DOI: 10.1002/adsc.201300864

Highly Efficient Catalytic Dimerization of Styrenes *via* Cationic Palladium(II) Complexes

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Received: September 25, 2013; Revised: October 24, 2013; Published online: December 11, 2013

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300864.

Abstract: A highly efficient head-to-tail dimerization of a styrene was developed using a cationic palladium(II)-catalyzed selective C–C bond forming reaction. The complex $[\mathrm{AllylPd(PPh_3)}]^+\mathrm{OTf}^-$, which is believed to generate 'palladium hydride' (Pd–H), catalyzed the dimerization of various styrenes in excellent yields as single isomers. This Pd(II)-catalyzed reaction provides a new economical C–C bond forming method.

Keywords: C–C bond formation; dimerization; palladium hydride; styrene

Introduction

Efficient catalysts for the dimerization or oligomerization of olefins have been extensively studied and developed in the industrial sector, because of the commerical importance of these catalysts for the production of α-olefins.[1,2] For these processes, Ziegler–Natta type Ti and Ni catalysts have been studied, and successfully applied to ethylene dimerization and oligomerization processes.[2] In academic research, these types of catalysts have received attention because of the importance of discovering new C–C bond-forming reactions.[3] Using catalysts which operate by related mechanisms, the development of diverse single C–C bond-forming reactions has been studied for various organic reactions.[4–7] For example, diverse Ni-, Co-, and Pd-catalyzed co- and hetero-dimerizations of ethylene and styrene have been developed.[5–7] These new catalytic systems have been successfully applied to selective C–C bond formation. Furthermore, enantioselective syntheses of commercial non-steroidal anti-inflammatory drugs (NSAID) such as ibuprofen, and the total syntheses of natural products with intricate methyl-bearing stereogenic centers have been reported using these catalytic systems.[8,9]

For selective styrene head-to-tail dimerization, several catalytic systems have been reported (Figure 1).[10–12] This reaction could be a test reaction to develop various co- and hetero-dimerization reactions. In addition, it could yield various 1,3-diphenyl-1-butene derivatives. Stable metal hydride complexes, such as Ru hydride, can catalyze the reaction in good yields.[10] Also, cationic Ni and Pd complexes have been used for styrene dimerization, oligomerization, and polymerization.[4,11–13] Currently, cationic Pd-catalyzed systems have shown promising results for the selective dimerization of styrene with less oligomerization or polymerization than other catalysts.[12] However, these Pd-catalyzed systems needed an additional Lewis acid such as $\mathrm{In(OTf)_3}$,[12c] $\mathrm{Cu(OTf)_2}$[12d] or $\mathrm{BF_3{\cdot}OEt_2}$,[12g–i] to generate active catalytic species or activate vinylarenes, and generally elevated temperatures and/or pressures were needed for high turnover number.[12c–i] Hence, the development of an operationally simple, highly catalytic, and selective Pd-based

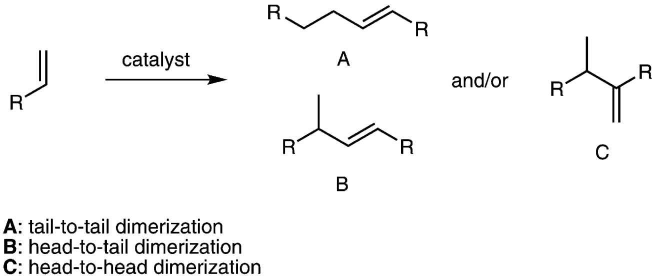
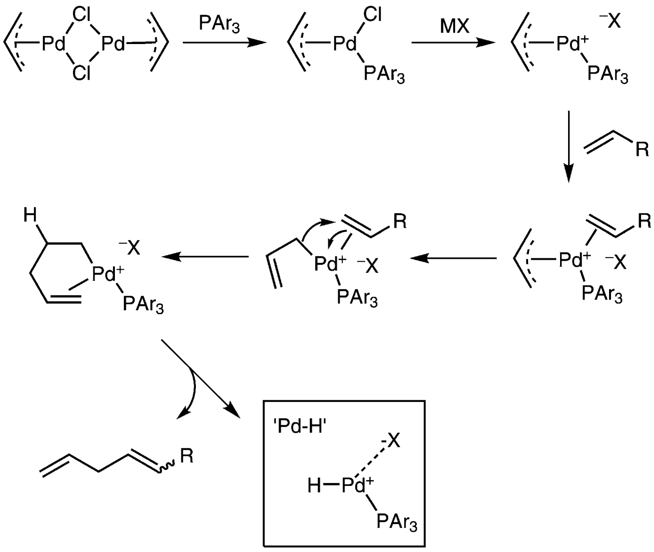
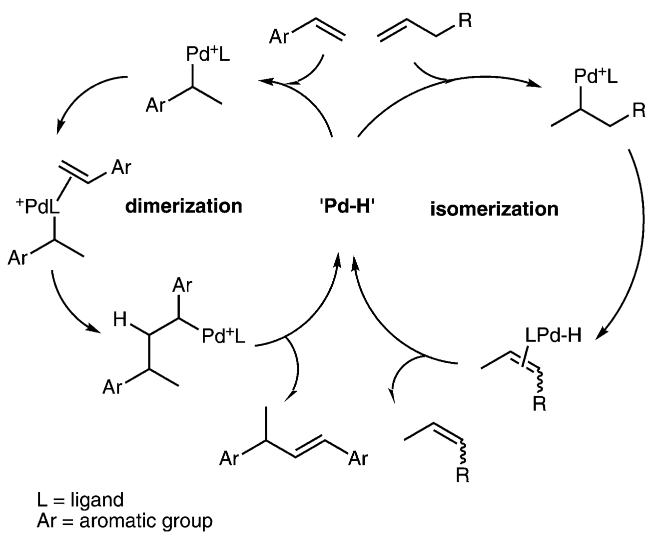


