[Ru((*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl)(H)(MeCN)(THF)$_2$](BF$_4$), a Catalyst System for Hydrosilylation of Ketones and for Isomerization, Intramolecular Hydrosilylation, and Hydrogenation of Olefins

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*Summary: (R)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl ((R)-BINAP) reacted with cis-[Ru(MeCN)$_2$(COD)(η^3-C$_3$H$_5$)](BF$_4$) (COD = cycloocta-1,5-diene) to generate two isomers of [Ru(MeCN)((R)-BINAP)((1−3-η):(5,6-η)-C$_8$H$_{11}$)](BF$_4$) (**1**) that reacted with an excess of dihydrogen gas (pressure H$_2$ ∼1 atm, ambient temperature) in THF and methylene chloride (∼5:1) to generate [Ru((R)-BINAP)(H)(MeCN)(THF)$_2$](BF$_4$) (**2**). Reactions effected using 2 mol % **2** as catalyst include hydrogenation of (Z)-methyl α-acetamidocinnamate, hydrosilylation of ethyl acetoacetate by chlorodimethylsilane, tandem, stereoselective isomerization of (rac)-3-buten-2-ol via a partial kinetic resolution (ee of 3-buten-2-ol 42% S at 50% conversion) to initially generate (Z)-2-buten-2-ol, followed by isomerization of the enol to 2-butanone, and competing isomerization and intramolecular hydrosilylation of dimethyl-(2-propen-1-oxy)silane.*

Nearly all reported examples of enantioselective reactions catalyzed by chiral ruthenium(II)−bis(phosphine) complexes (the most common are of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)) are hydrogenations[1] and transfer hydrogenations[2] of olefins or ketones. These reactions generally occur with high turnover numbers and enantiomeric excesses (ee). Reports of other reductive-type additions to double bonds (transformations that usually involve oxidative additions, insertions, and reductive eliminations) catalyzed by ruthenium(II)−bis(phosphine) complexes are rare and tend to require either reactive substrates or elevated temperatures.[3] Of the nearly 200 reports describing ruthenium−BINAP or related catalysts, we are aware of only two examples that catalyze such reactions: hydrosilylation of reactive nitrones[3e] and one isomerization of an olefin.[4] Both the enormous success of chiral ruthenium(II)−bis(phosphine) complexes as catalysts for enantioselective hydrogenations and their near-absence in other reductive-type additions to double bonds encouraged us to extend ruthenium−BINAP chemistry to the catalyst system described in this report. We have developed a moderately air-stable, crystalline complex of ruthenium(II) and (*R*)-BINAP that undergoes facile hydrogenation to produce a catalyst system

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(3) We limit our discussion to bis(phosphine) ligands because of the high success obtained with their use in homogeneous catalysis and because, in general, multidentate, chiral ligands are required to obtain high ee values. For examples of high enantioselectivity obtained using monodentate, chiral phosphine ligands see: (a) Hayashi, T.; Niizuma, S.; Kamikawa, T.; Suzuki, N.; Uozumi, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9101. For examples of Ru(bis(phosphine))-catalyzed reactions other than hydrogenations, see the following. For isomerization of olefins: (b) Frauenrath, H.; Philipps, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 274. (c) Frauenrath, H.; Kaulard, M. *Synlett* **1994**, 517. For intramolecular hydrosilylation of ketones, (d) Burk, M. J.; Feaster, J. E. *Tetrahedron Lett.* **1992**, *33*, 2099. For hydrosilylation of nitrones: (e) Murahashi, S.-I.; Watanabe, S.; Shiota, T. *J. Chem. Soc., Chem. Commun.* **1994**, 725.

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(6) We identified, but did not quantify, propylene in solution by ^{1}H NMR spectroscopy.

(7) The two isomers of **1** were produced in a ratio of 0.9:1.0. We believe they are diastereomers with opposite absolute configurations about the sp^2 carbons in (1−3-η):(5,6-η)-C$_8$H$_{11}$. We have been unable to separate the two isomers of **1** and confirm that they are diastereomers.

