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[Pd(acac)(L)₂][BF₄] (L = morpholine, diethylamine, dibutylamine, dioctylamine): synthesis, structure and their catalytic activity

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Abstract

Cationic acetylacetonate bis(secondary amine) palladium (II) complexes were synthesized by nitrile substitution of $[Pd(acac)(MeCN)_2][BF_4]$ with L (L = morpholine, diethylamine, dibutylamine, dioctylamine) which yielded $[Pd(acac)(L)_2][BF_4]$ as a mononuclear species with chelating acac ligand. An X-ray diffraction, NMR, IR and DFT study of $[Pd(acac)\{morpholine\}_2][BF_4]$ establishes the presence of hydrogen bonding between the morpholine ligand and $[BF_4]^-$ anion. Crystallographic defects in the crystal and presence of pseudocrystalline structure in solution of $[Pd(acac)(morph)_2][BF_4]$ were assumed to explain IR spectra features. Preliminary investigations into the polymerization of norbornene, dimerization of styrene, and telomerization of 1,3-butadiene with diethylamine were performed.

Keywords

Palladium, acetylacetonate, secondary amine, norbornene, 1,3-butadiene, styrene Introduction

The cationic palladium complexes are widely used as catalyst precursors in a variety of olefin transformations. Transition-metal-catalyzed olefin oligomerization and polymerization reactions constitute one of the most important industrial processes for forming polyolefins and α -olefins [1–4]. In the past decades, the late transition-metal palladium(II) and nickel(II) catalysts for olefin polymerization have attracted considerable attention in both the academic and industrial fields due to their low electrophilicity and more heteroatom tolerance [5–8]. Oligomerization (and polymerization) catalysis typically involves either a sensitive organometallic precursor or activators such as aluminum alkyls, usually with exclusion of air and water, with MAO being the activator of choice here [5,6]. Exceptions are cationic palladium-(II) complexes such [Pd(η^3 -allyl)(L)₂]Y (Y = BF₄, PF₆, SbF₆, BAF, etc) [9–16], [(L^L)PdMe(solv)]BAF (L^L= α -diimine, P^O, solv = MeCN, dmso) [5,17–20], [(α -diimine)Pd((CH₂)₃C(O)OCH₃)]BAF [5], [Pd(NCCH₃)₄](BF₄)₂ [11,21–23], [Pd(PPh₃)₃(NCCH₃)](BF₄)₂ [24,25], [(α -diimine)Pd(NCCH₃)₂][BF₄]₂ [26], [(α -diimine)Pd(μ -OH)]₂[BF₄]₂ [27], which require no cocatalyst for their activation toward olefins oligomerization and polymerization. Aluminum alkyls free cationic Pd-catalyzed systems with O⁻O-chelating ligands (O⁻O = β -diketonates or carboxylates) in combination with Lewis acids such as BF₃·OEt₂, In(OTf)₃ or Cu(OTf)₂ have shown promising results for oligomerization of ethylene [28], selective dimerization of styrene [29–33], polymerization of norbornene and its derivates [34–36].

Recently we reported synthesis of novel acetylacetonate cationic palladium complexes with mono-/bidentate phosphines, α -diimine and aniline ligands as well as the results of their usage as efficient precursors for the selective dimerization of styrene [33,37], telomerization of butadiene with diethylamine [38], polymerization of norbornene [37,39,40]. As part of our ongoing research in the field of late transition metals oligo-/polymerization catalysis, we describe here the synthesis of cationic palladium acetylacetonate complexes containing secondary amine ligands. Amines are ubiquitous ligands in transition-metal chemistry. They bind to metals in enzymes, classical coordination complexes, and organometallic compounds. In spite of their importance they were not often used in olefins oligo- and polymerization reaction as catalysts precursors. Compared to the large number of known bis(amine)palladium complexes, the palladium complexes that contain secondary amine ligands in *cis*-position are rare [41,42]. In order to examine the influence of the secondary amine structure on the catalytic properties, the addition polymerization of norbornene, dimerization of styrene, and telomerization of 1,3-butadiene with diethylamine with these complexes were also investigated.

1. Experimental Section

1.1. General procedures and materials

All air- and/or moisture-sensitive compounds were manipulated by using standard high-vacuum line, Schlenk, or cannula techniques under an argon atmosphere. Argon was purified before feeding to the reactor by passing through columns packed with oxygen scavenger (Fisher REDOX) and molecular sieve 5A (Aldrich), respectively. Diethyl ether, benzene and hexane were distilled from sodium-benzophenone. CH₂Cl₂, CH₃CN, diethylamine, morpholine, dibutylamine, and dioctylamine were distilled from CaH₂. Solvents were stored over molecular sieves. All glassware was dried for at least 3 h in a 150°C oven and cooled under an argon atmosphere. Styrene (99%, Aldrich) was purified by distillation under reduced pressure over CaH₂. Norbornene (Acros, 99%) were distilled from sodium-benzophenone and used as a solution (80 wt.%) in CH₂Cl₂. 1,3-butadiene (Aldrich, 98%) was used as received. BF₃·OEt₂ (Acros, 99%) was distilled over CaH₂ prior to use. Pd(acac)₂ was synthesized according to a literature procedure [43] and recrystallized from acetone. [Pd(acac)(MeCN)₂][BF₄] was prepared according to literature procedure [37]. All other reagents were obtained commercially and used as received. All NMR spectra were recorded at room temperature on Varian VXR-500S, Brucker DPX-250, or Brucker DPX-400 spectrometers. IR spectra were recorded on a Simex Infralum FT 801 spectrometer. TG/DSC measurements were performed with a Netzsch STA 449-F3 instrument. The products of the catalytic runs were analyzed by GC–MS (Shimadzu QP2010 Ultra, GSBP-5MS capillary column) and GC (Chromatec, Crystall 5000.2, SGE BPX-5 capillary column).

