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Layered Double Hydroxide Supported Nanoplatinum and Nanopalladium Catalyzed Allylation of Aldehydes: A Mechanistic Study

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Abstract: Layered double hydroxide (LDH)-supported nanoplatinum(0) and nanopalladium(0) catalysts were prepared by a simple ion exchange technique and subsequent reduction with hydrazine hydrate and used for the allylation of aldehydes to give moderate to good yields of homoallylic alcohols. Detailed mechanistic studies of LDH-Pd(0)-catalyzed allylation using XPS and TGA-MS reveal that a monoallyl-palladium complex is the key intermediate for the catalytic cycle.

Keywords: aldehydes; allylation; heterogeneous catalysis; monoallyl-palladium complex; nanoplatinum

Introduction

Homoallylic alcohols are versatile intermediates in the preparation of materials, natural products, and bioactive compounds. Palladium[1] and platinum[2] catalyzed allylation of aldehydes to homoallylic alcohols is a reliable and widely used methodology in modern organic synthesis. Allylation of aldehydes by homogeneous catalysis using palladium or platinum complexes[1,2] offers good to excellent yields of homoallylic alcohols but the non-recoverable expensive palladium or platinum metal restricts its use in industry. It is highly desirable to develop a new recoverable and reusable catalytic system with similar or better activity than the homogeneous system. The chemical industry has often favored heterogeneous catalysis, but the development of better catalysts has been hindered by the presence of numerous kinds of active sites and also by the low concentration of active sites. But recent developments in nanotechnology, mainly nanoparticles stabilized by solid supports,[3] have widen the scope of heterogeneous catalysts. Recently Cai et al.[3b] reported the allylation of aldehydes catalyzed by a silica-supported palladium(0) complex, but to our knowledge there is no report on the allylation of aldehydes catalyzed by a heterogeneous platinum(0) catalyst. Earlier[3a] a nanopalladium catalyst was prepared and evaluated for C–C bond forming reactions and later mechanistic studies were performed by isolating surface transient organometallic intermediates.[4] Herein we report the efficacy of layered double hydroxides (LDHs)-supported nanoplatinum and nanopalladium catalysts in the allylation reaction of aldehydes using allyl bromide, allyl alcohol and allyltributylstanne as allylating agents. Mechanistic studies were also undertaken in this work. This is the first example of a heterogeneous nanoplatinum-catalyzed allylation of aldehydes by allyltributylstanne.

Results and Discussion

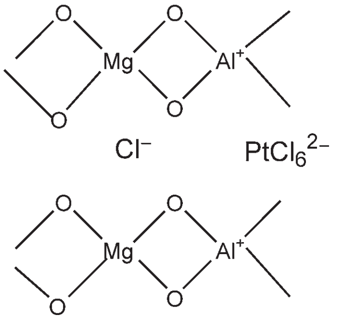
Preparation of LDH-Pt(0) and LDH-Pd(0)

LDHs have recently received much attention in view of their potential usefulness as materials, anion exchangers and more importantly as catalysts.[5a–e] The LDH consists of alternating cationic $M(II)_{1-x}M(III)_x(OH)_2{}^{x+}$ and anionic $A^{n-} \cdot z\,H_2O$ layers.[5f] The positively charged layers contain edge-shared metal M(II) and M(III) hydroxide octahedra, with charges neutralized by A^{n-} anions located in the interlayer spacing or at the edge of the lamellae. Small hexagonal LDH crystals with $Mg_{1-x}Al_x(OH)_2(Cl)_x \cdot z\,H_2O$ composition were synthesized following the existing procedures (here $x = 0.25$).[5g] Hexachloroplatinate was exchanged onto chloride-saturated LDH to obtain a light yellow-colored LDH-Pt(IV) and then reduced with hydrazine hydrate

$$\text{LDH-Cl} \xrightarrow{K_2PtCl_6} \text{LDH-}PtCl_6 \xrightarrow{N_2H_4 \cdot H_2O} \text{LDH-Pt(0)}$$

$$\text{LDH-Cl} \xrightarrow{Na_2PdCl_4} \text{LDH-}PdCl_4 \xrightarrow{N_2H_4 \cdot H_2O} \text{LDH-Pd(0)}$$

Scheme 1. Preparation of LDH-Pt and LDH-Pd catalysts.



