ELSEVIER

Journal of Molecular Catalysis A: Chemical 118 (1997) 55–61

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Effect of the CO_2H groups of carboxylated triarylphosphines on (COD)RhCl(PAr_3)-catalyzed isomerization of 1-octen-3-ol under phase transfer conditions

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Received 4 June 1996; accepted 30 August 1996

Abstract

Water soluble sodium salts of (COD)RhCl(PAr_3), where PAr_3 is $Ph_2P(C_6H_4$-2-COOH), $Ph_2P(C_6H_4$-3-COOH), $Ph_2P(C_6H_4$-4-COOH), $PhP(C_6H_4$-3-COOH$)_2$, or $P(C_6H_4$-3-COOH$)_3$, catalyze under phase transfer conditions the isomerization of 1-octen-3-ol to 3-octanone. The reaction rate depends on the position and number of the carboxyl groups in the phosphine ligand. (COD)RhCl[$Ph_2P(C_6H_4$-2-C_6H_4COOH], which exists as an equilibrium mixture with (COD)(H)RhCl(-$OCOC_6H_4$-2-PPh_2) is more reactive than the hydride-free catalysts. A hydride addition–elimination mechanism is suggested as the major pathway for the catalytic process.

Keywords: Double bond migration; 1-Octen-3-ol; Phase transfer catalysis; Rhodium

1. Introduction

In the course of our studies on water soluble transition metal catalysts, we have developed facile syntheses for various carboxylated triarylphosphines [1]. These ligands have already been applied in our laboratory [2–4], as well as by other researchers [5,6] to unique rhodium catalyzed hydrogenation, hydroformylation, oligomerization and polymerization processes. In this paper, we report on the effect of the position and the number of the carboxyl groups in the triarylphosphine ligands in (COD)RhCl(PAr_3), on the activity of the complexes as 1-octen-3-ol isomerization catalysts under phase transfer conditions, and show that the carboxylate moieties serve both as enhancer to water solubility and as handles for back extraction of the metal catalysts into organic solvents.

2. Experimental

2.1. General procedure for preparation of complexes *1–5*

A solution of 313 mg (0.64 mmol) of $[(COD)Rh(\mu\text{-}Cl)]_2$ in 3 ml of either CH_2Cl_2 or

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PII S1381-1169(96)00374-3

Table 1
Elemental analyses and carbonyl IR bands of complexes **1–5**

Complex	Molecular formula	C [a] (%)	H [a] (%)	Cl [a] (%)	$\nu_{C=O}$ (cm^{-1})
1	$C_{27}H_{27}ClO_2PRh$	58.72 (58.66)	4.99 (4.92)	6.20 (6.41)	1710
2	$C_{27}H_{27}ClO_2PRh$	58.53 (58.66)	4.63 (4.92)	6.44 (6.41)	1720
3	$C_{27}H_{27}ClO_2PRh$	58.95 (58.66)	4.85 (4.92)	5.92 (6.41)	1686 1617
4	$C_{28}H_{27}ClO_4PRh$	56.12 (56.35)	4.44 (4.60)	5.67 (5.94)	1721 1690
5	$C_{29}H_{27}ClO_6PRh$	54.08 (54.35)	4.13 (4.23)	5.40 (5.53)	1717 1695 1682

[a] Calculated values are given in parentheses.

$CHCl_3$ was treated, under exclusion of air, with 1.28 mmol of the appropriated carboxylated phosphine [1] in 3 ml of the same solvent. The orange solution was stirred at room temperature for 15 min, concentrated and treated with 15 ml of absolute ether. The precipitated complex was washed with ether and dried under reduced pressure. Elemental analyses and significant infrared bands are given in Table 1. Selected ^{1}H-, ^{13}C- and ^{31}P-NMR spectra are listed in Table 2. Most of the complexes do not have sharp melting points due to decomposition.

