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An Anionic Dinuclear BINAP−Ruthenium(II) Complex: Crystal Structure of $[NH_2Et_2][\{RuCl((R)\text{-}p\text{-}MeO\text{-}BINAP)\}_2(\mu\text{-}Cl)_3]$ and Its Use in Asymmetric Hydrogenation

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*Summary: Treatment of $[RuCl_2(COD)]_n$ with (R)-p-MeO-BINAP (p-MeO-BINAP = 2,2′-bis(bis(p-methoxyphenyl)-phosphino)-1,1′-binaphthyl) in toluene in the presence of triethylamine afforded the anionic dinuclear complex $[NH_2Et_2][\{RuCl((R)\text{-}p\text{-}MeO\text{-}BINAP)\}_2(\mu\text{-}Cl)_3]$ ((R)-**2**), whose structure has been determined by an X-ray crystallographic study. Complex **2** is an efficient catalyst for asymmetric hydrogenation of functionalized olefins and ketones.*

Recently, a number of monomeric BINAP−Ru(II) complexes (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) have been prepared and are effective catalysts for the asymmetric hydrogenations of a variety of olefins and ketones.[1−11] Although the BINAP−Ru complexes bearing halogen ligands are highly active catalysts, little information about their structure in organic solvents has been obtained.[12] A dinuclear complex formulated as $Ru_2Cl_4(BINAP)_2\cdot NEt_3$ (**1**), which is the first reported dinuclear BINAP−Ru(II) complex, was isolated by Ikariya *et al.*,[13] but its structure has not been elucidated. Herein we report the first X-ray

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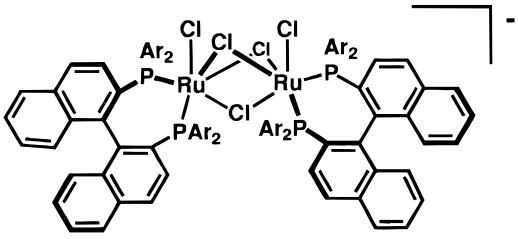
crystallographic characterization of such a dinuclear complex bearing *p*-MeO-BINAP (*p*-MeO-BINAP = 2,2′-bis(bis(*p*-methoxyphenyl)phosphino)-1,1′-binaphthyl) instead of BINAP, and thus the unique anionic dinuclear structure[14] is confirmed by X-ray analysis. Its catalytic activity for asymmetric hydrogenation is demonstrated.

Treatment of $[RuCl_2(COD)]_n$ with 1 equiv of (*R*)-*p*-MeO-BINAP[15] in the presence of excess amounts of triethylamine in toluene at reflux temperature for 8 h afforded $[NH_2Et_2][\{RuCl((R)\text{-}p\text{-MeO-BINAP})\}_2(\mu\text{-}Cl)_3]$ ((*R*)-**2**)[16] in addition to $RuHCl((R)\text{-}p\text{-MeO-BINAP})_2$



anion of (*R*)-**2**, Ar = *p*-MeO-C_6H_4

((*R*)-**3**).[17] Recrystallization afforded **2** as deep red crystals in 37% yield. The $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ exhibited AB quartets centered at δ 52.0 and 49.5 with a coupling constant of 38.0 Hz at room temperature. The ^{31}P and ^1H NMR spectral data of **2** are close to those for **1**.[13] These signals did not coalesce even at 80 °C, suggesting that the exchange among bridging and terminal chloride is slow.[18] In contrast to the original formulation of **1** as a neutral complex, we find by X-ray analysis that **2** consists of an anionic dinuclear *p*-MeO-BINAP−Ru part and a diethylammonium cation.

