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Journal of Organometallic Chemistry 619 (2001) 287–292

Journal of Organometallic Chemistry

New catalysts for the alternating copolymerization of 4-*tert*-butylstyrene/CO

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Received 4 July 2000; accepted 15 September 2000

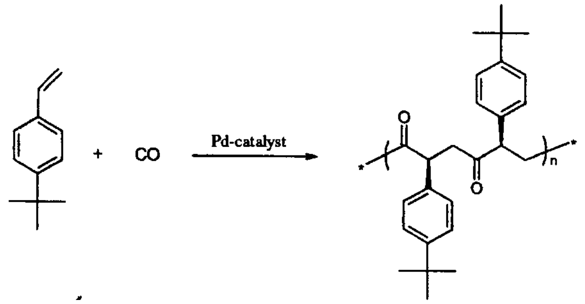
Abstract

New cationic palladium(II) complexes, containing C_S-nitrogen chelate ligands with pyrazol moieties, catalyze the copolymerization of styrene with CO under mild conditions, to produce a syndiotactic copolymer. Molecular weight and polydispersity for the obtained polymers are among the best reported for bisnitrogen planar ligands. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalysis; Copolymerization; Styrene; Carbon monoxide; Palladium complexes; Nitrogen ligands

1. Introduction

The copolymerization of carbon monoxide and alkenes using palladium catalyst is providing much interest [1–3]. Ethylene/carbon monoxide copolymerization has been widely studied and results have been best with diphosphine ligands. The high activity of these systems has raised industrial interest in the process [4–9]. Several groups are reporting on the exploration of new systems [10–15].



Scheme 1.

Chiral ligands have been successfully used for the copolymerization of carbon monoxide with propene [16,17] and styrene [18–21]. With styrene, however, only oligomers with low molecular weight are obtained with phosphine ligands. This has been attributed to a favoured β-hydride-elimination [1].

The first systems studied with styrene were Pd(II) catalyst based on planar 2,2′-bypiridine or 1,10-phenantroline to give syndiotactic poly(styrene-alt-CO) [22–24] (Scheme 1). This high stereochemical control (> 90%) has been attributed to a chain-end control due to the interaction of the growing chain with the incoming styrene unit, which inserts exclusively in the 2,1-fashion [3,25].

C_2-symmetric chiral N–N ligands have also been successfully explored to yield isotactic copolymers [18,19,25,26], although in some cases the chain-end control is more efficient than the enantiosite control caused by the ligand and this results in the formation of syndiotactic polymers [25].

C_1-symmetric chiral P–N ligands have been used to yield isotactic polymers due to the site-selective coordination of the olefin in the chiral environment generated by the ligand [21,25]. For these systems, using P–N ligands, high CO pressures and moderate temperatures are required.

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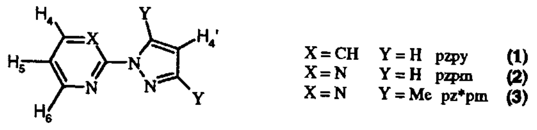
PII: S0022-328X(00)00670-7



Scheme 2. (*N*-*N*′)-Ligand systems.

Since planar N-N ligands are efficient and since there is an interest in exploring new types of ligands, we report on the synthesis of new well-defined cationic Pd (II) catalyst using the unsymmetrical chelate ligands 2-(1-pyrazolyl) pyridine (pzpy, **1**), 2-(1-pyrazolyl) pyrimidine (pzpm, **2**) and 2-(1-(3,5-dimethyl)pyrazolyl) pyrimidine (pz*pm, **3**), which yield syndiotactic alternating copolymers of 4-*tert*-butyl styrene and CO at mild pressure and temperature (Scheme 2).

2. Results and discussion

2.1. Synthesis and characterization of the palladium catalyst precursors [Pd(Me)(NCMe)(N–N′)]BAr′$_4$ (4–6)

The cationic complexes [Pd(Me)(NCMe)(N–N′)]-BAr′$_4$ were obtained by adding a previously prepared solution of the neutral complexes [PdCl(Me)(N–N′)] [27] to an equimolar solution of NaBAr′$_4$ in MeCN.

