Hydrogenation of organic substrates by isocyanide polymer-bound Rh(PPh$_3$) $_3$Cl

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Abstract

Rh(PPh$_3$)$_3$Cl undergoes easy and quantitative coordination to hydrophilic macromolecular isocyanides to give a supported rhodium complex which, activated at 50°C under 1 atm dihydrogen behaves as a versatile and recyclable catalyst for the hydrogenation of alkenes, alkynes, nitriles and nitrocompounds under mild conditions. Unsaturated aldehydes are converted into saturated aldehydes whereas nitriles are selectively converted into the corresponding imines or secondary amines depending on the reaction conditions.

Keywords: Hydrogenation; Cross-linked polymer; Isocyanide polymer; Supported catalyst; Rhodium

1. Introduction

Isocyano polymer supported complexes (**P**)–NC–ML$_n$ ((**P**)– = acrylic resin, M = transition metal, L = ligand) represent a promising approach to hybrid catalysis in view of the wide range of catalytic centres that can be immobilized to the polymeric supports [1]. We have recently investigated the catalytic activity of palladium(II) acetate coordinated to polymeric isocyanides and it was shown that such heterogeneous catalysts facilitate hydrogenation, isomerization and telomerization reactions of various organic substrates [2]. Moreover, a material obtained by syn-gas reduction of [((**P**)–NC)$_2$–(CO)$_2$(acac)Rh] was found to catalyse the

chemoselective hydrogenation of α,β-unsaturated aldehydes to saturated aldehydes [3].

We report here on the catalytic activity of isocyanide polymer-bound Rh(PPh$_3$)$_3$Cl towards hydrogenation reactions. The organic support was obtained upon copolymerization of 3-isocyanopropyl acrylate with oxytriethylene glycol methacrylate, in the presence of triethylene glycol dimethacrylate as the cross-linker [4].

2. Results and discussion

The reaction of Rh(PPh$_3$)$_3$Cl with the isocyano acrylic resin (**P**)–NC leads to the supported rhodium complex (**P**)–NC–RhCl(PPh$_3$)$_2$ [1].

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This complex was tested in the hydrogenation of 1-hexene at room temperature and atmospheric pressure but the gas uptake was extremely slow and after 24 h no reaction occurred. However, after heating overnight the complex in dichloromethane under 1 atmosphere dihydrogen a brown material (which will be referred to as (P)–NC–Rh) was obtained that was used in all reactions described here.
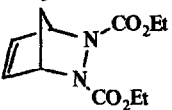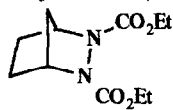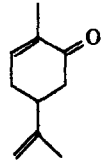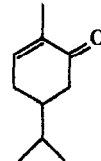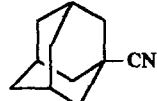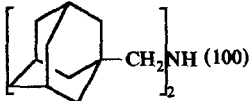
The first tests were carried out to study the catalytic activity, the stability and the reusability of the activated resin (P)–NC–Rh using 1-hexene as the substrate. (P)–NC–Rh catalysed the hydrogenation of 1-hexene at room temperature and ambient pressure with a turnover number as high as 55 h^{-1} (entry 1). The same resin was recycled six times with negligible loss of activity and, after the last cycle, its metal content was almost unchanged with respect to the initial amount.

Among the other alkenes tested in hydrogenation reactions (see Table 1), cyclohexene

Table 1
Scope of the investigated heterogeneous catalytic hydrogenations: 8.0 mmol substrates, substrate/supported rhodium = 160 mol/mol

