Application of [Ru((*R*)-BINAP)(MeCN)(1-3:5,6-η-C_8H_{11})](BF_4) as a catalyst precursor for enantioselective hydrogenations

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Abstract: A catalyst system employing [Ru((*R*)-BINAP)(MeCN)(1-3:5,6-η-C_8H_{11})](BF_4) as catalyst precursor was evaluated using the enantioselective hydrogenations of tiglic acid, α-acetamidocinnamic acid, itaconic acid, methyl tiglate, dimethyl itaconate, geraniol, ethyl acetoacetate, and dimethyl oxaloacetate as a series of typical substrates. Acetone and MeOH were used as model aprotic and protic solvents, respectively. The hydrogenation of substrates containing an α,β-unsaturated carboxylic acid functionality required stoichiometric quantities of NEt_3 to occur at reasonable rates in acetone solution, while in MeOH solution it did not. The enantioselectivities were typically higher in acetone than in MeOH. This catalyst system is among the more enantioselective ruthenium–BINAP type systems reported for the catalytic hydrogenation of substrates containing an α,β-unsaturated acid or ester functionality. The enantioselectivities for the hydrogenation of ketones ranged from poor (15%) to moderate (74%). 1,4-Dicarboxylate substrates with the prochiral olefin or ketone at the 2-position were all hydrogenated in good to high ee with the same enantioface selectivity both with our system and other catalysts reported in the literature. This raised the possibility that these substrates were hydrogenated through intermediates with similar structural features.

Key words: ruthenium, BINAP, enantioselective, hydrogenation, catalysis.

Résumé : Utilisant les hydrogénations énantiosélectives des acides tiglique, α-acétamidocinnamique et itaconique, du tiglate de méthyle, de l'itaconate de diméthyle, du géraniol, de l'acétoacétate d'éthyle et de l'oxaloacétate de diméthyle comme substrats typiques, on a évalué un système de catalyseur faisant appel au [Ru((*R*)-BINAP)(MeCN)(1,3,5,6-η-C_8H_{11})](BF_4) comme précurseur du catalyseur. On a utilisé l'acétone et le méthanol comme modèles de solvant respectivement aprotique et protique. Les énantiosélectivités sont généralement plus élevées dans l'acétone que dans le méthanol. Pour réaliser l'hydrogénation d'acides carboxyliques insaturés à une vitesse raisonnable dans l'acétone, il est nécessaire d'utiliser des quantités stoechiométriques de triéthylamine; ce n'est pas le cas dans le méthanol. Pour l'hydrogénation catalytique d'acides et d'esters α,β-insaturés, ce système de catalyseur se trouve parmi les systèmes de type ruthénium–BINAP les plus énantiosélectifs. Les énantiosélectivités pour l'hydrogénation des cétones vont de mauvaises (15%) à modérées (74%). Avec les substrats portant des 1,4-dicarboxylates et une oléfine ou une cétone prochirale en position 2, les hydrogénations conduisent à des ee allant de bons à élevés; notre système et les autres catalyseurs proposés antérieurement dans la littérature ont les mêmes sélectivités et ceci suggère que les hydrogénations de ces substrats se produisent par des intermédiaires possédant des caractéristiques structurales semblables.

Mots clés : ruthénium, BINAP, énantiosélectif, hydrogénation, catalyse.

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Introduction

Asymmetric catalysis by chiral transition metal complexes is among the most successful methods to synthesize optically active organic compounds. Of the hundreds of chiral ligands reported, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) is one of the most successful (for recent reviews on the use of BINAP in enantioselective catalysis, see ref. 1). While rhodium–BINAP systems are highly enantioselective catalysts for the hydrogenation of certain prochiral olefins (2), ruthenium–BINAP systems hydrogenate a much wider range of prochiral olefins and ketones with high enantioselectivities (3; for earlier references see 1*d*, *f*, and refs. cited therein).

We previously reported the synthesis of [Ru((*R*)-BINAP)(MeCN)(1-3:5,6-η-C_8H_{11})](BF_4) (**I**) and its use as a catalyst precursor for several catalytic processes (4). Compound **I** reacts with H_2 in acetone, THF, or MeOH solution to generate [Ru((*R*)-BINAP)(H)$(MeCN)_n(Sol)_{3-n}$](BF_4) (**II,** Sol = acetone, THF, or MeOH; n = 0–3), which we believe is the active catalyst for the described reactions.

The catalyst system **II** is distinguished from other ruthenium–BINAP catalysts by the combination of the following three features. First, it is reasonably well-defined. Second, the active catalyst is generated in high concentrations under

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mild conditions. In acetone, THF, or MeOH solution, the catalyst precursor **I** reacts under 1–2 atm of H_2 at room temperature to generate complex **II** in minutes. Third, the system has at least two readily available coordination sites (occupied by labile solvento ligands) to allow easy access by substrate molecules to the ruthenium centre. This feature is essential for the study of substrate–catalyst interactions.

We now report the use of **II** as a catalyst system for the enantioselective catalytic hydrogenation of a representative series of prochiral substrates. This work will define the utility of **II** as a catalyst system relative to the other ruthenium–BINAP catalyst systems reported in the literature, and it will explore any possible general trends in enantioselectivity by such catalysts. It is only through such trends that the general components of enantioselectivity (if they exist) by ruthenium–BINAP catalysts can be established.

Results and discussion

The nature of II

The MeCN ligand is rapidly exchanged between all the available vacant coordination sites in acetone solutions of **II** at room temperature. This exchange halts upon cooling to –80°C to give a static mixture of eight hydrides ranging from [Ru((*R*)-BINAP)(H)(acetone)$_3$](BF$_4$) to [Ru((*R*)-BINAP)(H)-(MeCN)$_3$](BF$_4$). These compounds all contain the hydride ligand in a coordination site *cis* to both phosphorus centres. This mutually *cis* disposition of the coordinated hydride and phosphorus centres presumably results from the high *trans influence* commonly observed for both of these types of ligands (5). In THF solution, the system exists mainly (~85%) as one diastereomer of the mono-MeCN complex [Ru((*R*)-(BINAP)(H)(MeCN)(THF)$_2$](BF$_4$). In MeCN solution, it exists solely as [Ru((*R*)-(BINAP)(H)(MeCN)$_3$](BF$_4$). To a first approximation, the system can be regarded as a source of the catalyst fragment "[Ru((*R*)-(BINAP)(H)]$^+$." For example, the solvento and MeCN ligands can all be displaced by arene donors to generate the corresponding [Ru((*R*)-(BINAP)(H)(η^6-arene)](BF$_4$) complexes (6).