General procedure for catalytic telomerizations of 1,3-butadiene. Palladium complex (0.013 mmol) and phosphine ligand (0.013 mmol) were added in a dried and sealed vessel under argon. The stainless steel autoclave was cooled with liquid nitrogen and 4.2 g (78 mmol) of 1,3-butadiene was condensed (volume and mass control). Afterwards cold (-15°C) diethylamine (5.4 mL, 42.5 mmol) was added via syringe into the cooled (-10°C) autoclave and the vessel was heated to the desired reaction temperature. After 3 h the autoclave was cooled to room temperature and 1 mL of benzene as internal standard was added. In general, the yield of telomers was determined by GC. The main product was isolated from the reaction mixture via distillation and analyzed by GC-MS and ¹H,¹³C NMR.

General procedure for catalytic dimerization of styrene.

A mixture of the styrene (132 mmol), 1.3 mL of CH_2Cl_2 , 2 mL C_6H_6 (internal standard), and palladium complex (4.4 µmol) were placed in a 25 mL glass flask equipped with a magnetic stirring bar. Dimerizations were initiated by the injection of boron compound.The reaction was carried out at 50 °C for 5 h with stirring. The conversion and selectivity were determined by GC. The main product was isolated from the reaction mixture via distillation and analyzed by GC-MS and ¹H,¹³C NMR.

General procedure for catalytic polymerization of norbornene.

Polymerizations were carried out in a 10-mL glass reactor equipped with a magnetic stirrer. The reactor was filled with norbornene as a solution in CH₂Cl₂, the solution was kept at desired temperature for 15 min and then the palladium complex was added. Polymerizations were initiated by the injection of boron compound. After stirring for a time needed, the polymers formed were precipitated in ethanol. The precipitated polymers were washed three times with ethanol, and dried in vacuum at 80 °C for 6 h.

1.2. Syntheses of complexes

Preparation of [Pd(acac)(NHEt₂)₂][BF₄] (1)

[Pd(acac)(MeCN)₂]BF₄ (0.5618 g, 1.5 mmol) was added slowly to solution of diethylamine (0.33 mL) in CH₂Cl₂ (10 mL) and stirred at room temperature for 1 h. The reaction mixture was cooled to -18 °C and stored overnight. The solvent was removed in vacuo, and the yellow residue was washed twice with Et₂O and dried under vacuum. Yield: 0.5244 g (80%). Anal. Calcd for C₁₃H₂₉BF₄N₂O₂Pd: C, 35.60; H, 6.66; F, 17.33. Found: C, 35.61; H, 6.42; F, 17.56. ¹H NMR (400.1 MHz, CDCl₃): δ 1.56 (dd, *J* = 7.2 Hz, 12H, CH₃, NHEt₂), 2.00 (s, 6H, CH₃ , acac), 2.55 (dq, *J* = 7.1 Hz, 14 Hz, 4H, CH₂ , NHEt₂), 2.87 (dq, *J* = 7,2 Hz, 14.5 Hz, 4H, CH₂ , NHEt₂, 4.18 (br., 2H, NH, NHEt₂), 5.40 (s, 1H, CH, acac). ¹³C{¹H} NMR (100.7 MHz, CDCl₃): δ 14.27 (CH₃ , NHEt₂), 26.21 (CH₃ , acac), 47.23 (CH₂ , NHEt₂), 101.28 (CH, acac), 186.70 (C=O, acac). ¹⁹F NMR (376.3 MHz, CDCl₃): δ -150.12 (s, 1F), -150.17 (d, J=1.1 Hz, 4F) (BF₄, the integral ratio of the two signals is 1:4 equal to the ¹⁰B/¹¹B isotopic ratio, natural isotopic abundance: ¹⁰B/¹¹B=19.4%/80.6%). ¹¹B NMR (128.3 MHz, CDCl₃): δ -1.17 (BF₄). ¹⁵N NMR (40.5 MHz, CDCl₃): δ -364.65 (J = 71.7 Hz).

Preparation of [Pd(acac)(morph)₂][BF₄] (2)

[Pd(acac)(MeCN)₂]BF₄ (0.5618 g, 1.5 mmol) was added slowly to solution of morpholine (0.26 mL) in CH₂Cl₂ (10 mL) and stirred at room temperature for 1 h. The reaction mixture was cooled to -18 °C and stored overnight. The solvent was removed in vacuo, and the yellow residue was washed twice with Et₂O and dried under vacuum. Yield: 0.6300 g (90%). Anal. Calcd for C₁₃H₂₅BF₄N₂O₄Pd: C, 33.47; H, 5.40; F, 16.29. Found: : C, 33.79; H, 5.41; F, 17.43. ¹H NMR (400.1 MHz, CDCl₃): δ 2.06 (s, 6H, CH₃, acac), 3.01 (br.d., *J* = 12.7 Hz, 4H, H^e, α-CH₂ in morph), 3.22 (qd, *J*=12.2, 3.4 Hz, 4H, H^a, α-CH₂ in morph), 3.73 (dd, *J* = 12.4, 3.1 Hz, 4H, H^e, β-CH₂ in morph), 3.90 (td (br.), *J* = 12.0, 1.3 Hz, 4H, H^a, β-CH₂ in morph), 4.65 (br.(dd), *J* = 10.5 Hz, 2H, H^a, NH in morph), 5.48 (s, 1H, CH, acac). ¹³C{¹H} NMR (100.7 MHz, CDCl₃): δ 26.28 (CH₃, acac), 50.01 (α-CH₂ in morph), 66.64 (β-CH₂ in morph), 101.85 (CH, acac), 186.98 (C=O, acac). ¹⁹F NMR (376.3 MHz, CDCl₃): δ -148.26 (br., *J* = 2 Hz,

