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Communication

# Catalytic Performances of Platinum Containing PLLA Macrocomplex in the Hydrogenation of $\alpha,\beta$ -Unsaturated Carbonyl Compounds

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**Abstract:** The synthesis of a bipyridine poly(lactic acid) carboxylic end-capped macroligand coordinated to a platinum center was reported. The reaction between the metal ion and the polymeric ligand was run in a very efficient way through a one-step synthesis and the complex was tested for selective hydrogenation of  $\alpha,\beta$ -carbonyl compounds. High selectivity was proven for double bond hydrogenation of 2-cyclohexen-1-one (up to 99%) and the production of 1-butanol from (E)-but-2-enal. Moreover, the catalytic system was still active after three catalytic cycles.

**Keywords:** poly(lactic acid); hydrogenation; polymer functionalization; macroligands

## 1. Introduction

The development of new catalysts is one of the breakthroughs of applied chemistry [1]. In the field of catalysis, hydrogenation plays a relevant role because this kind of process is largely used in the oil [2–4] and pharmaceutical [5,6] industries for refining or synthetic purposes. Furthermore, great interest has also been devoted to enantio [7] and chemo [8] selective conversions. Among all substrates, the multifunctional ones are quite challenging due to the possibility of the simultaneous transformation of one or all of the functionalities present. This normally induces a severe decrement of the hydrogenation selectivity and an interesting case study is represented by the  $\alpha,\beta$ -unsaturated carbonyl compounds [9]. Over the years, several systems have been developed for the selective hydrogenation of these substrates based on a plethora of metal frameworks (i.e., Cu [10], Au [11], Ni [12], Rh [13], Ru [14], Pd [15], and Pt [16,17]) with the aim to obtain a selective reduction of carbon–carbon or carbon–oxygen double bond or both. Among all available catalysts, noble metal based nanoparticles have astonishing properties of selectivity but still require a complex multi-step synthesis [18–21]. Recently, Bartoli et al. [22] proposed a new approach focused on the use of palladium bonded to a poly(lactic acid) macroligand. The catalytic system showed the same time advantages of a homogenous catalyst and the easy recyclability of a heterogeneous one. The use of Pd containing poly(lactic acid) systems is a well-established practice for selective hydrogenation of carbon–carbon double bonds [23–25], achieving great results for its selectivity and reusability.

In this paper, the use of a carboxylic end-capped poly(lactic acid) called macroligand was employed for the synthesis of platinum-based recyclable catalysts. The catalytic system was tested for selective hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds under several conditions to extend the use of macrocyclic ligands to the synthesis of other transition metal-containing catalysts.

## 2. Materials and Methods

### 2.1. Materials and Instrumentations

2-Cyclohexen-1-one, (E)-but-2-enal, dry  $\text{CH}_2\text{Cl}_2$  ( $\geq 99\%$ ), n-hexane ( $\geq 98\%$ ), acetonitrile ( $\geq 99\%$ ), chloroform ( $\geq 99\%$ ), deuteriochloroform ( $\text{CDCl}_3$ , 100%, 99.9 D), toluene ( $\geq 99\%$ ), hexadeuterodimethylsulfoxide ( $\text{DMSO-}d_6$ , 100%, 99.9 D), THF (HPLC grade,  $\geq 99.8\%$ ), and  $\text{PtCl}_2$  were purchased from Aldrich. L-lactide was purchased from Purac. 4-Methyl-4'-(hydroxymethyl)-2,2'-bipyridine (Bipy) was purchased from Imperial Chemical Industries (I.C.I.) ( $\geq 99.8\%$ ).

GC analyses were carried out on a Shimadzu 2010 (VFWAX column  $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ ) and GC-MS analyses were run using a Shimadzu GC-MS QP5050A (Petrocol™ column  $100\text{ m} \times 0.25\text{ mm} \times 0.5\text{ }\mu\text{m}$ ).

NMR analyses were performed with a Varian model GEMINI 400 MHz using  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  as the solvent. Integral errors were  $\pm 5\%$ .

GPC analyses were carried out with a Waters model binary HPLC 1525 system equipped with three columns (Shodex KF-802.5, KF-803, KF-804) and a refractive index detector Wyatt T-REX Optilab. Analyses were performed with THF as the eluant.

