ELSEVIER

Journal of Organometallic Chemistry 512 (1996) 45–50

Journal of Organometallic Chemistry

Aqueous organometallic chemistry: the mechanism of catalytic hydrogenations with chlorotris(1,3,5-triaza-7-phosphaadamantane)rhodium(I) [1]

Ferenc Joó [a,*], Levente Nádasdi [a], Attila Cs. Bényei [a], Donald J. Darensbourg [b]

[a] *Institute of Physical Chemistry, Lajos Kossuth University, Debrecen H-4010, Hungary*
[b] *Department of Chemistry, Texas A & M University, College Station, TX 77843, USA*

Received 22 May 1995; in revised form 11 September 1995

Abstract

The water-soluble phosphine complex of Rh(I), $RhCl(PTA)_3$ (**1**) was shown to be an active catalyst for the hydrogenation of various olefinic and oxo-acids, as well as of allyl alcohol and 4-sulfostyrene in aqueous solution under mild conditions. Detailed kinetic investigations were carried out with crotonic acid and allyl alcohol as substrates. The rate of hydrogenation of both compounds showed a sharp maximum as a function of pH at 4.7. Hydrogenation of itaconic, crotonic and α-acetamidocinnamic acid in D_2O led to 45–100% deuteration of the products with 25–100% stereoselectivity towards the α-carbon atom. These results, together with those of pH-static hydrogenation of complex **1**, suggest that water strongly assists the dehydrochlorination of **1** to yield the catalytically active monohydrido species $HRh(PTA)_3$ (**2**). Nevertheless, depending on the substrate and the pH of the solution the dihydridic pathway may remain partially operative.

Keywords: Rhodium; Hydrogenation; Phosphines

1. Introduction

Aqueous organometallic chemistry has recently become a well-established, independent field of study aimed, in part, at developing biphasic catalytic processes for industrial (e.g. hydroformylation and polymerization) and biological applications [1,2]. With respect to processes of industrial importance, it is anticipated that in the future more environmentally benign processes will use water as a solvent or cosolvent [3]. A successful and widely used method to achieve water-soluble organometallic catalysts is by slight modification of ligands commonly found in catalytically active transition metal complexes, e.g. by sulfonation, aminomethylation, or carboxylation of phosphine ligands [4]. However, water is a highly polar solvent with the ability to form strong hydrogen bonds, and hence can intricately affect the mechanism of catalysis.

In the course of our investigations of aqueous organometallic catalysis we have discovered that the mechanism of the hydrogenation of activated olefins catalyzed by $RhClP_3$ type (P = tertiary phosphine) complexes in aqueous solutions may contain two important steps not observed in olefin hydrogenation processes utilizing Wilkinson's catalyst in organic solvents. First, the sulfonated phosphines PPh_nAr_m ($Ar = C_6H_4$-m-SO_3Na, $n + m = 3$; $m = 1$ TPPMS; $m = 3$ TPPTS) easily add across an activated olefinic bond, like that in maleic acid, with the formation of the corresponding phosphonium salt [5]. This was shown, in the case of $RhCl(TPPMS)_3$, to lead to the formation of a phosphine deficient Rh(I) species [6]. Of alkenoic acids, E-2-butenoic (crotonic acid) reacted slowly with phosphines, and in that case the phosphonium salt formation did not influence the catalytic performance of $RhCl(TPPMS)_3$. Second, water facilitates the formation of $HRh^{I}P_x$ monohydrido species rather than the dihydride $H_2Rh^{III}ClP_3$, where x is dependent on the nature and the amount of excess phosphine [7]. Both of these processes are pH-dependent.

* Corresponding author.

[1] Dedicated to Professor Marvin D. Rausch on the occasion of his 65th birthday.

