Homogeneous hydrogenation of olefins catalyzed by a novel tetrarhodium(II) complex as precursor in aqueous solution

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Abstract

Hydrogenation of α,β-unsaturated alcohol, nitrile, aldehyde, ketone, carboxylic acid and amide catalyzed by a novel water-soluble complex $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ was investigated. The reactions were carried out in aqueous solution at room temperature under 1 atm of H_2. The results showed that this tetrarhodium(II) complex is efficient for the hydrogenation of both terminal and internal double bond with the selectivity of unhydrogenated carbonyl groups. Unsaturated ketone, amide and carboxylic acid were readily hydrogenated, and nitrile and aldehyde were slowly hydrogenated. The hydrogenation of allyl alcohol was accompanied with isomerization to propanal. The rate of the hydrogenation was first-order to the catalyst precursor. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogenation of simple olefins catalyzed by lantern-type dirhodium tetracarboxylate complexes has been studied [1,2]. Legzdins et al. [3] have found that complex $[Rh_2(O_2CCH_3)_4]$ can be protonated with strong but noncomplexing acids, and protonated solutions are active catalysts for the hydrogenation of unsaturated organic compounds only in the presence of other ligands, such as triphenylphosphine. The catalytic species was proposed to be a monomeric Rh(I) complex $[Rh(PPh_3)_3BF_4]$. Hui and Rempel [4] and Hui et al. [5] studied homogeneous hydrogenation of olefins catalyzed by the same compound, $[Rh_2(O_2CCH_3)_4]$, in a variety of organic solvents. They suggested a hydride, $[HRh_2(O_2CCH_3)_3]$, as an active species.

The chemistry of water-soluble catalysts is under rapid growth [6–9]. They have special uses in biochemistry [10], such as in membrane modification by selective hydrogenation and regeneration of $NAD(P)^+$. Recently, we isolated a new type of Rh(II) tetranuclear complex, $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ [11], which have acceptable water solubility and some similarities to $[Rh_2(O_2CCH_3)_4]$ in structure. We found that this complex has fairly efficient hydrogenation ability of some functional olefins in aqueous solution. Here, we report our preliminary results on hydrogenation of some olefins catalyzed by

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$[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ in aqueous solution at room temperature under 1 atm of hydrogen.

2. Experimental

2.1. Materials

The catalyst precursor, $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$, was prepared as previously reported and recrystallized from CH_2Cl_2–CH_3CN mixture [11]. Distilled water was used as solvent for hydrogenation. Substrates were used as received.

2.2. General data

The electronic spectra were measured on a Hitachi U-3500 spectrophotometer. The NMR spectra were recorded on a JEOL Alpha-400 FT-NMR spectrometer. GLC analyses were made on a Shimadzu GC-8A chromatograph with a 2-m column of diethylene glycol succinate on uniport B. X-ray diffraction studies were made by using a Rigaku AFC-7R automatic diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) from a rotating anode generator. The structure was solved and refined by using the teXsan crystallographic software package.

2.3. Hydrogenation

The reactions were carried out with a standard apparatus in aqueous solution at room temperature under a constant pressure (1 atm) of H_2. A liquid substrate was added to an aqueous solution of the catalyst precursor under H_2 atmosphere. When the substrate was a solid, H_2 was introduced to a mixture of catalyst and substrate in water. Kinetic measurements were made by following the consumption of hydrogen gas, which was assumed as insoluble in water.

2.4. Preparation of $[Rh_4(O_2CPr^n)_4Cl_4(CH_2=CHCN)_4]$

Into a mixture of CH_2Cl_2 and $CH_2=CHCN$ ($V/V = 1/2$, 6 ml), 20 mg (0.019 mmol) of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ was dissolved. The dark yellow solution gave brown crystals of $[Rh_4(O_2CPr^n)_4Cl_4(CH_2=CHCN)_4]$ on slow evaporation of solvent (yield 70%, 14 mg). Found C, 21.33; H, 3.17; Cl, 15.10. $C_{16}H_{38}Cl_4O_8Rh_4$ requires C, 21.31; H, 3.13; Cl, 15.72%. ^{1}H NMR (CDCl$_3$): δ +0.82 (t, 12H); 1.56 (h, 8H); 2.34 (t, 8H); 5.76 (4H); 6.15 (4H); 6.33 (4H).

