An Alternate Route to the Active Chiral Hydrogenation Catalysts [Ru(bisphosphine)(H)(solvent)$_3$]$^+$: Synthesis, Characterization, and Catalytic Evaluation

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We report an improved synthesis of *cis*-[Ru(CH_3CN)$_2$((1−3-η)-C_3H_5)((1,2:5,6-η)-C_8H_{12})]BF_4 and its use in the synthesis of [Ru(bisphosphine)((1−3:5,6-η)-C_8H_{11})(CH_3CN)]BF_4 (where bisphosphine = (*R*)-BINAP, (*R*)-Tol-BINAP). Thermolyses of the complexes [Ru(bisphosphine)((1−3:5,6-η)-C_8H_{11})(CH_3CN)]BF_4 afford [Ru(bisphosphine)((1−5-η)-C_8H_{11})]BF_4, which serve as convenient precatalysts to the active hydrogenation catalysts *fac*-[Ru(bisphosphine)(H)(sol)$_3$]BF_4 (sol = THF, acetone, *i*-PrOH). We compare the properties and activities of these catalysts with those of related, established systems.

Introduction

Enantioselective hydrogenation using catalysts containing ruthenium(II) and 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (BINAP), or related bisphosphines, is an important technology used widely in industrial and academic syntheses.[1] The scope of this process is broad, with catalysts usually exhibiting extraordinarily high turnover frequencies (TOF's), turnover numbers (TON's), and enantiomeric excesses (ee's). The ruthenium catalysts commonly employed in industrial-scale reactions, however, do not effect hydrogenations of tetrasubstituted olefin precursors at practical rates. For example, workers at Firmenich and the Genêt laboratories and this group only recently described catalyst mixtures suitable for production of (+)-*cis*-methyl dihydrojasmonate, a perfumery chemical, via hydrogenation of a tetrasubstituted olefin.[2] We and workers at Firmenich[3] also recently described a general synthesis of the active catalysts in these mixtures. These catalysts, of the form *fac*-[Ru(bisphosphine)(H)(sol)$_3$]BF_4 (sol = weakly coordinating solvento ligands, e.g., THF and acetone), were prepared from the zerovalent complex Ru((1,2:5,6-η)-C_8H_{12})((1−6-η)-C_8H_{10})—a versatile but challenging precursor.

As part of our ongoing efforts to prepare highly reactive ruthenium catalysts, we now describe in this report an alternate, convenient synthesis of the ruthenium precursor *cis*-[Ru(CH_3CN)$_2$((1−3-η)-C_3H_5)((1,2:5,6-η)-C_8H_{12})]BF_4 (**1**), its use in the synthesis of [Ru((*R*)-BINAP)((1−5-η)-C_8H_{11})]BF_4 (**2**) and the (*R*)-Tol-BINAP analogue (**3**), and the reactions of **2** and **3** with hydrogen to form the active catalysts *fac*-[Ru(bisphosphine)(H)(sol)$_3$]BF_4 (**4**, bisphosphine = (*R*)-BINAP; **5**, bisphosphine = (*R*)-Tol-BINAP; sol = THF, acetone, *i*-PrOH). The TOF and enantioselectivity of **4** as catalyst for the hydrogenation of (*Z*)-methyl α-acetamidocinnamate (MAC) are compared with those of [Ru((*R*)-BINAP)(H)(CH_3CN)$_n$(sol)$_{3-n}$]BF_4 (**6**; sol = acetone, methanol, n = 0−3)—the system reported previously by us[4] and Salzer[5]—and with those of the classic rhodium catalyst system [Rh((*R*)-BINAP)(sol)$_2$]BF_4 (**7**).

Results and Discussion

Syntheses and Characterization of Catalyst Precursors. Schrock et al.[6] reported that the reaction of Ru((1−3-η)-C_3H_5)$_2$((1,2:5,6-η)-C_8H_{12}) with [Ph_3C]BF_4 in mixtures of acetonitrile and methylene chloride gave *cis*-[Ru(CH_3CN)$_2$((1−3-η)-C_3H_5)((1,2:5,6-η)-C_8H_{12})]BF_4 (**1**) and $Ph_3CCH_2CH{=}CH_2$. We now report that **1** is more conveniently prepared using $HBF_4{\cdot}Et_2O$ rather than [Ph_3C]BF_4 as electrophile (Scheme 1). The reaction using $HBF_4{\cdot}Et_2O$ is faster, and it allows for easier isolation of the product, because $Ph_3CCH_2CH{=}CH_2$ is difficult to separate from **1**. Use of ≤1 equiv of $HBF_4{\cdot}Et_2O$ at 0 °C prevents formation of the undesired dication [Ru(CH_3CN)$_4$((1,2:5,6-η)-C_8H_{12})](BF_4)$_2$ via protonation of the allyl group in **1**. We reported earlier[4] that reaction between **1** and (*R*)-BINAP in acetone