SSDI 0022-328X(95)05946-6

Recently, we introduced the use of 1,3,5-triaza-7-phosphaadamantane (PTA) into organometallic catalysts in water [8,9]. It has been found that $RhCl(PTA)_3$, the analog of $RhCl(TPPMS)_3$, is an active catalyst for the selective reduction of unsaturated aldehydes to saturated aldehydes, using an aqueous sodium formate solution as the hydrogen source. One interesting property of PTA is that, despite being rather basic (pK_a 6.0) [10], it does not react with activated olefins. Hence, the effects of pH on the kinetics of hydrogenations catalyzed by $RhClP_3$ systems can be studied in the absence of the side reaction between the phosphine and the olefinic substrate. By utilizing an unactivated olefin, this side reaction can be further prevented. A detailed kinetic study was therefore undertaken to reveal the relative importance of the monohydridic and dihydridic pathways in hydrogenation of crotonic acid catalyzed by $RhCl(PTA)_3$ in aqueous solution. In addition, the hydrogenation of several other substrates (olefinic acids, 2-oxo-acids, allyl alcohol, 4-sulfostyrene) was also investigated.

2. Experimental details

2.1. Materials

PTA, $RhCl(PTA)_3$ and Z-α-acetamidocinnamic acid were prepared as described in the literature [8,11,12]. All other reagents were commercial products of Aldrich, Merck and Fluka and purified by recrystallization or distillation when necessary. For deuteration studies 99.9% D_2O from Cambridge Isotope Laboratories was used.

2.2. General methods

The extent of deuteration was calculated from the relative peak areas of ^1H NMR spectra of the products. NMR spectra were obtained on a Bruker WP 200 SY spectrometer. Deuterium distribution in 2-acetamido-3-phenylpropionic acid was deduced from the MS fragmentation pattern [13] of its methyl ester, obtained by esterification in HCl/methanol. Mass spectrometric measurements were made on a VG 7035 instrument (VG Analytical; direct sample introduction, 70 eV).

2.3. Hydrogenation experiments

Hydrogen uptake measurements were carried out using a thermostatted constant pressure gas burette [14]. Generally, the pH of the reaction mixtures was adjusted by titrating the solution of the substrate acids with NaOH (0.2 M) until the desired pH (4.70) was attained, as established by direct pH measurements using a conventional glass electrode. However, during the pH-variation studies an Na-phosphate buffer (0.1 M) of the required pH was used as solvent. In comparison with the unbuffered solutions of same pH, no specific salt effect was observed. In a typical experiment 20 ml of 4.5×10^{-2} M substrate solution was placed into the jacketed reaction flask under argon together with 6 mg (9.8×10^{-3} mmol) solid $RhCl(PTA)_3$ in a small cup made of filter paper and hung on a stainless steel hook. The reactor and the burette were subsequently filled with H_2 with several evacuation/refill cycles. The temperature was kept constant to ±0.1°C (typically at 37°C) using a Lauda K4R circulator. Reactions were started by dissolving the catalyst in the substrate solution. Independent of the experimental conditions, the reactions proceeded with no induction period and, therefore, initial rates were calculated from volume readings in the first 5 min. In all measurements the rate of hydrogen consumption was less than 50% of that of H_2 dissolution, as established by separate measurements under identical conditions, i.e. rate data were obtained in the truly kinetic region.

2.4. Isomerization studies

Isomerization of maleic to fumaric acid during the hydrogenation experiments was followed by high performance liquid chromatography (column: Nucleosil® 5 C18 (Macherey Nagel); eluent: methanol/water, containing 0.1% phosphoric acid, 1/1; room temperature, isocratic mode) using a Waters 501 pump, a 490E programable UV-vis detector and the Maxima integration software.

2.5. pH-static titrations

The jacketed reaction vessel was fitted with the base delivery tube of a Radiometer ABU 91 autoburette, a Radelkis OP08080 combined glass electrode connected to a PHM 93 pH meter, a gas inlet capillary and gas outlet tube connected to a bubbler. 50 ml doubly distilled, deaerated water was placed into the reactor and thoroughly bubbled with argon. $RhCl(PTA)_3$ was added in solid form against an argon stream. After closing the reactor the starting pH was adjusted by manual operation of the autoburette, the argon stream was changed for hydrogen and the solution was also stirred magnetically. The volume of base required to keep the pH constant was automatically recorded in time utilizing an IBM 486 PC.