UV-Vis analysis was carried out using a Varian model Cary 4000 UV-Vis spectrophotometer.

Fourier transform infrared spectroscopy (FTIR) was performed using a Shimadzu model IR Affinity-1, equipped with a Golden Gate single reflection diamond ATR accessory supplied by Specac.

Elemental analysis was carried out using a Perkin-Elmer 240 CHN model.

Differential calorimetric analyses were carried out using a Perkin Elmer Pyris-1-dsc. Samples were tested from  $40\text{ }^\circ\text{C}$  to  $180\text{ }^\circ\text{C}$  with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ .

Catalytic reactions: Homogeneous catalytic hydrogenations of  $\alpha,\beta$ -unsaturated substrates were carried out in a 150 mL stainless steel homemade autoclave thermostated in an oil bath ( $\pm 1\text{ }^\circ\text{C}$ ) containing a glass vessel. The substrate, solvent, and catalyst were introduced in the glass vessel, under a nitrogen atmosphere, then the autoclave was closed. The autoclave was pressurized at room temperature with hydrogen, then stirred and heated at the prefixed temperature for the established time. At the end of the reaction, the autoclave was rapidly cooled to room temperature, the gas vented, and the solution collected and transferred into a 50 mL Schlenk tube. A sample of the solution was taken for the GC and GC-MS analyses. Each test was repeated three times, and the mean value was reported.

### 2.2. Synthesis of Macroligand, Macrocomplex, and Reference Catalyst

#### 2.2.1. Synthesis of Macroligand PLLA-Bipy

In a Schlenk tube, L-lactide (4.00 g, 28.0 mmol) was heated at  $135\text{ }^\circ\text{C}$  under a nitrogen atmosphere in the presence of  $\text{Sn}(\text{Oct})_2$  (56.3 mg, 0.139 mmol) and Bipy (0.400 mmol) for 3 h. Afterward, the reaction mixture was allowed to cool to room temperature and residual crystalline L-lactide, which sublimated during the reaction, was removed mechanically from the Schlenk tube. The crude reaction product was then dissolved in  $\text{CH}_2\text{Cl}_2$  (20 mL) and precipitated upon the addition of n-hexane (30.0 mL), giving an off-white solid powder, which was separated from the solution by filtration, washed several times with n-hexane, and dried in vacuum at room temperature for 12 h.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta = 8.67$  (d, 1H,  $J = 1.7\text{ Hz}$ , H 6'), 8.53 (d, 1H,  $J = 1.7\text{ Hz}$ , H 6), 8.52 (s, 1H, H 3), 8.23 (s, 1H, H 3'), 7.21 (d, 1H,  $J = 2.1\text{ Hz}$ , H 5'), 7.19 (d, 1H,  $J = 2.6\text{ Hz}$ , H 5), 5.29 (s, 2H,  $\text{CH}_2$  on C4 of Bipy), 5.24–4.96 (bs, 135 CH, in chain), 4.37 (q, 1H,  $J = 2.3\text{ Hz}$ , CH end chain), 2.47 (s, 3H,  $\text{CH}_3$  of Bipy), 1.86–1.05 (bs, 406,  $\text{CH}_3$  PLA).

FT-IR ( $\text{cm}^{-1}$ ): 3007–2953 (w,  $\nu\text{CH}$ ), 1748 (s,  $\nu\text{CO}$ ), 1452 (m,  $\nu\text{asHCH}$ ), 1382 (m,  $\nu\text{CH}$ ), 1359 (m,  $\nu\text{HCH}$ ), 1180 (s,  $\nu\text{asCOC}$ ), 1128–1043 (s,  $\nu\text{CO}$ ), 995 (w,  $\nu\text{CCH}_3$ ), 871 (m,  $\nu\text{OCC}$ ).

Molecular weight (g/mol): 11,590, Polydispersity index: 1.9, Yields (wt.%): 93, Tg:  $55\text{ }^\circ\text{C}$ , Tf:  $161\text{ }^\circ\text{C}$ .

