

# Selective dimerization of styrene to 1,3-diphenyl-1-butene with bis( $\beta$ -diketonato)palladium/boron trifluoride etherate catalyst system

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## Abstract

The selective dimerization of styrene to 1,3-diphenyl-1-butene over Pd( $\beta$ -diketonate)<sub>2</sub>/BF<sub>3</sub>OEt<sub>2</sub> catalyst systems in both “phosphine-free” and “phosphine-modified” fashions has been investigated. For the Pd(acac)<sub>2</sub> + 2PR<sub>3</sub> + 7BF<sub>3</sub>OEt<sub>2</sub> catalyst system the turnover of 75,000 mol styrene/mol palladium for 7 h was reached at 70 °C with selectivity to dimers of 93%. Styrene dimers up to 95% consists of *trans*-1,3-diphenyl-1-butene. Catalytic activity and selectivity can be controlled by varying the reaction parameters. The nature of substituents on the  $\beta$ -diketonate did not affect the conversion of styrene. However, the selectivity to dimers increases almost linearly with decreasing acidity of  $\beta$ -diketonate ligand. The nature of the phosphine ligand has a strong effect on the conversion of styrene, but not on the selectivity. The order of the decrease in conversion parallels the increasing basicity (electronic effect) rather than steric properties of the phosphines. Reaction products were characterized with <sup>1</sup>H and <sup>13</sup>C NMR, IR, and GC–MS spectroscopies and GC analysis. Palladium hydride complexes are likely to be catalytically active species.

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## 1. Introduction

The dimerization of alkenes is an important method for the production of higher olefins, which find extensive application as industrial intermediates, as a source of new kinds of polymers, lubricants, detergents, and many other useful chemicals [1,2]. However, reports on late-transition metal catalyzed dimerization of styrene were very few, although palladium [3–10], cobalt [11], and nickel complexes [12–25] were widely used to catalyze the codimerization of styrene with  $\alpha$ -olefins. The first transition-metal complexes found to dimerize styrene in low yield and with poor selectivity were

based on palladium [3]. Later, a number of late transition-metal compounds were demonstrated to be efficient catalysts for the dimerization of styrene [26–34]. On the other hand, it has recently been found that several well-characterized Ziegler–Natta catalysts can also induce carbocationic polymerization of styrene and the line between the two processes is substantially blurred [35]. Exploring cationic, highly electrophilic palladium compounds as efficient initiators, Sen et al. [33,34] have demonstrated the carbocationic mechanism for the dimerization of styrene. In contrast, the conventional hydride mechanism has been frequently postulated for this reaction [3,26–32]. Some time ago, we showed that the interactions of Pd(acac)<sub>2</sub> and (acac)Pd(C<sup>3</sup>-acac)PR<sub>3</sub> with BF<sub>3</sub>OEt<sub>2</sub> in the presence of 1-hexene afford the formation of catalytically active, tetracoordinated square-planar palladium

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hydride complexes [36,37]. Pd(acac)<sub>2</sub>/BF<sub>3</sub>OEt<sub>2</sub> catalyst system is highly active in the trimerization of ethene, dimerization of propene, isomerization of 1-hexene, and telomerization of butadiene with amines [38]. At the same time, under comparable conditions, Pd(acac)<sub>2</sub>/BF<sub>3</sub>OEt<sub>2</sub> system catalyzes the polymerization of norbornene to give 2,7-enchained products, indicating a carbocationic polymerization mechanism [39].

We describe in this paper the results of the study of selective dimerization of styrene catalyzed by Pd(acac)<sub>2</sub>/BF<sub>3</sub>OEt<sub>2</sub> system in both “phosphine-free” and “phosphine-modified” fashions.

## 2. Experimental

All manipulations for air sensitive compounds were carried out under a stream of dry nitrogen using standard inert techniques.

### 2.1. Materials

Inert gases were purified before feeding to the reactor by passing them through columns packed with oxygen scavenger (Fisher REDOX) and molecular sieve 5A (Aldrich). Styrene (99%, Aldrich) was purified by distillation under reduced pressure over calcium hydride, CaH<sub>2</sub>. Boron trifluoride etherate (Aldrich, 99%) was distilled over CaH<sub>2</sub> prior to use. Benzene was distilled over sodium/potassium alloy (NaK) under dry nitrogen. Pd(β-diketonate)<sub>2</sub> complexes were synthesized according to a literature procedure [40] and recrystallized from benzene.

