ELSEVIER

Journal of Organometallic Chemistry 551 (1998) 49–53

Journal of Organometallic Chemistry

Kinetic studies on the selective hydrogenation of phenylacetylene catalyzed by [Rh(NBD)(PPh$_3$)$_2$]BF$_4$ (NBD = 2,5-norbornadiene) [1]

Miguel A. Esteruelas [b], Inmaculada González [a], Juana Herrero [a,*], Luis A. Oro [b,2]

[a] *Departamento de Química, Universidad de Cantabria, 39005-Santander, Spain*

[b] *Departamento de Química Inorgánica-Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, Zaragoza 50009, Spain*

Received 19 April 1997; received in revised form 8 June 1997

Abstract

The complex [Rh(NBD)(PPh$_3$)$_2$]BF$_4$ catalyzes the selective hydrogenation of phenylacetylene to styrene. In dichloromethane solution at 25°C, selectivities close to 80% are achieved. The reaction is first order in catalyst and substrate, and second order in hydrogen pressure, while the addition of triphenylphosphine inhibits the reduction. The mechanism deduced for this hydrogenation, on the basis of the above mentioned kinetic results, suggests that the reduction of the diolefin of the catalyst does not occur during the hydrogenation of the alkyne. © 1998 Elsevier Science S.A.

1. Introduction

Cationic rhodium and iridium complexes with the general formula [M(diene)L$_a$]$^+$ (a = 2 or 3) have been found to be active catalysts for the hydrogenation of olefins [1–7], dienes [8,9], internal alkynes [10] and ketones [11]. In solvents such as acetone, ethanol or acetonitrile, these compounds react with molecular hydrogen to give dihydrido-metal complexes [MH$_2$S$_x$L$_a$]$^+$ (M = Rh, Ir; S = solvent), which under catalytic conditions are in equilibrium with the corresponding monohydridos MHS$_y$L$_a$ (Eq. (1)). Both the dihydrido and monohydrido species are the active catalysts [12].

$$[MH_2S_xL_a]^+ \rightleftharpoons MHS_yL_a + H^+ \quad (1)$$

The reduction of terminal alkynes with these systems is not easy. In this sense, it has been proposed that the terminal alkynes, which are fairly acidic, destroy the active species by formation of alkynyl derivatives, according to Eq. (2) [10].

$$MHS_yL_a + RC{\equiv}CH \rightarrow M(C{\equiv}C-R)S_yL_a + H_2 \quad (2)$$

In spite of these difficulties, 1-hexyne can be successfully and selectively reduced to 1-hexene using 2-methoxyethanol and [Rh(NBD)(PPh$_2$Me)$_2$]$^+$ (NBD = 2,5-norbornadiene) as solvent and catalyst respectively [10], or using dichloromethane and [Rh(TFB){P(C$_6$H$_4$-4-R)$_3$}$_2$]$^+$ (TFB = tetrafluorobenzobarrelene) type complexes [13]. Recently, it has been also observed that the iridium complexes [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (COD = 1,5-

* Corresponding authors.

[1] Dedicated to Prof. Peter M. Maitlis, author of major advances in the understanding of homogeneous catalysis, on the occasion of his 65th birthday.

[2] Also corresponding author.

cyclooctadiene) catalyzes the selective hydrogenation of phenylacetylene to styrene in dichloromethane as solvent [14]. Kinetic and spectroscopic investigations indicate that the diolefin is not reduced during the reaction, and although the hydrido-akynyl complex $[IrH(C{\equiv}CPh)(COD)(\eta^2\text{-}^{i}Pr_2PCH_2CH_2OMe)]BF_4$ is the main species under catalytic conditions, the hydrogenation proceeds via the dihydrido intermediate $[IrH_2(COD)(\eta^2\text{-}^{i}Pr_2PCH_2CH_2OMe)]BF_4$ according to Eqs. (3)–(5), where the last equation is the rate-determining step [14].

$$\left[Ir(COD)\left(\eta^2-{}^{i}Pr_2PCH_2CH_2OMe\right)\right]BF_4 + H_2 \rightleftharpoons \left[IrH_2(COD)\left(\eta^2-{}^{i}Pr_2PCH_2CH_2OMe\right)\right]BF_4 \quad (3)$$

$$\left[IrH_2(COD)\left(\eta^2-{}^{i}Pr_2PCH_2CH_2OMe\right)\right]BF_4 + PhC{\equiv}CH \rightleftharpoons \left[IrH(CH{=}CHPh)(COD)\left(\eta^2-{}^{i}Pr_2PCH_2CH_2OMe\right)\right]BF_4 \quad (4)$$

$$\left[IrH(CH{=}CHPh)(COD)\left(\eta^2-{}^{i}Pr_2PCH_2CH_2OMe\right)\right]BF_4 + H_2 \rightarrow \left[IrH_2(COD)\left(\eta^2-{}^{i}Pr_2PCH_2CH_2OMe\right)\right]BF_4 + PhCH{=}CH_2 \quad (5)$$

