Phosphonate-Based Hybrid Materials for Catalysis? Supported Rhodium/2,2′-Bipyridine Complexes as Reduction Catalysts Under Hydrogen Pressure

Céline Maillet,[a] Pascal Janvier,[a] Marie-Jo Bertrand,[a] Thoniyot Praveen,[a] and Bruno Bujoli*[a]

Dedicated to Dr. Jean Villiéras on the occasion of his retirement

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Supported organometallic catalysts based on covalently immobilized rhodium/2,2′-bipyridine complexes are compared to the parent homogeneous system for the hydrogenation of ketones and carbon-carbon multiple bonds under hydrogen pressure. In alkaline methanol, the supported catalyst is more active for the reduction of C=C and C≡C bonds than for the hydrogenation of keto groups; this is in contrast with the analogous system in a homogeneous medium for which the opposite trend is observed.

Introduction

Nowadays, the chemical industry is under increased pressure to develop cleaner production technologies, and homogeneous catalysis offers a means to provide more effective processes and reduction of pollutants. A pitfall, however, is that the separation of the catalyst from the starting compound and products is difficult and often results in the loss of the catalytic material. Immobilized catalysts, either entrapped or grafted and obtained as insoluble supports, offer a potential solution that allows an easy separation of the reaction products by filtration, reducing both waste and costs.[1−5] We and others[6] have previously reported that the immobilization of organometallic catalysts onto solid supports could be performed using the binding properties of phosphonic acids [PO_3H_2]. Recently, we applied this strategy to the design of new phosphonate-based supported rhodium/2,2′-bipyridine complexes active for the hydrogenation of a variety of acetophenones under hydrogen pressure. This system was derived from the early work of Mestroni et al., who reported a high catalytic activity of rhodium complexed to 2,2′-bipyridine (bpy) for ketone hydrogenation in the presence of methanolic NaOH, where the $[Rh(bpy)_2]^+$ species was proposed as a catalyst.[7] In a preliminary work,[8] we have clearly shown how the catalytic performances could be improved by a careful optimization of the conditions employed for the preparation of the immobilized catalyst. In a final step, we wanted to know to what extent this supported catalyst could be used for the reduction of substrates other than acetophenones, and the results are described in this paper.

[a] Laboratoire de Synthèse Organique, UMR CNRS 6513, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cedex 03, France

Results and Discussion

In a previous study, a rhodium/2,2′-bipyridine complex functionalized by two phosphonic acid moieties (ligand **1** in Figure 1) was efficiently immobilized onto TiO_2 particles generated in situ.[8] After optimization of the heterogenization step, the resulting supported catalyst (labelled catalyst **A**) proved to be active for the reduction of aromatic ketones, such as 4′-methoxyacetophenone, under hydrogen pressure in alkaline methanol (Table 1, entry 1), similarly to the results reported by Mestroni et al.[7] for rhodium/2,2′-bipyridine complexes in a homogeneous medium in the same solvent. Moreover, the catalyst was recycled four times with no loss of activity (98% conversion after 21 hours for successive runs, using a 1.5% Rh/4′-methoxyacetophenone

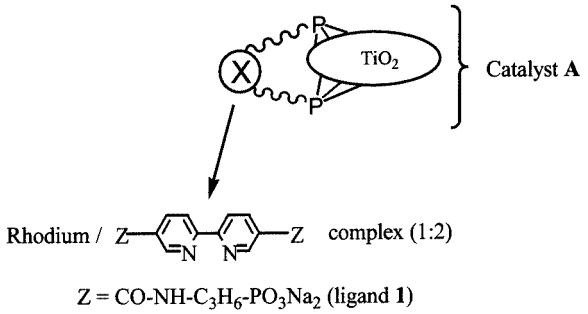

Figure 1. Schematic representation of the support bipyridine **A**

Table 1. Results from the hydrogenation of various substrates using catalyst **A** in alkaline methanol under 40 bar H_2[a]