### 2.2. Dimerization of styrene

Dimerizations were carried out in a glass reactor equipped with a magnetic stirrer under argon atmosphere without a solvent. The reactor was preliminary purged in vacuum and filled with argon, and then was filled with styrene and palladium precursor. Dimerizations were initiated by the injection of the boron compound. The reaction mixture was kept at room temperature for 30 min to form catalytically active species and then heated up to temperature desired. After stirring for a time needed, the reaction was terminated and styrene dimers were isolated by vacuum distillation (130 °C/1.3 × 10<sup>-2</sup> Torr). Special experiments showed that aromatic solvents, such as benzene and toluene, have no effect on the activity and selectivity of the dimerization. In contrast, polar solvents like acetone completely inhibit the reaction due to the formation of molecular complexes with BF<sub>3</sub> cocatalyst. GC/MS analysis showed that the rest consisted mainly of trimers. In standard runs the amount of palladium precursor was 5.0 × 10<sup>-5</sup> mol, the B/Pd ratio was 7, the styrene/Pd ratio was 52,500, the reaction time was 5 h, and the reaction temperature was 45 °C unless stated otherwise.

### 2.3. Characterization of products

NMR spectra were recorded in CDCl<sub>3</sub> at room temperature on a Bruker AMX-500 spectrometer with frequencies of 500 MHz for <sup>1</sup>H NMR and 125 MHz for <sup>13</sup>C NMR. Tetramethylsilane (TMS) was used as the internal standard. The IR spectrum was recorded on a “Perkin-Elmer-577” spectrometer. GC/MS data were obtained using a MAT-212 instrument (*T* = 100–300 °C, 20 m capillary column, SE-30 phase). Gas chromatography (GC) analyses were performed on a “Chrom-5” instrument (3.7 m column, SE-30 phase, nitrogen carrier gas, *T* = 240 °C). Mass spectra (MS) were recorded on a VCT Autospec Ultima instrument with GI 70 eV and DIP.

## 3. Results and discussion

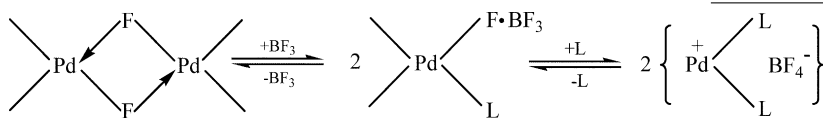
For the dimerization of styrene over the Pd(β-diketonate)<sub>2</sub>/BF<sub>3</sub>OEt<sub>2</sub> catalyst system, the yield and composition of products, as well as the catalyst activity, depend significantly on the reaction parameters applied such as cocatalyst/catalyst ratio (B/Pd), reaction temperature, the nature of phosphine ligand added and β-diketonate ligand at palladium. Preliminary experiments were made to check the activity of each of two components of the system, namely Pd(acac)<sub>2</sub> and BF<sub>3</sub>OEt<sub>2</sub>, as well as of PPh<sub>3</sub> at 45 °C. Neither Pd(acac)<sub>2</sub> nor PPh<sub>3</sub> was active in styrene transformation. Run with an amount of BF<sub>3</sub>OEt<sub>2</sub> corresponding to B/Pd = 25 ratio in standard conditions resulted in the complete conversion of styrene to polymer (*M<sub>v</sub>* = 31,500). NMR analysis showed the product to be atactic polystyrene typical of cationic initiators.

### 3.1. Influence of the cocatalyst to palladium ratio

To investigate the effect of the amount of cocatalyst, a set of runs was carried out with the B/Pd ratios from 1 to 25 at 45 °C. As one may see in Table 1, the conversion to dimers showed a broad maximum at B/Pd ratios from 7 to 10 and a further dramatic decrease due to cationic polymerization at higher ratios. The selectivity to dimers of 93% was maintained, while the B/Pd ratio changed from 1 to 7. Similar curves of activity versus cocatalyst/metal ratio is very common for the oligomerization and polymerization of alkenes and the increase in activity with increasing cocatalyst/metal ratio is usually explained by an equilibrium formation of the active complex from inactive precatalyst and cocatalyst, i.e. by an increasing number of active species.

