Journal of the Mexican Chemical Society
ISSN: 1870-249X
editor.jmcs@gmail.com
Sociedad Química de México
México

Montalvo, Liliana; Bolaños, Alberto; Cabrera, Armando

Catalytic Activity of Rhodium (I) Complexes with Bidentate Phosphinic Ligands in the Hydrogenation of Unsaturated Alycyclic Substrates

Journal of the Mexican Chemical Society, vol. 51, núm. 1, january-march, 2007, pp. 8-14
Sociedad Química de México
Distrito Federal, México

Available in: http://www.redalyc.org/articulo.oa?id=47551103

How to cite
Complete issue
More information about this article
Journal's homepage in redalyc.org

Scientific Information System
Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal
Non-profit academic project, developed under the open access initiative

Article

J. Mex. Chem. Soc. **2007**, *51(1)*, 8-14
© 2007, Sociedad Química de México
ISSN 1870-249X

Catalytic Activity of Rhodium (I) Complexes with Bidentate Phosphinic Ligands in the Hydrogenation of Unsaturated Alycyclic Substrates

Liliana Montalvo,[1] Alberto Bolaños,[2] Armando Cabrera[3]

[1] Departamento de Química, Facultad de Ciencias Naturales, Exactas y de la Educación, Universidad del Cauca, Popayán-Cauca-Colombia, Tel: 0057-2-8209800 ext. 2320, lmontalvo@unicauca.edu.co
[2] Departamento de Química, Facultad de Ciencias, Universidad del Valle Cali-Valle-Colombia, Apartado 25360, Tel: 0057-2-3334921, albolan@univalle.edu.co
[3] Instituto de Química, Universidad Nacional Autónoma de México Ciudad Universitaria, Coyoacán 04510, México D. F., México. arcaor1@servidor.unam.mx

Recibido el 6 de marzo del 2006; aceptado el 12 de septiembre del 2006

Abstract. $RhCl(dppe)_2$, $RhCl(dppp)_2$ and $RhCl(dppb)_2$, where dppe = diphenylphosphinoethane; dppp = diphenylphosphinopropane; dppb = diphenylphosphinobutane complexes were prepared by treating $RhCl_3.3H_2O$ with the appropriate di(tertiaryphosphine). These complexes were used as catalytic precursors in the hydrogenation of limonene, camphene and 1,5- cyclooctadiene at different concentrations and temperatures. It was found that the Rhodium complex having dppp as ligand was the best catalytic precursor.
Key words: Rhodium; bidentate phosphinic ligands; homogeneous catalysis; catalytic hydrogenation, unsaturated alycyclic compounds.

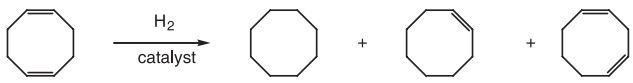
Resumen. Los complejos $RhCl(dppe)_2$, $RhCl(dppp)_2$ y $RhCl(dppb)_2$ donde dppe = difenilfosfino etano; dppp = difenilfosfinopropano; dppb = difenilfosfinobutano fueron preparados por el tratamiento del $RhCl_3.3H_2O$ con las fosfinas diterciarias apropiadas. Estos complejos fueron usados como precursores catalíticos en las reacciones de hidrogenación de limoneno, canfeno y 1,5-ciclooctadieno a diferentes concentraciones y temperaturas. Se encontró que el mejor precursor catalítico es el complejo de Rodio con el ligante dppp.
Palabras clave: Rodio, ligantes fosfínicos bidentados, catálisis homogénea; hidrogenación catalítica, alicíclicos insaturados.

Introduction

Organometallic and coordination compounds are used as catalytic promoters in homogeneous organic reactions. A very well known reaction is hydrogenation, in which one or more hydrogen atoms are added to an unsaturated substrate [1]. Hydrogen transference reactions, catalyzed by group VIII transition metals, having a variety of phosphorus-based atom donor ligands, have been used to reduce alkenes [2,3,4].

Wilkinson's catalyst [5], $RhCl(PPh_3)_3$, discovered in 1965, constitutes the first homogenous system routinely used for a considerable number of hydrogenation reactions in mild conditions.