Entry[a]	Substrate	Conversion (%)	Selectivity (%)
1	4′-methoxyacetophenone	>99	4′-methoxy-*sec*-phenethyl alcohol (100)
2	cyclohexanone	>99	cyclohexanol (100)
3	4-methylcyclohexanone	>99	4-methylcyclohexanol (100) *cis*/*trans*: 30:70[b]
4	2-heptanone	90	2-heptanol (100)
5	3-pentanone	95	3-pentanol (100)
6	6-methyl-5-hepten-2-one	>99	6-methylheptan-2-one (83) 6-methylheptan-2-ol (17)
7	cyclooctene	>99	cyclooctane (100)
8	1-octene	>99	octane (100)
9	*trans*-stilbene	>99	1,2-diphenylethane (100)
10	α-pinene	>99	α-pinane (93) 1,2,3,5- and 1,1,3,5-tetramethylcyclohexane (7)
11	1-octyne	>99	octane (100)
12	4-octyne	>99	octane (100)

[a] Catalyst **A**: 41 mg, 3 mL methanol, 47.5 μL 1 M NaOH [NaOH/Rh 5 equiv.], 0.95 mmol substrate [Rh/substrate = 1%], ambient temperature, 48 h. [b] A 70:30 ratio is obtained in homogeneous medium using 2,2′-bipyridine as ligand (ref.[7b]).

ratio) and the extent of rhodium leaching measured by ICP-MS analyses of the reaction medium upper phase was very low (≤0.065%).[8] It was thus of interest to know if our supported catalyst: (*i*) was also efficient for the reduction of aliphatic ketones (cyclic or linear), and (*ii*) was able to allow the selective reduction of C=O groups in the presence of C=C bonds.

As expected, catalyst **A** was active for the reduction of aliphatic ketones in good yields (Table 1, entries 2−5) but, surprisingly, in the case of 6-methyl-5-hepten-2-one, the reduction of the olefin proceeded faster than the hydrogenation of the ketone (Table 1, entry 6). For this reason, various alkenes and alkynes were tested in the same conditions, leading to a quantitative conversion into the corresponding alkanes (Table 1, entries 7−12). These results seemed somewhat in contradiction with data from the literature,[7] and we thus decided to compare the catalytic behavior of compound **A** and a closely related homogeneous system (Table 2), i.e. rhodium complexed to 2,2′-bipyridine (bpy) with a ligand/metal ratio of two, identical to that used for the preparation of the supported catalyst **A**. Obviously, the reaction rate for the hydrogenation of olefins is higher for the supported catalyst (Table 2, entries 1−4, 13−14); the same observation can be made in the case of 4-octyne, with an octane yield (after 8 hours) ten times higher for the supported rhodium-bipyridine complex (45%, entry 5) than for the homogeneous system (4%, entry 6). On the contrary, however, the homogeneous system is far more efficient than the supported counterpart for the reduction of C=O bonds (entries 7−8). Consistently, when the two types of function are present on the same substrate (e.g. 6-methyl-5-hepten-2-one) the regioselectivity of the reduction is radically different for the two systems, with the reduction of the C=C bond dominating with the solid catalyst **A** while the C=O bond is preferably hydrogenated with the Rh/bpy (1:2) complex in solution (entries 11−12), as reported by Mestroni et al. Moreover, some hydrogenation tests were performed with an aqueous solution of rhodium(I) complexed to ligand **1**, identical to that used for the preparation of catalyst **A** (ligand **1**/Rh = 2). With this biphasic catalytic system, after 15 hours, 6-methyl-5-hepten-2-one was quantitatively reduced to yield 6-methyl-5-hepten-2-ol with a 95% selectivity (Rh/substrate = 1%). Similarly, for the reduction of a mixture of cyclooctene and acetophenone (1:1), the reduction of the ketone took place first. These results are similar to those obtained with the 2,2′-bipyridine/rhodium complex (2:1) in homogeneous conditions, and are therefore consistent with the presence of similar active species in the two cases. This clearly indicates that the factor responsible for the change in selectivity (C=O versus C=C reduction) occurs during the immobilization process, i.e. when titanium isopropoxide is added.

The activity of compound **A** seems to be slowed down by the presence of the carbonyl function on the substrate. This was confirmed by testing a mixture of cyclooctene and acetophenone (1:1 molar ratio): after three hours the supported catalyst **A** shows only a poor conversion of cyclooctene (5%, entry 9) relative to cyclooctene on its own (95%, entry 1).