The interaction of Pd(acac)<sub>2</sub> with BF<sub>3</sub>OEt<sub>2</sub> in the presence of 1-hexene leads to catalytically active complexes, in which BF<sub>3</sub> can be bonded to Pd as a complexed BF<sub>4</sub><sup>-</sup> anion or via a fluorine atom as F·BF<sub>3</sub> [36,37]. Moreover, a rapid exchange between the bridging and the terminal fluorine atoms of coordinated BF<sub>4</sub><sup>-</sup> (anion “spinning”) and a presence of a tightly associated contact ion pair had been shown for the polymerization of norbornene derivatives with (η<sup>3</sup>-allyl)Pd(II) catalysts [41]. Therefore, the results obtained

might be explained by the equilibrium between a fluorine-bridged inactive and an active, tightly associated ion pairs of the palladium species:



\* Other ligands at Pd are omitted

The increasing amount of  $\text{BF}_3$  cocatalyst shifts the equilibrium to the active form and increases the ionic character of active species. The increased ionic character of active species resulted in increased chain propagation rate. An excess of  $\text{BF}_3\text{OEt}_2$  cocatalyst is not desirable for obtaining high dimerization activity and selectivity. Thus, it is possible to control the activity and selectivity *dimerization versus oligomerization* by varying the B/Pd ratio.

### 3.2. Variation of the $\beta$ -diketonate ligand

For chelated nickel catalysts, the activity and selectivity in the oligomerization of alkenes are greatly dependent on the nature of the chelate ligands around the metal [42]. In this context, it appeared of considerable interest to study the effect of chelate ligands at palladium on the activity and selectivity of the dimerization of styrene. The results are summarized in Table 2.

The nature of substituents on the  $\beta$ -diketone did not affect the conversion of styrene. However, a remarkable dependency of the selectivity of the catalyst on the acidity of the ligand was observed. It seems that the acidity of the ligand is dominating over the catalyst selectivity, the selectivity to dimers increasing almost linearly with decreasing acidity. Probably, a high degree of enolization and a related high acidity might cause a change of the optimum B/Pd ratio necessary for the maximum selectivity to dimers. The real reason for this observation is a subject of special studies.

### 3.3. Variation of the phosphine

In general, the phosphine ligand has a profound influence on both the activity and selectivity of transition-metal catalyst systems. Tolman [43] reviewed the effects of phosphine ligands on reactions or properties of metal complexes

for the first time and they were rationalized in terms of electronic and steric effects. Quantitative measures of electronic and steric effects were based on  $A_1$  carbonyl stretching

frequencies ( $\nu$ ) in  $\text{Ni}(\text{CO})_3\text{L}$  complexes and ligand cone angles ( $\theta$ ) of space-filling CPK models [43]. The influence of the phosphine added on the conversion and selectivity of  $\text{Pd}(\text{acac})_2 + 1\text{PR}_3 + 7\text{BF}_3\text{OEt}_2$  catalyst system is shown in Table 3. The selectivity of the catalyst system with various phosphine ligands seems to be highly similar and in all cases the dimers were formed with selectivity of about 92%. However, the conversion of styrene was substantially affected by the nature of phosphine. The highest conversion was observed with  $\text{PPh}_3$  and the lowest conversion was obtained with  $\text{P}(\text{C}_6\text{H}_{11})_3$ .

As may be seen in Table 3, the order of the decrease in conversion parallels the increasing basicity (electronic effect) rather than steric properties of the phosphines:  $\text{P}(\text{C}_6\text{H}_{11})_3$ , for example, is a stronger base than  $\text{PPh}_3$ . A reasonable explanation for this phenomenon might be that the phosphines with higher electron-donor properties, such as  $\text{P}(\text{C}_6\text{H}_{11})_3$ , enhance the electron density on the metal center, thus disfavoring the coordination of styrene and hence the conversion. Apparently, the results indicate strongly that the phosphine molecule remains complexed to palladium during the catalytic reaction.