Hydrogenations using II as catalyst

Figure 1 shows the representative substrates we hydrogenated using **I** as the catalyst precursor. Figure 1 also shows the major enantiomer of the hydrogenation products. Tables 1, 2, and 4 summarize our results.

Substrates containing an α,β-unsaturated acid or ester functionality

Hydrogenations were performed in MeOH as a model protic solvent. The hydrogenation of tiglic acid (**1a**) (Table 1, entry 1) was quantitative under mild conditions, giving 2-methylbutyric acid (**1c**) in high ee (90% (*R*)). The ee decreased to 72% (*R*) when the initial pressure of H_2 was increased from 3 to 55 atm (Table 1, entry 2). Attempts to hydrogenate methyl tiglate (**1b**) were unsuccessful under 3 atm of H_2 (Table 1, entry 3). This difference in reactivity between tiglic acid and methyl tiglate has been previously reported for another ruthenium–BINAP catalyst system (7).

We previously reported (4) that hydrogenation of (*Z*)-methyl α-acetamidocinnamate (MAC, **2b**) to *N*-acetylphenylalanine methyl ester (**2d**) in MeOH goes to completion in high ee (86% (*R*)) under mild conditions. This result is included for comparative purposes (Table 1, entry 6). Surprisingly, hydrogenation of the corresponding acid (α-acetamidocinnamic acid (**2a**)) under similar conditions proceeds much more slowly, with only 10% conversion after 94 h (Table 1, entry 4). To obtain complete conversion it was necessary to increase the pressure of H_2 to 100 atm, resulting in 46% ee (*R*) (Table 1, entry 5).

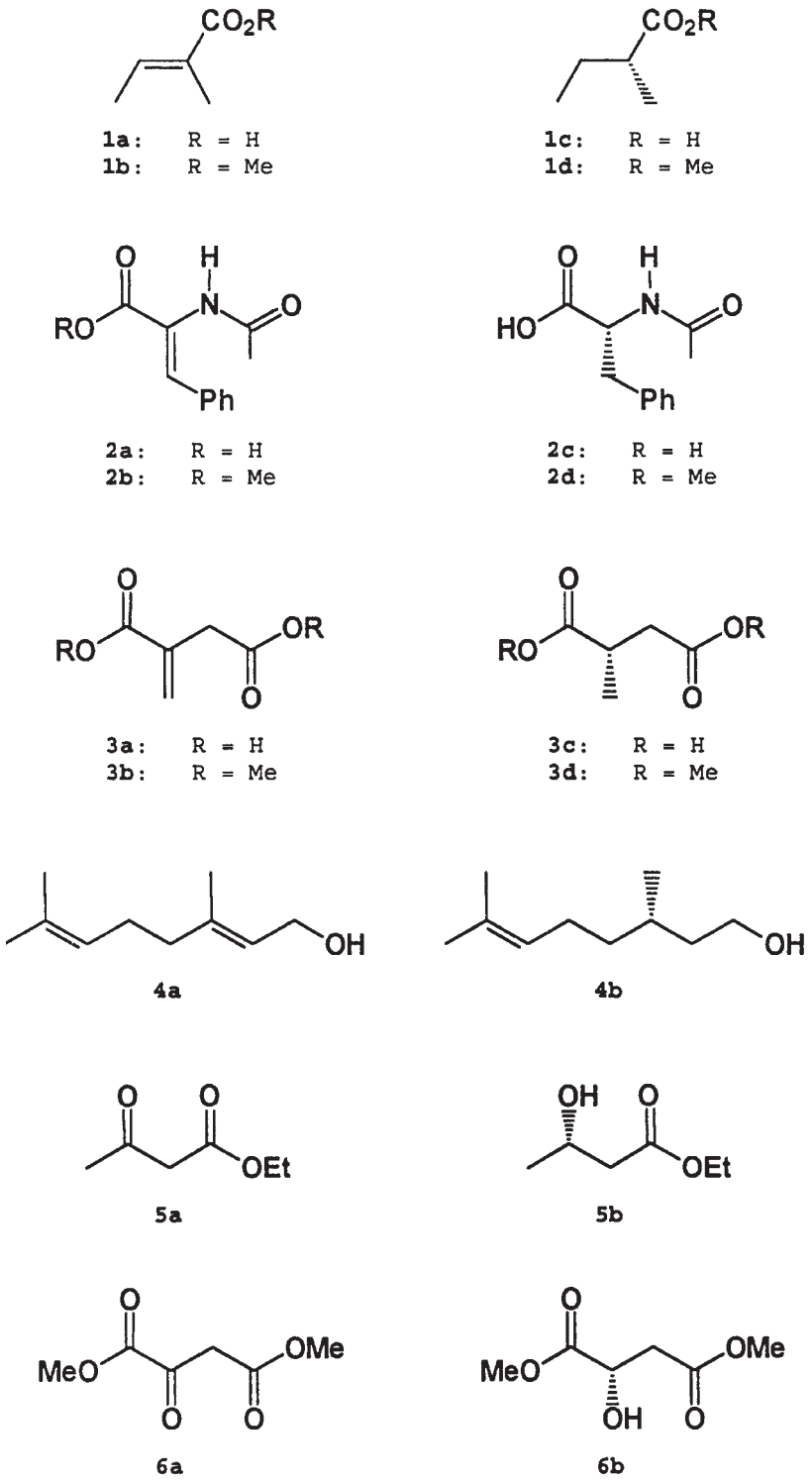
The hydrogenation of itaconic acid (**3a**) (Table 1, entry 7) proceeded smoothly under mild conditions giving methylsuccinic acid (**3c**) in 90% ee (*S*). The corresponding hydrogenation of dimethyl itaconate (**3b**) (Table 1, entry 8) under similar conditions was more successful, yielding dimethyl methylsuccinate (**3d**) in 95% ee (*S*). We note that the net enantioface selection by the catalyst for substrates **3a** and **3b** is the same as that for the structurally related substrates **2a** and **2b**.

