihydride *t,c*-**3b**

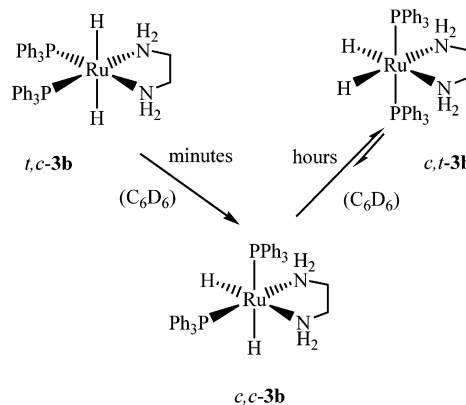


Table 4. NMR Properties of the *cis*-Dihydride Complexes *c,c*-**3** in C_6D_6

	Λ - <i>c,c</i> - 3a ^a	Δ - <i>c,c</i> - 3a	<i>c,c</i> - 3b
δ_H (ppm)	-5.65 (ddd)	-5.35 (ddd)	-6.00 (ddd)
$^2J_{HP_{trans}}$ (Hz)	100	102	99
$^2J_{HP_{cis}}$ (Hz)	32	33	33
$^2J_{HH}$ (Hz)	6	6	6
δ_H (ppm)	-15.4 (m)	-15.4 (m)	-15.75 (td)
$^2J_{HP}$ (Hz)	not resolved	not resolved	24
$^2J_{HH}$ (Hz)	6	6	6
δ_P (ppm)	55.5	57.5	56.5
δ_P (ppm)	84.0	84.0	83.5
$^2J_{PP}$ (Hz)	13	13	14

^a Arbitrarily assigned to the major isomer with ratios of intensities of peaks of 2:1= Λ : Δ . These assignments may need to be reversed.

The KO^tBu/H_2 method (eq 5) produces small amounts of side products in low concentrations that are difficult to remove. This might be because this reaction proceeds via unstable amido-amine complexes. The potassium selectride (KHB^sBu_3) method (eq 6) might proceed via the initial formation of (OC-6-22)- $RuH(HB^sBu_3)(PPh_3)_2((R,R)\text{-dach})$ (cf. *trans*- $RuH(HBH_3)((R)\text{-binap})(dppe)$ ¹⁰) followed by its decomposition, first to the *trans*-dihydride *t,c*-**3a**, and then rapidly to the observed mixture of *cis*-dihydrides that becomes enriched in *c,t*-**3a** over time.

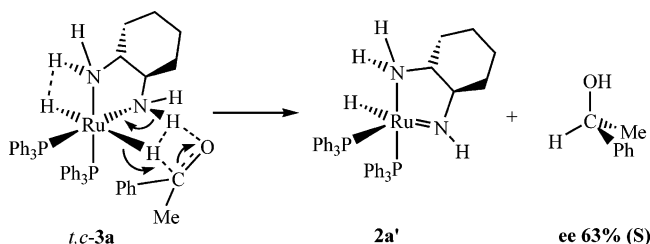
Some spectroscopic properties of the *cis*-dihydrides *c,c*-**3a** and *c,c*-**3b** are summarized in Table 4, while those of *c,t*-**3a** and *c,t*-**3b** are listed in Table 3. The NMR properties and X-ray crystal structure of *c,t*-**3a** have already been reported.¹¹ The *trans*-phosphine stereochemistry of *c,t*-**3b** was also verified by NMR using a ^{15}N labeled diamine in the complex $Ru(H)_2(PPh_3)_2(^{15}NH_2CH_2CH_2^{15}NH_2)$ (see the Experimental Section).

Reaction of the Dihydrides with Ketones and Alcohols.

Only the isomers of $RuH_2(PPh_3)_2(\text{diamine})$ with *cis*-phosphine ligands react with acetophenone ($PhMeC=O$) and benzophenone ($Ph_2C=O$). Cold solutions containing a mixture of the *trans*-dihydride *t,c*-**3a** and the amido complex **2a'** react with acetophenone to produce predominately (*S*)-phenylethanol (see below). This parallels the high activity of complex *t,c*-**3c** in rapidly transferring dihydrogen to acetophenone to produce 1-phenylethanol.¹⁸

The *cis,cis*-isomers Δ/Λ -*c,c*-**3a** and *c,c*-**3b** in solution at 20 °C are consumed completely within 3 min after the addition of acetophenone or benzophenone, while the *cis,trans*-isomers *c,t*-**3a** and *c,t*-**3b** remain unchanged. When dihydrogen is added, the *cis,cis*-dihydrides are regenerated, presumably via the *trans*-dihydrides *t,c*-**3**, while the amount of the dihydrides *c,t*-**3** still

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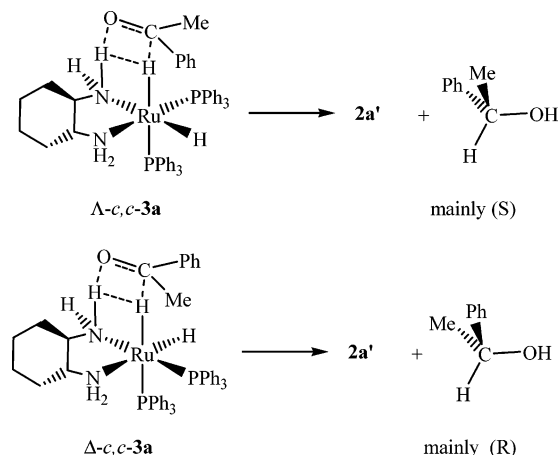
Scheme 4. Stoichiometric Hydrogenation of Acetophenone by *t,c*-**3a**

remains unchanged. This demonstrates that the *cis,cis*-isomers are potential catalysts for the hydrogenation of these ketones. In contrast, the *cis,trans*-isomers need at least several days to fully react and can even be detected after the addition of a large excess of PhCOMe. The *cis,trans*-isomers may have to isomerize to the *cis,cis*-isomer to react since the time scale of the reaction with the *c,t*-**3** compounds is similar to the time scale for the *c,t*-**3** to *c,c*-**3** isomerization. This is the explanation for the report of a reaction between *c,t*-**3a** and acetophenone in C₆D₆.¹¹

The metal-containing products of the stoichiometric reaction of benzophenone and acetophenone with *c,c*-**3a** or *c,c*-**3b** in benzene have not been completely characterized. These could be alkoxide complexes or the adducts of amido species and alcohols (see the Supporting Information). Only the *c,c*-**3a** isomer in a mixture of *c,c*-**3a**/*c,t*-**3a** reacts quickly with added *rac*-1-phenylethanol in C₆D₆ under Ar, probably to give H₂ and the alcohol adduct of **2a'**, RuH(OHCHMePh)(PPh₃)₂((*R,R*)-dach), with a broad ¹H NMR resonance at −20.4 ppm. This behavior was observed for the reaction of the amido–amine complex **2c'** with this alcohol.¹⁸

Enantioselective Stoichiometric Hydrogenation of Acetophenone by the Dihydride Isomers of **3a.** Solutions containing increasing amounts of the *trans*-dihydride *t,c*-**3a** (and smaller amounts of the *cis,cis*-dihydrides, *c,c*-**3a**) were prepared by reacting the amido–amine complex **2a'** in toluene at −20 °C with dihydrogen for time intervals increasing from 10 to 40 min. When these were reacted with PhCOMe for approximately 1 min at −20 °C, the conversion to 1-phenylethanol that was isolated after workup increased from 18 to 42% in accordance with the amount of *trans*-dihydride present, while the ee stayed at 63 ± 2% (*S*). The fact that the dihydrogen transfer to the ketone is very fast, even at −20 °C, supports the mechanism proposed below for the catalytic ketone hydrogenation. If the ketone is left in contact with the hydrides for longer periods of time (5–30 min at −20 °C), the *cis,cis*-dihydride isomers begin to react to give a higher conversion to the alcohol, but with a lower ee (50–30% (*S*)).

By examining the postulated structure of the transition state (Scheme 4), we can explain the production of the excess of the *S* enantiomer of 1-phenylethanol by hydrogen transfer to PhCOMe from the *trans*-dihydride *t,c*-**3a** that contains the optically active (*R,R*)-dach ligand. There is one axial NH aligned with the Ru–H bond at each side of this C₂-symmetrical molecule. Hydridic–protonic interactions are postulated to favor this alignment with a RuH⋯HN distance of 2.2 Å as is observed for *trans*-RuH₂(tmen)((*R*)-binap).¹⁷ The ketone approaches either side of the dihydride so that the oxygen forms a hydrogen bond with an axial NH. Then the smaller Me group fits between the bulky *cis*-PPh₃ ligands, while the carbonyl carbon is attacked

Scheme 5. Stoichiometric Hydrogenation of Acetophenone by the Diastereomers of *c,c*-**3a** To Produce 1-Phenylethanol

by the hydride. A concerted transfer of H[−] and H⁺ equivalents gives the (*S*)-alcohol and the amido–amine complex **2a'**. A similar mechanism has been established for *trans*-dihydrides **3c** and RuH₂((*R*)-binap)(tmen).¹⁸ The existence of rotamers of the PPh₃ ligands in *t,c*-**3a** could explain why the enantioselectivity is poor.