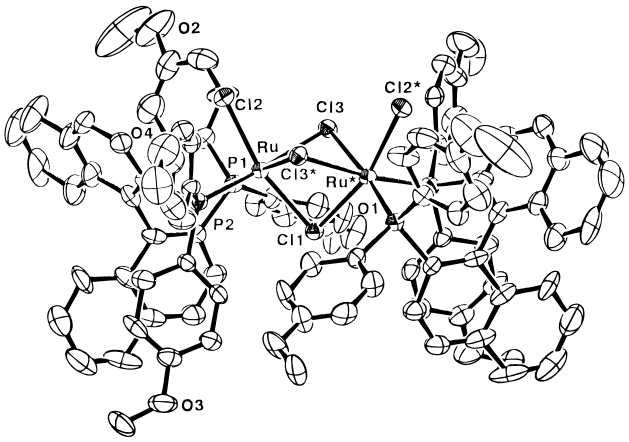


Figure 1. ORTEP drawing of the anionic part of (*R*)-**2** along with the numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−Cl(1) = 2.441(4), Ru−Cl(2) = 2.425(4), Ru−Cl(3) = 2.491(4), Ru−Cl(3*) = 2.513(4), Ru−P(1) = 2.285(4), Ru−P(2) = 2.259(4); Cl(1)−Ru−Cl(2) = 164.2(1), Cl(1)−Ru−Cl(3) = 80.0(1), Cl(1)−Ru−Cl(3*) = 79.5(1), Cl(2)−Ru−Cl(3) = 87.7(1), Cl(2)−Ru−Cl(3*) = 88.7(1), Cl(3)−Ru−Cl(3*) = 80.2(1), Cl(1)−Ru−P(1) = 95.9(1), Cl(1)−Ru−P(2) = 103.6(1), Cl(2)−Ru−P(1) = 94.7(1), Cl(2)−Ru−P(2) = 87.8(1), Cl(3)−Ru−P(1) = 94.0(1), Cl(3)−Ru−P(2) = 172.9(1), Cl(3*)−Ru−P(1) = 173.1(1), Cl(4)−Ru−P(2) = 94.3(1), P(1)−Ru−P(2) = 91.8(2).

Figure 1 shows the anionic part of (*R*)-**2**.[19] The halves of **2** are related by a C_2 axis passing through the bridging chloride Cl(1), and thus the $RuCl(\mu\text{-}Cl)_3RuCl$ core is confirmed. The geometry of each ruthenium center is roughly octahedral with little deviation of Cl−Ru−Cl, Cl−Ru−P, and P−Ru−P angles from 90° or 180°. The separation (3.33 Å) of the two ruthenium atoms (2.28−2.95 Å) is well outside the range for a Ru−Ru bond but is comparable to those (3.25−3.35 Å) of tris(chloro)-bridged Ru_2 complexes such as $Ru_2Cl_5(CHIRAPHOS)_2$,[20] $Ru_2Cl_4(CS)(PPh_3)_4$,[21] and $Ru_2Cl_4(DMSO)(DPPB)_2$ (dppb = 1,4-bis(diphenylphosphino)-

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(15) Synthesis of (*R*)-*p*-MeO-BINAP: 2,2′-Bis(bis(4-methoxyphenyl)-phosphino)-1,1′-binaphthyl was prepared by the reaction of 2,2′-dilithio-1,1′-binaphthyl with bis(4-methoxyphenyl)phosphinic chloride according to the literature method; mp >300 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.76 (s, 6H, OCH_3), 3.78 (s, 6H, OCH_3), 6.7−7.84 (m, 28H). ^{31}P NMR ($CDCl_3$, 161 MHz): δ 29.35. Low-resolution mass spectrum (LRMS): *m/e* 774 (M^+). Anal. Calcd for $C_{48}H_{40}O_6P_2$: C, 74.41; H, 5.20. Found: C, 73.84; H, 5.02. Treatment of (±)-2,2′-bis(bis(4-methoxyphenyl)phosphino)-1,1′-binaphthyl with 1 equiv of dibenzoyl-L-tartaric acid resulted in precipitation of a white solid which gave (+)-2,2′-bis-(bis(4-methoxyphenyl)phosphino)-1,1′-binaphthyl: mp >300 °C; $[\alpha]_D^{25}$ = +169.6° (*c* = 0.5, THF). Reduction of (+)-2,2′-bis(bis(4-methoxyphenyl)phosphino)-1,1′-binaphthyl by using trichlorosilane produced (*R*)-*p*-MeO-BINAP: mp 167−169 °C; $[\alpha]_D^{25}$ = +109.2° (*c* = 0.53, benzene). ^1H NMR (270 MHz, $CDCl_3$): δ 3.73 (s, 12H, OCH_3), 6.55−7.97 (m, 28H, aromatic). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ −17.2 (s). LRMS: *m/e* 742 (M^+). Anal. Calcd for $C_{48}H_{40}O_4P_2$: C, 77.62; H, 5.43. Found: C, 77.68; H, 5.24.