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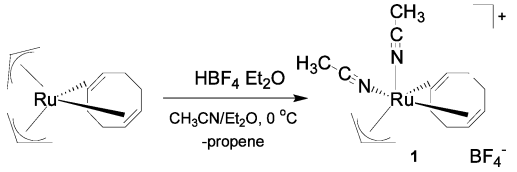
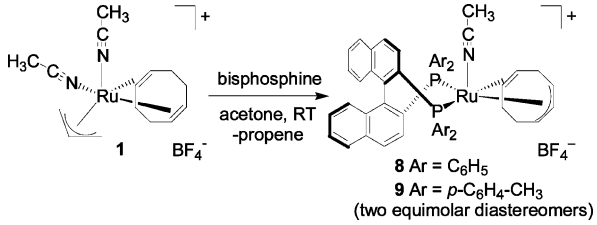
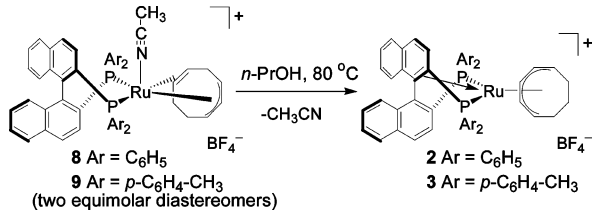
Scheme 1



Scheme 2



Scheme 3

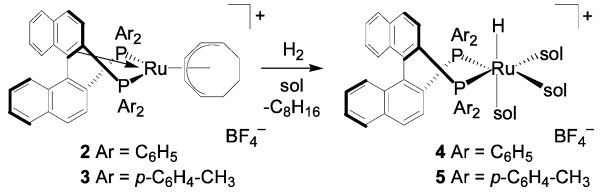


resulted in activation of an allylic C−H bond of 1,5-cyclooctadiene, and subsequent formation of propene and two equimolar diastereomers of [Ru((*R*)-BINAP)((1−3:5,6-η)-C_8H_{11})(CH_3CN)]BF_4 (**8**). We now report that this approach yields the related complex [Ru((*R*)-Tol-BINAP)((1−3:5,6-η)-C_8H_{11})(CH_3CN)]BF_4 (**9**), also isolated as a mixture of two equimolar diastereomers (Scheme 2).

The acetonitrile ligand in the diastereomers of **8** is sufficiently labile to allow exchange with excess $CH_3C^{15}N$ at room temperature to prepare **8**−$CH_3C^{15}N$.[7,8] This lability suggests that the acetonitrile can be removed by heating to generate more active acetonitrile-free species such as **2**. Indeed, heating the diastereomeric mixtures of **8** (containing BINAP) and **9** (containing Tol-BINAP) in *n*-propanol (80 °C, 2 h) resulted in loss of the acetonitrile ligand and isomerization of the (1−3:5,6-η)-C_8H_{11} ligand[9] to generate only one isomer of the conjugated (1−5-η)-C_8H_{11} species **2** and **3**, respectively (Scheme 3).

The BINAP and Tol-BINAP ligands in **2** and **3** act formally as six-electron donors (η^2,κ^2-biaryl coordination) via a metal−olefin bond and two metal−phosphorus bonds. Two compounds analogous to **2** and **3**, [Ru((1−5-η)-C_8H_{11})(P−P)]$^+$, were reported in 1997 by Pregosin and co-workers.[10] One analogue was made by

Scheme 4



reaction of Ru(P−P)$(OAc)_2$ (P−P = (6,6′-dimethoxybiphenyl-2,2′-diyl)bis(bis(3,5-di-*tert*-butylphenyl)phosphine), 2 HBF_4, and (1,2:5,6-η)-C_8H_{12}, while the other analogue was made by reaction of 0.5 [Ru$(CF_3CO_2)_2$((1,2:5,6-η)-C_8H_{12})]$_2$ with (6,6′-dimethoxybiphenyl-2,2′-diyl)-bis(diisopropylphosphine). Other complexes containing BINAP and related ligands coordinated to ruthenium in this manner have been studied widely by Pregosin's group and other groups.[11]

Generation and Characterization of Solvento Catalysts in the Absence of Substrate. We reported previously that complexes **2** and **3** react rapidly with excess hydrogen (pressure ∼1 atm) in solutions of acetone in the absence of substrate to yield cyclooctane[12] and *fac*-[Ru(bisphosphine)(H)(sol)$_3$]BF_4 (sol = acetone; **4**, bisphosphine = (*R*)-BINAP; **5**, bisphosphine = (*R*)-Tol-BINAP; Scheme 4).[3a] We have found in this subsequent research that the hydrido−solvento complexes **4** and **5** are not stable at room temperature for prolonged periods of time in the absence of substrate, and that the stability of these complexes is solvent dependent. Reaction of **2** with hydrogen carried out in acetone solution at room temperature quickly produced **4** in high yield, which then decomposed slowly over hours to generate mixtures of unidentified species. Reaction of **2** with hydrogen in THF solution at room temperature rapidly produced **4** (with sol = THF) that decomposed within minutes. Complex **4**, however, was generated in high yield at 0 °C in THF, and it was stable at this temperature for several hours. We found that **4** (sol = *i*-PrOH) is significantly less stable in *i*-PrOH solution—a solvent used commonly in catalytic ketone hydrogenations[13]—than in acetone or in THF. Remarkably, we found that compound **4** can be generated in *i*-PrOH by reaction with hydrogen and storage at ∼−60 °C. Compound **4** began to decompose in *i*-PrOH solution upon warming to −40 °C. The identity of the decomposition

