Synthesis of New Cationic BINAP–Ruthenium(II) Complexes and their Use in Asymmetric Hydrogenation [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl]

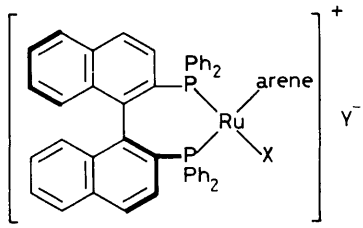
Kazushi Mashima,[a] Koh-hei Kusano,[a] Tetsuo Ohta,[a] Ryoji Noyori,[b] and Hidemasa Takaya*[a]

[a] *Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan*
[b] *Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan*

Reaction of $[RuX_2(arene)]_2$ (**1**) and (*S*)-BINAP gives cationic BINAP–ruthenium complexes of the formula $\{RuX(arene)[(S)\text{-binap}]\}Y$ (**2**) (X = Cl, Br, and I; Y = Cl, Br, I, BF_4, and BPh_4; arene = C_6H_6 and *p*-$MeC_6H_4CHMe_2$) which are efficient catalyst precursors for enantioselective hydrogenation of various prochiral alkenic and ketonic substrates [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl]; a crystal structure of (**2**) (with X = Cl, Y = BF_4) was obtained.

We report here the synthesis of new cationic BINAP–Ru^{II} complexes [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] which serve as excellent catalyst precursors for asymmetric hydrogenations.[1,2]

Treatment of $[RuCl_2(C_6H_6)]_2$ (**1a**)[3] with one equivalent of (*S*)-BINAP in an 8:1 mixture of ethanol and benzene at 50—55 °C for 40 min afforded a clear orange coloured solution, from which cationic complex (**2a**) was isolated as a reddish orange coloured solid in 90% yield.† Complex (**2b**) was synthesized in 94% yield from $[RuBr_2(C_6H_6)]_2$ (**1b**) and (*S*)-BINAP. A similar reaction of $[RuI_2(C_6H_6)]_2$ (**1c**) with (*S*)-BINAP afforded rather unstable (**2c**), which is prone to loss of the benzene ligand in solution. The chloride ion of (**2a**)



(**2**) arene = C_6H_6
a; X = Y = Cl
b; X = Y = Br
c; X = Y = I
d; X = Cl, Y = BF_4
e; X = Cl, Y = BPh_4

(**3**) arene = *p*-$MeC_6H_4CHMe_2$
a; X = Y = Cl
b; X = Y = Br
c; X = Y = I

† Satisfactory elemental analyses and consistent n.m.r. spectral data were obtained for all new complexes unless otherwise stated. ^{31}P n.m.r. data (162 MHz, $CDCl_3$, 85% H_3PO_4 as external standard): (**2a**) δ 30.3 and 38.3 (*J* 64.6 Hz); (**2b**) δ 29.8 and 37.1 (*J* 61.0 Hz); (**2c**) δ 28.2 and 36.1 (*J* 61.0 Hz); (**2d**) δ 29.8 and 37.8 (*J* 64.6 Hz); (**2e**) δ 30.2 and 37.9 (*J* 62.6 Hz); (**3a**) δ 24.5 and 41.2 (*J* 62.6 Hz); (**3b**) δ 24.7 and 41.0 (*J* 60.7 Hz); (**3c**) δ 24.7 and 41.6 (*J* 60.6 Hz); (**4**) δ 28.9 and 36.7 (*J* 62.6 Hz); (**5**) δ 23.0 and 39.3 (*J* 62.6 Hz).

Table 1. Asymmetric hydrogenation catalysed by cationic BINAP-Ru^{II} complexes (**2**) and (**3**).[a]

Substrate	Catalyst	S/C[b]	Solvent	H_2/ kg cm^{-2}	Temp. /°C	Time /h	E.e./%	Configuration[c]
Methyl 3-oxo-butanoate	(**2a**)	2000	MeOH	95	17	44	98	(*S*)[d,e]
	(**2c**)	2100	CH_2Cl_2	100	50	35	97	(*S*)[d]
	(**3c**)	2500	MeOH	100	30	35	99	(*S*)[d,e]
	(**3c**)	2200	MeOH–H_2O[f]	100	30	35	98	(*S*)[d]
N,*N*-Dimethyl-aminoacetone	(**3c**)	1100	EtOH–CH_2Cl_2[g]	105	30	40	99	(*S*)[h]
(*E*)-2-Methyl-2-butenoic acid	(**2d**)	1000	MeOH	4	20	92	89	(*S*)[i]
	(**3c**)	1300	MeOH	4	65	17	86	(*S*)[i]
2-(6-Methoxy-2-naphthyl)-propenoic acid	(**3c**)	200	MeOH	116	−20	17	96	(*S*)[j]
Geraniol	(**3c**)	1900	MeOH–H_2O[f]	100	20	8	96	(*R*)[k,l,m]
	(**3c**)	5000	MeOH	112	60	10	95	(*R*)[j,n]

