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Spectroscopic Study of the Interaction of the Pd(acac)(C^3-acac)PPh_3 Complex with BF_3OEt_2 in the Presence of PPh_3[1]

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Abstract—The interaction between the components of a catalytic system Pd(acac)(C^3-acac)PPh_3 + $n$$PPh_3$ + $m$$BF_3OEt_2$ (where n = 1–4, m = 0.25–4, and acac is the acetylacetonate ligand) in benzene is examined by UV and IR spectroscopy. With a relative excess of PPh_3 ($n > m$), acacH and $[Pd(acac)(PPh_3)_2]^+BF_4^-$ were the main products, whereas BF_2acac and a polynuclear complex of PdF_2 with PPh_3 also containing $Pd^{2+}(BF_4^-)_2$ units were formed with a relative excess of BF_3OEt_2 ($n < m$).

INTRODUCTION

Catalytic systems based on $Pd(acac)_2$ and BF_3OEt_2, including systems modified with PR_3 or H_2O, exhibit a relatively high activity in the selective dimerization of styrene, the telomerization of butadiene and isoprene with diethylamine, and the oligomerization of propylene. For these systems, the key role of unsaturated hydrocarbons in the formation of active complexes that are coordinatively unsaturated palladium hydrides, such as $[HPd(C_4H_6)_2]BF_4$, was found [1, 2].

In this work, we examined the effect of coordinated and free molecules of triphenylphosphine on the composition and structure of reaction products in the system Pd(acac)(C^3-acac)PPh_3 + $n$$PPh_3$ + $m$$BF_3OEt_2$ (n = 1–4; m = 0.25–4) in benzene. The interaction between the components of this system significantly depends on the ratio between PPh_3 and BF_3OEt_2. Systems with excess PPh_3 ($n > m$; group 1 of reaction systems) or BF_3OEt_2 ($n < m$; group 2 of reaction systems) were studied.

EXPERIMENTAL

Benzene (5–10 ml), a palladium complex with triphenylphosphine, and triphenylphosphine were successively added into a reaction vessel, which was purged with argon at room temperature with stirring. After the dissolution of these components, boron trifluoride etherate was added to the reaction vessel. The initial concentration of Pd(acac)(C^3-acac)PPh_3 was varied from 0.009 to 0.067 mol/l.

The product composition was analyzed by IR and UV spectroscopy. The IR spectra of products were measured using a Specord IR 75 spectrophotometer over a range of 2000–400 cm^{-1}. The solutions of precipitates in acetonitrile for measuring the IR spectra were prepared in a 1.5-ml densimeter ([Pd] = 0.02–0.04 mol/l), and photometric measurements were performed in cells 0.011 cm in thickness with KBr windows. The IR spectra of solid reaction products in mineral oil were also measured. The UV spectra over a range of 38000–28000 cm^{-1} were recorded using a Specord UV–VIS spectrophotometer and quartz cells 0.011–0.051 cm in thickness. The solutions of precipitates were prepared in acetonitrile ([Pd] = 0.0015–0.0022 mol/l).

The reaction was monitored by measuring the UV spectra of solutions. In this case, the reaction was performed in an argon atmosphere in a sealed quartz cell 0.011 cm in thickness. The initial concentration of the palladium triphenylphosphine complex in these experiments was 0.0045 mol/l.

RESULTS AND DISCUSSION

Analysis of changes in the absorption intensity at different points of the UV spectrum for the reaction systems of group 1 demonstrates that the intensity of UV absorption in the region 35000–30000 cm^{-1} increased with time (from 3 min to 1–3 h after the onset of the reaction). This fact is indicative of the formation of acetylacetonate anions and their complexes with BF_3 and the appearance of acacH. After 1–3 h, yellow crystalline precipitates appeared because of the interaction between the components of reaction systems; the formation of these precipitates lasted for 24 h. The UV spectrum of the reaction mixture after precipitation