Our comparison between the homogeneous and supported rhodium/bipyridine systems was extended to the case where the bpy/Rh ratio is 1. Mestroni et al. have shown that in such conditions the resulting complexes hydrogenate both olefins and ketones, as confirmed by the results described in Table 3 (entries 1/2, 9/10, 13/14). Even though the reaction rate observed for the reduction of C=C bonds is higher for the 1:1 complex, the reduction of the keto group is still favored. On the contrary, C=O versus C=C competitive reductions (entries 7/8, 11/12), performed with an analogue of catalyst **A** in which the initial ligand **1**/rhodium ratio used was equal to 1 (catalyst **B**), showed an increase of C=O reduction products, although the olefin reduction was still predominant. It is also worth noting that the hy-

Table 2. Comparison of performances of a Rh/bpy (1:2) complex with catalyst **A** for the reduction of various substrates in alkaline methanol under 40 bar H_2

Entry	Substrate	Reaction time (h)	Conversion (%)	Selectivity (%)
1 (supported)[a]	cyclooctene	3	95	cyclooctane (100)
2 (homogeneous)[b]	cyclooctene	3	18	cyclooctane (100)
3 (supported)[a]	1-octene	4	97	octenes[c] (5) octane (95)
4 (homogeneous)[b]	1-octene	4	2	octane (100)
		10	95	octenes[d] (14) octane (86)
5 (supported)[a]	4-octyne	8	90	octenes (49)[e] octane (51)
6 (homogeneous)[b]	4-octyne	8	41	octenes (90)[f] octane (10)
7 (supported)[a]	4′-methoxyacetophenone	3	0	4′-methoxy-sec-phenethyl alcohol (100)
		30	89	
8 (homogeneous)[b]	4′-methoxyacetophenone	3	93	4′-methoxy-sec-phenethyl alcohol (100)
9 (supported)[a]	acetophenone + cyclooctene	3	acetophenone (0) cyclooctene (5)	phenethyl alcohol (100) cyclooctane (100)
		7	acetophenone (20) cyclooctene (99)	
10 (homogeneous)[b]	acetophenone + cyclooctene	3	acetophenone (89) cyclooctene (0)	phenethyl alcohol (100) cyclooctane (100)
		7	acetophenone (97) cyclooctene (66)	
11 (supported)[a]	6-methyl-5-hepten-2-one	15	70	6-methylheptan-2-one (79) 6-methylheptan-2-ol (12) 6-methyl-5-hepten-2-ol (9)
12 (homogeneous)[b]	6-methyl-5-hepten-2-one	15	96	6-methylheptan-2-one (0.5) 6-methylheptan-2-ol (3.5) 6-methyl-5-hepten-2-ol (96)
13 (supported)[a]	3-methyl-2-buten-1-ol	24	43	3-methylbutan-1-ol (74) 3-methyl-3-buten-1-ol (26)
14 (homogeneous)[b]	3-methyl-2-buten-1-ol	24	13	3-methylbutan-1-ol (63) 3-methyl-3-buten-1-ol (37)

[a] Catalyst **A**: 41 mg, 3 mL methanol, 47.5 μL 1 M NaOH [NaOH/Rh 5 equiv.], 0.95 mmol substrate [Rh/substrate = 1%], ambient temperature. [b] Homogeneous conditions: sample taken from a mother liquor, corresponding to 2.97 mg of 2,2′-bipyridine, 2.34 mg of $[Rh(COD)Cl]_2$, 3 mL methanol, 47.5 μL 1 M NaOH [NaOH/Rh 5 equiv.], 0.95 mmol substrate [Rh/substrate = 1%], ambient temperature. [c] The major product is *trans*-2-octene (77%). [d] The major product is *trans*-2-octene (80%). [e] The major product is *cis*-4-octene (80%). [f] The major product is *cis*-4-octene (90%).

drogenation of alkenes and alkynes is slower for catalyst **B** (entries 3/4, 5/6).