### 3.4. Reaction temperature and reaction kinetics

The effect of reaction temperature on the dimerization of styrene over the  $\text{Pd}(\text{acac})_2 + 7\text{BF}_3\text{OEt}_2$  catalyst system modified with various amount of  $\text{PPh}_3$  ligand was studied at temperatures between 35 and 75 °C. As seen in Table 4, at lower temperatures of 35–45 °C the addition of phosphine led to the decrease in conversion of styrene. At higher temperatures of 60–70 °C the pattern of dependency was inverted; the highest turnover of 75,000 mol styrene per mol palladium with selectivity to dimers of 93.0% was reached at 70 °C with the

Table 1

Effect of cocatalyst/palladium ratio on the dimerization of styrene (St) over  $\text{Pd}(\text{acac})_2 + n\text{BF}_3\text{OEt}_2$  catalyst system

| B/Pd (ratio)    | St/Pd (ratio) | Catalyst ( $10^5$ mol) | Time (h) | Conversion (mol St/mol Pd) | Composition (mass%) |                      |
|-----------------|---------------|------------------------|----------|----------------------------|---------------------|----------------------|
|                 |               |                        |          |                            | Dimers              | Trimers and polymers |
| 1               | 52500         | 5                      | 5        | 2100                       | 93.0                | 7.0                  |
| 2               | 52500         | 5                      | 5        | 5900                       | 92.9                | 7.1                  |
| 5               | 52500         | 5                      | 5        | 15500                      | 93.5                | 6.5                  |
| 7               | 52500         | 5                      | 5        | 24000                      | 93.8                | 6.2                  |
| 10              | 52500         | 5                      | 5        | 23850                      | 90.9                | 9.1                  |
| 15              | 52500         | 5                      | 5        | 22100                      | 60.3                | 39.7                 |
| 25 <sup>a</sup> | —             | —                      | —        | —                          | —                   | —                    |

<sup>a</sup> Polymer product.

Table 2

Effect of the nature of the  $\beta$ -diketonate ligand on the dimerization of styrene (St) over  $\text{Pd}(\text{R}^1\text{C}(\text{O})\text{CHC}(\text{O})\text{R}^2)_2 + 7\text{BF}_3\text{OEt}_2$  catalyst system

| Substituent ( $\text{R}^1, \text{R}^2$ )                        | Acidity ( $\text{p}K_{\text{a}}$ ) | Conversion (mol St/mol Pd) | Composition (mass%) |                      |
|-----------------------------------------------------------------|------------------------------------|----------------------------|---------------------|----------------------|
|                                                                 |                                    |                            | Dimers              | Trimers and polymers |
| $\text{R}^1 = \text{CH}_3; \text{R}^2 = \text{C}_6\text{H}_5$   | 9.4                                | 22750                      | 95.0                | 5.0                  |
| $\text{R}^1 = \text{R}^2 = \text{CH}_3$                         | 9.0                                | 24000                      | 93.8                | 6.2                  |
| $\text{R}^1 = \text{CH}_3; \text{R}^2 = i\text{-C}_3\text{H}_7$ | 8.1                                | 22500                      | 90.2                | 9.8                  |
| $\text{R}^1 = \text{CF}_3; \text{R}^2 = \text{C}_6\text{H}_5$   | 6.8                                | 23000                      | 82.2                | 17.8                 |
| $\text{R}^1 = \text{R}^2 = \text{CF}_3$                         | 4.2                                | 23200                      | 49.2                | 50.8                 |

Experimental conditions:  $[\text{Pd}] = 5 \times 10^{-5}$  mol;  $\text{St}/\text{Pd} = 52,500$ ;  $45^\circ\text{C}$ ; 5 h.