1F), -148.31 (d, J = 2.5 Hz, 4F) (BF₄, the integral ratio of the two signals is 1:4 equal to the ¹⁰B/¹¹B isotopic ratio, natural isotopic abundance: ¹⁰B/¹¹B=19.4%/80.6%). ¹¹B NMR (128.3 MHz, CDCl₃): δ -1.01 (br.qnt, J = 2 Hz, BF₄). ¹⁵N NMR (40.5 MHz, CDCl₃): δ -385.3 (J = 72.1 Hz).

Preparation of [Pd(acac){NH(n-Bu)₂}₂][BF₄] (3)

[Pd(acac)(MeCN)₂]BF₄ (0.5618 g, 1.5 mmol) was added slowly to solution of dibutylamine (0.53 mL) in CH₂Cl₂ (10 mL) and stirred at room temperature for 1 h. The reaction mixture was cooled to -18 °C and stored overnight. The solvent was removed in vacuo, and the yellow residue was washed twice with Et₂O and dried under vacuum. Yield: 0.5700 g (69%). Anal. Calcd for C₂₁H₄₅BF₄N₂O₂Pd: C, 45.79; H, 8.23; F, 13.80. Found: CC, 45.96; H, 7.91; F, 14.36. ¹H NMR (250 MHz, CDCl₃): δ 0.96 (dd, *J* = 7.27 Hz, 12H, CH₃, NHBu₂), 1.37 (m, 8H, γ-CH₂, NHBu₂), 1.85 (m, 4H, β-CH₂, NHBu₂), 1.99 (s, 6H, CH₃, acac), 2.22 (m, 4H, β-CH₂, NHBu₂), 2.40 (m, 4H, α-CH₂, NHBu₂), 2.76 (m, 4H, α-CH₂, NHBu₂), 4.22 (br., 2H, NH, NHBu₂), 5.42 (s, 1H, CH, acac). ¹³C{¹H} NMR (50 MHz, CDCl₃): δ 13.90 (CH₃, NHBu₂), 20.54 (γ-CH₂, NHBu₂), 26.20 (CH₃, acac), 31.22 (β-CH₂, NHBu₂), 52.98 (α-CH₂, NHBu₂), 101.36 (CH, acac), 186.63 (C=0, acac).

Preparation of [Pd(acac){NH(n-Oct)₂}₂][BF₄] (4)

[Pd(acac)(MeCN)₂]BF₄ (0.5618 g, 1.5 mmol) was added slowly to solution of dioctylamine (0.90 mL) in CH₂Cl₂ (10 mL) and stirred at room temperature for 1 h. The reaction mixture was cooled to -18 °C and stored overnight. The solvent was removed in vacuo, and the yellow residue was washed twice with Et₂O and dried under vacuum. Yield: 0.9300 g (80%). Anal. Calcd for C₃₇H₇₇BF₄N₂O₂Pd: C, 57.32; H, 10.01; F, 9.80. Found: C, 57.49; H, 10.21; F, 10.34. ¹H NMR (400.1 MHz, CDCl₃): δ 0.87 (dd, J = 6.5 Yz, 12H, CH₃, NHOct₂), 1.29 (br., 40H, γ-η-CH₂, NHOct₂), 1.86 (m, 4H, β-CH₂, NHOct₂), 1.99 (s, 6H, CH₃, acac), 2.24 (m, 4H, β-CH₂, NHOct₂), 2.38 (m, 4H, α-CH₂, NHOct₂), 2.74 (m, 4H, α-CH₂, NHOct₂), 4.22 (br, 2H, NH, NHOct₂), 5.42 (s, 1H, CH, acac). ¹³C{¹H} NMR (100.7 MHz, CDCl₃): δ 14.17 (CH₃, NHOct₂), 22.72 (η-CH₂, NHOct₂), 26.15 (CH₃, acac), 27.32 (ζ-CH₂, NHOct₂), 29.19 (ε-CH₂, NHOct₂), 29.29 (δ-CH₂, NHOct₂), 29.37 (γ-CH₂, NHOct₂), 31.89 (β-CH₂, NHOct₂), 53.24 (α-CH₂, NHOct₂), 101.25 (CH, acac), 186.56 (C=O, acac). ¹⁹F NMR (376.3 MHz, CDCl₃): δ –150.48 (br., 1F), –150.54 (s, 4F) (BF₄, the integral ratio of the two signals is 1:4 equal to the ${}^{10}B/{}^{11}B$ isotopic ratio, natural isotopic abundance: ${}^{10}B/{}^{11}B=19.4\%/80.6\%$). ¹¹B NMR (128.3 MHz, CDCl₃): δ –1.19 (br.qnt, I = 1.56 Hz, BF₄). ¹⁵N NMR (40.5 MHz, CDCl₃): δ-373.4 (*J* = 68.3 Hz).