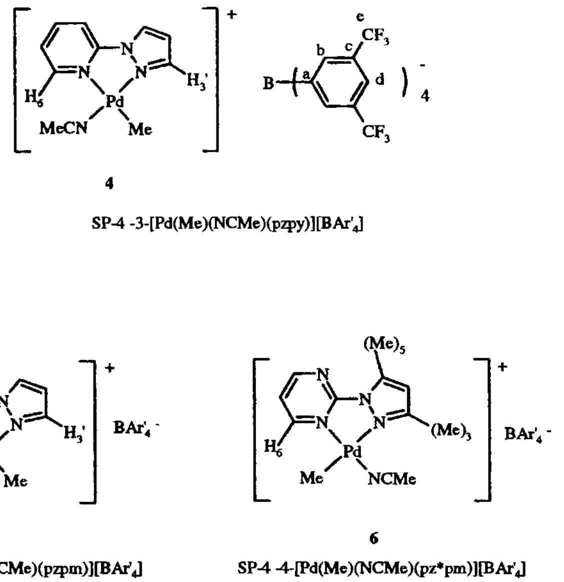
NOE difference NMR experiments showed that cationic precursors **4** and **5** had the methyl group *trans* to pyridine and pyrimidine ring, respectively, while **6** had the methyl group *trans* to the pyrazole moiety (Scheme 3). Because of the large *trans* influence of the methyl group, we should expect it to be coordinated *trans* to the less basic ring (pyrazole in compound **4** and pyrimidine in compounds **5** and **6**). We therefore believe that this stereochemistry cannot be explained in terms of electronic effects. The sterical hindrance caused by the hydrogen H_6 in compounds **4** and **5** may be larger than the one caused by the $H_{3'}$ of the pyrazole fragment, which could force the methyl to be *cis* to the pyrazole in both molecules. This agrees with the stereochemistry observed in **6**, where the steric demand of the methyl group $(Me)_3$ of the pyrazole ring is greater than the bulkiness of H_6, thus placing the methyl group trans to the pyrazole moiety.

Spectroscopic data suggest that these configurations are in agreement with the stereochemistry of the related [PdClMe(N–N)], although in the case of [Pd-ClMe(pz*pm)] there is also a minor isomer with the methyl ligand *trans* to the pyrimidine ring [27].

In the case of **6**, it is also noteworthy the fluxional behaviour found for the pz*pm ligand (**3**). An NOE experiment carried out at low temperature (243 K) reflects the expected NOE interaction between the methyl group and H_6. However, at room temperature an NOE effect has been found not only with this proton but also with H_4 being the observed percent of 2.4% for H_6 and 0.6% for H_4. This implies a process of Pd–N bond rupture, internal rotation of the ligand around the pz*–pm bond and reformation of the Pd–N bond. The two separated resonances for H_4 and H_6 at room temperature indicate that the process is in a slow exchange regime at this temperature. This Pd–N bond rupture is also observed in related Pd(II) complexes with this type of ligands [28].

2.2. Copolymerization experiments

Whereas C_2-symmetric bipyridyl-or phenantroline-type ligands are a well-known class of C_2-symmetric



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SP-4 -3-[Pd(Me)(NCMe)(pzpy)][BAr′$_4$]

5

SP-4 -3-[Pd(Me)(NCMe)(pzpm)][BAr′$_4$]

6

SP-4 -4-[Pd(Me)(NCMe)(pz*pm)][BAr′$_4$]

Scheme 3. Stereochemistry around palladium of compounds **4**, **5** and **6**.