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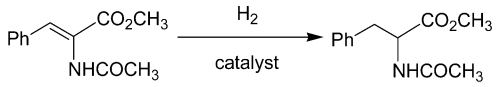
Table 1. Catalytic Hydrogenation of MAC[a]



entry	catalyst[b]	solvent	$P(H_2)$, atm	ee,[c] %	abs confign
1	Ru−BINAP/CH_3CN (**6**)	methanol	4	87	*R*
2	Ru−BINAP/CH_3CN (**6**)	acetone	4	92	*R*
3	Ru-Tol-BINAP/CH_3CN (**11**)	acetone	4	87	*R*
4	Rh−BINAP (**7**)	acetone	4	33	*S*
5	Rh−BINAP (**7**)	methanol	4	19	*S*
6	Ru−BINAP (**4**)	acetone	4	92	*R*
7[d]	Ru−BINAP (**4**)	acetone	1	96	*R*
8[d]	Ru−BINAP/CH_3CN (**6**)	acetone	1	96	*R*

[a] Reaction conditions: 2 mol % catalyst; [catalyst] = 2.6 mM; stir rate = 1100 rpm; T = 30 °C (except where noted otherwise). [b] Abbreviations: Ru−BINAP = *fac*-[Ru((*R*)-BINAP)(H)(sol)$_3$]BF_4 (**4**), Ru−BINAP/CH_3CN = [Ru((*R*)-BINAP)(H)$(CH_3CN)_n$(sol)$_{3-n}$]BF_4 (**6**), Rh−BINAP = [Rh((*R*)-BINAP)(sol)$_2$]BF_4 (**7**), and Ru-Tol-BINAP/CH_3CN = [Ru((*R*)-Tol-BINAP)(H)$(CH_3CN)_n$(sol)$_{3-n}$]BF_4 (**11**). [c] Hydrogenations were allowed to proceed for 48 h to ensure complete conversion of reactants to products before the absolute configurations and the ee's of the products were determined.[15,17] [d] Reaction carried out at 25 °C.

product has not been determined. In contrast, Pregosin et al. obtained the crystal structure of the sterically crowded compound [Ru((6,6′-dimethoxybiphenyl-2,2′-diyl)bis[3,5-di(*tert*-butyl)phenylphosphine])(H)(*i*-PrOH)$_2$]BF_4.[14] In all solvents, complex **4** contained the hydrido ligand in a coordination site cis to both phosphorus centers, as shown by the magnitude of the coupling between the phosphorus atoms and the hydride ($^2J_{P-H}$ typically ∼30 Hz). Further reaction with hydrogen under these conditions was not detected by NMR spectroscopy. Solutions of **4** did, however, react readily with deuterium (even at −78 °C) to generate **4**-*d* with concomitant formation of HD. No detectable quantities of η^2-dihydrogen complexes were observed. Addition of ≥3 equiv of acetonitrile to solutions containing **4** generated *fac*-[Ru((*R*)-BINAP)(H)$(CH_3CN)_3$]BF_4 (**10**) in quantitative yield.

Catalysis. The relative activity and enantioselectivity of these catalysts were evaluated using a common test reaction in enantioselective catalysis: the hydrogenation of MAC. Table 1 summarizes the reactions effected using 2 mol % **4**, **6** ([Ru((*R*)-BINAP)(H)$(CH_3CN)_n$(sol)$_{3-n}$]BF_4; sol = acetone, methanol, n = 0−3), and related complexes as catalysts. As we reported previously, there is one CH_3CN per Ru in solutions of **6**, but the CH_3CN ligand exchanges rapidly among all the Ru centers in solution at room temperature. We denote this mixture of hydrides generally as [Ru((*R*)-BINAP)(H)$(CH_3CN)_n$(sol)$_{3-n}$]BF_4 (n = 0−3).[7,15] As we reported previously,[15] the ee obtained using **6** as catalyst is higher in acetone than in methanol (Table 1, entries 1 and 2). The ee obtained in methanol is comparable to values reported for other ruthenium−((*R*)-BINAP) catalysts.[16]

