and benzene (10 mL). The mixture was subjected to hydrogenation for 7 h, and then it was filtered and concentrated. The crude product was separated by column chromatography on silica gel (hexanes/ethyl acetate = 10/1) to give 2[9] as a colorless solid (28 mg, 23%) and a mixture of two components (ratio = 6:1) as a colorless solid (88 mg, 72%). A pure sample of the major component was obtained from repetitive chromatography[10] of the mixture; it was characterized as 7: mp 107-108 °C (recrystallized from hexane/ether); $^1$H NMR (200 MHz) $\delta$ 7.58 ($\delta$, $J$ = 8.8 Hz, 2 H), 7.21 (m, 2 H), 7.04 (d, $J$ = 8.9 Hz, 1 H), 4.86 (s, 1 H), 3.05 (t, $J$ = 6.0 Hz, 2 H), 2.95 (t, $J$ = 6.4 Hz, 2 H), 2.06 (quin, $J$ = 6.1 Hz, 2 H); $^{13}$C NMR $\delta$ 148.81, 134.93, 130.98, 129.10, 126.94, 125.88, 124.31, 123.11, 117.15, 117.10, 30.73, 23.56, 22.12; MS (EI), $m/e$ (rel intensity) 184 (100, M$^+$), 183 (32), 181 (8), 169 (11), 167 (8), 165 (19), 152 (11), 82 (11), 76 (8); HRMS $m/e$ calcd for $C_{13}H_{12}O$ 184.0888, found 184.0893.

**7-Methyl-2,3-dihydrophenalen-4-ol (11).** Hydrogenation of 120 mg of phenalenone 10 (vide infra) gave 76 mg of 11 as a yellow solid: mp 149-150 °C (recrystallized from Skelly F/ether):[11] $^1$H NMR $\delta$ 7.75 (d, $J$ = 9.0 Hz, 1 H), 7.08 (m, 3 H), 4.95 (m, 1 H), 3.02 (t, $J$ = 6.2 Hz, 2 H), 2.97 (t, $J$ = 6.2 Hz, 2 H), 2.61 (d, $J$ = 0.6 Hz, 3 H), 2.05 (m, 2 H); $^{13}$C NMR $\delta$ 148.76, 133.10, 132.05, 131.08, 128.17, 124.13, 123.89, 123.26, 117.77, 116.59, 30.78, 23.77, 22.28, 19.41; MS (EI) $m/e$ (rel intensity) 198 (100, M$^+$), 183 (55), 165 (30), 152 (11), 82 (25); HRMS $m/e$ calcd for $C_{14}H_{14}O$ 198.1045, found 198.1053.

**2,3-Dihydro-1*H*-phenalene** was obtained as a solid, mp 82-84 °C, in 87% yield from ketone 3: $^1$H NMR[12] ($CCl_4$) $\delta$ 7.53 (d, $J$ = 8.1 Hz), 7.24 (t, $J$ = 7.1 Hz), 7.09 (d, $J$ = 6.8 Hz), 3.06 (t, $J$ = 5.9 Hz, 4 H), 2.06 (quin, $J$ = 5.8 Hz, 2 H); $^{13}$C NMR[13] ($CCl_4$) $\delta$ 135.34, 133.49, 129.85, 125.60, 124.76, 123.30, 31.10, 22.88; MS (EI) $m/e$ (rel intensity) 168 (100, M$^+$), 167 (59), 165 (40), 153 (46), 152 (30), 144 (24), 129 (15), 83 (27), 82 (22).

**General Procedure of Dehydrogenation Reactions of 2,3-Dihydro-1*H*-phenalenones.** The bomb was loaded with $Pd(OH)_2$ on carbon (402 mg), phenalenone 3 (57 mg, 0.31 mmol), acetic acid (0.5 mL), and benzene (5 mL). The mixture was heated at 100 °C for 40 h and then was filtered through a pack of silica gel and $Na_2CO_3$. The filtrate was concentrated in vacuo to give 1*H*-phenalenone (1) (available from Aldrich Chemical Co., Inc. as perinaphthenone) as a yellow crystalline solid, mp 153-155 °C (35 mg, 61%): $^1$H NMR $\delta$ 8.62 (dd, $J$ = 7.4, 1.2 Hz), 8.18 (dd, $J$ = 8.1, 1.1 Hz), 8.02 (d, $J$ = 8.2 Hz), 7.74 (m, 3 H), 7.58 (dd, $J$ = 8.2, 7.1 Hz), 6.74 (d, $J$ = 9.8 Hz); $^{13}$C NMR $\delta$ 185.79, 141.92, 134.99, 132.07, 131.99, 131.47, 130.48, 129.33, 129.06, 127.71, 127.43, 127.07, 126.60. (The $^1$H NMR spectrum matches that reported by the Aldrich Chemical Co., Inc.).[14]