### 2.2.2. Synthesis of the Macrocomplex Pt(PLLA-Bipy)Cl<sub>2</sub>

In a single neck round bottom flask, PLLA-Bipy (2.00 g, 0.14 mmol) and PtCl<sub>2</sub> (45 mg, 0.17 mmol) were dissolved in acetonitrile (20 mL) and refluxed for 16 h. Afterward, the reaction mixture was cooled to room temperature and the crude reaction product was recovered through filtration and washed three times with n-hexane. The yellow powder was dried in vacuum at room temperature for 12 h.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ = 9.70 (d, 1H, *J* = 1.7 Hz, H 6'), 9.54 (d, 1H, *J* = 1.7 Hz, H 6), 7.95 (s, 1H, H 3), 7.91 (s, 1H, H 3'), 7.42 (d, 1H, *J* = 2.1 Hz, H 5'), 7.37 (d, 1H, *J* = 2.6 Hz, H 5), 5.29 (s, 2H, CH<sub>2</sub> on C4 of Bipy), 5.26–5.05 (bs, 133CH, CH in chain), 4.37 (q, 1H, *J* = 2.3 Hz, CH end chain), 2.47 (s, 3H, CH<sub>3</sub> of Bipy), 1.86–1.05 (bs, 400 CH<sub>3</sub> end chain of PLA).

FT-IR (cm<sup>-1</sup>): 3012–2956 (w, νCH), 1749 (s, νCO), 1456 (m, νasHCH), 1384 (m, σCH<sub>3</sub>), 1359 (m, νHCH), 1182 (s, νasCOC), 1130–1041 (s, νCO), 966 (w, νCCH<sub>3</sub>), 871 (m, νOCC).

Yields (wt.%): 57 Tg: 59 °C Tf: 166 °C.

### 2.2.3. Synthesis of the Complex Pt(Bipy)Cl<sub>2</sub>

In a single neck round bottom flask, Bipy (80.0 mg, 0.4 mmol) and PtCl<sub>2</sub> (104 mg, 0.4 mmol) were dissolved in acetonitrile (20 mL) and refluxed for 16 h. Afterward, the reaction mixture was cooled to room temperature and the crude reaction product was recovered through filtration and washed three times with n-hexane. The yellow powder was dried in vacuum at room temperature for 12 h.

<sup>1</sup>H-NMR (DMSO, 400 MHz, ppm): δ = 9.16 (d, 1H, H6', *J* = 1.5 Hz), 8.92 (d, 1H, H6, *J* = 1.2 Hz), 8.48 (s, 1H, H3'), 8.42 (s, 1H, H3), 7.43 (d, 1H, H5, *J* = 1.2 Hz), 7.19 (d, 1H, H5', *J* = 1.5 Hz), 4.61 (s, 2H, CH<sub>2</sub>), 3.65 (OH), 2.36 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C-NMR (DMSO, 75 MHz, ppm): δ = 157.3 (s, C 4'), 153.1 (s, C 2,2'), 148.4 (s, C 6,6'), 147.8 (s, C 4), 128.5 (s, C 3), 125.1 (s, C 3'), 124.7 (s, C 5'), 121.2 (s, C5), 61.7 (s, CH<sub>2</sub>), 21.5 (s, CH<sub>3</sub>).

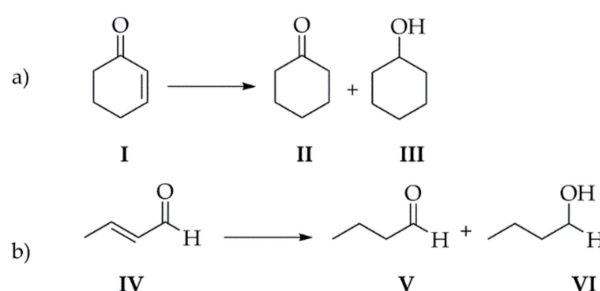
FT-IR (cm<sup>-1</sup>): 3421 (bs, νOH), 3066 (w, νCH aromatic), 2897 (w, νCH aliphatic), 1616 (s, νC=C), 1427 (s, ring breathing mode), 1056 (s, νCO).

Elemental analysis found (calc.): C: 29.59% (30.91%), H 3.32% (2.59%), N 5.95% (6.01%).

Yields (wt.%): 57.6.

### 2.3. Catalytic Experiments


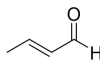
All the catalytic reactions were run with the formation of products according to the reaction scheme reported in Figure 1.