(8) Small amounts (<2−3%) of each of two other species formed as well as **1**. We tentatively identify one as [Ru(MeCN)$_2$((*R*)-BINAP)(η^3-C$_3$H$_5$)](BF$_4$), on the basis of NMR data. We purified **1** by recrystallization from a solution of methylene chloride−acetonitrile (∼1:3) by slow addition of diethyl ether (resulting in isolation of **1**·0.17MeCN·0.2Et$_2$O·0.56CH$_2$Cl$_2$). We could not detect [Ru(MeCN)$_2$((*R*)-BINAP)(η^3-C$_3$H$_5$)](BF$_4$) in recrystallized **1**. The amount of the other, unidentified impurity (∼2−3%) did not change, even after several recrystallizations of **1**. We believe this species to be in equilibrium with **1** in solution. We note that *fac*-[Ru((*R*)-BINAP)(H)(MeCN)$_3$](BF$_4$) is the only detectable species in solution upon hydrogenation of **1** followed by addition of excess acetonitrile.

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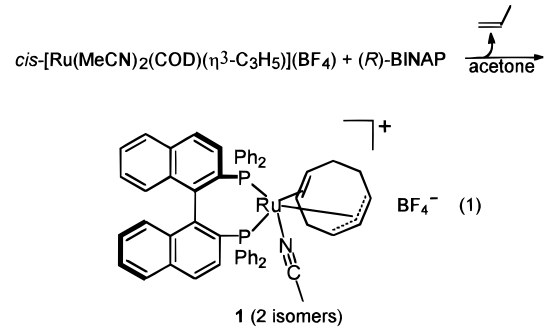
for hydrosilylation of ketones and for isomerization, intramolecular hydrosilylation, and hydrogenation of olefins.

We found that reaction between *cis*-[Ru(MeCN)$_2$(COD)(η^3-C_3H_5)](BF$_4$)[5] (COD = cycloocta-1,5-diene) and (*R*)-BINAP in acetone resulted in activation of an allylic C-H bond of COD and subsequent formation of propylene[6] and two isomers[7] of [Ru(MeCN)((*R*)-BINAP)((1−3-η):(5,6-η)-C_8H_{11})](BF$_4$) (**1**; eq 1).[8,9] Complex **1** was



isolated as moderately air-stable, lemon-yellow needles in 83% yield after recrystallization. Figure 1 shows the crystal structure of (*S′*)-**1** (*S′* designates the absolute configuration of the central allylic carbon (C(2)) in (1−3-η):(5,6-η)-C_8H_{11}).[10]

Compound **1** reacted in an excess of dihydrogen gas (pressure H_2 ~1 atm, room temperature) in mixtures of THF and methylene chloride (~5:1)[11] to yield cyclooctane[12] and the air-sensitive hydride [Ru((*R*)-BINAP)(H)(MeCN)(THF)$_2$] (BF$_4$) (**2**; eq 2).[13] Exchange of solvento ligands on **2** was facile, and it was necessary to cool solutions to −78 °C to obtain partially resolved

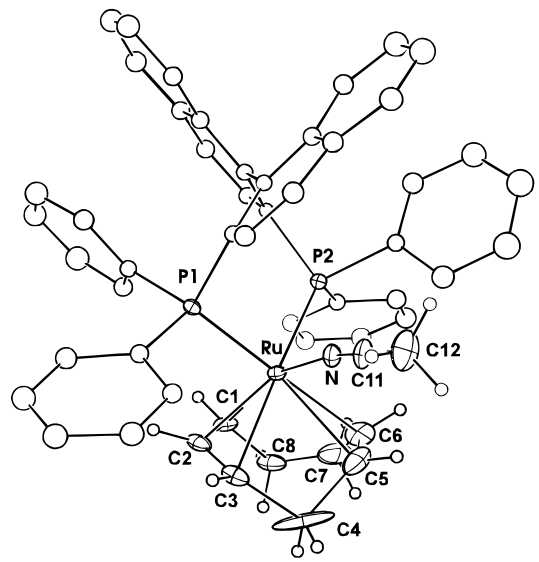
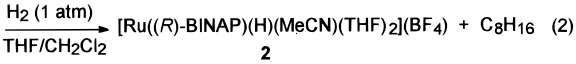


