A New Rhodium Trinuclear Complex containing highly protected Hydroxo Groups, [{Rh(binap)}$_3$(μ_3-OH)$_2$]ClO$_4$, responsible for Deactivation of the 1,3-Hydrogen Migration Catalyst of Allylamine [binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl]

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A new stable rhodium trinuclear complex, [{Rh(binap)}$_3$(μ_3-OH)$_2$]ClO$_4$ [binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] (**2**), formed when water deactivates the Rh^I–binap complex catalysed asymmetric 1,3-hydrogen migration of allylamine, has been isolated; an *X*-ray structural analysis of the deuterium derivative [{Rh[(+)-binap]}$_3$(μ_3-OD)$_2$]ClO$_4$ revealed a unique structure with two highly protected μ_3-hydroxo groups.

Recently we reported that cationic rhodium(I) complexes, [Rh(binap)L$_n$]ClO$_4$ [binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; L = solvent, diene, or binap] are excellent catalysts for enantioselective 1,3-hydrogen migration of allylamine to optically active enanime.[1] Among these catalysts the solvent complex, [Rh(binap)(solv.)$_n$]ClO$_4$, was the most active but the most sensitive to impurities such as water or oxygen. If the solvent or the substrate for the catalytic isomerisation with [Rh(binap)(MeOH)$_2$]ClO$_4$ (**1**) was not carefully dried, red-brown crystals gradually separated from the reaction mixture and isomerisation ceased. With excess of water ([H$_2$O]/[Rh] = 15) present in the reaction mixture, isomerisation stopped after only a few cycles and the red–brown solids precipitated rapidly. The same complex was obtained from the reaction of [Rh(binap)(MeOH)$_2$]ClO$_4$ (**1**) and triethylamine or ammonia in the presence of water. The complex is stable to air and does not show any catalytic activity for the isomerisation. Thus we consider that the formation of the red–brown complex results in the deactivation of the catalysis. In order to characterise the precipitates and to

$$\underset{(\mathbf{1})}{[\mathrm{Rh(binap)(MeOH)_2]ClO_4}} + \mathrm{H_2O}$$

$$\rightarrow \underset{(\mathbf{2})}{[\{\mathrm{Rh(binap)}\}_3\mathrm{(OH)_2]ClO_4}}$$

Scheme 1. *Reagents*: R_3N, acetone.

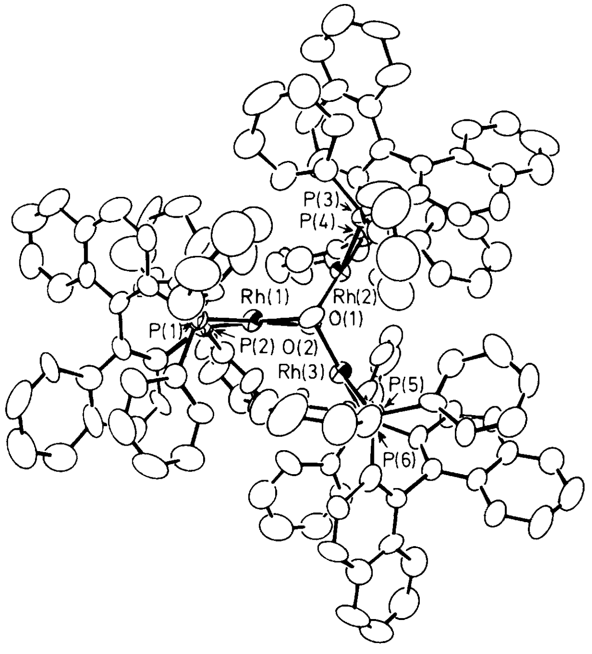

Figure 1. ORTEP drawing of a cation in the complex (*R*)-(+)-[$^2H_2$]-(**2**). Selected distances (Å) and angles (°): Rh(1)–Rh(2) 3.094(2), Rh(1)–Rh(3) 3.102(2), Rh(2)–Rh(3) 3.086(2), Rh(1)–P(1) 2.207(5), Rh(1)–P(2) 2.222(5), Rh(2)–P(3) 2.194(5), Rh(2)–P(4) 2.208(5), Rh(3)–P(5) 2.211(5), Rh(3)–P(6) 2.199(5), Rh(1)–O(1) 2.160(11), Rh(1)–O(2) 2.161(11), Rh(2)–O(1) 2.122(11), Rh(2)–O(2) 2.154(11), Rh(3)–O(1) 2.163(11), Rh(3)–O(2) 2.143(11); Rh(2)–Rh(1)–Rh(3) 59.75(4), Rh(1)–Rh(2)–Rh(3) 60.25(4), Rh(1)–Rh(3)–Rh(2) 60.00(4), P(1)–Rh(1)–P(2) 88.6(2), P(3)–Rh(2)–P(4) 88.1(2), P(5)–Rh(3)–P(6) 89.1(2), Rh(1)–O(1)–Rh(2) 92.5(4), Rh(1)–O(2)–Rh(2) 91.6(4), Rh(2)–O(1)–Rh(3) 92.2(4), Rh(2)–O(2)–Rh(3) 91.8(4), Rh(3)–O(1)–Rh(1) 91.7(4), Rh(3)–O(2)–Rh(1) 92.2(4). The angles between the least-squares planes through the two naphthyl rings in each binap ligand are 74.2(6), 75.5(6), and 72.9(6)°. Vibration ellipsoids are drawn at the 50% probability level.