Rhodium(I)-bis(ditertiaryphosphine) complexes of the general formula $Rh[Ph_2P(CH_2)_nPPh_2]_2Cl$, n = 1-4, have been previously prepared by treating $[Rh(cyclooctene)_2Cl]_2$ with the appropriate di(tertiary phosphine) [6]. These complexes have been used for catalytic hydrogenation of conjugated dicarboxylic acids.



Scheme 1: Products obtained in hydrogenation reaction of 1,5-cyclooctadiene.

In the present work, a rhodium system was synthesized using different phosphorus-based bidentate ligands, and was used as a catalytic promoter in the homogenous hydrogenation of cycloalkenes. It was observed that the number of carbon atoms between the two phosphorus atoms appears to have a very important influence on the process, as suggested by James [6].

Results and Discussion

Hydrogenation of 1,5- cyclooctadiene

1,5- cyclooctadiene was hydrogenated with $RhCl(dppe)_2$; $RhCl(dppp)_2$ and $RhCl(dppb)_2$ catalysts in the molar proportions substrate/catalyst: 1000/1; 500/1 at a temperature of 120 ºC and H_2 pressures of 50 and 72 bar. The analysis of these reactions was performed by gas chromatography and the resulting compounds were characterized by mass spectrometry. The analysis of chromatograms is reported in tables. These products are: cyclooctane (COA), cyclooctene (COE), and 1,4-cyclooctadiene (1,4-COD). (Scheme 1).

a) $RhCl(dppb)_2$ as promoter

Table 1 (A and B) shows that when catalyst concentration and temperature are kept constant, $RhCl(dppb)_2$ is selective at 72 bar pressure producing cyclooctane, whereas at 50 bar pressure, 1,5 cyclooctadiene yields cyclooctene in the same reaction time (18 hours). Table 1 (B and C) shows that when tem-

Table 1. Hydrogenation 1,5- COD with $RhCl(dppb)_2$ T = 120 °C.

	% 1,5- COD			% 1,4- COD			% COE			% COA		
	Pressure (bar)			Pressure (bar)			Pressure (bar)			Pressure (bar)		
	72	50		72	50		72	50		72	50	
	concentration			concentration			concentration			concentration		
Time (h)	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C
0	100	100	100	0	0	0	0	0	0	0	0	0
6	42	27.3		29.9	21.2		28.1	51.4		0	0	
9	39.6		1.51	20.6		0	39.8		28.2	0		70.29
12	31.28	8	0	27.63	33	0	37.5	59	1.14	3.5	0	98.86
18	0	0	0	0	0	0	2.05	96	0	97.5	4	100
24	0	0	0	0	0	0	0.8	38.3	0	99.2	61.7	100

perature and pressure are kept constant and the catalyst concentration is doubled, regioselectivity to the formation of cyclooctane is selectively obtained in 12 h and no isomerization products are detected.

b) $RhCl(dppp)_2$ as promoter

When Tables 2A and 2B are compared, the complex having a substrate/catalyst ratio of 500/1 showed no isomerization at 160 °C. After 6 h, the reaction remained practically constant and no regioselectivity was observed. The comparison of tables 3A and 3B shows that at identical catalyst concentration and temperature, the reaction was enhanced at a low pressure, corroborating data previously observed in table 1 (A and B), probably due to the fact that the mobility of the ligands in the coordination sphere is inhibited at higher pressures.

When comparing tables 1B and 3B, the same trend is observed. Table 3 (B and C) shows the results of experiments that were conducted at a pressure of 50 bar and a temperature of 120 °C (with 1000/1 and 500/1 substrate/catalyst ratio). It was observed that the ratio 500/1 was more effective as, after 6 h of reaction, no substrate was found, and almost all cyclooctene had been converted to cyclooctane. Table 3C also shows this behavior. Comparison of tables 1C and 3C demonstrates that the best catalyst is the one having bis-(diphenylphosphinopropane) ligand, since regioselectivity was obtained in 6 h, whereas, when using bis-(diphenylphosphinobutane) ligand, regioselectivity was obtained in 12 h.

c) $RhCl(dppe)_2$ as promoter

In Table 4A, no selectivity is observed with this catalyst, contrary to the trend observed with bis-(diphenylphosphinobutane) and bis-(diphenylphosphinopropane) catalysts. The reaction is slower, which suggests that the catalyst precursor formed a stable species with rhodium and did not easily reach a dissociative pathway in the process.