In order to investigate the generality of this mechanism for rhodium cationic complexes, we have carried out a kinetic study about the hydrogenation of phenylacetylene, catalyzed by $[Rh(NBD)(PPh_3)_2]BF_4$. In this paper, we report the results from this study.

2. Results and discussion

Complex $[Rh(NBD)(PPh_3)_2]BF_4$ efficiently catalyzes the sequential hydrogenation of phenylacetylene in dichloromethane solution. At 25°C and atmospheric pressure, selectivities close to 80% are achieved for the hydrogenation of the alkyne to the alkene, as illustrated in Fig. 1. Reduction of the double bond only begins to take place when most of the alkyne has been consumed. In the absence of the alkyne, styrene is hydrogenated to ethylbenzene at slower rates than those observed in the reduction of the acetylene triple bond. During the reduction of the C≡C triple bond the formation of norbornene or norbornane was not observed.

Initial hydrogenation rates were obtained from gas uptake experiments at 25°C. In order to determine the rate dependence on the various reaction components, hydrogenation runs were performed at different catalyst and substrate concentrations and at different hydrogen pressures. The data collected in Table 1 indicate that the reaction is first order in catalyst and substrate. Plots of $\log(-dV/dt)$ versus log([Catalyst]) and versus log([PhC≡CH]) give in both cases straight lines of slope 0.9. An analogous plot of $\log(-dV/dt)$ versus $\log(P(H_2))$ yields a straight line of slope 2.0, suggesting that the reduction of the alkyne is second order in hydrogen pressure. In addition, it should be mentioned that the hydrogenation of phenylacetylene was found to be inhibited by the addition of triphenyl phosphine

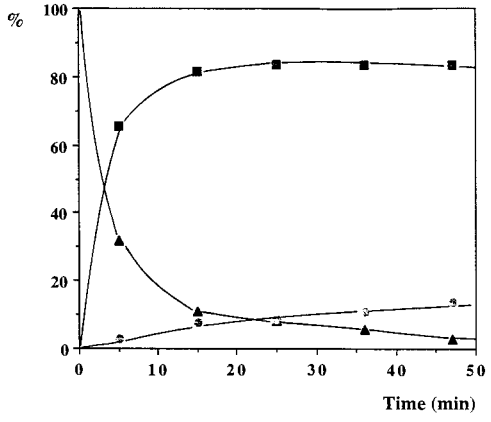

Fig. 1. Hydrogenation of phenylacetylene to styrene catalyzed by $[Rh(NBD)(PPh_3)_2]BF_4$ in dichloromethane at 25°C, 1 atm H_2, 1.6×10^{-3} M [Catalyst], 0.17 M PhC_2H. ▲Phenylacetylene; ■styrene; ●ethylbenzene.

(Fig. 2). In light of these results, a similar mechanism to that described by Eqs. (3)–(5) can be proposed (Eqs. (6)–(10)).

$$\underset{\mathbf{1}}{[Rh(NBD)(PPh_3)_2]}BF_4 + H_2 \overset{K_6}{\rightleftharpoons} \underset{\mathbf{2}}{[RhH_2(NBD)(PPh_3)_2]}BF_4 \quad (6)$$

$$\underset{\mathbf{2}}{[RhH_2(NBD)(PPh_3)_2]}BF_4 \overset{K_7}{\rightleftharpoons} \underset{\mathbf{3}}{[RhH_2(NBD)(PPh_3)]}BF_4 + PPh_3 \quad (7)$$

$$\underset{\mathbf{3}}{[RhH_2(NBD)(PPh_3)]}BF_4 + PhC{\equiv}CH \overset{K_8}{\rightleftharpoons} \underset{\mathbf{4}}{[RhH(CH{=}CHPh)(NBD)(PPh_3)]}BF_4 \quad (8)$$

$$\underset{\mathbf{4}}{[RhH(CH{=}CHPh)(NBD)(PPh_3)]}BF_4 + H_2 \overset{k_9}{\rightarrow} \underset{\mathbf{5}}{[RhH_2(NBD)(PPh_3)}BF_4 + CH_2{=}CHPh \quad (9)$$

$$\underset{\mathbf{5}}{[RhH_2(NBD)(PPh_3)]}BF_4 + PPh_3 \rightarrow \underset{\mathbf{1}}{[RhH_2(NBD)(PPh_3)_2]}BF_4 \quad (10)$$