3. Results and discussion

$RhCl(PTA)_3$ is an active catalyst for the hydrogenation of various water soluble unsaturated substrates under mild conditions (Scheme 1, Table 1).

$$R_1R_2C{=}CR_3R_4 + H_2 \longrightarrow R_1R_2CH{-}HCR_3R_4$$

Scheme 1.

Table 1
Specific rate of hydrogenation of various substrates by $[RhCl(PTA)_3]$ [a]

Substrate	Turnover (h^{-1})
1. Crotonic acid	331
2. Maleic acid	69
3. Fumaric acid	342
4. Itaconic acid	453
5. Allyl alcohol	188
6. 2-oxovaleric acid	98
7. Pyruvic acid	46
8. *p*-Sulfostyrene	158

[a] Conditions: $T = 37°C$; $c_{substrate} = 4.5\times10^{-2}$ mol dm^{-3}; $c_{[Rh(I)]} = 4.9\times10^{-4}$ mol dm^{-3}; $c_{hydrogen} = 6.6\times10^{-4}$ mol dm^{-3}; pH 4.70.

In general, the hydrogenation rate of unsaturated fatty acids is greater than that of 2-oxo-acids. Strikingly, fumaric acid is hydrogenated approximately five times faster than maleic acid, contrary to the behavior of Wilkinson's catalyst, which, in organic solvents, is considerably more active for hydrogenation of *cis*-rather than *trans*-olefins [15]. In this respect, $RhCl(PTA)_3$ resembles $RhCl(TPPMS)_3$ [16]. It is interesting to note that the fastest hydrogenation was observed with itaconic acid, although methyl itaconate is reduced slowly with $RhCl(PPh_3)_3$ in benzene [15]. During hydrogenation the originally yellow solutions slowly become brown, and the rate of this color change depends on the excess phosphine concentration, temperature, and pH of the solutions.

Detailed kinetic investigations show that the rate of crotonic acid hydrogenation is first order in the catalyst concentration (Fig. 1), levels off with crotonic acid concentration (Fig. 2) and varies in a slightly non-linear way with the partial pressure of dihydrogen (Fig. 3). A small excess of PTA decreases the rate considerably, however, the reaction is not completely inhibited even at higher excess of the phosphine (Fig. 4).

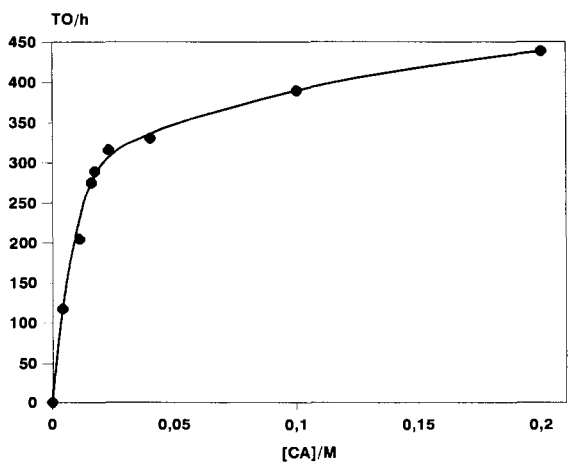

Fig. 1. Initial rate of crotonic acid hydrogenation as a function of substrate concentration. Conditions: $T = 37°C$; $c_{[Rh(I)]} = 4.9\times10^{-4}$ mol dm^{-3}; $c_{hydrogen} = 6.6\times10^{-4}$ mol dm^{-3}; pH 4.70.