Table 1
Copolymerization of 4-*tert*-butylstyrene and CO with **4**, **5** and **6** at 1 bar CO and r.t. [a]

Entry	Catalyst precursor	pCO (bar)	t (h)	% Conversion [b]	M_N (M_W/M_N)	Productivity (g (g Pd h)$^{-1}$)
1	**4**	1	24	38.45	21 440 (1.1)	8.83
2	**5**	1	24	55	36 353 (1.3)	11.75
3	**6**	1	24	25.78	15 720 (1.5)	5.88
4	**4**	1	48	67.49	72 360 (1.1)	7.75
5	**5**	1	48	68.88	70 680 (1.2)	7.05
6 [c]	**4**	1	24	43.15	30 380 (1.4)	19.86
7	**4**	5	24	14.59	15 570 (1.1)	3.42
8	**5**	5	24	10.73	7155 (1.2)	2.5

[a] Reaction conditions: solvent: 5 ml chlorobenzene, alkene/catalyst = 310.

[b] Styrene conversion calculated from the isolated polymer weight.

[c] Alkene/catalyst = 620.

planar ligands for the styrene/CO copolymerization reaction, few systems have been reported in which a nonsymmetrical N-N' planar ligand leads to similar activities and molecular weights [29]. The new complexes **4**, **5** and **6** were explored as catalysts in this reaction at mild conditions (room temperature and 1 bar CO) (Table 1).

The catalyst precursor **5** seemed the most active after 24 h, with a productivity of 11.75 g (g Pd h)$^{-1}$, although the cationic system **4** behaved in a similar way (entries 1 and 2). Increasing the reaction time from 24 to 48 h led, as expected, to higher conversions and molecular weights although the difference in activity between the two catalysts (**4** and **5**) narrowed, probably due to the combined effects of the increasing difficulty of the monomers to access the catalytic site and decomposition of catalyst **5** to palladium metal (entries 4 and 5). The molecular weights (20000–70000) and the polydispersities (1.1–1.3) are in the order of the best ones reported for bisnitrogen systems using styrene derivatives [24,26]. The activity and molecular weight obtained with catalyst precursor **6** were lower than those obtained with precursors **4** and **5** (entries 1–3). This lower productivity may be attributed to the sterically more demanding ligand pz*pm (**3**), as previously reported for other systems [25]. When the substrate/catalyst ratio is 620 for precursor **4**, productivity and molecular weight increased (entries 1 and 6).

We also studied the effect of CO pressure. When the CO pressure was increased to 5 bar, conversion and molecular weight decreased, although polydispersities remained stable (entries 7 and 8).

To compare the activity of the most active catalyst precursors **4** and **5**, we varied reaction times from 7 to 72 h and plotted styrene conversion against reaction time (Fig. 1). With catalyst **5** the initial reaction rate was higher but prolonged reaction time with **4**, however, resulted in similar conversions, as mention above.

All the systems we studied yield prevailing syndiotactic copolymers, which is indicative of a stereocontrol from the growing polymer chain (chain-control). Analysis of the decoupled ^{13}C spectra indicated a substantial degree of stereoregularity (ca. 85% of syndiotactic diads) by integration of the signals of the methylene carbon atoms. The greater resonance at 43.2 ppm was assigned to the syndiotactic *uu*-triad by comparison with the spectrum of the epimerized polymer and with literature values [18,21] (Fig. 2).

3. Conclusions

This study shows that new cationic palladium(II) compounds containing the bisnitrogen ligands pzpy (**1**), pzpm (**2**) and pz*pm (**3**) are active as catalyst precursors in the alternating CO/4-*tert*-butylstyrene copolymerization. The C_S-symmetry of the ligands did not seem to affect stereocontrol, which was determined by the chain end. These systems behave similar to the previously studied C_2-symmetric bipyridyl and phenantroline ligands that yield readily syndiotactic copolymers.

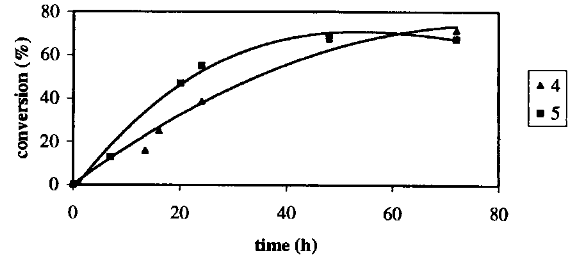


Fig. 1. Compared activity of catalysts **4** and **5**, containing ligands pzpy and pzpm, respectively.