Catalyst **11** ([Ru((*R*)-Tol-BINAP)(H)$(CH_3CN)_n$(sol)$_{3-n}$]BF_4; sol = acetone) was less enantioselective than the BINAP catalyst **6** in acetone (Table 1, entry 3). Notably, the enantioselectivities of **6** and **11** are significantly higher, with the opposite face selection, than that of the benchmark catalyst [Rh((*R*)-BINAP)(sol)$_2$]ClO_4 (**7**; sol = acetone, methanol; Table 1, entries 4 and 5). The TOF when using **7**, however, was greater than when using **6** by approximately 2 orders of magnitude (approximate TOF's (25 °C, 1 atm of H_2, acetone): **6**, 0.1 min^{-1}: **7**, 9.8 min^{-1}).[18] One factor contributing to this difference in TOF may be the presence of acetonitrile in **6**.[19] Indeed, use of the BINAP catalyst without an acetonitrile ligand in acetone (i.e., *fac*-[Ru((*R*)-BINAP)(H)(sol)$_3$]BF_4, sol = acetone, **4**) maintained the high enantioselectivity exhibited by **6** (Table 1, entries 7 and 8) while providing TOF's that are even slightly higher than those of **7** (TOF of **4** (25 °C, 1 atm of H_2, acetone): 11.9 min^{-1}).

Conclusions

We described a convenient synthesis of the known complex **1** and demonstrated its utility in the preparation of several catalyst precursors. Thermally induced isomerization of the (1−3:5,6-η)-C_8H_{11} ligand of **8** and **9** with loss of the acetonitrile ligand generated the highly reactive catalyst precursors **2** and **3**, respectively, where the BINAP-type ligands functioned as six-electron donors to the ruthenium center. Complexes **4** and **6** are the active catalysts generated quantitatively by reaction of **2** and **8**, respectively, with hydrogen. Addition of ≥3 equiv of acetonitrile to **4** generated **10**, the tris(acetonitrile) species, quantitatively. Complex **4** is the most reactive (acetonitrile-free) form of **6**; complex **10** is the least reactive (acetonitrile-rich) form of **6**. Complex **10** did not effect the catalytic hydrogenation of MAC. The change of **6** to **4** as catalyst resulted in a 100-fold increase in TOF.

Experimental Section

General Comments. Details describing our synthetic techniques, analytical techniques, analytical instrumentation, and purification of solvents appear elsewhere.[15,17,20] All reagents were used as received from Aldrich, except (*R*)-BINAP, which was purchased from Strem and recrystallized by established procedures before use.[21] (*Z*)-Methyl α-acetamidocinnamate,[15] [$RuCl_2$((1,2:5,6-η)-C_8H_{12})]$_n$,[22] Ru((1−3-η)-C_3H_5)$_2$((1,2:5,6-η)-C_8H_{12}),[22] and [Rh(bicyclo[2.2.1]hepta-2,5-diene)((*R*)-BINAP)]ClO_4 [16b] were prepared as described previously. The hydrogenations of (*Z*)-methyl α-acetamidocinnamate and the

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(18) The TOF's were determined by setting up and taking down the pressure reactor as quickly as possible during a hydrogenation and judging the extent of the reaction by ^{1}H NMR spectroscopy. Their values are to be taken as approximate.
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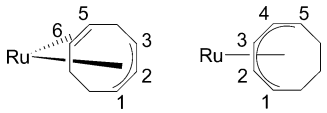

Figure 1. Illustration of the numbering schemes for the (1−3:5,6-η)-C_8H_{11} and (1−5-η)-C_8H_{11} ligands.

determination of ee and yield were carried out as we described previously.[15,17]

***cis*-[Ru(CH$_3$CN)$_2$((1−3-η)-C$_3$H$_5$)((1,2:5,6-η)-C$_8$H$_{11}$)]BF$_4$ (1).** A diethyl ether solution (54 wt %) of tetrafluoroboric acid (318 μL, 2.31 mmol) was added to a stirred solution of freshly sublimed Ru((1−3-η)-C_3H_5)$_2$((1,2:5,6-η)-C_8H_{12}) (748.0 mg, 2.57 mmol, sublimed under dynamic vacuum (ca. 0.05 mmHg) at 70 °C) in diethyl ether (5.0 mL) and acetonitrile (5.0 mL) at 0 °C. The resulting yellow solution was stirred for 5 min at 0 °C and stirred an additional 2 min while warming to room temperature. The reaction mixture was evaporated under reduced pressure, and the resulting yellow residue was washed with diethyl ether (5 × 5.0 mL) to remove excess Ru((1−3-η)-C_3H_5)$_2$((1,2:5,6-η)-C_8H_{12}). Slow addition of diethyl ether (5.0 mL over a 2 h period) to a saturated solution of the crude product in acetonitrile (1.3 mL) afforded yellow, highly air-sensitive microcrystals. The product was washed with diethyl ether (3 × 5.0 mL) and dried in vacuo to yield 631.8 mg of **1** (65% yield based on tetrafluoroboric acid). The typical yield for this procedure is ∼70%. The NMR spectra of this material were identical with those reported in the literature for **1**.[6]