Table 3

Effect of the nature of the phosphine ligand on the dimerization of styrene (St) over  $\text{Pd}(\text{acac})_2 + \text{IPR}_3 + 7\text{BF}_3\text{OEt}_2$  catalyst system

| $\text{PR}_3$                                             | $\nu$ ( $\text{cm}^{-1}$ ) | $\theta$ ( $^\circ$ ) | Conversion (mol St/mol Pd) | Composition (mass%) |                      |
|-----------------------------------------------------------|----------------------------|-----------------------|----------------------------|---------------------|----------------------|
|                                                           |                            |                       |                            | Dimers              | Trimers and polymers |
| $\text{PPh}_3$                                            | 2068.9                     | 145                   | 24250                      | 92.0                | 8.0                  |
| $\text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_3$           | 2066.3                     | 194                   | 23600                      | 91.1                | 8.9                  |
| $\text{P}(p\text{-ClC}_6\text{H}_4)_3$                    | 2072.8                     | 145                   | 23200                      | 91.4                | 8.6                  |
| $\text{P}(o\text{-CH}_3\text{OC}_6\text{H}_4)_3$          | 2058.3                     | 194                   | 16000                      | 91.9                | 8.1                  |
| $\text{P}(p\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4)_3$ | 2063.4                     | 145                   | 13200                      | 92.0                | 8.0                  |
| $\text{P}(\text{C}_6\text{H}_{11})_3$                     | 2056.1                     | 170                   | 3500                       | 91.8                | 8.2                  |

Experimental conditions:  $[\text{Pd}] = 5 \times 10^{-5}$  mol;  $\text{St}/\text{Pd} = 52,500$ ;  $45^\circ\text{C}$ ; 5 h.

P/Pd ratio of 2. Further increase in temperature to  $75^\circ\text{C}$  led to the decrease in conversion due to thermal decomposition of the catalyst.

Differential kinetic curves of dimerization rate versus reaction time for “phosphine-free” and “phosphine-modified” catalyst systems at higher temperatures are plotted in Fig. 1. The reaction rates refers to the formation of dimer products. Kinetic curves for  $\text{Pd}(\text{acac})_2 + 7\text{BF}_3\text{OEt}_2$  and  $\text{Pd}(\text{acac})_2 + \text{IPPh}_3 + 7\text{BF}_3\text{OEt}_2$  systems at  $60^\circ\text{C}$  showed a stationary segment followed with a rapid decrease. For the system modified with equimolar amount of phosphine the stationary segment is longer than that without phosphine, even

though the addition of phosphine led to a slight decrease in activity (curves 1 and 3). This illustrates a stabilizing effect of phosphine ligand. An existence of the stationary segment itself indicates zero order of reaction with respect to styrene and the constant concentration of active species. A rise of temperature to  $70^\circ\text{C}$  resulted in a rapid thermal decomposition (curves 2 and 4).

At the P/Pd ratio of 2 the activity profiles are changed completely. After some induction period, the curves passed through the maximum followed by a steady decline. At  $70^\circ\text{C}$  the activity after 7 h was 3500 mol St/mol Pd for an hour. Thus, the maximum conversion of 75,000 mol St/mol Pd for

Table 4

Effect of the reaction temperature on the dimerization of styrene (St) over  $\text{Pd}(\text{acac})_2 + n\text{PPh}_3 + 7\text{BF}_3\text{OEt}_2$  catalyst system

| Temperature ( $^\circ\text{C}$ ) | P/Pd (ratio) | Conversion (mol St/mol Pd) | Composition (mass%) |                      |
|----------------------------------|--------------|----------------------------|---------------------|----------------------|
|                                  |              |                            | Dimers              | Trimers and polymers |
| 35                               | 0            | 13450                      | 94.0                | 6.0                  |
|                                  | 1            | 12500                      | 92.6                | 7.4                  |
|                                  | 2            | 6200                       | 92.8                | 7.2                  |
| 45                               | 0            | 24000                      | 94.0                | 6.0                  |
|                                  | 1            | 22300                      | 92.6                | 7.4                  |
|                                  | 2            | 14500                      | 92.0                | 8.0                  |
| 60                               | 0            | 37100                      | 93.6                | 6.7                  |
|                                  | 1            | 42900                      | 93.0                | 7.0                  |
|                                  | 2            | 46300                      | 92.5                | 7.5                  |
| 70 <sup>a</sup>                  | 0            | 29300                      | 91.0                | 9.0                  |
|                                  | 1            | 54500                      | 92.9                | 7.1                  |
|                                  | 2            | 75000                      | 93.0                | 7.0                  |
|                                  | 3            | 24000                      | 91.8                | 8.2                  |
| 75 <sup>a</sup>                  | 0            | 15000                      | 93.2                | 6.8                  |
|                                  | 1            | 43000                      | 91.8                | 8.2                  |
|                                  | 2            | 59000                      | 92.5                | 7.5                  |

Experimental conditions:  $[\text{Pd}] = 5 \times 10^{-5}$  mol;  $\text{St}/\text{Pd} = 52,500$ ; 5 h.<sup>a</sup>  $\text{St}/\text{Pd} = 105,000$ ; 7 h.

