Synthesis and Characterization of Mono- and Tri-nuclear Ruthenium Complexes of 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl and Their Catalytic Activity†

Kazushi Mashima, Takahiro Hino and Hidemasa Takaya*
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

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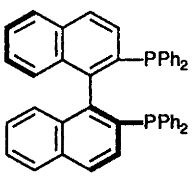
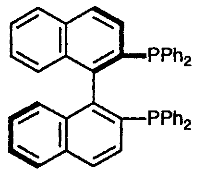
The structures of ruthenium(II) complexes formed in solution from [RuX{(*S*)-binap}(arene)]Y (*S*)-**3** (X, Y = halide and/or BF_4^-; binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; arene = benzene or *p*-cymene) depend on the solvent. In acetonitrile–methanol (1 : 1) dicationic complexes [Ru{(*S*)-binap}$(MeCN)_4$]X(Y) (*S*)-**4** (X = Y = Cl **a**; X = Cl, Y = BF_4 **b**; X = Y = Br **c**; or X = Y = I **d**) are predominantly formed, while monocationic species [RuX{(*S*)-binap}$(MeCN)_3$]X (*S*)-**6** (X = Cl **a**, Br **b** or I **c**) were observed in acetonitrile. These mono- and di-cationic species could not be isolated pure, while [$RuCl_2${(*S*)-binap}$(MeCN)_2$] (*S*)-**5** was isolated from (*S*)-**4a** or (*S*)-**6a** upon concentration of the reaction mixture. In methanol without donor molecules such as acetonitrile, cationic trinuclear complexes [Ru_3X_5{(*S*)-binap}$_3$]Y (*S*)-**7** (X = Y = Cl **a**; X = Cl, Y = BF_4 **b** or X = Y = Br **c**) were exclusively formed by heating at 60 °C or UV irradiation of a solution of (*S*)-**3**. The structure of (*S*)-**7** was characterized by spectral data and an X-ray crystallographic analysis of (*S*)-**7b** [orthorhombic, space group $P2_12_12_1$, $a = 26.328(5)$, $b = 18.140(3)$, $c = 26.374(4)$, $Z = 4$, $R' = 0.083$]. The relationship between the structure of the Ru^{II}(binap) complexes and their catalytic activities for asymmetric hydrogenation of methyl 3-oxobutanoate has been investigated.

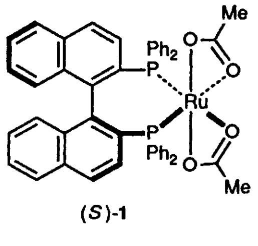
Transition-metal complexes possessing binap [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] or its derivatives have been used as catalysts for various types of asymmetric reactions.[1–11] Recently, we have reported that the complex [$Ru(OCOMe)_2$(binap)] **1** is an efficient catalyst for asymmetric hydrogenation of olefinic substrates.[2,3] However, it showed almost no catalytic activity for hydrogenation of α- and β-functionalized ketones such as methyl 3-oxobutanoate. On the other hand, addition of 2 equivalents of HX to complex **1** followed by removal of all volatiles *in vacuo* gives rise to highly efficient catalyst systems described by an empirical formula [RuX_2(binap)] **2** [equation (1)] for asymmetric hydrogenation of α- and β-functionalized ketones, giving the corresponding secondary alcohols in high enantioselectivity.[4] Recently, we have also synthesized well characterized cationic mononuclear ruthenium(II) dihalide complexes [RuX(binap)(arene)]Y **3** and showed that they are excellent catalysts for asymmetric hydrogenation of α- and β-functionalized ketones.[6] In spite of the high efficiency of catalysts **2** and **3** we know very little about their chemical behaviour in solution. Here we report several new Ru^{II}(binap) complexes formed under various conditions.[12] Their catalytic activities for hydrogenation of β-keto esters are discussed based on their structures.

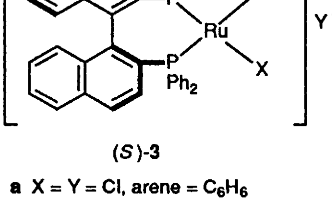
$$(S)\text{-}\mathbf{1} \xrightarrow[(b)\ \text{removal of the solvent}]{(a)\ 2HX,\ CH_2Cl_2} [RuX_2\{(S)\text{-binap}\}] \qquad (1)$$

(*S*)-**2**
a X = Cl
b X = Br


(*S*)-binap


(*R*)-binap


(*S*)-**1**


(*S*)-**3**

a X = Y = Cl, arene = C_6H_6
b X = Cl, Y = BF_4, arene = C_6H_6
c X = Y = Br, arene = C_6H_6
d X = Y = Br, arene = *p*-$MeC_6H_4Pr^i$
e X = Y = I, arene = *p*-$MeC_6H_4Pr^i$

Results and Discussion

Synthesis and Characterization of Ru^{II}(binap)(MeCN) *Complexes.*—The cationic mononuclear complex [RuCl{(*S*)-binap}(C_6H_6)]Cl (*S*)-**3a** was dissolved in acetonitrile–[$^2H_4$]methanol (1 : 1) in an NMR tube and the reaction was monitored by ^{31}P-{^1H} NMR spectroscopy. When the mixture was kept at 60 °C for 20 h signals due to (*S*)-**3a** disappeared and a new singlet

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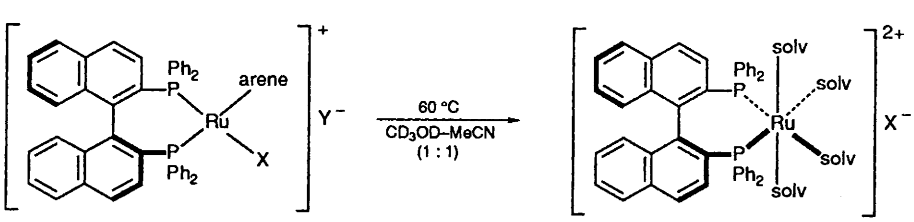
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

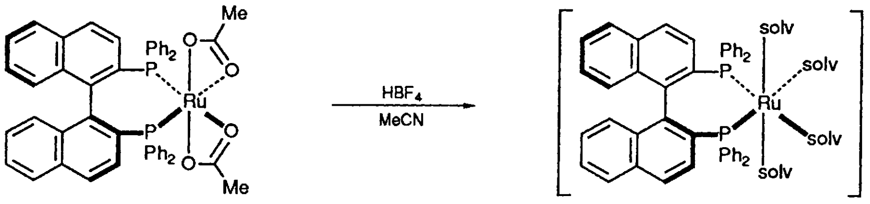


(2)

(S)-3

a X = Y = Cl, arene = C_6H_6
b X = Cl, Y = BF_4, arene = C_6H_6
d X = Y = Br, arene = p-$MeC_6H_4Pr^i$
e X = Y = I, arene = p-$MeC_6H_4Pr^i$

(S)-4
solv = MeCN
a X = Y = Cl
b X = Cl, Y = BF_4
c X = Y = Br
d X = Y = I



(3)

(S)-1

(S)-4e
solv = MeCN

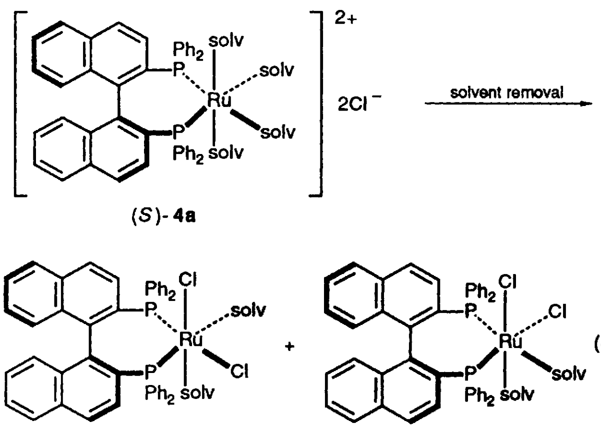
Table 1 ^{31}P-{^1H} NMR spectral data for new Ru^{II}(binap) complexes