To investigate the use of an aprotic solvent, the hydrogenations were carried out in acetone. The results of these reactions are reported in Table 2. As we previously reported (8), the hydrogenation of **2b** proceeds smoothly under mild conditions to give **2d** in higher ee (92% (*R*)) than does the hydrogenation in MeOH (86% (*R*)). This result is included for comparative purposes (Table 2, entry 6). The hydrogenation of **3b** also proceeded under mild conditions in acetone (Table 2, entry 10) to yield **3d** in similar ee to that obtained from the hydrogenation in MeOH (95% ee (*S*)). As was the case in MeOH, **1b** did not undergo hydrogenation in acetone (Table 2, entry 3). The hydrogenations of **1a**, **2a**, and **3a** were extremely slow under these conditions (4 atm H_2, 25°C, acetone), giving low to moderate conversions ranging from <10% to ~55% (Table 2, entries 1, 4, and 7, respectively). Even at 50°C and 4 atm of H_2 the hydrogenation of **3a** proceeded to a maximum of ~65% conversion (Table 2, entry 8). It is well known that addition of an equivalent of base (e.g., amines) for every acid unit in the substrate often (but not always) yields higher ee and rates for the hydrogenation of acid substrates using both ruthenium and rhodium catalyst systems (9). We examined this effect on the hydrogenations of the acids (**1a**, **2a**, and **3a**) in acetone. The hydrogenations of **1a** and **3a** (Table 2, entries 2 and 9, respectively) proceeded to completion under mild conditions in the presence of 1 equiv. of NEt_3 per acid group. Further, the ee improved from 90% (*R*) for **1a** and 90% (*S*) for **3a** in the absence of added base in MeOH to 95% ee (*R*) and 95% ee (*S*) with added base in acetone. The addition of 1 equiv. of NEt_3 did not enhance the rate of hydrogenation of **2a** (Table 2, entry 5).

Table 3 compares our results to the best results reported in the literature for other ruthenium–BINAP systems we are aware of. Apart from the hydrogenation of **2b**,[2] all the literature examples reported in Table 3 were performed in pure alcohol or binary alcohol–solvent solutions (solvent = THF or CH_2Cl_2), under mild temperatures (20–50°C), and under low to moderate pressures of H_2 (1–5 atm). The results obtained

[2] This is the only literature example we are aware of where **2b** is hydrogenated using a ruthenium–BINAP catalyst.

Fig. 1. Representative substrates and their respective hydrogenation products (major enantiomers shown) investigated using **I** as hydrogenation catalyst precursor.



with complex **I** as the catalyst precursor show it to be among the better ruthenium–BINAP systems examined to date for the hydrogenation of these substrates.

Inspection of Table 3 shows no real trends in the absolute configuration of the major enantiomer produced by hydrogenation of tiglic acid (**1a**) using ruthenium–BINAP catalyst systems. That methyl tiglate (**1b**) does not undergo hydrogenation but tiglic acid does suggests that substrates with one ester group that are not easily supported by chelation upon coordination to ruthenium will not undergo hydrogenation. Indeed, we observed no evidence of interaction between the active catalyst species **II** and an up to 100-fold excess of

Table 1. Hydrogenation of substrates containing an α,β-unsaturated carboxylic acid or ester functionality in MeOH using **I** as catalyst precursor.[a]

Entry	Substrate	H_2 (atm)	Temp. (°C)	Time (h)	% Conv.	% ee
1	**1a**	3	25	9.5	100	90 (*R*)
2	**1a**	55	25	17.5	100	72 (*R*)
3	**1b**	3	25	18	0	—
4	**2a**	4	35	94	10	—
5	**2a**	100	40	20	100	46 (*R*)
6[b]	**2b**	4	30	30	100	86 (*R*)
7	**3a**	4	25	20	100	90 (*S*)
8	**3b**	4	25	19	100	95 (*S*)

[a] Reaction conditions: 1 mol% catalyst, [Ru] = 3.0 mM.
[b] Reaction conditions: 2 mol% catalyst, [Ru] = 2.6 mM (ref. 4).

Table 2. Hydrogenation of substrates containing an α,β-unsaturated carboxylic acid or ester functionality in acetone using **I** as catalyst precursor.[a]

Entry	Substrate	N/S[b]	H_2 (atm)	Temp. (°C)	Time (h)	% Conv.	% ee
1	**1a**	0	4	25	20	<10	—
2	**1a**	1	4	25	18	100	95 (*R*)
3	**1b**	0	4	25	20	0	—
4	**2a**	0	4	25	20.5	<10	—
5	**2a**	1	4	25	20.5	<10	—
6[c]	**2b**	0	4	30	1	100	92 (*R*)
7	**3a**	0	4	25	18.5	~55	—
8	**3a**	0	4	50	18	~65	—
9	**3a**	2	4	25	18	100	95 (*S*)
10	**3b**	0	4	25	20.5	100	95 (*S*)

[a] Reaction conditions: 1 mol% catalyst, [Ru] = 3.0 mM.
[b] *N/S* is defined as moles of NEt_3 added per mole of substrate.
[c] Reaction conditions: 2 mol% catalyst, [Ru] = 2.6 mM (ref. 6).

Table 3. Comparison of Ru((*R*)-BINAP) catalyst systems in the hydrogenation of substrates containing an α,β-unsaturated carboxylic acid or ester functionality.

	Substrates					
Catalyst system	**1a**	**2a**	**2b**	**3a**	**3b**	Reference
$[Ru(BINAP)(C_8H_{11})(MeCN)](BF_4)$	95 (*R*)	46 (*R*)	92 (*R*)	95 (*S*)	95 (*S*)	4, 8
$Ru_2Cl_4(BINAP)_2(NEt_3)$	85 (*S*)	86 (*R*)	—	90 (*S*)	68 (*S*)	10–12
$RuHCl(BINAP)_2$	79 (*R*)	80 (*R*)	—	93 (*S*)	54 (*S*)	9*a*, 11, 12
$[RuH(BINAP)_2](PF_6)$	88 (*R*)	—	—	94 (*S*)	—	9*a*
$RuCl_2(RCN)_2(BINAP)$	84 (*S*)	—	—	89 (*S*)	—	10
$[RuI_2(p\text{-cymene})]_2$ + BINAP	87 (*R*)	—	—	—	—	13
Ru(BINAP)(2-methylallyl)$_2$ + 2 HBr	—	—	85 (*R*)[a]	—	—	14
Ru(BINAP)(2-methylallyl)$_2$	90 (*R*)	—	—	—	—	15
$Ru(BINAP)(OCOCH_3)_2$	94 (*R*)	—	—	—	—	16