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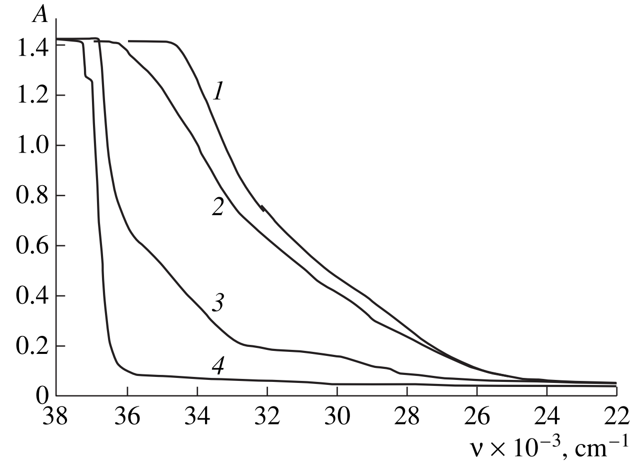


Fig. 1. UV spectra of a benzene solution of the system $Pd(acac)(C^3\text{-}acac)PPh_3 + 2PPh_3 + BF_3OEt_2$ (*1*) 3 min, (*2*) 1 h, and (*3*) 24 h after the onset of the process; (*4*) the UV spectrum of benzene.