1.3. Calculations

All density functional theory calculations were performed with the ORCA program.[44] All geometry optimizations were run with tight convergence criteria, using the BP86 functional,[45,46] making use of the resolution of the identity technique.[47] The applicability of gradient-corrected functionals as BP86 for the structural prediction of transition metal compounds and reliable determination of the kinetic balance are well documented [48–53]. The basis sets that were used were the Weigend–Ahlrichs basis sets [54,55]. Triple-ξ-quality basis sets with one set of polarization functions (def2-TZVP) were used for the palladium. The remaining atoms were described by slightly smaller def2-SVP basis sets. A scalar relativistic correction was applied using the zeroth-order regular approximation (ZORA) method [56–58]. Chemical shifts calculations were performed using IGLO-III (C, H, N, O) and def2-TZVPP basis sets.

1.4. X-ray Diffraction Studies

The diffraction data was collected on a Bruker X8Apex-II CCD diffractometer with MoK α radiation ($\lambda = 0.71073$ Å) by doing ω and φ scans of narrow (0.5°) frames at 296 K. The structure of [Pd(acac)(morph)₂]BF₄ was solved by direct methods and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2014/7 [59] in ShelXle program [60]. Absorption corrections were applied empirically with SADABS [61]. Crystallographic data and refinement details are given in Table 1, bond distances are summarized in Table S1. Further details may be obtained from the Cambridge Crystallographic Data Center on quoting the depository number CCDC 1510187. Copies of this information may be obtained free of charge from <u>http://www.ccdc.cam.ac.uk</u>.

Table 1

Crystal data			
Chemical formula	$C_{13}H_{25}BF_4N_2O_4Pd$		
M _r	466.56		
Crystal system, space group	Triclinic, <i>P</i> ⁻ 1		
Temperature (K)	296		
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.6812 (3), 9.8778 (3), 12.0872 (4)		
$\alpha, \beta, \gamma(^{\circ})$	68.380 (1), 80.563 (2), 80.062 (2)		
$V(\text{\AA}^3)$	943.39 (5)		
Ζ	2		
Radiation type	Μο Κα		
μ (mm ⁻¹)	1.04		

Experimental details for 2

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Crystal size (mm)	$0.20 \times 0.20 \times 0.15$		
Data collection			
Diffractometer	Bruker X8Apex		
Absorption correction	Multi-scan SADABS (Bruker-AXS, 2004)		
T_{\min}, T_{\max}	0.819, 0.860		
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	9237, 2883, 2686		
R _{int}	0.033		
θ _{max} (°)	23.9		
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.570		
Range of h, k, l	, $l \qquad h = -9 \rightarrow 9, k = -11 \rightarrow 11, l = -13 \rightarrow 13$		
Refinement			
$R[F^2 > 2\sigma(F^2)],$ wR(F ²), S	0.034, 0.099, 1.19		
No. of reflections	2883		
No. of parameters	268		
No. of restraints	12		
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement		
Weighting scheme	$w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0245P)^{2} + 2.8477P]$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3$		
$ \Delta\rangle_{\rm max}, \Delta\rangle_{\rm min} (e {\rm \AA}^{-3})$	0.71, -0.63		

Computer programs: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

2. Results and discussion

2.1. Synthesis and structure

 $[Pd(acac)(L)_2][BF_4]$ complexes **1-4** were prepared by following a similar procedure to that for the synthesis of $[Pd(acac)(NH_2Ar)_2][BF_4]$ complexes [40], combining the corresponding $[Pd(acac)(MeCN)_2][BF_4]$ with an slight excess of secondary amine ligand in CH_2Cl_2 at room temperature. After 2 h, removal of the solvent afforded the desired complexes as yellow solids, which were then washed with cold Et₂O. The complexes were characterized by NMR and EA.



The solid-state structure of **2** was determined by X-ray diffraction. Crystals of **2** were grown from CH₂Cl₂ solution by overlaying with Et₂O. An ORTEP plot of the asymmetric unit cell is reported in Figure 1. The crystallographic data, and structure refinement summary data for **2** are listed in Table 1 (see Experimental Section). The coordination around palladium center is square-planar with two O atoms ($d(Pd-O)_{av} = 1.995[4]$ Å) and two N atoms ($d(Pd-N)_{av} = 2.049[5]$ Å) of the organic ligands coordinated in a *cis*-geometry. The N–Pd–N bond angle (90.3°) show no angle deformation due to steric hindrance, and the O-Pd-O angle is 94.0°. The two coordination planes are almost exactly parallel, the dihedral angle being 1.2° only. Slightly disordered [BF₄]⁻ anions are in the second coordination sphere of Pd (d(Pd...B) = 5.329Å) between two morpholine ligands assuming the presence of hydrogen bonding between the NH group of the ligand and one of the fluorides attached to the [BF₄]⁻ anion. For comparison, in [Pd(acac)(dppp)][BF₄] the distance between Pd and B atoms is 9,319 Å [38], and anion is situated near phenyl ring of the diphosphine ligand.



Fig. 1. Crystal structure of **2** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



Fig. 2. Three-dimensional representations of the calculated structures of molecular models of **1** (a) and **2** (b).