**Figure 1.** Catalytic reaction pathways of (a) 2-Cyclohexen-1-one, (b) (E)-But-2-enal.

Experiments were carried out using the apparatus reported in the experimental methods using the conditions reported in Table 1. A 10 mL glass vessel was charged, under a nitrogen atmosphere with I or IV as the substrate (2.7 mmol), the catalyst (0.0027 mmol catalyst), and toluene (5 mL). The reactor was then pressurized with hydrogen and heated at 60 °C for the prefixed time, then cooled at room temperature. The reaction mixture was analyzed as above described. After three catalytic cycles, the catalyst was recovered by filtration and characterized.

**Table 1.** Catalytic performances of Pt(Bipy)Cl<sub>2</sub> (A) and Pt(PLLA-Bipy)Cl<sub>2</sub> (B) in the selective hydrogenation of 2-cyclohexen-1-one (I) and (E)-but-2-enal (IV) at 60 °C.

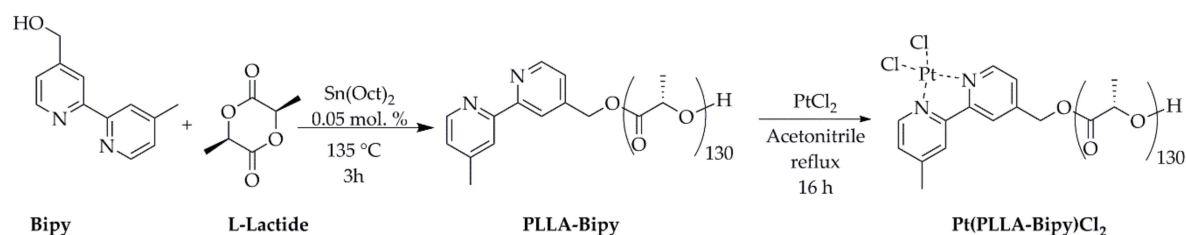
Run	Cat	Substrate	Time [h]	Pressure [MPa]	I [%]	II [%]	III [%]	IV [%]	V [%]	VI [%]	Conversion <sup>a</sup> [%]	TOF <sup>b</sup>
ID1	A		3	1.1	100	0	0	-	-	-	-	-
ID2	B		3	1.1	27	73	0	-	-	-	73	243
ID3	B		6	1.1	1	99	0	-	-	-	99	165
ID4	B <sup>c</sup>		3	1.1	61	39	0	-	-	-	39	130
ID5	B		3	2.2	5	95	-	-	-	-	95	317
ID6	B <sup>d</sup>		3	2.2	60	40	-	-	-	-	40	133
ID7	B		3	2.2	-	-	-	4	8	88	96	320
ID8	B		6	2.2	-	-	-	3	8	89	97	161
ID10	B <sup>e</sup>		3	2.2	-	-	-	9	4	87	91	303

<sup>a</sup> 60 °C, substrate (2.7 mmol), catalyst (0.0027 mmol), toluene (5 mL), <sup>b</sup> TOF defined as mmol (product) × (mmol Pt × h)<sup>-1</sup>, <sup>c</sup> Catalyst recycled after three cycles using catalytic conditions of ID2, <sup>d</sup> Catalyst recycled after three cycles using catalytic conditions of ID5, <sup>e</sup> Catalyst recycled after three cycles using catalytic conditions of ID7.

### 3. Results

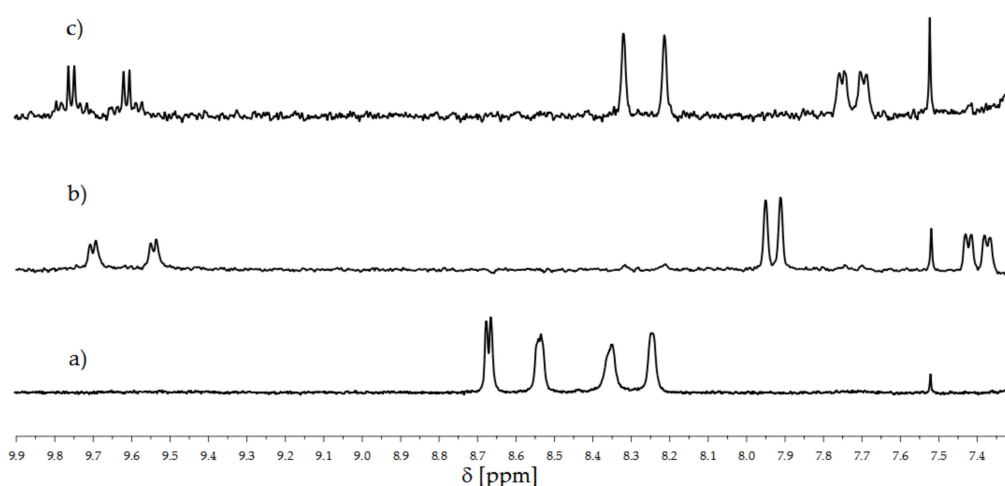
#### 3.1. Platinum Containing Poly(Lactic Acid) Macrocomplex

