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LETTERS TO THE EDITOR

Selective Dimerization of Styrene in the Presence of Catalysts of the Type $[(Acac)Pd(PR_3)_2]BF_4$ + $nBF_3 \cdot OEt_2$

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We have developed a simple method for preparing cationic palladium complexes $[(Acac)Pd(PR_3)_2]BF_4$ (**I**) starting from $Pd(Acac)_2$, PR_3, and $BF_3 \cdot OEt_2$ by the following general equation: $Pd(Acac)_2 + 2PR_3 + 2BF_3 \cdot OEt_2 \rightarrow [(Acac)Pd(PR_3)_2]BF_4 + 2OEt_2 + BF_2Acac$ (Acac is acetylacetonate; R = phenyl, *o*-tolyl, or *p*-tolyl).

Below we give as example the synthesis protocol for $[(Acac)Pd(PPh_3)_2]BF_4$ (**II**). A three-necked flask was successively charged at 20°C in an argon atmosphere with 1.641 mmol of bis(acetylacetonato)palladium, 3.282 mol of triphenylphosphine, and 40 ml of benzene. Then 3.282 mmol of $BF_3 \cdot OEt_2$ was added dropwise with vigorous stirring. A light yellow precipitate formed; it was filtered off, washed with benzene, and dried in a vacuum (10 mm Hg, 2 h, 20°C). Yield 91%, mp 174–176°C. Found, %: C 61.2; H 4.24; B 1.1; F 8.25; O 3.92; P 7.1; Pd 12.8. $PdC_{41} \cdot H_{37}O_2P_2BF_4$. Calculated, %: C 60.3; H 4.53; B 1.35; F 9.3; O 3.92; P 7.6; Pd 13.0. NMR spectra: ^1H, δ, ppm: 1.5 (CH_3), 5.6 (CH), 7.2–7.8 (CH arom.); ^{13}C, δ_C, ppm: 27.5 (CH_3), 102.3 (CH), 128–136 (arom.), 188.4 (C=O); ^{19}F, δ_F, ppm: –146.1 (BF_4); ^{11}B, δ_B, ppm: –0.56 (BF_4); ^{31}P, δ_P, ppm: 36 (PPh_3).

The other cationic complexes of type **I** (R = *o*-tolyl, *p*-tolyl) were prepared and characterized similarly.

We examined the dimerization of styrene in the presence of catalytic systems $[(Acac)Pd(PR_3)_2]BF_4$–$BF_3 \cdot OEt_2$. Under optimal reaction conditions (B/Pd 8, 75°C, R = Ph), the conversion of styrene into the target products exceeds that attained on the known palladium analogs [1–4] and reaches 153000 mol of styrene per g-atom of Pd in 7 h, with up to 91% content of dimers and up to 9% content of trimers.

The NMR spectra were recorded on a Varian VXR-500S spectrometer, solvent $(CD_3)_2CO$. Ampules were filled in an argon atmosphere. Benzene was dehydrated by the standard procedure [5]. Argon was thoroughly dried and deoxygenated according to [6]. Styrene dimers (100% 1,3-diphenyl-1-butene) were separated by vacuum distillation; the *cis/trans* ratio, according to ^1H NMR, was 95/5.

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