To gain more insight into the structure of the cationic species, we performed DFT calculations for the **1** and **2**. Within the limits of the basis set employed, the optimized geometry of **2** in gas phase was good representation of the structure obtained from the crystallographic studies (Figure 2). Calculated molecular models of **1** and **2** consistently showed the [BF₄]⁻ anion in a F₃BF...H–N–Pd orientation. For **2** d(H1-F1) = 1,72 Å, d(H2-F1) = 1,82 Å, B1–F1...H1 = 99.3°, B1–F1...H2 = 93.4°, N1–H1...F1 = 157.3°, N2–H2...F1 = 151.3° are characteristic for hydrogen bonding and close to that encountered in the crystal structure of cationic acetylacetonate *bis*-aniline analogue [40]. In the model of complex **1**

two fluorine atoms interacts with NH hydrogen and d(H1-F1) = 1,73 Å и d(H2-F2) = 1,73 Å, B1-F1...H1 = 101.5°, B1-F2...H2 = 101.1°, N1-H1...F1 = 169.0°, N2-H2...F2 = 169.3°. Consequently, hydrogen atoms in **1** are out of NPdN plane by 19 and 16 degrees. The cation-anion interactions in **2** were assessed by stepwise assembly of the complex starting from the $[Pd(acac)(morph)_2]^+$ cation. The electronic energy difference between the product and the components from which the product was composed were calculated. Upon introduction of the charge-compensating anion a large drop in energy (ΔE_e of -110 kcal/mol) is gained with the formation of $[Pd(acac)(morph)_2][BF_4]$ from $[[Pd(acac)(morph)_2]^+$ and $[BF_4]^-$. Within the accuracy of the computational methods, further calculations indicated that the effect of hydrogen bonding on the ΔE_{e} of ion-pairing is marginal and the interaction with the anion must be electrostatic in nature. When solvent effects were included with the COSMO model with CHCl₃ as solvent, the ΔE_e of ionpairing was only -46 kcal/mol. The morpholine-anion interaction showed $\Delta E_{\rm e}$ of -21.7 and -15.0 kcal/mol in gas phase and CHCl₃ respectively. Calculations performed on H...F bonding between BF₃ and morpholine indicate that the energy associated with the formation of this bond is only -3 kcal/mol, which is characteristic for hydrogen-fluorine bonds [62].

Comparison of the ¹H NMR chemical shifts of the NH group from diethylamine ligand in known palladium complexes showed strong dependence on the anion nature (Table 2, from strongly coordinating to weakly coordinating anions). From the NMR spectra of **1**, the hydrogen bonding-induced shifts of the signals for the NH-protons of diethylamine (Table 2) and for fluorine atoms in [BF₄]⁻ (Table 3), are also indicative of a slight H...F interaction.

Table 2

Complex	Chemical shift, ppm	Reference
[Pd(acac)(NHEt ₂) ₂](acac)	7.1	[41]
[Pd(acac)(NHEt ₂) ₂]BF ₄	4.18	—
[Pd(dmpe)(Me)(NHEt ₂)]BF ₄	3.64	[63]
[Pd(dmpe)(Me)(NHEt ₂)]BPh ₄	2.66	[63]

Comparison of the ¹H NMR chemical shifts of the NH group in diethylamine ligand

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Table 3

Комплекс	Chemical shift, ppm	Reference
[Pd(acac)(PPh ₃) ₂][BF ₄]	-153.6	[64]
[Pd(acac)(MeCN) ₂][BF ₄]	-152.1	[37]
[Pd(acac)(NHEt ₂) ₂][BF ₄]	-150.2	
[Pd(acac)(morph) ₂][BF ₄]	-148.3	
$[Pd(acac){NH(n-Oct)_2}_2][BF_4]$	-150.5	R

Comparison of the ¹⁹F NMR chemical shifts of the anion [BF₄]-



Fig. 3. Coordination of morpholine with palladium in 2.

For non-coordinated morpholine (OC_4H_8NH), eight protons attached to carbon give two resonances at 2.9 ppm and 3.6 ppm [65], while spectra of 2 give four resonances as illustrated in Figure 4. There are four multiples characterized for eight coordinated morpholine protons attached to carbon (Figure 3). This is expected since upon coordination to palladium, one chair conformation of morpholine is fixed. Proton H^e_{α} interacts with germinal proton H^a_α ($^2J_{ae}$ = 12,7 Hz) and with 3 vicinal protons, H^a_β , H^a_N , H^e_β (with smaller coupling constants), therefore its resonance appears as broadened doublets at 3.01 ppm (Fig. 4). Because proton H^a_{α} interacts with H^e_{α} , H^a_{β} , H^a_{N} and H^e_{β} its resonance appears as a quartet of doublets centered at 3.22 ppm with ${}^{2}J_{ae}$, ${}^{3}J_{aa}$, ${}^{3}J_{aa(N)} \approx 12.2$ Hz and ${}^{3}J_{ae}$ = 3.4 Hz. Proton H_{β}^{e} interacts with germinal proton H_{β}^{a} (² J_{ae} = 12.4 Hz) and with 2 vicinal protons H^a_{α} and H^e_{α} (with ${}^{3}J_{ae} = 3,1$ Hz) giving a doublet of doublets or broadened doublets at 3.73 ppm. Proton H^a_β is coupled to H^e_β , H^a_α , H^a_N and H^e_β giving a triplet of doublets centered at 3.90 ppm with ${}^{3}J_{aa}$ = 12,0 Hz, ${}^{2}J_{ae} \approx$ 1,3 Hz. Comparing the 1 H NMR spectrum of **2** with the reported spectra of neutral platinum morpholine complexes [65] one can see some features. Chemical shifts of H_{β} (3.73, 3.90 ppm) are more downfield than those of H_{α} (3.01, 3.22 ppm), while for the neutral platinum morpholine complexes the shifts are reversed. These feature may be caused by the small interaction of beta protons with the $[BF_4]$ - anion in second coordination sphere of Pd(II). The same trend is observed for **1**.

