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Palladium(II)–acetylacetonate complexes containing phosphine and diphosphine ligands and their catalytic activities in telomerization of 1,3-dienes with diethylamine

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ABSTRACT

A series of novel $[Pd(acac\text{-}O,O')(P^{\wedge}P)]BF_4$ and known complexes $[Pd(acac\text{-}O,O')(PR_3)_2]BF_4$ ($P^{\wedge}P$ = dppm (**1**), dppp (**2**), dppb (**3**), dppf (**4**); R = Ph (**5**), *p*-Tol (**6**), *i*-Pr (**7**); acac = 2,4-pentanedionato) were prepared by the reaction of $[Pd(acac\text{-}O,O')(MeCN)_2]BF_4$ (**1**) with appropriate ligands. Complex **2** was characterized by single-crystal X-ray analysis. Models of the structure and IR wavenumbers assignments of the cations of **1**–**4** were obtained by DFT calculations. Synthesized complexes were tested as catalysts in the telomerization of isoprene and butadiene with diethylamine. In the case of telomerization of butadiene with diethylamine high catalyst activity (e.g. TOF_{av} = 1940 h^{-1} and TON up to 17,480 for complex 5) was obtained.

1. Introduction

Telomerization, linear dimerization of 1,3-dienes with simultaneous addition of a nucleophile in a catalytic reaction, is a very efficient "green" organic transformation with an overall atom economy of 100%. Since its discovery 45 years ago [1,2], telomerization has attracted significant interest due to its robustness and versatility in the production of a wide variety of valuable products. Easily available starting materials are converted in the presence of a catalyst in a 100% atom efficient manner to give functionalized octa-2,7-dienes. The resulting products have been used as intermediates in the total synthesis of several natural products, as well as precursors for plasticizer alcohols, industrial monomers, solvents, corrosion inhibitors, and non-volatile herbicides [3–12]. Complexes of palladium are known to effectively catalyze the reaction of dienes with a variety of nucleophiles. It is also known that the palladium catalyzed dimerization of butadiene-type substrates can take place, leading to linear or cyclic products, with chemoselectivity depending on nature of nucleophiles and ligands appended to the reactive palladium center [13–15].

The telomerization process has been intensively studied by many industrial and academic laboratories [1,2,16–27]. Studies of the mechanism by Jolly et al. have led to the generally accepted basic catalytic cycle (for methanol), which has been crucial for further development [28–31]. Very recently, a detailed DFT studies of Pd -catalyzed 1,3-butadiene (**BD**) telomerization of methanol was reported [13,15].

A series of palladium complexes with phosphines, diphosphines and NHC (NHC = *N*-heterocyclic carbene) ligands were reported for the telomerization of dienes with amines, water and alcohols [7,12,14,32–34]. Beller and co-workers [35–43] reported the most selective, active, and productive catalyst, an $(NHC)Pd^0$ complex. In particular, the best-known Pd-catalyst for butadiene telomerization of diethylamine gives TON of 17,800 mol_{BD}/mol_{Pd}, and TOF of 890 h^{-1} [36,37].

We reported that acetylacetonate-based cationic palladium complexes with triarylphosphine ligands, $[Pd(acac)(PAr_3)_2]BF_4$, can be used as very efficient precursors for the selective dimerization of styrene (to the best of our knowledge the highest catalyst turnover number ever reported for this reaction was achieved) [44].

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Complexes of such type can be obtained in different manner: a) by acetylacetonate ligand abstraction from $Pd(acac)_2$ with $[CPh_3]BF_4$, $NaBPh_4$, $HBF_4{\cdot}OEt_2$, CF_3SO_3H followed by further phosphine–ligand addition [45–48], b) by reaction of Pd(0) complexes with acetylacetone followed by addition of $[CPh_3]BF_4$ [49], c) by consecutive haloids displacement from starting palladium complex using Tl(acac) and $AgClO_4$ [50], or d) by acetonitrile displacement [51,52]. Only one example of use of $[Pd(acac)(PPh_3)_2]BF_4$ in the telomerization of isoprene with amines was reported [53b].

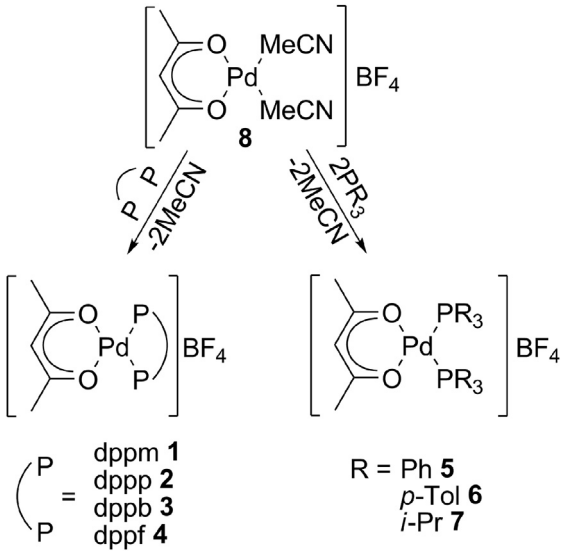
Here we report the results of synthesis of the novel palladium complexes $[Pd(acac)(P^{\frown}P)]BF_4$ ($P^{\frown}P$ = dppm, dppp, dppb, dppf) as well as results of $[Pd(acac)(PR_3)_2]BF_4$ or $[(acac)Pd(P^{\frown}P)]BF_4$-catalyzed telomerization of isoprene and butadiene with diethylamine.