Table 2. Hydrogenation 1,5- COD with $RhCl(dppp)_2$ T = 160 °C.

	% 1,5-COD		% COA		% COE	
	Pressure (bar)		Pressure (bar)		Pressure (bar)	
	60		60		60	
Time (h)	1000:1 A	500:1 B	1000:1 A	500:1 B	1000:1 A	500:1 B
0	100	100	0	0	0	0
6	0	0	15.54	38.9	84.46	61.1
24	0	0	65.07	39.8	34.93	60.15

In Table 4B, it can be observed that at low pressures, an induction time is required in order to obtain the active species, which could be explained by the formation, in these cases, of a stable moiety with rhodium, as was previously suggested.

Hydrogenation of camphene

The reactions were carried out at 120°C and H_2 pressures of 50 and 68 bar.

Scheme 2 shows the products obtained from the hydrogenation of camphene.

a) $RhCl(dppb)_2$ as promoter

The analysis of Table 5 (A and B) reveals the influence of catalyst concentrations in the reaction rate. After 18 h, regioselectivity to the formation of camphane was observed, probably due to the fact that an increase in catalyst concentration speeds up the reaction.

Table 3. Hydrogenation 1,5- COD with $RhCl(dppp)_2$ T = 120 °C.

	% 1,5- COD			% 1,4- COD			% COE			% COA		
	Pressure (bar)			Pressure (bar)			Pressure (bar)			Pressure (bar)		
	60	50		60	50		60	50		60	50	
	concentration			concentration			concentration			concentration		
Time (h)	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C
0	100	100	100	0	0	0	0	0	0	0	0	0
2	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C
3	100	100	100	0	0	0	0	0	0	0	0	0
4	42	27.3		29.9	21.2		28.1	51.4		0	0	
5	39.6		1.51	20.6		0	39.8		28.2	0		70.29
6	31.28	8	0	27.63	33	0	37.5	59	1.14	3.5	0	98.86
8	0	0	0	0	0	0	2.05	96	0	97.95	4	100
12	0	0	0	0	0	0	0.8	38.3	0	99.2	61.7	100
18	100	100	100	0	0	0	0	0	0	0	0	0
24	42	27.3		29.9	21.2		28.1	51.4		0	0	

Table 4. Hydrogenation 1,5- COD with $RhCl(dppe)_2$ T = 120 °C.

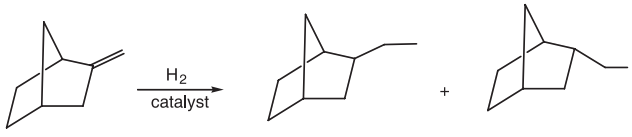
	% 1,5- COD			% 1,4- COD			% COE			% COA		
	Pressure (bar)			Pressure (bar)			Pressure (bar)			Pressure (bar)		
	60	50		60	50		60	50		60	50	
	concentration			concentration			concentration			concentration		
Time (h)	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C	1000:1 A	1000:1 B	500:1 C
0	100	100	100	0	0	0	0	0	0	0	0	0
6	100	100	100	0	0	0	0	0	0	0	0	0
12	100	100	67.9	0	0	0	0	0	32.1	0	0	0
18	78.7			0			21.3			0		
24		17.05	5.4		5.87	5.7		69.46	82.1		7.61	6.8

b) $RhCl(dppp)_2$ as promoter

Comparing tables 6A and 6B, it was found that when the substrate/catalyst ratio was 1000/1 and T = 120°C, the reaction occurred faster when pressure was lowered, as previously observed, probably because the lower pressure favors the ligand mobility into the catalytic species.

c) $RhCl(dppe)_2$ as promoter

Table 7A shows that camphene does not exhibit hydrogenation when substrate/catalyst ratio is 500/1, T is 120 °C and P is 68 bar, which confirms the modest reactivity of this ligand observed in previous reactions. In tables 7B and 7C, it is observed that when the concentration of catalyst is increased, the reaction occurs, albeit very slowly. Induction times are required, and the reaction is enhanced at lower pressure, as observed in other cases.