**4-Methyl-1*H*-phenalenone (10)** was obtained as a yellow solid starting from compound 9:[15] yield 354 mg (79%); mp 98-99 °C (recrystallized from EtOAc);[11] $^1$H NMR $\delta$ 8.62 (dd, $J$ = 7.4, 1.3 Hz), 8.13 (dd, $J$ = 8.0, 1.1 Hz), 8.05 (d, $J$ = 10.1 Hz), 7.90 (d, $J$ = 8.4 Hz), 7.70 (t, $J$ = 7.7 Hz), 7.41 (d, $J$ = 8.4 Hz), 6.73 (d, $J$ = 10.1 Hz), 2.73 (s, $CH_3$); $^{13}$C NMR $\delta$ 185.51, 140.82, 137.79, 134.97, 131.92, 131.13, 130.60, 130.10, 129.27, 128.46, 127.97, 126.18, 125.00, 19.29; MS (EI) $m/e$ (rel intensity) 194 (85, M$^+$), 165 (100), 139 (12), 82 (26), 52 (13); HRMS $m/e$ calcd for $C_{14}H_{10}O$ 194.0732, found 194.0735.

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**Supplementary Material Available:** $^1$H and $^{13}$C NMR for compounds 7, 10, and 11 (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and may be ordered from the ACS; see any current masthead page for ordering information.

(9) The $^1$H NMR spectrum of this compound is identical to that of the authentic compound obtained from the reduction of 3 with LAH/$AlCl_3$.[7a]

(10) The minor component was obtained in impure form. HRMS indicates a molecular formula of $C_{26}H_{22}O_2$.

(11) Duplicate elemental analyses did not produce satisfactory results.

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## Practical Synthesis of BINAP-Ruthenium(II) Dicarboxylate Complexes

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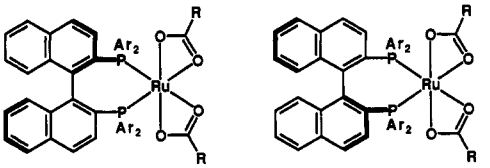
BINAP-Ru(II) dicarboxylate complexes of type 1 serve as excellent catalyst precursors for highly enantioselective hydrogenation of a wide range of prochiral functionalized olefins.[1] The stereoselective hydrogenation allows efficient asymmetric synthesis of terpenes,[2] amino acids,[3] isoquinoline alkaloids including morphines,[4] carbapenem antibiotics,[5] prostaglandins,[6] anti-inflammatory naproxen,[7] etc. This paper discloses a convenient procedure for the preparation of the significant Ru complexes using commercially available BINAP[8] and a Ru complex. This method is high-yielding and much simpler than our original procedure.[9,10]




Δ-(*R*)-1 Λ-(*S*)-1

a, Ar = $C_6H_5$; R = $CH_3$
b, Ar = $C_6H_5$; R = $C_6H_5$
c, Ar = 3,5-$(CH_3)_2C_6H_3$; R = $CH_3$

The present synthesis starting with $[RuCl_2(benzene)]_2$ consists of a high-temperature ligand exchange between benzene and optically pure BINAP[10] followed by displacement of the chlorides with carboxylates. Thus, when a mixture of $[RuCl_2(benzene)]_2$[11] and (*R*)- or (*S*)-BINAP (Ru:BINAP = 1.05:1) was heated in *N*,*N*-dimethylformamide (DMF) at 100 °C for 10 min, the exchange of the neutral ligands occurred facilely to give BINAP-$RuCl_2$ complexes. The chloride ligands were then displaced by acetates by treatment of the DMF solution with 20-fold excess of sodium acetates in methanol at room temperature