Complex	δ (J/Hz)
4a[a]	43.6 (s)
4b[a]	43.6 (s)
4c[a]	43.5 (s)
4d[a]	43.6 (s)
4e[a]	43.7 (s)
4e[b]	46.1 (s)
4f[b]	46.2 (s), −144 (spt, J_{PF} = 713, PF_6)
5[b,c]	54.8, 53.7 (ABq, J_{PP} = 35.2)
	51.7, 50.9 (ABq, J_{PP} = 35.2)
7a[b]	47.1 (s)
7b[b]	47.5 (s)
7c[b]	48.3 (s)

[a] Measured in CD_3OD–MeCN (1 : 1). [b] Measured in $CDCl_3$. [c] The ratio of the intensities of the two ABq signals was 9 : 1, q = quartet.

appeared at δ 43.6 which was assigned to the dicationic complex (S)-**4a** [equation (2) and Table 1]. The formation of the dicationic complex was supported by an alternative synthesis of dicationic complex (S)-**4e** by the addition of 2 equivalents of aqueous HBF_4 to a solution of complex (S)-**1** in acetonitrile. When all volatiles were removed under reduced pressure (S)-**4e** was obtained in quantitative yield [equation (3)]. The ^{31}P-{^1H} NMR spectrum of (S)-**4e** displayed a singlet at δ 43.7, which is comparable to that of dicationic complex (S)-**4a**. The ^1H NMR spectrum of (S)-**4e** in $CDCl_3$ exhibited two singlets at δ 2.27 and 2.29, which were assigned to two kinds of acetonitrile co-ordinated to ruthenium. Thus, co-ordination of four acetonitrile ligands to ruthenium in (S)-**3a** displaces two chloride anions and a benzene to afford dicationic complex (S)-**4a**.

Attempted isolation of complex (S)-**4a** by concentration of the solution failed, but the neutral complex [$RuCl_2${(S)-binap}-$(MeCN)_2$] (S)-**5** was obtained [equation (4)]. Elemental analysis established the stoichiometry of each ligand. The ^{31}P-{^1H} NMR spectrum in $CDCl_3$ displayed two sets of AB quartets (9 : 1 ratio) centred at δ 54.8 (J_{PP} = 35.2 Hz) and 53.7, and at δ 51.7 (J_{PP} = 35.2 Hz) and 50.9. The ^1H NMR spectrum of the major product exhibited two singlets due to two kinds of acetonitrile co-ordinated to ruthenium. Thus, the complex [{$RuCl_2$[(S)-binap](MeCN)}$_2$] can be ruled out by elemental analysis and ^1H NMR spectroscopy, though similar dinuclear complexes [{$RuCl_2(MeCN)(PPh_3)_2$}$_2$][13] and [Ru_2Cl_3(Me-CN)$_2$(dppb)$_2$]PF_6 [dppb = 1,4-bis(diphenylphosphino)butane][14] have been reported. The IR absorption at 2274 cm^{-1} assignable to ν(CN) of acetonitrile co-ordinated to ruthenium is comparable with values of 2243–2230 cm^{-1} reported for monomeric *trans*- and *cis*-[$RuCl_2(MeCN)_2(PPh_3)_2$].[13,15] These data supported the neutral monomeric structure of (S)-**5**. Although the spectral properties of the minor product have not been determined, except for the ^{31}P-{^1H} NMR spectrum, the above data suggest that (S)-**5** is a mixture of stereoisomers assignable to Λ- and Δ-(S)-**5**.



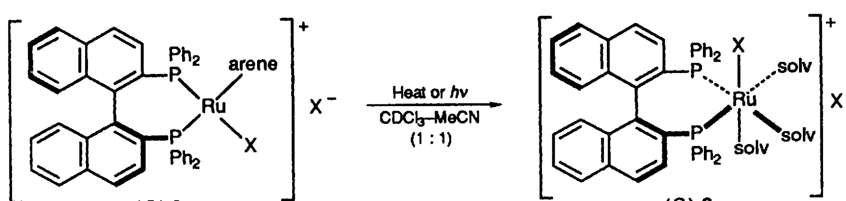
(4)

Λ-(S)-5 Δ-(S)-5

solv = MeCN

When complex (S)-**3b** was treated under the same conditions as for (S)-**3a**, a ^{31}P NMR singlet due to the dicationic complex (S)-**4b** bearing chloride and BF_4^- anions was observed at δ 43.6, the same chemical shift value as that for (S)-**4a**. Similar treatments of (S)-**3d** and (S)-**3e** afforded (S)-**4c** and (S)-**4d**, respectively, which also exhibited in the ^{31}P-{^1H} NMR spectra singlets at δ 43.5 and 43.6, in the same chemical shift region as those of (S)-**4a** and (S)-**4e** (Table 1).

In contrast to the formation of dicationic species in a mixture of acetonitrile and methanol, monocationic Ru^{II}(binap) complexes were formed in the absence of methanol. When a solution of the iodide complex (S)-**3e** in acetonitrile was heated at reflux for 24 h and then concentrated *in vacuo*, the



(S)-3 (S)-6

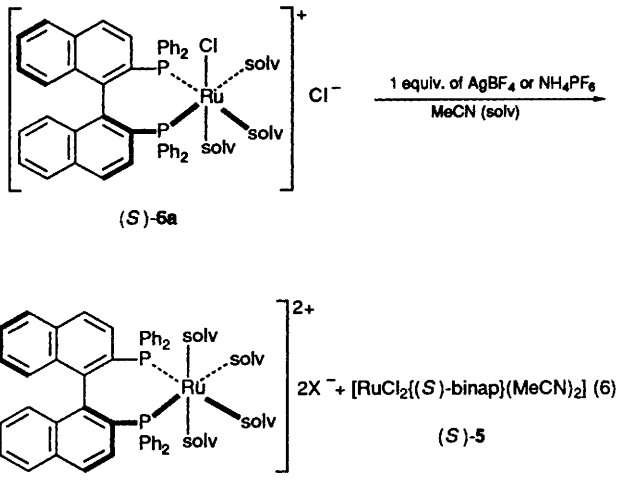
a X = Cl, arene = C_6H_6
d X = Br, arene = p-$MeC_6H_4Pr^i$
e X = I, arene = p-$MeC_6H_4Pr^i$

a X = Cl
b X = Br
c X = I

Table 2 Variable-temperature ^{31}P-{^1H} NMR spectral data and thermodynamic parameters calculated for the fluxional process of [RuX{(S)-binap}(MeCN)$_3$]X (S)-**6** in $CDCl_3$–MeCN (1 : 1)

Complex	δ at −30 °C (J/Hz)	Δν/Hz (at −30 °C)	T_c/K	$\Delta G^{\ddagger a}$/ kJ mol^{-1}
6a	47.7, 44.9 (ABq, J_{PP} = 32)	306	323	61.8
6b	48.4, 44.3 (ABq, J_{PP} = 31)	454	328	61.7
6c	46.5, 43.5 (ABq, J_{PP} = 30)	324	328	62.6

[a] $\Delta G^{\ddagger} = (1.987 \times 10^{-3})T_c[23.76 + \ln(T_c/k_c)]$ where $k_c = \pi(\Delta\nu)/2^{\frac{1}{2}}$.