Synthesis of bipyridine carboxylic end-capped poly(lactic acid) ligand is an advantageous procedure for the production of several molecular architectures [26]. In this work, the synthesis of Pt(PLLA-Bipy)Cl<sub>2</sub> was reported, according to the scheme reported in Figure 2.

**Figure 2.** Pathway for the synthesis of Pt(PLLA-Bipy)Cl<sub>2</sub> macrocomplex.

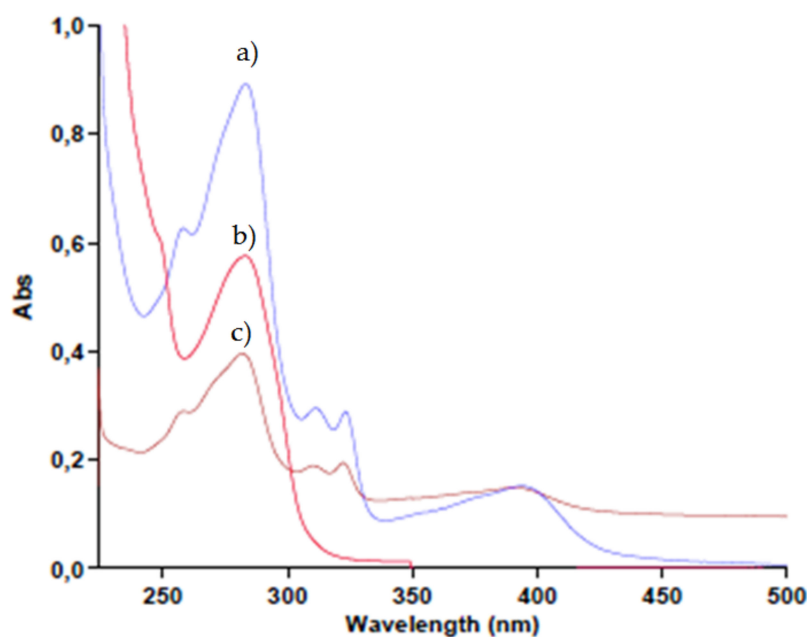
Synthesis of the ligand with carboxylic end-capped functionalization was proven by the presence of aromatic signals of Bipy in the region between 8.7–7.4 ppm (Figure 3a).

The formation of the platinum macrocomplex was detectable by <sup>1</sup>H-NMR spectra, through a comparison of spectra (a) and (b) as reported in Figure 3. The formation of the Pt complex did not affect the number of lactic acid units in the ligand because the reaction conditions were quite soft. The difference between hydrogen numbers was imputable to several issues: the first and the main relevant among them is the integral processing of the signals that were affected by noise and baseline correction. A% error in integral evaluations was reported in the experimental. Considering these points, the data for the macrocomplex and the macroligand are in good agreement among them. For a more precise molecular weight and fragment numbers, the value obtained from GPC analysis must be considered. After the coordination of the platinum ion, signals of aromatic hydrogen shifted to a higher ppm (Figure 3b) when compared with the non-coordinated ligand (Figure 3a). This behavior was in agreement with similar results observed for palladium coordination [26]. This phenomenon is due to the reduction of charge density on the aromatic ring caused by the modification of the π-orbitals of the Bipy due to the interaction of the electron doublet on the nitrogen atoms with the platinum orbital system as described by several theoretical studies [27,28]. Thermal properties of the complex were in good agreement with those previously reported for functionalized poly(lactic acid) [29].