With regard to the kinetic data, there is no doubt that Eq. (9) is the rate-determining step. Thus, the rate of formation of styrene is

$$d[\text{styrene}]/dt = k_9[\mathbf{4}]P(H_2) \quad (11)$$

The concentration of the key intermediate **4** can be determined as follows:

$$[Rh]_{Tot} = [\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}] + [\mathbf{4}] \quad (12)$$

since $K_6 = [\mathbf{2}]/[\mathbf{1}]P(H_2)$, $K_7 = [\mathbf{3}][PPh_3]/[\mathbf{2}]$ and $K_8 = [\mathbf{4}]/[\mathbf{3}][PhC_2H]$, we have $[\mathbf{1}] = [\mathbf{4}][PPh_3]/K_6K_7K_8[PhC_2H]P(H_2)$, $[\mathbf{2}] = [\mathbf{4}]\,[PPh_3]/K_7K_8[PhC_2H]$ and $[\mathbf{3}] = [\mathbf{4}]/K_8\,[PhC_2H]$ and finally

$$[\mathbf{4}] = \frac{K_6K_7K_8[Rh]_{Tot}[PhC_2H]P(H_2)}{[PPh_3]\{1 + K_6P(H_2) + K_6P_7P(H_2) + K_6K_7K_8[PhC_2H]P(H_2)\}} \quad (13)$$

Complex **1** is the main species under catalytic conditions. Thus, $\mathbf{1} \gg K_6P(H_2) + K_6K_7P(H_2) + K_6K_7K_8[PhC_2H]P(H_2)$, when $P(H_2) \leq \mathbf{1}$ and $[PPh_3]$ equilibrium $\cong [PPh_3]$ added. Therefore $[\mathbf{4}]$ can be written as follow:

$$[\mathbf{4}] \cong \frac{K_6K_7K_8[Rh]_{Tot}[PhC_2H]P(H_2)}{[PPh_3]} \quad (14)$$

Combining Eqs. (11) and (14), we obtained Eq. (15), where $[Rh]_{Tot}$ and $[PPh_3]$ are the concentrations of catalyst and added phosphine, respectively.

$$\frac{d[\text{styrene}]}{dt} \cong \frac{k_9K_6K_7K_8[Rh]_{Tot}[PhC_2H]\{P(H_2)\}^2}{[PPh_3]} \quad (15)$$

Inspection of Eq. (15) shows that the rate of the catalytic reaction is aproximately proportional to the concentra-

Table 1
Kinetic data for the hydrogenation of phenylacetylene to styrene catalyzed by $[Rh(NBD)(PPh_3)_2]BF_4$ in dichloromethane at 25°C

[Catalyst] 10^4 M	$[PhC_2H]$ 10 M	$P(H_2)$ atm	$[PPh_3]$ 10^5 M	$-dV/dt$ ml/min
1.14	0.76	1	–	1.20
1.55	0.76	1	–	1.38
2.07	0.76	1	–	2.10
2.41	0.76	1	–	2.34
1.55	0.62	1	–	1.30
1.55	1.25	1	–	2.20
1.55	1.47	1	–	2.55
1.55	1.89	1	–	3.30
1.55	0.76	0.61	–	0.52
1.55	0.76	0.72	–	0.80
1.55	0.76	0.81	–	0.90
1.55	0.76	0.84	–	1.17
1.55	0.76	1	0.9	1.30
1.55	0.76	1	1.9	1.14
1.55	0.76	1	2.6	1.06
1.55	0.76	1	3.0	1.05

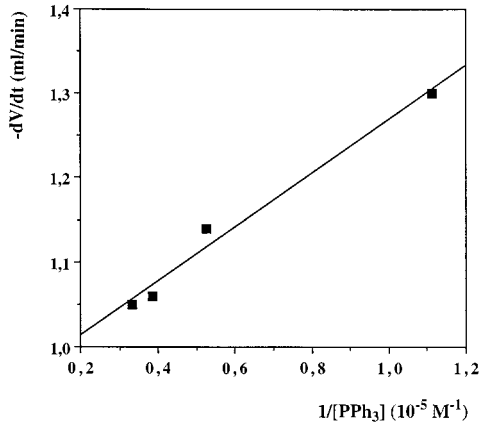

Fig. 2. Plot of the rate of hydrogenation of phenylacetylene to styrene versus $1/[PPh_3]$ in dichloromethane at 25°C, 1 atm H_2, 1.55×10^{-3} M [Catalyst], 0.067 M PhC_2H.

tions of catalyst and substrate, second order with respect to hydrogen pressure, and inversely proportional to the concentration of added phosphine, which agrees well with the experimental data.