Figure 1. Three possible modes of dimerization of α-olefins.



Scheme 1. Proposed mechanism of 'Pd–H' generation.



Scheme 2. Proposed mechanism of 'Pd–H'-catalyzed isomerization and dimerization.

catalyst for the styrene dimerization reaction is still needed.

Recently, we reported the regioselective Pd(II)-catalyzed isomerization of terminal olefins to internal olefins.[14] In this report, we showed that the [allylPd(PPh$_3$)]$^+$OTf$^-$ complex could isomerize terminal double bonds in good yields. This study demonstrated the utility of *in situ* generated 'Pd hydride' as an olefin isomerization catalyst (Scheme 1).[15]

We hypothesized that the conditions used to generate the putative 'Pd–H' for olefin isomerization might be applicable to selective head-to-tail styrene dimerization reactions (Scheme 2).

Results and Discussion

We used a catalytic system similar to that used in a previous isomerization study.[14] In the former works, non-polar solvents such as CH$_2$Cl$_2$ gave the best results to catalyze isomerization, and relatively polar solvents like THF gave poor conversions. Based on these results, ligand screening was performed using several different types of phosphines with CH$_2$Cl$_2$ as a solvent. Fortunately, the use of simple arylphosphine ligands **1** and **3** provided excellent yields and selectivities (entries 1 and 3, Table 1), but 2-furylphosphine did not give any product (entry 2, Table 1). Reactions with sterically encumbered phosphines **4** and **5** showed low conversion rates (entries 3 and 4, Table 1), and no product was obtained with bidentate phosphines **6** and **7** (entries 6 and 7, Table 1). In all experiments, only the head-to-tail dimerized *E*-isomer was obtained as a major product, regardless of the yield or type of ligand. Therefore, triphenylphosphine **1** was selected for further salt-effect studies.

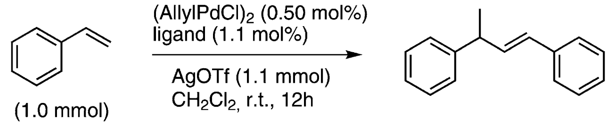
No reaction occurred in the absence of a silver salt (entry 1, Table 2). Although reactions with AgBF$_4$ and AgClO$_4$ showed excellent conversions (entries 5 and 6, Table 2), AgOTf was the best option for the target reaction in terms of yield and selectivity (entry 2, Table 1). When AgOAc and Ag$_2$CO$_3$ were used (entries 3 and 4, Table 2), the reaction did not occur. Furthermore, the use of NaBARF resulted in a low conversion rate (entry 7, Table 2).

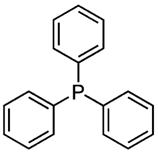
To investigate the efficiency of the optimized catalyst, the catalyst loading was further lowered. Even with 0.025 mol% catalyst loading (styrene/Pd = 4000), the reaction still showed complete conversion on a 10-g scale at room temperature, which produced 9.4 g of (*E*)-1,3-diphenyl-1-butene with a trace amount of the trimer.