Finally, the presence of rhodium metal that might be responsible for the chemoselectivity in favor of the C=C hydrogenation observed with catalyst **A** was ruled out by taking account of the following data: a blank experiment was run with a solid **C** obtained using the same deposition method as for the preparation of catalyst **A**, but without bipyridine. The resulting pale-yellow solid turned gray irreversibly after one test (due to the formation of rhodium metal under H_2 pressure), while the color of catalyst **A** was deep green and switched back to pale-yellow upon prolonged exposure to air. Moreover, in the case of 4′-methoxyacetophenone as the substrate, compound **C** led to a significant amount of by-products corresponding to the hydrogenation of the aromatic ring of the substrate, as expected for rhodium(0)-based heterogeneous catalysts.[9] No evidence for reduction of the phenyl ring was observed with catalyst **A** under the same conditions.

In conclusion, it is clear that the immobilization process is responsible for the catalytic behavior being significantly different from that of the parent homogeneous system. This phenomenon could arise from: (*i*) possible strong hydrogen-bonding of the ketones (compared to olefins) with the TiO_2 surface affecting their accessibility to the catalytic sites, and/or (*ii*) a mechanism different from that proposed by Mestroni et al. to explain the C=O selectivity for the hydrogenation of unsaturated ketones observed with the Rh/bpy (1:2) homogeneous system. In this mechanism,[7b] various species are present in equilibrium, while the situation is expected to be different in the solid state with the supported catalyst; for example, no variation of the rhodium to bipyridine **1** ratio is likely to occur for the immobilized catalyst because no mobility of the diamine is allowed due to its covalent attachment to the inorganic surface.

Work is in progress to understand the exact role of the inorganic network that might be of importance in the course of the reaction.[10] Finally, we would like to point

Table 3. Influence of the rhodium/bipyridine ratio using homogeneous and supported catalysts for the reduction of various substrates in alkaline methanol under 40 bar H_2

Entry	Substrate	Reaction time (h)	Conversion (%)	Selectivity (%)
1 (homogeneous)[a]	cyclooctene (Rh/ligand = 1:2)	3	18	cyclooctane (100)
2 (homogeneous)[a]	cyclooctene (Rh/ligand = 1)	3	100	cyclooctane (100)
3 (catalyst **A**)[b]	1-octene (Rh/ligand = 1:2)	4	97	octenes[c] (5) octane (95)
4 (catalyst **B**)[b]	1-octene (Rh/ligand = 1)	4	72	octenes[d] (9) octane (91)
5 (catalyst **A**)[b]	4-octyne (Rh/ligand = 1:2)	8	90	octenes (49)[e] octane (51)
6 (catalyst **B**)[b]	4-octyne (Rh/ligand = 1)	8	60	octenes (78)[f] octane (22)
7 (catalyst **A**)[b]	acetophenone + cyclooctene (Rh/ligand = 1:2)	7	acetophenone (20) cyclooctene (99)	phenethyl alcohol (100) cyclooctane (100)
8 (catalyst **B**)[b]	acetophenone + cyclooctene (Rh/ligand = 1)	7	acetophenone (63) cyclooctene (100)	phenethyl alcohol (100) cyclooctane (100)
9 (homogeneous)[a]	acetophenone + cyclooctene (Rh/ligand = 1:2)	3	acetophenone (89) cyclooctene (0)	phenethyl alcohol (100) cyclooctane (100)
10 (homogeneous)[a]	acetophenone + cyclooctene (Rh/ligand = 1)	3	acetophenone (95) cyclooctene (40)	phenethyl alcohol (100) cyclooctane (100)
11 (catalyst **A**)[b]	6-methyl-5-hepten-2-one (Rh/ligand = 1:2)	15	70	6-methylheptan-2-one (79) 6-methylheptan-2-ol (12) 6-methyl-5-hepten-2-ol (9)
12 (catalyst **B**)[b]	6-methyl-5-hepten-2-one (Rh/ligand = 1)	15	> 99	6-methylheptan-2-one(43) 6-methylheptan-2-ol (57) 6-methyl-5-hepten-2-ol (0)
13 (homogeneous)[a]	6-methyl-5-hepten-2-one (Rh/ligand = 1:2)	15	96	6-methylheptan-2-one (0.5) 6-methylheptan-2-ol (3.5) 6-methyl-5-hepten-2-ol (96)
14 (homogeneous)[a]	6-methyl-5-hepten-2-one (Rh/ligand = 1)	15	> 99	6-methylheptan-2-one (1) 6-methylheptan-2-ol (76) 6-methyl-5-hepten-2-ol (23)