[Ru((*R*)-BINAP)((1−3:5,6-η)-C$_8$H$_{11}$)(CH$_3$CN)]BF$_4$ (8). This compound was prepared as described previously,[4] with the only procedural improvement being recrystallization from acetonitrile/diethyl ether. Yield of **8**·0.4Et$_2$O: 90%. The amended spectroscopic data are listed below; the asterisks (*) denote resonances attributed to the labile diastereomer. The numbering schemes for the cyclooctadienyl ligands in **2**, **3**, **8**, and **9** are illustrated in Figure 1. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ −0.21 (m, 1H, H-7*), 1.05 (m, 1H, H-7′*), 1.41 (m, 1H, H-8*), 1.6−1.9 (m, 2H, H-8′* and H-8), 1.73 (s, 3H, CH_3CN*), 1.95 (m, 4H, H-8′ and CH_3CN), 2.16 (m, 1H, H-4), 2.4−2.6 (m, 3H, H-3*, H-4*, and H-7), 2.69 (m, 1H, H-4′), 2.87 (m, 1H, H-7′), 3.17 (m, 2H, H-1 and H-5), 3.26 (m, 2H, H-2* and H-4′*), 3.40 (m, 1H, H-3), 3.53 (m, 2H, H-2 and H-5*), 3.95 (m, 1H, H-1*), 4.89 (m, 1H, H-6*), 5.08 (m, 1H, H-6), 5.6−8.1 (aromatic). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ 4.8 (s, CH_3CN*), 4.9 (s, CH_3CN), 20.6 (s, C-4*), 21.2 (s, C-4), 24.9 (s, C-8), 25.3 (s, C-7*), 31.1 (s, C-3), 31.6 (s, C-8*), 35.6 (s, C-7), 36.7 (d, J_{P-C} = 14.5 Hz, C-3*), 55.8 (s, C-1*), 62.9 (s, C-5*), 66.2 (s, C-1), 71.2 (d, J_{P-C} = 27.5 Hz, C-5), 85.4 (s, C-2), 90.0 (s, C-2*), 99.3 (d, J_{P-C} = 12.0 Hz, C-6*), 117.3 (d, J_{P-C} = 8.5 Hz, C-6), 125−142 (aromatic, CH_3CN, and CH_3CN*). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 25 °C): δ 32.8 (d, $^2J_{P-P}$ = 33.5 Hz, 1P, P(A)), 35.7 (br d, $^2J_{P-P}$ = 38.5 Hz, 1P, P(A′)*), 45.6 (br d, $^2J_{P-P}$ = 38.5 Hz, 1P, P(B′)*), 46.9 (d, $^2J_{P-P}$ = 33.5 Hz, 1P, P(B)). MS (ESI): *m*/*z* calcd for $C_{54}H_{46}NP_2{}^{102}Ru$ ([M − BF$_4$]$^+$), 872.2; found, 872.2. Anal. Calcd for $C_{54}H_{46}BF_4NP_2Ru$·0.4Et$_2$O: C, 67.56; H, 5.10; N, 1.42. Found: C, 67.21; H, 4.92; N, 1.54.

[Ru((*R*)-Tol-BINAP)((1−3:5,6-η)-C$_8$H$_{11}$)(CH$_3$CN)]BF$_4$ (9). The method used for the preparation of **9** was the same as that used for **8**,[4] with substitution of (*R*)-Tol-BINAP for (*R*)-BINAP. The crude product was purified by recrystallization from a methylene chloride/diethyl ether solvent mixture. Yield: 75%. NMR spectroscopic data indicated that **9** was isolated as a solvated mixture (**9**·0.8Et$_2$O·0.3CH$_2$Cl$_2$) of a labile and a nonlabile diastereomer in a ratio of 1:1. The asterisks (*) denote resonances attributed to the labile isomer. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ −0.10 (m, 1H), 1.06 (m, 1H), 1.40 (m, 1H), 1.5−2.0 (m, 3H), 1.76 (br s, 3H, CH_3), 1.95 (br s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.0−2.3 (m, 1H,), 2.13 (s, 3H, CH_3), 2.16 (br s, 3H, CH_3), 2.3−2.6 (m, 3H), 2.43 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.48 (s, 6H, 2 × CH_3 overlapping), 2.67 (m, 1H), 2.84 (m, 1H), 3.19 (m, 4H), 3.36 (m, 1H), 3.46 (m, 2H), 3.91 (m, 1H), 4.84 (m, 1H), 5.02 (m, 1H), 5.7−8.6 (aromatic). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ 4.8 (br, CH_3CN*), 5.0 (s, CH_3CN), 20.5 (br, C-4*), 21.0 (s, $C_6H_4CH_3$), 21.1 (s, $C_6H_4CH_3$), 21.2 (s, C-4), 21.4 (s, 2 × $C_6H_4CH_3$ overlapping), 24.9 (d, J_{P-C} = 3.5 Hz, C-8), 25.4 (d, J_{P-C} = 5.5 Hz, C-7*), 30.5 (s, C-3), 31.6 (s, C-8*), 35.6 (d, J_{P-C} = 7.0 Hz, C-7), 36.2 (d, J_{P-C} = 9.0 Hz, C-3*), 55.5 (br, C-1*), 62.5 (br, C-5*), 66.2 (s, C-1), 70.8 (d, J_{P-C} = 26.5 Hz, C-5), 85.4 (s, C-2), 90.0 (br, C-2*), 98.8 (br, C-6*), 116.3 (d, J_{P-C} = 9.0 Hz, C-6), 122−142 (aromatic, CH_3CN, and CH_3CN*). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 25 °C): δ 31.1 (d, $^2J_{P-P}$ = 33.5 Hz, 1P), 34.0 (br d, $^2J_{P-P}$ = 38.5 Hz, 1P*), 43.9 (br d, $^2J_{P-P}$ = 38.5 Hz, 1P*), 45.2 (d, $^2J_{P-P}$ = 33.5 Hz, 1P). MS (ESI): *m*/*z* calcd for $C_{58}H_{54}NP_2{}^{102}Ru$ ([M − BF$_4$]$^+$), 928.3; found, 928.3. Anal. Calcd for $C_{58}H_{54}BF_4NP_2Ru$·0.8Et$_2$O·0.3CH$_2$Cl$_2$: C, 67.17; H, 5.74; N, 1.27; Cl, 1.93. Found: C, 66.98; H, 5.55; N, 1.48; Cl, 2.13.

