

Communication

An effective route for the synthesis of cationic palladium complexes of general formula $[(\text{Acac})\text{PdL}^1\text{L}^2]^+\text{A}^-$

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Abstract

A series of palladium complexes of general formula $[(\text{Acac})\text{PdL}^1\text{L}^2]^+\text{A}^-$, where $\text{L}^1, \text{L}^2 =$ phosphines and $\text{A} = \text{BF}_4, \text{CF}_3\text{SO}_3$, were synthesized. Preliminary studies show that the complexes are active in selective dimerization of styrene and addition polymerization of norbornene.

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Keywords: Boron trifluoride; Dimerization; Palladium; Styrene; Norbornene; Polymerization

1. Introduction

The cationic palladium complexes are widely used as catalyst precursors in a variety of olefin transformations. For more than 50 years palladium compounds have been intensively used as active and selective catalysts for reactions of many difficult substrates providing new useful synthetic organic products. Halide abstraction from neutral halide complexes in the presence of a weakly coordinating ligand represents a general route to palladium cationic complexes [1]. Systems on the basis on $\text{Pd}(\text{Acac})_2$ (where $\text{Acac} =$ acetylacetonate) and BF_3OEt_2 are very promising catalysts for selective oligomerization of vinyl monomers, the polymerization of norbornene and its derivatives as well as the telomerization of butadiene with amines [2–4].

We recently reported on mechanistic study on the interactions between $\text{Pd}(\text{Acac})_2$, PPh_3 and BF_3OEt_2 [5]. As a

key intermediate complex **1** was identified by IR spectroscopy (Scheme 1).

The existence of intermediate **1** is supported by isolation of complex $[(\text{Acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4$ (**2**) which is produced upon addition of 1 equiv. of PPh_3 to the reaction mixture.

We report here the synthesis of the cationic palladium complexes of general formula $[(\text{Acac})\text{PdL}^1\text{L}^2]^+\text{A}^-$, where $\text{L}^1, \text{L}^2 =$ phosphines and $\text{A} = \text{BF}_4$ or CF_3SO_3 . The compounds were characterized by elemental analysis, IR, ^1H , ^{13}C , ^{11}B , ^{19}F and ^{31}P NMR spectroscopy. Preliminary studies showed that the complexes are active in polymerization of norbornene and selective dimerization of styrene.

2. Results and discussion

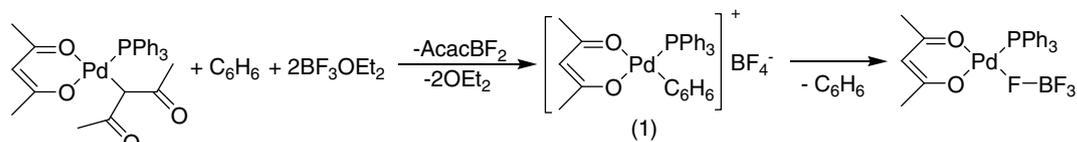
2.1. Complexes

The basic principle for the synthesis of the cationic palladium complexes are shown in Eqs. (1)–(4) presented in Scheme 2.

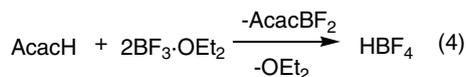
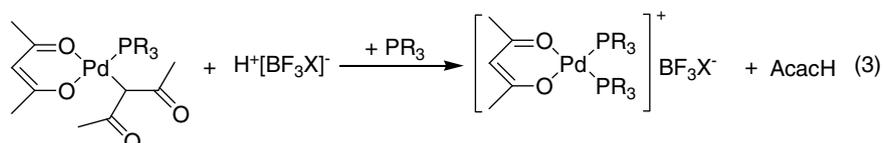
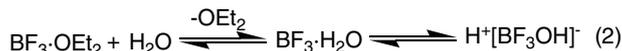
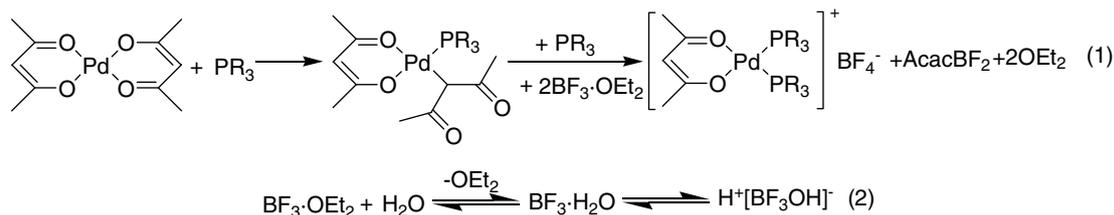
In Scheme 2, HBF_3OH , the product of intermolecular interaction between BF_3 and trace amounts of water in

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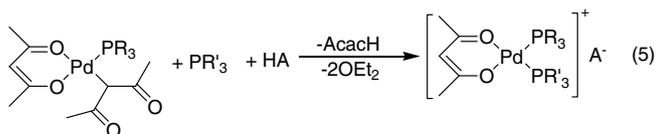
Scheme 1.