Scheme 2. The structure of LDH-$PtCl_6$.

to give the air-stable, black-colored LDH-Pt(0) catalyst. The LDH-Pd(0) catalyst was prepared according to the earlier report[3a] and was well characterized. Scheme 1 represents the synthesis of LDH-Pt and LDH-Pd catalysts. The possible structures for the catalysts are depicted in Scheme 2.

Characterization of the LDH-Pt(0) Catalyst

All the catalysts developed were well characterized by XRD, XPS, SEM-EDX and TEM. XRD patterns of the initial LDH and LDH-Pt(0) hardly differ in the range $2\theta = 3-65°$. The observed d_{003} basal spacing of the support that appeared at 7.8 Å remains unchanged after the anion exchange and subsequent reduction, which indicates that the $PtCl_6^{2-}$ and Pt(0) nanoparticles are mainly located at the edge-on surface in the respective samples. An XPS investigation of LDH-Pt(0) at Pt 4f level shows a $4f_{7/2}$ line at 72.87 eV and a $4f_{5/2}$ line at 75.19 eV (Fig. 1).[6] The average sizes of the nanoplatinum particles in the fresh and used LDH-Pt(0) were measured from TEM images and found to be in the range of 30–40 nm.

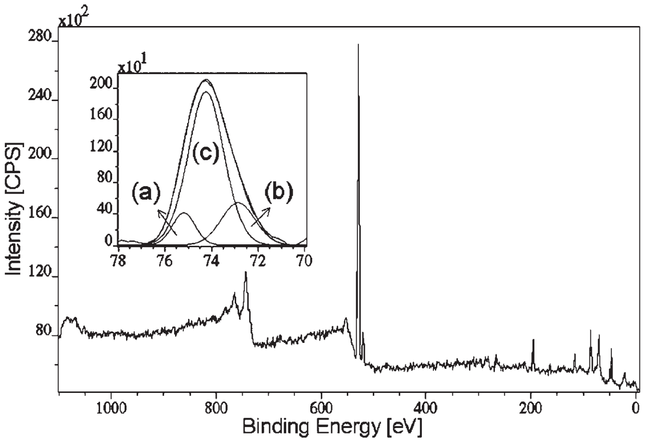
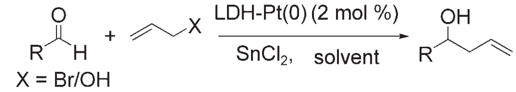


Figure 1. XPS survey scan of LDH-Pt(0). Inset shows the high resolution narrow scan showing peaks of (**a**) Pt $4f_{7/2}$, (**b**) Pt $4f_{5/2}$ and (**c**) Al 2p.

Table 1. Allylation of aldehydes by allyl bromide and allyl alcohol.



Entry	Aldehyde	Isolated yield [%]	
		A	B
1	C_6H_5CHO	88, 85[a]	62, 61[a]
2	*p*-NO_2-C_6H_4CHO	92	74
3	*o*-NO_2-C_6H_4CHO	90	74
4	*p*-MeO-C_6H_4CHO	85	50
5	*c*-C_6H_{11}-CHO	80	48

[A] Aldehyde:allyl bromide:$SnCl_2$ = 1:2:1.5 taken in 2 mL DMF; [B] Aldehyde:allyl alcohol:$SnCl_2$=1:3:3 taken in 2 mL DMI.

[a] Yields after 5th cycle.

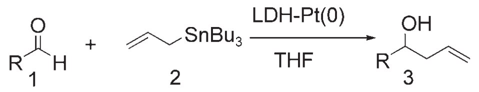
Allylation of Aldehydes with LDH-Pt and LDH-Pd Catalysts

The allylation reaction of aldehydes catalyzed by LDH-Pt(0) (2 mol %) at room temperature using allyl bromide or allyl alcohol as the allylating agent, gave the corresponding homoallylic alcohols in moderate to good yields. The results are summarized in Table 1.

After getting good results with allyl bromide and allyl alcohol, we turned our attention towards allyltributylstanne to extend the scope of our catalytic system. The addition of allyltributylstanne to benzaldehyde proceeded smoothly at room temperature in the presence of LDH-Pt(0) (5 mol %) (Table 2, entry1). Impressed by the result of benzaldehyde allylation, we examined the allylation of various aldehydes with allyltributylstanne using LDH-Pt and LDH-Pd catalysts (Table 2).

As per expectation, aldehydes with electron-donating group gave lower yields of product whereas the presence of electron-withdrawing groups produced better yields.