(S)-6a

2X$^-$ + [$RuCl_2${(S)-binap}(MeCN)$_2$] (6)

(S)-5

(S)-4
e X = BF_4
f X = PF_6

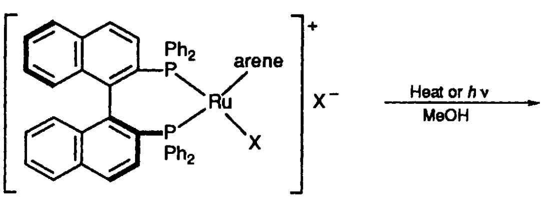
monocationic complex (S)-**6c** was obtained [equation (5)]. The ^{31}P-{^1H} NMR spectrum in $CDCl_3$ in the presence of a trace amount of acetonitrile exhibited a set of broad AB quartets at room temperature which afforded a sharp AB quartet centred at δ 46.7 (J_{PP} = 30 Hz) and 44.0 at −30 °C. The ^1H NMR spectrum in $CDCl_3$ containing a small amount of acetonitrile at −30 °C showed three singlets at δ 1.92, 2.05 and 2.65, which were assigned to three kinds of co-ordinated acetonitrile, along with a singlet at δ 2.00 due to free acetonitrile. These NMR spectra supported the structure of monocationic complex (S)-**6c**. Fluxionality in the structure of (S)-**6c** has been investigated by ^{31}P-{^1H} NMR spectroscopy in $CDCl_3$–acetonitrile (1 : 1). The broad AB quartet at room temperature became sharp at −30 °C to afford a sharp AB quartet centred at δ 46.5 (J_{PP} = 30 Hz) and 43.5, while at 55 °C a very broad signal centred at δ 44.9 was obtained. Coalescence of these AB pattern signals at 55 °C might be the consequence of a rapid replacement of iodide anions at two axial positions of (S)-**6c**. It is of interest that the observation of such a fluxional process is only possible for ruthenium(II) complexes co-ordinated by a chiral chelating ligand with C_2 symmetry. The $\Delta G^{\ddagger}$ value for this fluxional process was determined (Table 2). Unfortunately, when free acetonitrile was removed by concentration of the solution followed by washing the residue with diethyl ether, complex (S)-**6c** decomposed to give a complex mixture as shown by ^{31}P-{^1H} NMR spectroscopy.

In order to investigate the behaviour of the chloride complex (S)-**3a** in acetonitrile, it was dissolved in acetonitrile–$CDCl_3$ (1 : 1) in an NMR tube and the reaction was monitored by ^{31}P-{^1H} NMR spectroscopy. When the mixture was heated at 50 °C for 24 h signals due to (S)-**3a** disappeared and a new broad AB quartet assignable to a monocationic complex [RuCl{(S)-binap}(MeCN)$_3$]Cl (S)-**6a** appeared at δ 48 (J_{PP} = 30 Hz) and 45. Complex (S)-**6a** exhibited a similar fluxionality to that of (S)-**6c** on the variable-temperature measurement of ^{31}P-{^1H} NMR spectra (Table 2). In contrast to the iodide (see above), concentration of the solution of this mononuclear complex in acetonitrile did not allow the isolation of (S)-**6a**, but afforded the neutral complex (S)-**5**.

On the other hand, when the dibromide complex (S)-**3d** was dissolved in acetonitrile–$CDCl_3$ (1 : 1) in an NMR tube and then heated at 50 °C for 24 h no change was observed in the ^{31}P-{^1H} NMR spectrum, which showed that (S)-**3d** is stable under these conditions. As arene ligands co-ordinated to ruthenium can be replaced by another arene ligand under UV irradiation,[15,16] this mixture was irradiated. As expected, photochemical removal of the p-cymene ligand of (S)-**3d** gave a monocationic complex (S)-**6b**. This complex also exhibited a similar molecular fluxionality in $CDCl_3$–MeCN(1 : 1) as monitored by variable-temperature ^{31}P-{^1H} NMR measurement. The $\Delta G^{\ddagger}$ value was determined (Table 2).

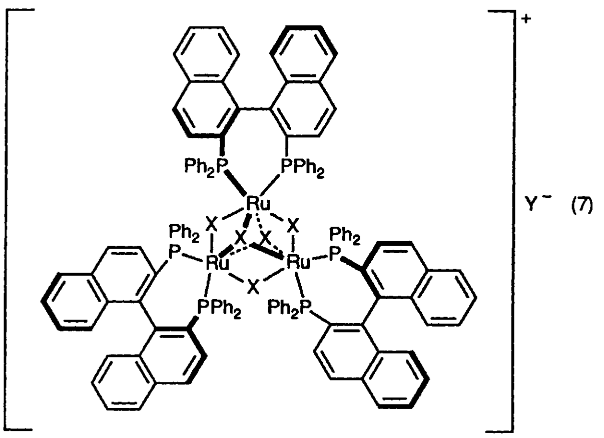
Isolation of the monocationic complex [RuCl{(S)-binap}(MeCN)$_3$]Y (Y = BF_4 or PF_6) was also attempted by exchanging one Cl$^-$ ion of (S)-**6a** by BF_4^- or PF_6^-, as for [RuCl(MeCN)$_3$(dppb)]PF_6.[14] However, a disproportionation occurred to give neutral complex (S)-**5** and dicationic (S)-**4e** or (S)-**4f** [equation (6)].

Formation of Cationic Trinuclear Ru(binap) *Complexes*.—A solution of complex (S)-**3a** in $CDCl_3$ was kept at 60 °C for 12 h and then the ^{31}P-{^1H} NMR spectrum was measured, showing no change. On the other hand, when a solution of (S)-**3a** was heated under similar conditions in the presence of a large excess of methanol, acetone, or ethyl 3-oxobutanoate the ^{31}P-{^1H} NMR spectra showed that a new trinuclear complex (S)-**7a** exhibiting a singlet at δ 47.1 has been predominantly formed along with a small amount of unidentified species [equation (7) and Table 1]. This shows that the use of a weakly co-ordinating polar solvent is important for the formation of cationic complex **7**. Complex (S)-**7a** was isolated in 62% yield as deep orange crystals when a solution of (S)-**3a** in methanol was heated at 60 °C for 12 h followed by recrystallization of the resulting precipitate from a mixture of dichloromethane, methanol and hexane.



(*S*)-**3**

a X = Cl, arene = C_6H_6
d X = Br, arene = p-$MeC_6H_4Pr^i$



(*S*)-**7**

a X = Y = Cl
b X = Cl, Y = BF_4
c X = Y = Br

Conductivity measurement of complex (*S*)-**7a** in dichloromethane revealed that it is cationic. One of the chloride anions was easily replaced by BF_4^- to afford (*S*)-**7b** in quantitative yield. Complex (*S*)-**3d** did not form the corresponding (*S*)-**7c** on heating the solution for a prolonged time (24 h). However, UV irradiation[15,16] of the solution caused liberation of the *p*-cymene ligand from (*S*)-**3d** to give (*S*)-**7c** in fair yield (40%).* In contrast, treatment of the iodoruthenium complex (*S*)-**3e** in a mixture of $CDCl_3$ and methanol at 60 °C for 6 h did not afford the corresponding trinuclear complex, but the $^{31}P-\{^1H\}$ NMR spectrum showed the formation of a transient species which exhibited an AB quartet (δ 9.4 and 75.2, J_{PP} = 38.4 Hz). This gradually disappeared to give a complex mixture. The UV irradiation of a solution of (*S*)-**3e** in methanol also did not afford the desired complex.

No fluxionality has been observed for (*S*)-**7a** based on the variable-temperature measurement of $^{31}P-\{^1H\}$ NMR spectra over the range −60 to 50 °C. The trinuclear structure was retained even in the presence of donor molecules such as triethylamine and dimethylacetamide at 60 °C. The lack of interaction of complex **7** with organic donor molecules might be the reason why it is inactive as a catalyst for the hydrogenation of β-keto esters (see below).

As previously reported,[4] the species **2** prepared by the addition of 2 equivalents of HCl to a solution of $[Ru(OCOMe)_2(binap)]$ **1** [equation (1)], has been used as a catalyst for asymmetric hydrogenation of α- and β-functionalized ketones. Interestingly, the $^{31}P-\{^1H\}$ NMR spectrum of the mixture prepared by the addition of 2 equivalents of HCl in aqueous methanol to a solution of (*R*)-**1** in CD_2Cl_2 showed an intense singlet at δ 48.9 due to (*R*)-**7a** along with a very small amount of unidentified species. Removal of all volatiles from this solution, however, afforded a complex mixture of Ru(binap) complexes, which converged again gradually on complex (*R*)-**7a** in $CDCl_3$–methanol (1:1). In contrast to the reaction of HCl, the $^{31}P-\{^1H\}$ NMR spectrum of the sample prepared by addition of 10 equivalents of aqueous HBr to (*R*)-**1** in $CDCl_3$–methanol (1:1) exhibited an AB quartet (δ 15.2 and 63.2, J_{PP} = 39.4 Hz) in addition to a singlet at δ 48.0 due to (*R*)-**7c**. The former signals gradually disappeared and finally only the singlet due to (*R*)-**7c** was observed. The former complex might be assignable to a halide-bridged dimeric complex of the type $[Ru_2Br_2(\mu\text{-}Br)_2\{(R)\text{-binap}\}_2]$, since a similar five-co-ordinate dinuclear complex $[Ru_2Cl_2(\mu\text{-}Cl)_2(dppb)_2]$ has been reported.[17] The properties of complex **7** will be discussed in relation to its catalytic activities (see below).