(16) Synthesis of (*R*)-**2**: A mixture of (*R*)-*p*-MeO-BINAP (202 mg, 0.27 mmol), $[RuCl_2(COD)]_n$ (76 mg, 0.27 mmol as monomeric form), toluene (30 mL), and triethylamine (1 mL) was heated at 110 °C for 8 h. In this period, the mixture became clear and reddish brown. Concentration of the solution gave a mixture of (*R*)-**2** and (*R*)-**3** as analyzed by ^{31}P NMR. Recrystallization of the above mixture from dichloromethane (3 mL) and ether (20 mL) gave (*R*)-**2** in 37% yield as deep red crystals. (*R*)-**2**: mp 120 °C dec. ^1H NMR (270 MHz, $CDCl_3$): δ 1.42 (t, 6H, *J* = 7.4 Hz, CH_2CH_3), 3.05 (m, 2H, $CHHCH_3$), 3.26 (m, 2H, $CHHCH_3$), 3.42 (s, 6H, OCH_3), 3.44 (s, 6H, OCH_3), 3.58 (s, 6H, OCH_3), 3.71 (s, 6H, OCH_3), 5.95 (dd, *J* = 1.3 and 8.6 Hz, 4H), 6.05−6.15 (m, 8H), 6.55−6.7 (m, 6H), 6.85−6.95 (m, 2H), 7.0−7.2 (m, 6H), 7.2−7.35 (m, 4H), 7.35−7.6 (m, 20H), 7.8−7.95 (m, 2H), 7.95−8.1 (m, 4H), 8.56 (broad s, 2H, H_2N). The ^1H NMR spectrum exhibited signals due to 1 equiv of dichloromethane and 2 equiv of diethyl ether. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 52.0 and 49.5 (*J* = 38.0 Hz). Anal. Calcd for $C_{100}H_{92}Cl_5NO_8P_4Ru_2(C_4H_{10}O)_2(CH_2Cl_2)$: C, 60.26; H, 5.29; N, 0.64. Found: C, 60.78; H, 4.97; N, 0.62.

(17) (*R*)-**3** was synthesized separately by the reaction of (*R*)-*p*-MeO-BINAP (200 mg, 0.27 mmol), $[RuCl_2(COD)]_n$ (36 mg, 0.13 mmol as monomeric form) in ethanol (30 mL), and triethylamine (1 mL) at reflux temperature in almost quantitative yield as a yellow powder. ^1H NMR (400 MHz, $CDCl_3$): δ −16.6 (tt, 1H, *J* = 14 and 24 Hz, Ru-*H*), 3.42 (s, 6H, OCH_3), 3.45 (s, 6H, OCH_3), 3.47 (s, 6H, OCH_3), 3.53 (s, 6H, OCH_3), 5.4−9.0 (m, 56H, aromatic protons). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 20.0 (t, *J* = 34 Hz), 34.6 (t).

(18) Temperature-dependent $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$) of (*R*)-**2**: δ 51.3 and 49.6 (*J* = 38 Hz) at 80 °C, 52.0 and 49.5 (*J* = 38 Hz) at room temperature (23 °C), 53.5 and 49.3 (*J* = 37 Hz) at −60 °C. Differences between two phosphorus signals ($\Delta\delta$) became small at high temperature ($\Delta\delta$: 4.2 at −60 °C, 2.5 at 23 °C, and 1.7 at 80 °C).

(19) Crystal data for (*R*)-**2**: orthorhombic, space group $C222_1$, fw = 2172.31 for $C_{109}H_{114}Cl_7O_{10}NP_4Ru_2$ (one dichloromethane and two diethyl ether solvent molecules), *a* = 21.464(4) Å, *b* = 22.770(4) Å, *c* = 25.656(4) Å, *V* = 12 538(3) Å^3, *Z* = 4, μ(Mo Kα) = 4.89 cm^{-1}, d_{calcd} = 1.151 g/cm^3. Diffraction data were collected on a Rigaku AFC-5R diffractometer. The 5444 unique reflections with $I > 3\sigma(I)$ were considered as observed. The crystal structures were solved by direct methods (SHELXS86: Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; p 175). A series of standard full-matrix least-squares refinement and Fourier synthesis revealed the remaining atoms. Hydrogen atoms bound to aromatic carbon atoms were located as fixed contributions after idealization (C−H = 0.95 Å). All calculations were performed using the TEXSAN crystallographic software package. Residual values for 555 parameters were *R* = 0.062 and R_w = 0.062.

