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Heterogeneous hydrogenation of bicyclo[2.2.2]octenes on Rh/TPPTS/LDH catalysts

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Abstract

The Rh-TPPTS complex was heterogenized onto layered double hydroxides (LDH) Zn_3AlCl and Co_2FeCO_3 using ion-exchange procedure. Before ion exchange, the Rh precursor $[Rh(cod)Cl]_2$ was dissolved together with the TPPTS ligand in deionised water and stirred for 12 h. After stirring, the LDH was added to the solution and stirred for another 24 h, then filtered, washed with deionised water, and dried under vacuum at room temperature for 16 h. The characterization of the catalysts was carried out using several techniques: ICP-AES, N_2 adsorption–desorption isotherms at −196 °C, thermal analysis, powder X-ray diffraction, XPS and DRIFTs. Substrates were prepared via Diels–Alder reaction of various 2*H*-pyran-2-ones with *N*-substituted maleimides in an aqueous medium with microwave irradiation. The catalytic tests were performed in a stirred stainless-steel autoclave using H_2 pressures in the range 20–40 atm, 30 mg catalyst and 30 mg substrate, at different temperatures. Hydrogenation of bicyclo[2.2.2]octenes showed that these strained and functionalized cycloadducts were inert to classic catalysts but could be hydrogenated by using ionic-immobilized Rh-ligand complexes on the LDH. The Rh-TPPTS/Zn_3AlCl was found to exhibit a pretty high activity and selectivity for such reactions leading to heteropolycyclic derivatives. The heterogeneous catalyst was easily recycled with no leaching.

Keywords: Cycloaddition; Microwaves; Hydrogenation; Heterogeneous catalysis; Rhodium; Bicyclo[2.2.2]octenes

1. Introduction

Bicyclo[2.2.2]octenes and their fused derivatives [1] as well as their hydrogenated analogues, bicyclo[2.2.2]octanes, [1c,2] have been shown to serve as useful building blocks in organic syntheses. Among them, bicyclo[2.2.2]oct-7-enes (bicyclo[2.2.2]oct-2-enes when unsubstituted) containing a free or protected amino group at the bridgehead carbon atom are very rare compounds [3a] and can be found in the skeleton of naturally occurring *Kopsia* alkaloids [3b] whereas analogous bicyclo[2.2.2]octanes have been only rarely described. During our recent investigation of the transformations of the 2*H*-pyran-2-ones and fused pyran-2-ones we synthesized a series of aminobicyclo[2.2.2]oct-7-enes bearing fused heterocyclic rings in their structure, such as a fused maleic anhydride moiety [4a] or a fused substituted succinimide moiety [4b,c]. The transformation of the bicyclo[2.2.2]oct-7-ene-2*exo*,3*exo*,5*exo*,6*exo*-tetracarboxylic acid 2,3:5,6-dianhydrides with hydrazine derivatives resulted in the preparation of the corresponding fused succinimides [5].

Over the past few years the developments in the field of green chemistry have been oriented towards adopting methods and processes that use less-toxic chemicals, produce smaller

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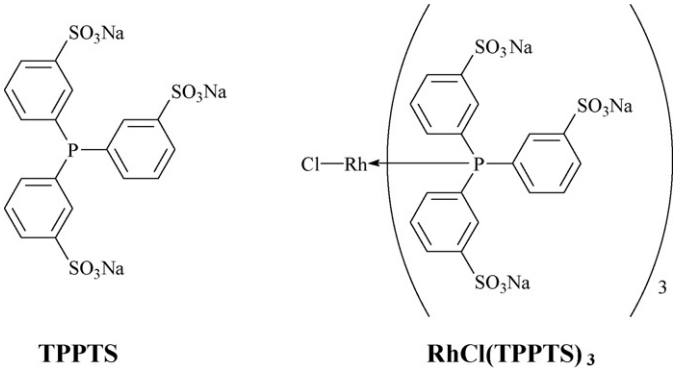


Scheme 1. TPPTS and $RhCl(TPPTS)_3$.

amounts of by-products and consume less energy [6]. Among them, microwave-assisted reactions [7] have attracted considerable attention and many efficient, eco-friendly syntheses of a variety of organic products were developed in water [5,8]. In pursuit of our studies on atom- and energy-economical reactions, we envisioned developing a sequential microwave-assisted cycloaddition reaction followed by a heterogeneous hydrogenation [9], which would represent an expedient route to complex functionalized heteropolycyclic derivatives.