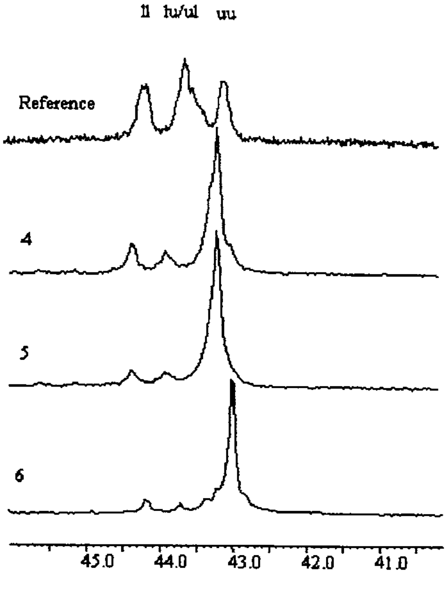


Fig. 2. Methylene carbon atom-region of the copolymers obtained with precursors **4**, **5** and **6**. The reference spectrum is epimerized poly (4-*tert*-butylstyrene-alt-CO).

4. Experimental

4.1. General procedure

All reactions were carried out in a nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were distilled and deoxygenated prior to use unless otherwise stated. The salt $NaBAr'_4$ ($Ar' = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$) was prepared according to reported methods [30]. Ligands **1** and **2** were prepared according to published methods [28]. Ligand **3** was prepared in a similar way.

^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini spectrometer with a ^{1}H resonance frequency of 300 MHz and on a Varian Mercury VX spectrometer with a ^{1}H resonance frequency of 400 MHz. Chemical shifts were reported relative to tetramethylsilane for ^{1}H and ^{13}C. Some assignments in NMR spectra were determined by ^{1}H-^{13}C-COSY, DEPT and NOE experiments. IR spectra (range 4000–400 cm^{-1}) were recorded on a Midac Grams/386 spectrophotometer in KBr pellets. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. The molecular weight of the copolymers and molecular weight distributions were determined by gel permeation chromatography (GPC-MALLS) measurements made in THF on a Waters 510 gel-permeation chromatography device using a three-serial column system (SHODEX K80M and PLGEL MIXED-D and MIXED-E linear columns) with a Wyatt mini-DAWN Light Scattering and a SHIMADZU RID-6A refractive index detector.

4.2. Synthesis of catalyst precursors

4.2.1. [Pd(Me)(NCMe)(pzpy)](BAr'₄) (**4**)

A previously prepared solution of [PdCl(Me)(pzpy)] [27] (0.05 g, 0.17 mmol) in 3 ml of CH_2Cl_2 was added to a solution of $NaBAr'_4$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$) (0.147 g, 0.17 mmol) in the minimum amount of MeCN. The light orange solution formed was stirred for about an hour, filtrated through Kieselghur and evaporated to dryness. The white-brownish compound was crystallised from CH_2Cl_2 / hexane. Yield: 75%. Anal. Found: C, 44.7; H, 2.1; N, 4.7. Calc. for $C_{43}H_{25}BF_{24}N_4Pd$: C, 44.1; H, 2.1; N, 4.8%. ^{1}H-NMR (400 MHz, $CDCl_3$, room temperature (r.t.): δ 8.15 (ddd, $^3J = 5.2$ Hz, $^4J = 1.6$ Hz, $^5J = 0.8$ Hz, 1H, H_6), 8.08 (d, $^3J = 3.2$ Hz, 1H, $H_{5'}$), 7.9 (ddd, $^3J = 8.4$ Hz, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 1H, H_4), 7.8 (d, $^3J = 2.0$ Hz, 1H, $H_{3'}$), 7.71 (s, 8H, H_b), 7.52 (s, 4H, H_d), 7.45 (td, $^3J = 8.4$ Hz, $^4J = 0.8$ Hz, $^5J = 0.8$ Hz, 1H, H_3), 7.23 (ddd, $^3J = 7.6$ Hz, $^3J = 5.2$ Hz, $^4J = 0.8$ Hz, 1H, H_5), 6.7 (dd, $^3J = 3.2$ Hz, $^3J = 2$ Hz, 1H, $H_{4'}$), 2.38 (s, 3H, CH_3CN), 1.21 (s, 3H, Pd–CH_3). ^{13}C-NMR (100.5 MHz, $CDCl_3$, r.t.): δ 161.9 (q, $J_{C-B} = 198.3$ Hz, C_a), 147.5 (s, C_6), 142.4 (s, $C_{3'}$ or C_4), 142.3 (s, C_4 or $C_{3'}$), 135 (s, C_b), 129.5 (s, $C_{5'}$), 129.1 (m, C_e), 126 (s, C_c), 124.4 (s, C_5), 123.3 (s, $CH_3\mathit{C}N$), 117.7 (s, C_d), 111.2 (s, $C_{4'}$ or C_3), 111.1 (s, C_3 or $C_{4'}$), 3.3 (s, $\mathit{C}H_3CN$), -0.8 (s, Pd–CH_3).