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(11) Use of $[RuCl_2(1,5\text{-cyclooctadiene})]_n$ requires heating in DMF at 160 °C for 20 min. Prolonged heating forms some Ru-carbonyl complexes.[10a]

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for 5 min. This one-pot, two-stage synthesis was accomplished easily within a short period, and extractive workup followed by concentration afforded the crude Ru(OCOCH$_3$)$_2$[(*R*)- or (*S*)-BINAP] in quantitative yield. Recrystallization from a toluene–hexane mixture gave an analytically pure sample in 85–91% yield. This procedure is operationally simple, reproducible, and applicable to the preparation of various related Ru complexes.

The BINAP–Ru complexes thus prepared exhibited identical reactivity and enantioselectivity in the hydrogenation as those obtained with the samples synthesized by the previous procedure. The crude diacetate complexes were also comparable. As noted earlier,[1] the conditions leading to satisfactory enantioselection are highly dependent on the structures of the olefinic substrates. Certain substrates such as N-acylated (*Z*)-1-benzylidene-1,2,3,4-tetrahydroisoquinolines were hydrogenated efficiently with the intermediary crude dichloroRu complex. For the synthesis of citronellol from geraniol, however, use of the diacetate complex is recommended to minimize the overreduction product; reaction with the dichloro Ru complex produced dihydrocitronellol (3–7%) in addition to the desired citronellol. Hydrogenation of $\alpha,\beta$-unsaturated carboxylic acids is much faster with the dicarboxylate complex than with the dichloro complex. The carboxylate ligands of Ru(OCOR)$_2$(BINAP) can be removed or replaced by other anionic ligands by the action of strong acids.[12]

## Experimental Section

**General.** DMF was distilled over molecular sieves 4A under argon to a Schlenk tube. Hexane and toluene were dried and degassed at refluxing temperature over sodium benzophenone ketyl under an argon stream for 6 h and distilled into Schlenk flasks. In a similar manner, methanol was distilled from magnesium turnings. Ion-exchanged water was degassed immediately before use. Argon gas was purified by passing through a column of the activated copper at 80 °C followed by a column of molecular sieves 4A. [RuCl$_2$(benzene)]$_2$ is used without purification. BINAP is available commercially or by the literature procedure.[13] (*R*)-2,2′-Bis[bis(3,5-dimethylphenyl)phosphino]-1,1′-binaphthyl was provided by Takasago Research Institute.[14]

**[(*R*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl]ruthenium Diacetate, Ru(OCOCH$_3$)$_2$[(*R*)-BINAP] (1a).** [RuCl$_2$(benzene)]$_2$ (800 mg, 1.60 mmol) and (*R*)-BINAP (1.89 g, 3.04 mmol) were placed in a dry 150-mL Schlenk tube containing a Teflon-coated magnetic stirring bar. The whole system was evacuated and then filled with argon. DMF (30 mL) was introduced, and the reddish brown suspension was heated at 100 °C for 10 min, resulting in the formation of a clear reddish brown solution. After the solution was cooled to room temperature, a degassed methanol solution (50 mL) of sodium acetate (5.20 g, 63.4 mmol) in another dry 80-mL Schlenk tube was introduced to the above prepared DMF solution of BINAP–Ru(II) complex. After the solution was stirred for 5 min at 25 °C, water (50 mL) and toluene (25 mL) were added and the resulting two layers were mixed by vigorous stirring. The upper organic layer was transferred into another 200-mL, long Schlenk tube (4 cm × 16 cm) with cannula. Use of such a long Schlenk tube is recommended to facilitate the subsequent recrystallization. The aqueous layer was further extracted with two 25-mL portions of toluene. The combined organic layers were washed with four portions of 10-mL water. This extraction procedure must be carried out under argon atmosphere. Removal of the solvent at 1 mmHg at 40 °C for 30 min with vigorous stirring followed by evacuation at 0.1 mmHg at 25 °C for 12 h gave 2.54–2.67 g of solid Ru(OCOCH$_3$)$_2$[(*R*)-BINAP] (99–104% crude yield based on BINAP). Under reduced pressure, the solution sometimes causes foaming, which can be avoided by heating the top part of the Schlenk tube with a drier. This crude material contains, in addition to Ru(OCOCH$_3$)$_2$-[(*R*)-BINAP], less than 5% of a complex showing, in $^{31}$P-NMR spectrum ($CDCl_3$ at 27 °C), two sets of doublets at $\delta$ 73.1 and 15.9 with a P–P coupling constant of 52 Hz. The crude complex is usable for enantioselective hydrogenation of olefinic substrates. The Ru complex was dissolved in toluene (25–35 mL), and hexane (75–105 mL) was very carefully put on the toluene solution. The resulting two-layer system was kept at 25 °C for 12 h and then at 4 °C for 3 days. Removal of the mother liquor was followed by washing with hexane (20 mL) and drying in vacuo, affording 2.17–2.33 g (85–91% yield) of pure Ru(OCOCH$_3$)$_2$[(*R*)-BINAP] as yellow fine needles or powdery crystals, mp 188–190 °C dec. Anal. Calcd for $C_{48}H_{38}O_4P_2Ru$: C, 68.5; H, 4.6. Found: C, 68.4; H, 4.5. The $^1$H, $^{13}$C, and $^{31}$P NMR and IR data are identical with reported data.[9]