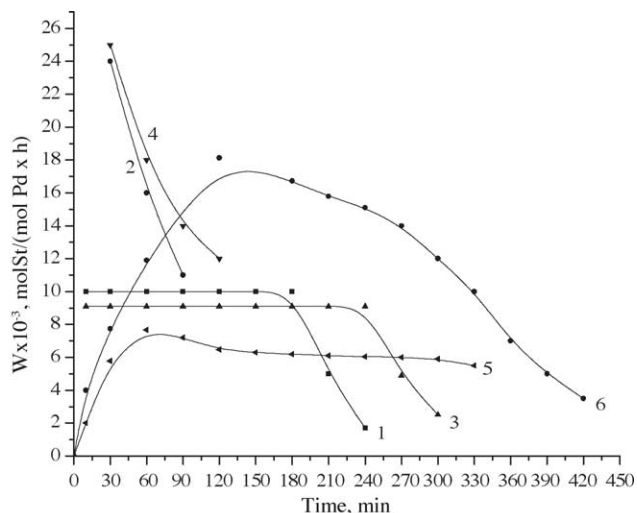
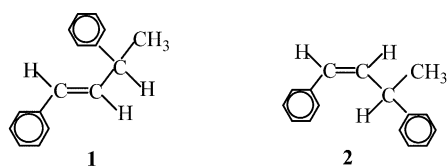


Fig. 1. Kinetic curves: Pd(acac)<sub>2</sub> + 7BF<sub>3</sub>OEt<sub>2</sub> system at 60 °C (1) and 70 °C (2); Pd(acac)<sub>2</sub> + 1PPh<sub>3</sub> + 7BF<sub>3</sub>OEt<sub>2</sub> system at 60 °C (3) and 70 °C (4); and Pd(acac)<sub>2</sub> + 2PPh<sub>3</sub> + 7BF<sub>3</sub>OEt<sub>2</sub> system at 60 °C (5) and 70 °C (6).

7 h was reached using the P/Pd ratio of 2 at 70 °C. The results were explained according to the proposed structure of active species formed in the systems.

### 3.5. Structure of the product and reaction mechanism

It has been established that the fractionation of reaction products affords exclusively to 1,3-diphenyl-1-butene. GC analysis showed that the dimer consists of *trans*-stereoisomer **1** up to 95% and the content of *cis*-isomer **2** is up to 5%. IR spectroscopy analysis also proved an existence of both isomers exhibiting bands at 965 and 910 cm<sup>-1</sup> attributable to δ<sub>C-H</sub> vibrations at the double bond in *trans* and *cis* structures, respectively [44].



*trans*-1,3-diphenyl-1-butene

*cis*-1,3-diphenyl-1-butene

Molar mass of  $M = 208$  of the dimer product was confirmed by the mass spectroscopy (Fig. 2). The <sup>1</sup>H NMR spectrum of 1,3-diphenyl-1-butene (Fig. 3a) shows the resonance peak at 1.98 ppm due to methyl group protons (protons at 4 position). The peak at 4.12 ppm is assigned to a methyne proton at the 3 position. The resonance peaks at 6.92 ppm are vinylic protons at the positions 1 and 2. The coupling constant for protons H<sup>1</sup> and H<sup>2</sup> ( $^2J = 15.27$  Hz) is quite similar to that reported in [30], therefore suggesting a *trans* double bond. Aromatic protons appear at 7.76 ppm. The <sup>13</sup>C NMR spectrum (Fig. 3b) presents six groups of resonances in the region from 20 to 150 ppm. The resonance peak at 21.76 ppm is due to the methyl group (carbon 4). The resonance peak at 43.00 ppm is the CH group (carbon 3). The