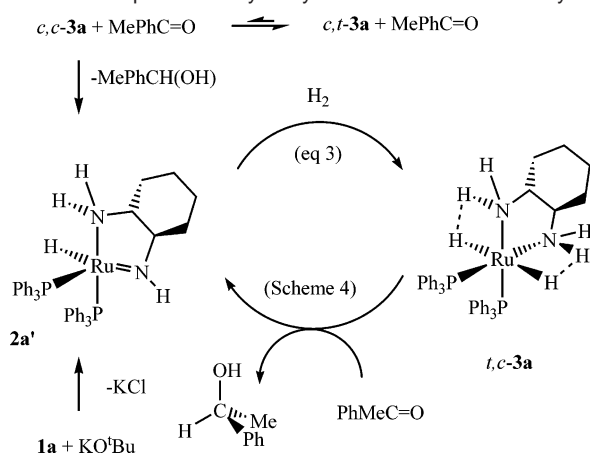
When a mixture containing predominantly the *cis,cis*-diastereomers Δ -*c,c*-**3a** and Λ -*c,c*-**3a** is reacted with acetophenone at 20 °C, an ee of 16–18% (*S*) is obtained. If it is assumed that the most important reason for stereoselectivity is the avoidance of the bulky *syn*-PPh₃ ligand by the large phenyl group of the acetophenone docked by hydrogen bonding in the second coordination sphere, then the following model provides a possible explanation for the reduction in enantioselectivity. The proposed transition state for Λ -*c,c*-**3a** should favor (*S*)-1-phenylethanol, whereas that for Δ -*c,c*-**3a** should favor the (*R*)-enantiomer (Scheme 5) with the assumption that the larger Ph group of the ketone is placed over the smaller hydride ligand. The result will be a low overall ee.

The very low reactivity of the dihydride *c,t*-**3a** with the ketone may be due to poor positioning of the amine protons and hydrides for the dihydrogen transfer reaction. The X-ray crystal structure of *c,t*-**3a**¹¹ revealed that these are not aligned by RuH⋯HN hydridic–protonic interactions unlike the *trans*-dihydride RuH₂((*R*)-binap)(tmen) that does react readily with ketones.^{17,18}

Hydrogenation of Acetophenone Catalyzed by Complexes **3a in Benzene.** The dihydride Ru(H)₂(PPh₃)₂((*R,R*)-dach) **3a** was reported to be an active catalyst for the hydrogenation of neat acetophenone to 1-phenylethanol with an enantiomeric excess of 60% (*S*).¹¹ However, the role of the different isomers of **3a** in catalysis was not studied.

Here we find that a mixture of about 85% Δ / Λ -*c,c*-**3a** and 15% *c,t*-**3a**⁴⁵ in benzene that is prepared according to eq 5 serves as an active catalyst precursor to hydrogenate PhCOMe to (*S*)-PhCH(OH)Me with an ee of about 50%. When a sample of this mixture of **3a** is left to isomerize to an equilibrium mixture of about 8% Δ / Λ -*c,c*-**3a**/92% *c,t*-**3a** in benzene, almost no catalytic activity is observed using exactly the same procedure. In general, we observe that the catalytic activity of **3a** decreases

(45) During catalyst preparation and loading, this mixture should evolve into a mixture of approx 75% *c,c*-**3a** and 25% *c,t*-**3a**.

Scheme 6. Proposed Catalytic Cycle and Routes into the Cycle

as the ratio of *c,c*-**3a**/*c,t*-**3a** decreases. Therefore, we can rule out *c,t*-**3a** as being the active catalyst or catalyst precursor in benzene.

Samples of **3a** that contain the *c,c*-**3a** isomer prepared according to eq 6 provide the alcohol in 55–61% ee (*S*) in catalytic hydrogenation reactions. Samples prepared according to eq 5 with similar amounts of *c,c*-**3a** give a product of lower ee (48–51% ee (*S*)). We suspect that a small amount of racemization of the (*R,R*)-dach ligand occurs by reversible β -hydride elimination from the amido–amine intermediate of reaction 5 to give an imine intermediate as in the formation of **6** discussed below. This would result in some loss of enantiopurity.

The 48–61% ee (*S*) of the product in the catalytic hydrogenation approaches the 63% ee of the alcohol observed in the stoichiometric reaction of predominantly the *trans*-dihydride *t,c*-**3a** with acetophenone at low temperature and not the ee of 16–18% (*S*) of the stoichiometric reaction of mainly Δ/Λ -*c,c*-**3a** (see above). Therefore, the *trans*-dihydride *t,c*-**3a** is the active catalyst along with the amido–amine complex **2a'**, whereas the isomers Δ/Λ -*c,c*-**3a** are only catalyst precursors to these active catalysts.

Scheme 6 shows the proposed catalytic cycle for the hydrogenation of acetophenone conducted in benzene solutions by analogy to that proposed for **2c'**/*t,c*-**3c**. The amido complex **2a'** reacts with H₂ to produce *t,c*-**3a** that rapidly transfers the hydride and proton to the ketone to produce 1-phenylethanol in 50–60% ee (*S*) (cf. Scheme 4). This transfer is apparently more rapid than the isomerization to Δ/Λ -*c,c*-**3a** because the ee obtained is 50–60% (*S*), not the 16–18% (*S*) resulting from the reaction of the *cis,cis*-isomers with acetophenone (cf. Scheme 5). Scheme 6 shows two possible entries into the cycle. The catalyst precursors can be *c,c*-**3a**, by the reactions of Scheme 5 to produce **2a'** and other ruthenium species, or **1a**, by reaction with base to produce mainly **2a'**. The reaction of *c,c*-**3a** with the ketone in benzene is very fast, and thus there is no induction period for catalyst formation while there is an induction period of several seconds starting with **1a** and a suspension of KO^tBu. The second entry, the addition of complex **1a** to a mixture of ketone and base under H₂, provides the most active system in benzene and gives the alcohol in 50–62% ee (*S*) depending on the conditions. The isomer *c,t*-**3a** is apparently not a good precatalyst in benzene but will, over the course of several hours, isomerize to *c,c*-**3a** that is a precatalyst.

Kinetic Study of the Hydrogenation of Acetophenone Catalyzed by Dihydrides **3a in Benzene.** The rates of hydrogenation as a function of concentrations of the dihydrides **3a**, ketone and dihydrogen in benzene, benzene-*d*₆, or 2-propanol were studied by withdrawing samples from a thermostated reactor at set time intervals and analyzing them by NMR and gas chromatography over a chiral column. The conditions for obtaining reproducible results are exacting (see the Experimental Section). It is necessary to determine by NMR the starting ratio of *c,c*-**3a**/*c,t*-**3a** isomers since only the *c,c*-**3a** isomers are effective catalyst precursors in benzene as shown in Scheme 6. Hence, fresh catalyst solutions have to be made up before each run. The activity of a precatalyst benzene solution enriched in *c,c*-**3a** decreases with time, decreasing as *c,c*-**3a** isomerizes to *c,t*-**3a**. When a solution of **3a** is added to the ketone solution under H₂ at the start of the hydrogenation reaction, the *c,c*-**3a** present at that instant rapidly reacts with the ketone to start the reaction.

The catalytic reaction in benzene was found to be first-order with respect to the initial concentration of *c,c*-**3a** in the catalyst mixture, first-order in dihydrogen concentration, and zero-order in ketone concentration (eq 7, $k_7 = 7.5 \pm 0.4 \text{ M}^{-1} \text{ s}^{-1}$) at ketone concentrations of less than 0.02 M (Table 5). The presence of 0.01 M PPh₃ or 0.05 M racemic 1-phenylethanol (Table 5, entries 4 and 5) did not significantly alter the reaction rate as expected on the basis of Scheme 6. The first-order dependence on the initial *c,c*-**3a** concentration is illustrated in Figure 2, while the first-order dependence on hydrogen concentration is demonstrated in Figures 3 and 4 (entries 2, 7, and 8 of Table 5). The approximately linear dependence of concentration with time throughout the reaction indicates that the catalytic reaction is independent of the ketone and alcohol concentrations.

$$\text{rate} = \frac{d[\text{alcohol}]}{dt} = \frac{-d[\text{ketone}]}{dt} = k_7[c,c\text{-}\mathbf{3a}]_{\text{initial}}[\text{H}_2],$$

$$k_7 = 7.5 \pm 0.4 \text{ M}^{-1} \text{ s}^{-1} \quad (7)$$

The second entry route into the catalytic cycle of Scheme 6 is the addition of **1a** to the KO^tBu/ketone/H₂/benzene mixture to form **2a'**. This results in a catalyst mixture that is about twice as active as one from **3a** on the basis of total ruthenium concentration. It seems that this route provides a better yield of **2a'**, but possibly at the expense of partial racemization of the (*R,R*)-dach ligand, as mentioned above.

