New Pyridine−Imidazoline Ligands for Palladium-Catalyzed Copolymerization of Carbon Monoxide and Styrene

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C_1-symmetrical pyridine–imidazoline ligands have been synthesised and used in the preparation of Pd^{II} complexes of general formula [PdMe(NCMe)(N-N′)][BAr′$_4$] [Ar′ = 3,5-$(CF_3)_2C_6H_3$]. The introduction of electronically different substituents in the imidazoline moiety determines the coordination position of the methyl group in the cationic complexes, which are catalyst precursors for the copolymerization of carbon monoxide and 4-*tert*-butylstyrene (TBS). Interestingly, the use of a precatalyst with a different stereochemistry provides copolymers with a different stereoregularity.

Introduction

Chelating nitrogen ligands have been reported to be the most efficient for the Pd-catalyzed alternating copolymerization of carbon monoxide and styrene.[1−6] Catalysts containing planar, achiral ligands give syndiotactic copolymers with high stereocontrol.[3,7,8] This stereoregularity 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 a 2,1-fashion.[3] Enantiomerically pure C_2-symmetrical N-N ligands yield highly isotactic copolymers due to the strict enantiomorphic site control provided by the chiral ligand.[9−11]

To the best of our knowledge there is only one example of a C_1-symmetrical bisnitrogen ligand. Surprisingly, the use of (*S*,*S*)-4,5-dihydro-4-methoxymethyl-3-phenyl-2-(2-pyridyl)oxazole provides a syndiotactic copolymer. It has been proposed that, due to a pronounced site-selective coordination of the olefin, the influence of the chirality of the growing chain is more efficient than the enantiosite control.[9,12,13] The related C_1-symmetrical phosphane−oxazoline ligands provide isotactic poly(styrene-*alt*-CO). It seems that with these ligands the enantioface discrimination is determined by the site-selective coordination of the olefin (*trans* to the P atom) and a secondary insertion of the incoming styrene units.[12]

Recently it has been reported that electronic effects in palladium catalysts modified with chiral ferrocenyldiphosphanes may increase the differentiation of the two coordinating P atoms and change the catalytic activity in the enantioselective copolymerization of carbon monoxide and propene dramatically.[14]

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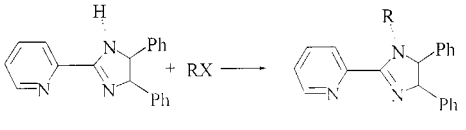
In this paper we show that the stereochemistry of the [PdMe(NCMe)(N-N′)][BAr′$_4$] complexes can be modified by changing the electronic properties of the C_1-symmetrical pyridine−imidazoline ligands. This fact influences the stereoregularity of the CO/TBS copolymers.

Results and Discussion

The pyridine−imidazoline ligand **1a** was prepared similarly to the oxazolines by reaction of 2-cyanopyridine with *meso*-1,2-diphenylethylenediamine but using $YbOTf_3$ as catalyst.[15,16] Further reaction of **1a** with BnBr, TsCl or Tf_2O, provided the 1-substituted-4,5-dihydro-4,5-diphenyl-2-(2-pyridyl)-imidazoles **1b**−**d**, respectively, in a racemic manner (Figure 1).[16] The neutral [PdClMe(N-N′)] complexes **2a**−**d** were isolated from the stoichiometric reaction of [PdClMe(cod)] (cod = 1,5-cyclooctadiene) and the ligands **1a**−**d** in anhydrous toluene.[17,18] The cationic palladium complexes [PdMe(NCMe)(N-N′)][BAr$_4$′] (**3a**−**d**) were prepared following reported procedures.[19]

The stereochemistry of the neutral complexes **2a**−**d** was assigned by means of NOE experiments at room temperature, showing that all the complexes have the methyl group coordinated *trans* to the pyridine ring. This is also confirmed by the downfield shift in the ^{1}H NMR spectra of the proton H_6, next to the N-pyridine atom, which is indicative of the presence of the chloride ligand in a *cis* position.[17] However, the cationic compounds [Pd(Me)(NCMe)(N-N′)][BAr′$_4$] (**3a**−**d**) show a different stereochemistry depending on the ligand. The ^{1}H NMR spectra of **3c**−**d** at



1a **1b** R = Bn
c R = Ts
d R = Tf

Figure 1. Synthesis of the pyridine-imidazoline ligands

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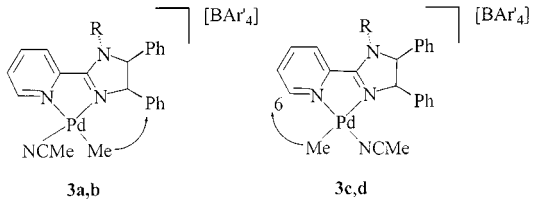

Figure 2. NOE difference experiments show the stereochemistry of the complexes

room temperature show a downfield shift of the Pd−Me signal to around δ = 1.[19] NOE difference experiments at room temperature allowed the determination of the stereochemistry of these complexes and showed that in the complexes **3a**−**b** the methyl group is *trans* to the pyridine moiety whereas it is *cis* in the complexes **3c**−**d** (Figure 2). Therefore the use of different substituents (R) with electron-donor or electron-withdrawing character results in an effective electronic determination in the methyl coordination. The methyl group is always coordinated *trans* to the less basic nitrogen of the ligand.

