ACS Catalysis

Research Article

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Hydrogenation of Biomass-Derived Levulinic Acid into γ-Valerolactone Catalyzed by Palladium Complexes

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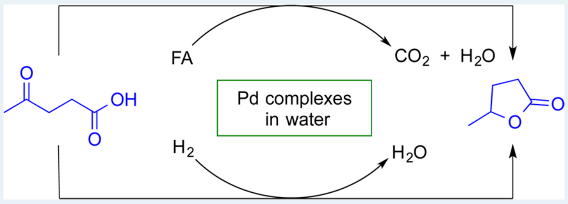
Ⓢ *Supporting Information*

ABSTRACT: The selective catalytic hydrogenation and cyclization of levulinic acid (LA) into valuable γ-valerolactone (GVL) catalyzed by different palladium compounds was achieved in water under mild conditions with high yields. Either formic acid (FA) or molecular hydrogen (H_2) was used as a hydrogen source. The precatalyst [(dtbpe)$PdCl_2$] (dtbpe = 1,2-(bis-di-*tert*-butylphosphino)ethane) (**1**) was highly active in the processes of LA hydrogenation (TON of 2100 and TOF of 2100 h^{-1}) and in the dehydrogenation of formic acid to produce H_2 and carbon dioxide. The catalytically active complexes [(dtbpe)Pd(H)Cl)] (**2**) and $[(dtbpe)_2Pd_2(\mu\text{-}H)_3]^+$ (**3**) and the catalytically inactive complex $[(dtbpe)_2Pd_2(\mu\text{-}H)\ (\mu\text{-}CO)]^+$ (**4**) all formed in situ and were identified as species resulting from FA decomposition.



KEYWORDS: *hydrogenation, palladium compounds, levulinic acid, γ-valerolactone, formic acid dehydrogenation*

INTRODUCTION

The continuing increase in demand for energy derived from fossil fuels has led to the search for alternative sustainable energy sources such as biomass. The conversion of biomass into useful chemicals represents a major challenge. The hydrogenation of levulinic acid to γ-valerolactone (GVL) is an important step in the transformation of biomass into biofuels.[1] GVL can be employed as a liquid fuel, food additive, or solvent.[2]

Currently, there are several methodologies for the hydrogenation of LA using homogeneous catalysts,[3] but to the best of our knowledge, palladium compounds are not included. In contrast, there are a great number of heterogeneous catalysts based on palladium. These catalysts are less active than ruthenium-supported catalysts.[4] Palladium heterogeneous catalysts such as Pd/C that have been used in LA hydrogenation under harsh reaction conditions (at 265 °C for 50 h)[5] produced low yields of GVL,[6] and they have been used in organic solvents instead of water.[7]

Formic acid (FA) can be used as an efficient and reversible storage material for hydrogen under very mild reaction conditions in the presence of suitable catalysts.[8] Decomposition of FA ($HCOOH \rightarrow H_2 + CO_2$) has been extensively studied with both heterogeneous[9] and homogeneous catalysts. The homogeneous catalysts are still the most active, and Ru,[10] Rh,[11] Fe,[12] and Ir[13] compounds are fairly common. FA is commonly used as a source of H_2 in catalytic hydrogenations of alkynes,[14] imines,[15] alcohols,[16] and nitroarenes.[17] Deng et al. first reported the use of FA for LA hydrogenation with Ru catalysts.[18]

Recently, Horváth et al. used Shvo-catalyst hydride ruthenium compounds to transform LA into GVL by transfer hydrogenation with FA.[19] We report the first use of palladium(II) complexes for LA hydrogenation, which resulted in very high activity by catalytic formic acid decomposition under mild conditions. We identified the catalytically active compounds **2** and **3** as species involved in this reaction, whereas **4** from FA dehydration was a catalytically inactive complex.

RESULTS AND DISCUSSION

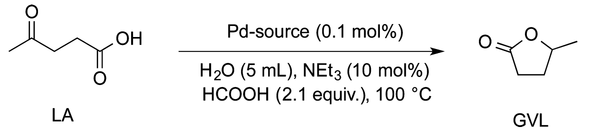
Catalytic Hydrogenation of Levulinic Acid with Palladium Compounds Using FA. Several palladium compounds were used to catalyze the LA by transfer hydrogenation using a slight excess of FA, and the results are shown in Table 1. This reaction occurred homogeneously, as confirmed by the mercury drop test (entries 3 and 9), without loss of activity. In general, compounds with alkyl diphosphines such as dippe (dippe = 1,2-(bis-di-isopropylphosphino)ethane) and dtbpe exhibited the highest activity, while complexes with aryl substituents such as dppe (1,2-bis(diphenylphosphino)ethane) were not active. It is known that [(dppe)$PdCl_2$] readily decomposes in aqueous media.[20]

In some cases, the stability of the different catalytic precursors is related to their resulting activity. Regarding such stability, Zhou reported[21] different Ir compounds with PNP ligands with distinct substituents for the hydrogenation of LA, where the trend of ^{i}Pr > ^{t}Bu > Cy > Ph was observed. The steric effect favors the stability of the catalytic precursors while preventing their decomposition. On the other hand, it has been reported that strong σ-donating ligands promote FA decomposition.[22]

Received: December 14, 2014
Revised: January 14, 2015
Published: January 20, 2015