The aim of this study was to investigate the hydrogenation of bicyclo[2.2.2]octenes over heterogeneous catalysts prepared via ionic exchange of Rh[TPPTS] (TPPTS—trisodium salt of 3,3′,3″-phosphanetriyl benzenesulfonic acid) complexes (Scheme 1) with double-layered hydroxides (LDH). Previous reports indicated that the triphenylphosphine (TPP)-substituted Rh catalyst $[HRh(CO)(TPP)_3]$ showed remarkable catalytic properties in the hydrogenation and hydroformylation of olefins [10]. The introduction of water-soluble moieties on the TPP ligand for the preparation of the trisodium salt of 3,3′,3″-phosphanetriyl benzenesulfonic acid (TPPTS) as a ligand of Rh, allowed the work in water. Indeed α- and β-unsaturated aldehydes were selectively hydrogenated with TPPTS-modified transition-metal complex catalysts, either with Ru or Rh [11]. For our purpose, such a behavior allowed immobilization of Rh complexes on LDH support via a typical ion exchange procedure. LDH-supported $Pd(TPPTS)_2Cl_2$ was previously found to be efficient for the Heck arylation of olefins [12a] and a unique LDH containing a chiral organic guest had been used for asymmetric C–C bond formation [12b]. Preparation of heterogeneous catalysts via the ion-exchange of LDH was also reported to increase the thermal stability of the immobilized ligands [13]. Also the $RhCl(TPPTS)_3$ complex was previously immobilized on a mesoporous SBA-15 [12c] for the heterogeneous hydrogenation of simple alkenes.

2. Experimental

2.1. Catalysts preparation

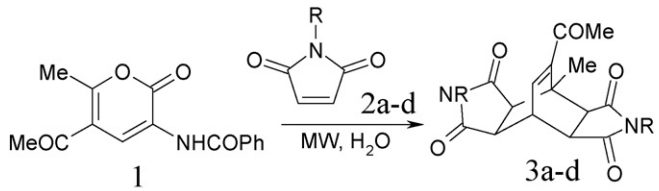
The heterogenization of the Rh-TPPTS complex was realized onto layered double hydroxides LDH1 $[Zn_{0.76}Al_{0.24}(OH)_2]Cl_{0.24}\cdot 0.8H_2O]$ (Zn_3AlCl) and LDH2 $[Co_{0.66}Fe_{0.34}(OH)_2](CO_3)_{0.17}\cdot 0.5H_2O]$ (Co_2FeCO_3). Both LDHs were prepared following methods described in the literature [14]. The ionic exchange capacity of LDH1 and LDH2 was of 1.1 and 2.1 mequiv. g^{-1}, respectively. Before ionic exchange, the Rh precursor $[Rh(cod)Cl]_2$ (0.25 mmol of metal) was dissolved together with the TPPTS ligand (1 mmol) in 50 mL of deionised water and stirred for 12 h. After stirring, the LDH (1 g) was added to the solution and stirred for another 24 h. The solution was filtered and the solid was washed with deionised water, and dried under vacuum at room temperature for 16 h.

2.2. Catalysts characterization

The characterization of the catalysts was carried out using several techniques. Chemical composition of the catalysts was determined using an ICP-AES Spectro equipment. N_2 adsorption–desorption isotherms of the LDH support were measured at liquid nitrogen temperature with a Micromeritics ASAP 2020. Prior to measurement, the samples were degassed at 150 °C under vacuum for more than 4 h. The specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) method in the p/p_0 (low case, according to IUPAC) range of 0.05–0.35. Pore size distribution curves were calculated from the adsorption branch of the isotherms with the Barrett–Joyner–Halenda (BJH) method, and pore sizes were obtained from the peak positions of the distribution curves. Both LDH support and exchanged catalysts were characterized by powder X-ray diffraction (XRD) using a Siemens D5000 X-ray diffractometer with nickel filtered Cu Kα radiation (λ = 1.5418 Å) at a scanning rate of 0.1° min^{-1} in the 2θ range of 10–80°. The XPS spectra were recorded with a Leybold Heraeus spectrometer with monochromated Al Kα radiation. The spectrometer energy scale was calibrated using the Au $4f_{7/2}$ peak (binding energy: 84.0 eV). For the calculation of the binding energies, the C 1s peak of the C–(C, H) component at 284.8 eV was used as an internal standard. The superficial composition of the investigated samples was determined using the apparatus software. The binding energies assigned to the Rh $3d_5$, Al $2p_3$, Zn $2p_3$, Co $2p_3$, Fe $2p_3$, O 1s, C 1s, P $2p_3$, and S $2p_3$ levels were analyzed. DRIFTs investigation of the catalysts was realized with a Nicolet 4700 spectrometer using the following parameters: 200 scans, 600–4000 cm^{-1} scan range, 4 cm^{-1} resolution. Thermal analysis, registering the TG curves, was carried out using a SETARAM 92 16.18 equipment by heating the samples in air up to 900 °C at a rate of 10 °C min^{-1}.