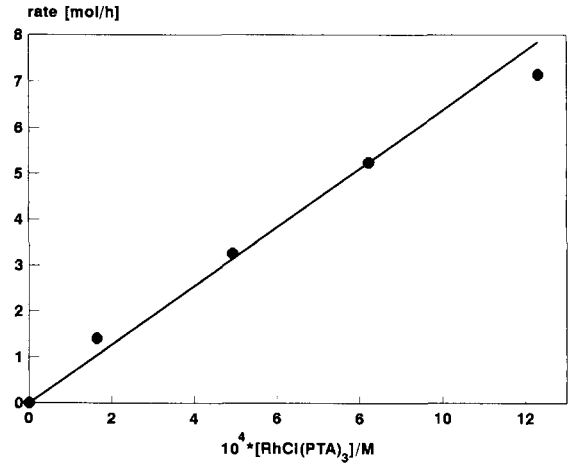

Fig. 2. Initial rate of crotonic acid hydrogenation as a function of $RhCl(PTA)_3$ concentration. Conditions: $T = 37°C$; $c_{substrate} = 4.5\times10^{-2}$ mol dm^{-3}; $c_{hydrogen} = 6.6\times10^{-4}$ mol dm^{-3}; pH 4.70.

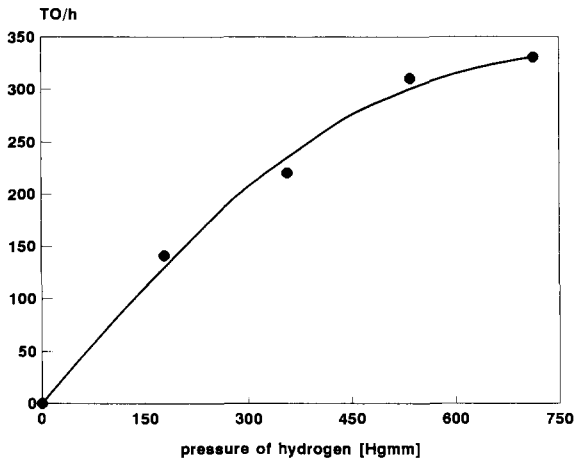

Fig. 3. Initial rate of crotonic acid hydrogenation as a function of partial pressure of hydrogen. Conditions: $T = 37°C$; $c_{[Rh(I)]} = 4.9\times10^{-4}$ mol dm^{-3}; $c_{substrate} = 4.5\times10^{-2}$ mol dm^{-3}; pH 4.70.

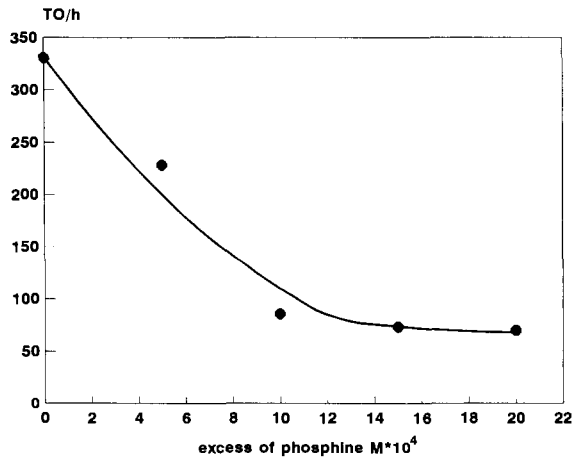

Fig. 4. Initial rate of crotonic acid hydrogenation as a function of excess phosphine. Conditions: $T = 37°C$; $c_{[Rh(I)]} = 4.9\times10^{-4}$ mol dm^{-3}; $c_{substrate} = 4.5\times10^{-2}$ mol dm^{-3}; $c_{hydrogen} = 6.6\times10^{-4}$ mol dm^{-3}; pH 4.70.