2.2. Isomerization of 1-octen-3-ol

A solution of 128 mg (1 mmol) of 1-octen-3-ol, 0.12 mmol of a phase transfer agent and 10 μl of *o*-xylene (internal standard) in 0.5 ml of toluene was heated to 104°C and treated with a preheated solution (98°C) of 0.02 mmol of the rhodium complex (**1, 2, 3, 4** or **5**) neutralized with an equivalent amount of $NaOCH_3$ in 0.5 ml of triply distilled water. The mixture was stirred vigorously under exclusion of air at 104°C (or at another desired temperature). At intervals of 1–10 min 2 μl samples were withdrawn from the organic layer and immediately frozen at −40°C. GC analyses were carried out on a 2 m long column packed with 10% stabilized DEGS on Chromosorb W, operated at 95°C. Representative results are summarized in Table 3.

3. Results and discussion

In analogy to the synthesis of $(COD)RhCl(PPh_3)$ from PPh_3 and

Table 2
^{31}P- and selected ^{1}H- and ^{13}C-NMR signals for complexes **1–5**

Complex	40.5 MHz ^{31}P {^{1}H} signal [a]	Coordinated COD signals									
		400 MHz ^{1}H-NMR (ppm) [b]					100 MHz ^{13}C-NMR (ppm) [b]				
		2H		2H	4H	2H	2H				C=O
1	32.2 (147) [c]	1.93 (1.75)		2.32 (2.41) (4.22)	3.78 (5.72) [d]	5.34	28.42	31.27	72.20	79.011	170.63
2	34.2 (150)	1.94	2.08	2.39	3.09	5.13	28.46	31.97	70.92	78.77	169.69
3	35.1 (152)	1.94	2.10	2.37	3.14	5.66	29.48	33.63	66.57	72.20	168.80 [e]
4	33.8 (150)	1.97	2.18	2.44	3.15	5.65 [f]	30.67	31.83	67.21	100.70	168.77 169.24
5	34.4 (152)	2.02	2.13	2.46	3.28	5.53	30.00	34.14	73.16	107.88	196.06

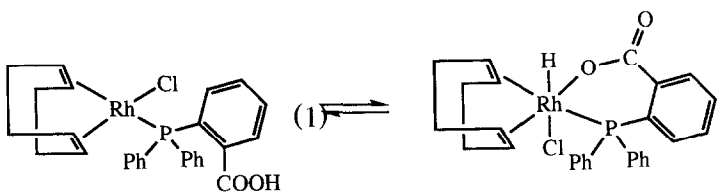
[a] Except for **1**, the measurements were performed in CD_3OD; values are given in ppm from 85% H_3PO_4; doublets, J_{P-Rh} are given in parentheses in Hz.
[b] Unless stated otherwise the ^{1}H- and ^{13}C-NMR of **1, 2,** and **3** were recorded in $CDCl_3$ and those of **4** and **5** in CD_3OD.
[c] Measured at 162 MHz in $CDCl_3$.
[d] The ^{1}H-NMR values in parentheses amount to 8% of the COD signals and corresponds to the protons of **6**.
[e] Measured at 67.5 MHz in CD_3OD.
[f] ^{1}H-NMR was measured in $CDCl_3$.

Table 3
Isomerization of 1-octen-3-ol by complexes **1–5** [a]

Rhodium complex	k_{obs} ($s^{-1} \times 10^{-2}$)	Conversion after 1 h (%) [b]
1	160.0±4.0	96
2	6.0±0.2	30
3	19.1±0.9	54
4	7.8±0.5	35
5	9.6±0.5	40

[a] Reaction conditions: 1 mmol of the substrate, 0.02 mmol of the rhodium complex (neutralized with $NaOCH_3$), 0.12 mmol of Aliquat 336, 0.5 ml of H_2O and 0.5 ml of toluene, at 104±0.2°C.
[b] Average of three experiments.