2. Results and discussion

2.1. Complex synthesis

The synthetic procedures followed for the preparation of complexes **1**–**7** are summarized in Scheme 1. Methodology requires complex **8**, which can be prepared starting from $Pd(acac)_2$, MeCN and $HBF_4{\cdot}OEt_2$ [47]. The cationic complexes were prepared in near quantitative yields. The structures of compounds **1**–**4** have been confirmed by the usual techniques (^1H, ^{13}C, ^{31}P, and ^{11}B NMR, FTIR, and elemental analysis). Due to the insolubility in available solvents complex **1** was characterized only by means of FTIR and elemental analysis. Structural details and Gibbs free energy for the cations of complexes **1**–**4** were obtained by our ZORA-BP86 calculations (Table 1, Fig. 1). Comparison between observed and DFT-calculated IR wavenumbers for complexes **1**–**4** is presented in Table 2. In addition, the structure of compound **2** was also confirmed by single-crystal X-ray diffraction analysis.

Complex $[Pd(acac)(dppp)]BF_4$ (**4**) crystallizes from CH_2Cl_2/Et_2O as light-yellow conglomerates of crystals. It possesses C2/c space group with a = 28.8084(6) Å, b = 14.2418(3) Å, c = 15.7720(3) Å, and β = 94.919(1) Å. In the crystal structure there are cations $[Pd(acac)(dppp)]^+$ with Pd(II) in a square planar coordination (Fig. 2) and highly disordered BF_4^- anions. The DFT calculated structure (Table 1) agrees well with the experimental data (Fig. 2). The Pd–O and Pd–P distances in the complexes described in literature are given in Table 3. As can be seen, all calculated and



Scheme 1.

Table 1
DFT-calculated (ZORA-BP86) structural parameters (bond lengths, Å; angles, °) and Gibbs free energy (kcal/mol) of reactions (see Scheme 1) for the cations of **1**–**4**.

	1	2	3	4
$[Pd-O]_{av}$	2.06	2.07	2.07	2.07
$[Pd-P]_{av}$	2.29	2.30	2.31	2.33
P–Pd–P	74.4	94.4	94.4	98.8
O–Pd–O	92.5	91.3	91.2	90.8
ΔG	−34.8	−44.7	−44.3	−40.7

observed distances are in a good agreement with the corresponding values of known phosphine-acetylacetonate Pd complexes.

Synthesis of the complex $[Pd(acac)(dppe)]BPh_4$ was reported by Basato et al. [46,60]. In spite of DFT-calculated Gibbs free energy of acetonitrile exchange reaction by dppe was of the same value (−45.4 kcal/mol) as for other diphosphines, our attempts to prepare complex with the similar cation $[Pd(acac)(dppe)]BF_4$ failed. The reaction of **8** with dppe was performed in CH_2Cl_2, but the complex generated was unstable and decomposed upon workup. ^{31}P NMR spectrum of the reaction mixture showed signals at 25.8, 58.0, and 63.5 ppm which we assigned to the complex cations with following formal fragments: dppe-bridged $[Pd(\mu\text{-dppe})Pd]^{2+}$, dicationic $[Pd(dppe)]^{2+}$ and monocationic $[Pd(dppe)]^+$ respectively. For comparison ^{31}P NMR chemical shifts for $[Pd_2(\mu\text{-dppe})\{PPh(C_6H_4S)_2\}_2]$ is 20.9 ppm [61], for $[Pd(dppe)_2](OAc)_2$ is 58.7 ppm, and for $(OAc)_2Pd(dppe)$ is 63.4 ppm [62]. We assume that this is due to the transformation of $[(acac)Pd(dppe)]BF_4$ to ½Pd(acac)$_2$ and ½$[Pd(dppe)_2](BF_4)_2$ with formation of dppe-bridged by-product by analogy with data reported for $Pd(OAc)_2$ [62–64] and $Pd(dppe)Cl_2$ [65]. The nature of this phenomenon is the subject of special study.

2.2. Telomerization of 1,3-butadiene with diethylamine

In exploratory experiments using individual complex **5** as catalyst we discovered that addition of boron trifluoride etherate as co-catalyst is not required to obtain active catalyst, opposite to the results for dimerization of styrene [44]. Optimum temperature was found to be 70 °C, at higher temperature catalyst decomposition occurs. Palladium complexes **1**–**8** were tested in the model reaction of diethylamine with 1,3-butadiene (Scheme 2, Table 4). Even at very low catalyst concentration conversions up to 91.0% and excellent selectivity (99.9%) were observed with complex **7**. To our delight whatever the ligand present on the palladium, only the linear telomerization product is formed. Telomerizations of butadiene with secondary amines show considerably higher selectivity

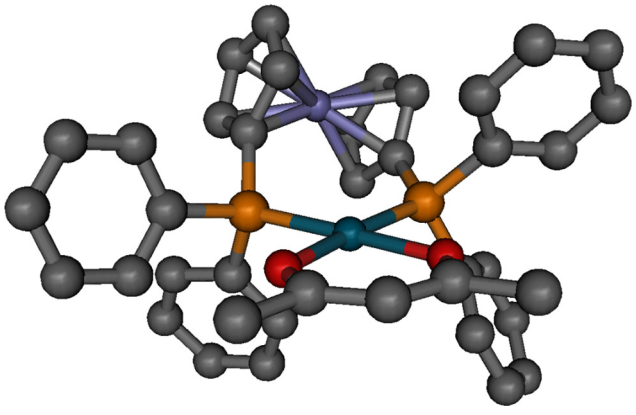


Fig. 1. Optimized structure for cation of complex **4**, hydrogen atoms are omitted for clarity.