Chemical shifts of beta protons in diethylamine ligand (1.56 ppm) is slightly downfield than those in non-hydrogen bonded [Pd(dmpe)(Me)(NHEt₂)]BPh₄ [63] (1.27 ppm) and in calculated cation of **1** ([1.28]_{*av.*} ppm, Table S2). ¹H and ¹³C NMR chemical shifts for **1** and **2** have been calculated using the BP86 and B3LYP functionals with IGLO-III/def2-TZVPP_{Pd} basis-set (Tables S2 and S3). Calculated chemical shifts were in good agreement with experimental data for both used functionals. Signals from NH-group of amines are shifted to low field due to the presence of hydrogen N–H...F bonds. For cation of complex **1** BP86 and B3LYP calculations showed δ (N-H) = 2.9 and 2.4 ppm respectively, which are similar to chemical shift reported for [Pd(dmpe)(Me)(NHEt₂)]BPh₄ complex with non-coordinating anion. As expected, upon introduction of the [BF₄]⁻ anion a major difference between resonance signals of NH protons of the molecular model of complex **1** (δ (NH) = 6.4 ppm) and its cation could be discerned.



Fig. 4. Fragment of ¹H NMR spectrum of 2

The IR spectra of complex **2** exhibit bands at 3260 (ν_1) cm⁻¹ and 3340 (ν_2) cm⁻¹ with peak intensity ratio of $A_1/A_2 \approx 15$. These bands are referred to the NH stretching vibrations of the ligand. Similar bands were observed in the spectrum of [(dmpe)Pd(Me)(NHEt₂)]BF₄ [63] (3264 cm⁻¹ μ 3384 cm⁻¹), and for [*trans*-(morph)₂Pd(OAc)₂] (3304 and 3173 cm⁻¹)

[66]. It is worth noting that the structure [66] of $trans-(morph)_2Pd(OAc)_2$] contains one crystallographically independent water molecule, which functions as a donor of two hydrogen bonds with the carboxyl oxygen atoms not coordinated to the metal and the acceptor of a hydrogen bond with the morpholine amino group. DFT calculations (BP86/def2-SVP_{C,H,N}/def2-TZVP_{Pd}) of vibrational spectra were used to elucidate the nature of these bands. The comparison of the experimental and calculated wavenumbers of the most intense vibrations and their assignment of complexes 1 and 2 are given in Tables S4-S7, respectively. It is seen from Tables S4-S7 that the experimentally measured vibrational wavenumbers of the species studied coincide well with the DFT theoretical predictions. Calculated NH bands wavenumbers (average) are 3253 cm⁻¹ (v_1) for **2** and 3357 cm⁻¹ (v_2) for its cation. Therefore, v_1 band refer to N-H...F bond vibrations which is offset by interaction with [BF₄]⁻. Subsequently, vibrational spectra of **2** were calculated with constrained Pd and B coordinates. The *l*(B-Pd) was varied from 4.5 Å to 6.5 Å, Table 4. During geometry optimization with l(B-Pd) = 6.0 Å and 6.5 Å one morpholine ligand is rotated ($\Delta E_{\rm e} \approx -10$ kcal/mol). In this case, NH bond is out of the N-Pd-N angle plane by 41.6° (l(B-Pd) = 6.0 Å) or 68.8° (l(B-Pd) = 6.5 Å). Furthermore, the experimental wavenumbers $v_1(N-H)$ and $v_2(N-H)$ are close to the calculated values with increasing B-Pd distance (Table S8). The results of the calculations can be summarized by assuming crystallographic defects in the crystal of **2**. In the obtained crystal of the complex [Pd(acac)(morph)₂][BF₄] in addition to the main structure, there are crystallographic defects, in which the anion [BF₄]⁻ is at greater distances from the cation than in primary structure (*l*(B-Pd) = 5,329 Å). This is also confirmed by the observation of only one band 3260 (v_1) cm⁻¹ in the IR spectrum of **2** in CH₂Cl₂. In addition, according to XRD two sets of coordinates were obtained for fluorine atoms in [BF₄]⁻ anion . In our opinion, this indicates the existence of two types $[BF_4]^-$ anions. Analysis of bond lengths and angles (Table S9) showed that the geometry of one of them were close to the tetrahedral.