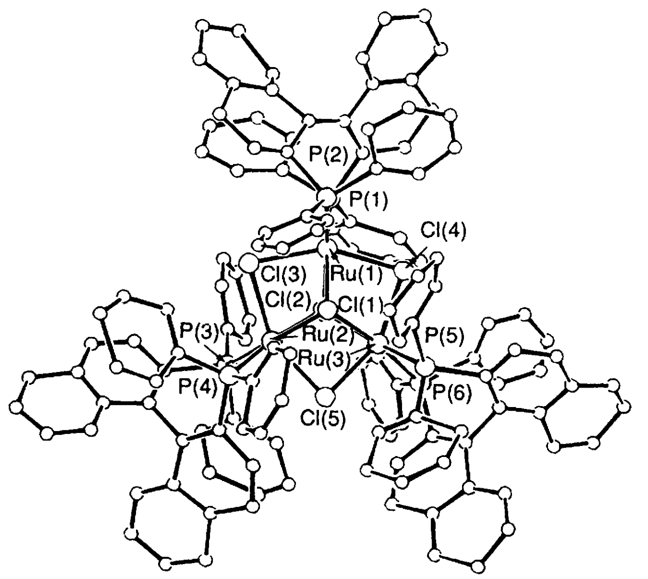


Fig. 1 An ORTEP drawing of complex (*S*)-**7b** with the atom numbering scheme

Crystal Structure of Cationic Trinuclear Complex (*S*)-**7b**.—The structure of cationic trinuclear complex (*S*)-**7b** (Fig. 1) was established by X-ray crystallography.[12] The complex has a cationic trinuclear $Ru_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3$ core, which is shown in Fig. 2 with the atom labelling scheme. A space-filling representation is shown in Fig. 3. Selected interactomic distances and angles are listed in Tables 3 and 4.

Bond distances between the three ruthenium atoms, Ru(1)–Ru(2) 3.383(3), Ru(1)–Ru(3) 3.334(3) and Ru(2)–Ru(3) 3.294(3) Å, are comparable to those reported (3.18–3.40 Å)[18,19] for the $Ru(\mu\text{-}Cl)_3Ru$ unit. These Ru–Ru bond distances are well outside the range (2.28–2.95 Å) expected for a Ru–Ru single bond.[19,20] The Ru–Cl [2.370(7)–2.557(8) Å] and Ru–P bond lengths [2.276(9)–2.303(9) Å] are normal and each ruthenium atom is co-ordinated in approximately octahedral geometry, as expected for Ru^{II}, defined by two phosphorus and four chloride atoms. The cationic molecule has pseudo D_3 symmetry. The trinuclear rhodium complex, $[\{Rh(binap)\}_3(\mu_3\text{-}OH)_2]^+$, has been reported to have a similar symmetry.[21] To the best of our knowledge, this is the first example of a trinuclear ruthenium complex with capping and edge-bridging halides determined by X-ray analysis,† though structures of trinuclear ruthenium complexes $[Ru_3O(OCOR)_6]$[23] and $[Ru_3Cl_5\{P(OEt)Ph_2\}_6]^+$

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* Although liberation of the aromatic ligand from (*S*)-**3c** might be easier than from (*S*)-**3d**, use of the latter as starting material is more convenient because it can be prepared readily in high purity. Purification of (*S*)-**3c** and its precursor $[\{RuBr_2(C_6H_6)\}_2]$ is not easy due to their low solubility in common organic solvents.

† Recently,[22] a similar trinuclear ruthenium(II) complex with 2,2′-bis(diphenylphosphino)-6,6′-dimethyl-1,1′-biphenyl has been reported.

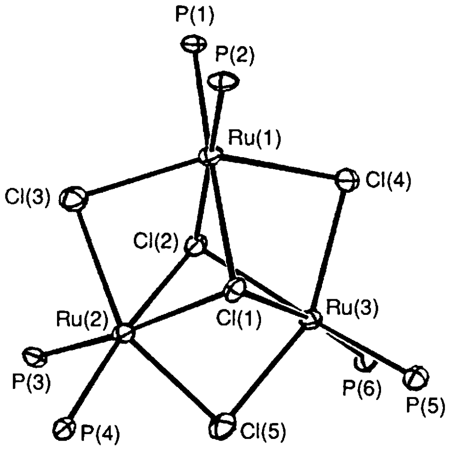


Fig. 2 An ORTEP drawing of the trinuclear cluster core of complex (*S*)-**7b** with the atom numbering scheme

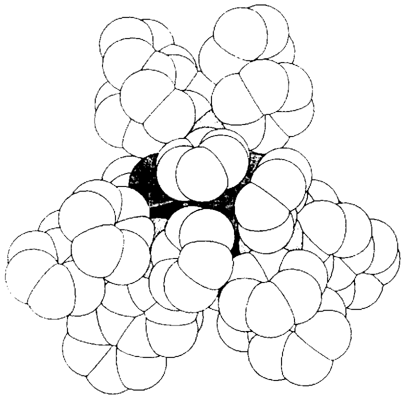


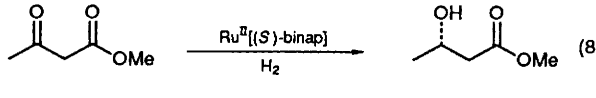
Fig. 3 Space-filling representation of complex (*S*)-**7b**. All hydrogens are omitted

Table 3 Selected bond distances (Å) of complex (*S*)-**7b**

Ru(1)–Ru(2)	3.383(3)	Ru(1)–Ru(3)	3.334(3)
Ru(2)–Ru(3)	3.294(3)	Ru(1)–P(1)	2.296(8)
Ru(1)–P(2)	2.283(9)	Ru(2)–P(3)	2.303(8)
Ru(2)–P(4)	2.276(9)	Ru(3)–P(5)	2.29(1)
Ru(3)–P(6)	2.303(9)	Ru(1)–Cl(1)	2.515(7)
Ru(1)–Cl(2)	2.530(6)	Ru(1)–Cl(3)	2.449(7)
Ru(1)–Cl(4)	2.451(7)	Ru(2)–Cl(1)	2.557(8)
Ru(2)–Cl(2)	2.470(7)	Ru(2)–Cl(3)	2.501(6)
Ru(2)–Cl(5)	2.370(7)	Ru(3)–Cl(1)	2.484(7)
Ru(3)–Cl(2)	2.556(8)	Ru(3)–Cl(4)	2.427(8)
Ru(3)–Cl(5)	2.375(7)		

having a $Ru_3(\mu\text{-}Cl)_4Cl$ core[24] and linear trinuclear complexes $[Ru_3Cl_8(PBu_3)_4]$[19b] and $[Ru_3Cl_{12}]^{4-}$ (ref. 19*c*) have been characterized by X-ray analyses. Each (*S*)-binap ligand coordinates to ruthenium to form a seven-membered chelate ring with λ conformation.

Catalytic Activities of Ru^{II}(binap) *Complexes for Hydrogenation of Methyl* 3-*Oxobutanoate*.—We chose asymmetric hydrogenation of methyl 3-oxobutanoate as a test reaction to investigate the catalytic activities of newly obtained Ru^{II}(binap) complexes [equation (8). The results are shown in Table 5.