Scheme 2: Products obtained in hydrogenation reaction of camphene.

Table 5. Hydrogenation camphene with $RhCl(dppb)_2$ T = 120 °C.

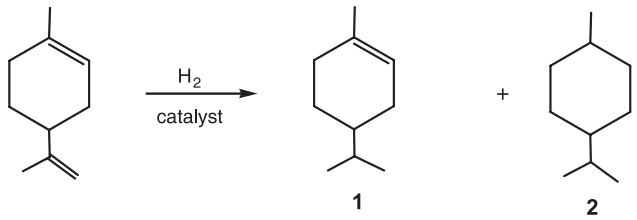
	% camphene		% camphane	
	Pressure (bar)		Pressure (bar)	
	50		50	
	Concentration		Concentration	
Time (H)	1000:1 A	500:1 B	1000:1 A	500:1 B
0	100	100	0	0
6	84.65	49	15.35	51
9	62.4		37.6	
12	39.34	25.4	60.66	74.6
15	36.9	17.23	63.1	82.77
18	25.75	0	74.25	100
24	18.79	0	81.21	100

Table 6. Hydrogenation camphene with RhCl(dppp)2 1000:1 T = 120 °C.

	% camphene		% camphane	
	Pressure (bar)		Pressure (bar)	
Time (H)	68 A	50 B	68 A	50 B
0	100	100	0	0
3		97		3
6	77.9	58.5	22.1	41.5
9		50.07		49.93
12		42.2		57.8
18	56.22	34.95	44.78	65.05
24	35.1	23.8	64.9	76.92

Hydrogenation of limonene

The reactions were carried out at 160 °C and 120 °C, and H_2 pressures of 50, 75 and 100 bar, during 24 h of reaction time. Scheme 3 shows the products obtained from the hydrogenation of limonene.



Scheme 3: Products obtained in reaction of hydrogenation of limonene.

a) $RhCl(dppb)_2$ as promoter

In Table 8A, it can be observed that reaction is regioselective, after 18 hours, in the reduction of the exocyclic double bond. After 48 hours, it is regioselective in the completion of substrate hydrogenation, which suggests that these processes are consecutive. When tables 8A and 8B are compared, it can be deduced that when pressure is decreased, selectivity is lost with this ligand, although the reaction becomes faster. When temperature is increased (Table 8B), and this is compared with Table 8C, it can be observed that in both reactions, induction time is required. However, in table 8C, when temperature is lowered, reaction becomes cleaner, yielding 80% of **1**.

Tables 8B and 9A show that when the catalyst concentration is increased, practically all limonene is found to have

Table 7. Hydrogenation camphene with $RhCl(dppe)_2$ T = 120 °C.

	% Camphene		% Camphane		% Camphene		% Camphane	
	Pressure (bar)				Pressure (bar)			
	68				68			
	Concentration				Concentration			
Time (h)	500:1 A	300:1 B	500:1 A	300:1 B	500:1 A	300:1 B	500:1 A	300:1 B
0	100	100	0	0	100	0	100	100
6	100	100	0	0	100	0	100	100
9	100	100	0	0	48.21	51.79	100	100
12	100	100	0	0	39.39	60.61	100	100
15	100		0		28.9	71.1	100	
18	100	0	0	100			100	0
24	100	0	0	100			100	0

Table 8. Hydrogenation limonene with RhCl(dppb)2 1000:1.