Under the optimized conditions, various styrenes were tested for dimerization. In all experiments, 1.0 mol% of the catalyst was used for experimental convenience on small-scale reactions. Styrenes with a *para*-substituent generated excellent results (entries 2–6, and 9, Table 3), regardless of the electronic properties of the substituent. *meta*-Bromo substrate produced a similar result (entry 8, Table 3), but a lower yield was observed with 2-fluorostyrene (entry 7, Table 3), possibly because of an electronic effect. In all cases, small amounts (3–5%) of trimmers were detected by GC/MS.[16]

With the less reactive α-methylstyrene,[12c] the reaction still occurred with an excellent conversion (> 99%). However, significant isomerization of the initial dimerized product occurred (^{1}H NMR ratio of expected (**a**):isomerized (**b**):trimers (**c**) = 1:0.8:0.2, Figure 2). Increased steric hindrance at the reaction site may explain the occurrence of isomerization.

Table 1. Selection of a ligand.





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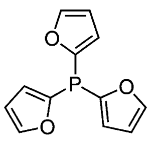

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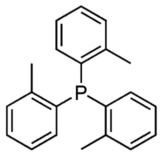

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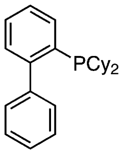

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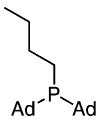

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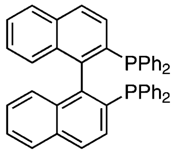

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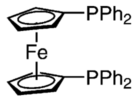

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Entry	Ligand[a]	Conversion[b] [%]	Yield[c,d] [%]
1	triphenylphosphine **1**	**95**	**93**
2	tri(2-furyl)phosphine **2**	1	–
3	tri(*ortho*-tolyl)phosphine **3**	**96**	**94**
4	2-(dicyclohexyl)phosphinodiphenyl **4**	15	15
5	*n*-butyldiadamantylphosphine **5**	53	31
6	*rac*-BINAP **6**	0	–
7	diphenylphosphinoferrocene **7**	0	–

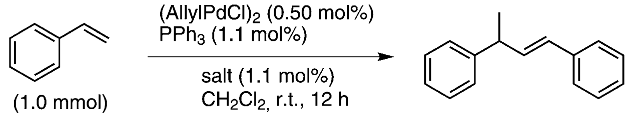
[a] Styrene (1.0 mmol), (allylPdCl)$_2$ (0.0050 mmol), ligand (0.011 mmol), AgOTf (0.011 mmol), and CH$_2$Cl$_2$ (3 mL) were used.

[b] Analyzed by GC/MS.

[c] Isolated yields.

[d] 3–5% of trimer was produced.

Table 2. Selection of a counterion.



Entry	Salt[a]	Conversion[b] [%]	Yield[c] [%]
1	none	0	–
2	AgOTf	**95**	**93**[e]
3	AgOAc	0	–
4	Ag$_2$CO$_3$	0	–
5	AgBF$_4$	**99**	**99**[d]
6	AgClO$_4$	**99**	**94**[e]
7	NaBARF[f]	46	46[e]

[a] The reaction conditions are the same as for entry 1 in Table 1, except for the salt.

[b] The crude products were analyzed by GC/MS.

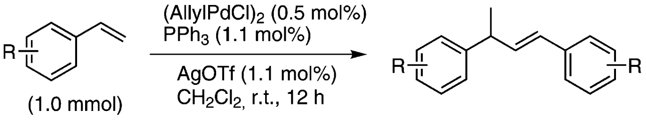
[c] Isolated yields.

[d] 14% of trimer was produced.

[e] 3–5% of trimer was produced.

[f] NaBARF = sodium tetrakis[(3,5-trifluoromethyl)phenyl]-borate.

Table 3. Dimerization of substituted styrenes.



Entry	Styrene (R =)[a]	Conversion[b] [%]	Yield[c,d] [%]
1	H	95	93
2	4-F	> 99	98
3	4-Br	> 99	99
4	4-AcO	95	90
5	4-Me	> 99	99
6	4-CF$_3$	90	85
7	2-F	60	58
8	3-Br	93	95
9	4-Cl	92	90

[a] Styrene (1.0 mmol), (allylPdCl)$_2$ (0.0050 mmol), PPh$_3$ (0.011 mmol), swalt (0.011 mmol), and CH$_2$Cl$_2$ (3 mL) were used.

[b] The crude products were analyzed by GCMS.

[c] Isolated yields.

[d] 3–5% of trimers were included.