If the addition of dihydrogen to **2a'** is the turnover limiting step of Scheme 6 as it is for **2c'** ($k = 110 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C),¹⁸ then a rate law like that of eq 7 would be expected except that the concentration of the amido complex **2a'** is used instead of $[c,c\text{-}\mathbf{3a}]_{\text{initial}}$ (eq 8).

$$\text{rate} = \frac{d[\text{alcohol}]}{dt} = k_8[\mathbf{2a'}][\text{H}_2] \quad (8)$$

We conclude that k_8 is $8 \text{ M}^{-1} \text{ s}^{-1}$ or slightly greater depending on the yield of catalyst **2a'** from the precatalyst *c,c*-**3a** or **1a**. The rate constant increases with temperature, but the interpretation of the temperature dependence will be complicated by the presence of the various dihydride and alkoxide equilibria.

Figure 5 shows three runs at higher catalyst and ketone concentrations. As mentioned previously, when mainly *c,t*-**3a** is present, there is almost no catalytic activity. When 75% *c,c*-

Table 5. Dependence of the Zero Order Rate of Production of Alcohol on the Concentrations of the Precatalyst *c,c*-**3a** and Hydrogen in Benzene^a

run	[Ru] _{total} , M	% <i>c,c</i> - 3a (±5%)	[<i>c,c</i> - 3a] _{init.} , M (±5%)	[H ₂], M	v ₀ , initial rate, M ⁻¹ s ⁻¹ (±5%)	k = v ₀ /([<i>c,c</i> - 3a][H ₂]), M ⁻¹ s ⁻¹	%conversion/% ee
1	1.1 × 10 ⁻⁴	35	3.6 × 10 ⁻⁵	0.013	3.5 × 10 ⁻⁶	6.9 ± 0.5	7/61; 31/55
2	2.2 × 10 ⁻⁴	35	7.7 × 10 ⁻⁵	0.013	7.8 × 10 ⁻⁶	7.7 ± 0.5	16/60; 30/59; 73/55
3	3.3 × 10 ⁻⁴	40	1.3 × 10 ⁻⁴	0.013	1.3 × 10 ⁻⁵	7.5 ± 0.5	49/62; 96/61
4	2.2 × 10 ⁻⁴	40	8.8 × 10 ^{-5b}	0.013	9.5 × 10 ⁻⁶	8.2 ± 0.5	15/63; 90/55
5	2.2 × 10 ⁻⁴	40	8.8 × 10 ^{-5c}	0.013	9.4 × 10 ⁻⁶	8.1 ± 0.5	
6	2.2 × 10 ⁻⁴	10	2.2 × 10 ^{-5d}	0.013	2.8 × 10 ⁻⁶	9 ± 1	14/60; 24/58
7	2.2 × 10 ⁻⁴	40	8.8 × 10 ⁻⁵	0.021	1.37 × 10 ⁻⁵	7.6 ± 0.5	20/59; 77/58
8	2.2 × 10 ⁻⁴	30	6.6 × 10 ⁻⁵	0.029	1.40 × 10 ⁻⁵	7.3 ± 0.5	32/58; 96/56
9	1.1 × 10 ⁻³	75	8 × 10 ^{-4e}	0.013	4 × 10 ⁻⁵ to 1.2 × 10 ^{-4e}	4 to 12	8/47; 30/50

^a [Acetophenone]₀ = 0.0167 except for run 9 where it is 0.167 M; constant [H₂] = 0.013 M (5 atm), 0.021 M (8 atm), or 0.029 M (11 atm); 293 K; [Ru]_{tot} = [active *c,c*-**3a**] + [inactive *c,t*-**3a**]. ^b [PPh₃] = 0.01 M. ^c [rac-1-phenylethanol]₀ = 0.05 M. ^d A solution of 35% *c,c*-**3a** after sitting for 2.5 h. ^e [acetophenone]₀ = 0.167 M (Figure 5).

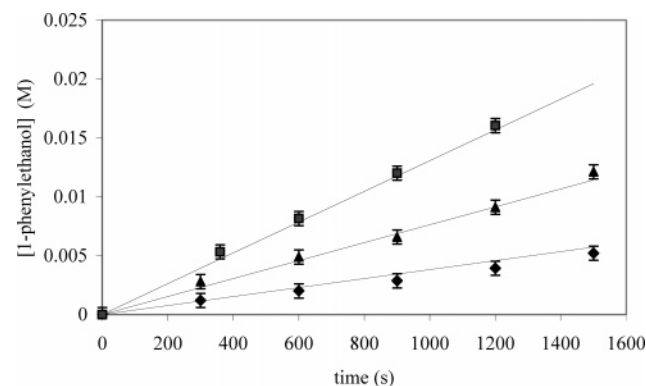


Figure 2. Plots of production of 1-phenylethanol as a function of time in the hydrogenation of acetophenone (0.0167 M) by precatalyst **3a** in benzene at 20 °C, 5 atm H₂, with total initial concentrations of **3a** of 3.3 × 10⁻⁴ M (40% *c,c*-**3a**, ■), 2.2 × 10⁻⁴ M (35% *c,c*-**3a**, ▲), and 1.1 × 10⁻⁴ M (35% *c,c*-**3a**, ◆). The solid lines represent the numerical integration of eq 7 with $k_7 = 7.5 \text{ M}^{-1} \text{ s}^{-1}$ with the initial conditions as indicated above. The ee values decrease from 60 to 55% (S) over the course of the reaction.

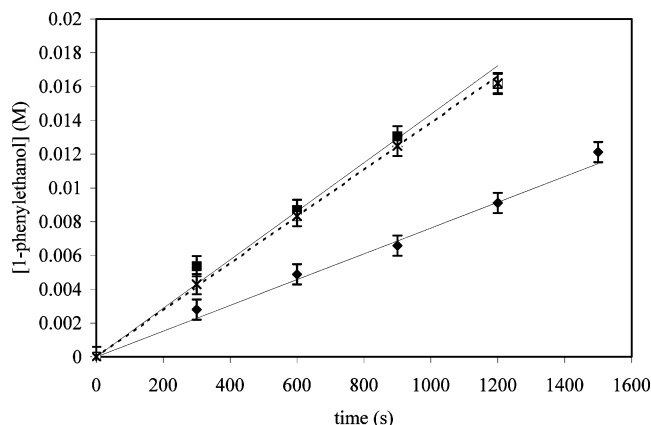


Figure 3. Plots of 1-phenylethanol concentration as a function of time in the hydrogenation of acetophenone (0.0167 M) by precatalyst **3a** in benzene at 20 °C, with total initial concentrations of **3a** of 2.2 × 10⁻⁴ M and constant hydrogen concentrations of 0.0132 M (5 atm, 35% *c,c*-**3a**, ◆), 0.0212 M (8 atm, 40% *c,c*-**3a**, ×), and 0.0292 M (11 atm, 30% *c,c*-**3a**, ■). The solid lines (dotted line for the 8 atm run) represent the numerical integration of eq 7 with $k_7 = 7.5 \text{ M}^{-1} \text{ s}^{-1}$ and the hydrogen concentrations as indicated. The ee values decrease from 60 to 57% (S) over the course of the reaction.

3a is present, there is good activity and the plot of conversion versus time curves upward. The initial rate is lower than that expected on the basis of eq 8, while the maximum rate is slightly higher than expected (Table 5, entry 7). A possible explanation for the former low rate might be an inhibition by ketone; this has been observed previously for the related ketone hydrogena-

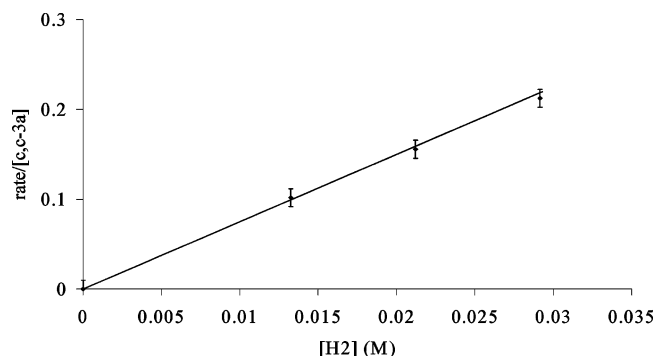


Figure 4. Plot of rate of alcohol formation divided by the starting concentration of the isomer *c,c*-**3a** as determined by NMR versus the hydrogen concentration. The slope of the line is the rate constant, $k_7 = 7.5 \text{ M}^{-1} \text{ s}^{-1}$.