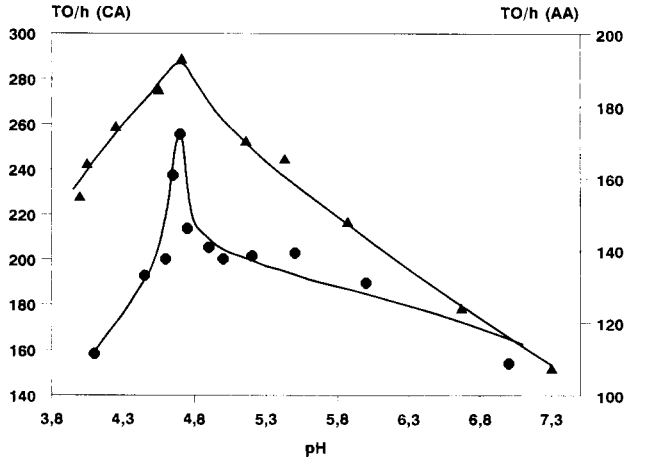

Fig. 5. Dependence of reaction rate of hydrogenation of crotonic acid (▲) and allyl alcohol (●) on pH. Conditions: $T = 37°C$; $c_{[Rh(I)]} = 4.9 \times 10^{-4}$ mol dm^{-3}; $c_{substrate} = 4.5 \times 10^{-2}$ mol dm^{-3}; $c_{hydrogen} = 6.6 \times 10^{-4}$ mol dm^{-3}.

All these findings could be interpreted in terms of a classical dihydridic mechanism [17] of hydrogenations catalyzed by Wilkinson-type rhodium phosphine complexes (CA = crotonic acid, BA = butyric acid):

$$RhCl(PTA)_3 + H_2 \rightleftharpoons (H)_2RhCl(PTA)_2 + PTA \quad (1)$$

$$(H)_2RhCl(PTA)_2 + CA \rightleftharpoons (HCA)(H)RhCl(PTA)_2 \quad (2)$$

$$(HCA)(H)RhCl(PTA)_2 + H_2 \rightarrow (H)_2RhCl(PTA)_2 + BA \quad (3)$$

Although this simplified scheme does not show all the possible elementary steps, the overall rate of such a reaction sequence should be independent of pH since no proton is involved in any of the consecutive reactions.

Contrary to this observation, the hydrogenation of crotonic acid is very strongly influenced by the pH (Fig. 5). The maximum rate occurs at pH 4.7, which coincides with the pK_a of crotonic acid [18], hence it was necessary to study the hydrogenation of allyl alcohol and 4-sulfostyrene as 'non-ionizable' substrates as a function of pH as well. In both cases a maximum rate is achieved at pH 4.7. Therefore, this value refers merely to changes in the mechanism brought about by varying pH, and the incidence with the pK_a of crotonic acid is only coincidental.

Through the use of pH-static measurements, it has been established that in aqueous solutions the reaction of $RhCl(PTA)_3$ and H_2 results in proton liberation (Eq. (4)) [9]. This reaction can be interpreted as a reductive dehydrochlorination of an intermediate Rh(III) dihydride which has previously been reported in the literature [19]. The driving force for this process comes from the high solvation energy of the ionic products, particularly H^+, in water [20]. In this respect $RhCl(PTA)_3$ behaves similarly to $RhCl(TPPMS)_3$.

Table 2
Distribution of deuterium between carbon atoms of various substrates [a]

Substrate	Product 1 (%)	Product 2 (%)	Product 3 (%)
α-acetamido cinnamic acid	0	0	100
Itaconic acid	45	0	55
Crotonic acid	75	15	10

[a] Conditions: $T = 37°C$; $c_{substrate} = 4.5 \times 10^{-2}$ mol dm^{-3}; $c_{[Rh(I)]} = 4.9 \times 10^{-4}$ mol dm^{-3}; $c_{hydrogen} = 6.6 \times 10^{-4}$ mol dm^{-3}; pH 4.70.

$$RhCl(PTA)_3 + H_2 \rightleftharpoons HRh(PTA)_3 + Cl^- + H^+ \quad (4)$$

From the kinetic measurements it is highly probable that the monohydride, formed in reaction (4), catalyses the hydrogenation of crotonic acid through the following steps (L = PTA or H_2O):

$$HRh(PTA)_3 + CA \rightleftharpoons HRh(CA)(PTA)_2 + PTA \quad (5)$$

$$HRh(CA)(PTA)_2 + L \rightleftharpoons [(HCA)Rh(PTA)_2L] \quad (6)$$

$$[(HCA)Rh(PTA)_2L] + H^+ \rightarrow [Rh(PTA)_2L]^+ + BA \quad (7)$$

$$[Rh(PTA)_2L]^+ + H_2 \rightleftharpoons HRh(PTA)_2L + H^+ \quad (8)$$

It should be emphasized that numerous other equilibria, involving phosphine, water, chloride and carboxylate coordination, and the reaction of the respective species with dihydrogen, should also be regarded. However, all considerations result in the conclusion that part, if not all, of the product is formed on a pH-dependent, monohydridic pathway.