	% limonene			% 1			% 2		
	Temperature			Temperature			Temperature		
	160 °C	120 °C		160 °C	120 °C		160 °C	120 °C	
	Pressure (bar)			Pressure (bar)			Pressure (bar)		
Time (h)	100 A	50 B	50 C	100 A	50 B	50 C	100 A	50 B	50 C
0	100	100	100	0	0	0	0	0	0
6	14	95.79	100	86	4.2	0	0	0	0
9		10.59	29.5		75.04	71.62		14.37	0
12	11	5.03	21	89	79.29	70.62	0	15.68	8.4
18	0	3.79	16.72	100	69.16	69.52	0	27.05	8.88
24	0	1.76	7.85	74.5	35.87	80.07	25.5	62.36	12.08
48	0			0			100		

Table 9. Hydrogenation limonene with catalyst 500:1 P = 50 bar.

	% limonene		% 1		% 2	
	$RhCl(dppb)_2$	$RhCl(dppe)_2$	$RhCl(dppb)_2$	$RhCl(dppe)_2$	$RhCl(dppb)_2$	$RhCl(dppe)_2$
	Temperature		Temperature		Temperature	
Time (h)	160 °C A	120 °C B	160 °C A	120 °C B	160 °C A	120 °C B
0	100	100	0	0	0	0
6	91.2	100	8.4	0	0	0
9	4.98	44.85	75.92	55.25	19.11	0
12	3.12	36	73.02	59.6	23.86	4.3
18		32.85		59.43		4.69
24	2.5	21.67	48.8	73.21	35.24	5.12

reacted after 9 h, which corroborates the previous finding that a higher catalyst concentration speeds up the reaction.

b) $RhCl(dppp)_2$ as promoter

It can be observed that when temperature is lowered an induction time is required, and, after 18 h, 90% of **1** is formed (Tables 10 A and B). In table 10B, after 6 h, regioselectivity occurs and 80% of **1** is formed; however, at 160 °C this regioselectivity is lost. When tables 11A and 11B are compared, it can be seen that an increase in catalyst concentration does not have an important influence on selectivity.

c) $RhCl(dppe)_2$ as promoter

The catalyst precursor requires induction time and favors limonene hydrogenation to a lesser degree than when using catalysts $RhCl(dppb)_2$ and $RhCl(dppp)_2$ (table 9 B); confirming the assumption that the named $RhCl(dppe)_2$ is not a good catalyst, due to the stability of the five member ring that it forms with rhodium.

After the analysis of all the results, it is confirmed that in the case of 1,5- cyclooctadiene hydrogenation, a high pressure of H_2 (72 bar) produces the reduction of a single unsaturated bond. At a lower pressure (50 bar), however, the reaction tends toward the formation of cyclooctane. The same behavior is observed for the other two substrates (camphene and limonene). These findings suggest that at a lower pressure the mobility of the ligands is greater, and vacant sites for the activation of the substrate and the hydrogen molecule can be quickly generated.

High pressure probably favors the stability of the species, and no lability of the hydride moieties is formed until a vacant site is generated.

One reason that isomerization is prevented from being produced with $RhCl(dppp)_2$ may be that, in order for catalytic hydrogenation to be produced, it is necessary that the catalyst release a ligand, in order to produce a vacant site where olefin

Table 10. Hydrogenation limonene with $RhCl(dppp)_2$ 1000:1 y P = 65 bar.

	% limonene		% 1		% 2	
	Temperature		Temperature		Temperature	
Time (h)	120 °C A	160 °C B	120 °C A	160 °C B	120 °C A	160 °C B
0	100	100	0	0	0	0
6	98.83	6.75	1.17	79.05	0	14.2
18	3.78	1.68	86.97	63.9	9.25	34.42
24	0	0	89.13	63.53	10.86	36.5

Table 11. Hydrogenation limonene with $RhCl(dppp)_2$ T = 120 °C y P = 50 bar.