4.2.2. [Pd(Me)(NCMe)(pzpm)](BAr'₄) (**5**)

Compound **5** was obtained from [PdCl(Me)(pzpm)] [27] as a white-brownish solid in a similar way to compound **4**, although it does not analyse as a pure solid. Yield: 72%. ^{1}H-NMR (300 MHz, $CDCl_3$, r.t.): δ 8.74 (dd, $^3J = 4.8$ Hz, $^4J = 2.4$ Hz, 1H, H_4), 8.57 (dd, $^3J = 3.2$ Hz, $^4J = 0.8$ Hz, 1H, $H_{5'}$), 8.33 (dd, $^3J = 5.2$ Hz, $^4J = 2.4$ Hz, 1H, H_6), 7.84 (dd, $^3J = 2.4$ Hz, $^4J = 0.8$ Hz, 1H, $H_{3'}$), 7.71 (s, 1H, H_b), 7.52 (s, 1H, H_d), 7.14 (dd, $^3J = 5.2$ Hz, $^3J = 4.8$ Hz, 1H, H_5), 6.76 (dd, $^3J = 3.2$ Hz, $^3J = 2.4$ Hz, 1H, $H_{4'}$), 2.32 (s, 3H, CH_3CN), 1.3 (s, 3H, Pd–CH_3). ^{13}C-NMR (100.5 MHz, $CDCl_3$, r.t.): δ 161.9 (q, $J_{C-B} = 198.3$ Hz, C_a), 161.6 (s, C_6), 156.3 (s, C_4), 143.8 (s, $C_{3'}$), 135 (s, C_b), 132.3 (s, $C_{5'}$), 129.2 (m, C_e), 126 (s, C_c), 123.3 (s, $CH_3\mathit{C}N$), 120.8 (s, C_5), 117.7 (s, C_d), 111.2 (s, $C_{4'}$), 3.2 (s, $\mathit{C}H_3CN$), -0.1 (s, Pd–CH_3).

*4.2.3. [Pd(Me)(NCMe)(pz*pm)](BAr'₄)* (**6**)

Compound **6** was synthesised from [PdCl(Me)(pz*pm)] [27] following a similar procedure to compound **4** and isolated as a light grey solid. Yield: 82.1%. Anal. Found: C, 44.6; H, 2.3; N, 5.6. Calc. for $C_{44}H_{28}BF_{24}N_5Pd$: C, 44.1; H, 2.3; N, 5.8%. ^{1}H-NMR (400MHz, $CDCl_3$, r.t.): δ 8.8 (dd, $^3J = 4.8$ Hz, $^4J = 2.2$ Hz, 1H, H_4), 8.48 (dd, $^3J = 6$ Hz, $^4J = 2.2$ Hz, 1H, H_6), 7.71 (s, 8H, H_b), 7.53 (s, 4H, H_d), 7.29 (dd, $^3J = 6$ Hz, $^3J = 4.8$ Hz, 1H, H_5), 6.19 (s, 1H, $H_{4'}$), 2.7 (s, 3H, $(Me)_3$ or $(Me)_5$), 2.35 (s, 3H, CH_3CN), 2.23 (s, 3H, $(Me)_5$ or