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butane).[22] It is noteworthy that the formation of a stable Ru(II) complex such as (*R*)-**2** is attributed to the presence of the triaryl phosphine of the BINAP ligand, which might be one of the reasons the BINAP−Ru(II) complexes are superior catalyst precursors for hydrogenations compared to other ruthenium complexes bearing alkyl-substituted phosphine ligands. The bridging chloride Cl(1) *trans* to a terminal chloride has a Ru−Cl distance (2.441(4) Å) shorter than that of the bridging chloride atoms *trans* to phosphine atoms (2.491(4) Å). This might be explained in terms of the weaker *trans* effect of the Cl ligand compared to that of the phosphorus ligand. The dihedral angle between the two naphthyl planes of **2** is 70.4°, a value of which lies in the range (66−75.7°) found for $[RuCl(\eta^6\text{-}C_6H_6)((S)\text{-BINAP})]^+$ [6] and ruthenium carboxylate complexes $Ru(OCOR)_2$-(BINAP).[4,7]

Complex **2** is an excellent catalyst precursor for the asymmetric hydrogenation of ketonic and olefinic substrates, exhibiting almost the same catalytic activity and enantioselectivity for the hydrogenation as with BINAP complexes. When (*R*)-**2** was used as a catalyst, hydrogenation of methyl 3-oxobutanoate under standard conditions (H_2 100 kg/cm^2, methanol−dichloromethane, 27 h, *s*/*c* = 4000) afforded methyl (*R*)-3-hydroxybutanoate in >99% *ee*.[23] The hydrogenation of tiglic acid by using (*R*)-**2** (THF−ethanol−NEt_3, H_2 4 kg/cm^2, 13.5 h, *s*/*c* = 170) led to (*R*)-2-methylbutanoic acid in 73% *ee*,[24] a value slightly lower than that (81% *ee*) obtained by the BINAP analogue.

Thus, we have elucidated structural details of the anionic dinuclear ruthenium complex **2** by single-crystal X-ray analysis and showed that **2** exhibits high catalytic activity and enantioselectivity. We continue in our efforts to determine the structures of catalytically active species derived from **2**.[25]

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Supporting Information Available: Text giving experimental details for the preparation of (*R*)-*p*-MeO-BINAP and tables of final positional parameters, final thermal parameters, and all bond distances and angles and a drawing with the numbering scheme (for (*R*)-**2** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead for ordering information and Internet access instructions.

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(23) Asymmetric hydrogenation of tiglic acid: Tiglic acid (175 mg, 1.75 mmol) was treated in the presence of (*R*)-**2** (9.6 mg, 5.3 mmol) in THF (10 mL), ethanol (10 mL), and triethylamine (0.4 mL) under H_2 (4 kg/cm^2) at 30 °C for 13.5 h. GC analysis showed no substrate and a single product, 2-methylbutanoic acid. Concentration and bulb-to-bulb distillation gave pure product. The produced acid was derivatized to the amide of (*R*)-(1-(1-naphthyl)ethyl)amine with diethyl cyanophosphonate as a condensation reagent. HPLC analysis of the amide synthesized (Chemco Nucleosil 100-3, 4.6 mm × 250 mm, hexane−ether (7:3), 1 mL/min, t_R = 19 and 23 min; 13.4:86.6) showed 73% *ee* as the *R* isomer.

(24) Asymmetric hydrogenation of methyl 3-oxobutanoate: A mixture of methyl acetoacetate (0.70 g, 6.0 mmol) and (*R*)-**2** (3.1 mg, 1.5 μmol) in methanol (3 mL) and dichloromethane (1 mL) was stirred at 30 °C for 27 h under H_2 (100 kg/cm^2). GC analysis of the reaction mixture showed no substrate and a lone product. It was identified by ^{1}H NMR of the product purified by bulb-to-bulb distillation (0.59 g). The MTPA ester of methyl 3-hydroxybutanoate obtained was analyzed by ^{1}H NMR. Diastereomeric signals of methyl at the C4 position of the butanoate was observed only at 1.34 ppm, which indicated that the enantiomeric excess is >99%, because these signals of the MTPA ester derived from racemic methyl 3-hydroxybutanoate appear at 1.34 and 1.45 ppm in a similar integrated ratio.

(25) Hydrogenation catalyzed by dinuclear ruthenium complexes: Daniel, E.; Chau, K.-Y.; James, B. R. *Inorg. Chim. Acta*, in press. Joshi, A. M.; MacFarlane, K. S.; James, B. R. *J. Organomet. Chem.* **1995**, *488*, 161.