**Figure 3.** Magnification of the NMR spectra in the aromatic region of (a) PLLA-Bipy, (b) Pt(PLLA-Bipy)Cl<sub>2</sub> and (c) [Pt(PLLA-Bipy)Cl<sub>2</sub>]<sub>2</sub> recovered after ID4.

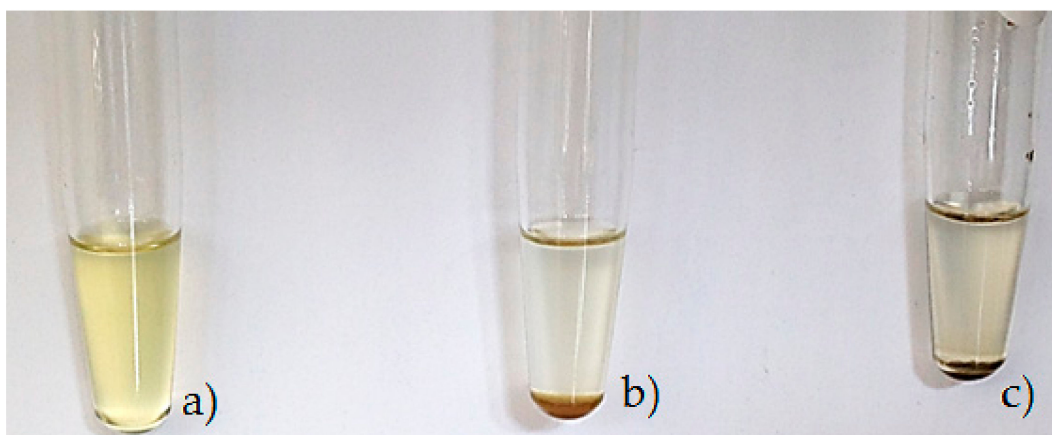
The effect of orbitals interactions was also appreciable in the UV–Vis spectra reported in Figure 4. Pt(PLLA-Bipy)Cl<sub>2</sub> (c) and Pt(Bipy)Cl<sub>2</sub> (a) showed a maximum absorption at 287 nm and a secondary absorption at 314 and 384 nm while PLLA-Bipy (b) showed only the absorption at 287 nm. Additional absorption bands were an evident proof of the coordination of Pt to Bipy moieties, in agreement with the NMR spectra above reported.



**Figure 4.** UV–Vis spectra of (a) Pt(Bipy)Cl<sub>2</sub>, (b) PLLA-Bipy and (c) Pt(PLLA-Bipy)Cl<sub>2</sub> collected in CH<sub>2</sub>Cl<sub>2</sub> solution (M = 0.005 mol/L).

### 3.2. Catalytic Experiments

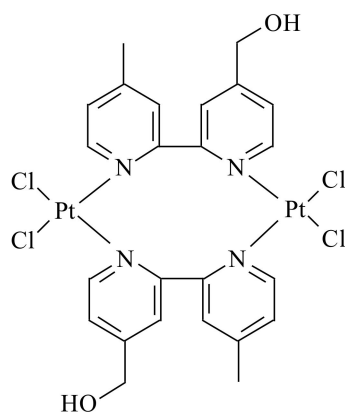
The most important advantage for the use of Pt(PLLA-Bipy)Cl<sub>2</sub> is the lack of solubility in the reaction medium at room temperature, while it was completely soluble under catalytic conditions (see Figure 5). This behavior, known as the “ponytail” effect, allows catalysis to be carried out in the homogeneous phase while the catalyst may be easily separated at the end of the process as a heterogeneous system. In contrast, the Pt(Bipy)Cl<sub>2</sub> complex did not show this property.



**Figure 5.** The catalytic reaction mixture of (a)  $\text{Pt}(\text{PLLA-Bipy})\text{Cl}_2$  under reaction conditions, (b)  $\text{Pt}(\text{PLLA-Bipy})\text{Cl}_2$  before and after catalysis at room temperature, (c)  $\text{Pt}(\text{Bipy})\text{Cl}_2$  at room and reaction temperature.

Catalytic performances of  $\text{Pt}(\text{PLLA-Bipy})\text{Cl}_2$  and  $\text{Pt}(\text{Bipy})\text{Cl}_2$  were tested under different conditions of time and pressure as shown in Table 1.