DOI: 10.1021/cs5020095
ACS Catal. 2015, 5, 1424–1431

Table 1. LA Hydrogenation Using FA as a Hydrogen source



entry	[cat]	*T* (h)	GVL (%)^{a}	TON	TOF (h^{-1})
1	[(dippe)$PdMe_2$]	5	30	300	60
2	[(dtbpe)$PdMe_2$]	5	100	1000	200
3^{b}	[(dtbpe)$PdMe_2$]	5	100	1000	200
4	[(dtbpe)$PdMe_2$]	1	52	520	520
5	[(dippe)$PdCl_2$]	5	100	1000	200
6	[(dippe)$PdCl_2$]	1	nd	-	-
7	[$(PMe_3)_2PdCl_2$]	5	5	50	10
8	[(dtbpe)$PdCl_2$]	1	100	1000	1000
9^{b}	[(dtbpe)$PdCl_2$]	1	100	1000	1000
10^{c}	[(dippf)$PdCl_2$]	5	28	280	56
11	[(dppe)$PdCl_2$]	5	nd	-	-
12^{d}	[(dtbpe)$PdCl_2$]	1	70	2100	2100
13^{d,e}	[(dtbpe)$PdCl_2$]	1	27	810	810
14^{e}	[(dtbpe)$PdCl_2$]	1	100	1000	1000
15^{f}	[(dtbpe)$PdCl_2$]	1	5	50	50
16^{f}	[(dtbpe)Pd(H)Cl]	1	65	650	650
17^{g}	[(dtbpe)$PdCl_2$]	1	100	1000	1000
18^{h}	[(dtbpe)$PdCl_2$]	5	98	980	196

[a] All yields were determined by GC-MS. [b] Hg drop test (0.34 mmol). [c] Without solvent. [d] With 0.03 mol % of **1**. [e] Loaded in air atmosphere. [f] Without NEt_3. [g] With 1 equiv of FA and 33 mol % of NEt_3. [h] At 80 °C. nd: not detected.

The compound [(dtbpe)$PdCl_2$] (**1**) was synthesized according to the methodology described by Yamamoto et al.[23] However, the crystal structure of compound **1** has not been reported previously. Yellow crystals suitable for X-ray studies were obtained by slow evaporation of a THF/CD_2Cl_2 solution, and the corresponding ORTEP representation is depicted in Figure 1. The compound **1** used in this study shows the highest activity for the current reaction. However, when chlorines are replaced by CH_3− in [(dtbpe)$PdCl_2$] (**1**) (entries 1−4), the decomposition of methyl complexes by reductive elimination to yield Pd(0) and ethane[24] led to lower activity. In addition to the different complexes shown in Table 1, Pd, Ni, Pt, and Ru catalyst sources were also used (see Supporting Information), but these compounds were not active.

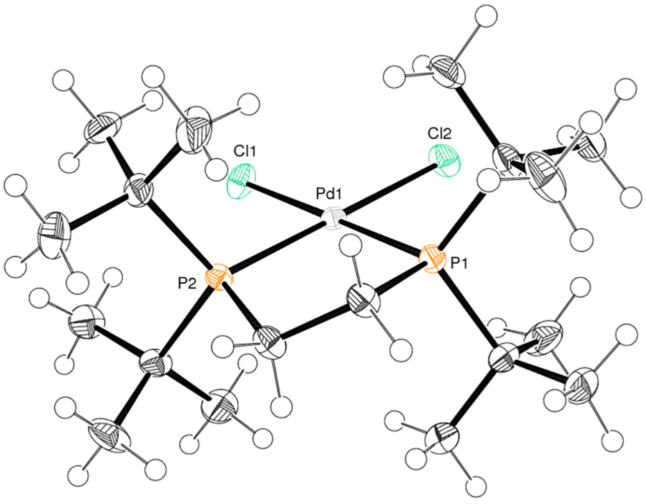


Figure 1. ORTEP diagram for [(dtbpe)$PdCl_2$] **1** (thermal ellipsoids are drawn at 50% probability) used as catalyst precursor. Selected distances (Å) and angles (deg): Pd(1)−P(1) = 2.2717(8), Pd(1)−P(2) = 2.2687(8), Pd(1)−Cl(1) = 2.3689(8), Pd(1)−Cl(2) = 2.3516(8), P(2)−Pd(1)−P(1) = 89.37(3), P(1)−Pd(1)−Cl(2) = 89.72(3), P(2)−Pd(1)−Cl(2) = 178.77(3), P(1)−Pd(1)−Cl(1) = 179.60(3), Cl(2)−Pd(1)−Cl(1) = 90.30(3).

Notably, when the reaction was loaded under an uncontrolled atmosphere, catalyst decomposition was observed. In fact, the LA conversion to produce GVL exhibited a TON of 810 compared to 2100 when the reaction was loaded under inert atmosphere with 0.03 mol % of **1** (entries 12 and 13). Additionally, the compounds **1** and [(dtbpe)Pd(H)Cl)] (**2**) were used for the LA hydrogenation without NEt_3 (entries 15 and 16). Only compound **2** was catalytically active in the reaction, which suggests that the chlorine removal by the base is an important step to generate the active catalytic species. The catalytic reaction was successful with the use of 1 equiv of FA (entry 17), but it needed a higher amount of NEt_3, because the base accelerates the FA decomposition.

The FA decomposition with Pd complexes also depended on the presence of water. When the reaction was carried out without water or nonaqueous solvents such as 1,4-dioxane or THF, the hydrogenation process was inhibited (Table 2), indicating that the use of nonaqueous solvents favors the formation and stabilization of compound [$(dtbpe)_2Pd_2(\mu\text{-}H)(\mu\text{-}CO)]^+$ (**4**), which does not promote the FA decomposition. The highest FA decomposition occurred in aqueous media. Although the precatalyst **1** is poorly soluble in water at room temperature, the reaction mixture dissolved immediately when heated.