(Me)$_3$), 1 (s, 3H, Pd–CH$_3$). ^{13}C-NMR (75.4 MHz, CDCl$_3$, r.t.): δ 161.9 (q, $J_{C-B} = 198.2$ Hz, C$_a$), 160.6 (s, C$_6$), 156 (s, C$_4$), 135 (s, C$_b$), 129.1 (m, C$_e$) 126.5 (s, C$_c$), 122.9 (s, CH$_3$*C*N), 119.3 (s, C$_5$), 117.7 (s, C$_d$), 113.5 (s, C$_{4'}$), 15.4 (s, (Me)$_3$ or (Me)$_5$), 13.3 (s, (Me)$_5$ or (Me)$_3$), 5.5 (s, *C*H$_3$CN), 3.4 (s, Pd–CH$_3$).

4.3. Copolymerization reactions — general procedure

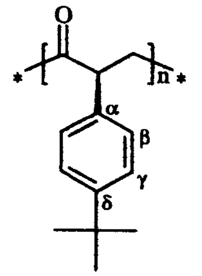
The 4-*tert*-butylstyrene was passed through a small column of Al_2O_3 prior to use. Chlorobenzene was used as purchased from Aldrich.

In a typical procedure the cationic precursor **4**, **5** or **6** (0.0125 mmol) was dissolved in 5 ml of chlorobenzene in a previously flushed Schlenk and the N_2 atmosphere replaced with CO. 4-*tert*-Butylstyrene (0.7 ml, 3.875 mmol) was then introduced and the reaction was allowed to take place at r.t. and 1 bar of CO. The experiments under 5 bar of CO pressure were carried out in a 100 ml stainless steel Berghoff autoclave. The reaction mixture was introduced into the autoclave by suction and the pressure level was kept constant by continuous feeding from a gas reservoir. Reaction times varied from 7 to 96 h. Work-up included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution dropwise into 100 ml of rapidly stirring methanol. The off-white powder was collected by filtration, washed with methanol and dried in a vacuum oven at 70°C overnight. Percentage conversions were calculated from the weight of the isolated polymeric material.

The polymers were purified by reprecipitation and then polymer weights were measured. The copolymers were dissolved in the minimum amount of THF, the solutions were filtered over a 0.22 μm filter and added dropwise to stirring methanol. The solid was then filtered and dried as previously stated.

4.4. Copolymer characterization

^{1}H-NMR (300 MHz, CDCl$_3$, r.t): δ 7.0 (d, $^3J = 8.1$ Hz, 2H, H$_\beta$ or H$_\gamma$), 6.59 (d, $^3J = 8.1$ Hz, 2H, H$_\gamma$ or H$_\beta$), 4.11 (t, $^3J = 6.9$ Hz, 1H, CH), 3 (dd, $^2J = 18.1$ Hz, $^3J = 6.9$ Hz, 1H, CH$_2$), 2.64 (dd, $^2J = 18.1$ Hz, $^3J = 6.9$ Hz, 1H, CH$_2$), 1.23 (s, 9H, C(CH$_3$)$_3$). ^{13}C-NMR (75.4 MHz, CDCl$_3$, r.t.): δ 206.9 (–C(O)–), 149.8 (C$_\delta$), 134.3 (C$_\alpha$), 128.2 (C$_\gamma$), 125.6 (C$_\beta$), 52.9 (CH), 43.2 (CH$_2$), 34.5 (C(CH$_3$)$_3$), 31.5 (C(CH$_3$)$_3$). IR (KBr, cm^{-1}): ν 1709 (C=O).



Acknowledgements

We thank the Spanish Ministerio de Educación y Cultura for financial support (DGES PB-97-0407-C05-01, DGES PB-98-0315 and 2FD97-1565) and for awarding a research grant (to A.B.). We also thank Ramón Guerrero (Servei de Recursos Cientifics, Universitat Rovira i Virgili) for carrying out the NOE and ^{1}H-^{13}C-COSY experiments.

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