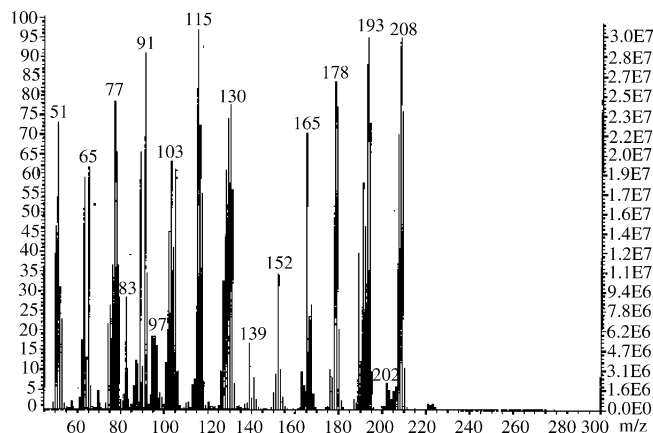


Fig. 2. Mass spectrum of 1,3-diphenyl-1-butene.

peak at 135.65 ppm is vinyl carbon at the 1 position. Second vinyl carbon resonates at 138.10 ppm. The resonance peak at 146.63 ppm is from the aromatic carbon, bonded to the C<sup>3</sup> carbon. Other aromatic carbons appear in the region from 126.65 to 129.23 ppm.

Indeed, Sen et al. [33,34] have suggested a carbocationic mechanism for the dimerization of styrene over [Pd(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> and Pd(PPh)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> complexes. Such a carbocationic mechanism would be very sensitive to the temperature and to the presence of nucleophiles; i.e. the reaction would be favoured at low temperature and inhibited by nucleophiles, as was shown for the carbocationic polymerization

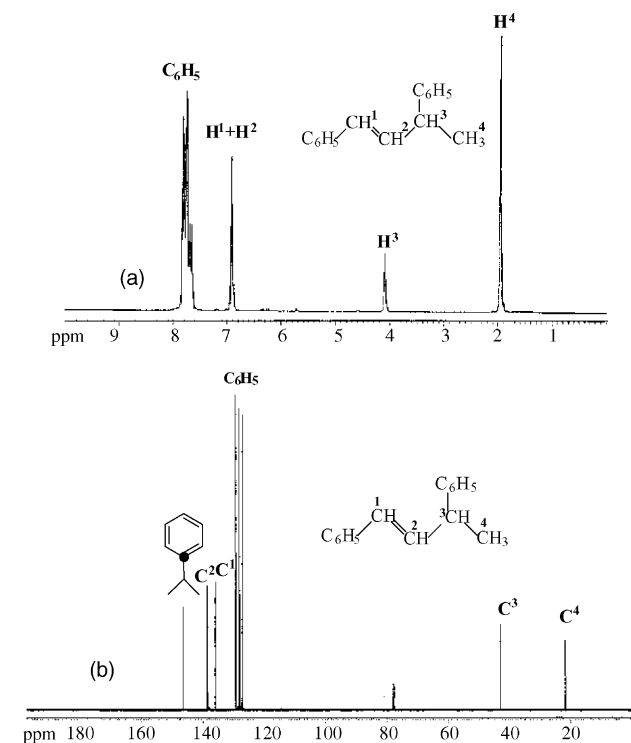
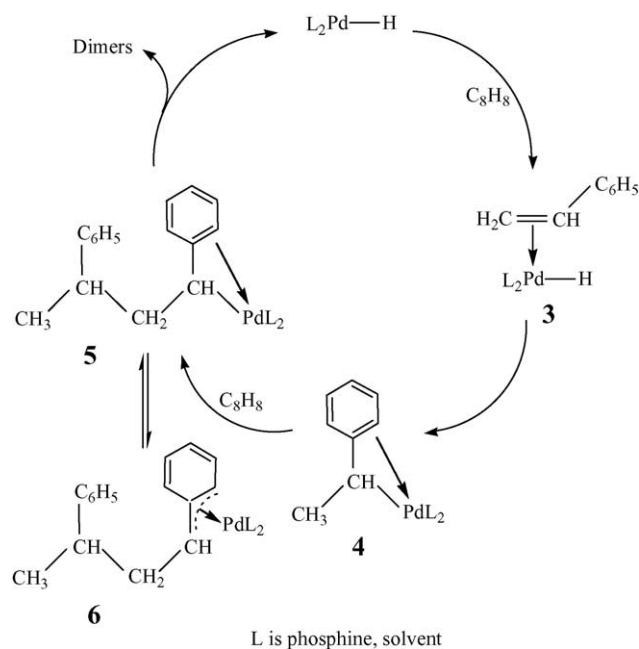


Fig. 3. NMR spectra of 1,3-diphenyl-1-butene in CDCl<sub>3</sub>: <sup>1</sup>H NMR (a) and <sup>13</sup>C NMR (b).



