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Short communication

Cationic palladium(II)–acetylacetonate complexes bearing α-diimine ligands as catalysts in norbornene polymerization

D.S. Suslov [a], M.V. Pahomova [a], P.A. Abramov [b,c], M.V. Bykov [a], V.S. Tkach [a,*]

[a] Irkutsk State University, ul. K. Marksa, 1, Irkutsk 664003, Russia
[b] Nikolaev Institute of Inorganic Chemistry SB RAS, pr-kt Akad. Lavrentieva, 3, Novosibirsk 630090, Russia
[c] Novosibirsk State University, ul. Pirogova, 2, Novosibirsk 630090, Russia

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ABSTRACT

A variety of palladium(II)–acetylacetonate complexes bearing α-diimine ligands were synthesized by the reaction of $[Pd(acac)(MeCN)_2]BF_4$ with N N ligands. When activated with $BF_3 \cdot OEt_2$, these complexes provide access to a new class of alkylating agent free Pd–diimine catalyst systems. Catalyst screening for the vinyl addition polymerization of norbornene showed their high activities of 10^2–10^4 $kg_{pol}\ mol_{cat}^{-1}\ h^{-1}$.

1. Introduction

In the past decades, late-transition metal catalysts for olefin polymerization have attracted considerable attention in both the academic and industrial fields [1–3]. This was sparked by the discovery of Brookhart and coworkers in 1995 that α-diimine complexes of palladium(II) and nickel(II), after activation with methylaluminoxane, provide very active catalysts for the production of high-molecular-weight polyolefins [4]. Since this discovery, numerous palladium(II) complexes with α-diimine ligands have been prepared and the ability to produce polyolefins with various types of branches and copolymers with a variety of polar-functionalized olefin was explored [5–14]. Their higher tolerance of polar functional groups in the monomer has since been recognized as a key advantage over early transition metal catalyst systems, and much effort has thus been devoted to the design of new ligand frameworks for improved catalyst performance.

Polymerization (and oligomerization) by Pd–α-diimine based catalysts typically involves either a sensitive organometallic precursor (Fig. 1b, c) or activators such as aluminum alkyls or perfluoroaryl boranes (Fig. 1a), and hence must be carried out under carefully controlled conditions, usually with exclusion of air and water [1,2]. Boron trifluoride etherate, $BF_3 \cdot OEt_2$, has emerged as a simple but effective activator that is relatively inexpensive and easy to use. In particular, palladium catalytic systems with O O-chelating ligands (O O = β-diketonates or carboxylates) activated with $BF_3 \cdot OEt_2$ co-catalysts are very promising catalysts for selective oligomerization of ethylene [15] and vinyl arenes [16] and the polymerization of norbornene [17,18] and its derivates [19]. Recently we reported the synthesis of novel acetylacetonate cationic palladium complexes with mono- and bidentate phosphine ligands as well as the results of its usage as very efficient precursors for the selective dimerization of styrene [16] and telomerization of butadiene with diethylamine [20]. Therefore, to expand the variety of such catalytic systems, we report in this communication a new class of α-diimine-based palladium catalyst systems. A variety of palladium(II)–acetylacetonate complexes bearing α-diimine ligands are evaluated as catalysts for the first time and shown to be highly active catalysts for norbornene polymerization reaction.

2. Experimental section

2.1. General information

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified argon with standard vacuum-line Schlenk, or cannula techniques.

2.2. Materials

2,3-Dimethylaniline, 2,6-diisopropylaniline, 2,3-butanedione, and glyoxal (40 wt.% solution in water) were purchased from Aldrich

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* Corresponding author.
E-mail address: tkach@chem.isu.ru (V.S. Tkach).

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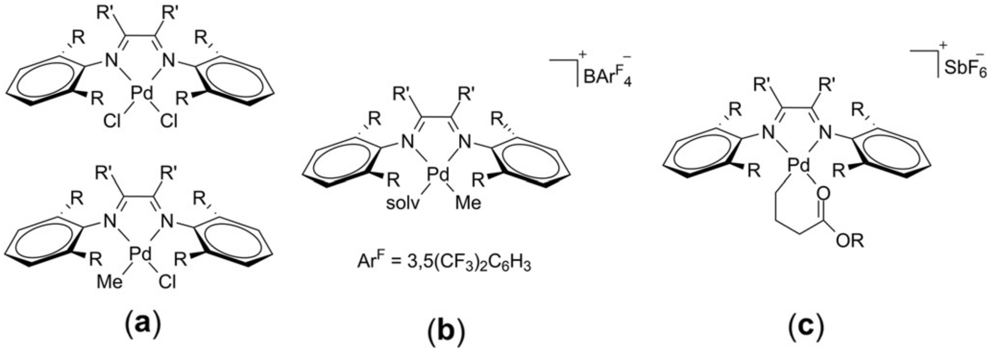


Fig. 1. The main classes of α-diimine palladium complexes reported in literature as useful precursors. See some review articles for details: [1–3].