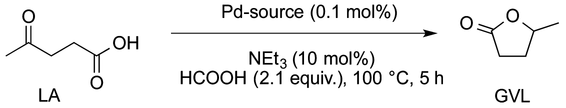
Detection of Intermediates. A reaction among complex **1**, NEt_3, and FA in water as the solvent was carried out with the aim of identifying the intermediates generated during the FA decomposition (Scheme 1). [(dtbpe)PdH(Cl)] (**2**) was identified as the main product. Compound **2** was also prepared by an alternative synthesis.[25]

The reaction between compound **2** and FA is represented in Scheme 2, which promptly produced H_2 and a mixture of complexes **1** and **2b′** at room temperature. The ^{1}H NMR spectrum for complex **2b′** showed a broad singlet at 8.44 ppm assigned to the formate CH moiety, whereas in $^{31}P\{^{1}H\}$, a broad singlet was observed at 48.8 ppm. The formation of palladium diformate has been proposed previously in FA decomposition. However, palladium diformates have not been isolated.[26] When the reaction was heated to 100 °C and maintained for 1 h, the amount of H_2 increased. The formation of compound **4** and CO_2 was observed after 2 h, along with the total consumption of FA. Clearly, the formation of compound **4** is favorable in the absence of water. In spite of longer heating, no change in composition was detected.

Using a similar mixture of **2**, **4**, and **3** in Tol-d_8, as depicted in Scheme 1, the formation of GVL was observed until the mixture was heated to 80 °C after 1 h (Figure 2). Compounds **2** and **3** disappeared, and the amount of LA decreased, but **4** prevailed in solution. Although the solution was heated for a longer time, its composition did not change. The full transformation of LA was not completed since it was in excess, and the catalyst decomposed to **4**.

Complex **3** is a rare example of a binuclear trihydride palladium complex that could be structurally characterized by the addition of NBu_4PF_6 and slow evaporation of an acetone/THF solution to yield suitable crystals for a single-crystal X-ray

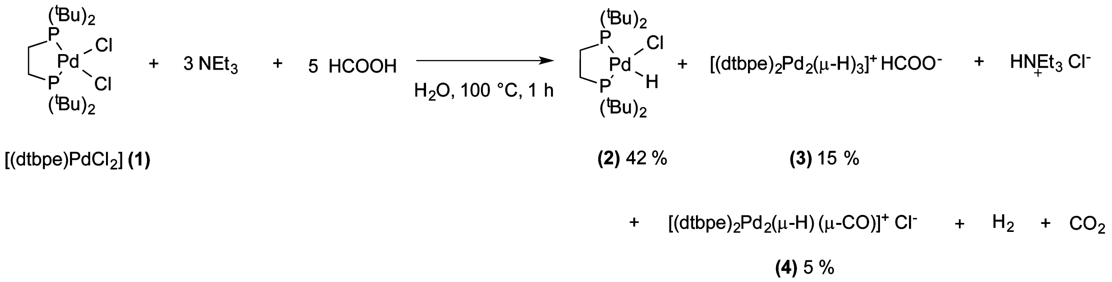
Table 2. Solvent Effect in Levulinic Acid Hydrogenation with FA



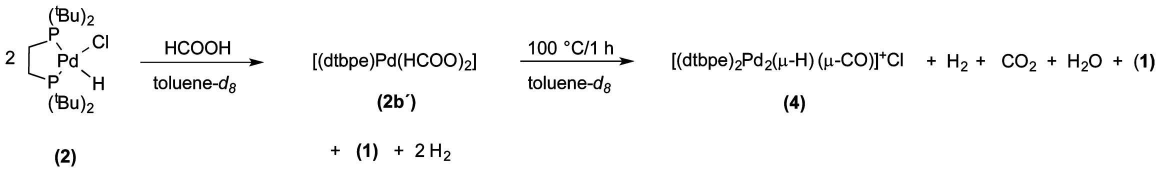
entry	Pd source	solvent	GVL (%)[a]	TON	TOF (h^{-1})
1	[(dippe)$PdCl_2$]	none	5	50	10
2	[(dippe)$PdMe_2$]	none	nd	-	-
3	[(dippf)$PdCl_2$]	none	28	280	56
4	[(dtbpe)$PdCl_2$]	none	77	770	154
5	[(dippe)$PdCl_2$]	1,4-dioxane	9	90	18
6	[(dtbpe)$PdCl_2$]	H_2O	100	1000	200
7	[(dtbpe)$PdCl_2$]	THF	3	30	6

[a] All yields were determined by GC-MS. nd: not detected.

Scheme 1. Reactivity of [(dtbpe)$PdCl_2$] in the FA/NEt_3 System



Scheme 2. Reactivity of 2 with FA



determination of the anion exchanged product **3a** (Figure 3). The ^{1}H NMR spectrum for complex **3** showed key resonances such as one quintet at −6.6 ppm with $^{2}J_{H-P} = 54$ Hz, whereas in $^{31}P\{^{1}H\}$, **3** was observed as a singlet at 108.42 ppm to four equivalent phosphorus atoms. These NMR data in solution suggest only one type of hydride, consistent with the crystal structure determined for complex **3a**. There are three bridging hydrides, and the following distances show a highlighted asymmetry: Pd(2a)−H(01) = 1.60 Å, Pd(1a)−H(03) = 1.79 Å, Pd(2a)−H(03) = 1.96 Å. Closely related trihydride complexes of Pt[25] and Ni[27] have been reported, showing a quick scrambling of hydrides in solution.

Compound **4** (Figure 4) turned out to be an inactive complex for LA hydrogenation. A proposal for its formation is depicted in Figure 5, which probably occurs via the reaction of a hydride and carbonyl. The carbonyl is a byproduct of the FA dehydration (HCOOH → H_2O + CO), a reaction that has been reported with palladium.[28] The preparation of this kind of Pd(I) compound obtained via the reduction of Pd(II) complexes with methanol was first reported by Milstein et al.[29] Recently, several closely related compounds similar to **4** have been reported.[30] Amber-colored crystals suitable for X-ray diffraction analysis of **4a** were isolated after slow evaporation of an acetone/THF solution upon anion exchange with PF_6NBu_4.