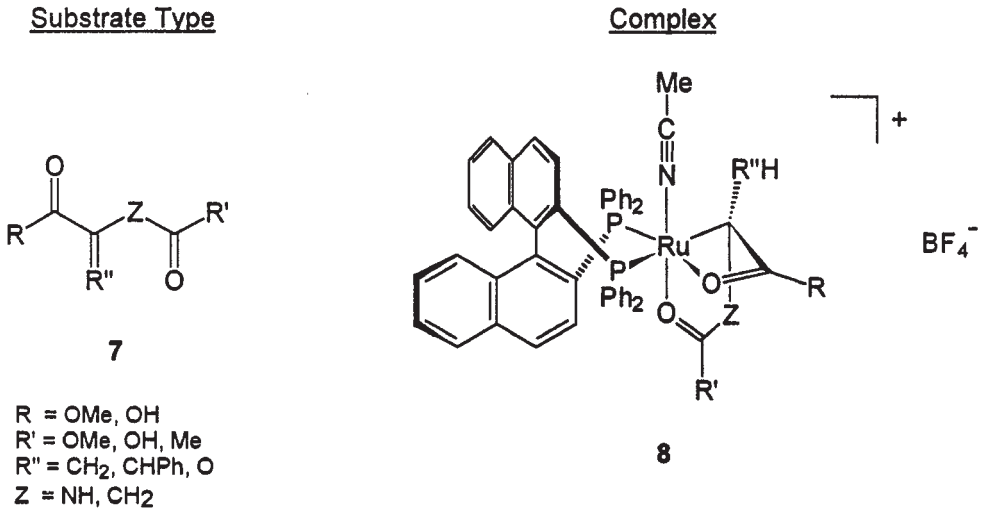
[a] Reaction performed under 100 atm of H_2.

methyl tiglate in acetone solution.[3] The acids and other esters studied in this report all react stoichiometrically (1:1) with **II** to generate a variety of products. The structures of these ruthenium–substrate compounds are under investigation in our laboratories.

Substrates **2a**, **2b**, **3a**, and **3b** are hydrogenated with good to excellent ee and with the same enantioface selectivity. Figure 2 shows that these substrates all contain the same basic framework, a 1,4-dicarbonyl unit with the prochiral functionality at the 2-position (**7**). That hydrogenation of **2a**, **2b**, **3a**, and **3b** all proceed with the same face selectivity for most, if not all reported ruthenium–BINAP systems (Table 3) under similar conditions, raises the possibility that they proceed through structurally related intermediates. Figure 2 illustrates one possible structure type for such a species (**8**). We suggest this structure based on the recently

[3] $[Ru((R)\text{-BINAP})(H)(MeCN)_n(acetone)_{3-n}](BF_4)$ (n = 0–3) was the only species detected by ^{31}P NMR spectroscopy.

Fig. 2. Model for a possible common intermediate structure type.



reported (6) crystallographically characterized compound we isolated from the reaction of MAC (**2b**) with **II** (Fig. 2, **8**, R = OMe, R′ = Me, R′′ = CHPh, Z = NH). If such species form with these and other related substrates, and if these species contribute to the enantioselection by the catalytic hydrogenation must be investigated by experiment.

The role of NEt_3 as promoter for the hydrogenation of tiglic acid and itaconic acid in acetone is unknown. We have found, however, that reaction of tiglic acid with **II** in acetone results in immediate protonolysis of the Ru—H bond to generate a Ru-tiglato complex (eq. [1]). Reaction of Ru—D (formed by deuteration of **I** with D_2) resulted in the formation of the Ru-tiglato complex and concomitant formation of HD. We were unable to identify the absolute configuration of the tiglato complex about the ruthenium centre. We postulate that it is the Δ configuration on the basis of the arguments previously reported for the related complex Ru((*R*)-BINAP)($O_2CCMe{=}CHMe)_2$ (17). Two possible roles of the NEt_3 as promoter for hydrogenations of unsaturated acids may therefore be to enhance the rate of carboxylate exchange on such complexes, or to prevent protonolysis of the Ru—H bond by deprotonating the acid substrate. King and others have reported that NEt_3 decomposes (perhaps via a β-hydride elimination (18)) upon reaction with $[RuCl_2(COD)]_n$ and (*R*)-BINAP, or similar bis(phosphines), from 110 to 140°C to generate $[Et_2NH_2](Ru_2Cl_5((R)\text{-}(BINAP)_2)$ (19). It seems unlikely, however, that such a process occurs under H_2 at 25°C using **II** as catalyst (Table 2, entries 2, 5, and 9). The reasons why NEt_3 is not required to promote these hydrogenations in MeOH is unknown.

Geraniol

We found that the enantioselectivity for the hydrogenation of geraniol (**4a**) using **II** as catalyst was inversely dependent on the pressure of H_2. The sense of the enantioselectivity inverted and its magnitude increased when the pressure of H_2 was increased from 1 atm (Table 4, entries 1–3). The maximum ee, 86% (*S*), was obtained at 100 atm of H_2. Noyori and co-workers (20) reported increases in ee from 70 to 98% (*S*) when the pressure of H_2 was increased from 4 to 100 atm using Ru((*R*)-BINAP)($O_2CMe)_2$ as catalyst precursor. Sowa and co-workers (21) found that the isomerization of geraniol to γ-geraniol occurs at a rate comparable to that of hydrogenation using $[Et_2NH_2](Ru_2Cl_5((S)\text{-Tol-BINAP})_2)$ (Tol-BINAP = (di-*p*-tolylphosphino)-1,1′-binaphthyl) as catalyst precursor. The enantioselectivity for the direct hydrogenation of geraniol was found to be opposite to that for the direct hydrogenation of γ-geraniol, resulting in an inversion of enantioselectivity over the course of the catalytic hydrogenation. Our results indicate that use of **II** as catalyst results in similar behaviour. We report, however, that reaction of **II** with geraniol in the absence of H_2 results in a complex mixture of olefin isomerization products, not just formation of γ-geraniol.