[a] Hydrogenations were carried out in 0.2—8.7 M solution of the substrate (2.3—13.9 mmol). Conversions of the starting material were complete unless otherwise described. [b] Substrate to catalyst ratio. [c] Determined by the sign of optical rotation. [d] Determined by h.p.l.c. analysis after conversion to the ester of (+)-methoxy(trifluoromethyl)phenylacetic acid [(+)-MTPA]. [e] The dimethyl acetal of methyl 3-oxobutanoate was formed in 1.1—3.4% yield. The formation was avoided by use of 95—99% aqueous methanol as solvent. [f] MeOH : H_2O = 95 : 5. [g] EtOH : CH_2Cl_2 = 5 : 2. [h] Determined based on ^1H n.m.r. (400 MHz) spectrum after conversion to the ester of (+)-MTPA. [i] Determined by h.p.l.c. analysis of the amide derived from the product and (*R*)-1-(1-naphthyl)ethylamine. [j] Enantiomeric excess of methyl ester of naproxen was determined by h.p.l.c. analysis (Chiralcel OD column, 4.6 × 250 mm, hexane : propan-2-ol = 99 : 1). [k] Determined by h.p.l.c. analysis of the amide prepared by condensation of (*R*)-1-(1-naphthyl)ethylamine and citronellic acid, obtained by the Jones oxidation. [l] The conversion was 91%. [m] Dihydrocitronellol (0.3%) was detected by g.l.c. [n] Dihydrocitronellol (0.6%) was detected by g.l.c.

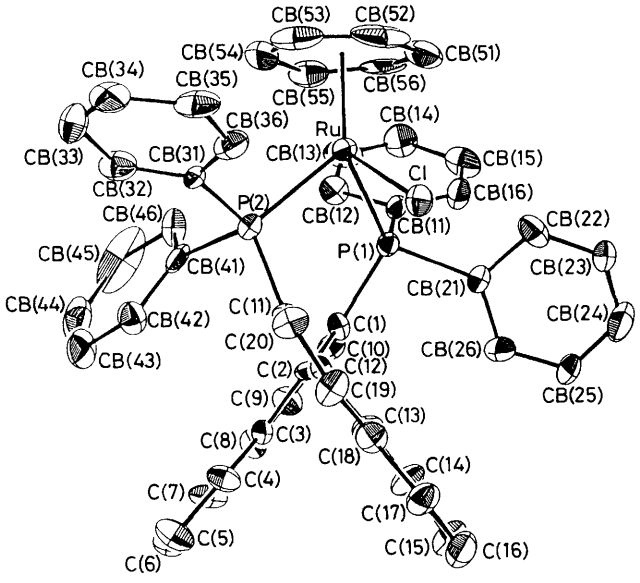


Figure 1. An ORTEP drawing of {$RuCl(C_6H_6)$[(*S*)-binap]}$^+$. Selected interatomic distances (Å) and angles (°): Ru–P(1) 2.379(3), Ru–P(2) 2.334(3), Ru–Cl 2.393(4), Ru–C_6H_6 1.770; P(1)–Ru–P(2) 91.4(1), P(1)–Ru–Cl 89.1(1), P(2)–Ru–Cl 84.9(1), P(1)–Ru–C_6H_6 126.3, P(2)–Ru–C_6H_6 129.8, Cl–Ru–C_6H_6 122.5. C_6H_6 is the centroid of benzene co-ordinated to ruthenium.

could be replaced by BF_4^- or BPh_4^- by treatment with $AgBF_4$ in dichloromethane or $NaBPh_4$ in methanol to afford complexes (**2d**) and (**2e**), respectively. The *p*-cymene complexes (**3a**) and (**3b**), prepared by the reaction of $[RuCl_2(p\text{-cymene})]_2$ (**1d**)[3b] or $[RuBr_2(p\text{-cymene})]_2$ (**1e**)[4] with (*S*)-BINAP in 94% and 97% yields, respectively, are more stable than the corresponding benzene complexes (**2**), and even iodide complex (**3c**) could be isolated in pure form in 94% yield by the reaction of $[RuI_2(p\text{-cymene})]_2$ (**1f**)[4]‡ and (*S*)-BINAP in a 4 : 1 mixture of ethanol and dichloromethane. When (*S*)-*p*-TolBINAP [*p*-TolBINAP = 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl] was allowed to react with (**1a**) or (**1d**), the cationic complexes {$RuCl(C_6H_6)$[(*S*)-*p*-tolbinap]}Cl (**4**) and {$RuCl(p\text{-cymene})$[(*S*)-*p*-tolbinap]}Cl (**5**) were obtained in 95% and 96% yields, respectively.

An ORTEP view of the complex (**2d**) determined by *X*-ray crystallography§ is shown in Figure 1. The ruthenium atom has a pseudo-octahedral geometry defined by chloride, two phosphorus atoms of BINAP, and a tridentate benzene ligand. Bond lengths of Ru–P(1) [2.379(4) Å] and Ru–P(2) [2.333(3) Å] are nonequivalent. Another characteristic

‡ Complex (**1f**)[4] was conveniently prepared by stirring a solution of ruthenium trichloride hydrate and 4 equiv. of *p*-mentha-1,5-diene in 90% ethanol at 50 °C for 5 h followed by dropwise addition of the resulting orange coloured mixture to a solution of excess KI in 50% ethanol. An air-stable purple coloured solid precipitated and was collected on a glass filter and dried *in vacuo* to give (**1f**) in 76% yield.

