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Selective dimerization of styrene to 1,3-diphenyl-1-butene with bis(β-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(β-diketonate)$_2$/BF$_3$OEt$_2$ catalyst systems in both "phosphine-free" and "phosphine-modified" fashions has been investigated. For the Pd(acac)$_2$ + 2PR$_3$ + 7BF$_3$OEt$_2$ 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 β-diketone did not affect the conversion of styrene. However, the selectivity to dimers increases almost linearly with decreasing acidity of β-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 ^{1}H and ^{13}C NMR, IR, and GC–MS spectroscopies and GC analysis. Palladium hydride complexes are likely to be catalytically active species.

Keywords: Boron trifluoride; Dimerization; Palladium; Phosphine; Styrene

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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 α-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)$_2$ and (acac)Pd(C^3-acac)PR$_3$ with BF$_3$OEt$_2$ in the presence of 1-hexene afford the formation of catalytically active, tetracoordinated square-planar palladium

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hydride complexes [36,37]. $Pd(acac)_2/BF_3OEt_2$ 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, $Pd(acac)_2/BF_3OEt_2$ 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 $Pd(acac)_2/BF_3OEt_2$ 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_2. Boron trifluoride etherate (Aldrich, 99%) was distilled over CaH_2 prior to use. Benzene was distilled over sodium/potassium alloy (NaK) under dry nitrogen. $Pd(\beta\text{-diketonate})_2$ 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 ($130\,^{\circ}C/1.3 \times 10^{-2}$ 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_3 cocatalyst. GC/MS analysis showed that the rest consisted mainly of trimers. In standard runs the amount of palladium precursor was 5.0×10^{-5} 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 $CDCl_3$ at room temperature on a Bruker AMX-500 spectrometer with frequencies of 500 MHz for ^1H NMR and 125 MHz for ^{13}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 ($T = 100$–$300\,^{\circ}C$, 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, $T = 240\,^{\circ}C$). 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 $Pd(\beta\text{-diketonate})_2/BF_3OEt_2$ 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 $Pd(acac)_2$ and BF_3OEt_2, as well as of PPh_3 at 45 °C. Neither $Pd(acac)_2$ nor PPh_3 was active in styrene transformation. Run with an amount of BF_3OEt_2 corresponding to B/Pd = 25 ratio in standard conditions resulted in the complete conversion of styrene to polymer ($M_v = 31{,}500$). 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 $Pd(acac)_2$ with BF_3OEt_2 in the presence of 1-hexene leads to catalytically active complexes, in which BF_3 can be bonded to Pd as a complexed BF_4^- anion or via a fluorine atom as $F{\cdot}BF_3$ [36,37]. Moreover, a rapid exchange between the bridging and the terminal fluorine atoms of coordinated BF_4^- (anion “spinning”) and a presence of a tightly associated contact ion pair had been shown for the polymerization of norbornene derivatives with (η^3-allyl)Pd(II) catalysts [41]. Therefore, the results obtained