This conclusion is supported by the results of deuteration experiments, where unsaturated acids were hydrogenated with H_2 in D_2O catalyzed by $RhCl(PTA)_3$. The products were found to be extensively deuterated as illustrated in Scheme 2.

($R = CH_2COOH$, $R' = H$: itaconic acid; $R = C_6H_5$, $R' = H$: acetamidocinnamic acid; $R = H$, $R' = CH_3$: crotonic acid)

The distribution of deuterium at full conversion (Table 2) reveals some interesting differences between the

$$R'—CH=C(R)—COOH \xrightarrow{H_2,\ D_2O} \begin{cases} R'—CH_2—CH(R)—COOH & (1) \\ R'—CHD—CH(R)—COOH & (2) \\ R'—CH_2—CD(R)—COOH & (3) \end{cases}$$

Scheme 2.

three substrates studied. The sterically hindered acetamidocinnamic acid derivative is hydrogenated slowly, but it is fully deuterated and the label is exclusively on the α-carbon atom (**3**). This implies that hydrogenation proceeds on a pathway including a protonolysis (deuterolysis) step similar to that in Eq. (7), and that H/D exchange on the rhodium is insignificant on this time scale (hours). Itaconic acid is also exclusively deuterated on the α-carbon (**3**), however, 45% of the product remains undeuterated (**1**) implying the dihydridic mechanism is operative too. The dihydridic mechanism is even more significant when utilizing crotonic acid as the substrate, where 75% of the product formed results from that pathway and there is only a slight directing effect of the substituents, resulting in an almost even distribution of the label on the α- and β-carbon atoms. Similar deuteration experiments have already been described in the literature using Rh(I) complexes of various sulfonated phosphines as catalysts [13]. Based on detailed NMR investigations it was concluded that labeling of the products occurred via an [Rh]–H $\rightleftarrows$ [Rh]–D exchange, although a protonation step, as suggested here, could not be ruled out completely. It would be premature to speculate on the exact causes of the selectivity in the deuteration of the above substrates. However, it is important to stress that in aqueous systems highly enantioselective hydrogenations [21] can be achieved only if (i) the probability of monohydridic mechanism is decreased, e.g. by a careful choice of pH, and/or (ii) the transfer of hydrogen from the metal center onto the olefin, and consequently the protonolysis, proceeds regio- and stereospecifically.

Both dihydridic and monohydridic mechanisms give rise to the reversible formation of an intermediate rhodium-alkyl species (reactions (2) and (6)). If this potential equilibrium is not shifted significantly to the right, olefin isomerization may occur. Under standard reaction conditions (see Table 1), the formation of fumaric acid during the hydrogenation of maleic acid was not observed. This is in agreement with our expectations since in the $RhCl(PTA)_3$ catalyzed system fumaric acid is much more reactive than maleic acid. However, when hydrogenations were carried out using 5 v/v% H_2 in Ar, and the reactions were stopped at low conversions, 14–17% fumaric acid was detected by HPLC. This does not necessarily imply that reduction of maleic acid catalyzed by $RhCl(PTA)_3$ proceeds via isomerization to fumaric acid followed by hydrogenation; this pathway cannot be excluded but our kinetic results do not allow for this distinction.

