Highly active and selective palladium catalyst for hydroesterification of styrene and vinyl acetate promoted by polymeric sulfonic acids

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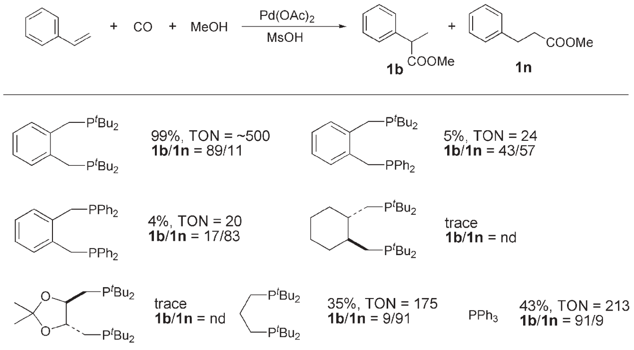
Highly efficient, selective and recyclable palladium catalyst systems for hydroesterification of styrene and vinyl acetate were realized by using 1,2-bis(di-*tert*-butylphosphinomethyl)benzene as ligand and polymeric sulfonic acids of limited SO_3H loadings as promoter.

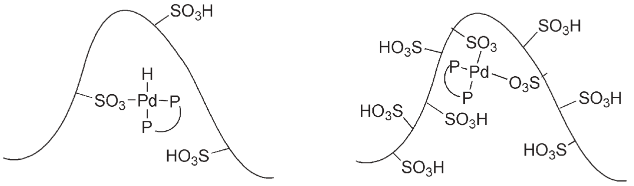
Palladium-catalysed hydroesterification is a long-known useful method of high atom economy to synthesize esters from olefins or other unsaturated compounds with alcohols under CO atmosphere.[1] Extensive and intensive research and development have been carried out for the reaction of methylacetylene and propylene toward the goal of commercial exploitation. Hydroesterification of polar olefins, however, has been relatively little studied. In general, besides the activity and selectivity of the reaction, stability and recovery of the palladium catalyst are also factors to be scrutinized for commercial exploitation. Since the reaction is usually effected in the presence of acidic promoters, how to minimize the corrosion of the reaction vessel is another important factor. Our study, initiated with these requirements in mind, has found that palladium species generated from $Pd(OAc)_2$ or $Pd_2(dba)_3$, 1,2-bis(di-*tert*-butylphosphinomethyl)benzene (DTBPMB) and polymeric sulfonic acids of relatively low loading of SO_3H functionality catalyze the reaction of styrene[2] and vinyl acetate[3] efficiently, which will be disclosed in the present communication.[4] There is a large demand for the branched structured products formed from vinylarenes and vinyl acetate in applications to pharmaceutical and polymer industries.

Preliminary experiments to screen phosphine ligands in styrene hydroesterification (Scheme 1) have revealed that DTBPMB[5] is the ligand of choice to display high yield and selectivity for the branched product (**1b**). Thus, a typical experiment using styrene (10.0 mmol) and methanol (1.0 mL) was run in the presence of $Pd(OAc)_2$ (0.02 mmol), DTBPMB (0.02 mmol) and methanesulfonic acid (0.15 mmol) at room temperature for 18 h under 6 atm of carbon monoxide. Analysis of the reaction mixture by GLC showed the formation of **1b** and **1n** in a near 100% total yield (**1b**/**1n** = 89/11).† As summarized in Scheme 1, however, the performance of other phosphine ligands was much lower, suggesting that even a very minor change in the structure dramatically affects it. Our results that the diphosphines except DTBPMB preferentially formed the linear product (**1n**) agree with the finding first reported by Sugi and Bando[2f] that 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane form **1n** as the major product. The preferential formation of **1b** in the reaction using PPh_3 also agrees with precedents.[2b,d,6] However, the selective formation of **1b** observed by the use of DTBPMB is totally unexpected.



Scheme 1 Ligand effect in the palladium-catalysed hydroesterification of styrene (reagents and conditions: styrene 10.0 mmol, MeOH 1.0 mL, CO 6 kg cm^{-2}, $Pd(OAc)_2$ 0.02 mmol, CH_3SO_3H 0.15 mmol, P/Pd = 2, room temperature for 17 h).