$[(COD)Rh(\mu\text{-}Cl)]_2$ [7] the dirhodium complex was treated with 2 eq. of (a) $Ph_2PC_6H_4$-2-COOH, (b) $Ph_2PC_6H_4$-3-COOH, (c) $Ph_2PC_6H_4$-4-COOH, (d) $PhP(C_6H_4\text{-}3\text{-}COOH)_2$ and (e) $P(C_6H_4\text{-}3\text{-}COOH)_3$. The products obtained from the latter four carboxylated phosphines proved, by virtue of their elemental analyses, their IR and multinuclear NMR spectra (see Tables 1 and 2), to be monorhodium compounds (cf. [8]) with the following formulas: $(COD)RhCl(Ph_2PC_6H_4\text{-}3\text{-}COOH)$ (**2**), $(COD)RhCl(Ph_2PC_6H_4\text{-}4\text{-}COOH)$ (**3**), $(COD)RhCl[PhP(C_6H_4\text{-}3\text{-}COOH)_2]$ (**4**) and $(COD)RhCl[P(C_6H_4\text{-}3\text{-}COOH)_3]$ (**5**). The main features of their spectra proved to resemble those of $(COD)RhCl(PPh_3)$ [8–12] apart from the signals characteristic for the carboxyl moieties. In contrast to complexes **2–5** which show strong ArCOOH carbonyl IR bands between 1682 and 1721 cm^{-1}, the product of $[(COD)Rh(\mu\text{-}Cl)]_2$ and $Ph_2PC_6H_4$-2-COOH showed a broad absorption in the carbonyl region with two discrete (medium) peaks at 1686 and 1617 cm^{-1}. We interpret this spectrum in terms of equilibrium **1** ⇄ **6** (Eq. (1)) in which an intramolecular oxidative addition–reductive elimination takes place.



1 **6**

Support in the formation of **6** can be found both in the appearance of a weak Rh–H band at 2005 cm^{-1} [13] and Rh–O absorptions at 388, 424 and 454 cm^{-1} [14] and the appearance of two sets of ^1H signals in the ^1H-NMR spectrum that correspond to the two rhodium compounds **1** and **6**. The integration of the peaks indicates that the major and minor products amount to 92% and 8%, respectively (see Table 2). In addition, a dd signal for the Rh–H appears at −12.80 ppm (J_{P-H} = 18 Hz, J_{Rh-H} = 15 Hz) (see e.g., Ref. [15]). It should be recalled that we have already observed a similar intramolecular cyclization when the rhodium–pyrazole complex $[Rh(CO)_2(\mu\text{-}pz)]_2$ had been reacted with $Ph_2PC_6H_4$-2-COOH. In that case $Rh(CO)(H\text{-}pz)(Ph_2PC_6H_4\text{-}2\text{-}COO)$ (characterized by X-ray diffraction analysis) has been obtained [2]. Upon treatment of the equilibrium mixture of **1** and **6** with $NaOCH_3$ both compounds were converted into the normal sodium salt of the normal carboxylic acid, **1**.

The sodium salts of all five rhodium complexes were shown to catalyze, under phase transfer conditions, the transformation of 1-octen-3-ol to 3-octanone via the corresponding enol tautomer [16] (Eq. (2)).

$$CH_3(CH_2)_4CH(OH)CH{=}CH_2 \rightarrow [CH_3(CH_2)_4C(OH){=}CHCH_3 \rightarrow CH_3(CH_2)_4COCH_2CH_3 \quad (2)$$

In most of our experiments, a two liquid phase system of water and toluene was used. The extraction of the metal complex into the organic layer is assumed to take place via liquid

anion exchange with lipophilic quaternary ammonium salts according to Eq. (3).

$$(COD)RhCl(Ph_2PC_6H_4COO^-)_{(aq)} + R_4N^+X_{(org)-} \rightleftarrows R_4N^+[(COD)RhCl(Ph_2PC_6H_4COO)]^-_{(org)} + X^-_{(aq)} \quad (3)$$

The main characteristic of this extraction is the lack of any direct interaction of the onium cation with the metal. The preferred phase transfer agent was tricaprylmethylammonium chloride (Aliquat 336®), though other onium salts were found to be active as well (vide infra)). In the absence of a phase transfer catalyst the allylic alcohol hardly reacted.