Figure 1. Crystal structure of (*S′*)-**1**·0.5$C_2H_4Cl_2$, as determined by X-ray diffraction. The positions of the hydrogen atoms are based on geometries of the parent carbon atoms. Non-hydrogen atoms are represented at the 20% probability level. Hydrogen atoms are shown with artificially small thermal parameters for (1−3-η):(5,6-η)-C_8H_{11} and are not shown for (*R*)-BINAP. Selected bond lengths (Å): Ru−C(1), 2.260(11); Ru−C(2), 2.165(11); Ru−C(3), 2.289(10); Ru−C(5), 2.395(14); Ru−C(6), 2.402(12); Ru−P(1), 2.332(2); Ru−P(2), 2.378(2); Ru−N, 2.075(9).



NMR spectra.[14] The magnitude of the coupling between the phosphorus atoms and the hydride (28 Hz) indicated that the hydride occupied a coordination site *cis* to both phosphines. We did not detect (by NMR spectroscopy) further reaction between **2** and dihydrogen gas under these conditions. Addition of excess acetonitrile (acetonitrile−ruthenium ~5:1) to **2** resulted in quantitative formation of *fac*-[Ru((*R*)-BINAP)(H)(MeCN)$_3$](BF$_4$) (**3**).[15]

Table 1 summarizes the reactions we effected using 2 mol % **2** as catalyst. The rate, the yield, and the magnitude of the ee for hydrogenation of methyl α-acetamidocinnamate (Table 1, entry 1) are comparable to those reported for other rhodium− and ruthenium−BINAP complexes as catalysts.[16] Reaction between **2** and *rac*-3-buten-2-ol (**4**; Table 1, entry 2) resulted in a stereoselective isomerization to generate significant quantities of the simple enol (*Z*)-2-buten-2-ol (maximum concentration ~0.055 M). We were unable to detect (using NMR spectroscopy) the *E* isomer in solution. Although this enol was previously generated via isomerization of **4** using rhodium-bis(phosphine) catalysts,[17] the rhodium catalysts were substantially less stereose-

(9) For other examples of ruthenium complexes containing (1−3-η):(5,6-η)-C_8H_{11}, see: Ashworth, T. V.; Nolte, M. J.; Reimann, R. H.; Singleton, E. *J. Chem. Soc. Chem. Commun.* **1977**, 937. Bouachir, F.; Chaudret, B.; Neibecker, D.; Tkatchenko, I. *Angew. Chem.* **1985**, 347. Ashworth, T. V.; Chalmers, A. A.; Liles, D. C.; Meintjies, E.; Singleton, E. *Organometallics* **1987**, *6*, 1543.

(10) Crystals suitable for structure determination by X-ray diffraction were obtained by liquid-liquid diffusion of methanol into a 1,2-dichloroethane solution of **1** at room temperature. Crystal data: M_r = 1008.21; monoclinic, space group $P2_1$ (No. 4); a = 12.8559(8) Å, b = 13.0675(8) Å, c = 14.9401(9) Å, β = 91.678(6)°, V = 2508.8(3) Å^3, Z = 2, d_{calcd} = 1.335 g cm^{-3}; crystal size 0.56 × 0.08 × 0.06 mm; μ(Cu Kα) = 4.040 mm^{-1}. Data were measured using a Siemens P4/RA diffractometer with Cu Kα radiation (λ = 1.541 78 Å; maximum $2q$ = 110.0°); 3315 independent reflections (3179 with $I > 2\sigma(I)$) were measured. The structure was solved via direct methods (SHELX-86[19]). Full-matrix, least-squares refinement on F^2 (SHELXL-93 yielded R_1 = 0.043 ($I > 2\sigma(I)$) and wR2 = 0.1306 (all data).