	% limonene		% 1		% 2	
	Concentration		Concentration		Concentration	
Time (h)	1000:1 A	500:1 B	1000:1 A	500:1 B	1000:1 A	500:1 B
0	100	100	0	0	0	0
6	100	86	0	14	0	0
9	3.17	2.75	79.85	76.44	16.99	20.81
12	2.42	2.29	75.95	53.04	21.63	34.67
24	1.38		74.55		24.07	

can be coordinated. It seems that in the case of the diphenylphosphino propane ligand, one of these ligands can be released more easily, while in the case of diphenylphosphino butane, perhaps allows the ligand to be partially released from the sphere of coordination, due to its size, which would make this catalyst less effective than bis-(diphenylphosphino) propane. On the other hand, a reason for the modest activity presented by the $RhCl(dppe)_2$ catalyst is that a five member ring is formed with the Metal-Ligand catalyst, forming a stable species that does not dissociate easily and, therefore, does not generate the vacant site indispensable to the production of the reaction. When pressure is lowered, it is observed that induction time is required. At such pressure, a dissociative step is suggested.

At high pressures, hydride formation is favored, but this must be less labile than at low pressures and cannot then be easily transferred to alkene.

A possible explanation for induction times being required for the occurrence of hydrogenation reactions at low pressures and not being required at high pressures, is that these reactions occur by different mechanisms:

Conclusions

In almost all the reactions between the substrates and the $RhCl(dppe)_2$ catalyst, it was observed that an induction time is required, probably due to the formation of the stable five member ring.

When the catalyst concentration was increased, the reactions of the substrates with the catalysts occurred faster; this finding confirming that reaction speed is a function of catalyst concentration.

All reactions between the substrates and the catalysts were favored at a lower hydrogen pressure (50 bar), reinforcing a dissociative pathway in these conditions. The precursor $RhCl(dppp)_2$ allowed the reactions to occur faster, probably due to the fluxionality of the six member ring formed between the catalyst promoter and the rhodium complex.

The seven member ring formed with the $RhCl(dppb)_2$ ligand could promote its partial dissociation from the coordinative sphere, making this species less effective in a dissociative process.

Experimental

The toluene (solvent) was purified and deoxygenated prior to its use. $RhCl(dppe)_2$, $RhCl(dppp)_2$ and $RhCl(dppb)_2$ complexes were synthesized as follows: Stoichiometric amounts of $RhCl_3.3H_2O$ and the ligands, bis-(diphenylphosphino) ethane, bis-(diphenylphosphino) propane and bis-(diphenylphosphino) butane 1:2 were dissolved in purified acetone . The mixture was refluxed for five hours, under a nitrogen atmosphere, yielding a precipitate that was filtered, and recrystalized from acetone and ether. The ligands, dppe, dppp and dppb, as well as the substrates limonene, camphene and 1,5- cyclooctadiene, were obtained from Aldrich Co. Ultrapure H_2 gas was obtained from Aga-Gas-Co. The reaction products were analyzed on a JEOL JMS-AX505H-A GC-MS, equipped with a 25m x 0.25 mm glass capillary column, packed with 5% phenyl silicone.

General catalytic procedure

The reactions of hydrogenation of limonene, camphene and 1,5- cyclooctadiene with catalytic precursors $RhCl(dppe)_2$, $RhCl(dppp)_2$ and $RhCl(dppb)_2$, were carried out as follows: A solution of the unsaturated compound (100 – 500 mmol) and the catalytic precursor (1 mmol) in 10 mL of dry toluene (in a Schlenk tube), was transferred to a 45 mL stainless steel autoclave (PARR), magnetically stirred, and purged with N_2. After this reaction was taken to the desired pressure (H_2), it was warmed in an oil bath at different temperatures. At the end of the reaction time, the reactor was cooled, and the gas was liberated. The solution was analyzed by GC – MS to quantify the reaction products.

Acknowledgements

We would like to thank the Cauca University and the Valle University, both of Colombia, and the National Autonomous University of Mexico, for financing this research project.

References

1. Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Gold, L. A. *Homogeneous Hydrogenation*, Kluwer Academic, Dordrecht, **1994**.
2. Brieger G.; Nestrick, T. *Chem. Rev.* **1974**, *74*, 567-580.
3. Johnstone, R. A.W.; Wilby, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129-167.
4. Zassinovich, G.; Mestroni, G. *Chem. Rev*. **1992,** *92***,** 1051-1068.
5. Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A.* **1966**, 1711-1732.
6. James, B. R.; Mahajan, D. *Can. J. Chem.* **1979,** *57***,** 180-187.