elucidate the mechanism of the deactivation of the catalysis by water, we prepared the complex separately, determined the structure by *X*-ray crystallography, and examined the physical properties of the complex.

On addition of 50 µl of aqueous ammonia (1.43 M) to an acetone solution (2 ml) of (**1**) (79.6 mg), a precipitate appeared immediately and deep red–brown needles of [{Rh(binap)}$_3$(OH)$_2$]ClO$_4$ (**2**)† (29.8 mg, 42%) were isolated after one day at room temperature.

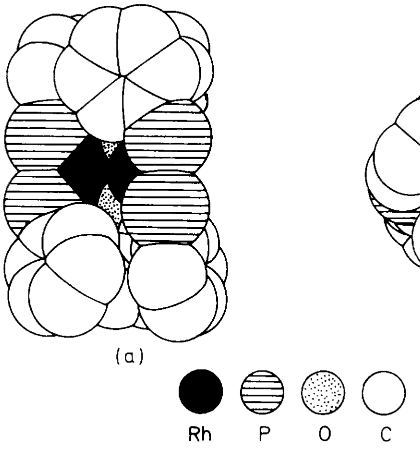

Figure 2. Space-filling representation [(a) side view; (b) top view] of the central part of the cation in (*R*)-(+)-[$^2H_2$]-(**2**). (Naphthyl groups, phenyl groups stacked with naphthyl rings, and hydrogens omitted for clarity) (filled atoms = Rh, scored atoms = P, dotted atoms = O, and open atoms = C).

Unexpectedly, when the reaction was carried out in [$^2H_6$]acetone, deuterium was incorporated in the product and [{Rh(binap)}$_3$(OH)$_{2-x}$(OD)$_x$]ClO$_4$, which showed a medium intensity OD absorption at 2650 cm^{-1} as well as the OH signal at 3590 cm^{-1}, was isolated. The intensity ratio $\nu_{OH}:\nu_{OD}$ depended on the reaction conditions. Unlike most transition metal hydroxo complexes,[2] however, once the complex (**2**) is formed, its hydroxo protons do not exchange with deuterium of D$_2$O even in the presence of strong acids or bases such as conc. DCl or NaOD. This was confirmed by ^{1}H n.m.r. and i.r. spectroscopy. From these results the incorporation of deuterium into (**2**) may be explained as follows; OD$^-$ is produced by H–D exchange between water and [$^2H_6$]acetone under basic conditions, probably *via* an enolate ion (CD$_3$)CO$^-$=CD$_2$, and then reacts with 'Rh(binap)$^+$' forming the deuterium derivatives of (**2**).

Single crystals suitable for *X*-ray analysis were formed in an n.m.r. tube from an equimolar mixture of [Rh{(*R*)-(+)-binap}(MeOH)$_2$]ClO$_4$ (*R*)-(+)-(**1**) and *N*,*N*-dimethyl-2-methylprop-2-enylamine in [$^2H_6$]acetone (room temp. 1 yr). The sharp ν_{OH} absorption at 3590 cm^{-1} in the i.r. spectrum disappeared and a new band appeared at 2650 cm^{-1} due to ν_{OD} and in the ^{1}H n.m.r. spectrum the OH proton signal at δ −0.84 almost disappeared. The *X*-ray crystallographic analysis‡ of [{Rh[(*R*)-(+)-binap)]}$_3$(OD)$_2$]ClO$_4$ (*R*)-(+)-[$^2H_2$]-(**2**)

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† *Data* for (**2**): m.p. 144 °C (decomp.); ^{1}H n.m.r. (CDCl$_3$, 100 MHz) δ −0.84 (m, 2H, OH), 5.9—8.0 (m, 90H, ar.), 10.6 (br. s, 6H, ar.); ^{31}P-{^{1}H} n.m.r. (CD$_2$Cl$_2$, 40.25 MHz, downfield from external 85% H$_3$PO$_4$) 50.32 p.p.m. (d, J_{P-Rh} 195.6 Hz); i.r. (CsI disk) 3590s (O–H), 1590s (C=C), 1050vs (ClO$_4$), 815s, 745vs, and 695vs (ar.) cm^{-1}; satisfactory elemental analyses were obtained (C, H, and Cl).