Entry	Substrate	Time (h)	T (°C)	P (atm)	Conv. %	Products (Yield %)
1[a]	1-hexene	3	RT	1	100	n-hexane (100)
2[a]	cyclohexene	6	RT	1	100	cyclohexane (100)
3[b]		24	RT	1	98	(99)
4[b]	"	15	50	1	99	" (97)
5[a]	phenylacetylene	16	RT	1	100	ethylbenzene (100)
6[c]	trans-2-hexenal	29	RT	1	100	hexanal (100)
7[c]	cynnamaldehyde	70	RT	20	75	3-phenylpropanal (99)
8[c]		10	RT	1	92	(95)
9[c]	citral	40	RT	1	87	citronellal (74)
10[a]	valeronitrile	12	RT	10	100	dipentylamine (94)
11[c]		48	RT	10	95	(100)
12[d]	adiponitrile	9	RT	30	65	polymer
13[b]	benzonitrile	8	RT	10	85	N-benzylidene-benzylamine (93) dibenzylamine (7)
14[b]	"	12	RT	30	100	dibenzylamine (78)
15[d]	p-chlorobenzonitrile	30	RT	10	92	N-p-chlorobenzylidene--p-chlorobenzylamine (93) dibenzylamine (7)
16[c]	nitrobenzene	16	50	1	100	aniline (100)

[a] In 2 ml CH$_3$OH.
[b] In 4 ml CH$_3$OH.
[c] In 2 ml CH$_2$Cl$_2$.
[d] In 3 ml CH$_2$Cl$_2$.

gave quantitative conversion into cyclohexane at ambient conditions in 6 h (entry 2) whereas diethyl 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate, whose hydrogenation at the olefinic double bond is a key step in the synthesis of bicyclo[2.1.0]pentane [5], reached complete transformation into diethyl 2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate in 24 h at ambient conditions (entry 3), and in 15 h at 50°C and 1 atm H_2 (entry 4).

Phenylacetylene gave 100% ethylbenzene after 16 h at ambient conditions (entry 5) showing that, in contrast to isocyano-supported palladium acetate [2], no oligomerization reaction takes place.
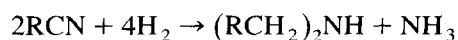
With the aim of studying the chemo- and regio-selectivity of the supported rhodium complex polyfunctional substrates such as trans-2-hexenal, cinnamaldehyde, carvone and citral have been submitted to catalytic hydrogenation.

Trans-2-hexenal was hydrogenated selectively to hexanal (entry 6), by that feature most rhodium catalysts have, preferential reduction of $C = C$ double bonds [6]. Cinnamaldehyde reacted slower than trans-2-hexenal, and gave selectively 3-phenylpropanal with a conversion as high as 75% after 70 h at 20 atm (entry 7).

The hydrogenation of carvone highlights the regioselectivity of the catalyst: after 10 h reaction 2-methyl-5-isopropyl-2-cyclohexenone was obtained in high yield (entry 8).

In the case of citral the hydrogenation was directed preferentially towards the conjugated double bond, affording citronellal in 74% yield (at 87% conversion) after 40 h at ambient conditions (entry 9 and Fig. 1). No decarbonylation was observed for any of the carbonyl compounds tested.

Aliphatic nitriles were hydrogenated by (P)–NC–Rh to give the corresponding secondary amines according to the reaction

$$2RCN + 4H_2 \rightarrow (RCH_2)_2NH + NH_3$$

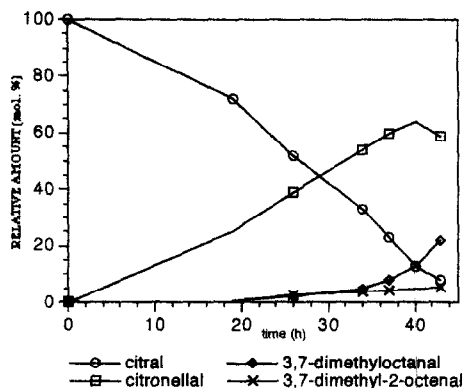Valeronitrile was the most reactive nitrile tested and was converted quantitatively into

Fig. 1. Product distribution for supported rhodium-catalysed hydrogenation of citral: 8.0 mmol citral, 0.05 mmol supported rhodium, 2 ml CH_2Cl_2, 1 atm H_2, room temperature.