[Ru((*R*)-BINAP)((1−5-η)-C$_8$H$_{11}$)]BF$_4$ (2). Complex **8** (100.7 mg, 0.105 mmol) was dissolved partially in *n*-propanol (40.0 mL) under an atmosphere of argon. The reactor was sealed, and the mixture was stirred with heating (80 °C) for 40 min to generate an amber solution. The solvent was removed under reduced pressure with heating (80 °C) to give a yellow solid. The solid was heated (80 °C) under vacuum for a total of 2 h. The solid was passed quickly through a plug of neutral alumina (Brockman I) under nitrogen using methylene chloride as eluent. Slow addition of *n*-pentane (80 mL) to a solution (2.0 mL) of the recovered solid in methylene chloride afforded a yellow powder that was collected by filtration, washed with *n*-pentane (2 × 20 mL), and dried in vacuo to yield 57.8 mg (60%) of **2** as an amber yellow microcrystalline powder. ^{1}H NMR (599.9 MHz, CD_2Cl_2, 25 °C): δ −0.15 (apparent q, J = 15.0 Hz, 1H, exo H-7), 0.07 (apparent t, J = 15.0 Hz, 1H, H-6), 0.84 (apparent t, J = 15.0 Hz, 2H, overlapping H-4 and endo H-7), 1.00 (br, 1H, H-6′), 1.54 (apparent t, J = 15.0 Hz, 1H, H-8), 1.86 (br, 1H, H-8′), 2.20 (br, 1H, H-5), 4.65 (br, 1H, H-1), 5.46 (br, 2H, overlapping H-2 and H-3), 6.0−8.3 (aromatic). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ 18.9 (s, C-7), 23.2 (d, J_{P-C} = 2.0 Hz, C-6), 27.3 (s, C-8), 58.5 (apparent t, J_{P-C} = 3.5 Hz, C-1), 64.0 (d, J_{P-C} = 35.0 Hz, BINAP C-2), 71.6 (dd, J_{P-C} = 20.0, 2.0 Hz, C-5), 91.0 (s, C-2), 96.2 (s, C-4), 97.8 (dd, J_{P-C} = 5.5, 4.0 Hz, BINAP C-1), 114.1 (d, J_{P-C} = 9.5 Hz, C-3), 123−148 (aromatic). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 25 °C): δ −6.0 (d, $^2J_{P-P}$ = 44.5 Hz, 1P), 63.9 (d, $^2J_{P-P}$ = 44.5 Hz, 1P). HRMS (ESI): *m*/*z* calcd for $C_{52}H_{43}P_2{}^{102}Ru$ ([M − BF$_4$]$^+$), 831.1884; found, 831.1883. Anal. Calcd for $C_{52}H_{43}BF_4P_2Ru$: C, 68.01; H, 4.72. Found: C, 67.26; H, 4.82.