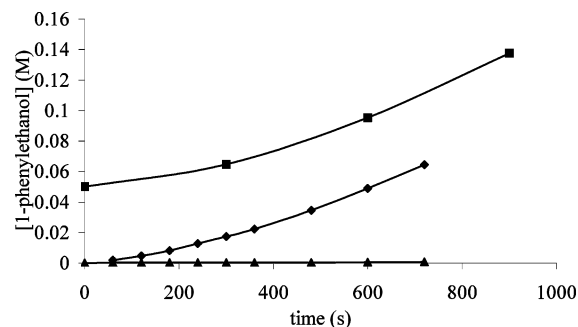


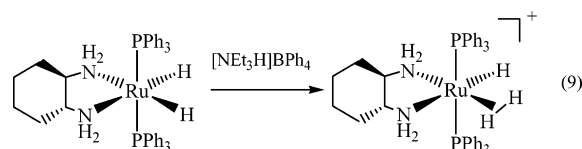
Figure 5. Plot of 1-phenylethanol concentration versus time during the hydrogenation (5 atm) of acetophenone (0.167 M) in benzene at 20 °C catalyzed by 0.0011 M **3a** as 75% *c,c*-**3a**/25% *c,t*-**3a** (◆) or >95% *c,t*-**3a** (▲) or >95% *c,t*-**3a** that was preactivated by reaction with 0.05 M racemic 1-phenylethanol for 15 min under H₂ before (■). The ee range from 49 to 51% (S).

tion precatalyst $\text{RuHCl}\{(\text{R,R})\text{-}(\text{PPh}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH})_2\text{C}_6\text{H}_{10}\}$.³¹ The latter acceleration might be due to the high concentration of the alcohol product that assists in the activation of dihydrogen as observed in 2-propanol.

The upper curve in Figure 5 demonstrates that the *trans*-phosphine isomer *c,t*-**3a** can be activated by reaction with excess racemic 1-phenylethanol (0.05 M) for 15 min under H₂ before adding the ketone. Again there is also increasing activity with time. Lower concentrations of the dihydride *c,t*-**3a** and alcohol do not display this activation phenomenon. The higher concentration of this acidic alcohol may allow the protonation of this dihydride to give a transient dihydrogen complex that loses H₂ to produce an alkoxide complex $\text{RuH}(\text{OCHMePh})(\text{PPh}_3)_2$ ((*R,R*)-dach). This alkoxide complex might then isomerize to

the *trans*-isomer and eliminate alcohol to give the ketone hydrogenation catalyst **2a'**. Thus, catalytically inactive *c,t*-**3a** is converted into active **2a'**. Chaudret and co-workers have reported observing the first steps of such a reaction sequence.⁴¹ The *cis*-dihydride *cis*-RuH₂(dppm)₂, dppm = PPh₂CH₂PPh₂, reacts with phenol to produce first the dihydrogen-bonded complex *trans*-Ru(H...HOPh)(H)(dppm)₂ along with the dihydrogen complex *trans*-[Ru(H₂)(H)(dppm)₂][OPh], and then the alkoxide complex *trans*-RuH(OPh)(dppm)₂.

While no dihydrogen-bonded or dihydrogen complexes have been detected by reaction of complex **3a** with alcohols under H₂ thus far, the related dihydrogen complex (OC-14)-[Ru(η²-H₂)(H)(PPh₃)₂((*R,R*)-dach)]BPh₄ (**4**) with *trans*-phosphines has been observed in solution by reacting *c,t*-**3a** with [HNEt₃][BPh₄] under 1 atm H₂ (eq 9). Equation 9 shows that the dihydride *c,t*-**3a** is more basic than triethylamine in THF. Therefore, it is reasonable that the acidic alcohol 1-phenylethanol could protonate this dihydride when in high enough concentration. Noyori and co-workers have reported evidence for the formation of *trans*-[Ru(H₂)(H)((*S*)-tolbinap)((*S,S*)-dppe)]⁺ in alcohol solution.²⁸



The dihydrogen compound **4** is only stable in solution under an atmosphere of H₂ gas. The ¹H NMR spectrum of the salt in THF-*d*₈ shows a single triplet at −10.65 ppm (*J*_{HP} = 15.0 Hz) for the hydride and dihydrogen ligands in rapid exchange, while a singlet and a quartet at 52.0 ppm in the ³¹P{¹H} and ³¹P NMR spectra, respectively, are consistent with the presence of three coordinated hydrogens and mutually *trans*-PPh₃ ligands. When a solution of the salt in THF-*d*₈ is sealed under deuterium gas, the ¹H NMR spectrum shows the presence of the three observable isotopomers, **4**-H₃, **4**-H₂D, and **4**-HD₂. After equilibration under a large excess of deuterium gas, only **4**-HD₂ was detected. The hydride region of the ¹H{³¹P} NMR spectrum of this species shows a nonbinomial quintet with an averaged HD coupling constant of 4.5 Hz, which was used to calculate a ¹*J*_{HD} coupling constant of 13.5 Hz in the HD ligand. This value is consistent with the presence of an elongated dihydrogen ligand with an H–H distance of 1.2 Å.^{46,47} The dihydrogen complexes [RuH(H₂)(PCy₃)₂(L)]⁺, L = bipy or phen, have very similar properties to complex **4**.⁴⁸

Study of the Hydrogenation of Acetophenone Catalyzed by Dihydrides **3a in 2-Propanol.** Solutions of **3a** in 2-propanol in the absence of added base change over time and have variable catalytic activity in the hydrogenation of acetophenone. The plots of 1-phenylethanol production versus time in the catalytic hydrogenation reactions are curved with decreasing rate with increasing time (see the Supporting Information). The initial rates are higher than those for corresponding conditions with benzene as a solvent. The ee values increase with time from 56

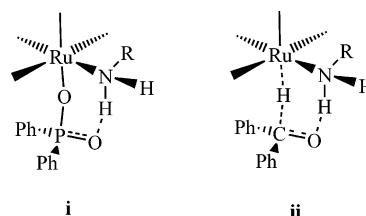
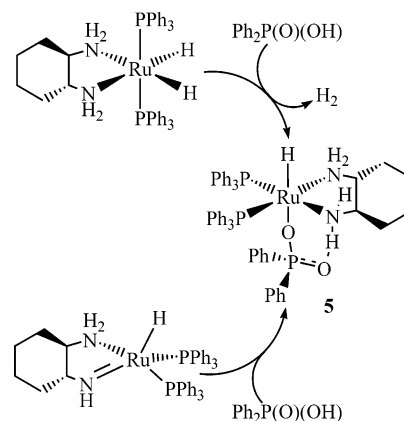


Figure 6. Structure i, analogous to the transition state structure ii.

Scheme 7. Preparation of the Phosphinate Complex **5**



to 60% (*S*) in 2-propanol, while they decrease in benzene. The complexities of this system would require further extensive investigation.

Diphenylphosphinate Complex with Similar Structure to the Proposed Transition State for Ketone Hydrogenation in Benzene. The diphenylphosphinate group has been used as an analogue (Figure 6, i) of the transition state for the transfer of hydride and proton from a ruthenium transfer hydrogenation catalyst Ru(η⁶-arene)(RC₆H₄SO₂NCH₂CH₂NH₂)(H), arene = cymene, R = CH₂=CH–, to benzophenone (Figure 6, ii).⁴⁹

In a similar approach, the reaction of diphenylphosphinic acid with complex **3a** (Scheme 7) resulted in the slow evolution of H₂ gas and the gradual formation of the sparingly soluble, air-stable diphenylphosphinato complex, **5**, which was isolated as pale yellow air-stable crystals. This compound was also prepared by adding solid diphenylphosphinic acid to a freshly prepared solution of **2a'**, whereupon **5** was formed without the evolution of H₂ gas. Two diastereomers are in the unit cell of a crystal of **5**. The structure of each consists of a distorted octahedron, with *cis*-phosphines and with the hydride ligand trans to the coordinated phosphinato oxygen. In one isomer (Figure 7), there is a PO...HN hydrogen bond between the noncoordinated phosphinato oxygen (P=O) and the amine hydrogen (H1BB) of the dach ligand that is axial with respect to the Ru–N–C–C–N– ring. The O(2B)...N(1B) distance is 2.944(5) Å. A ketone oxygen is proposed to form a similar hydrogen bond to an axial NH in the concerted hydrogen transfer transition state (Scheme 4), and thus this diastereomer of **5** is an interesting transition state analogue. The other isomer in the crystal has a PO...HN hydrogen bond with a longer O(2A)...N(2A) distance of 3.016(5) Å involving an amine hydrogen that is bisectonal⁵⁰ with respect to the five-membered ring. The latter hydrogen bond is similar to the one observed in Ru(η⁶-arene)(RC₆H₄-

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(50) Bisectonal: between axial and equatorial. See Luger, P.; Bülow, R. *J. Appl. Crystallogr.* **1983**, *16*, 431–432 for ring descriptor classifications.