2.3. Preparation of the reaction substrates

A mixture of 2*H*-pyran-2-one **1** (1 mmol) and *N*-substituted maleimide **2** (2.1 mmol) in 3 mL of distilled water was irradiated in the focused-microwave equipment (discover by CEM Corporation, Matthews NC) for the time specified (the final temperature was set to 150 °C, the power to 100 W, and the ramp time 3 min) (Scheme 2). Thereafter, the reaction mixture was cooled to room temperature; the precipitated solid was filtered off and washed with water (0.5–1 mL). Crude solid prod-



Run	Starting compounds **1** and **2**		Product **3**
	R	**2**	
1	H	**2a**	**3a**
2	Me	**2b**	**3b**
3	Et	**2c**	**3c**
4	Ph	**2d**	**3d**

Scheme 2. Synthesis of bicyclo[2.2.2]octenes.

ucts **3a**–**d** obtained after microwave irradiation were crystallized from EtOH.

2.4. Catalytic tests and analysis of the products

The catalytic tests were performed in a stirred stainless-steel autoclave using H_2 pressures in the range 20–40 atm, 30 mg catalyst and 30 mg substrate **3**, at different temperatures. All the experiments were carried out in EtOAc. The analysis of the reaction products was made on a Knauer HPLC equipped with a chiral column EC 150/4 RESOLVOSIL BSA-7, UV–vis detector. The eluent used was 25% MeCN/75% H_3PO_4 0.1%. For analytical purposes the products **4** and **5** were separated by the silica gel chromatography using a solution of EtOAc with cyclohexane (40/60) as eluent. Identification of the components was made on the basis of ^{1}H and ^{13}C NMR analysis. ^{1}H NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer at 29 °C and 300 MHz using TMS as an internal standard. ^{13}C NMR spectra were recorded on the same instrument at 75.5 MHz and are referenced against the central line of the solvent signal (DMSO-d_6 septet at δ = 39.5 ppm). The coupling constants (J) are given in Hz. They corresponded to the following data: *N*-[9-*Acetyl*-2,3,3*a*,4*a*,5,6,7,7*a*,8,8*a*-*decahydro*-8-*methyl*-1,3,5,7-*tetraoxo*-4,8-*ethenobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**3a**) [4c]. ^{1}H NMR (DMSO-d_6): δ 1.86 (s, 3H, Me), 2.15 (s, 3H, COMe), 2.99 (d, 2H, J = 8.3 Hz, 7a-H, 8a-H), 4.24 (d, 2H, J = 8.3 Hz, 3a-H, 4a-H), 7.36 (s, 1H, 10-H), 7.53 (m, 3H, Ph), 7.89 (m, 2H, Ph), 8.69 (s, 1H, N*H*COPh), 11.15 (s, 2H, 2 × NH); ^{13}C NMR (DMSO-d_6): δ 18.1, 27.7, 41.0, 44.1, 50.3, 57.6, 127.5, 128.1, 131.1, 135.3, 138.8, 142.5, 167.4, 175.7, 177.0, 196.2. *N*-[9-*Acetyl*-2,3,3*a*,4*a*,5,6,7,7*a*,8,8*a*-*decahydro*-2,6,8-*trimethyl*-1,3,5,7-*tetraoxo*-4,8-*ethenobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**3b**) [4c]. ^{1}H NMR (DMSO-d_6): δ 1.90 (s, 3H, Me), 2.08 (s, 3H, COMe), 2.69 (s, 6H, 2 × Me), 3.11 (d, 2H, J = 8.2 Hz, 7a-H, 8a-H), 4.31 (d, 2H, J = 8.2 Hz, 3a-H, 4a-H), 7.20 (s, 1H, 10-H), 7.56 (m, 3H, Ph), 7.91 (m, 2H, Ph), 8.75 (s, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 18.2, 24.3, 27.9, 41.2, 43.0, 49.0, 57.7, 127.5, 128.1, 131.2, 135.3, 138.1, 142.4, 167.7, 174.3, 175.5, 196.3. *N*-[9-*Acetyl*-2,6-*diethyl*-2,3,3*a*,4*a*,5,6,7,7*a*,8,8*a*-*decahydro*-8-*methyl*-1,3,5,7-*tetraoxo*-4,8-*ethenobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**3c**). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.89 (6H, t, J = 7.2 Hz, 2 × NCH$_2$C*H*$_3$), 1.92 (3H, s, Me), 2.09 (3H, s, COMe), 3.08 (2H, d, J = 8.1 Hz, 7a-H, 8a-H), 3.27 (4H, q, J = 7.2 Hz, 2 × NC*H*$_2$CH$_3$), 4.30 (2H, d, J = 8.1 Hz, 3a-H, 4a-H), 7.25 (1H, s, 10-H), 7.56 (3H, m, Ph), 7.90 (2H, m, Ph), 8.75 (1H, s, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 12.7, 18.1, 27.3, 32.6, 41.2, 42.8, 48.8, 57.8, 127.5, 128.1, 131.2, 135.4, 138.4, 142.4, 167.7, 173.9, 175.1, 195.9. *N*-[9-*Acetyl*-2,3,3*a*,4*a*,5,6,7,7*a*,8,8*a*-*decahydro*-8-*methyl*-1,3,5,7-*tetraoxo*-2,6-*diphenyl*-4,8-*ethenobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**3d**). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.96 (3H, s, Me), 2.25 (3H, s, COMe), 3.39 (2H, d, J = 8.3 Hz, 7a-H, 8a-H), 4.57 (2H, d, J = 8.3 Hz, 3a-H, 4a-H), 7.11 (4H, m), 7.48 (10H, m), 7.87 (2H, m) (3 × Ph, 10-H), 8.83 (1H, s, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 17.8, 28.1, 41.5, 43.4, 49.0, 57.9, 126.8, 127.4, 128.1, 128.4, 128.9, 131.2, 132.0, 135.3, 137.7, 143.5, 167.9, 173.4, 174.6, 197.0. *N*-[9-*Acetyldecahydro*-8-*methyl*-1,3,5,7-*tetraoxo*-4,8-*ethanobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**4a**). ^{1}H NMR (DMSO-d_6): δ 1.66 (s, 3H, Me), 1.90 (s, 3H, COMe), 2.14 (d, 2H, J = 6.4 Hz, 10-H), 2.42 (t, 1H, J = 6.4 Hz, 9-H) 2.90 (d, 2H, J = 8.1 Hz, 7a-H, 8a-H), 4.15 (d, 2H, J = 8.1 Hz, 3a-H, 4a-H), 7.55 (m, 3H, Ph), 7.90 (m, 2H, Ph), 8.50 (s, 1H, N*H*COPh), 11.10 (s, 2H, 2 × NH); ^{13}C NMR (DMSO-d_6): δ 18.0, 27.2, 32.4, 41.0, 41.8, 43.9, 49.7, 57.3, 127.6, 128.1, 131.3, 135.6, 167.9, 174.2, 175.6, 192.1. *N*-[9-*Acetyldecahydro*-2,6,8-*trimethyl*-1,3,5,7-*tetraoxo*-4,8-*ethanobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**4b**). ^{1}H NMR (DMSO-d_6): δ 1.69 (s, 3H, Me), 1.83 (s, 3H, COMe), 2.09 (d, 2H, J = 6.6 Hz, 10-H), 2.40 (t, 1H, J = 6.6 Hz, 9-H) 2.75 (s, 6H, 2 × Me), 2.98 (d, 2H, J = 8.1 Hz, 7a-H, 8a-H), 4.22 (d, 2H, J = 8.1 Hz, 3a-H, 4a-H), 7.57 (m, 3H, Ph), 7.89 (m, 2H, Ph), 8.53 (s, 1H, N*H*COPh); ^{13}C NMR (DMSO-d_6): δ 17.9, 24.2, 27.5, 32.9, 40.8, 41.5, 44.2, 48.5, 56.6, 127.4, 128.0, 131.3, 135.1, 167.0, 173.5, 175.1, 190.1. *N*-[9-*Acetyl*-2,6-*diethyldecahydro*-8-*methyl*-1,3,5,7-*tetraoxo*-4,8-*ethanobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**4c**). ^{1}H NMR (DMSO-d_6): δ 0.91 (6H, t, J = 7.0 Hz, 2 × NCH$_2$C*H*$_3$), 1.70 (3H, s, Me), 1.85 (3H, s, COMe), 2.12 (2H, d, J = 6.5 Hz, 10-H), 2.43 (1H, t, J = 6.5 Hz, 9-H),