[Ru((*R*)-Tol-BINAP)((1−5-η)-C$_8$H$_{11}$)]BF$_4$ (3). Complex **9** (46.7 mg, 0.046 mmol) was dissolved partially in *n*-propanol (18.7 mL) under an atmosphere of nitrogen. The reactor was sealed, and the mixture was stirred with heating (80 °C) for 40 min to generate an amber solution. The solvent was removed under reduced pressure with heating (80 °C) to give a mustard yellow solid. The solid was heated (80 °C) under vacuum for a total heating time of 2 h. The solid was passed quickly through a plug of neutral alumina (Brockman I) under nitrogen using methylene chloride as eluent. Addition of hexanes (100 mL) to a solution (2.0 mL) of the recovered solid in methylene chloride afforded a mustard yellow powder that was collected by filtration, washed with hexanes (2 × 20 mL), and dried in vacuo to yield 33.9 mg (75%) of **3** as an amber yellow microcrystalline powder. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 27 °C): δ −0.19 (apparent q, J = 13.5 Hz, 1H), 0.14 (apparent t, J = 14.5 Hz, 1H), 1.73 (s, 3H), 2.42 (s, 3H), 2.41 (s, 3H), 2.53 (s, 3H), 4.53 (br, 1H), 5.28−5.38 (m, 2H), 5.41 (td, J = 7.0, 2.0 Hz, 1H), 5.80 (dd, J = 8.0, 2.0 Hz, 2H), 5.91 (d, J = 9.0 Hz, 1H), 6.10−6.19 (m, 2H), 7.10−7.63 (m, 24H), 7.78 (d, J = 7.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 8.08−8.17 (m, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 27 °C): δ 19.0 (s, C-7), 20.9 (s, CH_3), 21.5 (s, CH_3), 21.6 (s, 2 overlapping CH_3), 23.1 (d, J_{P-C} = 2.5 Hz, C-6), 27.3 (s, C-8), 58.8 (s, C-1), 64.1 (d,

J_{P-C} = 35.0 Hz, Tol-BINAP C-2), 71.3 (d, J_{P-C} = 20.0 Hz, C-5), 91.1 (s, C-2), 95.8 (s, C-4), 97.0 (br d, J_{P-C} = 10.0 Hz, Tol-BINAP C-1), 113.8 (d, J_{P-C} = 9.2 Hz, C-3), 120−148 (aromatic). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, 27 °C): δ −8.4 (d, $^2J_{P-P}$ = 44.5 Hz, 1P), 64.1 (d, $^2J_{P-P}$ = 45.0 Hz, 1P). HRMS (ESI): *m*/*z* calcd for $C_{56}H_{51}P_2{}^{102}Ru$ ($[M - BF_4]^+$), 887.2510; found, 887.2511. Anal. Calcd for $C_{56}H_{51}BF_4P_2Ru$: C, 69.07; H, 5.28. Found: C, 68.01; H, 5.33.

***fac*-[Ru((*R*)-BINAP)(H)(sol)$_3$]BF$_4$ (4; sol = Acetone-d_6).** Complex **2** (16.0 mg, 1.74 × 10^{-5} mol) was dissolved in acetone-d_6 (0.6 mL) and reacted with hydrogen, as outlined above for the synthesis of **11** (sol = acetone-d_6). ^1H NMR (400.1 MHz, acetone-d_6, 25 °C): δ −19.80 (apparent t, $^2J_{P-H}$ = 30.5 Hz, Ru−H), 6.0−8.5 (aromatic). Free cyclooctane was observed in the ^1H NMR spectrum at ca. 1.5 ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, acetone-d_6, 25 °C): δ 71.2 (d, $^2J_{P-P}$ = 49.5 Hz, 1P), 79.7 (d, $^2J_{P-P}$ = 49.5 Hz, 1P).

***fac*-[Ru((*R*)-BINAP)(H)(sol)$_3$]BF$_4$ (4; sol = THF-d_8).** Complex **2** (7.5 mg, 8.17 × 10^{-6} mol) was dissolved in THF-d_8 (0.7 mL) in an NMR tube under an atmosphere of argon. The tube was cooled to 0 °C, injected with 10 mL of hydrogen using a gastight syringe, and shaken periodically over 30 min (maintaining the temperature of the reaction mixture ∼0 °C) to generate a yellow-orange solution. ^1H NMR (400.1 MHz, THF-d_8, 0 °C): δ −23.26 (br, Ru−H), 6.0−8.5 (aromatic). Free cyclooctane was observed in the ^1H NMR spectrum at ca. 1.5 ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, THF-d_8, 0 °C): δ 75.0 (d, $^2J_{P-P}$ = 51.5 Hz, 1P), 81.6 (d, $^2J_{P-P}$ = 51.5 Hz, 1P).