Scheme 2. R = Ph, *o*-CH₃C₆H₄, *p*-CH₃C₆H₄, *o*-CH₃OC₆H₄; X = F, OH.

the solvent (Eq. (2)), initiates the protolysis of the Pd–C bond (Eq. (3)). The formed AcacH reacts with BF₃OEt₂ to give HBF₄ (Eq. (4)) which continues the further protolysis (Eq. (3)). The procedure of protonation and removing of acetylacetonate ligand from co-ordination sphere of palladium is not new. This process has been already observed during kinetic studies [6] and in preparation of some complexes [(Acac)PdL₂]BF₄ by interaction of Pd(Acac)₂ with [Ph₃C]BF₄ [7] or with HBF₄OEt₂ [8] followed by addition of L.

In our case the general synthetic procedure includes addition of 2 equiv. of BF₃OEt₂ to a benzene solution of 1 equiv. of Pd(Acac)₂ and 2 equiv. of PR₃. Solid complexes **2**, **3**, **4**, **5** were isolated as yellow or orange crystals in about 90% yields.

A route for the synthesis of complexes with diverse ligands and anions is shown in Eq. (5). Complexes **5** and **6** were synthesized in this manner and obtained as powders in nearly 95% yield. One equivalent of a Brønsted acid (HBF₄OEt₂ or HSO₃CF₃) was added into a benzene solution of an equimolar mixture of Pd(Acac)₂ · PPh₃ and PR₃.

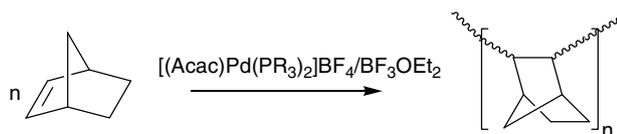
R = Ph, cyclohexyl; A = BF₄, CF₃SO₃

2.2. Catalytic activity of the complexes

Complexes **2**, **3**, **4**, **5** activated with boron trifluoride etherate were used as catalysts in the addition polymerization of norbornene and selective styrene dimerization. Preliminary experiments were made to check the activity for each of two components of the system, namely complex **2** and BF₃OEt₂ at 60 °C. Complex **2** showed no activity in styrene and norbornene transformations. Run with an amount of BF₃OEt₂ corresponding to B/Pd = 25 ratio at 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 for cationic initiators. No polymeric products were observed when norbornene was used as substrate at the same conditions.

Styrene could be dimerized to a mixture of *trans*- and *cis*-1,3-diphenyl-1-butenes in the presence of the [(Acac)-Pd(PR₃)₂]BF₄ + 5BF₃OEt₂ catalyst system. GC analysis showed that the dimers consist of the *trans*-stereoisomer up to 95% and the content of the *cis*-isomer is up to 5%. IR spectroscopy analysis also proved the existence of both isomers exhibiting bands at 965 and 910 cm⁻¹ attributable to δ_{C–H} vibrations at the double bond in *trans* and *cis* structures, respectively [9]. The molar mass of the dimer product (*m/z* = 208) was confirmed by the mass spectrometry. The ¹H and ¹³C NMR spectra of the dimer products are identical to those described in Ref. [10], indicating 1,3-diphenyl-1-butene is the main product.

Norbornene (bicyclo[2.2.1]hept-2-ene) and its derivatives can be polymerized via ring-opening metathesis (ROMP), olefin addition polymerization and also cationic or radical polymerization [11]. The increasing interest in the addition polymerization of norbornene (bicyclo[2.2.1]hept-2-ene) and its derivatives is due to the attractive properties of these polymers, which show high glass transition temperatures, high optical transparency, low dielectric constant and low birefringence [12]. Therefore the addition polymers of norbornene and its derivatives are attractive materials for the manufacture of microelectronic and optical devices. The $[(\text{Acac})\text{Pd}(\text{PR}_3)_2]\text{BF}_4 + 25\text{BF}_3\text{OEt}_2$ system catalyzes the polymerization of norbornene via the vinyl-addition route:



The ^{13}C NMR and IR spectroscopy data of the polynorbornene obtained showed 2,3-enchaind repeating units of polymer backbone.