Fig. 5. IR spectra of 0.05M [Pd(acac)(morph)₂]BF₄ in the range of 1000-1200 cm⁻¹ (KBr, 0.07 mm)

The IR spectrum of the crystal of complex **2** in the 1150–1000 cm⁻¹ range exhibited three bands from the antisymmetric stretching vibration of the tetrahedral anions. In an ideal tetrahedral anion these vibrations are triply degenerate and the IR spectrum should exhibit one band. In the crystal under the influence of the surrounding cations the anion tetrahedral symmetry is distorted. Accordingly, in the spectrum of **2** we observed three bands at 1118, 1083, and 1032 cm⁻¹. Moreover, distortion of idealized tetrahedral geometry of the anion [BF₄]⁻ leads to appearance in the spectrum of the symmetric stretching vibration at 785 cm⁻¹, forbidden in the infrared absorption spectrum. In the IR spectra of solution of **2** (MeCN, CH₂Cl₂) these three bands (1120, 1087, and 1036 cm⁻¹ in MeCN; 1121, 1082, and 1041 cm⁻¹ in CH₂Cl₂) were also registered. As can be seen from the IR spectra for the solution and the crystal of 2 (Figure 5) full bands width (L) at half maximum(A/2) are similar ($L_{crystal} = 123 \text{ cm}^{-1}$ and $L_{solution} = 102 \text{ cm}^{-1}$). Therefore, the pseudocrystalline structures are present in the solution of **2**, presumably consisting of a several pairs of cations and anions. The opposite is observed in the IR spectrum of model compound (NBu₄)BF₄ in CH₂Cl₂: only one band appeared at 1060 cm⁻¹. The FT-IR spectrum of (NBu₄)BF₄, recorded as Nujol mull, displays three bands (1099, 1050, and 1034 cm⁻¹). Full bands width (*L*) at half maximum(A/2) for solution and crystal of (NBu₄)BF₄ are rather different ($L_{crystal} = 104 \text{ cm}^{-1}$ and $L_{solution} = 55 \text{ cm}^{-1}$). This indicates that cation-anion interaction is disturbed whereby this vibration remains degenerate (Figure S1).

2.2. Catalysis

Telomerization of 1,3-butadiene with diethylamine. Telomerization, linear dimerization of 1,3-dienes with simultaneous addition of a nucleophile in a catalytic reaction, is a very efficient "green" organic transformation. Easily available starting materials are converted in the presence of a catalyst in a 100% atom efficient manner to The resulting products have been used as give functionalized octa-2,7-dienes 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 [67-69]. A series of palladium complexes with phosphines, diphospines and NHC (NHC = N-heterocyclic carbene) ligands were reported for the telomerization of 1,3butadiene (BD) with amines, water and alcohols [38,67,68,70-78]. In exploratory experiments using individual complexes 1-4 as catalysts we discovered that addition of tertiary phosphine is required to obtain active catalyst (Table 6), opposite to the results obtained previously for [Pd(acac)(NHEt₂)₂][BF₄] [42]. Even at very low catalyst concentration conversions up to 89.1% and excellent selectivity (99.9%) were observed with complex **3** in combination with P^iPr_3 . To our delight whatever the ligand present on the palladium, only the linear telomerization product is formed. The ligand structure is known to influence the product ratio in the telomerization reaction, but factors explaining the changes in chemo- and regioselectivity remained unraveled. For complex 3 with $P(OEt)_3$ ligand reduced yield was observed (Table 6).

Table 6

Telomerization of 1,3-butadiene with diethylamine

2 + NHEt ₂ $\xrightarrow{3/PR_3 (0.0013 \text{ mol}\%)}$ NEt ₂					
Entry	Catalyst ^[a]	Yield ^[b] , %	Selectivity ^[c] , %	TOF ^[d] , mol _{BD} /(mol _{Pd} ·h)	TON ^[d] , mol _{BD} /mol _{Pd}
1	1-4	0.3-0.9	99.9	~5-20	~20-60
2	3 +PPh ₃	85.7	99.9	1710	5140
3	3 +2PPh ₃	71.5	99.9	1430	4290
4	$3 + \mathbf{P}^n \mathbf{B} \mathbf{u}_3$	84.2	99.9	1680	5050
5	$3 + \mathbf{P}^{i}\mathbf{P}\mathbf{r}_{3}$	89.1	99.9	1780	5350
7	3 +P(OEt) ₃	54.2	99.9	1080	3250
8	$3+P^ptol_3$	84.3	99.9	1690	5060

^[a] Reaction conditions: BD:Pd = 6000, Et₂NH:Pd = 3270, 1.3·10⁻⁵ mol Pd (0.016 mol% with respect to 1,3-butadiene), 70°C, 3 h; ^[b] Yield of octa-2,7-dienyldiethylamine. ^[c]Selectivity toward octa-2,7-dienyldiethylamine. ^[d]Catalyst turnover frequency(number) with respect to BD

Styrene dimerization. Diverse Ni-, Co-, and Pd-catalyzed co- and heterodimerizations of ethylene and styrene have been developed. These new catalytic systems have been successfully applied to selective C–C bond formation [12,64,79–87]. Furthermore, enantioselective syntheses of commercial non-steroidal anti-inflammatory drugs such as ibuprofen, and the total syntheses of natural products with intricate methylbearing stereogenic centers have been reported using these catalytic systems. This reaction could be a test reaction to develop various co- and heterodimerization reactions [12]. In contrast to reactions with BD, complexes **1**-4 activated by treatment with BF₃·OEt₂ showed styrene oligomerization. Styrene was converted with $1-4/nBF_3$ ·OEt₂ highly chemo- and stereospecifically to the head-to-tail dimer (E)-1,3-diphenyl-1-butene as the exclusive dimerization product (Table 7). To investigate the effect of the amount of co-catalyst, a set of runs was carried out with the B/Pd ratios from 5 to 15 at 50°C. As one may see in Table 7, the conversion to dimers (selectivity) showed dramatic decrease due to cationic polymerization at higher ratios initiated by Lewis acid. The selectivity to dimers of 97% was obtained using **2** as catalyst with B/Pd molar ratio of 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 conversion of styrene with various amine ligands (entries 1, 4, 8, 12, Table 7) seems to be similar. However, the selectivity of the catalyst system was substantially affected by the nature of secondary amine. The highest selecivity was obtained with morpholine ligand and the lowest conversion was obtained with NH(ⁿOct)₂. As may be seen in Table 7, the order of the decrease in selectivity parallels the increasing basicity [88] (electronic effect). Apparently, the results indicate strongly that the amine molecule remains complexed to palladium during the catalytic reaction.