[1]

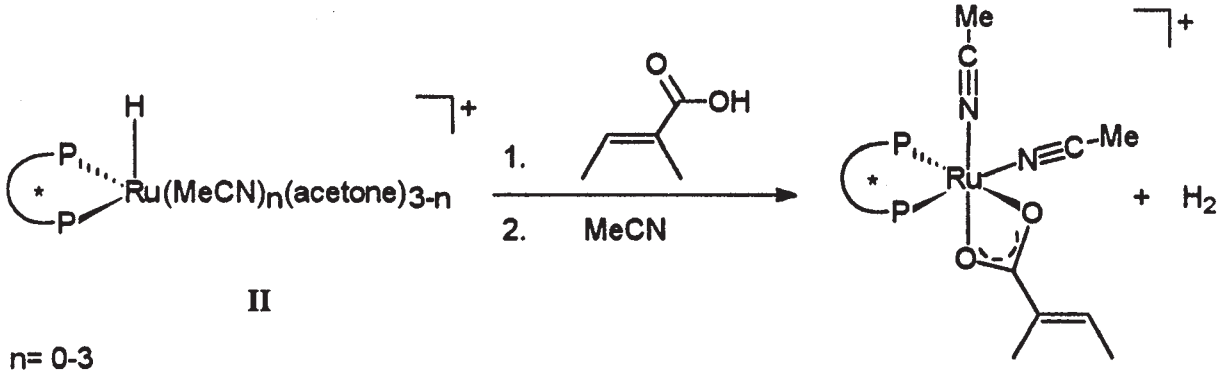


Table 4. Hydrogenation of an allylic alcohol and ketones in MeOH using **I** as catalyst precursor.[a]

Entry	Substrate	H_2 (atm)	Temp. (°C)	Time (h)	% Conv.	% ee
1	**4a**	1	25	5	100	21 (*R*)
2	**4a**	4	25	5	100	70 (*S*)
3	**4a**	100	25	0.25	100	86 (*S*)
4	**5a**	100	50	24	100	15 (*S*)
5[b]	**5a**	100	50	24	100	20 (*R*)
6[c]	**6a**	100	50	28	100	74 (*S*)

[a]Reaction conditions: 1 mol% catalyst, [Ru] = 3.0 mM.
[b]10 equiv. of LiCl added.
[c]Reaction done in acetone.

α- and β-Keto esters

The hydrogenation of ethyl acetoacetate (**5a**) to ethyl 3-hydroxybutyrate (**5b**) (Table 4, entry 4) proceeded in a quantitative fashion, but in low ee (15% (*S*)). Takaya and coworkers (22) reported that addition of 2 equiv. of HX (e.g., X = Cl, Br) to Ru((*R*)-BINAP)$(O_2CMe)_2$ followed by removal of all volatiles in vacuo gave rise to highly efficient catalysts which hydrogenate various β-keto esters with greater than 98% ee. The addition of 10 equiv. of LiCl to **I** (Table 4, entry 5) increased the ee, but only to 20% and in the opposite absolute configuration (*R*). The role of LiCl is unclear but the enantioselectivity of complex **II** remains poor compared to other reported ruthenium–BINAP systems which often yield enantiomeric excesses greater than 95% for the hydrogenation of such substrates (23).

Examining the structural framework of the model substrates for our catalyst system (Fig. 2, **7**) led to our use of dimethyl oxaloacetate (**6a**). Dimethyl oxaloacetate has similar structural characteristics to dimethyl itaconate (**3b**) where the olefinic bond is replaced by a carbonyl functionality. The hydrogenation of **6a** proceeded to completion (100 atm H_2, 50°C, acetone, Table 4, entry 6) yielding dimethyl hydroxysuccinate (**6b**) in 74% ee (*S*). Although the ee is moderate, it is a substantial increase from the hydrogenation of ethyl acetoacetate. Further, the hydrogenation product (**6b**) resulted from the same enantioface selection as those for the hydrogenations of **2b** and **3b**. These findings support the possibility that substrates with similar structural features proceed through structurally related intermediates (Fig. 2).

Conclusions

Complex **II** is among the more effective ruthenium–BINAP catalysts reported for the asymmetric hydrogenation of substrates containing an α,β-unsaturated carboxylic acid or ester functionality. Its success in the asymmetric reduction of ketones is only moderate. Prochiral substrates with the general structure **7** shown in Fig. 2 are hydrogenated with the same enantioface selection. Extrapolations of these results from mechanistic investigations of one combination of substrate, catalyst, and reaction conditions are precarious in their nature because of the large number of variables involved in such reactions. That substrates of the general structure **7** are hydrogenated with the same enantioface selection raises the possibility that a general trend may exist in these catalyst systems. Further investigations into the true significance of this apparent general trend in enantioselection by ruthenium–BINAP catalysts are underway in our laboratories.

Experimental

Materials and methods

All operations were performed under an Ar atmosphere using standard Schlenk techniques. The solvents were dried and distilled under an Ar atmosphere before use by standard methods (24). The Ar (Praxair, 99.998%) was passed through a drying train containing 3 Å molecular sieves and P_4O_{10} before use. Trace quantities of oxygen were removed from the H_2 (Praxair, 99.99%) by passage through an Alltech Oxy-Trap. All commercial reagents (Aldrich or Fluka) were recrystallized or distilled under an Ar atmosphere before use. [Ru((*R*)-BINAP)-(MeCN)(1-3:5,6-η-C_8H_{11})](BF_4) (4), (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetylchloride (25), [Rh(η^4-norbornadiene)(DIPHOS)](ClO_4) (26), and dimethyl oxaloacetate (27) were prepared using established procedures.

Unless stated otherwise, all ^1H, ^{13}C, and ^{31}P NMR spectra were measured with a Bruker AM-400 spectrometer operating at 400.1 MHz, 100.6 MHz, and 161.9 MHz, respectively. ^1H and ^{13}C NMR chemical shifts are reported in ppm (δ) relative to TMS, using the solvent as an internal reference. ^{31}P NMR chemical shifts are reported in ppm (δ) relative to an 85% H_3PO_4 external reference. Mass spectra were measured using a Kratos MS50 spectrometer. Microanalyses were performed at the University of Alberta Microanalysis Laboratory. Optical rotations were measured with a Perkin–Elmer 241 polarimeter at 589 nm using 1.0 dm cells. Specific rotations, $[\alpha]_D$, are reported in degrees per decimeter at 25°C, and the concentration (*c*) is given in grams per 100 mL.

Hydrogenation procedure

A glass pressure reactor (Lab Glass) was employed for hydrogenation reactions where the pressure of H_2 was ≤ 4 atm. For reactions requiring elevated pressures, a Parr cell-disruption bomb was used. A typical hydrogenation procedure is described below.

Under an Ar atmosphere, the catalyst precursor (**I**) (0.010 mmol), substrate (1.0 mmol), and NEt_3 (1 equiv. per acid unit as required, Table 2), were introduced into the reactor. The dry, deoxygenated solvent (MeOH or acetone) was then added (3.8 mL), and the solution was stirred for 5 min. The atmosphere was then replaced by H_2, and the solution was allowed to react under the prescribed conditions (Tables 1, 2, and 4). On completion of the reaction, the sol-

vent was removed under reduced pressure, and the products were worked up as detailed below. Complete conversion and identification of the products were confirmed by CIMS and (or) ^{1}H NMR analyses.