On the basis of these experimental results and considering previously reported experimental and computational data,[12b,25,31] a proposal for a catalytic cycle is represented in Figure 5. Compound **2** was initially formed, accompanied by the subsequent production of triethylamine chlorhydrate and **2a**. Without NEt_3 (Table 1, entry 15), only 5% of the LA was transformed, indicating that NEt_3 is necessary to remove chlorides. It has been reported that the catalytic conversion of FA in the absence of tertiary amines is extremely slow.[12c]

The addition of formate ion to compound **2a** may generate a hydride-metal formate of palladium (**2b**), which plays a key role in the catalytic cycle.[31b] Even when **2b** and **2c** were not observed by NMR, which was probably due to a fast *β*-H elimination to yield CO_2 and dihydride **2c**, the LA hydrogenation to 4-HVA (4-hydroxyvaleric acid) and its cyclization was still efficiently achieved. The reaction between complexes **2** and the dihydride **2c** can produce the compound **3**, a reaction that has been described for platinum.[25] The inactive complex **4** can be produced by a reaction between **2a′** and carbonyl compound **2f**.[32]

As shown in Figure 6, the catalyst was successfully recycled. After each reaction of LA hydrogenation, small amounts of compound **1**, NEt_3HCl, and compound **4** were usually recovered after all volatiles were removed, and the residue was later used as a catalyst in the next reaction. The slight decrease in activity can be attributed in part to the withdrawal of a small amount of catalyst from the sample being taken to quantify the products, as well as the increasing amount of inactive complex **4**.

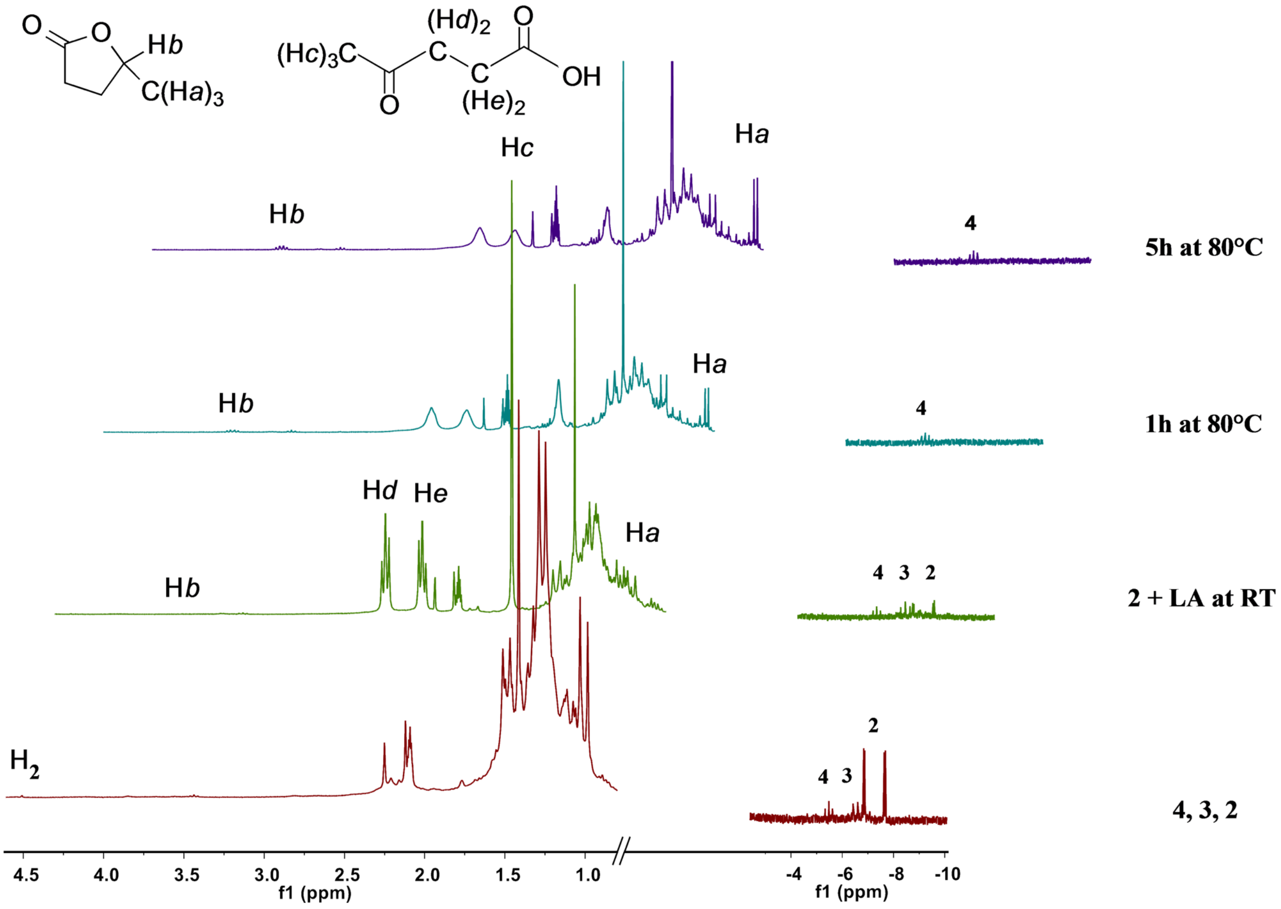


Figure 2. ^{1}H NMR monitoring of compound **2** with LA to GVL in Tol-d_8.