The mechanism summarized by Eqs. (6)–(10) merits some additional comment, the reaction of $[Rh(NBD)(PPh_3)_2]BF_4$ with molecular hydrogen most likely should give a short-lived intermediate, *cis*-$[RhH_2(NBD)(PPh_3)_2]BF_4$, which must have the stereochemistry shown in Fig. 3. In agreement with this proposal Crabtree and co-workers have observed that the iridium complexes $[Ir(COD)(PR_3)_2]^+$ ($PR_3 = PPh_3$, PPh_2Me) react with molecular hydrogen at -80°C in dichloromethane to give the dihydrido *cis*-$[IrH_2(COD)(PR_3)_2]^+$, which have the stereochemistry shown in Fig. 3. When the dichloromethane solutions of these complexes are warmed to -20°C, in the absence of an excess of H_2, hydrogen is partly lost to give $[Ir(COD)(PR_3)_2]^+$. In acetone, the reactions lead to the cations $[IrH_2(acetone)_2(PR_3)_2]^+$ [15]. In contrast to these compounds, the also dihydrido derivative *cis*-$[IrH_2(COD)(dppm)]BF_4$ (dppm = bis(diphenylphosphino)methane) is stable, even at room temperature, neither losing molecular hydrogen nor transferring it to the coordinated 1,5-cyclooctadiene [16].

Intermediate *cis*-$[RhH_2(NBD)(PPh_3)_2]BF_4$ is six-coordinate and thus coordinatively saturated. So, one arm of the chelating NBD ligand or triphenylphosphine must be dissociated from the coordination sphere of the metal before the reaction with the alkyne. In this context, it should be mentioned that spectroscopic studies on the addition of molecular hydrogen to the also saturated complex $[Rh(NBD)(PPhMe_2)_3]^+$ suggest that it is $PPMe_2$, rather than one arm of the diene ligand, which dissociates prior to addition of hydrogen [12]. Furthermore, in the complex *cis*-$[RhH_2(NBD)(PPh_3)_2]BF_4$, the dissociation of the phosphine *trans* disposed to the hydrido ligand should be favored due to high *trans* effect of the hydrido and the large steric hindrance experienced by the triphenylphosphine groups, which are mutually *cis* disposed.

If the alkyne fills the site of the dissociated phosphine, the alkyne would then be *cis* to one hydride but *trans* to the other. So, if the *cis*-hydrido migrates to the alkyne and the stereochemistry does not change further, the resulting hydrido-alkenyl intermediate would have *trans* stereochemistry. This *trans* coordination would not facilitate the reductive elimination of styrene in the next step, explained why a new reaction with molecular hydrogen is necessary for the formation of the olefin.

The selectivity observed in the reduction of phenylacetylene may have kinetic reasons. Fig. 1 shows that phenylacetylene is hydrogenated at a rate which is much greater than the rate at which styrene is reduced. The same behavior has been observed for the hydrogenation of 2-hexyne to *cis*-2-hexene catalyzed by $[Rh(NBD)(PR_3)_2]^+$ [10], and for the hydrogenation of phenylacetylene to styrene catalyzed by $[Ir(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)]BF_4$ [14]. In these cases, it has been argued that the alkyne competes strongly with the olefin for coordination sites at the metal center. Consequently, the higher coordination ability of phenylacetylene, in comparison with styrene, could favor the displacement of triphenylphosphine from *cis*-$[RhH_2(NBD)(PPh_3)_2]BF_4$ and therefore the alkyne hydrogenation.

In contrast to these cationic systems, the selectivity observed for the hydrogenation of phenylacetylene catalyzed by $OsHCl(CO)(P^iPr_3)_2$ appears to be thermodynamically controlled [17]. The independent study of the reduction of C≡C

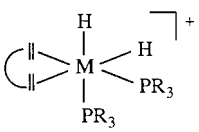

Fig. 3.

and C=C bonds indicates that the latter is kinetically favored. However, the vinyl complex Os{(E)-CH=CHPh}Cl(CO)(P^iPr_3)$_2$ [18] is the main species under catalytic conditions; this complex represents a thermodynamic sink that causes virtually all the osmium present in solution to be tied up this form, and consequently, the kinetically unfavored pathway becomes the only one available in the presence of phenylacetylene [17]. However, kinetic reasons seems to be operative in the above mentioned rhodium and iridium complexes.