Chemical and used as received. Norbornene (Acros, 99%) was distilled from sodium-benzophenone and used as a solution (80 wt.%) in CH_2Cl_2. CH_2Cl_2, and CH_3CN were distilled from CaH_2. Solvents were stored over molecular sieves. $BF_3 \cdot OEt_2$ (Acros, 99%) was distilled over CaH_2 prior to use. All glassware was dried for at least 3 h in a 150 °C oven and cooled under an argon atmosphere. $[Pd(acac)(MeCN)_2]BF_4$ [21] and α-diimine ligands [10,14,22,23] were prepared according to literature procedures and characterized by NMR and elemental analysis. All NMR spectra were recorded at room temperature on a Varian VXR-500S spectrometer or a Brucker Avance-400 spectrometer. IR spectra from KBr pellets were recorded on a Simex Infralum FT 801 spectrometer. Elemental analyses were measured using a CHN Thermo Finnigan Flash EA 1112 instrument. TG/DSC measurements were performed at a heating rate of 10 °C min^{-1} with a Netzsch STA 449-F3 instrument. DFT calculations were performed with the ORCA-An ab Initio, Density Functional and Semiempirical Program Package (v.2.8.0) [24] (for details see Electronic supplementary information, ESI) using the BP86 functional.

2.3. X-ray diffraction studies

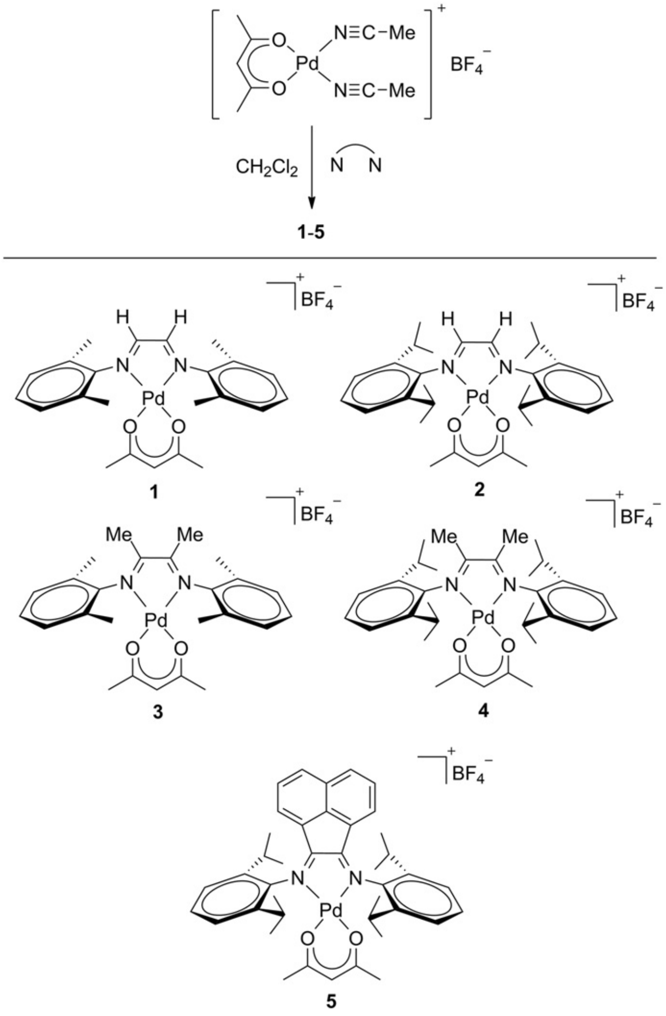
The diffraction data were collected on a Bruker X8Apex CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$) by doing φ and ω scans of narrow (0.5°) frames at 296 K. The structure of **4** was solved by a direct method and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with the SHELXTL program set [25]. Absorption corrections were applied empirically with the SADABS program [25]. All non-hydrogen atoms in the cation of **4** were refined anisotropically. The hydrogen atoms were refined in their geometrically calculated positions; a riding model was used for this purpose. The BF_4^- anion was found to be disordered over two close positions with 0.75/0.25 occupancy ratio. Since anions are highly disordered with small occupancies, their atoms were refined in isotropic approximation. Further details may be obtained from the Cambridge Crystallographic Data Center on quoting the depository number CCDC 1019356. This information may be obtained free of charge from http://www.ccdc.cam.ac.uk.

2.4. General procedure for the synthesis of cationic palladium complexes $[Pd(acac)(ArN = C(R)C(R) = NAr)]BF_4$

A glass reactor was used to add in small portions 1 equiv. of $[Pd(acac)(MeCN)_2]BF_4$ to α-diimine ligand dissolved in 15 mL of CH_2Cl_2, and the reaction mixture was stirred for 1 h at room temperature. The resulting dark orange solution was then filtered, and the solvent of the filtrate was removed under reduced pressure. The product was washed with cold hexane and dried under vacuum. Complexes **1** and **2** (see Scheme 2) were prepared according to the procedure described previously [26].

2.5. General procedure for norbornene polymerization

In a Schlenk-flask norbornene was mixed as a solution in the solvent CH_2Cl_2. The solution was kept at a fixed temperature and the metal precatalyst followed by $BF_3 \cdot OEt_2$, which were applied as a solution in CH_2Cl_2, was added. The polymerization was quenched after the respective time by the addition of 15 mL of ethanol. The polymer precipitate was filtered off, washed with ethanol (10 mL), and dried under vacuum at 50 °C for 6 h.



Scheme 1. Synthesis of palladium complexes **1**–**5**.