Table 2. Allylation of aldehydes with allyltributylstanne using LDH-Pt(0).



Entry	Aldehyde	Isolated yield [%]	
		Reflux[a]	RT[b]
1	C_6H_5CHO	83,82[c],82[d]	75
2	*p*-Br-C_6H_4CHO	85,85[d]	78
3	*p*-Cl-C_6H_4CHO	84	75
4	*o*-NO_2-C_6H_4CHO	90	85
5	*p*-NO_2-C_6H_4CHO	90,88[c],87[d]	85
6	*p*-MeO-C_6H_4CHO	65	60[e]
7	*c*-$C_6H_{11}CHO$	60	55[e]
8	C_6H_4-$(CH_2)_2$-CHO	72	60[e]
9	*trans*-Cinnamaldehyde	74	62[e]

Reaction conditions: aldehyde (1 mmol), allyltributylstanne (1.2 mmol), THF (3 mL), LDH-Pt(0) (5 mol %).

[a] Reaction time 9 h.

[b] Reaction time 48 h.

[c] Yield after 5th cycle.

[d] LDH-Pd(0) (5 mol %).

[e] LDH-Pt(0) (10 mol %).

Aromatic α,β-unsaturated and aliphatic aldehydes also underwent the allylation reaction in the presence of LDH-Pt(0) (10 mol %) at room temperature and with 5 mol % catalysts at reflux temperature in THF. THF is found to be the best solvent for this reaction among the solvents studied.[7] The use of LDH-Pd(0) (5 mol %) gave an almost similar chemical yield (Table2, entries 1,2,5) but LDH-$PtCl_6$, LDH-$PdCl_4$, K_2PtCl_6 and Na_2PdCl_4 gave lower yields (Table 3).

Here we observed that LDH-Pt(0) or LDH-Pd(0) gave better yields than the Pt(IV) or Pd(II) precursor, which is completely different in the case of homogeneous catalysis.[2b] Pd(dba), dppe or Pd $(PPh_3)_4$ gave poor yields when compared to $PdCl_2(PPh_3)_2$ or the $PdCl_2$(dppf) complex. These results suggest that here in heterogeneous catalysis some different kind of mechanism is operative. Among the catalysts screened, LDH-Pt(0) is found to be the best.

Table 3. Comparison of activity of different catalysts in the allylation of benzaldehyde.[a]

Entry	Catalyst	Isolated yield [%]
1	LDH-Pt(0)	83, 75[b]
2	LDH-Pd(0)	82, 72[b]
3	LDH-$PtCl_6$	62
4	LDH-$PdCl_4$	60
5	K_2PtCl_6	45
6	Na_2PdCl_4	40

[a] Benzaldehyde (1 mmol), allyltributylstanne (1.2 mmol) THF (3 mL) refluxed under nitrogen for 9 h.

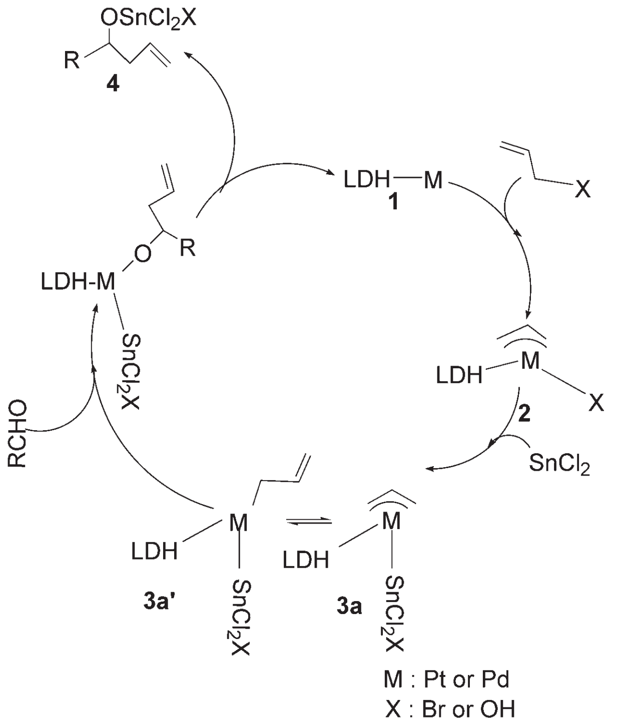
[b] Reaction conducted at room temperature for 48 h.