(8)

When complex (*S*)-**2a** or (*S*)-**3e** was used as catalyst the hydrogenation proceeded smoothly and (*S*)-methyl 3-hydroxybutanoate was obtained in high yield and in high enantioselectivity (runs 1 and 2).[4a,6a] Dicationic complex (*S*)-**4e** exhibited almost no catalytic activity at 35 °C, and a small amount of the dimethyl acetal of methyl 3-oxobutanoate was formed (run 3). Complex (*S*)-**5**, which has two chloride ligands bound to ruthenium, had no catalytic activity at 20 °C, while at 55 °C hydrogenation proceeded smoothly to give methyl (*S*)-3-hydroxybutanoate (runs 4 and 5). Partial loss of enantioselectivity (93% enantiomeric excess), however, was observed at elevated temperature. In contrast, carefully prepared single crystals of (*S*)-**7a** and (*S*)-**7c** were found to be totally inert (runs 6 and 7). Therefore, complex **7** is a compound outside of the catalytic cycle. As can be seen from the crystal structure of (*S*)-**7b** (Fig. 3), the trinuclear cluster core is almost buried in bulky aromatic rings, which should prevent interaction of donor molecules and substrates with ruthenium atoms. On the other hand, when powdery (*S*)-**7a** was used without purification the hydrogenation proceeded smoothly (run 8). These facts suggest that a very small amount of catalytically active Ru^{II}(binap) complexes (less than 5%) contained in a crude sample of (*S*)-**7a** acts as a catalyst to give a reasonable rate of hydrogenation and high enantioselectivity. As described before, the reaction mixture obtained by addition of 2 equivalents of HCl to **1** contains mainly the cationic trinuclear complex **7a** and a small amount of unidentified Ru^{II}(binap) species. The residue obtained by concentration of the above reaction mixture [*cf.* equation (1)] is a complex mixture, but it is really an excellent catalyst.[4] The presence of a trace amount of acid and water, perhaps, caused the collapse of complex **7a** upon concentration to give various unidentified Ru^{II} [(*S*)-binap] species which served as excellent catalysts.

Table 4 Selected angles (°) of complex (*S*)-**7b**

P(1)–Ru(1)–P(2)	91.8(3)	P(1)–Ru(1)–Cl(1)	173.3(3)
P(1)–Ru(1)–Cl(2)	93.9(3)	P(2)–Ru(1)–Cl(1)	94.4(3)
P(2)–Ru(1)–Cl(2)	173.7(3)	Cl(1)–Ru(1)–Cl(2)	80.0(2)
P(3)–Ru(2)–P(4)	90.2(3)	P(3)–Ru(2)–Cl(1)	171.6(3)
P(4)–Ru(2)–Cl(1)	98.1(3)	P(5)–Ru(3)–P(6)	89.2(3)
P(5)–Ru(3)–Cl(1)	92.5(3)	P(6)–Ru(3)–Cl(1)	171.9(3)
Ru(1)–Cl(1)–Ru(2)	83.7(2)	Ru(1)–Cl(1)–Ru(3)	83.7(2)
Ru(1)–Cl(2)–Ru(2)	85.1(2)	Ru(1)–Cl(2)–Ru(3)	81.9(2)
Ru(1)–Cl(3)–Ru(2)	86.2(2)	Ru(1)–Cl(4)–Ru(3)	86.2(3)
Ru(2)–Cl(1)–Ru(3)	81.6(2)	Ru(2)–Cl(2)–Ru(3)	81.9(2)
Ru(2)–Cl(5)–Ru(3)	87.9(2)	Cl(1)–Ru(1)–P(1)	173.3(3)
Cl(1)–Ru(1)–P(2)	94.4(3)	Cl(1)–Ru(1)–Cl(2)	80.0(2)
Cl(1)–Ru(1)–Cl(3)	79.4(2)	Cl(1)–Ru(1)–Cl(4)	80.4(3)
Cl(2)–Ru(1)–P(1)	93.9(3)	Cl(2)–Ru(1)–P(2)	173.7(3)
Cl(2)–Ru(1)–Cl(3)	79.3(2)	Cl(2)–Ru(1)–Cl(4)	79.4(3)
Cl(3)–Ru(1)–P(1)	102.4(3)	Cl(3)–Ru(1)–P(2)	96.9(3)
Cl(3)–Ru(1)–Cl(4)	152.8(2)	Cl(4)–Ru(1)–P(1)	95.8(3)
Cl(4)–Ru(1)–P(2)	102.7(3)	Cl(1)–Ru(2)–P(3)	171.6(3)
Cl(1)–Ru(2)–P(4)	98.1(3)	Cl(1)–Ru(2)–Cl(2)	80.4(2)
Cl(1)–Ru(2)–Cl(3)	77.6(2)	Cl(1)–Ru(2)–Cl(5)	78.2(2)
Cl(2)–Ru(2)–P(3)	91.2(3)	Cl(2)–Ru(2)–P(4)	173.4(3)
Cl(2)–Ru(2)–Cl(3)	79.5(2)	Cl(2)–Ru(2)–Cl(5)	82.5(2)
Cl(3)–Ru(2)–P(3)	100.8(3)	Cl(3)–Ru(2)–P(4)	106.6(3)
Cl(3)–Ru(2)–Cl(5)	151.9(3)	Cl(5)–Ru(2)–P(3)	100.9(3)
Cl(5)–Ru(2)–P(4)	90.9(3)	Cl(1)–Ru(3)–P(5)	92.5(3)
Cl(1)–Ru(3)–P(6)	171.9(3)	Cl(1)–Ru(3)–Cl(2)	80.1(2)
Cl(1)–Ru(3)–Cl(4)	81.5(2)	Cl(1)–Ru(3)–Cl(5)	79.6(2)
Cl(2)–Ru(3)–P(5)	172.1(3)	Cl(2)–Ru(3)–P(6)	98.5(3)
Cl(2)–Ru(3)–Cl(4)	79.4(2)	Cl(2)–Ru(3)–Cl(5)	80.6(2)
Cl(4)–Ru(3)–P(5)	96.7(3)	Cl(4)–Ru(3)–P(6)	106.2(3)
Cl(4)–Ru(3)–Cl(5)	154.4(3)	Cl(5)–Ru(3)–P(5)	101.2(3)
Cl(5)–Ru(3)–P(6)	92.3(3)		

Experimental

Optically pure 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap) was synthesised by the method previously reported.[25] Complexes **1**[2] and **3**[6] were prepared according to the literature

Table 5 Hydrogenation of methyl 3-oxobutanoate catalysed by Ru^{II}[(*S*)-binap] complexes to give methyl (*S*)-3-hydroxybutanoate[a]

Run	Complex	Substrate/ catalyst	$P(H_2)$/ Kg cm^{-2}	*T*/°C	*t*/h	Yield (%)	Enantiomeric excess %
1[b]	(*S*)-**2a**	1400	83	27	40	97	>99
2[c]	(*S*)-**3e**	2500	100	30	35	96	99
3	(*S*)-**4e**	1000	100	35	40	0	—
4	(*S*)-**4a**	1000	97	20	60	1	—
5	(*S*)-**4a**	1000	97	55	156	69	93
6	(*S*)-**7a**[d]	2000	90	20	48	0	—
7	(*S*)-**7c**[d]	1000	100	30	40	0	—
8	(*S*)-**7a**[e]	1000	100	30	40	97	98

[a] Reactions were carried out in methanol. In some cases the dimethyl acetal was obtained in up to 30% yield. [b] Data taken from ref. 4(*a*). [c] Data taken from ref. 6(*a*). [d] Single crystals obtained by carefully repeated recrystallization were used as catalyst. [e] Powdery (*S*)-**7a** containing <5% unidentified Ru^{II}(binap) complexes was used as the catalyst.

procedures. Silver tetrafluoroborate was obtained from Aldrich. All manipulations involving air- and moisture-sensitive compounds were carried out by the use of the standard Schlenk technique under an argon atmosphere purified by passage through a BASF-Catalyst R3-11 column. All solvents were purified by distillation under argon after drying over calcium hydride or sodium–benzophenone.