3. Conclusions

This study has revealed that in dichloromethane as solvent the mechanism for the selective hydrogenation of phenylacetylene to styrene catalyzed by [Rh(NBD)(PPh_3)$_2$]BF_4 is similar to that previously descrited for the same reaction catalyzed [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)]BF_4. These reactions do not imply the reduction of the dienes of the catalysts, which remain coordinated during the processes, in contrast to that previously reported for related systems in coordinating solvents, where dihydrido and monohydrido derivatives of the types [$MH_2S_x(PR_3)_2$]$^+$ and $MHS_y(PR_3)$ (M = Rh, Ir; S = solvent) are the active species.

4. Experimental details

All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures and distilled under argon prior to use. Phenylacetylene (Merck) was purified by distillation. Complex [Rh(NBD)(PPh_3)$_2$]BF_4 was prepared as described in literature [1].

4.1. Kinetic studies

The catalytic reactions were followed, at constant pressure, by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256). The analysis of the products of the catalytic reactions was carried out on a Perkin–Elmer 8500 gas chromatograph with a flame ionization detector and an FFAP on Chromosorb 6HP 80/100 mesh (3.6 m × 1/8 in.) column at 220°C. In a typical procedure, the substrate dissolved in dichloromethane (20 ml) was added to a solution of the catalyst in dichloromethane (20 ml), under argon atmosphere. This solution was syringed through a silicon septum into a 50-ml flask attached to a gas buret, which was in turn connected to a Schlenk manifold and had been previously evacuated and refilled with hydrogen three times. The flask was then immersed in a 25°C bath and the mixture was vigorously shaken during the run.

Acknowledgements

We thank the DGICYT (Projects PB95-0806 and PB94-1186, Programa de Promoción General del Conocimiento) and the Comisión Mixta Caja Cantabria-Universidad de Cantabria for financial support.

References

[1] J.R. Shapley, R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 91 (1969) 2816.
[2] R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 98 (1976) 2134.
[3] R.H. Crabtree, H. Felkin, G.E. Morris, J. Organomet. Chem. 141 (1977) 205.
[4] R. Usón, L.A. Oro, J. Artigas, R. Sariego, J. Organomet. Chem. 179 (1979) 65.
[5] R.H. Crabtree, Acc. Chem. Res. 12 (1979) 331.
[6] R. Usón, L.A. Oro, M.J. Fernández, R. Sariego, Rev. Acad. Ciencias Zaragoza 35 (1980) 87.
[7] R.H. Crabtree, P.C. Demon, D. Eden, J.M. Michelcic, C.A. Parnell, J.M. Quirk, G.E. Morris, J. Am. Chem. Soc. 104 (1982) 6994.
[8] R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 98 (1976) 4450.
[9] R. Usón, L.A. Oro, N.J. Fernández, J. Organomet. Chem. 193 (1980) 127.
[10] R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 98 (1976) 2143.
[11] R.R. Schrock, J.A. Osborn, J. Chem. Soc., Chem. Commun., (1970) 567.
[12] P.A. Chaloner, M.A. Esteruelas, F. Joó, L.A. Oro, Homogeneous Hydrogenation, Kluwer Academic Publishers, Dordrecht, 1994.
[13] R. Usón, L.A. Oro, R. Sariego, M. Valderrama, C. Rebullida, J. Organomet. Chem. 197 (1980) 87.
[14] M.A. Esteruelas, A.M. Lopez, L.A. Oro, A. Perez, M. Schulz, H. Werner, Organometallics 12 (1993) 1823.
[15] R.H. Crabtree, H. Felkin, T. Fillebeen-Khan, G.E Morris, J. Organomet. Chem. 168 (1979) 183.
[16] M.A. Esteruelas, M. Oliván, L.A. Oro, M. Schulz, E. Sola, H. Werner, Organometallics 11 (1992) 3659.
[17] A. Andriollo, M.A. Esteruelas, U. Meyer, L.A. Oro, R.A. Sanchez-Delgado, E. Sola, C. Valero, H. Werner, J. Am. Chem. Soc. 111 (1989) 111.
[18] H. Werner, M.A. Esteruelas, H. Otto, Organometallics 5 (1986) 2295.