**[(*S*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl]ruthenium Dibenzoate, Ru(OCOC$_6$H$_5$)$_2$[(*S*)-BINAP] (1b).** A mixture of [RuCl$_2$(benzene)]$_2$ (81.3 mg, 0.163 mmol) and (*S*)-BINAP (192.3 mg, 0.309 mmol) in DMF (7 mL) was heated at 100 °C for 10 min. The resulting solution was combined with sodium benzoate (890 mg, 6.18 mmol) in a mixture of methanol (7 mL) and water (2 mL) and stirred at 25 °C for 5 min. The above workup gave the crude material (313.2 mg, 105% yield). Recrystallization from the bilayer system consisting of toluene (3 mL) and hexane (18 mL) afforded pure Ru(OCOC$_6$H$_5$)$_2$[(*S*)-BINAP] (266.4 mg, 89% yield) as yellowish brown fine needles: mp 188–190 °C dec.; $^1$H NMR ($CDCl_3$) $\delta$ 6.2–8.1 (m, aromatic protons); $^{31}$P NMR ($CDCl_3$) $\delta$ 65.22 (s); $^{13}$C NMR ($CDCl_3$) $\delta$ 125.3–134.9, 182.4; IR (KBr) 1599, 1551, 1507, 1418 cm$^{-1}$. Anal. Calcd for $C_{58}H_{42}O_4P_2Ru$: C, 72.1; H, 4.4. Found: C, 72.2; H, 4.4.

**[(*R*)-2,2′-Bis[bis(3,5-dimethylphenyl)phosphino]-1,1′-binaphthyl]ruthenium Diacetate (1c).** A mixture of [RuCl$_2$(benzene)]$_2$ (52.5 mg, 0.105 mmol) and (*R*)-2,2′-bis[bis(3,5-dimethylphenyl)phosphino]-1,1′-binaphthyl (144.8 mg, 0.197 mmol) in DMF (3 mL) was heated at 100 °C for 10 min, and the resulting solution was treated with a methanol (4 mL) solution of sodium acetate (321 mg, 3.91 mmol) at 25 °C for 5 min. This afforded the crude material (195 mg, 104% yield), which was then dissolved in methanol (10 mL). Addition of water (10 mL) to the methanol solution resulted in precipitation, giving pure 1c (132 mg, 70% yield) as a yellow solid: mp 185–189 °C dec.; $^1$H NMR ($CDCl_3$) $\delta$ 1.76 (s), 1.81 (s), 2.36 (s), 6.51–7.64 (m, aromatic protons); $^{31}$P NMR ($CDCl_3$) $\delta$ 64.25 (s); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.16, 21.82, 23.45, 124.4–138.3, 187.3; IR (KBr) 1525, 1502, 1454, 1414 cm$^{-1}$. Anal. Calcd for $C_{56}H_{54}O_4P_2Ru$: C, 70.5; H, 5.7. Found: C, 70.5; H, 5.8.

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