2.5. Preparation and isolation of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CH_2CONH_2)_2]$

2.5.1. Preparation of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CH_2CONH_2)_2]$

In 2 ml CH_2Cl_2 15 mg (0.014 mmol) of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ was stirred with 6.0 mg (0.082 mmol) of $CH_3CH_2CONH_2$ for 2 h at room temperature. After filtration, 6 ml pentane was added. The solution gave brown crystals on slow evaporation of solvent (10 mg, 70%). Found C, 24.92; H, 3.85; Cl, 13.80; N, 2.87. $C_{22}H_{42}Cl_4N_2O_{10}Rh_4$ requires C, 25.21; H, 4.04; Cl, 13.53; N, 2.67%. ^{1}H NMR data (CDCl$_3$): δ +0.82 (t, 12H); 1.18 (t, 6H); 1.5 (m, 12H); 2.32 (q, 4H); 2.33 (t, 8H). The single crystal for X-ray diffraction study was obtained from its CH_2Cl_2 solution layered with pentane.

2.5.2. Isolation of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CH_2CONH_2)_2]$

After hydrogenation of $CH_2=CHCONH_2$ (50.0 mg, 0.70 mmol) in 1.5 ml of water catalyzed with $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ (6.4 mg, 0.006 mmol) for 3 h, the reaction solution was extracted with $CHCl_3$ (1 ml × 3). To this extract was added equivalent volume of toluene. This solution gave brown crystals (3 mg) on slow evaporation of solvent, which was identified as $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CH_2CONH_2)_2]$ based on ir and ^{1}H NMR spectra.

2.6. X-ray crystallography of $[Rh_4(O_2CPr^n)_4$-$Cl_4(CH_2=CHCN)_4]$ and $[Rh_4(O_2CPr^n)_4$-$Cl_4(CH_3CH_2CONH_2)_2]$

A crystal was mounted on a glass fiber with grease in a cold nitrogen stream. The data were collected using the ω–2θ technique to the maximum 2θ value of 55°. The structure was solved by direct methods (SHELXS-86 [12]) and expanded using Fourier techniques. The structure of the former complex was refined to $R = 0.038$ ($R_w = 0.044$) and that of the latter to $R = 0.026$ ($R_w = 0.034$). Details concerning the crystal structure investigation for $[Rh_4(O_2CPr^n)_4Cl_4$-$(CH_2=CHCN)_4]$ (CCDC No. 139665) and for $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CH_2CONH_2)_2]$ (CCDC No. 139664) are available on request from the Director of the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK.

3. Results and discussion

3.1. Catalytic hydrogenation of olefin

The tetrarhodium(II) compound $[Rh_4(O_2$-$CPr^n)_4Cl_4(CH_3CN)_4]$ was found to catalyze the hydrogenation of both terminal and internal double bond of a variety of functional monoenes homogeneously in aqueous solution at room temperature under 1 atm of hydrogen (Table 1). No hydrogenation of carbonyl function groups was observed. However, $Me_2C=$ $CHCO_2H$ could not be hydrogenated probably due to steric congestion around its double bond. The hydrogenation of the olefinic aldehyde were slow compared to the other substrates. In the case of allyl alcohol as substrate, there invariably occurred to some extent the isomerization to CH_3CH_2CHO. For example, when the reaction was performed in water ($[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4] = 4.0$ mM, $[CH_2=CHCH_2OH] = 0.40$ M), we obtained 40% hydrogenated product (C_3H_7OH) and 60% isomerization product (CH_3CH_2CHO) (Entry 5