2.97 (2H, d, $J = 8.0$ Hz, 7a-H, 8a-H), 3.26 (4H, q, $J = 7.0$ Hz, 2 × NCH_2CH$_3$), 4.20 (2H, d, $J = 8.0$ Hz, 3a-H, 4a-H), 7.58 (3H, m, Ph), 7.88 (2H, m, Ph), 8.54 (1H, s, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 12.6, 17.6, 27.4, 32.5, 32.8, 40.8, 41.7, 42.5, 44.3, 57.5, 127.4, 128.1, 131.3, 135.6, 167.4, 173.1, 174.8, 191.7. *N*-[9-*Acetyldecahydro*-8-*methyl*-1,3,5,7-*tetraoxo*-2,6-*diphenyl*-4,8-*ethanobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**4d**). ^{1}H NMR (DMSO-d_6): δ 1.73 (3H, s, Me), 2.09 (3H, s, COMe), 2.21 (2H, d, $J = 6.5$ Hz, 10-H), 2.47 (1H, t, $J = 6.5$ Hz, 9-H) 3.12 (2H, d, $J = 8.3$ Hz, 7a-H, 8a-H), 4.39 (2H, d, $J = 8.3$ Hz, 3a-H, 4a-H), 7.09 (4H, m, Ph), 7.45 (9H, m, Ph), 7.84 (2H, m, Ph), 8.62 (1H, s, NH). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 17.5, 27.7, 32.5, 41.0, 41.5, 44.0, 49.1, 57.2, 125.7, 126.6, 127.5, 128.0, 129.0, 131.1, 132.2, 135.4, 167.8, 174.1, 175.2, 191.9. *N*-[2,3,3*a*,4*a*,5,6,7,7*a*,8,8*a*-*decahydro*-9-(1-*hydroxyethyl*)-8-*methyl*-1,3,5,7-*tetraoxo*-4,8-*ethenobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**5a**). ^{1}H NMR (DMSO-d_6): δ 1.24 (3H, d, $J = 6.7$ Hz, CH_3CHOH), 1.86 (3H, s, Me), 2.81 (1H, s, OH), 3.00 (2H, d, $J = 8.3$ Hz, 7a-H, 8a-H), 4.02 (1H, q, $J = 6.7$ Hz, C*H*OH), 4.27 (2H, d, $J = 8.3$ Hz, 3a-H, 4a-H), 6.70 (1H, s, 10-H), 7.56 (3H, m, Ph), 7.90 (2H, m, Ph), 8.82 (1H, s, N*H*COPh), 11.15 (2H, s, 2 × NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 17.9, 23.9, 41.2, 43.8, 50.1, 57.4, 75.8, 127.6, 128.2, 131.2, 135.2, 138.5, 143.4, 167.6, 174.9, 176.8. *N*-[2,3,3*a*,4*a*,5,6,7,7*a*,8,8*a*-*decahydro*-9-(1-*hydroxyethyl*)-2,6,8-*trimethyl*-1,3,5,7-*tetraoxo*-4,8-*ethenobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**5b**). ^{1}H NMR (DMSO-d_6): δ 1.23 (d, 3H, $J = 6.8$ Hz, CH_3CHOH), 1.83 (s, 3H, Me), 2.72 (s, 6H, 2 × Me), 2.80 (s, 1H, OH), 3.01 (d, 2H, $J = 8.1$ Hz, 7a-H, 8a-H), 4.06 (q, 1H, $J = 6.8$ Hz, C*H*OH), 4.29 (d, 2H, $J = 8.1$ Hz, 3a-H, 4a-H), 6.71 (s, 1H, 10-H), 7.55 (m, 3H, Ph), 7.90 (m, 2H, Ph), 8.74 (s, 1H, N*H*COPh); ^{13}C NMR (DMSO-d_6): δ 18.1, 24.1, 24.5, 40.9, 42.7, 50.1, 57.4, 74.6, 127.5, 128.1, 131.0, 135.2, 138.0, 143.7, 167.6, 174.8, 176.6. *N*-[2,6-diethyl-2,3,3*a*,4*a*,5,6,7,7*a*,8,8*a*-*decahydro*-9-(1-*hydroxyethyl*)-8-*methyl*-1,3,5,7-*tetraoxo*-4,8-*ethenobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**5c**). ^{1}H NMR (DMSO-d_6): δ 0.90 (6H, t, $J = 7.2$ Hz, 2 × NCH$_2$CH_3), 1.26 (3H, d, $J = 6.8$ Hz, CH_3CHOH), 1.85 (3H, s, Me), 2.83 (1H, s, OH), 3.03 (2H, d, $J = 8.0$ Hz, 7a-H, 8a-H), 3.25 (4H, q, $J = 7.1$ Hz, 2 × NCH_2CH$_3$), 4.08 (1H, q, $J = 6.8$ Hz, C*H*OH), 4.28 (2H, d, $J = 8.0$ Hz, 3a-H, 4a-H), 6.68 (1H, s, 10-H), 7.53 (3H, m, Ph), 7.89 (2H, m, Ph), 8.80 (1H, s, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 12.8, 18.0, 24.1, 32.4, 41.3, 42.7, 48.7, 57.9, 74.9, 127.3, 128.0, 131.1, 135.3, 138.2, 142.0, 167.9, 172.9, 174.5. *N*-[2,3,3*a*,4*a*,5,6,7,7*a*,8,8*a*-*decahydro*-9-(1-*hydroxyethyl*)-8-*methyl*-1,3,5,7-*tetraoxo*-2,6-*diphenyl*-4,8-*ethenobenzo*[1,2-*c*:4,5-*c*′]*dipyrrol*-4(1*H*)-*yl*]*benzamide* (**5d**). ^{1}H NMR (DMSO-d_6): δ 1.26 (3H, d, $J = 6.7$ Hz, CH_3CHOH), 1.89 (3H, s, Me), 2.85 (1H, s, OH), 3.10 (2H, d, $J = 8.2$ Hz, 7a-H, 8a-H), 4.00 (1H, q, $J = 6.7$ Hz, C*H*OH), 4.37 (2H, d, $J = 8.2$ Hz, 3a-H, 4a-H), 6.73 (1H, s, 10-H), 7.10 (4H, m, Ph), 7.45 (9H, m, Ph), 7.85 (2H, m, Ph), 8.84 (1H, s, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 18.0, 23.4, 41.4, 43.0, 49.1, 57.7, 74.3, 125.8, 126.7, 127.2, 128.1, 128.8, 131.1, 132.3, 135.5, 138.1, 142.9, 167.8, 173.8, 175.1.