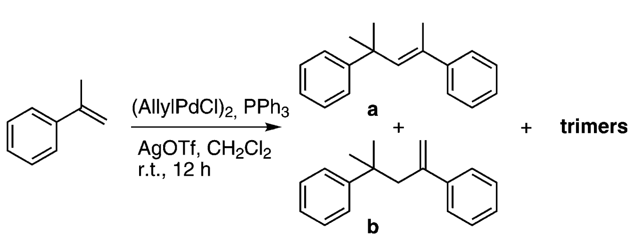


Figure 2. Dimerization of α-methylstyrene.

Conclusions

In summary, we have developed an exceptionally efficient Pd(II)-catalyst for the dimerization of various styrenes. With styrene, the reaction afforded complete conversion with 0.025 mol% catalyst on a 10-g scale at room temperature. Regardless of the substituent, the optimized catalytic system generally produced the desired products in excellent yields. In addition, α-methylstyrene resulted in dimerization products with isomerization. Further studies toward hetero-dimerization and an enantioselective version of this reaction using a chiral ligand are underway.

Experimental Section

General Information

All solvents were dried by standard methods prior to use. Dichloromethane was distilled from calcium hydride under nitrogen and stored over molecular sieves. Reactions requiring air-sensitive manipulations were conducted under an inert atmosphere of nitrogen by using Schlenk techniques or a Vacuum Atmospheres glove-box. Reagents such as silver salts, $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$ (NaBARF), phosphine ligands, and $[(allyl)PdCl]_2$ were purchased from Aldrich or Strem Co. Ligands for co-dimerization, $[(allyl)PdCl]_2$, silver salts, and NaBARF were stored in a Vacuum Atomspheres drybox. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 F254 plates. NMR experiments were performed using $CDCl_3$ with $CHCl_3$ ($\delta = 7.26$) as an internal standard.

General Procedure of Cationic Pd(II)-Catalyzed Styrene Dimerization

In an Ar-charged drybox, Schlenk tube was charged with $[(allyl)PdCl]_2$ (0.5 mol%), ligand (1.10 mol%), and silver salt (1.10 mol%), and then mixture was dissolved in dry CH_2Cl_2 (2.0 mL mmol^{-1} of styrene). The prepared catalyst was stirred at room temperature for 10 min, and then taken out. Into the solution of the activated pre-catalyst, styrene in dry CH_2Cl_2 (1.0 mL mmol^{-1} of olefin) was added, and the resulting mixture was stirred at ambient temperature under a N_2 atmosphere. After the reaction, the solvent was evaporated, and the crude product was filtered through a short pad silica then evaporated. The crude product was analyzed by GC/MS and NMR without further purification.

Preparative-Scale Procedure of Pd(II)-Catalyzed Styrene Dimerization[17]

The premixed catalyst in dry CH_2Cl_2 (15 mL) was prepared by the above-mentioned procedure using $[(allyl)PdCl]_2$ (0.012 mol%, 0.011 mmol, 4.0 mg), PPh_3 (0.027 mol%, 0.027 mmol, 7.1 mg), and AgOTf (0.027 mol%, 0.027 mmol, 6.9 mg). The prepared catalyst was stirred at room temperature for 10 min, and then taken out. Into the solution, 10 g of styrene (96 mmol) in dry CH_2Cl_2 (25 mL) were added dropwise slowly, and the resulting mixture was stirred at ambient temperature for 12 h under an N_2 atmosphere. After filtration and evaporation, the desired product including a trace amount of trimer was obtained as a colorless oil; yield: 9.6 g.

1,3-Diphenylbut-1-ene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.24 (m, 10 H), 6.48–6.47 (m, 2 H), 3.74–3.70 (m, 1 H), 1.56–1.53 (d, J = 9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.8, 137.8, 135.4, 128.7, 127.5, 126.4, 42.8, 21.4; GC/MS (EI): m/z = 208 (M$^+$).

1,3-Di(4-fluorophenyl)but-1-ene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.18 (m, 4 H), 7.02–6.94 (m, 4 H), 6.37–6.20 (m, 2 H), 3.65–3.56 (m, 1 H), 1.44–1.42 (d, J = 6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.8, 163.2, 160.6, 160.0, 141.3, 133.7, 129.0, 128.6, 127.9, 127.7, 127.6, 127.5, 115.5, 115.2, 115.1, 41.8, 21.5; GC/MS (EI): m/z = 244 (M$^+$).

1,3-Di(4-bromophenyl)but-1-ene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.10 (m, 8 H), 6.32–6.31 (d, J = 3 Hz, 2 H), 3.62–3.55 (m, 1 H), 1.44–1.42 (d, J = 6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.3, 136.3, 135.4, 131.6, 129.1, 127.9, 127.8, 120.9, 120.1, 42.1, 21.1; GC/MS (EI): m/z = 366 (M$^+$).