Nuclear magnetic resonance (^{1}H, ^{13}C and ^{31}P-{^{1}H}) spectra were measured on JEOL JNM-GX400 and EX-270 spectrometers. Gas chromatographic (GLC) analyses were conducted on a Hitachi 263-30 instrument equipped with a flame ionization detector. Liquid chromatography was carried out on a Shimadzu LC-4A instrument equipped with a UV detector. Conductivity[26] was measured by Horiba DS-8F apparatus. Elemental analyses were performed at the Elemental Analysis Center of Kyoto University. All melting points were measured in sealed tubes with a Yanagimoto–Seisakusyo Micro melting point apparatus and were not corrected.

^{31}P-{^{1}H} *NMR Spectra of Complexes* **4a**–**4d** *in Acetonitrile–Methanol* (1:1).—To complex **3a** (15 mg, 1.7 × 10^{-2} mmol) in an NMR tube was added [$^2H_4$]methanol–acetonitrile (1:1, 1.0 cm^3) and the solution was kept at 60 °C for 20 h. Then the ^{31}P-{^{1}H} NMR spectrum was measured. Similarly, spectra were recorded for complexes **3b**, **3d** and **3e**; the data are shown in Table 1.

Preparation of [Ru{(*S*)-binap}$(MeCN)_4$][BF_4]$_2$ (*S*)-**4e**.—To a solution of complex (*S*)-**1** (0.16 g, 0.19 mmol) in a mixture of acetonitrile (5 cm^3) and dichloromethane (5 cm^3) was added an aqueous solution of HBF_4 (*ca.* 2.5 equivalents). All volatiles were removed under reduced pressure to give (*S*)-**4e** as a semi-solid in quantitative yield, m.p. 207–217 °C (decomp.) (Found: C, 57.0; H, 4.20; N, 4.85. Calc. for $C_{52}H_{44}B_2F_8N_4P_2Ru\cdot0.5CH_2Cl_2$: C, 57.1; H, 4.10; N, 5.05%); ν_{max}(Nujol) 2296 (CN), 1053 cm^{-1} (BF_4); δ_H($CDCl_3$) 7.69–6.71 (32 H, m, aromatic protons), 5.30 (1 H, s, CH_2Cl_2), 2.29 (6 H, s, MeCN) and 2.27 (6 H, s, MeCN).

Preparation of [$RuCl_2${(*S*)-binap}$(MeCN)_2$] (*S*)-**5**.—A solution of complex (*S*)-**3a** (28.8 mg, 33.0 μmol) in acetonitrile (2.0 cm^3) and methanol (2.0 cm^3) was heated at 60 °C for 20 h. The resulting pale yellow mixture was concentrated *in vacuo* to afford (*S*)-**5** as a yellow solid in quantitative yield.

An analytical sample of complex (*S*)-**5** was prepared as follows. A solution of (*S*)-**3a** (0.10 g, 0.11 mmol) in acetonitrile (20 cm^3) was heated at 60 °C for 20 h to give a clear yellow solution. All volatiles were removed under reduced pressure. The resulting yellow residue was recrystallized from dichloromethane–diethyl ether (1:1) to give (*S*)-**5** (0.09 g, 84% yield) as a yellow solid, m.p. 85–100 °C (decomp.) (Found: C, 63.5; H, 4.70; N, 3.30. Calc. for $C_{48}H_{38}Cl_2N_2P_2Ru\cdot0.5CH_2Cl_2$: C, 63.4; H, 4.30; N, 3.05%); ν_{max}(Nujol) 2274 cm^{-1} (CN); δ_H($CDCl_3$) 8.08–6.27 (32 H, m, aromatic protons), 5.30 (1 H, s, CH_2Cl_2), 2.00 (3 H, s, MeCN) and 1.80 (3 H, s, MeCN).

Table 6 Crystal data and data collection parameters for complex **7b**

Formula	$C_{132}H_{96}BCl_5F_4P_6Ru_3\cdot CH_2Cl_2$
M	2520.27
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	26.328(5)
b/Å	18.140(3)
c/Å	26.374(4)
Z	4
U/Å^3	12 596(4)
D_c/g cm^{-3}	1.329
F(000)	5112
Radiation	Mo-Kα
Reflections measured	+*h*, +*k*, +*l*
Crystal size/mm	0.24 × 0.38 × 0.45
μ/cm^{-1}	6.26
Scan mode	2θ–θ
T/°C	25
Scan speed/° min^{-1}	5
Scan width/°	1.1 + 0.5tanθ
Background count/s	5
$2\theta_{max}$/°	60
No. of variables	1388
Goodness of fit	4.90

^{31}P-{^{1}H} *NMR Spectra of Complexes* **6a**–**6c** *in Acetonitrile*.—A solution of complex **3a** (20 mg, 2.3 × 10^{-2} mmol) in acetonitrile–$CDCl_3$ (1:1, 1.0 cm^3) in a sealed NMR tube was kept at 50 °C for 1 d, then the ^{31}P-{^{1}H} NMR spectrum was measured. The same procedure was used for complexes **3d** and **3e**, and the spectral data obtained are shown in Table 1.

Preparation of [RuI{(*S*)-binap}$(MeCN)_3$]I (*S*)-**6c**.—A solution of complex (*S*)-**3e** (0.13 g, 0.12 mmol) in acetonitrile (12 cm^3) was heated at reflux temperature for 24 h. The resulting pale yellow solution was concentrated *in vacuo* to afford (*S*)-**6c** as a yellow solid in quantitative yield; ν_{max}(Nujol) 2282 cm^{-1} (CN); δ_H($CDCl_3$ at −30 °C) 7.86–6.40 (32 H, m, aromatic protons), 2.65 (3 H, s, co-ordinated MeCN), 2.05 (3 H, s, co-ordinated MeCN), 2.00 (free MeCN) and 1.92 (3 H, s, co-ordinated MeCN).

Preparation of [Ru_3Cl_5{(*S*)-binap}$_3$]Cl (*S*)-**7a**.—A solution of complex (*S*)-**3a** (0.32 g, 0.37 mmol) in methanol (60 cm^3) was stirred at 60 °C for 12 h. The resulting solid (0.27 g, 93% yield) was collected and washed with methanol. Recrystallization from a mixture of dichloromethane, methanol and hexane gave (*S*)-**7a** (0.18 g, 62% yield) as orange plates, m.p. 170–180 °C (decomp.) (Found: C, 64.9; H, 4.25. Calc. for $C_{132}H_{96}Cl_6P_6$-