3. Results and discussions

Several techniques provided evidences about the intercalation of the Rh(I)-TPPTS ligands inside the LDH layers. The catalysts structure was confirmed by XRD analysis. The XRD patterns of pure LDH contain a diffraction plane at 11.4 (2θ) (which corresponds to a d value of 7.7 Å), which is typical for such materials. After the docking of the complex an additional plane appeared at a 2θ around 5 (which corresponds to a d value of 15.2 Å), which is in perfect agreement with the literature data for such materials thereby, proving the complex docking [12]. However, exchange was not complete, as the diffraction peak due to planes (0 0 3) of the starting LDHs is still recorded in both cases. The presence of this plane confirms the increase of the interlayer distance caused by the intercalation of the complex (Fig. 1).

Table 1 compiles the chemical composition and the surface areas of the investigated catalysts. The TPPTS loading was determined from the thermal analysis by determining the mass loss in the catalysts. Docking of the Rh(I)-TPPTS complex caused an important decrease of the surface area to ca. 50% of the original

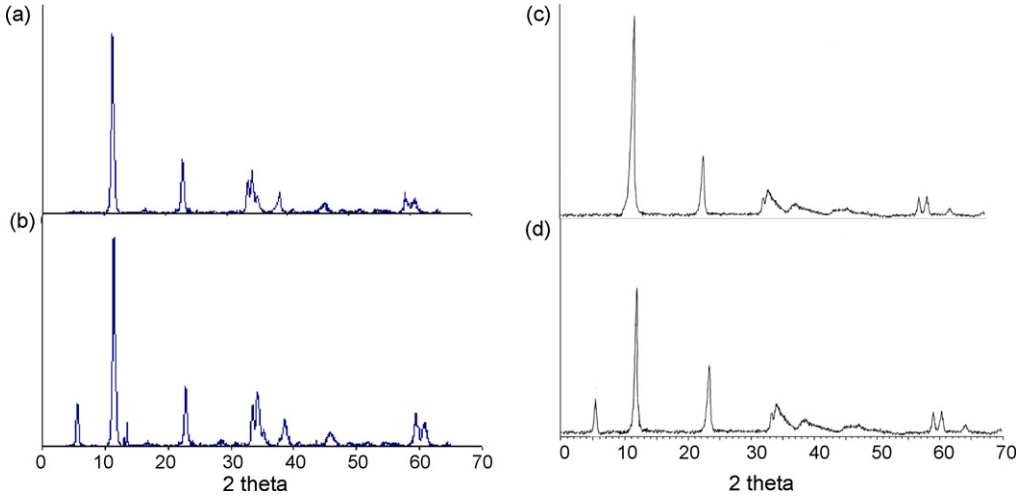


Fig. 1. XRD patterns of LDH1 (a and b) and LDH2 (c and d): (a and c) before docking and (b and d) after docking with Rh/TPPTS complex.