On the basis of the foregoing experiments, we examined the Pd–DTBPMB catalysed hydroesterification in the presence of commercial polymeric sulfonic acid resins, such as Amberlyst® 15 and Nafion® NR-50, which proved to generate much less active palladium species (yield < 5% at SO_3H/Pd = 45–8.0) than monomeric acids such as methanesulfonic acid under the same conditions. However, we have found that a polymeric sulfonic acid of a relatively low loading of the SO_3H functionality works as efficiently as the monomeric sulfonic acids (Scheme 2; the SO_3 anion may dissociate to accommodate a CO ligand while the carbonylation is in progress[1,7]). Thus, the reaction in the presence of a polymeric acid PS–SO_3H-30‡ (SO_3H/Pd = 4.5) under otherwise identical conditions afforded 97% yield of the esters with 88% selectivity for **1b**. On the other hand when a sample of PS–SO_3H-100‡ (SO_3H/Pd = 5.3) was used, the reaction gave only traces of **1b** and **1n**. To generate active H–Pd species, we do need an acid promoter. However, if the local acid concentration in the close proximity of palladium is too high, more than two SO_3H



Scheme 2 High (left) and low (right) performance resins.

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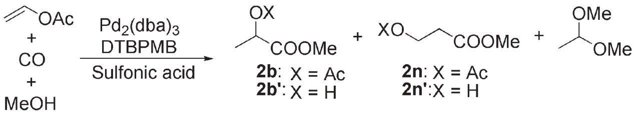
Table 1 Hydroesterification of vinyl acetate[a]



Run	Acid	Conv.[b] (%)	Ester yield[c] (%)	Ester distribution **2b/2b′/2n/2n′**	Acetal yield (%)
1	Wang resin–SO_3H[d]	91	70.4	72.2/0.2/27.2/0.2	4.8
2	CH_3SO_3H	100	60.8	66.4/5.9/21.7/5.9	21.0

[a] Procedure and conditions: Vinyl acetate 10 mmol, MeOH 1.0 mL, $Pd_2(dba)_3$ 0.01 mmol (0.02 mmol with respect to Pd), DTBPMB 0.02 mmol, acid 0.092 mmol, initial CO pressure 6 kg cm^{-2}, 60 °C, 1.5 h. [b] Conversion of vinyl acetate. [c] Total yield of **2b**, **2b′**, **2n** and **2n′**. [d] Derived from Argonaut 800351 Wang resin. SO_3H content = 0.37 mmol g^{-1} (by ICP analysis) for this particular sample.

Table 2 Reaction of vinyl acetate: Catalyst recycling[a]

Recycle	Ester yield (%)	TON for esters	Ester distribution **2b/2b′/2n/2n′**	Acetal yield (%)
Pristine	82.1	32.8×10^2	76.2/0.6/22.7/0.5	5
1	89.4	35.8×10^2	72.1/0.6/26.6/0.7	6
2	83.5	33.4×10^2	74.6/0.4/24.7/0.3	4
3	84.9	33.9×10^2	73.8/0.4/25.3/0.4	5

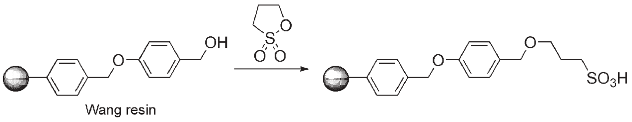
[a] Procedure and conditions: Vinyl acetate 40 mmol, MeOH 4.0 mL, $Pd_2(dba)_3$ 0.005 mmol (0.01 mmol with respect to Pd), DTBPMB 0.01 mmol, Wang resin-SO_3H (derived from Argonaut 800351 Wang resin) 0.048 mmol, initial CO pressure 10 kg cm^{-2}, 40 °C, 24 h.

groups may interact with the palladium species to prevent the H–Pd species formation or coordination of the phosphine ligand.[7]

Since PS–SO_3H-30 and -100 were synthesized by treating commercial polystyrene beads with chlorosulfonic acid in dichloromethane, the sulfonation may not have uniformly proceeded. To further confirm the effect of acid density, we prepared another type of polymeric sulfonic acids by the reaction of Wang resins with propanesultone (Scheme 3), which is envisioned to afford more uniformly sulfonated resins.§