[a] Homogeneous conditions: sample taken from a mother liquor, corresponding to 2.97 mg (or 1.48 mg) of 2,2′-bipyridine, 2.34 mg of $[Rh(COD)Cl]_2$, 3 mL methanol, 47.5 μL 1 M NaOH [NaOH/Rh 5 equiv.], 0.95 mmol substrate [Rh/substrate = 1%], ambient temperature. [b] Catalyst **A**: 41 mg or Catalyst **B**: 21.3 mg, 3 mL methanol, 47.5 μL 1 M NaOH [NaOH/Rh 5 equiv.], 0.95 mmol substrate [Rh/substrate = 1%], ambient temperature. [c] Major product is *trans*-2-octene (77%). [d] Major product is *trans*-2-octene (68%). [e] Major product is *cis*-4-octene (80%). [f] Major product is *cis*-4-octene (87%).

out that different chemoselectivities can be obtained with ligand **1** depending on the conditions selected for its use: either biphasic catalysis or supported catalysis.

Experimental Section

Typical Procedure for the Preparation of the Supported 2,2′-Bipyridine Rhodium Complex A and the Evaluation of the Catalytic Activity: Ligand **1** was prepared as previously described.[11] The following procedure used for the synthesis of catalyst **A** was the result of an optimization study described previously.[8] Ligand **1** (233.6 mg, 0.48 mmol) was suspended in 40 mL of a distilled water/2-propanol mixture (1:1) and 2 mL of 1 M sodium hydroxide was added. After complete dissolution, $[Rh(COD)Cl]_2$ (59.2 mg, 0.12 mmol) was added and the mixture was stirred for 48 hours at room temperature. Titanium tetra-*iso*-propoxide (1.6 mL) was then added in one portion and the mixture stirred for two days. The reaction medium was then centrifuged. Analysis of the phosphorus (UV/Visible) and rhodium (X-ray fluorescence) content[8] in the supernatant liquid showed that the amount of residual phosphorus was exactly 4 times as high as the amount of residual rhodium. Thus, no variation of the Rh/ligand **1** ratio occurred during the heterogenization step. The solid was washed four times with distilled water in the centrifugation tubes, then three times with acetone and was finally collected by filtration through a Millipore apparatus. The resulting yellow powder (990 mg of catalyst **A**) was dried at room temperature in air. In agreement with the UV/Visible and X-ray fluorescence measurements mentioned above, chemical analyses of the catalyst **A** [Rh: 2.21; P: 2.74; N: 2.30] showed Rh/P (calculated 0.25; found 0.24) and Rh/N (calculated 0.125; found 0.13) values indicative of a rhodium/ligand **1** ratio of 1:2 on the supported catalyst. Catalyst **A** (41 mg) was then transferred into a 30 mL stainless steel glass-coated autoclave. Methanol (3 mL), 1 M sodium hydroxide aqueous solution (47.5 μL; NaOH/Rh = 5) and the substrate (with a 1.0 mol % rhodium/substrate ratio) were then added. The autoclave was purged three times with argon, followed by three times with hydrogen and the final H_2 pressure was adjusted to 40 bar. The mixture was stirred (200 rpm) at room temperature for the desired reaction time and then centrifuged. The liquid phase was then sep-

arated and analyzed by gas chromatography to determine the conversion and reaction yields. Catalyst **B** was prepared according to the procedure described for the synthesis of catalyst **A**, except that 118.4 mg of $[Rh(COD)Cl]_2$ were used, yielding a pale yellow solid (1.02 g).

The reaction products obtained from the catalytic tests were analyzed by gas chromatography on a Hewlett−Packard HP 6890 chromatograph with a J & W Scientific DB-1701 column (l = 30 m, *i.d.* = 0.25 mm), equipped with a FID detector (N_2 as carrier gas). To ensure a good separation of the products, a Macherey−Nagel LIPODEX E column (l = 25 m, *i.d.* = 0.25 mm) was used in the case of 1-octene, 4-octyne and 1-octyne (He as carrier gas [1.3 mL/min], oven temperature 38 °C).

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