Reaction Mechanism

In order to clarify the mechanism of the allylation reaction catalyzed by LDH-Pt(0) and LDH-Pd(0), we first investigated the role of tin species in the allylation of aldehydes. We performed allylation of aldehydes with allyl alcohol and allyl bromide in the presence of excess amount of stannous chloride and, as expected, the yields were good (Table 1). But when the same reactions were performed under identical conditions excluding the stannous chloride, no product formation was observed. So we thought that the stannous chloride is necessary to facilitate the allylation of aldehyde to give the corresponding homoallylic alcohol. The plausible mechanism is shown in Scheme 3.

To validate this mechanistic cycle we tried to trap the intermediate **2** or **3**, but our attempts have failed. Then, instead of using stannous chloride, we have taken an organotin reagent, namely allyltributylstanne, and treated it with LDH-Pd(0). Here we chose LDH-Pd(0) instead of LDH-Pt(0) because in XPS the Pt signal was overlapped by an Al signal.

A mixture of LDH-Pd(0) and allyltributylstanne was refluxed in THF under argon. Then the solid material was filtered off, washed with THF and vacuum dried to get the surface transient organometallic (STO-1) intermediate. This STO-1 was then subjected to XPS analysis (Fig. 2). A high resolution narrow scan XPS spectra of Pd on deconvolution shows a set of two lines each at 337.02 eV ($3d_{5/2}$) 342.35 eV ($3d_{3/2}$) and 335.10 eV ($3d_{5/2}$) 340.31 eV ($3d_{3/2}$) (Fig.3). The latter set of lines is attributed to unreacted Pd(0). The high resolution narrow scan of STO-1 for Sn shows the $3d_{5/2}$ line at 486.35 eV



Scheme 3. Plausible mechanism for the allylation.

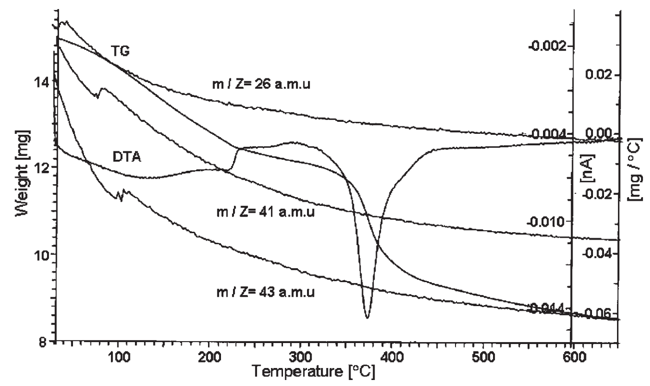


Figure 3. TGA-DTA-MS thermogram of STO-1.

and $3d_{3/2}$ lines at 494.88 eV, which indicate the presence of a Pd–Sn bond[4] (Fig. 2). The deconvoluted C 1 s XPS spectrum of STO-1 displays four lines at 283.70, 284.60, 285.95 and 288.01 eV. Although specific assignment is difficult but we could say that there are four types of carbon bonds most likely to be Pd–C, Sn–C, C–C and a carbon impurity in the LDH-Cl precursor of the LDH-Pd catalyst.[4]

STO-1 was then subjected to TGA-MS (Fig. 3) and the observed *m/z* values of the evolved gas fragments are 26, 41 and 43 a.m.u. corresponding to C_2H_2, C_3H_5 and C_3H_7, respectively (Scheme 4). The *m/z* value corresponding to allyltributylstanne was not detected, which suggests that the mass fragments observed are the pyrolysis products of surface transient organometallic intermediate (allyl)PdSnBu$_3$.

Heating of the STO-1 with 4-nitrobenzaldehyde in THF yielded the corresponding homoallylic alcohol. By XPS and TGA-MS analysis of the surface transient organometallic intermediate, we postulate that in this catalytic reaction, oxidative addition of allyltributylstanne, has taken place in LDH-Pd(0) to produce STO-1, followed by insertion of the aldehyde into the Pd–C bond to form **4** and finally reductive elimination of **5** from the intermediate **4** completes the catalytic cycle. Unfortunately we were not able to isolate **4**.