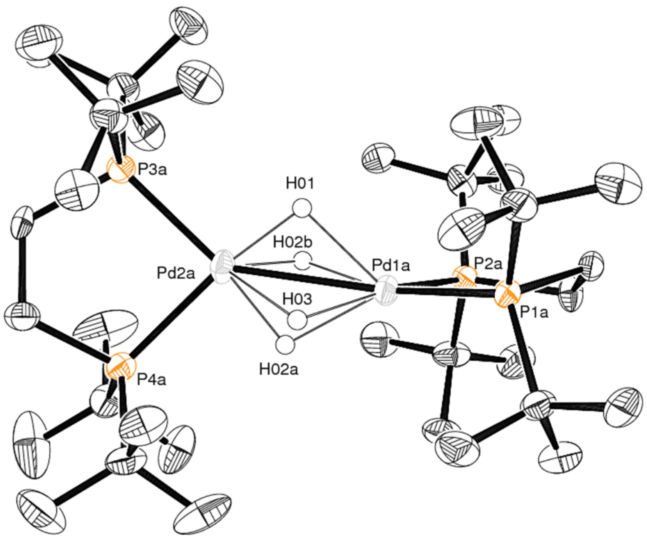


Figure 3. ORTEP diagram for compound **3a** (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms (except hydride ligands) and PF_6^- anion have been omitted for clarity. Selected distances (Å); and angles (deg): Pd(1a)−P(1a) = 2.2690(16), Pd(1a)−P(2a) = 2.3471(17), Pd(1a)−Pd(2a) = 2.6935(7), Pd(1a)−H(03) = 1.79, Pd(1a)−H(02b) = 1.78, Pd(1a)−H(02a) = 1.88, Pd(2a)−P(3a) = 2.2899(17), Pd(2a)−P(4a) = 2.3278(17), Pd(2a)−H(03) = 1.96, Pd(2a)−H(02b) = 1.50, Pd(2a)−H(01) = 1.60, Pd(2a)−H(02a) = 1.62; P(1a)−Pd(1a)−P(2a) = 89.50(6), P(1a)−Pd(1a)−Pd(2a) = 149.47(5), P(2a)−Pd(1a)−Pd(2a) = 119.26(4).

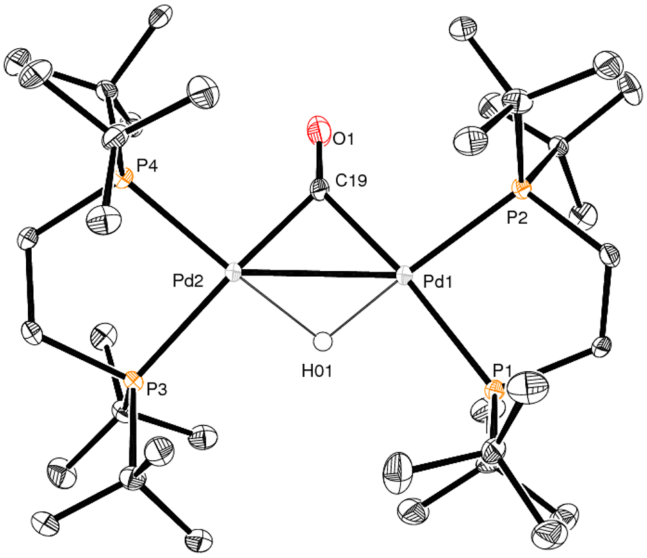


Figure 4. ORTEP diagram for compound **4a** (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms (except hydride ligand) and PF_6^- anion have been omitted for clarity. Selected distances (Å); and angles (deg): Pd(1)−P(2) = 2.3698(14), Pd(1)−P(1) = 2.3885(14), Pd(1)−Pd(2) = 2.7810(5), Pd(1)−H(01) = 1.75(6), Pd(2)−P(4) = 2.3680(14), Pd(2)−P(3) = 2.4102(13), Pd(2)−H(01) = 1.89(7), C(19)−O(1) = 1.149(6), C(19)−Pd(2) = 2.021(5), C(19)−Pd(1) = 2.032(5); Pd(2)−C(19)−Pd(1) = 86.6(2), C(19)−Pd(1)−P(1) = 173.36(15), P(1)−Pd(1)−Pd(2) = 127.90(4), Pd(2)−Pd(1)−H(01) = 42(2), P(4)−Pd(2)−H(01) = 177(2).

