Review

Cyclopalladated complexes derivates of phenylhydrazones and their use as catalysts in ethylene polymerization

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Abstract

New cyclopalladated complexes (Pd-A, Pd-B, Pd-C) were used as catalysts in ethylene polymerization. All of them show good activity, especially at a temperature of 80 °C. The molecular weight and molecular weight distribution obtained correspond to single-site catalysts, producing polymers with narrow molecular weight distribution.

The melting points correspond to linear polyethylene. UV–visible spectroscopy studies were used to determine possible polymerization mechanisms.

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Contents

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1. Introduction

Transition metals and organometallic complexes are known for their catalytic activity in homogeneous reactions for obtaining a variety of chemicals and materials such as pharmaceuticals, solvents, commodities, and special polymers [1–3].

An example in organometallic chemistry is the chemistry of cyclopalladated compounds. In recent years numerous examples of cyclopalladated complexes with different ligands have been made. Although practically every report on cyclopalladation ended with a mechanistic discussion, only a few were directly aimed at the elucidation of intimate mechanisms and were supported by kinetic data [4].

As an agent for the intermolecular activation of C–H bonds, palladium(II) was historically classified as a typical electrophile. Such a conclusion has been made on the basis of the general properties of this element and its location in the products of the cyclopalladation of complex molecules. On the other hand, Takahashi and Tsuji reported that cyclopalladation of asymmetrically substituted azobenzene leads to a palladium–carbon σ bond formed preferentially with the benzene ring having and electron-donating group [5]. In general, palladium complexes have been a subject of interest due to their applications in organic synthesis. Various cyclopalladated complex with tridentate N-donor ligands have been reported to produce mononuclear structures, while tridentate imines present dinuclear as well as mononuclear structures [6–9].

Ortega and Anorg [10] reported the synthesis and characterization of cyclopalladated complexes starting from the reaction of palladium chloride and hydrazones. Additionally, the reaction of the complexes with lithium phenylacetylide was studied, which yields $Ph_2-N-N=C(CH_3)-CH=N-N(Ph)(o-C_6H_4-C\equiv C-Ph)$.

On the other hand, the polymerization of olefins has been intensely studied in our group [11–14]. Ziegler–Natta catalysts all of which are the basis of the huge plastics industry. Together with this catalysts, metallocene catalysts started being studied, but they were not taken much into account until the discovery of an efficient co-catalyst called methylaluminoxane (MAO). At present new co-catalysts are being studied that are capable of forming the active species for polymerization. Generally, these catalysts are based on the metals zirconium, titanium, hafnium, etc., which in the polymerization of olefins show high activity, but in the presence of monomers with polar groups their activity decreases due to poisoning of their active center, which prevents the preparation of copolymers with polar groups. Attempts are being made to solve these problems using several techniques, such as protection of the polar groups or the use of long-chain olefins where the polar group is farther away than twice the olefin connection. On the other hand, recently the investigation of catalysts of the so-called Brookhart type has become very important. Here the metallic center is a transition metal such as nickel or palladium whose structure and low hydroxyphilicity allow the incorporation of monomers with functions [15–17].

Late transition metal complexes used in combination with methylaluminoxane or borane derivates are highly attractive catalytic systems for the preparation of polyolefins with tailor-made architecture.

Brookhart and coworkers disclosed the synthesis of a series of new square planar nickel(II) and palladium(II) derivates bearing a substituted α-diimine ligand as precursors for the preparation of polyolefins with special chain topology [18]. These systems are capable of polymerizing ethylene to higher molecular weight polymers with activities comparable to the metallocene catalyst systems when activated with methylaluminoxane. Important for the polymerization activity are the substituents, which have to be bulky groups. The task of these substituent is to fill up the coordination spheres bellow and above the square plane of the complex and thus enable the growing polymer chain to stay coordinated to the metal center [19].