The data on the dimerization of styrene and polymerization of norbornene using palladium cationic complexes **2–5** as catalyst precursors are shown in Table 1.

The phosphine ligand has a profound influence on both the activity and selectivity of transition metal catalyst systems. Tolman [13] reviewed the effects of phosphine ligands on reactions or properties of metal complexes for the first time and they were rationalized in terms of electronic and steric effects. Quantitative measures of electronic and steric effects were based on A_1 carbonyl stretching frequencies (ν) in $\text{Ni}(\text{CO})_3\text{L}$ complexes and ligand cone angles (θ) of space-filling CPK models [13]. The values of TON and TOF in the styrene dimerization and norbornene polymerization (Table 1) are better correlated with the electronic properties of phosphines than with their steric properties. Reasonable explanation of this phenomenon might be that the phosphines with higher electron-donor properties, such as $\text{P}(o\text{-CH}_3\text{OC}_6\text{H}_4)_3$, enhance the electron density on the

metal center, thus disfavoring the coordination and transformation of substrate. In the case of **5** in the presence of an excess of BF_3OEt_2 a formation of cationic Pd complexes with chelate $\text{P}(o\text{-CH}_3\text{OC}_6\text{H}_4)_3$ ligands is also possible and is a subject of special studies.

3. Experimental

3.1. Materials

All reactions were carried out under argon or nitrogen using standard Schlenk techniques. Reagent grade chemicals were purchased from commercial suppliers and used as received unless otherwise stated. $\text{Pd}(\text{Acac})_2$ was additionally recrystallized from acetone. $\text{Pd}(\text{Acac})_2\text{PPh}_3$ was prepared according to the literature [14]. Inert gases were purified before feeding to the reactor by passing them through columns packed with oxygen scavenger (Fisher REDOX) and molecular sieves 5A (Aldrich), respectively. 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 and norbornene (99%, Aldrich) were distilled over sodium/potassium alloy (NaK). Methanol was dried over Mg.

3.2. Physical measurements

The IR spectra of suspensions of the complexes in Nujol were recorded on the Specord M-80 spectrometer in KBr cell. The IR spectra for polymer samples were recorded using a KBr pellet technique with a Nicolet Fourier transform infrared (FT-IR) spectrometer. The NMR spectra were recorded on a Varian VXR-500S spectrometer. NMR tubes were filled in argon atmosphere. Viscosity measurements were carried out in 1,2,4-trichlorobenzene at 25 °C using Ubbelohde viscometer. Calorimetric analysis was done using a DSC Q100 instrument. Gas chromatography (GC) analyses were performed on a “Chrom-5” instrument (3.7 m column, SE-30 phase, nitrogen carrier gas, $T = 240$ °C).

Table 1

Dimerization of styrene and polymerization of norbornene over $[(\text{Acac})\text{Pd}(\text{PR}_3)_2]\text{BF}_4 + n\text{BF}_3\text{OEt}_2$ catalyst system

Complex	Styrene dimerization ^a			Norbornene polymerization ^b			Electronic and steric properties of PR_3		
	TOF (h^{-1})	TON (mol Pd/mol styrene)	Composition (mass %)		Activity (kg NB/(mol Pd · h))	Yield (g)	$[\eta]$ (dL/g)	ν (cm^{-1})	θ (°)
			Dimers	Trimers					
2	13500	66225	93	7	5500	2.8	0.68	2068.9	145
3	12900	62690	93	7	5300	2.7	0.63	2066.6	194
4	11200	55670	93	7	4000	2.05	0.50	2066.7	145
5			Traces	Traces		Traces		2058.6	194

^a Experimental conditions: $[\text{Pd}] = 3.7 \times 10^{-6}$ mol, B/Pd = 5, styrene/Pd = 120000, 6 h, 70 °C.

^b Experimental conditions: $[\text{Pd}] = 1 \times 10^{-6}$ mol, B/Pd = 25, norbornene/Pd = 38000, 60 °C, 3.8 g of norbornene, total volume of 7 ml, 30 min.