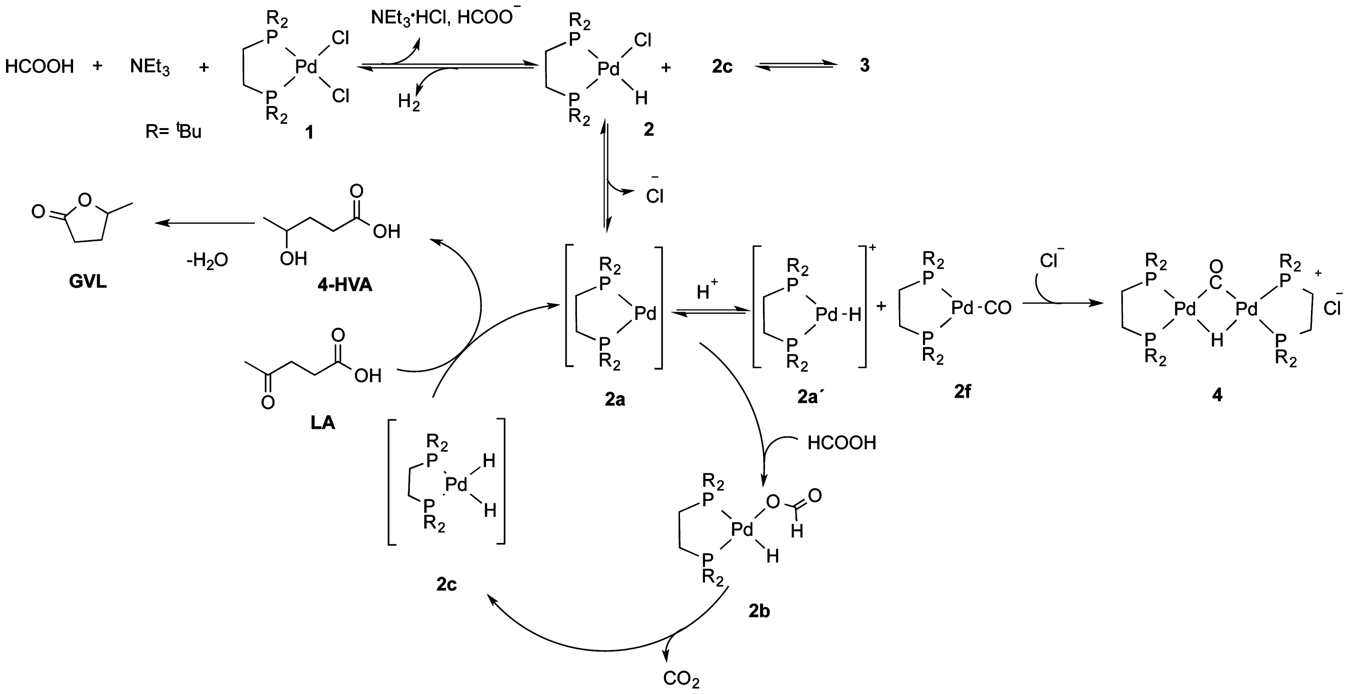


Figure 5. Mechanistic proposal for LA hydrogenation with formic acid.

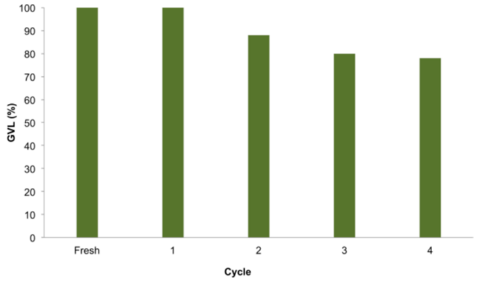
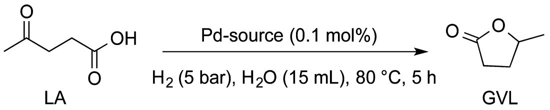


Figure 6. Catalyst recycling [(dtbpe)PdCl$_2$] study in the hydrogenation of levulinic acid into GVL.

Table 3. Hydrogenation of LA with Palladium Compounds Using Hydrogen Pressure



entry	Pd source	GVL (%)[a]	TON	TOF (h^{-1})
1	[(dippe)PdCl$_2$]	72	720	144
2	[(dtbpe)PdCl$_2$]	100	1000	200
3[b]	[(dtbpe)PdCl$_2$]	30	1500	300
4	[(dcype)PdCl$_2$]	34	340	68
5	[(dppe)PdCl$_2$]	9	90	18
6	[(dippf)PdCl$_2$]	22	220	44
7	{[(O^{i}Pr)$_3$P]$_2$PdCl$_2$]}	11	110	22
8	[(dippe)PdMe$_2$]	27	270	54
9	[(dtbpe)PdMe$_2$]	100	1000	200
10	[(dppdtbpf)PdCl$_2$]	7	70	14
11	[(PEt$_3$)$_2$PdMe$_2$]	3	30	6

[a] All yields were determined by GC-MS. [b] With 0.02 mol % of [(dtbpe)PdCl$_2$].

Catalytic Hydrogenation of Levulinic Acid with Palladium Compounds Using H$_2$. LA hydrogenation produced GVL as a single product using relatively low hydrogen pressure at 80 °C for 5 h (Table 3). A series of palladium complexes with diphosphine ligands was active. In the case of [(dtbpe)PdCl$_2$], the best catalytic activity was obtained. A trend in the activity similar to the formic acid reducing system is highlighted. Complexes with electron-donating and voluminous ligands exhibited a higher rate of activity. Notably, LA hydrogenation using hydrogen pressure was more efficient (TON 1500) versus the formic acid reducing system (TON 980) at 80 °C.

CONCLUSIONS

LA hydrogenation using palladium complexes as catalysts was achieved by transfer hydrogenation with formic acid under mild conditions, where complex **1** had the highest rate of activity. Also, it was possible to identify the compounds **3** and **4** from FA decomposition, and the formation of **4**, a catalytically inactive complex in LA hydrogenation, reduced the efficiency of the process. When hydrogen pressure was used, the reaction was catalyzed under milder conditions and with higher efficiency by palladium compounds, avoiding CO formation to produce **4**.

EXPERIMENTAL SECTION

General Considerations. Unless stated otherwise, all processes were performed using an MBraun glovebox (<1 ppm of H$_2$O and O$_2$). Levulinic acid (98% purity), triethylamine (purity ≥99.5%), FA (reagent grade ≥95%), dppdtbpf (1-diphenylphosphino-1′(di-*tert*-butylphosphino)ferrocene), triisopropyl phosphite 95%, dippf (1,1′-bis(diisopropyl)-ferrocene) 97%, and tetrabutylammonium hexafluorophosphate 98% were purchased from Sigma-Aldrich and deoxygenated. All water used was distilled and deoxygenated under argon flow. Ultrahigh-purity hydrogen (5.0, Praxair) was used. THF-d_8, toluene-d_8, CDCl$_3$, and methylene chloride-d_2 for NMR experiments were purchased from Sigma-Aldrich and stored over 3 Å molecular sieves in a glovebox. The bisphosphine ligands dippe (1,2-bis(diisopropylphosphino)ethane),[33] dtbpe (1,2-(bis-di-*tert*-butylphospino)ethane),[34] [(COD)$PdCl_2$],[35] [(dippe)$PdMe_2$], [(dtbpe)$PdMe_2$],[36] [(dippe)$PdCl_2$], [$(PMe_3)_2PdCl_2$], [(dtbpe)$PdCl_2$], [(dcype)$PdCl_2$], [(dppe)$PdCl_2$], [(dippf)$PdCl_2$], [$((O^iPr)_3P)_2PdCl_2$], and [(dppdtbpf)$PdCl_2$][23] were prepared as described in the literature.