*Tiglic acid (**1a**)*

The product residue from the hydrogenation in MeOH was dissolved in CH_2Cl_2 and passed through a Florisil plug to remove the catalyst. The solvent was then removed under reduced pressure, and the residue was converted to the corresponding diastereomeric amides of (*S*)-(–)-α-methylbenzylamine (28). The ee and absolute configuration were determined by comparison of the ^{1}H NMR spectrum of the derivatized residue to that of the corresponding amide derivatives prepared from (±)-2-methylbutyric acid and authentic (*S*)-(+)-2-methylbutyric acid, respectively.

To the acetone–NEt_3 product residue was added 10% aq. HCl (10 mL). The solution was filtered, and the filtrate extracted with Et_2O (5 × 40 mL). The combined organic layers were washed with 5% aq. HCl (3 × 8 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give 2-methylbutyric acid. The ee and absolute configuration were then determined as described above. NMR data for the (*S*, *S*) diastereomer: ^{1}H (400.1 MHz, $CDCl_3$), δ: 0.84 (t, *J* = 7.4 Hz, 3H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.39 (m, 1H), 1.46 (d, *J* = 6.9 Hz, 3H), 1.64 (m, 1H), 2.10 (apparent sextet, *J* = 6.9 Hz, 1H), 5.14 (apparent quintet, *J* = 7.2 Hz, 1H), 5.89 (br s, 1H), 7.15–7.40 (aromatic, 5H); NMR data for (*R*, *S*) diastereomer: ^{1}H (400.1 MHz, $CDCl_3$), δ: 0.92 (t, *J* = 7.4 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 1.38 (m, 1H, overlapped with (*S*, *S*) diastereomer), 1.47 (d, *J* = 6.9 Hz, 3H), 1.64 (m, 1H, overlapped with (*S*, *S*) diastereomer), 2.09 (apparent sextet, *J* = 6.9 Hz, 1H, overlapped with (*S*, *S*) diastereomer), 5.13 (apparent quintet, *J* = 7.2 Hz, 1H, overlapped with (*S*, *S*) diastereomer), 5.89 (br s, 1H, overlapped with (*S*, *S*) diastereomer), 7.15–7.40 (m, 5H, aromatic, overlapped with (*S*, *S*) diastereomer).

*α-Acetamidocinnamic acid (**2a**)*

The product residue was converted to the corresponding diastereomeric amides of (*S*)-(–)-α-methylbenzylamine (28). The absolute configuration of the product was determined by comparison of its optical rotation to that of the reported optical rotation of (*R*)-(–)-*N*-acetylphenylalanine (**2b**) ($[\alpha]^{27}_D$ = –40.3°, *c* = 1.0, MeOH) (29). The ee was determined by ^{1}H NMR analysis (400 MHz, $CDCl_3$) of the resulting diastereomeric amides.[4] NMR data of the diastereomeric amides: ^{1}H (400.1 MHz, $CDCl_3$), δ: 1.21 (d, *J* = 7.0 Hz, 3H; (*R*, *R*) diastereomer), 1.40 (d, *J* = 7.0 Hz, 3H; (*R*, *S*) diastereomer), 1.88 (s, 3H; (*R*, *R*) diastereomer), 1.95 (s, 3H; (*R*, *S*) diastereomer), 2.92 (m, 2H; (*R*, *S*) diastereomer), 2.97 (dd, *J* = 13.4, 8.8 Hz, 1H; (*R*, *R*) diastereomer), 3.10 (dd, *J* = 13.4, 6.1 Hz, 1H; (*R*, *R*) diastereomer), 4.70 (m, 2H), 4.91 (apparent quintet, *J* = 7.0 Hz, 1H; (*R*, *R*) diastereomer), 4.97 (apparent quintet, *J* = 7.0 Hz, 1H; (*R*, *S*) diastereomer), 6.49 (d, *J* = 7.7 Hz, 1H), 6.72 (m, 3H), 7.00–7.45 (m, 20H). N*H* signals not observed.

*Itaconic acid (**3a**)*

The product residue was converted directly to the dimethyl ester with CH_2N_2 (30), whereas the acetone–NEt_3 product was first worked up in a manner similar to that described for tiglic acid (**2a**), and then treated with CH_2N_2. The product was then dissolved in CH_2Cl_2 and passed through a Florisil plug to remove the catalyst. The solvent was removed under reduced pressure to yield dimethyl methylsuccinate. The ee and absolute configuration were then determined as described in the dimethyl itaconate (**3b**) hydrogenation work-up.

*Dimethyl itaconate (**3b**)*

The products of the MeOH and acetone reactions were treated in a similar manner. The product residue was dissolved in CH_2Cl_2 and passed through a Florisil plug to remove the catalyst. The solvent was removed under reduced pressure, yielding dimethyl methylsuccinate. The ee was spectroscopically determined (^{1}H NMR, CD_2Cl_2) upon addition of chiral lanthanide shift reagent ((+)-Eu(tfc)$_3$))[5] (31). The absolute configuration of the product was determined by comparison of its optical rotation to that of authentic (*R*)-dimethyl methylsuccinate ($[\alpha]^{25}_D$ = +4.8°, *c* = 4.0, $CHCl_3$).

*Geraniol (**4a**)*

The product residue was purified by flash distillation and reacted with (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetylchloride (25). The ee was determined by ^{1}H NMR spectroscopy of the diastereomeric esters.[6] The absolute configuration of the product was determined by comparison of its rotation with the reported optical rotation of (*R*)-citronellol ($[\alpha]^{25}_D$ = +5.12°, *c* = 21.0, $CHCl_3$) (32). NMR data for the diastereomeric esters: ^{1}H (400.1 MHz, $CDCl_3$), δ: 0.90 (d, *J* = 6.3 Hz, 3H; (*R*, *S*) diastereomer), 0.91 (d, *J* = 6.3 Hz, 3H; (*R*, *R*) diastereomer), 1.19 (m, 2H), 1.33 (m, 2H), 1.51 (m, 4H), 1.59 (s, 6H), 1.68 (s, 6H), 1.74 (m, 2H), 1.95 (m, 4H), 3.50 (br s, 3H; (*R*, *S*) diastereomer), 3.56 (br s, 3H; (*R*, *R*) diastereomer), 4.37 (m, 4H), 5.06 (m, 2H), 7.35–7.70 (m, 10H, aromatic). ^{1}H NMR signals for individual diastereomers were assigned when overlap did not occur.