Table 1
Hydrogenation of olefins by $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ as catalyst precursor[a]

Entry	Substrate	Reaction Time (h)	Conversion (%)[b]
1	⟍⟍⟍OH	4	73[c,d]
2	⟍⟍CHO	4	29[c]
3	⟍⟍COCH₃	4	100[c,e]
4	⟍⟍CN	4	51[c,f]
5	⟍⟍OH	2	100[d]
6	⟍⟍CHO	4	66
7	⟍⟍COCH₃	2	100[e]
8	⟍⟍CN	4	100[f]
9	⟍⟍CO₂H	2	100[e]
10	⟍⟍CO₂H	6	100[e]
11	$Me_2C=CHCO_2H$	2	0[e]
12	⟍⟍NH₂	1	71[e,g]
13	⟍⟍C(O)NH₂	3	100[e]

[a] Conditions: [Cat.] = 4.0 mM; [Sub.] = 0.40 M; 1 atm H_2; $T = 298$ K; solvent = H_2O, otherwise designated.
[b] The conversion was determined by GLC, otherwise designated.
[c] The solvent was an aqueous acetic acid solution (pH = 2.45).
[d] The conversion includes the isomerization product.
[e] The conversion was determined by ^1H NMR.
[f] Precipitate was formed immediately on addition of the substrate.
[g] Reaction solution became brown from yellow immediately on addition of the substrate.

in Table 1). In the absence of olefin, no measurable absorption of hydrogen was observed. The CH_3CN axial ligands of this catalyst precursor dissociate extensively in aqueous solution with the retention of the $[Rh_4(O_2CPr^n)_4Cl_4]$ core skeleton [11]. The UV–Vis spectra of the catalyst in olefin aqueous solutions showed no significant change of the absorption bands (Table 2) except the lowest energy band around 670 nm, which indicates that there is interaction between functional olefin and the catalyst precursor at axial positions, and that the skeletal core of this complex is conserved. When acrylonitrile was added to the reaction solution, there immediately appeared a precipitate, which

Table 2
Electronic spectra of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ in various aqueous solutions

Solvent	λ_{max} /nm (log ε)			
H_2O	680 (2.3)	465sh	314 (4.1)	271 (4.2)
8.32 mM $HClO_4$	682 (2.2)	465sh	314 (4.1)	270 (4.2)
0.30 M NaOH	674 (2.4)	465sh	314 (4.1)	270 (4.2)
0.20 M HBF_4	677 (2.2)	465sh	314 (4.1)	270 (4.2)
0.015 M HAA[a]	661 (2.1)	465sh	313 (4.0)	269 (4.3)
0.015 M AL[b]	660 (2.1)	470sh	313 (3.9)	269 (4.3)
0.015 M ALN[c]	668 (2.1)	470sh	313 (4.0)	269 (4.3)
0.014 M AA[d]	667 (2.2)	465sh	313 (4.0)	269 (4.3)

[a] HAA = acrylic acid.
[b] AL = acrolein.
[c] ALN = acrylonitrile.
[d] AA = acrylamide.

was confirmed as $[Rh_4(O_2CPr^n)_4Cl_4(CH_2=CHCN)_4]$ with the nitrile molecules at the axial sites by X-ray crystallography. The precipitation of the catalyst precursor caused the hydrogenation reaction to slow down. When the hydrogenation reaction was performed in NaOH solution, the complex was quickly reduced to rhodium metal. When carried out in a solution of noncomplexing strong acid, HBF_4, the hydrogenation rate slowed down. Representative plots of hydrogen uptake are shown in Fig. 1, which shows the double bonds in $CH_2=CHCOCH_3$ and $CH_2=CHCO_2H$ were quantitatively hydrogenated, and 32% of $CH_2=CHCH_2OH$ was hydrogenated.