Hydrogenation of LA with FA Using Pd Complexes. In a typical experiment, a 25 mL Schlenk flask equipped with a Rotaflo valve and a magnetic stirring bar was loaded with 0.4 g (3.37 mmol) of LA, 1.7 mg (0.03 mmol) of [Pd(dtbpe)Cl_2], and 5 mL of distilled water. Then, 350 mg (7.22 mmol) of FA and 35 mg (0.3 mmol) of NEt_3 were added. The reactor was heated to 100 °C, which was maintained for 1 h. CO_2 was detected and identified by $^{13}C\{^1H\}$ NMR when the vessel was opened, then the pH was determined between 3 and 4. The reaction mixture was extracted with 5 × 20 mL of ethyl acetate, and the solvent was removed by vacuum.

H_2 and CO_2 Detection from Hydrogenation of LA with FA Using Pd Complexes. At the end of a typical experiment of LA hydrogenation, the mixture of gases from the reaction was bubbled into a cooled NMR tube (WILMAD NMR tube equipped with J. Young valve) that contained $CDCl_3$, and then was analyzed by NMR.

Hg (0) Poisoning Test. Homogeneity tests were performed following the described procedures. In addition to the reactants, two mercury drops were added to the mixture. After reaction completion, the solution was filtered and analyzed by GC-MS.

Reaction of [(dtbpe)$PdCl_2$] with FA and NEt_3. A 25 mL Schlenk flask equipped with a Rotaflo valve and a magnetic stirrer was charged with an aqueous solution (3 mL) of [(dtbpe)$PdCl_2$] (60 mg, 0.12 mmol) and HCOOH (29.3 mg, 0.6 mmol), and after that, triethylamine was added (36.7 mg, 0.36 mmol). The mixture was stirred for 1 h at 100 °C in an oil bath. Afterward, the heating was stopped, and a green solution was obtained. Also, the solvent and other volatile products were removed under reduced pressure. The green-brownish solid was dissolved in THF, a white-yellowish solid was precipitated ($HNEt_3^+Cl^-$ and **1**), the solution was filtrated through a sintered glass filter and washed with THF to obtain a dark green solution, and then the solvent was evaporated under reduced pressure. The green solid was dissolved in toluene, forming a purple solution and an orange-brownish solid (compound **3**). The solution was again filtrated through a sintered glass filter and washed with toluene, producing a dark red solution. Finally, the solvent was evaporated in vacuo and dried for 5 h. Selected spectroscopic data: [(dtbpe)Pd(H)Cl] (**2**): Yield 45%. ^1H NMR (300 MHz, 25 °C, toluene-d_8,): δ, 1.48 (d, $^2J_{H-P}$ = 12.6 Hz, 4H, ($\mathbf{CH_2}$)), 1.25 (d, $^2J_{H-P}$ = 12.6 Hz, 36H, C($\mathbf{CH_3}$)$_3$), −7.68 (dd, $^2J_{\text{H-Ptrans}}$ = 228, $^2J_{\text{H-Pcis}}$ = 13.5 Hz, 1H, Pd-**H**). ^{31}P NMR (121 MHz, 25 °C, toluene-d_8): δ, (d, 109.95 $^2J_{PP}$ = 12 Hz).

*[(dtbpe)$_2$Pd$_2$(μ-H)$_3$]$^+$ (HCOO)$^-$***(3)**. Yield 15%. Anal. Calcd for (**3**) $C_{37}H_{84}O_2Pd_2P_4$: C, 49.50; H, 9.43. Found: C, 48.37; H, 8.66. ^1H NMR (300 MHz, 25 °C, THF-d_8): δ, 8.5 (s, 1H, **H**COO), 2.1 (d, $^2J_{H-P}$ = 12 Hz, 8H, -$\mathbf{CH_2}$-), 1.3 (d, $^2J_{H-P}$ = 15 Hz, 72H, -$\mathbf{CH_3}$-), −6.6 (quin, $^2J_{H-P}$ = 54 Hz, 3H, Pd-**H**). $^{31}P\{^1H\}$ NMR (121 MHz, 25 °C, THF-d_8): δ, 108.42, (br, s). The FAB$^+$ spectrum was produced using 3-nitrobenzyl alcohol (m-NBA) as the matrix, $[M - (-H_2) - Cl]^+$ at *m*/*z* 851. Elemental analyses out of range were probably due to the presence of small amounts of **1**.