Table 7 Atomic coordinates of $[Ru_3Cl_5\{(S)\text{-binap}\}_3]^+$ **7b**

Atom	*x*	*y*	*z*
Ru(1)	0.372 9(1)	0.262 3(1)	0.953 74(8)
Ru(2)	0.313 20(9)	0.313 0(1)	1.061 83(8)
Ru(3)	0.427 26(9)	0.238 7(1)	1.066 76(8)
P(1)	0.350 9(3)	0.170 2(4)	0.898 2(3)
P(2)	0.398 4(3)	0.337 4(5)	0.889 1(3)
P(3)	0.240 0(3)	0.261 0(5)	1.093 5(3)
P(4)	0.292 2(3)	0.422 9(5)	1.097 8(3)
P(5)	0.502 3(4)	0.292 7(4)	1.090 1(3)
P(6)	0.447 0(3)	0.139 0(5)	1.117 1(3)
Cl(1)	0.397 8(3)	0.351 6(4)	1.022 3(2)
Cl(2)	0.343 0(3)	0.191 9(4)	1.031 0(2)
Cl(3)	0.291 3(3)	0.322 8(4)	0.969 8(2)
Cl(4)	0.452 8(3)	0.205 7(4)	0.981 3(3)
Cl(5)	0.371 0(3)	0.287 8(4)	1.128 5(2)
C(1)	0.388(1)	0.217(2)	0.804(1)
C(2)	0.393(1)	0.163(2)	0.844(1)
C(3)	0.430(1)	0.109(2)	0.839(1)
C(4)	0.464(1)	0.103(2)	0.794(1)
C(5)	0.458(1)	0.160(2)	0.756(1)
C(6)	0.493(2)	0.151(2)	0.720(2)
C(7)	0.491(2)	0.205(2)	0.678(2)
C(8)	0.460(1)	0.267(2)	0.679(1)
C(9)	0.426(1)	0.255(2)	0.727(1)
C(10)	0.423(1)	0.208(2)	0.759 1(9)
C(11)	0.357(1)	0.267(2)	0.802(1)
C(12)	0.349(1)	0.335(2)	0.836(1)
C(13)	0.324(1)	0.387(2)	0.829(1)
C(14)	0.284(1)	0.392(2)	0.789(1)
C(15)	0.283(1)	0.330(2)	0.756(1)
C(16)	0.244(1)	0.335(2)	0.727(1)
C(17)	0.231(2)	0.276(3)	0.690(2)
C(18)	0.260(2)	0.226(3)	0.698(2)
C(19)	0.306(2)	0.244(3)	0.748(2)
C(20)	0.316(2)	0.282(2)	0.765(1)
C(21)	0.176(1)	0.379(2)	1.134(1)
C(22)	0.179(1)	0.321(2)	1.098(1)
C(23)	0.141(1)	0.318(2)	1.064(1)
C(24)	0.100(1)	0.361(2)	1.066(1)
C(25)	0.100(1)	0.419(2)	1.097(1)
C(26)	0.053(1)	0.463(2)	1.102(1)
C(27)	0.056(1)	0.528(2)	1.134(1)
C(28)	0.095(1)	0.534(2)	1.164(2)
C(29)	0.136(2)	0.491(2)	1.161(1)
C(30)	0.133(1)	0.428(2)	1.132(1)
C(31)	0.221(1)	0.391(2)	1.177(1)
C(32)	0.273(1)	0.410(2)	1.163(1)
C(33)	0.309(1)	0.396(2)	1.206(1)
C(34)	0.301(1)	0.379(2)	1.255(1)
C(35)	0.243(1)	0.362(2)	1.264(1)
C(36)	0.228(1)	0.340(2)	1.320(1)
C(37)	0.175(1)	0.330(2)	1.326(1)
C(38)	0.136(1)	0.342(2)	1.290(1)
C(39)	0.149(1)	0.354(2)	1.242(1)
C(40)	0.199(1)	0.365(2)	1.230(1)
C(41)	0.561(1)	0.185(2)	1.142(1)
C(42)	0.559(1)	0.227(2)	1.103(1)
C(43)	0.596(1)	0.224(2)	1.072(1)
C(44)	0.633(1)	0.173(2)	1.081(1)
C(45)	0.634(1)	0.121(2)	1.118(1)
C(46)	0.669(1)	0.065(2)	1.120(1)
C(47)	0.664(2)	0.009(3)	1.148(2)
C(48)	0.630(2)	0.030(2)	1.190(2)
C(49)	0.597(1)	0.085(2)	1.192(1)
C(50)	0.596(1)	0.133(2)	1.150(1)
C(51)	0.519(1)	0.194(2)	1.184(1)
C(52)	0.470(1)	0.171(2)	1.178(1)
C(53)	0.433(2)	0.200(2)	0.210(1)
C(54)	0.431(2)	0.222(2)	1.257(1)
C(55)	0.488(1)	0.243(2)	1.266(1)
C(56)	0.500(1)	0.281(2)	1.313(1)
C(57)	0.559(2)	0.294(2)	1.325(1)
C(58)	0.597(2)	0.286(3)	1.280(2)
C(59)	0.583(1)	0.250(2)	1.240(1)
C(60)	0.533(1)	0.233(2)	1.235(1)
C(61)	0.347(1)	0.079(1)	0.930(1)
C(62)	0.312(1)	0.039(1)	0.941(1)
C(63)	0.319(1)	−0.015(2)	0.969(1)
C(64)	0.363(2)	−0.027(2)	0.982(1)
C(65)	0.409(2)	−0.004(2)	0.980(1)
C(66)	0.403(1)	0.055(2)	0.950(1)
C(71)	0.289(1)	0.164(2)	0.866(1)
C(72)	0.249(1)	0.218(2)	0.865(1)
C(73)	0.204(1)	0.213(2)	0.843(1)
C(74)	0.198(1)	0.158(2)	0.815(1)
C(75)	0.243(2)	0.111(2)	0.807(2)
C(76)	0.286(1)	0.110(2)	0.831(1)
C(81)	0.460(1)	0.323(2)	0.854(1)
C(82)	0.498(1)	0.275(2)	0.862(1)
C(83)	0.542(1)	0.265(2)	0.830(1)
C(84)	0.545(1)	0.289(2)	0.791(1)
C(85)	0.511(2)	0.346(2)	0.780(1)
C(86)	0.463(1)	0.361(2)	0.806(1)
C(91)	0.403(1)	0.437(2)	0.907(1)
C(92)	0.359(1)	0.469(2)	0.926(1)
C(93)	0.369(2)	0.532(2)	0.938(1)
C(94)	0.413(1)	0.575(2)	0.939(1)
C(95)	0.445(2)	0.532(3)	0.919(2)
C(96)	0.438(2)	0.466(2)	0.910(2)
C(101)	0.231(1)	0.215(1)	1.159(1)
C(102)	0.278(1)	0.197(2)	1.189(1)
C(103)	0.282(1)	0.168(2)	1.239(1)
C(104)	0.240(2)	0.157(3)	1.252(2)
C(105)	0.189(2)	0.187(3)	1.225(2)
C(106)	0.188(1)	0.208(2)	1.175(1)
C(111)	0.217 2(9)	0.181(1)	1.055 2(9)
C(112)	0.212(1)	0.182(2)	1.004(1)
C(113)	0.199(2)	0.128(2)	0.975(1)
C(114)	0.194(1)	0.064(2)	0.994(1)
C(115)	0.203(1)	0.047(2)	1.051(1)
C(116)	0.217(1)	0.111(2)	1.071(1)
C(121)	0.246(1)	0.478(2)	1.069(1)
C(122)	0.237(1)	0.543(2)	1.100(1)
C(123)	0.200(2)	0.584(2)	1.082(2)
C(124)	0.174(2)	0.558(2)	1.020(2)
C(125)	0.187(2)	0.501(2)	1.002(2)
C(126)	0.227(2)	0.454(2)	1.019(1)
C(131)	0.343(1)	0.493(2)	1.100(1)
C(132)	0.376(1)	0.506(2)	1.060(1)
C(133)	0.414(2)	0.564(3)	1.064(2)
C(134)	0.414(1)	0.605(2)	1.117(1)
C(135)	0.382(1)	0.594(2)	1.157(1)
C(136)	0.344(1)	0.539(2)	1.155(1)
C(141)	0.514(2)	0.376(2)	1.035(1)
C(142)	0.516(1)	0.438(2)	1.053(1)
C(143)	0.515(2)	0.470(3)	1.015(2)
C(144)	0.546(2)	0.449(2)	0.975(2)
C(145)	0.548(1)	0.375(2)	0.957(1)
C(146)	0.532(1)	0.335(2)	0.992(1)
C(151)	0.508(1)	0.356(2)	1.146(1)
C(152)	0.469(1)	0.385(2)	1.164(1)
C(153)	0.468(1)	0.438(2)	1.207(1)
C(154)	0.519(1)	0.461(2)	1.219(1)
C(155)	0.562(2)	0.426(2)	1.196(2)
C(156)	0.567(2)	0.364(2)	1.162(1)
C(161)	0.494(1)	0.064(2)	1.090(1)
C(162)	0.506(2)	0.009(2)	1.123(1)
C(163)	0.544(1)	−0.043(2)	1.109(1)
C(164)	0.558(1)	−0.033(2)	1.073(1)
C(165)	0.547(1)	0.021(2)	1.040(1)
C(166)	0.517(1)	0.073(2)	1.049(1)
C(171)	0.398(1)	0.072(2)	1.123(1)
C(172)	0.394(2)	0.050(2)	1.170(2)
C(173)	0.354(2)	−0.030(2)	1.188(1)
C(174)	0.322(2)	−0.049(2)	1.153(2)
C(175)	0.328(1)	−0.006(2)	0.103(1)
C(176)	0.366(2)	0.048(2)	1.092(1)

$Ru_3{\cdot}3CH_3OH$: C, 65.4; H, 4.40%); δ_H ($CDCl_3$) 7.81–6.42 (96 H, m, aromatic protons) and 3.47 (9 H, s, CH_3OH); Λ (CH_2Cl_2) 79 S cm^2 mol^{-1} (25 °C).