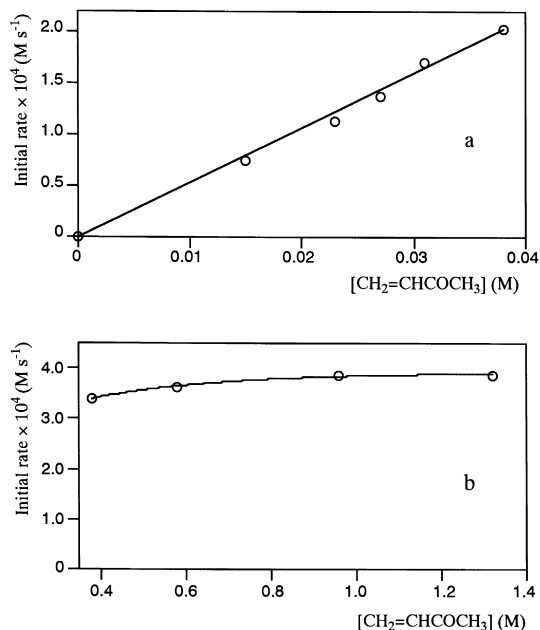Fig. 2. Dependence of the initial rate of hydrogen consumption on the concentration of methyl vinyl ketone at 298 K, 1 atm H_2 ([Cat.] = 2.0 mM).

A kinetic study was performed by examination of the initial rates of the gas consumption for the substrates of $CH_2=CHCOCH_3$ and $CH_2=CHCO_2H$. The initial rate of hydrogen consumption showed a first order dependence on $[CH_2=CHCOCH_3]$ at its low concentrations (Fig. 2a) to near zero-order one at high concentrations (Fig. 2b) of the substrate. A linear

Fig. 1. Time profile of hydrogen consumption ([Cat.] = 4.0 mM; [Sub.] = 0.40 M; T = 300 K).
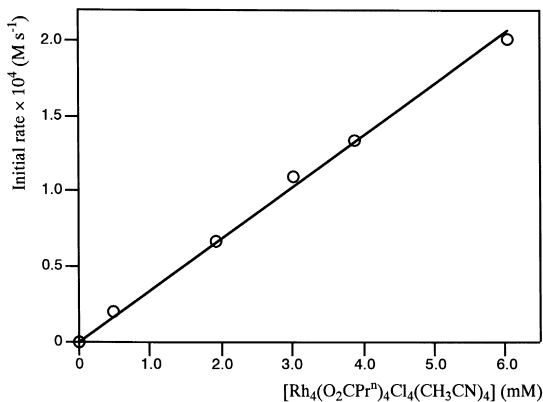

Fig. 3. Dependence of the initial rate of hydrogen consumption on the concentration of the catalyst precursor under high [olefin] condition ([Sub.] = [$CH_2=CHCO_2H$] = 0.47 M; T = 305 K; 1 atm H_2).
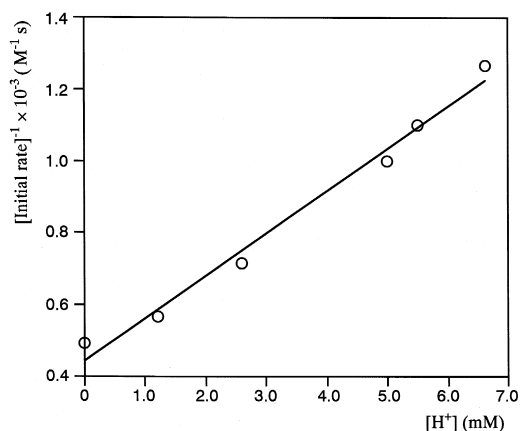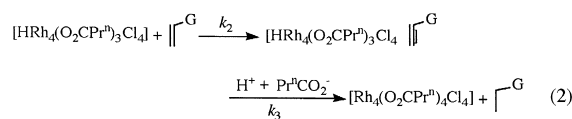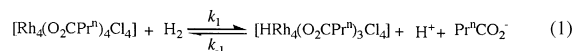
Fig. 4. Dependence of the initial rate of hydrogen consumption on $[H^+]$ ($[Cat.] = 2.0$ mM; $[Sub.] = [CH_2=CHCOCH_3] = 0.038$ M; $T = 298$ K).