The reaction of styrene (styrene 20 mmol, MeOH 2.0 mL, $Pd_2(dba)_3$ (0.01 mmol with respect to Pd metal), DTBPMB = 0.01 mmol, CO = 6 atm, room temperature, 18 h) was carried out in the presence of a new resin derived from Algonaut 800351 Wang resin (0.25 g corresponding to 0.13 mmol of SO_3H; SO_3H/Pd = 13) to give 97% yield of the esters with selectivity for **1b** of 86%. Likewise another resin derived from Aldrich 47703-6 Wang resin (0.25 g corresponding to 0.053 mmol of SO_3H; SO_3H/Pd = 5.3) gave 95% yield and 87% **1b** selectivity.

Vinyl acetate has been a substrate that does not conform to hydroesterification successfully since the reaction usually accompanies side reactions such as alcoholysis of the acetate functionality and the formation of acetals coming from acetaldehyde.[3] Very recently a patent application has disclosed a new catalyst system that can circumvent these drawbacks by using a limited quantity of a sulfonic acid promoter in conjunction with DTBPMB ligand.[3c] We have found that the new procedure of hydroesterification using the polymeric sulfonic acids, DTBPMB and a palladium complex could be successfully extended to vinyl acetate (Table 1). Thus hydroesterification of vinyl acetate with methanol in the presence of the Argonaut 800351-derived sulfonic acid gave 70% carbonylation yield (**2b** + **2b′** + **2n** + **2n′**) with a very minor extent of methanolysis that afforded hydroxyl esters (**2b′**, **2n′**) as compared with the reaction using CH_3SO_3H. In addition, the formation of the acetal byproduct was also suppressed.



Scheme 3 Derivation of a Wang resin to the corresponding sulfonic acid.

The resin–Pd complex recovered by stripping the volatiles retains the activity to allow repeated use as summarized in Table 2, suggestive of the stability of the catalyst system.

In summary, this communication discloses the high performance of the DTBPMB ligand and favorable effect of the polymeric sulfonic acid resin of low loading of the SO_3H functionality to synthesize branched esters starting with styrene and vinyl acetate.

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Notes and references

† The reaction did not work under the same conditions in the absence of acid promoters. Camphor- and *p*-toluene-sulfonic acids used in place of methanesulfonic acid displayed similar activity and selectivity, but the performance of trifluoromethanesulfonic acid was much poorer.

‡ *Synthesis* of PS–SO_3H-30 and -100: To a suspension of 1 g of commercial polystyrene crosslinked with 1% divinylbenzene (50–100 mesh) in dichloromethane was added a solution of 30 or 100 μL of chlorosulfonic acid in dichloromethane (5 mL) at 0 °C and the mixture was stirred for 30 min at room temperature. After overnight standing, the mixture was treated with acetic acid (1.0 mL) and was filtered. The resulting resin was washed successively with water, tetrahydrofuran and dichloromethane and was dried at room temperature.

§ *Synthesis* of Wang resin–SO_3H: A sample of Algonaut 800351 Wang resin (2.0 g, OH loading = 1.22 mmol g^{-1}) was added to a suspension of sodium hydride (4.9 mmol; washed with hexane (2 mL, three times)) in *N*-methylpyrrolidone (20 mL). After heating the mixture for 1 h at 60 °C, propanesultone (12.2 mmol) was added and the mixture was further heated for another 60 min at the same temperature, left to stand overnight and was treated with methanol. The filtered off resin was washed successively with dilute hydrochloric acid–tetrahydrofuran, tetrahydrofuran and dichloromethane and was dried. The SO_3H content was 0.53 mmol g^{-1} (ICP). Note that even though the catalog number of the starting Wang resin is the same, the OH loading given in the specification is inconsistent and dependent on a particular sample. Another Wang resin–SO_3H (SO_3H content = 0.21 mmol g^{-1}, as analyzed by ICP analysis) was synthesized from Aldrich 47703-6 Wang resin similarly, but in this case, the starting resin was treated with PhONa (1 equiv.) in *N*-methylpyrrolidone at 80 °C for 2 h to convert potentially catalyst-poisoning benzylic chloride impurity to the corresponding phenoxy ether, prior to the synthesis.

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