Preparation of $[Ru_3Cl_5\{(S)\text{-binap}\}_3]BF_4$ (*S*)-**7b**.—To a dark red solution of complex (*S*)-**7a** (0.33 g, 0.14 mmol) in dichloromethane (20 cm^3), was added a mixture of $AgBF_4$ (29.8 mg, 0.15 mmol) and dichloromethane (5 cm^3). The orange mixture was stirred for 2 h at room temperature. The precipitated AgCl was filtered off and the dark red solution was concentrated *in vacuo* to afford (*S*)-**7b** (0.37 g, quantitative yield) as a brown solid. Recrystallization from a mixture of dichloromethane (20 cm^3), methanol (2 cm^3) and hexane (20 cm^3) followed by drying at room temperature *in vacuo* (10^{-3} mmHg, *ca.* 0.133 Pa) afforded a dark red solid (0.20 g, 56% yield), m.p. 260–280 °C (decomp.) (Found: C, 64.7; H, 4.15. Calc. for $C_{132}H_{96}BCl_5F_4P_6Ru_3{\cdot}0.5CH_2Cl_2$: C, 64.3; H, 3.95%); ν_{max}(Nujol) 1055 cm^{-1} (BF_4); δ_H($CDCl_3$) 7.84–6.41 (96 H, m, aromatic protons) and 5.30 (1 H, s, CH_2Cl_2); Λ (CH_2Cl_2) 101 S cm^2 mol^{-1} (25 °C). For X-ray crystallography, wet samples were used directly since removal of solvent under reduced pressure causes collapse of the crystals due to partial loss of the solvent of crystallization.

Preparation of $[Ru_3Br_5\{(S)\text{-binap}\}_3]Br$ (*S*)-**7c**.—A mixture of complex (*S*)-**3d** (0.48 g, 0.47 mmol) and methanol (60 cm^3) was irradiated by a UV lamp at room temperature for 24 h. Complex (*S*)-**7c** precipitated as a light brown solid (0.17 g, 40% yield), m.p. 190–200 °C (decomp.) (Found: C, 57.9: H, 3.85. Calc. for $C_{132}H_{96}Br_6P_6Ru_3{\cdot}1.5CH_2Cl_2$: C, 57.7; H, 3.60%); δ_H($CDCl_3$) 8.04–5.93 (96 H, m, aromatic protons) and 5.23 (3 H, s, CH_2Cl_2); Λ (CH_2Cl_2) 60 S cm^2 mol^{-1} (25 °C).

Crystal Structure of $[Ru_3Cl_5\{(S)\text{-binap}\}_3]BF_4$ (*S*)-**7b**.—A bright orange crystal of complex (*S*)-**7b** was sealed in a glass capillary under an argon atmosphere in the presence of a mixture of dichloromethane and hexane, and then transferred to a goniostat on a Rigaku AFC-5R diffractometer. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima of orthorhombic symmetry and systematic absences (h 0 0) with h = odd, (0 k 0) with k = odd and (0 0 l) with l = odd corresponding to the unique space group $P2_12_12_1$. The details of the data collection and the final cell dimensions, obtained from a least-squares refinement of 2θ values of 50 independent reflections in the range of $20 < 2\theta < 30°$, are given in Table 6.

The 6139 unique raw intensity data with $|F_o| > 3\sigma(F_o)$ (a total of 19 712 reflections were collected) were converted into the structure factors and corrected for Lorentz and polarization effects. Inspection of the standard three reflections measured after every 50 reflections showed no systematic variation in intensity. Corrections for absorption and extinction effects were not made.

The ruthenium atom was located by the direct method.[27] A series of standard block-diagonal least-squares refinements and Fourier synthesis revealed the remaining atoms. Atoms of BF_4 and solvated dichloromethane were located by Fourier difference synthesis. The hydrogen atoms were not located. All non-hydrogen atoms of the complex and dichloromethane were refined with anisotropic thermal parameters to give $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.103$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.083$. The weighting scheme $1/w = \sigma_c{}^2 + (0.023|F_o|)^2$ was employed.[28] Final Fourier difference maps indicated no significant peak with > 1.13 e $Å^{-3}$. Selected bond distances and angles are summarized in Tables 3 and 4 and atomic coordinates are listed in Table 7.

Additional material available from the Cambridge Crystallographic Data comprises thermal parameters and remaining bond lengths and angles.

Addition of HCl *to Complex* (*R*)-**1**.—To a solution of complex (*R*)-**1** (39.2 mg, 46.6 μmol) in CD_2Cl_2 (1 cm^3) was added 1.14 mol dm^{-3} hydrochloric acid in 90% methanol (88.5 μl, 101 μl) at room temperature. The resulting dark red solution was stirred at room temperature for 2.5 h. The $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibited an intense singlet at δ 48.9 due to (*R*)-**7a**. The solvent was removed *in vacuo* to give a dark brown solid. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the solid in $CDCl_3$ showed that the trimer had partially collapsed and a complex mixture was formed.

Addition of HBr *to Complex* (*R*)-**1**.—To a solution of complex (*R*)-**1** (5.0 mg, 5.9 μmol) in $CDCl_3$–methanol (1 : 1, 0.5 cm^3) in an NMR tube was added aqueous 47% hydrobromic acid (0.01 cm^3, 58 μmol) at room temperature, and then the $^{31}P\text{-}\{^1H\}$ NMR spectrum was monitored. After 30 min at room temperature, the spectrum exhibited an intense AB quartet (δ 15.2 and 63.2, J_{PP} = 39.4 Hz) in addition to a singlet at δ 48.0 due to (*R*)-**7c**. After 5 d only the singlet at δ 48.0 was observed.

Catalytic Hydrogenation of Methyl 3-Oxobutanoate.—Typical procedures are as follows. A solution of complex **3e** (6.2 mg, 5.6 μmol) and methyl 3-oxobutanoate (1.61 g, 13.9 mmol) in methanol (1.6 cm^3) was degassed by three freeze–pump–thaw cycles and then placed in an autoclave. Hydrogen was introduced (100 kg cm^{-3}), and then the mixture was stirred at 30 °C for 35 h. After the pressure of hydrogen had been released and the solvent evaporated, the residue was distilled under reduced pressure to give a colourless oil (1.60 g, 98% yield). GLC analysis [capillary column, type FFS. PEG-20M (25 m), 80 °C, 1 kg cm^{-2} He] indicated that methyl 3-hydroxybutanoate (96%) and the dimethyl acetal of methyl 3-oxobutanoate (4%) were obtained. The enantioselectivity of methyl 3-hydroxybutanoate (99% enantiomeric excess) was determined by HPLC analysis [Nucleosil 100-3, eluted with hexane–diethyl ether (8 : 2)] of the (+)-(*R*)-2-methoxy-2-trifluoromethylphenylacetic acid ester of methyl 3-hydroxybutanoate.

Conclusion

The Ru^{II}(binap) dihalide complexes **3** form mononuclear mono- and di-cationic complexes depending on the solvent. Use of a mixture of acetonitrile and methanol led to the formation of dicationic complexes **4**, while in acetonitrile monocationic species **6** were predominantly formed. Attempted isolation of **4a** and **6a** by removal of the solvent resulted in the formation of the neutral dichloride **5**, while disproportionation to **4e** or **4f** and **5** has been observed upon displacement of one of the chloride anions in **6a** by $BF_4{}^-$ or $PF_6{}^-$. In methanol, cationic trinuclear complexes **7** have been formed whose molecular structures have been determined by spectroscopic and X-ray analyses. They are totally inert as catalysts for hydrogenation of methyl 3-oxobutanoate, although when partially decomposed are excellent catalysts. These findings show the catalytic activity and stereoselectivity of Ru^{II}(binap) complexes are highly dependent on the solvent, additives, impurities, *etc.* and, therefore, utmost efforts have to be made to find the most appropriate reaction conditions.

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