Under copolymerization conditions the coordination of carbon monoxide and the migratory insertion of the methyl group take place to form an acyl species; the styrene coordinates in the vacant position. The electronic effects of these ligands could therefore affect the steroregularity of the copolymer obtained with the catalytic precursors. The new Pd^{II} complexes with imidazoline-containing ligands were tested as catalysts for the alternating CO/TBS copolymerization. In a typical experiment **3a**−**d** were placed in chlorobenzene under 1 bar CO and TBS was added (Table 1).

Table 1. Alternating CO/TBS copolymerization catalysed by [PdMe(NCMe)(N-N′)][BAr′$_4$][a]

Entry	Precursor	Productivity[b] [g(gPd × h)$^{-1}$]	Stereoregularity (*l* diads) [%]	M_N (M_W/M_N)
1	**3a**	2	65	42200 (1.1)
2	**3b**	8.9	52	49750 (1.5)
3	**3c**	7	15	59250 (1.2)
4	**3d**	12.8	18	39700 (1.5)

[a] Reaction conditions: 0.0125 mmol catalyst, [TBS]/[cat] = 620, 5 mL chlorobenzene, p(CO) = 1 bar, 24 h at room temperature. [b] Productivity calculated from the isolated copolymer.

As Table 1 shows, introducing electron-withdrawing groups (entries 3 and 4) leads to a greater proportion of *u* diads giving highly syndiotactic copolymers. With the substituents H and Bn (entries 1 and 2 respectively) such a clear effect is not observed, probably due to the smaller electronic differentiation of the two rings (pyridine and imidazoline), although there is a bigger proportion of *l* diads. The degree of stereoregularity was evaluated from the ^{13}C NMR spectrum of the copolymers by integrating the signals in the region of the methylene carbon atom using the epimerized copolymer as reference (Figure 3). The molecular weights were high and similar in all the cases. In general, we did not find any relation between the nature of the R substituent and the activity of the catalytic systems.

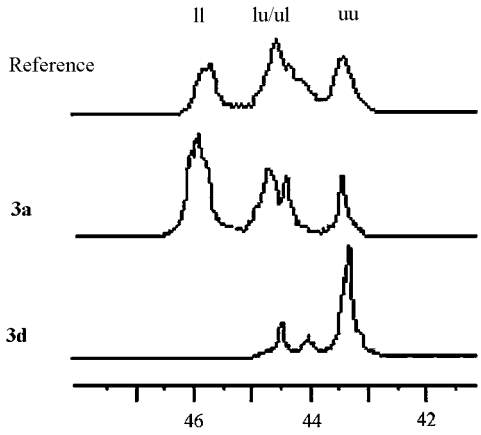

Figure 3. Comparative ^{13}C NMR spectrum of the copolymers in the region of the methylene carbon atom using the epimerized copolymer as reference

In conclusion, we have prepared pyridine−imidazoline ligands with several substituents in the imidazoline moiety and their related [Pd(Me)(NCMe)(N-N′)][BAr$_4$′] complexes. Interestingly, the nature of the substituents determines the stereochemistry of the complexes. The Pd^{II} complexes are active as catalysts in the CO/TBS copolymerization reaction and show that the electronic properties of the ligands strongly influence the stereoregularity of the copolymers. We are currently studying how this electronic discrimination affects the different steps of the catalytic reaction.

Acknowledgments

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[16] 2-Cyanopyridine and *meso*-1,2-diphenylethylenediamine were refluxed in chlorobenzene during 72 h using $YbOTf_3$ as catalyst. ^{1}H NMR (400 MHz, $CDCl_3$, room temp.): δ = 8.63 (ddd, ^3J = 5.0, ^4J = 1.8, ^5J = 1.1 Hz, 1 H, H_6), 8.36 (dt, ^3J = 7.7, ^4J = 1.1, ^5J = 1.1 Hz, 1 H, H_3), 7.81 (td, ^3J = 7.7, ^4J = 1.8 Hz, 1 H, H_4), 7.40 (ddd, ^3J = 7.7, ^3J = 5.0, ^4J = 1.1 Hz, 1 H, H_5), 7.02−6.94 (m, 10 H, $H_{arom.}$), 5.51 (s, 2 H, CHN); $C_{20}H_{17}N_3$ (299.37): calcd. C 80.2, H 5.4, N 14; found C 79.3, H 5.0, N 13.8.