Under the conditions given in the experimental section the isomerization proved to be independent of the concentration of the catalyst and was found to be first order in the substrate. Some representative k_{obs} values are listed in Table 3.

The Table indicates that the rate depends both on the location, and on the number of carboxyl groups in the phosphine ligand. Catalyst **3**, in which the carboxyl moiety is *para* to the phosphorous atom has been shown to be more efficient than complex **2** in which the substituent is at the *meta* position. An increase in rate has been observed when two or three carboxyl functions had been introduced into the catalyst as in **4** and **5**. Among the five catalysts, **1** proved to be the most active one. This can be rationalized in terms of the existence of equilibrium (1) in which the rhodium hydride **6** can readily supply the hydride required for the isomerization process. The hydride can be provided also by some solvents (such as toluene [17]) (vide infra). Application of either benzene or chloroform, instead of toluene as solvent in **2–4** catalyzed reaction, caused significant retardation in rate. Furthermore, substitution of the toluene by octadeuteriotoluene (and the H_2O by D_2O) in the isomerization of the carbinol by **2** revealed a primary deuterium isotope effect $k_H/k_D = 1.9$. It is notable however, that the water does not play a part in the isomerization process. Replacement of H_2O by D_2O (leaving unlabeled $C_6H_5CH_3$ as the organic phase) did not affect the rate to any extent.

Since the cyclic isomer of complex **1** is converted by bases into hydride-free salts, we expected catalyst **1** to be more active at lower than at higher pH. In fact, the rate of isomerization of 1-octen-3-ol by **1** was found to increase slightly upon increasing pH. Under the conditions of the experimental section, the initial rates (and conversions after 1 h) for the **1**-catalyzed isomerization reaction were 0.84 (62), 1.06 (96) and 1.28 M $min^{-1} \times 10^{-1}$ (100%) at pH 4, 7 and 8.5, respectively. We attribute the increase in rate under basic conditions to the enhanced extractability of the anion $[(COD)RhCl(Ph_2PC_6H_4COO)]^-$ into the organic substrate-containing layer.

The influence of several quaternary onium salts on **1**- and **3**-catalyzed reaction (2) is summarized in Table 4. Although the variations in rate by the different phase transfer agents are

Table 4
Isomerization of 1-octen-3-ol by **1** and **3** in the presence of several quaternary onium salts [a]

Catalyst	Onium salt	Initial rate (mM $min^{-1} \times 10^{-1}$)
1	none	0.01
1	$[(C_4H_9)_4N]Br$	0.68
1	$[(C_4H_9)_4P]Br$	0.76
1	$[C_6H_5CH_2N(C_2H_5)_3]_3Cl$	0.85
1	$[C_{16}H_{33}N(CH_3)_3]Br$ [b]	0.88
1	$[C_8H_{17})_3NCH_3]Cl$	1.06
3	none	0.06
3	$[(C_4H_9)_4N]Br$	0.22
3	$[(C_4H_9)_4P]Br$	0.36
3	$[(C_4H_9)_3NCH_3]Br$	0.40
3	$[(C_6H_{13})_4N]I$	0.40
3	$[C_6H_5CH_2N(C_2H_5)_3]Cl$	0.413
3	$[(C_7H_{15})_4N]Br$	0.425
3	$[C_8H_{17})_3NCH_3]Cl$	0.577