First,  $\text{Pt}(\text{Bipy})\text{Cl}_2$  was tested as a reference catalyst to evaluate its behavior in the hydrogenation of 2-cyclohexen-1-one as a model substrate. The results of ID 1 showed the total inactivity of this catalyst as shown by the absence of hydrogenation products after catalysis. In contrast, the reaction performed in the presence of  $\text{Pt}(\text{PLLA-Bipy})\text{Cl}_2$  as the catalyst achieved a conversion of 73% and a total selectivity for the reduction of the carbon–carbon double bond in the same conditions. After increasing the reaction time from 3 to 6 h, the catalytic performances of  $\text{Pt}(\text{PLLA-Bipy})\text{Cl}_2$  reached a conversion of 99% with a total selectivity toward the reduction of carbon–carbon unsaturation (ID3). The catalyst was still active and selective after three catalytic cycles, although the conversion dropped to 39%. This was probably due to the formation of higher hindered  $[\text{Pt}(\text{PLLA-Bipy})\text{Cl}_2]_2$  (Figure 6) instead of a merely Pt leaching, according to a theoretical study reported by Kawanishi et al. [30]. This hypothesis was supported by the NMR spectra of the recovered catalysts (Figure 3c), where the resonances of the Bipy ligands slightly shifted and the spectrum did not show any signal of free Bipy. A further increment of hydrogen pressure from 1.1 to 2.2 MPa gave a conversion of 95% with total selectivity. Under these conditions, the catalyst deactivation after three catalytic runs was the same as ID4. This result supports the deactivation mechanism above-mentioned and exclude the formation of nanoparticles that are more active than molecular complexes [31].



**Figure 6.** Structure of the hypothesized dimeric specie  $[\text{Pt}(\text{PLLA-Bipy})\text{Cl}_2]_2$ .

The solubility of the catalytic system Pt(PLLA-Bipy)Cl<sub>2</sub> is very different from the behavior of other heterogeneous systems previously described [32,33] as it acts as a non-supported catalyst during the reaction, leaving the C=O functionality untouched.

Different results were obtained in the hydrogenation of (E)-but-2-enal using the complex Pt(PLLA-Bipy)Cl<sub>2</sub> in the same conditions of the previously reported experiments. In these tests, a conversion of 96–97% was reached using a reaction time of 6 h and a hydrogen pressure of 2.2 MPa (ID7 and ID8). During the hydrogenation of an  $\alpha,\beta$ -unsaturated aldehyde, a remarkable selectivity was achieved toward the complete hydrogenation of the C=C double bond, but also of the -CHO group with the formation of 1-butanol (selectivity 88–89%) and butanal (selectivity 3–4%).

The different products formed during the two hydrogenations may be attributed to the high reactivity of the aldehydic group (-CHO) of (E)-but-2-enal if compared with the carbonyl group (=CO) of 2-cyclohexen-1-one.

In the hydrogenation of (E)-but-2-enal the recyclability of the catalyst was very high, and the conversion was reduced by only 5% after three catalytic cycles.

#### 4. Conclusions

In this research, the possibility of realizing the synthesis of bipyridine carboxylic end-capped poly(lactic acid) based macroligand was reported. The macroligand was used for the synthesis of a platinum-containing macrocomplex through a facile one-step coordination procedure. The new Pt macrocomplex showed high activity and selectivity for the hydrogenation of the carbon-carbon double bond of 2-cyclohexen-1-one to the corresponding saturated ketone. In contrast, in the hydrogenation of (E)-but-2-enal, a very promising selectivity toward the formation of 1-butanol (up to 89%) was achieved.

Furthermore, the catalyst was easily recycled even if it underwent a partial deactivation, especially in the reduction of cyclohexanone, while it remained almost constant after three catalytic runs in the hydrogenation of (E)-but-2-enal.

**Author Contributions:** Conceptualization: M.B., L.R., and M.F.; Methodology: B.M., M.B., L.R., and G.P.; Formal analysis: B.M., G.P., and E.P.; Resources: L.R. and M.F.; Writing—original draft preparation: M.B.; Writing—review and editing: L.R., M.F., and E.P.; Supervision: M.F.; Funding Acquisition: M.F.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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