Reusability of the Catalyst

The catalysts were recovered by simple filtration and washed with acetone and oven-dried .The catalyst was reused and consistent activity was noticed even after

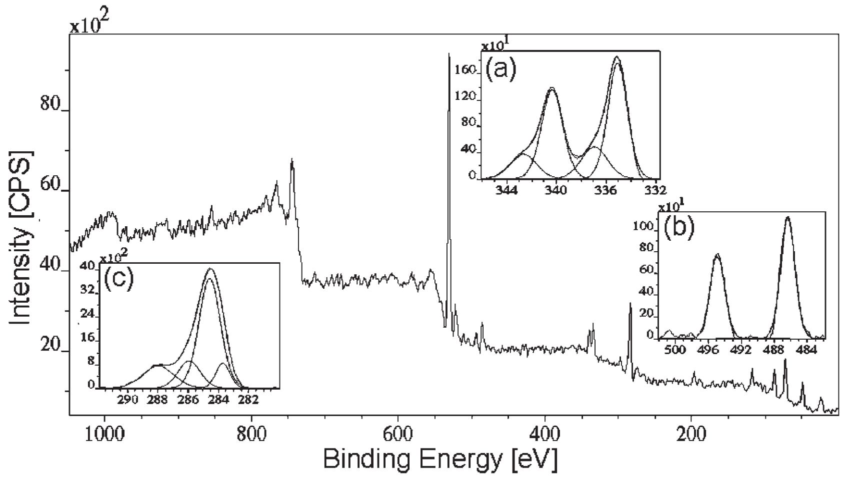
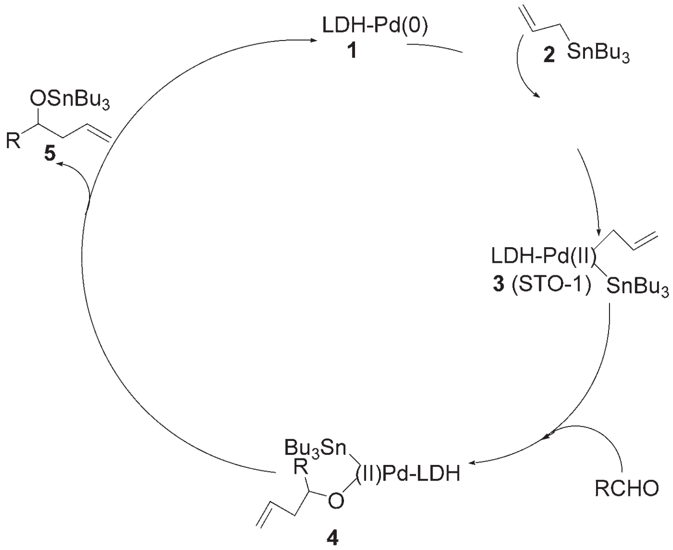


Figure 2. XPS survey scan of STO-1 along with **a**) Pd 3d of STO-1, **b**) Sn 3d of STO-1, **c**) C 1 s of STO-1



Scheme 4. Allylation of aldehydes using LDH-Pd(0).

the fourth cycle (Table 2, entries 1 and 5). When a fresh reaction was conducted with the filtrate obtained at the end of the allylation reaction, no product formation was observed. Moreover, the absence of Pt in the filtrate was determined by AAS. The platinum content of the catalyst was found to be almost the same in the fresh catalyst and in the used catalyst after the fifth cycle by SEM-EDX. This clearly rules out the possibility of leaching of platinum from the support.

Conclusion

In summary, LDH-Pt(0) and LDH-Pd(0) catalysts were successfully employed in the allylation of aldehydes to give homoallylic alcohols in high yields. Moreover, the mechanistic study revealed that a monoallyl-palladium-tin complex was the key intermediate in our heterogeneous system as opposed to the biallylpalladium complex in the homogeneous media as observed by Yamamoto et al.[2b] Finally, the simple procedure, easy recovery and reusability of the catalytic systems are expected to contribute to the development of benign chemical processes and products.

Experimental Section

General Remarks

FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer.^{1}H NMR spectra were recorded on a Bruker (300 MHz) spectrophotometer using $CDCl_3$ as solvent and TMS as the internal standard. XPS spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. X-ray powder diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using CuKα radiation. The particle size and external morphology of the samples were observed on a JEOL JEM-100CX transmission electron microscopy (TEM). SEM-EDX was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. Thermogravimetric (TG), differential thermal analysis and mass spectra of the evolved gas during the thermal decomposition of catalyst were studied on a TGA/SDTA Mettler Toledo 851^e system coupled to an MS Balzers GSD 300T, using open alumina crucibles, containing samples weighing about 8–10 mg with a linear heating rate of $10\,^{\circ}C\ min^{-1}$. All known compounds were characterized by comparing their physical data with those in the literature. Solvents used for experiments were dried and distilled according to literature procedures. All the reactants were commercially available and used without purification.