Table 1
The chemical composition and the surface areas of the investigated catalysts

Catalyst	Chemical composition						Specific surface area ($m^2\ g^{-1}$)
	Zn:Al ratio	Rh:Al ratio	Rh:Fe ratio	Co:Fe ratio	Rh (wt.%)	TPPTS (wt.%)	
LDH1	3:1	–	–	–	–	–	94
LDH2	–	–	–	2	–	–	90
Rh/TPPTS LDH1	3:1	0.43	–	–	2.51	7.63	51
Rh/TPPTS LDH2	–	–	0.12	2	2.51	7.63	48

Table 2
XPS binding energies and atomic Rh:Zn and Rh:Co XPS ratios

Catalyst	XPS binding energies (eV)						XPS composition	
	Al 2p	Zn $2p_3$	Co $2p_3$	Fe $2p_3$	P 2p	Rh $3d_5$	Rh:Zn ratio	Rh:Co ratio
LDH1	74.1	1021.7	–	–	–	–	–	–
LDH2	–	–	782.9	711.2	–	–	–	–
Rh/TPPTS LDH1	73.9	1021.6	–	–	132.6	308.2	0.052	–
Rh/TPPTS LDH2	–	–	782.9	711.2	132.6	308.2	–	0.041

value, although the layered structure is not altered, according to the PXRD diagrams.

The chemical composition of these catalysts was confirmed by the XPS analysis (Table 2). For the initial LDH, all the elements exhibited typical binding energies in oxidic structures. The docking of the complexes via ion exchange was not accompanied by any change in the binding energies, thus confirming that the structure of the LDH materials was not damaged during their deposition. Also, the binding energy of Rh corresponded to (I) state, that shows the complexation caused no change in its oxidation state [15].

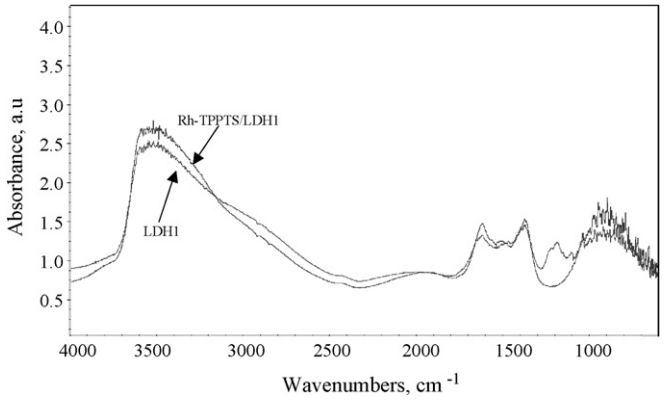
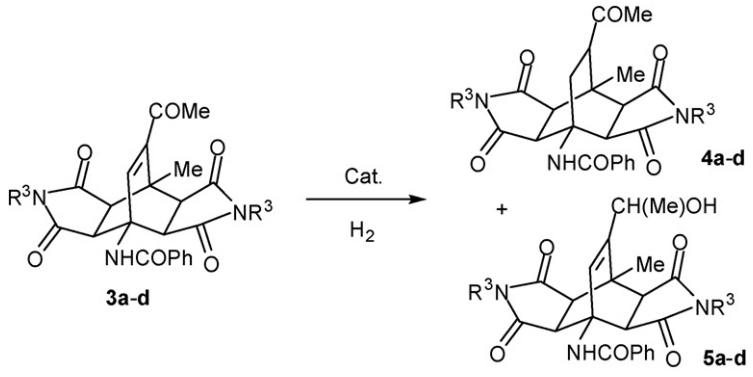


Fig. 2. DRIFTs spectra for fresh and docked Rh-TPPTS/LDH1 catalysts.

DRIFTs provided additional information about the docking of the ligands. Fig. 2 shows the DRIFTs spectra for fresh and docked Rh(I)-TPPTS/LDH1 catalysts. The bands in the window 1100–1300 cm^{-1} correspond to S=O vibrations in TPPTS [16].

Scheme 3 describes the reactions occurred during the hydrogenation of bicyclo[2.2.2]octenes **3** on Rh-TPPTS/LDH catalysts.

Hydrogenation of the structures **3** required a selective hydrogenation of the bridge C=C bond, preserving the entire structure intact. Experiments carried out with the homogeneous Rh-TPPTS catalyst, both in water and in EtOAc solvents, led to very low conversions (less than 4%) for reaction times of 96 h. This behavior can be explained by the insolubility of these substrates in water, while EtOAc is not a typical solvent for the Rh-TPPTS catalyst. The heterogeneization of this catalyst using an ion-exchange procedure and LDH (layered double hydroxides) as support therefore appeared as a logical solution. The immobilization of cationic or anionic metal complexes via ion-exchange with an appropriate ionic support may indeed be used as a strategy leading to stable catalysts.



Scheme 3. Hydrogenation of bicyclo[2.2.2]octenes on Rh-TPPTS/LDH catalysts.