Formation of *cis,fac*-$(H)_2RhCl(TPPTS)_3$ from $RhCl(TPPTS)_3$ and H_2, in the presence of excess TPPMS, has been observed by ^{31}P NMR, and the complex was found to be a poor hydrogenation catalyst [22]. The related complexes *cis-mer*-$[LRh(H)(PTA)_3]^+$ (L = Cl- or H_2O) and *cis*-$[Rh(H)(H)(PTA)_4]Cl$ were shown to form in the reaction of $RhCl(PTA)_3$ and H_2 in the presence of excess PTA [9]. This is in agreement with our finding that excess PTA decreases the rate of hydrogenation, but does not inhibit the reaction completely.

The temperature dependence of the overall rate in such a complex catalytic system obviously cannot be characterized by one activation energy. From measurements in the 10–60°C temperature range, a temperature quotient of 42 kJ mol^{-1} could be calculated for the hydrogenation of crotonic acid catalyzed by $RhCl(PTA)_3$. This value is fairly close to the activation energies established for maleic acid (52 kJ mol^{-1}) and fumaric acid (54 kJ mol^{-1}) hydrogenations in unbuffered aqueous solutions, catalyzed by $RhCl(TPPMS)_3$ [16].

4. Conclusions

The studies described herein on the catalytic hydrogenation of simple water-soluble olefinic substrates with $RhCl(PTA)_3$ as catalyst illustrate the importance of ionic equilibria in aqueous organometallic catalysis. Specifically, the high solvation power of water facilitates reactions with ionic products, such as reductive dehydrochlorination of Rh(III)-hydrides, changing the active rhodium species in the catalytic system. This changes the entire mechanism of the catalyzed reaction leading to unusual rates and selectivities as exemplified by the greater hydrogenation rate of fumaric acid relative to maleic acid. It is concluded that knowledge of the effect of pH on the outcome of aqueous organometallic reactions and its control is essential in devising selective catalytic syntheses.

Acknowledgements

This work has been jointly supported by the National Science Foundation (CHE91-19737 and INT-9313951) and the Hungarian Academy of Sciences (30.008/134/90). Financial support by the Hungarian National Scientific Research Foundation (OTKA grants T7527, F4021) and by the Ministry of Culture and Education (MKM 209/92) is gratefully acknowledged. Thanks are due to Albright and Wilson, Ltd. for a gift of tetrakis(hydroxymethyl)-phosphonium chloride. Support to buy an HPLC facility was provided by the TEMPUS scheme of EU (2237/90). We are grateful to Dr. Zoltán Dinya of L. Kossuth University for recording mass spectra. The help given by Tara J. Decuir (Texas A&M University) in writing the manuscript is gratefully acknowledged. L. Nádasdi is grateful for a stipend from Universitas Foundation (Kereskedelmi Bank Rt) Hungary.

References

[1] (a) W.A. Herrmann and C.W. Kohlpaintner, *Angew. Chem., Int. Ed. Engl., 32* (1993) 1524; (b) P. Kalck and F. Monteil, *Adv. Organomet. Chem., 34* (1992) 219; (c) D.V. McGrath, R.H. Grubbs and J.W. Ziller, *J. Am. Chem. Soc., 113* (1991) 3611; (d) D.J. Darensbourg, F. Joó, Á. Kathó, J.N.W. Stafford, A. Bényei and J.H. Reibenspies, *Inorg. Chem., 33* (1994) 175; (e) F. Joó, N. Balogh, L.I. Horváth, Gy. Filep, I. Horváth and L. Vígh, *Anal. Biochem., 194* (1991) 34; (f) B. Maresca and A.R. Cossins, *Nature, 365* (1993) 606.

[2] P.A. Chaloner, M.A. Esteruelas, F. Joó and L.A. Oro, *Homogeneous Hydrogenation (Catalysis by Metal Complexes)*, Kluwer Academic, Dordrecht, Netherlands, 1994.

[3] (a) R.A. Sheldon, *CHEMTECH, 24* (1994) 38; (b) C.-J. Li, *Chem. Rev., 93* (1993) 2023.