*Ethyl acetoacetate (**5a**)*

The product residue was purified by flash distillation and reacted with (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetylchloride (25). The ee and absolute configuration were determined by comparison of the ^{1}H NMR of the derivatized residue to that of the diastereomeric Mosher's esters of (±)-3-hydroxybutyrate and authentic ethyl (*R*)-(–)-3-hydroxybutyrate, respectively. NMR data for the diastereomeric esters: ^{1}H NMR (400.1 MHz, $CDCl_3$): (*R*, *R*) diastereomer, δ: 1.23 (t, *J* = 7.1 Hz, 3H), 1.34 (d, *J* = 6.3 Hz, 3H), 2.57 (dd, *J* = 16.0, 4.7 Hz, 1H), 2.72 (dd, *J* = 16.0,

[4] The ratio of the acyl peaks at δ = 1.94 (s, CH_3, *S*) and δ = 1.78 (s, CH_3, *R*) were used to determine the ee. The ratio of these peaks was 1:1 for racemic *N*-acetyl phenylalanine.

[5] The ratio of the methoxy signals (ca. 4 ppm) were used to determine the ee. The ratio of these peaks was 1:1 for racemic dimethyl methylsuccinate.

[6] The ratio of the methyl peaks at δ = 0.91 (d, *J* = 6.4 Hz, CH_3, *R*) and δ = 0.90 (d, *J* = 6.4 Hz, CH_3, *S*) were used to determine the ee. The ratio of these peaks was 1:1 for racemic β-citronellol.

8.5 Hz, 1H), 3.49 (br s, 3H), 4.13 (qd, J = 7.1, 1.3 Hz, 2H), 5.57 (m, 1H), 7.3–7.7 (m, 5H, aromatic); (*R*, *S*) diastereomer, δ: 1.19 (t, J = 7.1 Hz, 3H), 1.43 (d, J = 6.3 Hz, 3H), 2.53 (dd, J = 16.0, 5.0 Hz, 1H), 2.68 (dd, J = 16.0, 8.3 Hz, 1H), 3.55 (br s, 3H), 4.06 (q, J = 7.1 Hz, 2H), 5.57 (m, 1H), 7.3–7.7 (m, 5H, aromatic).

*Dimethyl oxaloacetate (**6a**)*

The product residue was dissolved in CH_2Cl_2 and passed through a Florisil plug to remove the catalyst. The solvent was removed under reduced pressure, and the residue was reacted with (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetylchloride (25). The ee was determined by comparison of the ^{1}H NMR spectrum of the derivatized residue to that of the Mosher's esters of (±)-dimethyl hydroxysuccinate (see achiral hydrogenation for NMR data). The absolute configuration was determined by comparison with the optical rotation of authentic (*S*)-(–)-dimethyl hydroxysuccinate ($[\alpha]^{25}_D$ = –8.85°, c = 5.2, MeOH).

Achiral hydrogenation of dimethyl oxaloacetate

A stainless-steel autoclave was charged with [Rh(η^4-norbornadiene)(DIPHOS)](ClO_4) (6.9 mg, 0.01 mmol), dimethyl oxaloacetate (160.0 mg, 1.0 mmol), and acetone (3.8 mL). The solution was stirred for 5 min, and the atmosphere was then replaced with H_2. The solution was allowed to react for 75 h at 50°C and 100 atm H_2. The product was worked up as described for the hydrogenation of dimethyl oxaloacetate with **I** as catalyst precursor and reacted with (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetylchloride (25). NMR spectroscopic data: ^{1}H (300.1 MHz, $CDCl_3$): (*R*, *R*) diastereomer, δ: 2.88 (dd, J = 16.7, 8.4 Hz, 1H), 2.96 (dd, J = 16.7, 5.0 Hz, 1H), 3.60 (s, 3H), 3.63 (br s, 3H), 3.81 (s, 3H), 5.72 (dd, J = 8.4, 5.0 Hz, 1H), 7.42 (m, 3H), 7.60 (m, 2H); (*R*, *S*) diastereomer, δ: 2.92 (dd, J = 16.9, 8.9 Hz, 1H), 3.02 (dd, J = 16.9, 4.0 Hz, 1H), 3.55 (br s, 3H), 3.70 (s, 3H), 3.76 (s, 3H), 5.71 (dd, J = 8.9, 4.0 Hz, 1H), 7.42 (m, 3H), 7.60 (m, 2H).

Hydrogenation of [Ru((*R*)-BINAP)(1-3:5,6-η-C_8H_{11})(MeCN)](BF_4) (I) in acetone-d_6