Table 3
Hydrogenation of bicyclo[2.2.2]octenes[a]

Entry	Catalyst	3	H_2 (atm)	T (°C)	Conversion (%)[b]	Selectivity **4/5** (%)[b]
1	Rh-TPPTS/LDH1	**3a**	20	80	46	55
2	Rh-TPPTS/LDH1	**3a**	40	80	83	67
3	Rh-TPPTS/LDH1	**3b**	40	80	55	63
4	Rh-TPPTS/LDH1	**3c**	40	80	45	54
5	Rh-TPPTS/LDH1	**3c**	40	50	22	58
6	Rh-TPPTS/LDH1	**3d**	40	80	26	53
7	Rh-TPPTS/LDH2	**3a**	40	80	62	48
8	Rh-TPPTS/LDH2	**3b**	40	80	44	47

[a] Conditions: substrate **3** (30 mg), catalyst (30 mg), EtOAc (8 mL), 24 h.
[b] Determined by HPLC and NMR analysis.

The hydrogenation of the compounds **3a–d**, differing only in *N*-substituent (R^3), was conducted using our prepared ionic-immobilized Rh complexes, and the results are presented in Table 3. The commercially available Rh/C, Pd/C and Ir/C catalysts exhibited no catalytic activity in the range of the temperatures and pressures investigated, irrespective of the conditions in which they were pre-activated. The supported catalyst A (Rh-TPPTS/LDH1) was found to be active in the hydrogenation and led to the formation of the acetyl derivative **4a** and the alcohol **5a** (entry 1). The conversion and selectivity in favour of the hydrogenation of the C–C double bond was then improved at a higher pressure (entry 2). A similar trend was observed for the hydrogenation of cycloadducts **3b–d** (entries 3, 4, 6), the selectivity varying from 53% up to 63%. At a lower temperature (entry 5), the hydrogenation reaction was still possible and the selectivity in the C=C hydrogenation product was not significantly affected. The activity of the Rh-TPPTS/LDH1 catalyst was sensible to steric hindrance as a large substituent (such as Ph in **3d**) led to a loss of activity and selectivity (entry 6). We also found that the chemical composition of the LDH significantly influenced the hydrogenation results, as the use of LDH2 lowered the selectivity but preserved acceptable conversions for the cycloadducts **3a** and **3b** (entries 7 and 8).

Even though the activity was not extremely high, we envisaged testing the recyclability of the system. The supported catalysts were recycled without any significant loss of activity and selectivity (Fig. 3). Three successive hydrogenation reactions of substrate **3a** using recycled catalyst A (conditions entry 2, Table 3) were performed, and after each step the catalyst was separated via centrifugation without any additional treatment. A slight decrease in the conversion and selectivity was observed during all the process. No leaching of the immobilized rhodium complexes occurred, as the same ICP-AES analyses were obtained for the re-used catalysts. This result further confirms that the Rh complex is inside the interlayer space, and not merely adsorbed on the external surface of the crystallites.

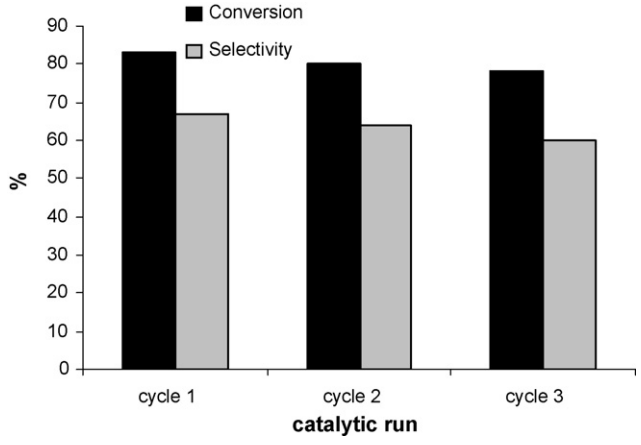


Fig. 3. Recycling test for the hydrogenation of bicyclo[2.2.2]octene **3a** in the presence of the Rh-TPPTS/LDH1 catalyst.

4. Conclusions

Hydrogenation of bicyclo[2.2.2]octenes investigated in this study in the presence of supported catalysts showed that these strained and functionalized cycloadducts were inert to classic catalysts but could be hydrogenated by using ionic-immobilized Rh-ligand complexes on the LDH. The Rh-TPPTS/Zn_3AlCl was found to exhibit a pretty high activity and selectivity for such reactions leading to heteropolycyclic derivatives. The heterogeneous catalyst was easily recycled with no leaching. The search for new ligands or other heterogeneous systems is currently underway in our groups and will be reported on in due course.

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