dipentylamine after 12 h at 10 atm and room temperature (entry 10). 1-Cyanoadamantane, under the same reaction conditions, took 48 h to afford the corresponding secondary amine in 95% conversion and 100% yield (entry 11). The hydrogenation of adiponitrile was carried out under 30 atm H_2 and afforded, after 9 h, a white solid which has not been thoroughly characterized, but whose elemental analysis, IR features (3431, NH st; 2944, CH_2 st; 2246 (w) CN st; 1460, CH_2 δ; 1405) and solubility characteristics (insoluble in all solvents, soluble in dilute HCl) indicate it as a polymer (or oligomer, depending on the value of n) with the formula $NC-(CH_2)_5-NH[(CH_2)_6NH]_n-(CH_2)_5-CN$.
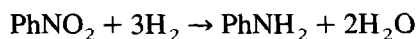
When aromatic nitriles were submitted to hydrogenation it was possible to isolate in high yield the imine formed according to

$$2ArCN + 3H_2 \rightarrow ArCH=NCH_2Ar + NH_3$$

Benzonitrile afforded 85% conversion and 93% yield in imine at 10 atm and RT (entry 13) whereas p-chlorobenzonitrile gave, under the same conditions, 93% yield (at 92% conversion) of the corresponding imine.

Carrying out the hydrogenation of benzonitrile under more severe conditions (30 atm H_2) it was possible to convert the substrate into dibenzylamine with 78% selectivity (entry 14).

The reaction of nitriles indicates that the supported catalyst is stable in the presence of nitrogen compounds such as ammonia and aliphatic amines. In order to test its stability towards water and aromatic amines we have carried out the hydrogenation of nitrobenzene that occurs according to

$$PhNO_2 + 3H_2 \rightarrow PhNH_2 + 2H_2O$$

The results obtained at 50°C and 1 atm H_2 (entry 16) show that (P)–NC–Rh catalyses the quantitative reduction of nitrobenzene into aniline in 16 h (entry 16).

In order to gain information about the possible active species anchored to the isocyanide polymer we have recorded IR and XPS spectra of the activated resin before and after catalysis. The non-activated resin showed an IR absorption at 2160 cm^{-1} that remained nearly unchanged after activation and after several catalytic runs. This indicates that (a) the catalytic centres remain attached via isonitrile to the bulk of the polymer, (b) NC functionalities are not hydrogenated under reaction conditions, (c) the electronic character of the supported rhodium is the same, both in (P)–NC–Rh(PPh$_3$)$_2$Cl and in the activated resin (P)–NC–Rh. This was confirmed by XPS analysis. The samples analysed (e.g. (P)–NC–Rh(PPh$_3$)$_2$Cl, (P)–NC–Rh and the resin used in the hydrogenation of 1-hexene) showed nearly the same spectrum in the region of rhodium signals and, in particular, the peaks attributable to Rh $3d_{5/2}$ were located at 308.5 ± 0.2 eV for the resin (P)–NC–Rh(PPh$_3$)$_2$Cl, and at 308.3 ± 0.2 eV for both the activated and the recycled resins. These findings may be rationalised allowing that the oxidation state of the supported rhodium is the same in all samples (and therefore equal to that of the starting Wilkinson complex, i.e., +1) and that the activation under hydrogen might serve to produce Rh(I) hydrides attached, via isonitriles, to the polymeric ligands. The binding energy found for the rhodium(I)hydride Rh(H)(CO)(PPh$_3$)$_2$ (308.5 eV) [7] is very close to that found by us in the supported rhodium of the activated resin.

3. Experimental

Chromatographic analyses were carried out on a Varian Vista 6000 instrument by using a capillary 30 m Carbowax 20M column or on a Hewlett Packard 5890 chromatograph using a 25 m SPB-1 capillary column. GC–MS analyses were performed using a HP 5890 chromatograph (30 m SE30 column) coupled with a mass selective detector HP 5970B, 70 eV. IR spectra were recorded on a Perkin Elmer 883 spectrometer. XPS measurements were performed by a Leybold LHS10 spectrometer equipped with a non-monochromated twin anode (MgK α/AlK α). The correction for sample charging was accomplished by choosing the C 1s main component as a binding energy reference (284.8 eV). NMR spectra were recorded on a Bruker AM500 instrument. Conversions were calculated by GLC analyses as moles of hydrogenated product per mole of starting unsaturated compound by using the internal standard method.