[4] (a) S. Ahrland, J. Chatt, N.R. Davies and A.A. Williams, *J. Chem. Soc.*, (1958) 276; (b) I. Tóth, B.E. Hanson and M.E. Davis, *Organometallics, 9* (1990) 675; (c) V. Ravindar, H. Hemling, H. Schumann and J. Blum, *Synth. Commun., 22* (1992) 841; (d) J.W. Ellis, K.N. Harrison, P.A.T. Hoye, A.G. Orpen, P.G. Pringle and M.B. Smith, *Inorg. Chem., 31* (1992) 3026; (e) O. Herd, K.P. Langhans, O. Stelzer, N. Weferling and W.S. Sheldrick, *Angew. Chem., Int. Ed. Engl., 32* (1993) 1058; (f) W. A. Herrmann, C.W. Kohlpaintner, H. Bahrmann and W. Konkol, *J. Mol. Catal., 73* (1992) 191.

[5] (a) C. Larpent and H. Patin, *Tetrahedron, 44* (1988) 6107; (b) C. Larpent and G. Meignan, *Tetrahedron Lett., 27* (1993) 4331.

[6] A. Bényei, J.N.W. Stafford, Á. Kathó, D.J. Darensbourg and F. Joó, *J. Mol. Catal., 84* (1993) 157.

[7] F. Joó, P. Csiba and A. Bényei, *J. Chem. Soc., Chem. Commun.*, (1993) 1602.

[8] (a) D.J. Darensbourg, F. Joó, M. Kannisto, Á. Kathó and J.H. Reibenspies, *Organometallics, 11* (1992) 1990; (b) D.J. Darensbourg, F. Joó, M. Kannisto, Á. Kathó, J.H. Reibenspies and D.J. Daigle, *Inorg. Chem., 33* (1994) 200.

[9] D.J. Darensbourg, N.W. Stafford, F. Joó and J.H. Reibenspies, *J. Organomet. Chem., 488* (1995) 99.

[10] K.J. Fisher, E.C. Alyea and N. Shahnazarian, *Phosphorus, Sulfur, Silicon Relat. Elem., 48* (1990) 37.

[11] D.J. Daigle, A.B. Pepperman, Jr. and S.L. Vail, *J. Heterocyclic Chem., 11* (1974) 407.

[12] A.H. Blatt (ed.), *Organic Syntheses*, Vol. 2, Wiley, New York, 1947, p. 1.

[13] J. Bakos, R. Karaivanov, M. Laghmari and D. Sinou, *Organometallics, 13* (1994) 2951.

[14] Z. Tóth, F. Joó and M.T. Beck, *Inorg. Chim. Acta, 42* (1980) 153.

[15] B.R. James, *Homogeneous Hydrogenation*, Wiley, New York, 1973, pp. 204–248.

[16] F. Joó, L. Somsák and M.T. Beck, *J. Mol. Catal., 24* (1984) 71.

[17] J.A. Osborne, F.H. Jardine, J.F. Young and G. Wilkinson, *J. Chem. Soc.*, (1966) 1711.

[18] R.C. Weast, M.J. Astle and W.H. Beyer (eds.), *CRC Handbook of Chemistry and Physics*, 64th edn., CRC Press, Boca Raton, FL, D-167.

[19] (a) F. Joó and E. Trócsányi, *J. Organometal. Chem., 231* (1982) 63; (b) V.V. Grushin, *Acc. Chem. Res., 26* (1993) 279; (c) V.V. Grushin and H. Alper, *J. Org. Chem., 58* (1993) 4794.

[20] Ref. [15], pp. 1–2.

[21] (a) L. Lecomte, D. Sinou, J. Bakos, I. Tóth and B. Heil, *J. Organometal. Chem., 370* (1989) 277; (b) I. Tóth, B.E. Hanson and M.E. Davis, *Tetrahedron Asymmetry, 1* (1990) 913; (c) A. Kumar, G. Oehme, J.P. Roque, M. Schwarze and R. Selke, *Angew. Chem., Int. Ed. Engl., 33* (1994) 2197.

[22] C. Larpent and H. Patin, *J. Organometal. Chem., 335* (1987) C13.