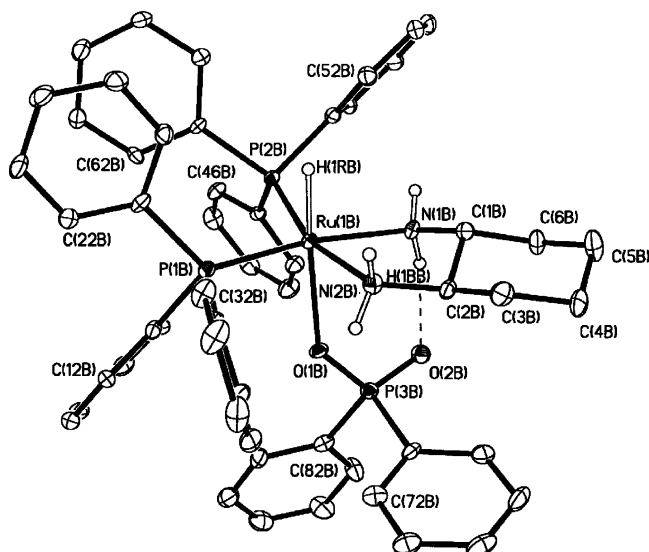
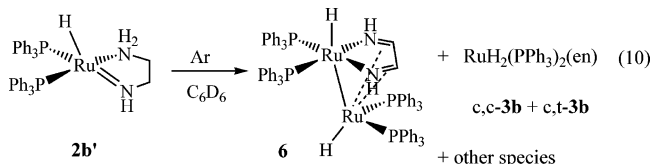


Figure 7. Molecular structure of isomer B of $\text{RuH}(\text{O}_2\text{PPh}_2)(\text{PPh}_3)_2((R,R)\text{-dach})$ **5**.

$\text{SO}_2\text{NCH}_2\text{CH}_2\text{NH}_2)(\text{O}_2\text{PPh}_2)$ with $\text{O}\cdots\text{N}$ 2.972(3) Å.⁴⁹ One difference is the much shorter Ru–O distance in the latter complex of 2.155(3) Å where the oxygen is trans to a Ru–C bond than in complex **5** (Ru–O 2.295(3) or 2.298(3)) where oxygen is trans to a Ru–H bond. In solution, there must be rapid isomerization between the hydrogen-bonded structures of **5** because only one hydride resonance (broad triplet) and three inequivalent phosphorus resonances are observed by ^1H and ^{31}P NMR, respectively.

Decomposition of 2b'. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the amido–amine complex **2b'** indicate that this compound decomposes in C_6D_6 under Ar via a dehydrogenation of the ethylenediamine ligand (eq 10) to produce two dihydride species, *c,c*-**3b** and *c,t*-**3b**, and at least two other complexes, one of which is likely to be the dinuclear complex **6**. After 60 min, all of the amido complex **2b'** is gone. Therefore, hydrogen is transferred from one molecule of **2b'** to another to generate the dihydrides and the diimine species. This process may be initiated by β -hydride elimination from the amido–amine ligand in **2b'**, a process that is shut down by the methyl groups in the stable complex $\text{RuH}(\text{NHCM}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ (**2c'**).



To reduce the complexity of the reaction, acetophenone was added to act as the dihydrogen acceptor in place of equivalents of **2b'**. Indeed, the main product of the reaction of **1b** with KO^tBu in the presence of PhCOMe under Ar in C_6D_6 is the dinuclear complex $\text{Ru}_2\text{H}_2(\text{PPh}_3)_4(\text{HN}=\text{CHCH}=\text{NH})$ **6**, which can be isolated from this reaction in a yield of about 30% but still contaminated by at least one other compound that also appears to have an imine ligand on the basis of ^1H NMR.

The determination of the crystal structure of complex **6** reveals that it is composed of the rare diimine ligand, 1,4-diazabutadiene, $\text{HN}=\text{CHCH}=\text{NH}$,⁵¹ that bridges between two $\text{RuH}(\text{PPh}_3)_2$ fragments (Figure 8). The diimine is bonded in a

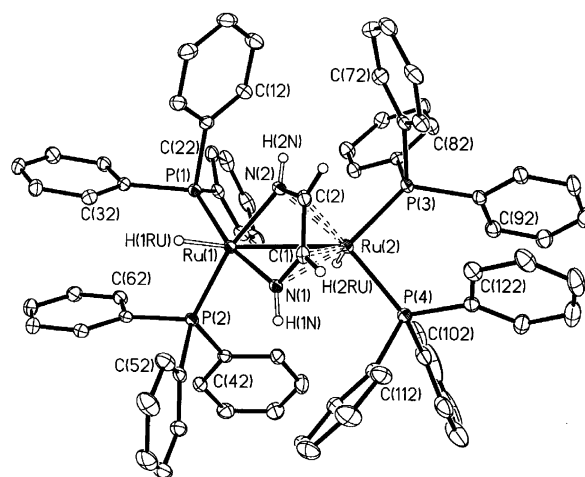


Figure 8. Structure and atomic numbering of the diazabutadiene complex **5**.

σ -fashion by the nitrogens to Ru(1) and in an $\eta^2\text{-C}=\text{N}$, $\eta^2\text{-C}'=\text{N}'$ π -fashion to Ru(2). The planar Ru(1)–diimine grouping acts like an η^5 -cyclopentadienyl analogue in its bonding to the second ruthenium. This type of $\eta^2;\eta^4$ -bridging diimine interaction has been observed previously in the structures of derivatives of the compounds $\text{M}_2(\text{RN}=\text{CHCH}=\text{NR})(\text{CO})_4(\text{X}_2)$, $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$, $\text{R} = \text{alkyl, aryl}$,^{52–54} where X_2 represents a bridging carbonyl, alkyne, or $\text{Ru}(\text{CO})_4$ unit. Therefore, the diimine bridges between two “ $\text{MX}(\text{CO})_2$ ” groups in this case. Such complexes have imine CH resonances in the ^1H NMR spectrum that range between 5 and 8 ppm (cf. 5.1 ppm for **6**). The Ru–Ru distances fall in the range from 2.7 to 2.9 Å, similar to that of **6** (Ru(1)–Ru(2) 2.9735(3)).

The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR signals of **6** in C_6D_6 are concordant with a molecular mirror plane containing the two inequivalent Ru–H groups. The $\text{CH}=\text{N}$ ^1H NMR resonance is a doublet at 5.1 ppm, and pairs of PPh_3 ligands produce singlets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 70.0 and 70.5 ppm. The hydride resonances are triplets at –7.15 and –19.85 ppm in the ^1H NMR spectrum.

The decomposition of the amido–amine complex **2a'** under Ar may also produce a similar dinuclear complex (a disordered crystal structure with some of the features of **6** was obtained in one case) along with a multitude of other compounds.

Conclusions

The reactive amido–amine complexes $\text{RuH}(\text{NH}-\text{R}-\text{NH}_2)-(\text{PPh}_3)_2$ **2** can be prepared by dehydrohalogenation of the complexes $\text{RuHCl}(\text{diamine})(\text{PPh}_3)_2$ **1**. The stability of the amido complexes decreases as the diamine changes in the order $\text{NH}_2\text{-CMe}_2\text{CMe}_2\text{NH}_2 > (R,R)\text{-dach} > \text{en}$. The last complex decomposes to dihydrides and an interesting dinuclear complex **6** with a bridging $\eta^2;\eta^4$ -diazabutadiene ligand.

The amido–amine complexes react with dihydrogen to produce a succession of dihydride isomers $\text{RuH}_2(\text{diamine})-(\text{PPh}_3)_2$ **3** when the diamine is (R,R) -dach or en: first, the *trans*-

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dihydride isomers, then the *cis,cis*-isomers, and finally an equilibrium mixture of the *cis,cis*- and *cis,trans*-isomers. This isomerization possibly proceeds via two trigonal twists of the octahedral coordination geometry. The fast, stoichiometric, enantioselective reduction of acetophenone by the *cis,cis*- and *trans,cis*-dihydride isomers of $\text{RuH}_2((R,R)\text{-dach})(\text{PPh}_3)_2$ is a significant mechanistic result. The low enantiomeric excess in the alcohol produced in the reactions of the *c,c*-**3a** diastereomers indicates that these isomers are only precatalysts, while the 63% ee from reaction with *t,c*-**3a** strongly suggests that this *trans*-dihydride is the catalyst in benzene and in 2-propanol. The original report¹¹ that the dihydride *c,t*-**3a** is likely to be within the catalytic cycle is incorrect, although this isomer can serve as a precatalyst when reacted with an alcohol. This is yet another instance where an isolated, stable “catalyst” turns out to be only a precatalyst. Thus, the *cis*-phosphine isomers are more reactive than the *trans*-phosphine one. The very active and selective Noyori-type catalysts for the asymmetric H_2 -hydrogenation of ketones contain a chelating, enantiopure diphosphine ligand and thus necessarily have phosphorus donors that are mutually *cis*. This appears to be an important structural feature of the catalysts.

The turnover-limiting step in the hydrogenation of acetophenone in benzene catalyzed by the dihydrides appears to be the activation of dihydrogen at the amido–amine complex, as it is for the *tmen* system **2c'**/*t,c*-**3c**. The complex $\text{RuH}(\text{O}_2\text{PPh}_2)(\text{PPh}_3)_2((R,R)\text{-dach})$ is a good model of the transition state for the concerted transfer of hydride and proton to the ketone. The mechanism when the solvent is phenylethanol/benzene or neat 2-propanol is more complex and would require extensive additional study. The catalyst is more active in the presence of alcohol. 2-Propanol is the solvent of choice in Noyori's enantioselective catalysts for ketone hydrogenation.