Table 7Dimerization of styrene

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	1-4 (0.)	0033 mol%)/BF 50°C, 5 h	F3·OEt2	
Entry ^[a]	Complex	[B] ₀ :[Pd] ₀	Selectivity ^[b] [%]	TON ^[c]
1	1	5	81	15200
2	1	10	70	25000
3	1	15	57	28400
4	2	5	93	10000
5	2	7	97	16500
6	2	10	87	17800
7	2	15	65	21800
8	3	5	71	13000
9	3	7	67	20000
10	3	10	62	25100
11	3	15	56	28000
12	4	5	63	16000

^[a] BF₃·OEt₂ as co-catalyst was used, 5 h, n_{Pd} = 4.4 µmol, 1.3 mL CH₂Cl₂ + 2 mL C₆H₆ (internal standard), t = 50°C ^[b] The crude products were analyzed by GC-FID. Trimers were also detected (GC-MS). ^[c] mol_{st}/mol_{Pd}.

Norbornene polymerization. Norbornene (NB) and its derivatives are representative cyclic olefin monomers which can be polymerized according to three different schemes: metathesis, addition and isomerization mechanisms. These features make norbornenes very attractive monomers for macromolecular design of polymers with required properties. Each polymerization mechanism leads to a polymer type that is different in structure and properties from the other. Palladium based catalysts usually polymerize norbornene via a vinyl addition mechanism. Vinyl polynorbornene (PNB) has received considerable attention owing to its optical, dielectric and mechanical properties for technical application [89]. The catalytic performance of 1-3 in the polymerization of norbornene in the presence of $25 \text{ eq } BF_3 \cdot OEt_2$ displayed moderate yields and activities in the order of $10^5 \text{ g}_{PNB} \text{ mol } Pd^{-1} \text{ h}^{-1}$ (Table 8). Obtained PNB were soluble in toluene and 1,2,4-trichlorobenzene. The structures of the Pd(II) complexes highly affected the molecular weights PNB, which increases with the increasing of basicity of amine ligands [88]. The palladium catalysts **4** with *n*-dioctylamine showed no activity in polymerization. Although

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different molecular weights were obtained, same NMR spectra were observed for those polynorbornenes [90]. Thermogravimetric analyses (TGA/DSC) of the polymers show typical high decomposition temperatures between 400–420°C.

Table 8

Polymerization of norbornene



Complex ^[a]	[B] ₀ /[Pd] ₀ ^[b]	Time [h]	Yield [%]	Activity ^[c]	$M_{\rm v}^{\rm [d]}$
1	25	4	56	1.3·10 ⁵	2.3
2	25	4	51	1.2·10 ⁵	1.2
3	25	4	31	$0.7 \cdot 10^{5}$	3.5
4	25	4		_	

^[a] $V_0 = 10$ mL, CH₂Cl₂, [NB]₀/[Pd]₀ = 10000, t = 25 °C, $n_{Pd} = 1.33 \mu mol$; ^[b] BF₃·OEt₂ as cocatalyst was used; ^[c] In units of (g of PNB) (mol of Pd)⁻¹ h⁻¹; ^[d] M_v ·10⁻⁶, obtained by capillary viscosimetry in 1,2,4-trichlorobenzene using the Mark–Houwink coefficients $\alpha =$ 0.56, $K = 7.78 \cdot 10^{-4}$ dL/g [91,92]

Conclusions

New cationic palladium complexes containing secondary amine ligands were prepared in good yields. An X-ray diffraction, NMR, IR and DFT study of $[Pd(acac)(morph)_2][BF_4]$ establishes the presence of hydrogen bonding between the morpholine ligand and $[BF_4]^-$ anion. We assume that in the obtained crystal of $[Pd(acac)(morph)_2][BF_4]$ in addition to the main structure, there are crystallographic defects, in which the anion $[BF_4]^-$ is at greater distances from the cation than in primary structure. IR spectroscopy study showed that the ion-associates are present in the solution of $[Pd(acac)(morph)_2][BF_4]$, presumably consisting of a several pairs of cations and anions. The tests of the $[Pd(acac)(L)_2]BF_4$ (L = morpholine, diethylamine, dibutylamine, dioctylamine) complexes as catalyst in the polymerization of norbornene, dimerization of styrene, and telomerization of 1,3-butadiene with diethylamine showed their moderate activities in these reactions. The reported study was funded by RFBR, according to the research project No. 31 16-33-60115\15 mol_a_dk.

Supporting Information. Calculated and experimental NMR, IR spectral data, Cartesian coordinates for the calculated species, and crystallographic data for **2** (in CIF format).

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- New acetylacetonate bis(secondary amine) palladium (II) complexes were synthesized
- XRD/IR/NMR/DFT studies shows hydrogen bonding between the amine ligands and [BF₄]⁻
- Presence of pseudocrystalline structure in solution of complexes were assumed
- Complexes are active in the telomerization of 1,3-butadiene with diethylamine
- Complexes are active in the polymerization of norbornene, dimerization of styrene