§ Orange coloured crystals of (**2d**) suitable for an *X*-ray diffraction study were grown by slow diffusion of hexane into a saturated solution of (**2d**) in dichloromethane. *Crystal data*: for (**2d**), $C_{51}H_{40}BCl_3F_4P_2Ru$; M = 1009.06, orthorhombic, space group $P2_12_12$, a = 20.141(2), b = 18.504(1), c = 12.241(1) Å, U = 4562.0(7) Å^3, Z = 4, D_c = 1.469 g cm^{-3}, crystal size; 0.22 × 0.48 × 0.58 mm, μ (Mo-K_α) = 6.368 cm^{-1}. The structure was solved by the Patterson method and refined *via* block-diagonal least-squares and Fourier techniques. Atoms of BF_4 and two molecules of disordered dichloromethane were located at positions defined by difference Fourier synthesis as having 0.5 occupancy. All hydrogen atoms were placed at the calculated positions. All non-hydrogen atoms were refined as anisotropic thermal parameters. Carbon atoms of dichloromethane, B of BF_4, and hydrogen atoms were refined as isotropic thermal parameters. The structure was refined to final residuals of R = 0.078 and R_w = 0.093 for 728 variables and 4177 observed reflections (absorption corrected) with $|F_o| > 3\sigma(F_o)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

feature is the dihedral angle between two naphthyl planes. The value of 75.7(2)° for complex (**2d**) is comparable to that of 74.4° for {Rh(norbornadiene)[(*R*)-binap]}ClO_4[5] and much larger than the value of 65.6° found for $Ru(OCOCMe_3)_2$[(*S*)-binap].[1]

Thus, complexes (**2**) and (**3**) can be prepared in high yields and in high purity. Moreover we found that the arene ligands are easily liberated under the catalytic conditions to afford co-ordinatively unsaturated species which exhibit sufficient catalytic activity and selectivity in the hydrogenation of a number of unsaturated substrates. Some representative examples are shown in Table 1. Methyl 3-oxobutanoate was hydrogenated in the presence of the cationic (*S*)-BINAP-Ru^{II} complexes under hydrogen (95—100 kg cm^{-2}) in methanol or dichloromethane to give methyl (*S*)-3-hydroxybutyrate in 97—99% enantiomeric excess (e.e.). Geraniol was hydrogenated in the presence of (**3c**) to (*R*)-citronellol in 96% e.e., where the allylic and nonallylic double bonds were well differentiated. (*E*)-2-Methyl-2-butenoic acid and 2-(6-methoxy-2-naphthyl)propenoic acid were converted to (*S*)-2-methylbutanoic acid and (*S*)-naproxen in up to 89 and 96% e.e., respectively.

We gratefully acknowledge Professor M. A. Bennett (Australian National University) for his helpful discussions and financial support from the Ministry of Education, Science and Culture, Japan (No. 62065005, 63106004, 63540415).

Received, 15th March 1989; Com. 9/01137D

References

1 T. Ohta, H. Takaya, and R. Noyori, *Inorg. Chem.*, 1988, **27**, 566.
2 R. Noyori, M. Ohta, Yi Hsiao, M. Kitamura, T. Ohta, and H. Takaya, *J. Am. Chem. Soc.*, 1986, **108**, 7117; H. Takaya, T. Ohta, N. Sayo, H. Kumobayashi, S. Akutagawa, S. Inoue, I. Kasahara, and R. Noyori, *ibid.*, 1987, **109**, 1596, 4129; T. Ohta, H. Takaya, M. Kitamura, K. Nagai, and R. Noyori, *J. Org. Chem.*, 1987, **57**, 3174; M. Kitamura, Yi Hsiao, R. Noyori, and H. Takaya, *Tetrahedron Lett.*, 1987, **28**, 4829; R. Noyori, T. Ohkuma, M. Kitamura, T. Takaya, N. Sayo, H. Kumobayashi, and S. Akutagawa, *J. Am. Chem. Soc.*, 1987, **109**, 5856; M. Kitamura, T. Ohkuma, S. Inoue, N. Sayo, H. Kumobayashi, S. Akutagawa, T. Ohta, H. Takaya, and R. Noyori, *ibid.*, 1988, **110**, 629.
3 (a) R. A. Zelonka and M. C. Baird, *Can. J. Chem.*, 1972, **50**, 3063; (b) M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.
4 R. O. Gould, C. L. Jones, T. A. Stephenson, and D. A. Tocher, *J. Organomet. Chem.*, 1984, **264**, 365.
5 K. Toriumi, T. Ito, H. Takaya, T. Souchi, and R. Noyori, *Acta Crystallogr., Sect. B*, 1982, **38**, 807.