1,3-Di(4-acetoxyphenyl)but-1-ene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.24 (m, 4 H), 7.05–6.99 (m, 4 H), 6.42–6.26 (m, 2 H), 3.68–3.58 (m, 1 H), 1.45–1.43 (d, J = 6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.6, 169.5, 149.7, 149.0, 143.0, 135.3, 128.1, 127.8, 127.2, 126.9, 121.8, 121.5, 121.4, 42.1, 21.2; GC/MS (EI): m/z = 324 (M$^+$).

1,3-Di(4-*tert*-butylphenyl)but-1-ene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.32 (m, 8 H), 6.58–6.48 (m, 2 H), 3.78–3.69 (m, 1 H), 1.59–1.56 (d, J = 6 Hz, 3 H), 1.44 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.1, 149.0, 142.8, 135.0, 134.8, 128.2, 127.1, 126.0, 125.5, 125.4, 42.1, 34.6, 31.7, 22.8, 21.3, 14.3; GC/MS (EI): m/z = 320 (M$^+$).

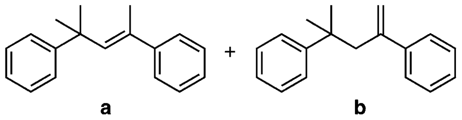
1,3-Di(4-trifluoromethylphenyl)but-1-ene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.40 (m, 8 H), 6.50–6.49 (m, 2 H), 3.81–3.72 (m, 1 H), 1.55–1.53 (d, J = 6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.3, 140.9, 136.9, 130.0, 129.1, 128.7, 127.8, 126.5, 126.2, 125.7, 122.6, 119.0, 42.7, 21.0; GC/MS (EI): m/z = 344 (M$^+$).

1,3-Di(2-fluorophenyl)but-1-ene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–6.99 (m, 8 H), 6.64–6.43 (m, 2 H), 4.04–3.94 (m, 1 H), 1.48–1.46 (d, J = 6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.3, 161.9, 136.2, 132.4, 128.5, 127.9, 127.3, 125.2, 124.3, 124.1, 121.6, 115.9, 115.5, 36.2, 20.2; GC/MS (EI): m/z = 244 (M$^+$).

1,3-Di(3-bromophenyl)but-1-ene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.20 (m, 8 H), 6.39–6.38 (m, 2 H), 3.70–3.61 (m, 1 H), 1.52–1.49 (d, J = 9 Hz, 3 H); ^{13}C NMR δ (75 MHz, $CDCl_3$): δ = 147.6, 139.5, 135.9, 130.4, 130.2, 130.1, 129.6, 129.1, 127.9, 126.1, 125.0, 124.9, 122.8, 122.8, 42.4, 21.0; GC/MS (EI): m/z = 364 (M$^+$).

1,3-Di(4-chlorophenyl)but-1-ene: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.28–7.14$ (m, 8H), 6.35–6.23 (m, 2H), 3.62–3.53 (m, 1H), 1.42–1.40 (d, $J = 6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 143.8$, 135.9, 135.4, 132.8, 132.1, 128.8, 128.7, 127.9, 127.5, 42.0, 21.2; GC/MS (EI): $m/z = 276$ (M^+).

Mixture of a and b from Co-dimerization of α-Methylstyrene (NMR ratio = 1:0.8 based on olefinic-H): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.51–7.31$ (m, 10H), 6.28 (s, olefinic H of **a**, 1H), 5.29 (s, olefinic H of **b**, 1H), 4.93 (s, olefinic H of **b**, 1H), 2.98 (s, CH_2 of **b**, 2H), 1.71 (s, CH_3 of **b**, 3H)., 1.66 [s, $(CH_3)_2$ of **b**, 6H], 1.37 [s, $(CH_3)_2$ of **a**, 6H]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.6$, 150.6, 149.5, 149.1, 146.8, 145.0, 142.5, 141.0, 138.9, 137.8, 136.4, 128.3, 128.2, 127.9, 126.6, 126.3, 126.0, 125.9, 117.0, 49.7, 40.3, 40.2, 39.3, 38.8, 38.1, 31.2, 29.6, 29.1, 17.3; MS (EI): $m/z = 236$ (M^+).



Acknowledgements

Financial supports provided by the KRICT (SI-1304) and the US NSF (CHE 1057818) are gratefully acknowledged.

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[16] In all cases, trace amounts of trimers (3–5%) were detected and tentatively assigned by GC/MS.

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