‡ *Crystal data* for (*R*)-(+)-(**2**): C$_{132}$H$_{96}$ClD$_2$O$_6$Rh$_3$, *M* = 2312.26, monoclinic, space group *P*2$_1$, *a* = 17.534(4), *b* = 23.222(2), *c* = 16.398(4) Å, β = 120.5(1)°, *U* = 5689(2) Å^3, *Z* = 2, D_c = 1.350, D_m = 1.32(1) g cm^{-3} (at 16 °C), µ(Cu-K_α) = 50.23 cm^{-1}, λ = 1.54178 Å (graphite-monochromated), *F*(000) = 2360; 9676 measured reflections (Rigaku-Denki Rotaflex rotating anode *X*-ray generator and Rigaku-Denki AFC diffractometer), *T* = 21 ± 2 °C, ω–2θ scan, 2θ ≤ 125°, heavy atom method, refined by block-diagonal least-squares methods. *R* = 0.0545, R_w = 0.0637 [$w = 1.0/\sigma^2(F_o)$], for 6967 observed reflections [$F_o \geq 6\sigma(F_o)$] and 1288 parameters. A perchlorate anion is disordered; three positions were assigned on the basis of the electron density maxima. The absolute configuration (*R*) of the (+)-binap ligand was determined in a previous study.[3] All numerical calculations were carried out on an ACOS S850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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.

$$2(\mathbf{1}) + 2\,R_3NH^+OH^- \rightarrow$$
$$\text{`}[(\text{binap})Rh(\mu\text{-}OH)_2Rh(\text{binap})]\text{'} + 2\,R_3NH^+ClO_4^- + 4\,MeOH$$
$$(\mathbf{3})$$

$$(\mathbf{3}) + (\mathbf{1}) \rightarrow (\mathbf{2}) + 2\,MeOH$$

Scheme 2

revealed a trinuclear monocation with pseudo-D_3 symmetry having two triply bridging hydroxo groups on each side of an approximately regular Rh_3 triangle (Figure 1). The fairly long Rh–Rh distances (av. 3.09 Å) may imply the absence of Rh–Rh bonding. Each Rh atom is co-ordinated almost in an approximately square plane formed by two phosphorus atoms of a binap ligand and two hydroxo oxygen atoms; the co-ordination plane is approximately perpendicular to the Rh_3 triangle and all the rhodium atoms have oxidation states of +1. This is the first example of a rhodium complex having μ_3-OH groups, although several rhodium hydroxo complexes[4] and transition metal complexes with μ_3-hydroxo groups[5,6] are known. Similar $M_3(OH)_2$ cores are found in $[Cu_3(OH)_2(C_{18}H_{24}N_6O_3)]^{4+}$ (ref. 5) and $Ni_3(\sigma\text{-}CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)_2(\mu_3\text{-}OH)_2$.[6]

The failure of the hydroxo proton of (**2**) to exchange with D_2O may be understood from the unique structure. The hydroxo groups sit in small cavities above and below the rhodium triangle; each one is surrounded by the three phenyl rings of the three binap ligands. The size of the cavity is just that of an OH group as visualised in the space-filling representations, Figure 2; an OH^- or OH_3^+ group could not leave or enter the hole.§ It has been briefly mentioned elsewhere[7] that reaction of $[Rh(\text{diphos})(\text{solv.})_n]^+$ with OMe^- or NEt_3 in methanol gives a methoxo complex $[\{Rh(\text{diphos})\}_3(\mu_3\text{-}OMe)_2]^+$, with a Rh_3O_2 core analogous to that of (**2**). However, $[Rh(\text{binap})(\text{solv.})_n]^+$, having the bulky binap ligand, produced only the hydroxo complex (**2**), and none of the corresponding methoxo complex under similar reaction conditions. This can also be understood from the structure of the cation of (**2**) described above; there is not enough space for MeO^- to replace OH^-.

A plausible mechanism for the formation of (**2**) is outlined in Scheme 2. The presence of water in the catalytic system may produce OH^- and result in the formation of (**2**). (**2**) is stable to hydrolysis as described above and does not dissociate into a catalytically active mononuclear species. Thus water deactivates the isomerisation catalysis.

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§ The openings of the cavities are estimated to have a diameter of at most 2.0 Å, which is much smaller than the van der Waals diameter of an oxygen atom.