$$-\frac{d[H_2]}{dt} = \frac{k_1 k_2 [Rh_4][H_2][olefin]}{k_{-1}[H^+][Pr^nCO_2^-] + k_2[olefin]} \qquad (3)$$

$$-\frac{d[H_2]}{dt} = \frac{\Delta n(H_2)}{V_s \times \Delta t} \quad (M\ s^{-1}) \qquad (4)$$

$$\frac{-1}{d[H_2]/dt} = \frac{1}{k_1[Rh_4][H_2]} + \frac{k_{-1}[Pr^nCO_2^-]}{k_1 k_2 [Rh_4][H_2][olefin]}[H^+] \qquad (5)$$

Scheme 2.

from the initial linear part of the H_2 consumption and estimated by Eq. (4), where $\Delta n(H_2)$ is the initial consumption of H_2 gas (in unit of mol) during the initial short time, Δt, and V_s represents the volume of the reaction solution. Eq. (3) explains the experimentally observed dependence of the initial rate of hydrogen uptake on the concentration of the substrate and of the catalyst shown in Figs. 2 and 3, respectively. Eq. (3) can be rewritten as Eq. (5). The observed linear dependence of the inverse of the initial rate on $[H^+]$ is consistent with Eq. (5).

3.2. Molecular structures of rhodium complexes

3.2.1. $[Rh_4(O_2CPr^n)_4Cl_4(CH_2=CHCN)_4]$

This compound immediately formed on the addition of acrylonitrile to the hydrogenation reaction solution. The ORTEP view is shown in
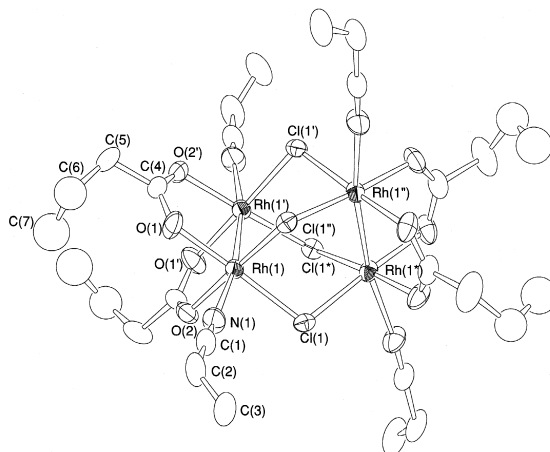
dependence of the initial rate on the concentration of the catalyst ($[Rh_4(O_2CPr^n)_4Cl_4(CH_3-CN)_4]$) in the hydrogenation of $CH_2=CHCO_2H$ at its high concentrations was observed (Fig. 3). Fig. 4 shows the linear dependence of the inverse of the initial rate on the proton concentration in the hydrogenation of $CH_2=CHCOCH_3$.

These results are in parallel to a mechanism similar to that proposed by Rempel et al. for $[Rh_2(O_2CCH_3)_4]$-catalyzed hydrogenation. It is a stepwise mechanism including a heterolytic splitting of hydrogen at the first step (Eq. 1) forming an active hydride species (with release of H^+), which reacts further with olefin substrate, and quickly releasing the hydrogenated product upon the attack of H^+ (Eq. 2). The observation of the isomerization of allyl alcohol to propanal is a supporting evidence for the stepwise addition of H_2 [13,14] (Scheme 1).