The dehydrogenation of the amine ligand during amido–amine formation, as observed for the ethylenediamine complex, could explain why the dihydrides prepared by the $\text{RuHCl}((R,R)\text{-dach})(\text{PPh}_3)_2/\text{KO}^t\text{Bu}/\text{H}_2$ route provide 1-phenylethanol of lower ee when used as hydrogenation catalysts than dihydrides prepared by the $\text{RuHCl}((R,R)\text{-dach})(\text{PPh}_3)_2/\text{K}^{\text{sec}}\text{Bu}_3\text{BH}$ route. The dehydrogenation and rehydrogenation of the *dach* ligand could result in some racemization of this ligand and cause the formation of other diastereomers of $\text{RuH}_2(\text{dach})(\text{PPh}_3)_2$.

Experimental Section

General. All preparations and manipulations were carried out under hydrogen, nitrogen, or argon atmospheres with the use of standard Schlenk, vacuum line, and glovebox techniques in dry, oxygen-free solvents. All of the chemicals were purchased from Aldrich Chemical Co. unless otherwise noted. The 99.5% ^{15}N -labeled ethylenediamine was obtained from CDN Isotopes. Instruments and the methods of solvent purification have been described previously.¹⁸ The acetophenone was distilled and deoxygenated before use.

X-ray Structure Analysis. Crystals were obtained by the slow diffusion of either diethyl ether or hexanes into THF or benzene solutions of the desired compounds under a nitrogen atmosphere. Data were collected on a Nonius Kappa-CCD diffractometer using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$; see the Supporting Information). The CCD data were integrated and scaled using the DENZO-SMN software package, and the structures were solved and refined using SHELXTL V5.0. Wherever reported, hydrides were located and refined with isotropic thermal parameters.

Synthesis. $\text{RuHCl}(\text{PPh}_3)_3$. A modification of the reported procedure⁵⁵ was used to prepare this complex. A solution of triethylamine

(10 mL) in toluene (150 mL) was degassed with hydrogen and $\text{RuCl}_2(\text{PPh}_3)_3$ (20.0 g, 20.9 mmol) added under a flow of hydrogen gas. The resulting mixture was refluxed for 2 h under hydrogen with vigorous stirring. The mixture was then cooled to room temperature and then in ice (1 h), and the purple solid was filtered under argon, washed with ethanol ($3 \times 20 \text{ mL}$), then ether ($2 \times 20 \text{ mL}$), and dried under vacuum (17.2 g, 89%). ^1H NMR (C_6D_6 , δ): -17.9 (q, $J_{\text{HP}} = 26 \text{ Hz}$, 1H, RuH), 7.5–7.0 ppm (m, 45H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR: 58.8 ppm (s, br).

$\text{RuHCl}(\text{PPh}_3)_2((R,R)\text{-dach})$ (1a**).**¹¹ $\text{RuHCl}(\text{PPh}_3)_3$ (600 mg, 0.65 mmol) and $(R,R)\text{-dach}$ (80 mg, 0.70 mmol) were mixed in an atmosphere of N_2 , 4 mL of THF was added, and the reaction mixture was stirred for 4 h, producing a dark yellow solution that was filtered. In a few instances, a small amount of an insoluble deep blue compound, thought to be (OC-6-32)- $\text{RuHCl}(\text{PPh}_3)_2((R,R)\text{-dach})$, was recovered. The filtrate was concentrated to 1.5 mL in vacuo, and 5 mL of hexanes was added to give a yellow precipitate. This was filtered, washed with 5 mL of hexanes, and dried in vacuo to give **1a** as a pale yellow powder (470 mg, 93%). Yellow crystals were obtained by layering a C_6D_6 solution with hexanes. **1a**: E. A. Calcd for $\text{C}_{42}\text{H}_{45}\text{ClN}_2\text{P}_2\text{Ru}$: C, 64.98; H, 5.84; N, 3.61. Found: C, 62.97; H, 5.63; N, 3.87. IR (Nujol), cm^{-1} : 1987 (s), 1957 (s) (ν_{RuH}), 3332 (s), 3270 (m), 3229 (m) (ν_{NH}). ^1H NMR (C_6D_6 , δ): -17.99 (t, $^2J_{\text{HP}} = 26 \text{ Hz}$, 1H, RuH), 0.12–0.31 (m, 2H, CH), 0.45 (br, 2H, NH), 0.8–0.98 (m, 4H, CH), 1.75–2.04 (m, 3H, CH), 2.38 (br, 2H, NH), 2.83 (t, 1H, CH), 6.96–7.20, 8.00 (m, 30H, Ph). $^{31}\text{P}\{^1\text{H}\}$: 70.6 ppm (s). (OC-6-32)- $\text{RuHCl}(\text{PPh}_3)_2((R,R)\text{-dach})$: ^1H NMR ($\text{DMF-}d_7$, δ): -12.07 (t, $^2J_{\text{HP}} = 21.75 \text{ Hz}$, 1H, RuH), 0.4–4.48 (m, 14H), 7.63–7.91 (m, 30H, Ph). $^{31}\text{P}\{^1\text{H}\}$: 48.06 ppm (s).

$\text{RuHCl}(\text{PPh}_3)_2(\text{en})$ (1b**).**³⁵ $\text{RuHCl}(\text{PPh}_3)_3$ (600 mg, 0.65 mmol) and en (40 mg, 0.67 mmol) were mixed in an atmosphere of N_2 , 3 mL of THF was added, and the resulting mixture was stirred for 4 h under N_2 . It was filtered and reduced in vacuo to about 1 mL, and 10 mL of hexanes was added to precipitate a yellow solid after being stirred for 10 min. The precipitate was collected by filtration, washed with 2 mL of hexanes, and dried in vacuo for 1 h. This was recrystallized twice to remove free PPh_3 by adding hexanes to a concentrated solution of **1b** in CH_2Cl_2 . Yield of **1b** as a pale yellow powder: 460 mg (>95%). ^1H NMR (C_6D_6 , δ): -18.15 (t, $^2J_{\text{HP}} = 26 \text{ Hz}$, 1H, RuH) 1.60, 1.85, 2.05, 2.40, (br s, 8H, CH_2 and NH_2), 6.9–7.2, 7.85, (m, 30H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): 70.0 ppm (s).

Preparation of a Solution of $\text{RuH}(\text{PPh}_3)_2((R,R)\text{-HNC}_6\text{H}_{10}\text{NH}_2)$ (2a'**).** The monohydride **1a** (62 mg, 0.08 mmol) and KO^tBu (20 mg, 0.18 mmol) were mixed in an atmosphere of N_2 , C_6D_6 (1.0 mL) was added, and the reaction mixture was stirred for 15 min, resulting in the formation of **2a'**. The NMR data were quickly collected without isolation, using the filtered, dark red reaction mixture. ^1H NMR (hydride region, C_6D_6 , δ): -20.70 (br t, $^2J_{\text{HP}} = 33 \text{ Hz}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): 72.5 (d, $^2J_{\text{PP}} = 24.5 \text{ Hz}$), 73.0 ppm (d, $^2J_{\text{PP}} = 24.5 \text{ Hz}$).

Observation of $\text{RuH}(\text{PPh}_3)_2(\text{NHCH}_2\text{CH}_2\text{NH}_2)$ (2b'**).** The monohydride **1b** (60 mg, 0.08 mmol) and KO^tBu (20 mg, 0.18 mmol) were mixed in an atmosphere of N_2 , C_6D_6 (0.6 mL) was added, and the reaction mixture was stirred for 3 min, resulting in the formation of a red solution. This was frozen by cooling with liquid N_2 , H_2 gas was added, and the mixture was warmed to room temperature. The ^1H NMR spectrum, obtained 3 min after melting, showed the presence of an amido species **2b'** (37%) and the three dihydride isomers *t,c*-**3b** (2%), *c,c*-**3b** (54%), *c,t*-**3b** (7%), and a small amount of the dinuclear compound **6**. ^1H NMR (hydride region, C_6D_6 , δ) **2b'**: -20.9 (br t, $^2J_{\text{HP}} = 33 \text{ Hz}$). *t,c*-**3b**: -5.9 (t, $^2J_{\text{HP}} = 20$). *c,c*-**3b**, *c,t*-**3b**, and **6** (see below). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): **2b'**: 72.0 (br), 73.1 ppm (br); *t,c*-**3b**: 86.0 (s); *c,c*-**3b**, *c,t*-**3b** and **6** (see below).