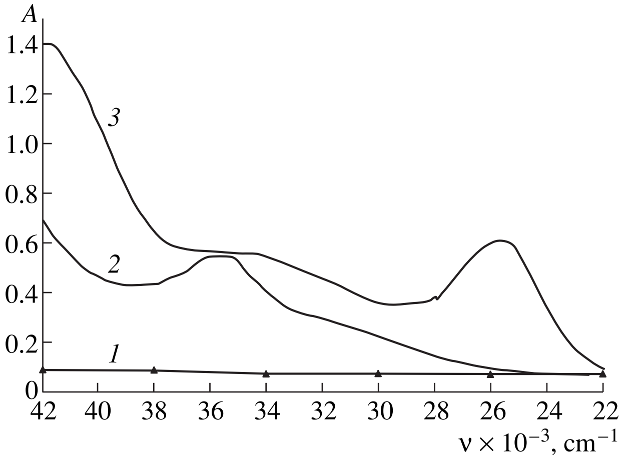


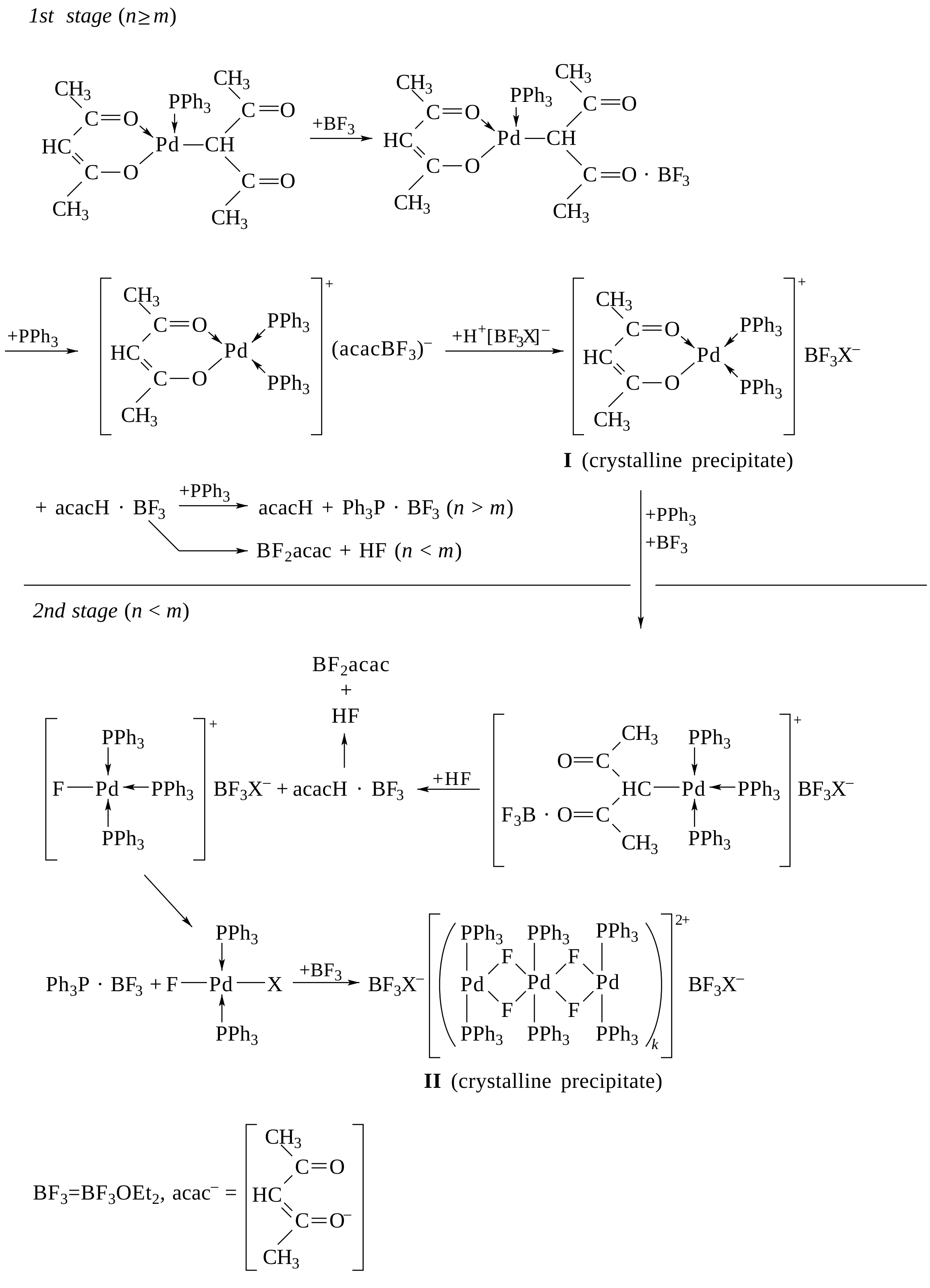
Fig. 2. UV spectra of (*1*) acetonitrile and the acetonitrile solutions of precipitates separated from the systems (*2*) $Pd(acac)(C^3\text{-}acac)PPh_3 + 2PPh_3 + BF_3OEt_2$ ($[Pd]_{initial}$ = 0.0045 mol/l; l = 0.0113 cm) and (*3*) $Pd(acac)(C^3\text{-}acac)PPh_3 + 2PPh_3 + 4BF_3OEt_2$ ($[Pd]_{initial}$ = 0.0045 mol/l; l = 0.0214 cm).

(solution over the precipitate) exhibited a long-wavelength wing of the band of PPh_3 (at 36000 cm^{-1}) and the wing of the band of the enol form of acetylacetone (at 37000 cm^{-1}). This spectrum did not contain an intense band at 34400 cm^{-1}, which is typical of BF_2acac (Fig. 1). The UV spectra of the precipitate solutions in acetonitrile exhibited an intense absorption band of PPh_3 (at 36000 cm^{-1}) and a weaker band of chelate rings (30300 cm^{-1}) (Fig. 2, spectrum *2*). The bands of the acetylacetonate chelate ring (1564 and 1520 cm^{-1}), a band of the BF_4^- anion (1033 cm^{-1}), and a group of bands of the coordinated triphenylphosphine (750–700 cm^{-1}) were detected in the IR spectra of precipitates. These data suggest that the interaction between the components of the reaction systems of group 1 results in the formation of complex **I**, which is precipitated (see the scheme). At the same time, acacH and BF_3, which remain in the solution, do not react with each other to form BF_2acac because of the appearance of the molecular complexes $PPh_3 \cdot BF_3$ with a much lower acceptor ability than that of BF_3OEt_2.