Scheme 1. Catalytic cycle based on the  $\beta$ -hydrogen transfer route.

of norbornene over the  $\text{Pd}(\text{acac})_2 + 25\text{BF}_3\text{OEt}_2$  system [39]. The opposite observation of higher reaction rates at higher temperatures for both “phosphine-free” and “phosphine-modified” systems led us to discard this mechanism for the system we employed. Although we have not carried out detailed mechanistic studies of the interaction of  $\text{Pd}(\text{acac})_2$  and  $\text{PPh}_3$  ligand with  $\text{BF}_3\text{OEt}_2$  in the presence of styrene, we favour a mechanism that involves a palladium hydride species (Scheme 1). In principle, the scheme is similar to the commonly accepted hypothesis concerning olefin oligomerization by transition-metal catalysts. Activation of the precatalyst in the presence of styrene leads to a coordinately unsaturated  $\text{Pd-H}$  species, which is able to add styrene. Two monodentate phosphine can coordinate to the palladium center with both *cis* and *trans* fashions. Clearly, if the insertion of monomer into the  $\text{Pd-H}$  bond involves the adjacent in-plane sites, it is only in the *cis* form that chain growth can occur. The observed induction period (Fig. 1) might be explained by the transformation of initially formed inactive *trans* structure to the active *cis* structure.

The addition of the styrene molecule to the palladium hydride provides **3**.  $\text{Pd} \rightarrow \text{C}_2$  insertion of the monomer into the  $\text{Pd-H}$  bond leads to **4**. Further  $\text{Pd} \rightarrow \text{C}_2$  insertion of the second styrene molecule into the  $\text{Pd-C}$  bond regenerates **5**. The palladium intermediate **5** retains its 16-electron configuration owing to the edge coordination of the phenyl ring of the last inserted styrene. This dimer chain might be stabilized in a secondary way by the  $\eta^3$ -benzyl-palladium bond affording **6**, which cannot undergo  $\beta$ -elimination process. The high selectivity toward a head-to-tail dimerization product might be explained by the formation of intermediates **5** and **6** with the stabilization of the active species [13,26,31]. Finally,  $\beta$ -elimination through a  $\eta^3 \leftrightarrow \eta^1$  isomerization terminates the

chain, giving 1,3-diphenyl-1-butene and regenerating the palladium hydride active species.

#### 4. Conclusion

The selective dimerization of styrene to 1,3-diphenyl-1-butene over  $\text{Pd}(\beta\text{-diketonate})_2/\text{BF}_3\text{OEt}_2$  catalyst systems in both “phosphine-free” and “phosphine-modified” fashions has been investigated. For  $\text{Pd}(\text{acac})_2 + 2\text{PR}_3 + 7\text{BF}_3\text{OEt}_2$  catalyst system the turnover of 75,000 mol styrene per mol palladium for 7 h was reached at  $70^\circ\text{C}$  with selectivity to dimers of 93%. Styrene dimers up to 95% consists of *trans*-1,3-diphenyl-1-butene. Catalytic activity and selectivity can be controlled by varying the reaction parameters. The nature of substituents on the  $\beta$ -diketonate did not affect the conversion of styrene. However, the selectivity to dimers increases almost linearly with decreasing acidity of  $\beta$ -diketonate ligand. The nature of the phosphine ligand has a strong effect on the conversion of styrene, but not on the selectivity. The order of the decrease in conversion parallels the increasing basicity (electronic effect) rather than steric properties of the phosphines. The highest conversion was observed with  $\text{PPh}_3$  and the lowest conversion was obtained with  $\text{P}(\text{C}_6\text{H}_{11})_3$ . Palladium hydride complexes are suggested to be catalytically active species.

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