Observation of the Successive Formation of the Dihydrides *t,c*-3a**, Δ/Λ -*c,c*-**3a** and *c,t*-**3a**.** (a) Complex **1a** (31 mg, 0.04 mmol) and KO^tBu (10 mg, 0.09 mmol) were mixed in an atmosphere of N_2 ,

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toluene- d_8 (0.6 mL) at $-20\text{ }^{\circ}\text{C}$ was added, and the resulting mixture was stirred for 10 min while it warmed to room temperature and was filtered and frozen in liquid N_2 . Hydrogen gas was added, and the mixture was allowed to warm to $-78\text{ }^{\circ}\text{C}$ and stored at that temperature for 45 min. ^1H and ^{31}P spectra were taken at -60 , -20 , and $25\text{ }^{\circ}\text{C}$. At low temperatures, they clearly showed the conversion of **2a'** to the dihydride species *t,c*-**3a** that then started isomerizing to Δ -*c,c*-**3a** and Λ -*c,c*-**3a** at $-20\text{ }^{\circ}\text{C}$ and totally disappearing at room temperature after **2a'** was consumed (Figure 1). *t,c*-**3a**: ^1H NMR (hydride region, toluene- d_8 , δ): -5.40 (t, $^2J_{\text{HP}} = 18\text{ Hz}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8): 86.5 ppm (s). Similar experiments were conducted using C_6D_6 to monitor the conversion of the *c,c*-**3a** isomers to *c,t*-**3a**.

Ru(H)₂(PPh₃)₂((R,R)-dach) (3a, Enriched in Isomer *c,t*-3a). THF (2 mL) was added to the monohydride **1a** (1.0 g, 1.28 mmol) and potassium tri-*sec*-butylborohydride (1.5 g of a 1.0 M solution, 1.7 mmol), and the mixture was stirred for 2 h under nitrogen. The resulting mixture was filtered and evaporated to dryness. Hexanes (10 mL) and a few drops of 2-propanol were added, precipitating a bright yellow solid. This was collected by filtration, washed with hexanes, and dried under vacuum to give the yellow solid (782 mg, 82%) as a mixture of *c,t*-**3a** (72%), Δ -*c,c*-**3a** (8%), and Λ -*c,c*-**3a** (20%).⁵⁶ Crystals of *c,t*-**3a** were obtained by diffusion of hexanes into an ether solution as described previously.¹¹ E. A. Calcd for $\text{C}_{42}\text{H}_{46}\text{N}_2\text{P}_2\text{Ru}$: C, 68.0; H, 6.2; N, 3.9. Found: C, 67.3; H, 6.2; N, 3.3. IR (Nujol): 1833 (s), 1944 (s) cm^{-1} (ν_{RuH}), 3266 (w), 3282 (w), 3327 (m), 3337 (w) cm^{-1} (ν_{NH}). ^1H NMR (C_6D_6 , 300 MHz, δ) *c,t*-**3a**: -18.26 (t, $^2J_{\text{HP}} 26.7\text{ Hz}$, 2H), 0.17 (m, 2H), 0.37 (t, 2H), 0.96 (d, 4H), 1.20 (m, 4H, $\text{CH}_2 + \text{NH}_2$), 2.04 (d, $J_{\text{HH}} 6.3\text{ Hz}$, 2H, NH_2), 7.02 (t, $^3J_{\text{HH}} 7.2\text{ Hz}$, $6H_{\text{para}}$), 7.15 (dd, $^3J_{\text{HH}} 7.2$, 6.6 Hz , $12H_{\text{meta}}$), 8.18 (dt, $^3J_{\text{HH}} 6.6$, $^3J_{\text{PH}} + ^2J_{\text{PH}} 3.9\text{ Hz}$, $12H_{\text{ortho}}$). Δ -*c,c*-**3a**: -15.5 (dt, $^2J_{\text{HP}} 23$, $^2J_{\text{HH}} 6\text{ Hz}$, RuH), -5.5 (ddd, $^2J_{\text{HP}} 103$, 34 , $^2J_{\text{HH}} 6\text{ Hz}$, RuH), 0.1 – 2.1 (m, 14H, CH, NH), 6.1 (s br, $2H_{\text{ortho}}$), 6.9 – 8.0 (m, 28 H). Λ -*c,c*-**3a**: -15.4 (dt, $^2J_{\text{HP}} 23$, $^2J_{\text{HH}} 6\text{ Hz}$, RuH), -5.6 (ddd, $^2J_{\text{HP}} 100$, 32 , $^2J_{\text{HH}} 6\text{ Hz}$, RuH), 0.0 (br, 2H), 0.1 (br, 2H), 0.3 – 2.1 (8H), 2.3 (m, 2H), 2.6 (m, 2H), 6.9 – 8.0 (m, 30 H). $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6) *c,t*-**3a**: 67.2 ppm (s); Δ -*c,c*-**3a**: 84.4 (d, $^2J_{\text{PP}} 13.7\text{ Hz}$), 57.7 (d, $^2J_{\text{PP}} 13.7\text{ Hz}$); Λ -*c,c*-**3a**: 84.6 (d, $^2J_{\text{PP}} 13.7\text{ Hz}$), 55.5 (d, $^2J_{\text{PP}} 13.7\text{ Hz}$).

Ru(H)₂(PPh₃)₂((R,R)-dach) (3a, Enriched in Isomers *c,c*-3a). Complex **1a** (200 mg, 0.26 mmol) and KO^tBu were mixed in an atmosphere of N_2 , toluene (1.5 mL) was added, and the mixture was stirred for 3 min, yielding a dark red solution, which was filtered. H_2 was bubbled through the filtrate for 2 min while being stirred, and then 15 mL of hexanes was added. After being stirred for 1 h, the light beige precipitate was collected by filtration and dried in vacuo to give a yellow powder (150 mg, 0.20 mmol; 78%) as a mixture of Δ -*c,c*-**3a** (30%), Λ -*c,c*-**3a** (55%), and *c,t*-**3a** (15%).⁵⁶ NMR properties as above.

Ru(H)₂(PPh₃)₂(en) (3b as a Mixture of Isomers *c,c*-3b and *c,t*-3b). Complex **1b** (360 mg, 0.50 mmol) and KO^tBu (60 mg, 0.52 mmol) were mixed in an atmosphere of N_2 , THF (2 mL) was added, and the mixture was stirred for 1 min, yielding a dark red solution, which was filtered. H_2 was bubbled through the filtrate for 2 min while being stirred, and then 20 mL of hexanes was added. After being stirred for 30 min, the brown precipitate was collected by filtration and dried in vacuo to give an orange solid (154 mg, 0.24 mmol, 45%) as a mixture of *c,c*-**3b** (85%) and *c,t*-**3b** (15%). ^1H NMR (C_6D_6 , 300 MHz, δ) *c,c*-**3b**: -15.7 (td, $^2J_{\text{HP}} 24$, $^2J_{\text{HH}} 6\text{ Hz}$, RuH), -6.0 (ddd, $^2J_{\text{HP}} 99$, 33 , $^2J_{\text{HH}} 6\text{ Hz}$, RuH), 0.8 – 1.6 (m, 5H, CH, NH), 1.8 (s br, 1H), 2.0 (s br, 1H), 2.2 (s br, 1H), 5.8 (s br, $1H_{\text{ortho}}$), 6.9 – 7.1 (m, 17H), 7.7 (td, 6H), 7.8 (m, 6H). *c,t*-**3b**: -18.35 (t, $^2J_{\text{HP}} 27\text{ Hz}$, 2H), 1.2 (m, 4H), 1.4 (m, 4H), 7.0 (m, 6H), 7.15 (m, 12H), 8.10 (dt, $^3J_{\text{HH}} 7$, $^3J_{\text{PH}} + ^2J_{\text{PH}} 4\text{ Hz}$, $12H_{\text{ortho}}$). $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6 , δ) *c,c*-**3b**: 83.5 (d, $^2J_{\text{PP}} 14\text{ Hz}$), 56.5 (d, $^2J_{\text{PP}} 14\text{ Hz}$, P trans to hydride); *c,t*-**3b**: 66.0 ppm (s). *cis,trans*-**Ru(H)₂(PPh₃)₂(H₂¹⁵N-(CH₂)₂¹⁵NH₂)**: ^1H NMR (C_6D_6 , δ): -18.26 (AA' part of AA'MM'X₂ where A, A' = ^1H , M, M' = ^{15}N , X = ^{31}P , $^2J_{\text{HP}} 26.9$, $^2J_{\text{HNtrans}} 7.5$, $^2J_{\text{HNcis}} -0.8$, $^2J_{\text{HH}} 6.5$, $^2J_{\text{NN}} < 1\text{ Hz}$, RuH).