(11) Methylene chloride was required to dissolve **1** at high enough concentrations to obtain satisfactory NMR spectra of **2**. Compound **2** rapidly decomposes in the presence of methylene chloride at room temperature. It was therefore necessary to keep these solutions of **2** at −78 °C as much as possible. The catalytic reactions were carried out at lower concentrations of **1** (see Table 1) and, except for one reaction (Table 1, entry 2), in the absence of methylene chloride.

(12) Identified and quantified by ^{1}H NMR spectroscopy and by gas chromatography (retention time confirmed by comparison to an authentic sample). ^{1}H NMR spectra measured of solutions early in the hydrogenation showed the presence of cyclooctene (~30% versus cyclooctane), indicating that cyclooctene is initially formed by hydrogenation of (1−3-η):(5,6-η)-C_8H_{11} in **1**.

(13) The rapid exchange of solvento ligands did not allow us to isolate **2**. We characterized **2** by ^{1}H and ^{31}P NMR spectroscopy. The solution also contained [Ru(R)-BINAP)(H)(MeCN)$_2$(THF)](BF$_4$) (~15%) that resulted from reaction between **2** and the excess acetonitrile present in crystals of **1**. Two other species with ^{31}P NMR spectra similar to that of **2** existed in solution in amounts too small to allow integration by NMR spectroscopy. We identify one as [Ru((*R*)-BINAP)(H)(MeCN)$_3$](BF$_4$) (on the basis of its ^{31}P NMR spectrum), and we propose that the other is [Ru((*R*)-BINAP)(H)(THF)$_3$](BF$_4$).

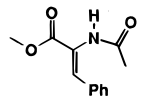
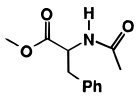
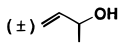
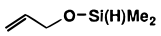
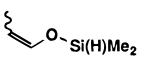
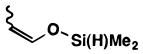
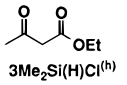
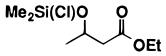
(14) ^{1}H NMR (400.1 MHz, −78 °C): δ −13.05 (app t, J = 28.0 Hz, 1H), 2.74 (s, 3H, CH_3CN), 6.00−8.72 (m, aromatic). ^{31}P{^{1}H} NMR (161.9 MHz, −78 °C): δ 72.22 (d, J_{P-P} = 49.6 Hz, 1P), 81.34 (d, J_{P-P} = 49.8 Hz, 1P).

(15) ^{1}H NMR (400.1 MHz, −78 °C): δ −13.48 (app t, J = 24.1 Hz, 1H), 1.84 (s, 3H, CH_3CN), 1.87 (s, 3H, CH_3CN), 2.22 (s, 3H, CH_3CN), 6.00−8.85 (m, aromatic). ^{31}P{^{1}H} NMR (161.9 MHz, −78 °C): δ 64.22 (d, J_{P-P} = 40.1 Hz, 1P), 69.89 (d, J_{P-P} = 40.5 Hz, 1P).

(16) Noyori, R.; Ikeda, T.; Ohkuma, T.; Widhalm, M.; Kitamura, M.; Takaya, H.; Akutagawa, S.; Sayo, N.; Saito, T.; Taketomi, T.; Kumobayashi, H. *J. Am. Chem. Soc.* **1989**, *111*, 9134. For the rhodium−BINAP-catalyzed hydrogenation of the corresponding acid, see: Miyashita, A.; Takaya, H.; Souchi, T.; Noyori, R. *Tetrahedron* **1984**, *40*, 1245.

(17) Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958.