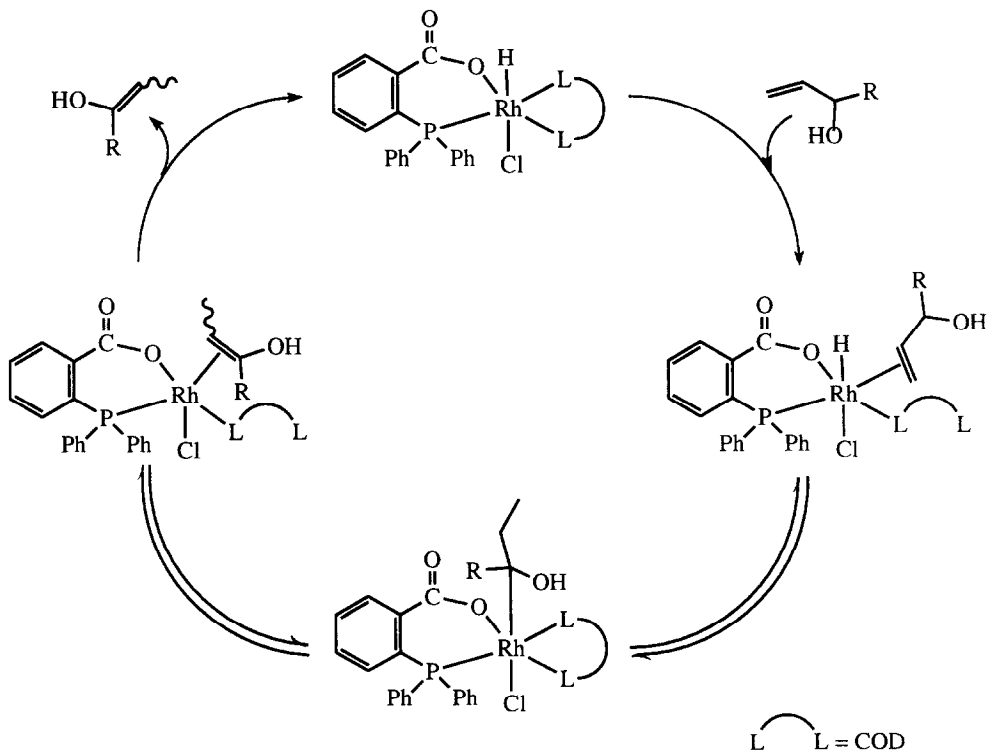
[a] Reaction conditions: 1 mmol of substrate, 0.02 mmol of rhodium complex (neutralized by $NaOCH_3$), 0.12 mmol of the onium salt, 0.5 ml of H_2O and 0.5 ml of toluene at 104 ± 0.2°C.
[b] In the presence of this PTC agent the reaction stopped after 20 min when the conversion reached 46%.

not sizable, these variations proved to be alike in both catalytic systems. The effectiveness of the onium salts seems to be associated mainly (or even entirely) with their extraction ability. Small onium salts and salts of low accessibility were shown to be the least efficient. The quaternary phosphonium ion proved somewhat more efficient than the corresponding ammonium salt. A similar behavior of the phase transfer agents has already been observed in the $RhCl_3$-catalyzed isomerization of 1-octen-3-ol [18]. However, in contrast to the latter catalyst system, where the onium salts both extract the metal ion into the organic phase, and play a part in the catalytic process, in the present case the sole function of the phase transfer agent is metal extraction. Thus, when a second portion of either the same or a different quaternary ammonium salt was added to the organic layer *after* phase separation, no change in rate of the catalytic process occurred.