Preparation of LDH-$PtCl_6$

LDH-Cl (Mg:Al = 3:1, 2 g) was suspended in 150 mL of an aqueous solution of K_2PtCl_6 (0.388 g, 0.8 mmol,) and stirred at 25 °C for 24 h under a nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 500 mL of water and vacuum-dried to obtain LDH-$PtCl_6$.

Preparation of LDH-Pt(0)

LDH-$PtCl_6$ (1 g) was reduced with hydrazine hydrate (1 g, 20 mmol) in ethanol (10 mL) for 3 h under a nitrogen atmosphere, then filtered and washed with ethanol to give an air-stable, black powder (0.374 mmol Pt per gram).

Allylation of Aldehydes using Allyl Bromide

In an oven-dried, 10-mL, round-bottom flask were charged benzaldehyde (1 mmol), allyl bromide (2 mmol), stannous chloride (1.5 mmol) and LDH-Pt(0) (2 mol %) and DMF (2 mL) and stirred at room temperature under a nitrogen atmosphere. After the completion of the reaction as monitored by TLC, the catalyst was filtered and the filtrate was diluted with 10 mL ethyl acetate and washed with 1 N HCl solution followed by saturated aqueous NaCl solution and the organic layer was concentrated to afford the crude reaction mixture. This crude reaction mixture was subjected to column chromatography and the pure product was separated using 3% ethyl acetate in hexane.^{1}H NMR (300 MHz,$CDCl_3$): δ = 2.2(br, 1H), 2.42–2.55 (m, 2H), 4.7 (t, J = 6.78 Hz, 1H), 5.10–5.20 (m, 2H), 5.65–5.85 (m, 1H), 7.15–7.35(m, 5H).

All products were identified by NMR and matched with authentic data as reported in the literature.[3b]

Allylation of Aldehydes using Allyl Alcohol

In an oven-dried, 10-mL, round-bottom flask were charged benzaldehyde (1 mmol), allyl alcohol (3 mmol), stannous chloride (3 mmol), LDH-Pt(0) (2 mol %) and 1,3-dimethyl-2-imidazolidinone (DMI) (2 mL) and stirred at room temperature under a nitrogen atmosphere. After the completion of the reaction as monitored by TLC, the catalyst was filtered and the filtrate was diluted with 10 mL ethyl acetate and washed with 1 N HCl solution followed by saturated aqueous NaCl solution and the organic layer was concentrated to afford the crude reaction mixture. This crude reaction mixture was subjected to column chromatography and the pure product was separated using a mixture of ethyl acetate and hexane.

Allylation of Aldehydes using Allyltributylstanne

In an oven-dried, 10-mL, round-bottom flask were charged benzaldehyde (1 mmol), allyltributylstanne (1.2 mmol) and LDH-Pt(0) (5 mol %) and dry THF (3 ml) and stirred at room temperature under a nitrogen atmosphere. After the completion of the reaction as monitored by TLC, the catalyst was filtered and the filtrate was concentrated to afford the crude reaction mixture. This crude reaction mixture was subjected to column chromatography and the pure product was separated using a mixture of ethyl acetate and hexane.

Preparation of STO-1

LDH-Pd(0) (1000 mg, Pd 1.5 mmol) and allyltributylstanne (1 mL) were charged in a 10-mL, round-bottom flask, 5 mL dry THF was added and the mixture refluxed under argon for 3 h. Then the solid material was filtered and washed with THF twice and vacuum dried for 1 h to afford STO-1 (1040 mg). STO-1 was analyzed for tin by SEM-EDX and the tin content was found to be 0.11 mmol per gram. Next STO-1 was subjected to XPS analysis for Pd, Sn and C. Then STO-1 (1000 mg) and 4-nitrobenzaldehyde (30 mg, 0.2 mmol) were mixed with 3 mL dry THF and refluxed under N_2 for 10 h to get the corresponding homoallylic alcohol.

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[7] Benzaldehyde (1 mmol), allyltributylstanne (1.2 mmol), LDH-Pt(0) and solvent (3 mL) were refluxed under nitrogen for 9 h. Isolated yields: dry THF (83%), THF:water = 9:1 (75%), toluene (65%) CH_3CN (60%), CH_3CN: water = 9:1 (55%), and DMF (50%).