3.1. Synthesis of the polymeric complexes

The polymeric ligand was synthesized by the procedure described in Ref. [4]. A solution of Rh(PPh$_3$)$_3$Cl in dichloromethane was added with vigorous stirring to the polymeric isocyanide which had been previously swollen in a minimum amount of dichloromethane. The initial molar ratio between the metal and the macromolecular ligand was 1.0. The mixture was further stirred for 2 h. The solid was thereafter recovered by filtration, washed with dichloromethane (4 ×), acetone (2 ×), diethyl ether (2 ×), and eventually dried in vacuo.

Elemental analysis (w/w, %): C = 56.61; H = 6.83; N = 1.12; Rh = 7.1. Infrared: ν_{NC} = 2160 cm^{-1}. The supported complex is air-stable, insoluble in all solvents, swells in halogenated solvents, methanol, dimethylformamide and water and shrinks in diethyl ether or petroleum ether.

3.2. Hydrogenation reactions

3.2.1. Atmospheric pressure

A Schlenk tube was charged with the activated catalyst (71 mg, 0.05 mmol of rhodium), the substrate (8.0 mmol) and the solvent (methanol or methylene chloride) and stirred under 1 atm H_2 at the desired temperature (room temperature or 50°C).

3.2.2. Reactions under pressure

A stainless steel autoclave was charged with the activated catalyst (71 mg, 0.05 mmol of rhodium), the substrate (8.0 mmol) and the solvent (methanol or methylene chloride) and pressurized with H_2 to the desired pressure. The mixture was stirred at room temperature.

After stopping the reactions, the recovered suspensions were filtered and the liquid phase was analysed by GLC and/or GC–MS. The hydrogenated products were isolated by evaporation of the solvent in the filtrate or by column chromatography and identified by comparison of their MS spectra, IR and NMR spectra and retention times in GC analysis with those of authentic samples. The resins were washed with CH_2Cl_2 (twice), acetone (once) and diethyl ether (twice), dried in vacuo and opportunely recycled.

3.3. N,N-p-Chlorobenzylidene-p-chlorobenzyl-amine

^{1}H NMR (CDCl$_3$, ppm): 4.77 (2-H, s), 7.70 (2-H, d, J = 8.5 Hz), 7.39 (2-H, d, J = 8.5 Hz), 7.31 (2-H, d, J = 8 Hz), 7.26 (2-H, d, J = 8 Hz), 8.34 (1-H, s). ^{13}C NMR (CDCl$_3$, ppm): 160.8, 137.6, 136.9, 134.4, 132.8, 129.4, 129.2, 128.9, 128.6, 64.2. IR (Nujol mull): 3022, 1642, 1593, 1487, 1403, 1090, 1046, 1013, 861, 823, 811, 799, 510, 485 cm^{-1}. MS (70 eV): m/e (relative intensity) 267 (4), 265 (19), 264 (14), 263 (M$^+$, 28), 262 (14), 151 (9), 127 (33), 126 (14), 125 (100), 89 (25).

3.4. Di(1-adamantyl)methylamine

^{1}H NMR (CD$_3$OD, ppm): 4.59 (1-H, s), 2.80 (4-H, s), 2.03 (6-H, bs), 1.76 (12-H, pseudo-quartet, J = 12.4 Hz), 1.70 (12-H, d, J = 2.5 Hz). ^{13}C NMR (CD$_3$OD, ppm): 63.3, 40.5, 37.4, 33.8, 29.4. IR (KBr): 3148, 2909, 2849, 1572, 1401, 1106 cm^{-1}. MS (70 eV): m/e (relative intensity) 313 (5), 178 (100), 176 (20), 149 (22), 79 (8).

Acknowledgements

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