***fac*-[Ru((*R*)-BINAP)(H)(sol)$_3$]BF$_4$ (4; sol = *i*-PrOH-d_8).** Complex **2** (13.1 mg, 1.43 × 10^{-5} mol) was dissolved in a mixture of CD_2Cl_2 (0.2 mL) and *i*-PrOH-d_8 (0.5 mL) in an NMR tube under an atmosphere of argon. The tube was cooled to −60 °C and injected with 8 mL of hydrogen using a gastight syringe. The tube was then removed briefly from the cooling bath, shaken vigorously, and returned to the bath in order to maintain the temperature near −60 °C. NMR spectra collected at −50 °C showed that the resulting orange solution contained **4** and ∼10% of unknown decomposition products. ^1H NMR (400.1 MHz, CD_2Cl_2/*i*-PrOH-d_8, −50 °C): δ −23.6 (br, Ru−H), 6.0−8.5 (aromatic). The decomposition products had broad signals at −0.86 and −10.6 ppm. Free cyclooctane was observed in the ^1H NMR spectrum at ca. 1.5 ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2/*i*-PrOH-d_8, −50 °C): δ 73.9 (d, $^2J_{P-P}$ = 49.0 Hz, 1P), 88.9 (br, 1P). The decomposition products had signals at 37.5, 49.1, 53.9, and 61.3 ppm.

***fac*-[Ru((*R*)-Tol-BINAP)(H)(sol)$_3$]BF$_4$ (5; sol = Acetone-d_6).** Complex **3** (8.9 mg, 9.1 × 10^{-6} mol) was dissolved in acetone-d_6 (0.7 mL) in an NMR tube under an atmosphere of argon. The tube was cooled to 0 °C, injected with 10 mL of hydrogen using a gastight syringe, and shaken to generate a light yellow-orange solution. ^1H NMR (400.1 MHz, acetone-d_6, 0 °C): δ −19.95 (apparent t, $^2J_{P-H}$ = 31.0 Hz, 1H, Ru−H), 1.88 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 6.19 (d, *J* = 8.5 Hz, 1H), 6.30 (d, *J* = 8.5 Hz, 1H), 6.45 (m, 4H), 6.80 (apparent t, *J* = 7.0 Hz, 1H), 6.90 (apparent t, *J* = 8.5 Hz, 1H), 7.21−7.39 (m, 11H), 7.57−7.73 (m, 7H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.95 (m, *J* = 8.5 Hz, 1H). Free cyclooctane was observed in the ^1H NMR spectrum at ca. 1.5 ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, acetone-d_6, 0 °C): δ 70.2 (d, $^2J_{P-P}$ = 50.5 Hz, 1P), 78.2 (d, $^2J_{P-P}$ = 50.5 Hz, 1P).

***fac*-[Ru((*R*)-Tol-BINAP)(H)(sol)$_3$]BF$_4$ (5; sol = THF-d_8).** Complex **3** (8.5 mg, 8.7 × 10^{-6} mol) was dissolved in THF-d_8 (0.7 mL) and reacted with hydrogen at 0 °C as outlined above. NMR spectroscopic data collected at 0 °C indicated that the resulting orange solution contained **5** and a product of decomposition (∼12%). ^1H NMR (400.1 MHz, THF-d_8, 0 °C): δ −23.5 (apparent t, $^2J_{P-H}$ = 31.0 Hz, 1H, Ru−H), 1.89 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 6.37 (d, *J* = 8.5 Hz, 2H), 6.48 (m, 2H), 6.80 (apparent t, *J* = 7.5 Hz, 2H), 6.89 (apparent, *J* = 7.5 Hz, 2H), 7.10−7.23 (m, 6H), 7.40−7.48 (m, 4H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.75−7.83 (m, 4H), 7.96 (m, 2H). Free cyclooctane was observed in the ^1H NMR spectrum at ca. 1.5 ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, THF-d_8, 0 °C): 48.0 (d, $^2J_{P-P}$ = 42.0 Hz, dec), 61.5 (d,$^2J_{P-P}$ = 42.0 Hz, dec), 73.7 (d, $^2J_{P-P}$ = 51.0 Hz, 1P), 80.2 (d, $^2J_{P-P}$ = 51.0 Hz, 1P).

***fac*-[Ru((*R*)-Tol-BINAP)(H)(sol)$_3$]BF$_4$ (5; sol = *i*-PrOH-d_8).** Complex **3** (9.2 mg, 9.4 × 10^{-6} mol) was dissolved in a mixture of CD_2Cl_2 (0.2 mL) and *i*-PrOH-d_8 (0.5 mL) in an NMR tube under an atmosphere of argon. This mixture was reacted with hydrogen at −60 °C as outlined above for **4**, with sol = *i*-PrOH-d_8. NMR spectra collected at −60 °C showed that the resulting orange solution contained **5** and ∼10% of unknown decomposition products. ^1H NMR (400.1 MHz, CD_2Cl_2/*i*-PrOH-d_8, −60 °C): δ −24.2 (br, Ru−H), 1.77 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 6.0−8.5 (aromatic). The decomposition products had broad signals at −0.89 and −10.6 ppm. Free cyclooctane was observed in the ^1H NMR spectrum at ca. 1.5 ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2/*i*-PrOH-d_8, −60 °C): δ 72.0 (d, $^2J_{P-P}$ = 47.5 Hz, 1P), 89.1 (br, 1P). The decomposition products had signals at 35.8, 48.1, and 58.9 ppm.

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