Table 1. Reactions Catalyzed by 2[a]

Substrate(s)	Product	T(°C)	Rate (time)[b]	Yield (ee)
 + H_2 (4 atm)		30	2.7×10^{-2}[c] T.O./min	100% (86% (*R*))[d]
 4		25	2.2 T.O./min[e]	42% (at maximum)
		25	0.1 T.O./min	100%
 5		25	1.6 T.O./min	94%[f]
		60	(~48h)	100%[g]
 + $3Me_2Si(H)Cl$[h]		60	0.6 T.O./min (1.5h)	100%(7% (*R*))

[a] All reactions were carried out using 2 mol % **2** in THF unless stated otherwise. Compound **2** was generated before addition of substrate by hydrogenation of **1** ([**2**] = 2.6 mM, pressure H_2 = 1 atm, ~2 min), followed by purging of the solution with argon gas (~1 min). [b] Value in parentheses is the time required for complete reaction: number of turnovers/min = (mol of substrate)/(mol of catalyst)t. [c] Reaction carried out in methanol. [d] See the Supporting Information for determination of yields, ee's, and absolute configurations. [e] Initial rate of isomerization; reaction carried out in a mixture of THF and CH_2Cl_2 (~20:1). [f] 87% *Z* and 13% *E* isomers. The remaining product (6%) was 2,2-dimethyl-1-oxa-2-silacyclopentane. [g] Generated as a mixture of monomer and polymer.[18] [h] Excess chlorodimethylsilane was used to minimize the effect of its loss from evaporation on hydrosilylation.

lective than complex **2** and generated the enol as a mixture of isomers. A partial kinetic resolution of the *R* and *S* enantiomers of *rac*-**4** occurred during the isomerization. The ee of **4** was 42% *S* at 50% conversion (time 60 min, reaction mixture composition 50% **4**, 42% enol, 8% 2-butanone). The rate of isomerization of the enol to 2-butanone (Table 1, entry 3) varied little over the course of the reaction. Reaction of dimethyl(2-propen-1-oxy)silane (**5**) with **2** (Table 1, entry 4) resulted in competing intramolecular hydrosilylation and isomerization to generate (*Z*)-dimethyl(1-propen-1-oxy)silane (81%), (*E*)-dimethyl(1-propen-1-oxy)silane (13%), and 2,2-dimethyl-1-oxa-2-silacyclopentane (6%, resulting from intramolecular hydrosilylation). Both silyl enol ethers underwent intramolecular hydrosilylation to generate 2,2-dimethyl-1-oxa-2-silacyclopentane upon heating to 60 °C (Table 1, entry 5). We believe that hydrosilylation of the silyl enol ethers proceeded via reverse isomerization to regenerate **5**. The hydrosilylation of ethyl acetoacetate by chlorodimethylsilane (Table 1, entry 6) proceeded at a reasonable rate, but with low ee. To the best of our knowledge, **2** is the first reported ruthenium(II)−BINAP complex to catalyze hydrosilylations of olefins and ketones.

We propose that **2** was the active catalyst generated by reaction between **1** and dihydrogen gas. The facile substitution of the solvento ligands in **2** (assuming that acetonitrile is displaced during catalysis) and the ability of the hydride ligand to undergo insertion and elimination reactions allow the ruthenium center to present the equivalent of four vacant coordination sites during catalysis. Further, **2** is not sterically hindered, the ruthenium center is in a low oxidation state, and it apparently undergoes oxidative additions, insertions, and reductive eliminations. The combination of these abilities distinguishes **2** from previously reported ruthenium-bis(phosphine) complexes, and we believe it accounts for the activity of **2** toward the catalytic reactions we present in this communication. Finally, this catalyst system will, in principle, lend itself well to mechanistic investigations because the proposed active catalyst can easily be generated in high concentrations.

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Supporting Information Available: Text giving experimental procedures and analytical data for all new compounds and a full report on the X-ray structure of **1**, including tables of experimental details, atomic coordinates, interatomic distances and angles, torsional angles, and anisotropic thermal parameters (36 pages). Ordering information is given on any current masthead page.

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