3.3. Preparation of [(Acac)Pd(PPh₃)₂]BF₄ (2)

BF₃OEt₂ (0.41 ml, 3.282 mmol) was dropped into a solution of Pd(Acac)₂ (0.5000 g, 1.641 mmol) and PPh₃ (0.8611 g, 3.282 mmol) in 40 ml of benzene. A lemon-yellow crystalline solid began to precipitate during the addition. The solid was filtered, washed with benzene and dried *in vacuo* (91% yield). M.p. 174–176 °C. ¹H NMR (acetone-*d*₆), δ 1.5 [s, 6H, –CH₃ of Acac], 5.6 [s, 1H, –CH of Acac], 7.2–7.8 [m, 30H, –PPh₃]; ¹³C NMR (acetone-*d*₆), δ 27.5 [–CH₃ of Acac], 102.3 [–CH of Acac], 128–136 [–PPh₃], 188.4 [–C=O]; ¹⁹F{¹H} NMR (CD₂Cl₂) δ –153.51 [s, 1F], –153.56 (s, 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 (acetone-*d*₆) δ –0.56 [BF₄, quintet, 1:4:6:4:1, J_{B-F} = 1.1 Hz]; ³¹P{¹H} NMR (acetone-*d*₆) δ 36.0 [–PPh₃]. IR (cm^{–1}) 1523, 1565 [C=C and C=I bonds in Acac group]; 1590 [C=C bond of benzene ring]; 1465, 1478 [CH₃– of Acac group]; 1020–1150 [BF₄]; 730; 750; 960; 980 [C–H bonds of benzene ring]; 511; 522; 543 [deformation vibrations of P–C bonds and benzene ring]. Anal. Calc. for C₄₁H₃₇BF₄O₂P₂Pd: Pd, 13.0; C, 60.3; H, 4.5; P, 7.6; B, 1.35; F, 9.3. Found: Pd, 12.8; C, 61.2; H, 4.3; P, 7.1; B, 1.1; F, 8.25%.

3.4. Preparation of [(Acac)Pd(P(*o*-CH₃C₆H₄)₃)₂]BF₄ (3)

BF₃OEt₂ (0.41 ml, 3.282 mmol) was dropped into a solution of Pd(Acac)₂ (0.5000 g, 1.641 mmol) and P(*o*-CH₃C₆H₄)₃ (0.9991 g, 3.282 mmol) in 40 ml of benzene. An orange crystalline solid began to precipitate during the addition. The solid was filtered, washed with benzene and dried *in vacuo* (90% yield). M.p. 194–196 °C. ¹H NMR (acetone-*d*₆), δ 1.5 [s, 6H, –CH₃ of Acac], 2.4 [s, 18H, –CH₃ in benzene ring], 5.5 [s, 1H, –CH of Acac], 7.2–7.6 [m, 24H, protons in benzene ring]; Anal. Calc. for C₄₇H₄₉BF₄O₂P₂Pd: Pd, 11.8; C, 62.7; H, 5.5. Found: Pd, 12.0; C, 63.0; H, 5.8%.

3.5. Preparation of [(Acac)Pd(P(*p*-CH₃C₆H₄)₃)₂]BF₄ (4)

BF₃OEt₂ (0.41 ml, 3.282 mmol) was dropped into a solution of Pd(Acac)₂ (0.5000 g, 1.641 mmol) and P(*p*-CH₃C₆H₄)₃ (0.9991 g, 3.282 mmol) in 40 ml of benzene. A yellow crystalline solid began to precipitate during the addition. The solid was filtered, washed with benzene and dried *in vacuo* (92% yield). M.p. 185–190 °C. ¹H NMR (acetone-*d*₆), δ 1.5 [s, 6H, –CH₃ of Acac], 2.4 [s, 18H, –CH₃ in benzene ring], 5.5 [s, 1H, –CH of Acac], 7.2–7.6 [m, 24H, protons in benzene ring]; Anal. Calc. for C₄₇H₄₉BF₄O₂P₂Pd: Pd, 11.8; C, 62.7; H, 5.5. Found: Pd, 11.4; C, 62.2; H, 5.3%.

3.6. Preparation of [(Acac)Pd(P(*o*-CH₃OC₆H₄)₃)₂]BF₄ (5)

BF₃OEt₂ (0.41 ml, 3.282 mmol) was dropped into a solution of Pd(Acac)₂ (0.5000 g, 1.641 mmol) and P(*o*-CH₃-

OC₆H₄)₃ (1.1569 g; 3.282 mmol) in 40 ml of benzene. An orange-yellow crystalline solid began to precipitate during the addition. The solid was filtered, washed with benzene and dried *in vacuo* (89 % yield). M.p. 125–127 °C. ¹H NMR (acetone-*d*₆), δ 1.5 [s, 6H, –CH₃ of Acac], 3.8 [s, 18H, –OCH₃ in benzene ring], 5.5 [s, 1H, –CH of Acac], 7.2–7.6 [m, 24H, protons in benzene ring]. Anal. Calc. for C₄₇H₄₉BF₄O₈P₂Pd: Pd, 10.7; C, 56.6; H, 5.0. Found: Pd, 10.4; C, 57.1; H, 4.8%.