Observation of (OC-14)-[Ru(H)₂(H)(PPh₃)₂((R,R)-dach)]BPh₄ (4). Cold THF- d_8 ($-30\text{ }^{\circ}\text{C}$, 0.6 mL) was added to a mixture of *c,t*-**3a** (30 mg, 0.04 mmol) and [HNEt₃]BPh₄ (17 mg, 0.04 mmol) in an NMR tube. The mixture was then sealed under hydrogen gas. The NMR spectra showed the clean formation of the dihydrogen salt [RuH(H)₂-(PPh₃)₂(dach)]BPh₄. ^1H NMR (THF- d_8) δ : -10.65 (t, $^2J_{\text{HP}} = 15.0\text{ Hz}$, 3H, RuH), 0.37 – 2.67 (m, 14H), 6.69 – 7.71 (m, 50H). $^{31}\text{P}\{^1\text{H}\}$ δ : 51.9 ppm (s).

RuH(PPh₃)₂(Ph₂PO₂)((R,R)-dach) (5). A suspension of diphenylphosphinic acid (87 mg, 0.40 mmol) in THF (5 mL) was added with stirring to a solution of the dihydride *c,t*-**3a** (300 mg, 0.40 mmol) in THF (5 mL). Evolution of H_2 gas was accompanied with the formation of a yellow crystalline solid over a period of 4 h. The solid was collected by filtration, washed with ether and then hexanes, and dried under vacuum (353 mg, 92%). A crystal from this preparation was chosen for the X-ray diffraction study. ^1H NMR (C_6D_6 , δ): -21.93 (br t or td, $^2J_{\text{HP}} = 20.2$, $^3J_{\text{HP}} 4.2\text{ Hz}$, 1H, RuH), 0.21 – 3.25 (m, 12H), 2.47 (b, 1H, NH), 5.55 (b, 1H, NH), 6.90 – 8.20 (m, 40H). $^{31}\text{P}\{^1\text{H}\}$ NMR: 71.1 (d, $^2J_{\text{PP}} 38.6\text{ Hz}$), 69.0 (d), 25.0 (s). IR (Nujol): 2000 cm^{-1} (ν_{RuH}), 3207 (br), 3251 , 3279 , 3319 , 3324 , 3333 , 3340 cm^{-1} (ν_{NH}). E. A. $\text{C}_{54}\text{H}_{55}\text{N}_2\text{O}_2\text{P}_3\text{Ru}$, Calcd: C, 67.70; H, 5.79; N, 2.92. Found: C, 67.27; H, 5.98; N, 2.76.

RuH₂(PPh₃)₄(HN=CH-CH=NH) (6). Complex **1b** (100 mg, 0.14 mmol), KO^tBu (31 mg, 0.28 mmol), and acetophenone (18 mg, 0.15 mmol) were mixed, 1 mL of THF was added, and the resulting mixture was stirred for 4 h under N_2 , giving a red-brown suspension that was filtered to leave a white solid (KCl) and a dark red-brown filtrate. About 10 mL of hexanes was added to the filtrate, and the mixture was stirred for 1 h to produce a yellow-brown suspension. A yellow solid was collected by filtration and dried in vacuo (32%). Recrystallization from THF/hexanes did not result in the separation of **6** from the other species present. A recrystallization from benzene/hexanes gave crystals of **6** in one instance. **6**: ^1H NMR (C_6D_6 , δ): 6.9 – 7.8 (m, Ar), 5.10 ppm (d, $J = 6\text{ Hz}$, $\text{CH}=\text{NH}$), -7.15 ppm (t, $^2J_{\text{HP}} 23\text{ Hz}$, RuH), -19.85 ppm (t, $J 30\text{ Hz}$, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): 70.0 (s), 70.5 ppm (s). Other species: ^1H NMR (C_6D_6 , δ): 5.35 (d, $J = 6\text{ Hz}$, $\text{CH}=\text{NH}$), -9.55 (m, RuH), -13.30 (t, $J = 32\text{ Hz}$, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): 67.0 ppm (s).

Kinetic Measurements. (a) General. Kinetic runs were carried out at constant pressures of H_2 using a 50-mL Parr hydrogenator reactor. A constant temperature ($20\text{ }^{\circ}\text{C}$) was maintained by use of a Fisher Scientific Isotemp 1016D water bath. All solutions were handled under an Ar or N_2 atmosphere in a glovebox. It is important that the glovebox is free of traces of vapors such as CH_2Cl_2 and HCl that react with the dilute solutions of the dihydrides. The benzophenone should be deoxygenated and distilled before use and the solvent dried, distilled, and deoxygenated carefully. For runs in benzene, standard solutions of acetophenone (0.083 M), **3a** (0.0055 M), and **1a** (0.0026 M) were prepared by dissolving the required amounts of acetophenone and ruthenium complexes in 10 mL (for ketone) or 5 mL (for catalyst precursors) of C_6H_6 . In parallel, a solution of **3a** in C_6D_6 was prepared to determine by use of NMR the *c,c*-**3a**(active)/*c,t*-**3a**(inactive) ratio at the time of the addition of the solution of **3a** to the reactor. For runs in 2-propanol, standard solutions of acetophenone (0.083 M) and **3a** (0.0013 M) were prepared by dissolving the required amounts in 10 mL of 2-propanol. These standard solutions were further diluted to the required concentrations. In all of the runs (except for the run described in section f), the solution of the ketone, followed by the solution of a ruthenium complex, was injected into the already-thermostated reactor under the required H_2 pressure to give a final working volume of 5 mL. The reaction time was measured from the time of the injection of the precatalyst solution. Anisole (phenylmethyl ether) was added as internal standard when needed (see below). In the cases when base was needed, a suspension of potassium *t*-butoxide (10 mg, 0.089 mmol) was added. Solutions containing **3a** were always prepared and handled last to keep the time from making the stock solution to injection at

(56) The assignment of the major isomer to the Λ configuration is not certain.

approximately 10 min and hence to ensure a known ratio of isomers in the precatalyst. The largest errors in the kinetic study are the approximately 5% error in the estimate of the percentage of the isomer *c,c*-**3a** and 5% error in the determination of the initial rates.

(b) Sampling and Sample Analysis. In all of the kinetic runs, sampling was done at regular time intervals of 5 min for a total reaction time of 25 min. The samples were withdrawn from the reactor with a syringe against a flow of hydrogen. The pressure in the reactor dropped to nearly atmospheric during the sampling time of about 10 s. These samples were analyzed for conversion and ee using a Perkin-Elmer Autosystem XL gas chromatograph with Chrompack capillary column ChirasilDex CB 25 m \times 0.25 mm). The carrier gas was H₂ at column pressure of 5 psi, with an oven temperature of 130 °C, injector temperature of 250 °C, and FID temperature of 275 °C. The retention times were: anisole 3.0 min, acetophenone 5.0 min, (*R*)-1-phenylethanol 8.5 min and (*S*)-1-phenylethanol 9.1 min. The injected sample volume was 1 μ L.

(c) Effect of Added PPh₃. The hydrogenation of a solution containing acetophenone (0.0167 M) and **3a** (2.2×10^{-4} M) in benzene was conducted for 10 min, and during this time, two samples were withdrawn to establish a baseline rate. Then a benzene solution (0.2 mL) containing PPh₃ (14 mg, 0.053 mmol) was injected, giving the final PPh₃ concentration of 0.01 M in the reaction mixture. After the addition of PPh₃ solution, sampling was continued as described in section b.

(d) Effect of Added 1-Phenylethanol. A standard solution of *rac*-1-phenylethanol (0.5 M) in C₆H₆ (5 mL) was prepared under Ar. After a baseline rate was verified by withdrawing one sample at 5 min, 0.3 mL of alcohol stock solution was injected into the reactor to give the starting alcohol concentration of 0.03 M. Other reaction conditions: [**3a**] = 2.2×10^{-4} M, [acetophenone] = 0.0167 M, [anisole internal standard] = 0.0167 M, H₂ pressure 5 atm, temperature 273 K.

(e) Kinetics with RuHCl(PPh₃)₂((*R,R*)-dach) as Catalyst Precursor. For this run, a suspension of potassium *t*-butoxide (10 mg, 0.089 mmol) in C₆H₆ (0.2 mL) was added after the solution of **1a** was injected into the reactor, giving the final concentration of base of 0.011 M. Timing was started after the base was added. Reaction conditions: [**1a**] = 2.1×10^{-4} and 1.0×10^{-4} M, [acetophenone] = 0.0167 M, H₂ pressure 5 atm, temperature, 273 K.

(f) Activation of *c,t*-3a** by Reaction with *rac*-MeHC(OH)Ph.** A solution (4 mL) containing *c,t*-**3a** and *rac*-MeHC(OH)Ph in benzene was stirred under 5 atm H₂ at 20 °C. After 15 min, a solution containing anisole and acetophenone was injected, giving a total volume of the reaction mixture of 5 mL and the following concentrations: [*c,t*-**3a**] = 0.0011 M, [*rac*-MeCH(OH)Ph] = 0.05 M, [acetophenone] = 0.167 M, and [anisole] = 0.17 M. The reaction time was measured from the addition of the ketone. Samples were taken as described above.

(g) Numerical Analysis. The differential equations were approximated and integrated using dynamic models on a spreadsheet.⁵⁷

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Supporting Information Available: Further details of the synthetic and kinetic studies (PDF). Crystallographic data in electronic form (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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