[(dtbpe)$_2$Pd$_2$(μ-H) (μ-CO)]$^+$Cl **(4)**. Yield 5%. Anal. Calcd for (**4**): $C_{37}H_{81}OPd_2P_4Cl$: C, 48.61; H, 8.93; Cl, 3.88. Found: C, 48.03; H, 8.54. ^1H NMR (300 MHz, 25 °C, THF-d_8): δ, 0.98 (d, $^2J_{H-P}$ = 15 Hz, 72H, -$\mathbf{CH_3}$-)-5.45 (quin, $^2J_{H-P}$ = 42 Hz, 1H, Pd-**H**). $^{31}P\{^1H\}$ NMR (121 MHz, 25 °C, THF-d_8): δ, s, 75.66. The FAB+ spectrum was produced using 3-nitrobenzyl alcohol (m-NBA) as the matrix, $[M + H - Cl]^+$ at *m*/*z* 879. IR (ATR, solid) 1801 cm^{-1} (ν C=O). Elemental analyses out of range were probably due to the presence of minute amounts of **1**.

[(dtbpe)$_2$Pd$_2$(μ-D) (μ-CO)]$^+$Cl ***(4d)***. $^{31}P\{^1H\}$ NMR (121 MHz, 25 °C, THF-d_8): δ, 76.30 (1:1:1) $^2J_{\text{D-P}}$ = 6.5 Hz.

Hydrogenation of LA with Molecular Hydrogen Using [(dtbpe)$PdCl_2$]. Catalytic tests were carried out in 100 mL stainless steel Parr autoclaves. In a typical experiment, the reactor was loaded with 0.4 g (3.37 mmol) of LA, 1.7 mg (0.0033 mmol) of [(dtbpe)$PdCl_2$], and 15 mL of distilled water. After that, it was pressurized with 5 bar of H_2 at room temperature and heated at 80 °C for 5 h. The reaction mixture was extracted with 5 × 20 mL of ethyl acetate and the solvent was removed by vacuum

Catalyst Recycling Experiments. Catalyst recycling was done on a prepared sample as follows: 1.67 mg of [(dtbpe)$PdCl_2$], 0.4 g (3.37 mmol) of LA, and 5 mL of distilled water were charged in an autoclave, then 350 mg (7.22 mmol) of FA was added followed by 35 mg (0.3 mmol) of NEt_3. Finally, the components were stirred at room temperature in a vessel for a few minutes and heated at 100 °C for 1 h. The LA was converted into GVL quantitatively, as determined by GC-MS. Then, all volatiles were removed, and the residue containing the regenerated compound **1** was later used as a catalyst in the next reaction using the same reagents.

Conversion and selectivity of the catalytic reactions were determined via GC-MS analyses performed on an Agilent 5975C system equipped with a 30m DB-5MS capillary (0.32 mm ID) column. Mass spectrometry (MS-FAB+) was performed by USAI-UNAM using a Thermo-Electron DFS. ^1H, $^{13}C\{^1H\}$. $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature on a 300 MHz Varian Unity spectrometer in toluene-d_8, THF-d_8, or CD_2Cl_2, unless otherwise stated. ^1H and $^{13}C\{^1H\}$ chemical shifts (δ, ppm) are reported relative to the residual proton resonance in the corresponding deuterated solvent. $^{31}P\{^1H\}$ NMR spectra were referenced to an external 85% H_3PO_4 solution. All air-sensitive NMR samples in this work were handled under an inert atmosphere using thin-wall (0.38 mm) WILMAD NMR tubes equipped with J. Young valves. The IR spectra were determined on an FTIR/FIR spectrum 400 PerkinElmer 1600 series. Elemental analyses were carried out on a PerkinElmer 2400 CHNS Elemental Analyzer.

X-ray Structure Determination. Crystals in the form of pale yellow prisms (**1**), colorless plates (**3a**), and brown plates (**4a**) were mounted under LVAC FOMBLIN Y on glass fiber and immediately placed under a cold nitrogen stream on an Oxford Diffraction Gemini "A" Diffractometer with a CCD area detector, a sealed tube X-ray radiation source with λ Mo Kα = 0.71073 Å, and a graphite monochromator at 130 K. Unit cell constants were determined with a set of 15/3 narrow frame/runs (1° in ω) scans. Data sets consisted of 183, 335, and 202 frames of intensity data collected with a frame width of 1° in ω for **1**, **3a**, and **4a**, respectively, and a crystal-to-detector distance of 55.00 mm.

The collected frames were integrated using an orientation matrix determined from the narrow frame scans. CrysAlisPro and CrysAlis RED software packages[37] were used for data collection and data integration. Analysis of the integrated data did not reveal any decay. Final cell constants were determined by global refinement of the 3895 ($\theta < 26°$), 7578 ($\theta < 29.5°$), and 4284 ($\theta < 29.3°$) reflections for **1**, **3a**, and **4a** respectively. Collected data were corrected for absorbance using analytical numeric absorption correction[38] with a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections.

Structure solution and refinement were carried out with SHELX-2013[39] and SHELXL-2013 software, and ORTEP-3 for Windows[40] was used for molecular graphics. WinGX[41] software was used to prepare material for publication. Full-matrix least-squares refinement was carried out by minimizing $(Fo^2 - Fc^2)^2$. All non-hydrogen atoms were refined anisotropically. H atoms attached to Pd atoms were located in a difference map and fixed to positions for geometry of metal centers, finally were refined isotropically with U_{iso} (H) = 1.5 Ueq for (Pd). H atoms attached to C atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C−H = 0.98−0.99 Å and U_{iso} (H) = $1.5U_{eq}$ (C), or 1.2 U_{eq} (C) for methylene and methyl groups.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The following files are available free of charge on the ACS Publications website at DOI: 10.1021/cs5020095.

Supplementary data including the results of hydrogenation, NMR spectra, and crystal data (PDF)

Crystallographic information for selected compounds (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank CONACYT 0178265 and DGAPA-UNAM (IN-201010) for their financial support for this work. C.O.-C. also thanks CONACYT for a graduate studies grant. We also thank Dr. Alma Arévalo for technical assistance. We dedicate this contribution to the memory of Prof. Armando Cabrera (1944-2014).

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