Compound **I** (19.5 mg, 2.03×10^{-5} mol) was partially dissolved in acetone-d_6 (0.6 mL) in an NMR tube under an Ar atmosphere. At room temperature, the tube was flushed with H_2, pressurized (1–2 atm), and shaken until a deep orange–yellow solution was generated (~5 min). The H_2 atmosphere was replaced by Ar, and the resulting solution was analyzed by ^{1}H and ^{31}P NMR spectroscopy at –80°C. NMR spectroscopic analysis indicated a mixture of eight ruthenium-hydrido species ([Ru((*R*)-BINAP)(H)$(MeCN)_n((CD_3)_2CO)_{3-n}$]($BF_4$), where n = 0–3) and cyclooctane were present. At –80°C, D_2 (5.0 mL) was injected into the headspace of the tube. The tube was removed from the cooling bath, shaken for ~15 s, and then immediately placed in a precooled (–80°C) NMR probe. The ^{31}P NMR spectrum at –80°C remained unchanged, while the ^{1}H NMR spectrum indicated that exchange of all ruthenium-hydrido species with D_2 (to form ruthenium-deutero species) had occurred with concomitant formation of HD. NMR spectroscopic data of the hydrides (A-H): ^{1}H (400.1 MHz, $(CD_3)_2CO$, –80°C), δ: –19.87 (br, A), –19.60 (apparent t, $^2J_{H-P}$ = 30 Hz, B), –19.45 (br, C), –19.26 (apparent t, $^2J_{H-P}$ = 30 Hz, D), –13.50 (apparent t, $^2J_{H-P}$ = 25 Hz, E), –13.20 (apparent t, $^2J_{H-P}$ = 25 Hz, F), –13.15 (dd, $^2J_{H-P}$ = 28 Hz, $^2J_{H-P}$ = 24 Hz, G), –12.88 (apparent t, $^2J_{H-P}$ = 27 Hz, H), 1.65–2.35 (12 s, Ru-NCCH_3), 6.00–8.50 (aromatic); ^{31}P{^{1}H} (161.9 MHz, $(CD_3)_2CO$), δ: 59.4 (d, $^2J_{P-P}$ = 43.0 Hz, A), 60.8 (d, $^2J_{P-P}$ = 46.4 Hz, B), 63.2 (d, $^2J_{P-P}$ = 44.2 Hz, F), 63.6 (d, $^2J_{P-P}$ = 40.6 Hz, E), 66.0 (d, $^2J_{P-P}$ = 43.0 Hz, A), 68.2 (d, $^2J_{P-P}$ = 46.0 Hz, C),[7] 69.6 (d, $^2J_{P-P}$ = 40.6 Hz, E), 71.2 (d, $^2J_{P-P}$ = 49.6 Hz, D), 71.5 (d, $^2J_{P-P}$ = 42.9 Hz, G), 74.2 (d, $^2J_{P-P}$ = 47.0 Hz, H), 75.4 (d, $^2J_{P-P}$ = 42.9 Hz, G), 76.5 (d, $^2J_{P-P}$ = 46.4 Hz, B), 79.3 (d, $^2J_{P-P}$ = 49.6 Hz, D), 80.3 (d, $^2J_{P-P}$ = 44.2 Hz, F), 82.7 (d, $^2J_{P-P}$ = 47.0 Hz, H). Approximate percentages of hydrido species present: A(3), B(14), C(5), D(22), E(15), F(15), G(11), H(15). Although we were unable to assign individual structures for each hydride, we have independently prepared *fac*-[Ru((*R*)-BINAP)(H)$(MeCN)_3$](BF_4) which corresponded to hydride E.

Stoichiometric reaction of [Ru((*R*)-BINAP)(H)$(MeCN)_n(Sol)_{3-n}$](BF_4) (II, n = 0–3) with tiglic acid in acetone

A Schlenk flask was charged with **I** (40.0 mg, 4.18×10^{-5} mol), tiglic acid (4.2 mg, 4.18×10^{-5} mol), and acetone (4.0 mL) under an Ar atmosphere. At room temperature, the flask was flushed with H_2, pressurized (1–2 atm), and shaken until a deep orange–yellow solution was generated (~5 min). The H_2 atmosphere was then replaced by Ar. To this solution was added MeCN (2.6 mL, 4.98×10^{-5} mol), and the flask was shaken (~5 min) to ensure complete reaction. The solvent was removed under reduced pressure, and the remaining orange solid was washed with hexanes (3 × 5 mL). The isolated solid was stored under an Ar atmosphere at –30°C. The product readily loses MeCN in vacuo. NMR spectroscopic data of the complex: ^{1}H (400.1 MHz, $(CD_3)_2CO$), δ: 1.45 (apparent t, $CH_3CHC(CH_3)CO_2Ru$, $^4J_{H-H}$ = 1.5 Hz, $^5J_{H-H}$ = 1.2 Hz), 1.56 (dd, $CH_3CHC(CH_3).CO_2Ru$, $^3J_{H-H}$ = 7.2 Hz, $^5J_{H-H}$ = 1.2 Hz), 2.01 (s, CH_3CN), 2.03 (s, CH_3CN), 6.45 (dq, $CH_3CHC(CH_3)CO_2Ru$, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.5 Hz), 6.58–7.89 (m, 32H, BINAP). ^{31}P{^{1}H} (161.9 MHz, $(CD_3)_2CO$), δ: 52.6 (dd, $^2J_{P-P}$ = 37.5 Hz), 56.9 (d, $^2J_{P-P}$ = 37.5 Hz). ^{13}C{^{1}H} (100.6 MHz, $(CD_3)_2CO$), δ: 2.4 (CH_3CN), 4.65 (CH_3CN), 10.72 and 13.90 ($CH_3CHC(CH_3)CO_2Ru$), 123.99 (CH_3CN), 124.14 (CH_3CN), 124.42–141.45 (BINAP and $CH_3CHC(CH_3)CO_2Ru$), 185.46 ($CH_3CHC(CH_3)CO_2Ru$).

Stoichiometric reaction of [Ru((*R*)-BINAP)(D)$(MeCN)_n(Sol)_{3-n}$](BF_4) (II, n = 0–3) with tiglic acid in acetone-d_6

Compound **I** (13.5 mg, 1.41×10^{-5} mol) was partially dissolved in acetone-d_6 (~0.8 mL) in an NMR tube under an Ar atmosphere. At room temperature, the tube was flushed with D_2, pressurized (1–2 atm), and shaken until a deep orange–yellow solution was generated (~5 min). The D_2 atmosphere was replaced by Ar, and the solution was then transferred to an NMR tube containing tiglic acid (1.41 mg, 1.41×10^{-5}

[7] The corresponding ^{31}P{^{1}H} NMR signal was obscured by resonances attributed to hydrides D and G ca. 71.3 ppm.

mol) under an Ar atmosphere. To this solution was added excess CD_3CN (2.0 μL, 3.83×10^{-5} mol) via a gas-tight syringe. The solution was immediately analyzed by ^1H NMR. The product was exclusively formed with concomitant formation of HD. ^1H (400.1 MHz, $(CD_3)_2CO$), δ: 1.45 (apparent t, $CH_3CHC(CH_3)CO_2Ru$, $^4J_{H-H}$ = 1.5 Hz, $^5J_{H-H}$ = 1.1 Hz), 1.46–1.52 (br m, partially deuterated cyclooctane), 1.56 (dd, $CH_3CHC(CH_3)CO_2Ru$, $^3J_{H-H}$ = 7.2 Hz, $^5J_{H-H}$ = 1.1 Hz), 1.99 (s, CH_3CN), 3.26 (br t, HD, $^1J_{H-D}$ = 240 Hz), 6.45 (dq, $CH_3CHC(CH_3)CO_2Ru$, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.6 Hz), 6.58–7.89 (m, 32H, BINAP). $^{31}P\{^1H\}$ (161.9 MHz, $(CD_3)_2CO$), δ: 52.6 (dd, $^2J_{P-P}$ = 37.5 Hz), 56.9 (d, $^2J_{P-P}$ = 37.5 Hz).

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