[17] Selected data for **1d** as an example: ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 8.78 (ddd, ^3J = 4.8, ^4J = 1.8, ^5J = 1.0 Hz, 1 H, H_6), 7.96 (dt, ^3J = 7.7, ^4J = 1.0, ^5J = 1.0 Hz, 1 H, H_3), 7.87 (td, ^3J = 7.7, ^4J = 1.8 Hz, 1 H, H_4), 7.49 (ddd, ^3J = 7.7, ^3J = 4.8, ^4J = 1.0 Hz, 1 H, H_5), 7.11−6.99 (m, 10 H, $H_{arom.}$), 5.98 (d, ^3J = 8.7 Hz, 1 H, CHN), 5.92 (d, ^3J = 8.7 Hz, 1 H, CHN); $C_{21}H_{16}F_3N_3O_2S$ (431.43): calcd. C 58.46, H 3.74, N 9.74, S 7.43; found C 58.85, H 3.82, N 9.42, S 7.28.

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[19] Selected data for **2d** as an example: ^{1}H NMR (400 MHz, $CDCl_3$, room temp.): δ = 9.27 (ddd, ^3J = 5.1, ^4J = 1.7, ^5J = 0.8 Hz, 1 H, H_6), 8.32 (ddd, ^3J = 7.9, ^4J = 1.2, ^5J = 0.8 Hz, 1 H, H_3), 8.15 (td, ^3J = 7.9, ^4J = 1.7 Hz, 1 H, H_4), 7.83 (ddd, ^3J = 7.9, ^3J = 5.1, ^4J = 1.2 Hz, 1 H, H_5), 7.24−6.69 (m, 10 H, H_{arom}), 6.11 (s, 2 H, CHN), 0.45 (s, 3 H, Pd−CH_3); $C_{22}H_{19}ClF_3N_3O_2PdS$ (588.32): calcd. C 45.0, H 3.3, N 7.1; found C 45.4, H 3.8, N 6.5.

[20] The standard synthesis is described in ref. 7. As representative examples **3b** and **3d** are chosen. Selected data for **3b**: ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 8.44 (dd, ^3J = 5.2, ^4J = 1.8 Hz, 1 H, H_6), 7.98 (dd, ^3J = 8.1, ^4J = 1.0 Hz, 1 H, H_3), 7.86 (td, ^3J = 8.1, ^4J = 1.8 Hz, 1 H, H_4), 7.72 (s, 8 H, H_{arom}), 7.53 (s, 4 H, H_{arom}), 7.43 (ddd, ^3J = 8.1, ^4J = 5.2, ^5J = 1.0 Hz, 1 H, H_5), 7.36−6.77 (m, 15 H, H_{arom}), 5.54 (d, ^3J = 11.7 Hz, 1 H, CHN), 5.43 (d, ^3J = 11.7 Hz, 1 H, CHN), 5.11 (d, ^2J = 17.6 Hz, 1 H, CH_2), 4.45 (d, ^2J = 17.6 Hz, 1 H, CH_2), 2.27 (s, 3 H, CH_3CN), 0.56 (s, 3 H, Pd−CH_3); $C_{62}H_{41}BF_{24}N_4Pd$ (1415.2): calcd. C 52.6, H 2.9, N 3.9; found C 50.8, H 2.9, N 3.4. Selected data for **3d**: ^{1}H NMR (400 MHz, $CDCl_3$, room temp.): δ = 8.51 (dt, ^3J = 5.6, ^4J = 0.8 Hz, 1 H, H_6), 8.41 (ddd, ^3J = 7.8, ^4J = 1.4, ^5J = 0.8 Hz, 1 H, H_3), 8.24 (td, ^3J = 7.8, ^4J = 1.5 Hz, 1 H, H_4), 7.76 (ddd, ^3J = 7.8, ^3J = 5.6, ^4J = 1.4 Hz, 1 H, H_5), 7.72 (s, 8 H, H_{arom}), 7.53 (s, 4 H, H_{arom}), 7.2-6.64 (m, 10 H, H_{arom}), 6.09 (d, ^3J = 8.0 Hz, 1 H, CHN), 6.01 (d, ^3J = 8.0 Hz, 1 H, CHN), 1.5 (s, 3 H, CH_3CN), 1.06 (s, 3 H, Pd−CH_3); $C_{56}H_{34}BF_{27}N_4O_2PdS$: calcd. C 46.2, H 2.4, N 3.8, S 2.2; found C 48.3, H 2.4, N 3.7, S 2.3.

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