In order to study new catalytic systems based on palladium, this paper presents the results of novel mononuclear cyclopalladated complexes of the type $PdCl(Ph_2N-N=CR_1-CR_2=N-NPh_2)$, where $R_1 = R_2 = H$ (Pd-A), $R_1 = H$, $R_2 = CH_3$ (Pd-B), $R_1 = R_2 = CH_3$ (Pd-C), having a very well-defined structure, and their use as catalysts in ethylene polymerization. The results of the study of catalytic systems are reported.

2. Experimental

2.1. Catalysts

The palladium compounds were synthesized and characterized as described in the literature [10].

2.2. Catalytic system

The UV–visible studies were carried out on the initiator systems at 60 °C under the polymerization conditions. Cyclopalladated complex (Pd-A) activated with MAO was studied by UV–visible spectroscopy.

2.3. Polymerization

Materials: Toluene (J.T. Baker) was used as solvent. Methylaluminoxane (WITCO) and metallocene (Boulder Scientific Company) were used without purification. All manipulations were carried out in a nitrogen atmosphere using Schlenk's technique.

Polymerization: Polymerizations were carried out in a 600 mL Parr reactor with mechanical agitation, and temperature, and ethylene consumption control. The reagents were introduced into the reactor by means of syringes in the following order: toluene, MAO, ethylene, and finally the palladium catalyst. The reaction was ended by addition

of acidified methanol. The polymer was then washed with acetone.

Polymer characterization: Catalytic activity was evaluated from the polymer weight obtained in every polymerization in g polymer/mmol of catalyst × pressure × reaction time. A Bruker Vector 22 spectrometer was used to obtain the FTIR spectra of the polyethylenes as films. Molecular weight and molecular weight distribution in trichlorobenzene were determined using a Waters 2000 Chromatograph at 135 °C. Differential scanning calorimetry (DSC) measurements were performed on TA Instrument DSC 2920 under a nitrogen atmosphere. Samples were melted at 180 °C, quenched from 180 °C to room temperature, and reheated from room temperature to 180 °C at a rate of 10 °C/min. The melting temperatures were determined from the second heating curve.

3. Results and discussion

Cyclopalladated complexes were studied as initiator systems in ethylene polymerization, their structures are described in Fig. 1.

One of the most important characteristics of the complexes studied is that they have a single chloride group, and that is why the polymerization mechanism turns out to be extremely important, because in most of the studies of ethylene polymerization, the "non-metallocene" complex presents two σ ligands in its structure.

To be able to understand the possible reaction mechanisms UV–visible spectroscopic studies of the catalytic system were also made. Also, the ethylene polymerizations were carried out at different temperatures.

3.1. Catalytic activity

It was found that the polymerization temperature was one most important operational factors in the polymerization. For the Pd-A, Pd-B and Pd-C complexes the activities increase with temperature regardless of the complex used. The activity data are shown in Fig. 2.

The activities obtained for the three complexes studied are high, that is to say, greater than 100, as normally obtained for "non-metallocene" complexes.
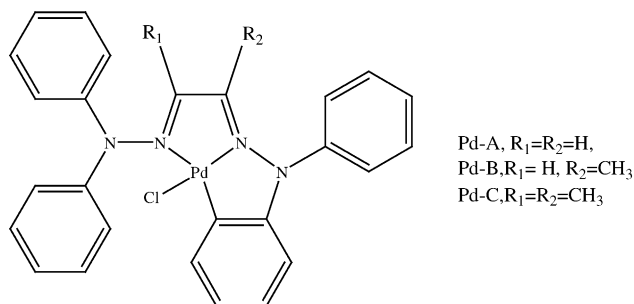

Fig. 1. Scheme of cyclopalladated complexes.