3.7. Preparation of [(Acac)Pd(PPh₃)₂]CF₃SO₃ (6)

HCF₃SO₃ (0.144 ml, 1.641 mmol) was dropped into a solution of Pd(Acac)₂ · PPh₃ (0.9303 g, 1.641 mmol) and PPh₃ (0.4306 g, 1.641 mmol) in 40 ml of benzene. An orange crystalline solid began to precipitate during the addition. The solid was filtered, washed with benzene and dried *in vacuo* (95% yield). M.p. 165–167 °C. ¹H NMR (acetone-*d*₆), δ 1.5 [s, 6H, –CH₃ of Acac], 5.6 [s, 1H, of –CH Acac], 7.2–7.8 [m, 30H, –PPh₃]; ¹⁹F{¹H} NMR (CDCl₃) δ –78.5 [s, CF₃SO₃]. Anal. Calc. for C₄₂H₃₇F₃O₃P₂SPd: C, 57.4; H, 4.2. Found: C, 57.9; H, 4.8%.

3.8. Preparation of [(Acac)Pd(PPh₃)(PCy₃)]BF₄ (7)

HBf₄ · OEt₂ (0.225 ml, 1.641 mmol) was dropped into a solution of Pd(Acac)₂ · PPh₃ (0.9303 g, 1.641 mmol) and PCy₃ (0.4600 g, 1.641 mmol) in 40 ml of benzene. A yellow crystalline solid began to precipitate during the addition. The solid was filtered, washed with benzene and dried *in vacuo* (93% yield). ¹H NMR (CD₂Cl₂), δ 1.0–2.2 [m, 33H, P(C₆H₁₁)₃], 1.3 [s, 3H, –CH₃ of Acac], 2.1 [s, 3H, –CH₃ of Acac], 5.5 [s, 1H, –CH of Acac], 7.2–7.8 [m, 15H, PPh₃]; ³¹P{¹H} NMR (CD₂Cl₂) δ 36.1 [d, 1P, J_{P-P} = 30 Hz, PPh₃], 47.1 [d, 1P, J_{P-P} = 30 Hz, PCy₃]. Anal. Calc. for C₄₁H₅₅BF₄O₂P₂Pd: C, 59.0; H, 6.6. Found: C, 59.1; H, 6.6%.

3.9. Dimerization of styrene

Dimerizations were carried out in a glass reactor equipped with a magnetic stirrer under nitrogen or argon atmosphere without a solvent. The reactor was evacuated and filled with inert gas, and then styrene and palladium precursor were added. 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 the desired temperature. After stirring for a time needed, the reaction was terminated and styrene dimers were isolated by vacuum distillation (130 °C/1.3 × 10^{–2} Torr).

3.10. Polymerization of norbornene

Polymerizations were carried out in a 10 ml glass reactor equipped with a magnetic stirrer. The reactor was evacu-

ated and filled with nitrogen, and then a toluene solution of norbornene was added. The solution was kept at the desired temperature for 15 min and a solution of **2** in toluene:nitromethane (80:20% vol.) was added. Polymerizations were initiated by the injection of the boron compound. After stirring for a time needed, the polymers formed were precipitated in acidified ethanol. The precipitated polymers were washed three times with ethanol, and dried *in vacuo* at 80 °C for 6 h. Polymerization runs were carried out at least three times to ensure reproducibility. The IR spectra of polymers show the absence of any double bond absorbance at 1620–1680 cm⁻¹ and exhibit a strong absorbance at 1452–1474 cm⁻¹ due to $\delta_{\text{H-C-H}}$ stretching modes of bridging CH₂ groups. Disappearance of these peaks would definitely indicate the formation of 2,7-enchaind polymer units [15,16]. Assignment of methylene and methine ¹³C NMR resonances of the polymers was made using DEPT editing of the ¹³C NMR spectrum. ¹³C NMR (1,2,4-trichlorobenzene), δ 31.0, 32.5, 36 and 38 and [-CH groups], 20, 23.5 and 27 [-CH₂ non-bridging groups], 30–32, 32.6, 36.5 [-CH₂ bridging group]. The DSC and TGA analyses of the polynorbornene were carried out for representative samples with various intrinsic viscosities. The glass transition temperatures are about 310 °C. The polymer samples decomposed in the range from 400 to 410 °C.

Acknowledgements

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