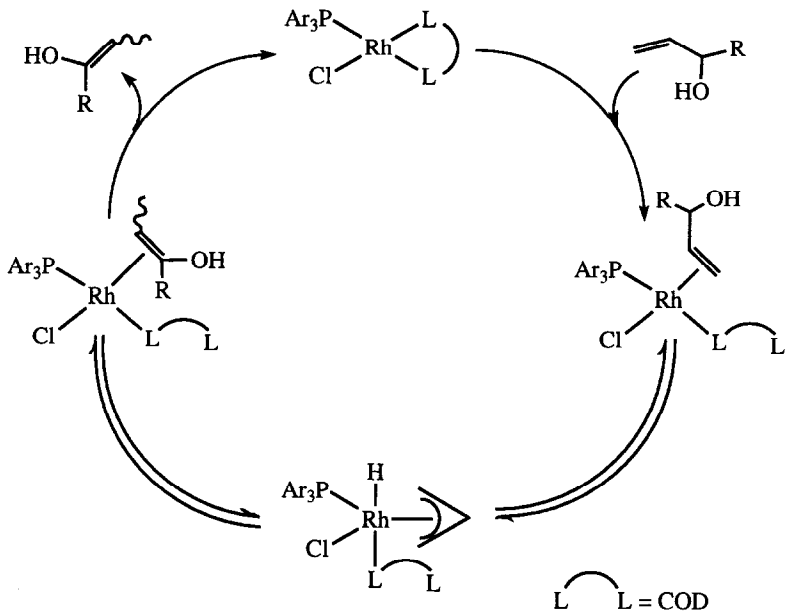
Isomerization of 1-octen-3-ol in the presence of **1–5** was found to have the same kinetic features between 80 and 100°C. Therefore, we could express the observed rate constants in this region of temperatures, in terms of Arrhenius plots form which we found that for each of the five systems $E_a \approx 11$ kcal mol^{-1}. This value which is lower than that of typical chemically-controlled, but higher than that of purely diffusion-controlled reactions [19] suggests that both processes contribute to the progress of the catalysis.

3.1. Mechanistic considerations

Two major mechanisms have been proposed for transition metal-catalyzed double bond migration in allylic compounds [20]. The first involves addition of an *M*–H bond to give an alkyl metal complex that undergoes nondegenerate β-hydrogen elimination to form a new C=C bond. The second one is based on a metal-assisted 1,3-hydrogen shift via a π-allyl



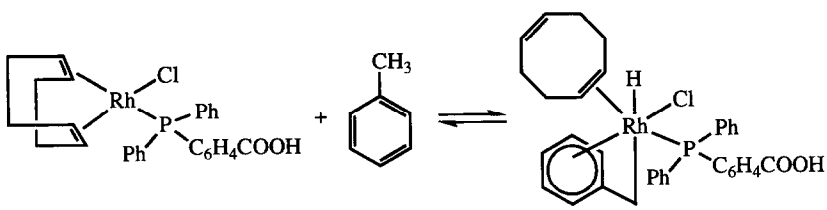
Scheme 1.



Scheme 2.

metal complex. In addition an alkoxide pathway which is specific for allyl alcohol isomerization has been suggested [21]. In this mechanism, which has been observed mainly in ruthenium-catalyzed processes, the metal forms initially a metal alkoxide of the allylic alcohol which in turn undergoes β-CH elimination and transformation into a π-oxopropenyl intermediate [21]. Since in our system neither substitution of the H_2O by D_2O, nor the labeling of the substrate hydroxyl with deuterium, had any effect on the rate, the alkoxide mechanism cannot play a significant role in our catalyses.

The superior catalytic activity of **1** over **2** and **3** can be rationalized best in terms of the hydride addition–elimination pathway shown as Scheme 1. This mechanism requires the preexistence of a metal hydride species. Thus, it is understandable why in the presence of toluene (that can form a rhodium hydride according to Eq. (4) [17]) the isomerization is faster than in benzene.



(4)

The existence of a primary isotope effect in toluene indicates that the formation of the hydride by this solvent is rate limiting. Since however the process takes place also in the presence of benzene, the π-allyl route shown as Scheme 2 as an alternative or as a coexisting mechanism cannot be excluded.

Acknowledgements

We thank the Israel Science Foundation (administered by the Israel Academy of Sciences and Humanities) and the partnership agreement between the Hebrew University of Jerusalem and the Technical University of Berlin for fi-

nancial support of this study, and Degussa, Hanau for the valuable gift of rhodium trichloride.

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