Pd-A, $R_1=R_2=H$,
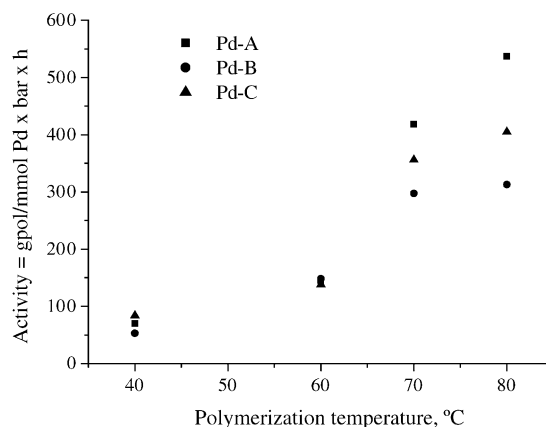Pd-B, $R_1= H$, $R_2=CH_3$
Pd-C, $R_1=R_2=CH_3$

Fig. 2. Effect of temperature on catalytic activity for the Pd-A, Pd-B, Pd-C complexes.

On the other hand, the strong dependence of the catalytic activity of the cyclopalladated/MAO system on polymerization temperature was initially thought to be just the activation energy required for polymerization. When it was recognized that the active species is the palladium ion, then one explanation for the polymerization temperature dependence could be the activation energy needed to produce the ionic species.

With the purpose of studying the polymerization mechanism, a UV–visible spectroscopic study was carried out.

3.2. Studies of catalytic activity by UV–visible spectroscopy

The UV–visible spectroscopy studies were supported by analysis and polymerization tests, and in addition the UV–visible spectroscopic investigation of several zirconocene/MAO systems has been recently reported [20–21].

This technique was found to be very effective for the observation of the successive elementary steps yielding cationic active species. Ultraviolet and visible (UV–vis) spectroscopy measures transitions between the electronic energy levels of a molecule. In organic compounds the transitions generally
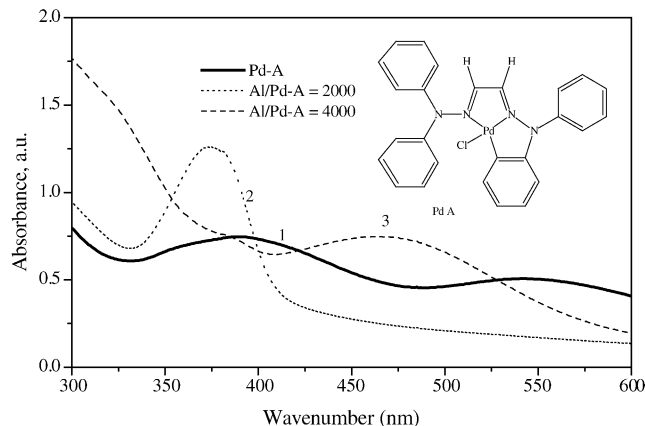

Fig. 3. UV–visible spectrum of cyclopalladated complex (Pd-A) with MAO, in toluene at 60 °C at different Al/Pd ratios.