The rate law was obtained as Eq. (3) by assuming $k_3 \gg k_2$, k_1, and k_{-1} (Scheme 2). The initial rate ($-d[H_2]/dt$) was determined

$$[Rh_4(O_2CPr^n)_4Cl_4] + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [HRh_4(O_2CPr^n)_3Cl_4] + H^+ + Pr^nCO_2^- \qquad (1)$$

$$[HRh_4(O_2CPr^n)_3Cl_4] + \|{\overset{G}{\ }} \xrightarrow{k_2} [HRh_4(O_2CPr^n)_3Cl_4 \ \|{\overset{G}{\ }}$$

$$\xrightarrow[k_3]{H^+ + Pr^nCO_2^-} [Rh_4(O_2CPr^n)_4Cl_4] + \ulcorner^G \qquad (2)$$

Scheme 1.

Fig. 5. ORTEP drawing of $[Rh_4(O_2CPr^n)_4Cl_4(CH_2=CHCN)_4]$. Atoms are represented by the thermall ellipsoids at the 30% probability level with hydrogen atoms omitted. The C(7) ellipsoid shows one of the two sites for the disordered methyl carbon atom of the butyrate ligand.
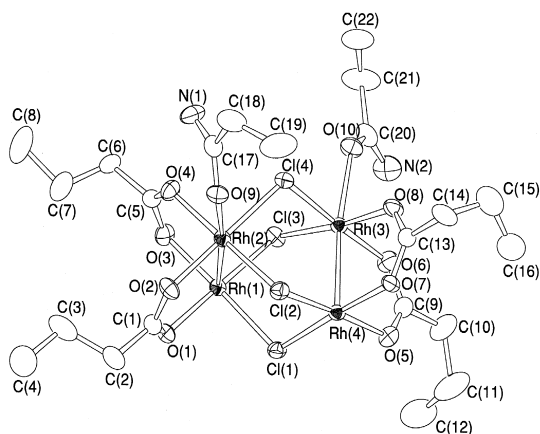
Fig. 6. ORTEP drawing of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CH_2-CONH_2)_2]$. Atoms are represented by the thermal ellipsoids at the 50% probability level with hydrogen atoms omitted. The C(12) ellipsoid shows one of the two sites for the disordered methyl carbon atom of the butyrate ligand.

Fig. 5. This result shows that the axial ligands can be readily substituted by other donor ligands, indicating axial position is relatively active for reactions. The Rh–Rh bond length is 2.5387(9) Å and Rh–Cl is 2.32 Å (ave.), which are similar to those of its parent $[Rh_4(O_2CPr^n)_4-Cl_4(CH_3CN)_4]$. The Rh–$O_{eq}$ lengths (ave. 2.04 Å) and Rh–N length (2.237(6) Å) are consistent with those of similar dinuclear species $[Rh_2-(O_2CR)_4L_2]$ [15].

3.2.2. $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CH_2CONH_2)_2]$

This compound was isolated by extraction with $CHCl_3$ from a hydrogenated reaction solution of $CH_2=CHCONH_2$. Unlike $[Rh_4-(O_2CPr^n)_4Cl_4(CH_2=CHCN)_4]$ or $[Rh_4-(O_2CPr^n)_4Cl_4(CH_3CN)_4]$, it has only two axial ligands (Fig. 6). The distances of Rh–Rh (ave. 2.542 Å) and Rh–Cl bonds (ave. 2.32 Å) are similar to those of its analogues. At least in the crystal, this complex is polymeric; the axial vacant sites of the rhodium atoms are occupied by carboxylate oxygen atoms of neighbouring complexes in short contact $[Rh(1)\cdots O(1)^* = 2.541(2)$ Å, $Rh(4)\cdots O(7)^{**} = 2.517(2)$ Å,

where atoms with * or ** belong to two neighbouring complexes].

4. Conclusion

The present tetrarhodium(II) complex $[Rh_4-(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ can catalyze hydrogenation of a variety of olefinic compounds in a mild condition in aqueous solution. Most of the catalyst can be recovered simply by extraction with organic solvents. However, the original axial ligands, CH_3CN, had been substituted by other coordinating compounds if there is any in the reaction solution.

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