The UV spectra of the reaction systems with a relative excess of BF_3OEt_2 (group 2) within the first minutes from the onset of the interaction are characterized by changes similar to those described above. The absorption intensity increases at 37000 cm^{-1}, which corresponds to the formation of acacH, and in a region of 35000–30000 cm^{-1}, which corresponds to the formation of acetylacetonate anions and their complexes with BF_3. Moreover, an intense characteristic band of BF_2acac (34400 cm^{-1}) appeared (Fig. 3, spectra *1* and *2*). After 1–3 h, yellow crystalline precipitates occurred because of interactions in the reaction systems; the formation of these precipitates lasted for 24 h. The UV spectrum of the reaction mixture after precipitation contained an intense absorption band at 34400 cm^{-1} (Fig. 3, spectrum *3*). This absorption indicates the formation of a considerable amount of BF_2acac, the relative concentration of which varied from 34 ($n = 1$, $m = 2$) to 71–77% ($n = 1$, $m = 4$; $n = 3$, $m = 4$), as compared with the theoretically possible amount (Fig. 2). The UV spectra of acetonitrile solutions of isolated precipitates exhibited a medium-intensity band at 36000 cm^{-1} (PPh_3) and a more intense band at 25800 cm^{-1}, which is associated with transitions from occupied orbitals possessed by lone electron pairs of F and P atoms to unoccupied orbitals primarily localized at the Pd atom (Fig. 2, spectrum *3*). A band of the BF_4^- anion (1033 cm^{-1}) and a group of bands of coordinated triphenylphosphine in the region 750–700 cm^{-1} were detected in the IR spectra of the precipitates under study. We propose structure **II** (see Scheme 1) based on the parameters of IR and UV spectra and the elemental analysis of these precipitates. For the reaction systems of group 2, special experiments performed at higher concentrations of components with the formation of precipitates in considerable amounts confirmed all of the above spectral characteristics and structure **II**. Thus, with excess BF_3OEt_2 (reaction systems of group 2), both C^3-bonded and chelate acetylacetonate ligands are removed from palladium and transfer to boron to form BF_2acac. The resulting polynuclear complex of PdF_2 with PPh_3 also includes units containing $Pd^{2+}(BF_4^-)_2$.

Consequently, the relative concentrations of PPh_3 and BF_3OEt_2 dramatically affect the interaction between the components in the systems under discussion. In the systems with excess PPh_3, the first step of

$BF_3 + HX \longrightarrow H^+[BF_3X]^-$, when X = F, OH



Scheme 1.

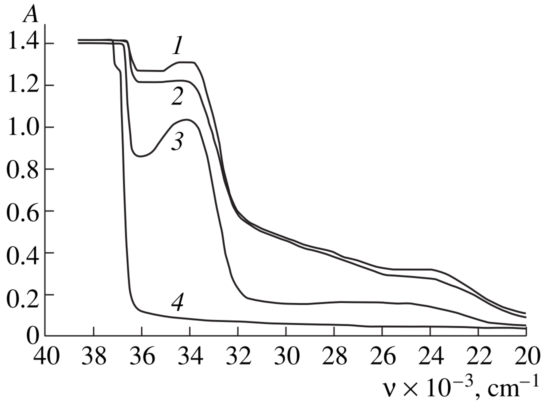


Fig. 3. UV spectra of a benzene solution of the system $Pd(acac)(C^3\text{-}acac)PPh_3 + 2PPh_3 + 4BF_3OEt_2$ (*1*) 5 min, (*2*) 1 h, and (*3*) 24 h after the onset of the process; (*4*) the UV spectrum of benzene.

this reaction takes place with the abstraction of the C^3-bonded acetylacetonate ligand and the formation of complex **I** and acacH. With excess BF_3OEt_2, the coordination of PPh_3 to palladium facilitates the abstraction of both C^3-bonded and chelate acetylacetonate ligands, and complex **II** and a considerable amount of BF_2acac are formed. Thus, the composition and structure of palladium complexes can be purposefully controlled by varying the ratio between PPh_3 and BF_3OEt_2, and the pathways for the formation of catalytically active systems can be chosen. For example, a high-performance catalyst for styrene dimerization was formed by the interaction between the components of the $Pd(acac)_2 + 2PPh_3 + 7BF_3OEt_2$ system. This catalyst made it possible to dimerize 75000 mol of styrene into 1,3-diphenyl-1-butene per 1 g-atom Pd in 7 h with up to 93% selectivity [3].

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