Pd A R$_1$=R$_2$=H
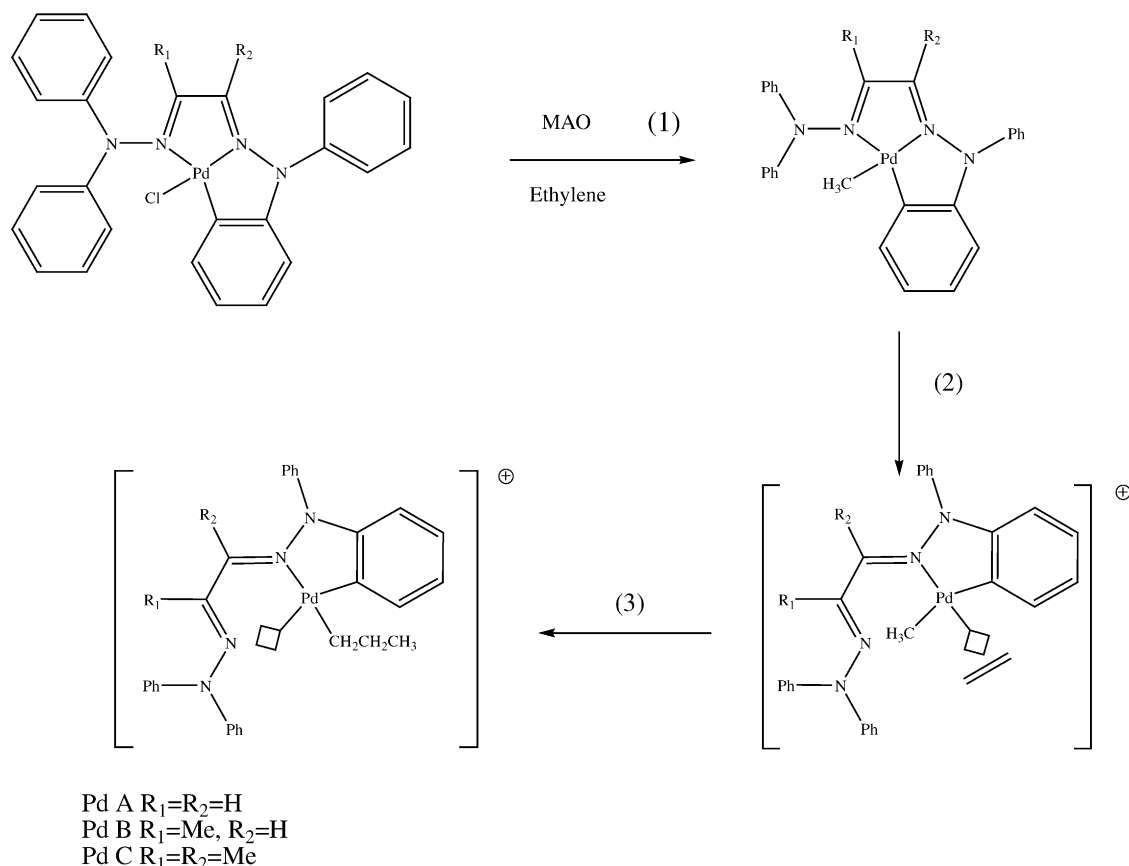Pd B R$_1$=Me, R$_2$=H
Pd C R$_1$=R$_2$=Me

Fig. 4. Mechanism of ethylene polymerization using Pd-A, Pd-B and Pd-C as catalyst.

occur between a bonding or a lone-pair orbital and an unoccupied non-bonding or anti-bonding orbital. In organometallic complexes, ligand to metal charge transfer (LMCT) can occur as well. In LMCT, electron density is transferred from the ligand orbital to the metal orbitals. If only transitions between the electron energy levels were involved, the UV–visible spectra of all compounds would consist of fairly sharp lines. Instead of sharp peaks, however, smooth curves are recorded, because any change in the rotational and vibrational energy levels, and interactions of solute molecules with the solvent blur out the rotational and vibrational fine structure.

In Fig. 3, it is presents a UV–visible spectrum of a palladium complex with maximum at 350 and 549 nm, which are the charge transfer transitions from ligand to Pd metal, i.e., an LMCT transition.

Two successive LMCT band shifts have been detected for the Pd-A/MAO catalyst system with increasing [Al]/[Pd] ratios (Fig. 3): (1) an LMCT band shift to higher energies at [Al]/[Pd] = 2000 (hypsochromic shift), and (2) a shift to lower energies with increasing [Al]/[Pd] = 4000 (bathochromic shift). These two shifts can be understood as produced by methylation and cationization, respectively, of the cyclopalladated complex Pd-A.

In Fig. 4, step 1 are observed, the replacement of the chloride by the more electron-donating methyl group results in an increase in the electron density at the palladium metal center. As a result, more energy is needed to push the electrons from thee ligand to Pd, and an LMCT band shift to higher energies, i.e. to shorter wavelengths, is detected.

It has been concluded that this LMCT shift arises from monomethylation. Palladium is left with one methyl group and a positive charge in addition to the ligand. The charge

Table 1
Molecular weight, molecular weight distribution, melting temperature of polyethylene obtained with Pd-A, Pd-B, Pd-C catalyst

Catalyst	T (°C)	Activity*	T_m (°C)	M_w ($\times 10^{-3}$)	M_w/M_n
Pd-A	40	70	138	195	2.1
Pd-A	60	145	136	150	2.2
Pd-A	70	418	137	143	2
Pd-A	80	537	136	87	2.2
Pd-B	40	53	137	150	1.7
Pd-B	60	148	136	139	1.9
Pd-B	70	297	135	115	2.1
Pd-B	80	313	136	74	1.7
Pd-C	40	84	137	245	2.1
Pd-C	60	138	136	201	2.1
Pd-C	70	356	135	99	2
Pd-C	80	405	136	98	1.9

Polymerization conditions—solvent: toluene (100 mL), P = 4 bar, time = 60 min, MAO WITCO al 10%; Al/Pd ratio = 4000, Ω = 1000 rpm; activity = g pol/mmol Pd × barxh.
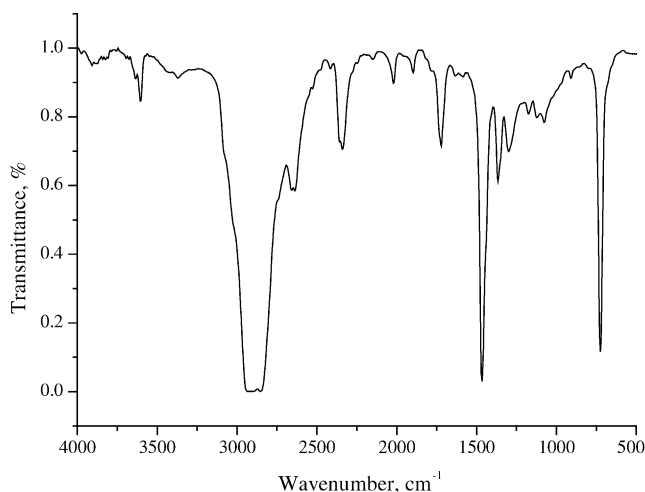
Fig. 5. FTIR for polyethylene obtained with Pd-A complex/MAO.

transfer from ligand to electron-poor Pd, therefore, requires less energy, and an LCMT band shift to lower energies, i.e. to longer wavelengths, is seen (see Fig. 4, step 2). As it is observed in the reaction mechanism, to generate the vacancy in the metallic atom, it is proposed the rupture of the Pd–N bond of the side non-orthopalladated, since it presents smaller energy bond.

Finally, Fig. 4 step 3 shows the regeneration of the d orbital vacancy of palladium in the complexes.

3.3. Polymer characterization

Table 1 shows the molecular weight and molecular weight distribution of polymers obtained with different complexes. At $40\,°C$, all of them present higher values. Chain transfer processes start becoming important at higher temperatures, regardless of the complexes used, and for that reason the molecular weights decrease.

On the other hand, the molecular weight distribution is approximately 2, corresponding to polymerization via metallocene catalysis, associated with one active species in the polymerization process [11].

The melting temperature (T_m) of polymers obtained corresponding to lineal polyethylene.

The FTIR spectrum displayed signals correspond to a typical polyethylene: at 2930 and $2845\,cm^{-1}$, assigned to C–H stretching of –CH$_2$ and –CH$_3$ groups. Approximately at $1462\,cm^{-1}$ there is a signal corresponding to bending of the –CH$_2$ group, and at $719\,cm^{-1}$ a signal corresponding to rocking of the $(-CH_2-CH_2-)_n$ group with $n > 3$ (see Fig. 5) [22].

4. Conclusions

New palladium complexes have been active in ethylene polymerization. They showed high catalytic activities partic-

ularly at $80\,°C$. On the other hand, melting temperature indicates that the polyethylenes obtained are linear. The molecular weight distribution correspond to single-site catalysis, producing polymers with narrow molecular weight distribution.

Studies of UV–visible spectroscopy determined that two shifts can be understood as produced by methylation and cationization, respectively, of the cyclopalladated complexes.

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