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Communications

Dipyridophenazine as Electronic Tunable Ligands for the Palladium-Catalyzed Synthesis of Polyketones

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Summary: A series of Pd—methyl complexes, ***1a—6a****, with 11-R-dipyrido[3,2-a:2′,3′-c]phenazine ligands (dppz-R) being electronically modified with an R sustituent, efficiently catalyze CO/styrene copolymerization under mild conditions. Increased catalytic activity is observed on increasing the electron-donating character of the remote R substituent in the order* $R = NO_2 < COOH < Cl < H < CH_3 < NH_2$.

Over the last few years several families of palladium precatalysts for alternating CO/olefin copolymerization have been developed, with the common feature being at least one chelating ligand.[1] Despite intense research on this reaction over the past decade, the major drawback to the industrial production of polyketones is still low catalyst activity and metallic palladium deposition during the process of polymer synthesis.[2] This catalyst decomposition is of particular importance for palladium catalysts bearing nitrogen ligands,[1a,3] which are the most active ones for CO/styrene copolymerization.[4] The decomposition of such catalysts mostly takes place after β-H elimination (a possible chain-end termination reaction), since the palladium—hydride species formed are very unstable and CO may substitute the coordination of the N ligand, precipitating black palladium. Therefore, investigations aimed at finding more stable catalysts for this process are still of interest. Catalysts with enhanced stability have been obtained by the coordination of two chelating nitrogen ligands to the palladium precursor. Although dissociation of one ligand must occur to generate two

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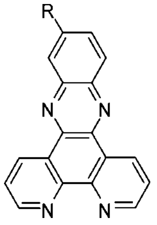
(3) Recent examples of palladium—methyl catalysts with nitrogen ligands: (a) Durand, J.; Zangrando, E.; Stener, M.; Fronzoni, G.; Carfagna, C.; Binotti, B.; Kamer, P. C. J.; Mueller, C.; Caporali, M.; van Leeuwen, P. W. N. M.; Vogt, D.; Milani, B. *Chem. Eur. J.* **2006**, *12*, 7639. (b) Schaetz, A.; Scarel, A.; Zangrando, E.; Mosca, L.; Carfagna, C.; Gissibl, A.; Milani, B.; Reiser, O. *Organometallics* **2006**, *25*, 4065. (c) Scarel, A.; Durand, J.; Franchi, D.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Mosca, L.; Seraglia, R.; Consiglio, G.; Milani, B. *Chem. Eur. J.* **2005**, *11*, 6014.

(4) Unexpected 1,2-styrene insertion explains the polymer production of a P—P-based palladium catalyst: Nozaki, K.; Komaki, H.; Kawashima, Y.; Hiyama, T.; Matsubara, T. *J. Am. Chem. Soc.* **2001**, *123*, 534.

10.1021/om700524v CCC: $40.75

Scheme 1. Dipyridophenazine Ligands (dppz-R)



Ligand	R
1	NH_2
2	CH_3
3	H
4	Cl
5	COOH
6	NO_2

vacant positions at palladium for the polymerization reaction, the presence of free ligand in the reaction medium greatly increases the stability of the catalytic systems.[5]

Our approach to increase catalyst stability has been the use of planar-around-metal ligands whose electronics could be easily tuned.[6] 11-R-dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligands (R = NH_2 (**1**), Me (**2**), H (**3**), Cl (**4**), COOH (**5**), NO_2 (**6**); referred to here as dppz-R),[7] which can be considered as π-extended phenanthrolines,[8] were chosen (Scheme 1). Due to the π-delocalization present in the phenazine backbone, we envisaged that the electronic properties of R could be transferred to the metal and affect its reactivity. Electronic effects have been observed for substituted diphosphine ligands in the related palladium-catalyzed CO/ethylene polymerization. The rate-enhancing effect of the electron-donating substituents has been related to the decreased strength of the interaction of the β-ketone moiety in the growing polymer chain with the metal center, which can favor the opening of the five- or six-membered oxametallacycle involved in the progress of the reaction.[9]

The ligands presented in this work have been previously used for the Ru-catalyzed water-gas shift reaction.[10] It must be here noted that during preparation of this work, Milani et al. reported the novel use of unsubstituted dppz as a ligand for this reaction.[11] We prepared isolated single-site polymerization catalysts via a two-step procedure (Scheme 2).[12] Reaction of ligands **1–6** with [PdClMe(cod)] (cod = 1,5-cyclooctadiene) in refluxing dichloromethane gave insoluble products, which were filtered and washed to remove free cyclooctadiene.[13] Further reaction of the insoluble products with NaBArF (BArF = $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$) to abstract chlorine afforded the cationic palladium−methyl complexes **1a–6a** as slightly soluble dark red-brown solids.[14]

Table 1. CO/*tert*-Butylstyrene Copolymerization with 1a–6a[a]

entry	precursor	R	productivity[b] (g of PK/g of Pd)	M_w[c] (M_w/M_n)	T_g[d] (°C)
1	**1a**	NH_2	2669	1.0×10^5 (1.7)	154
2	**2a**	CH_3	2153	4.3×10^4 (2.0)	153
3	**3a**	H	1332	3.6×10^4 (1.9)	152
4	**4a**	Cl	722	3.9×10^4 (1.8)	151
5	**5a**	COOH	240	4.0×10^4 (2.1)	150
6	**6a**	NO_2	259	4.6×10^4 (1.9)	142

[a] Reaction conditions: 5 μmol catalyst; TBS/Pd = 3270; 8 mL of CH_2Cl_2; 1 bar of CO; room temperature; 24 h. [b] Calculated from weighed polyketone (PK). [c] Measured at 25 °C against polystyrene standards. [d] Determined by DSC.

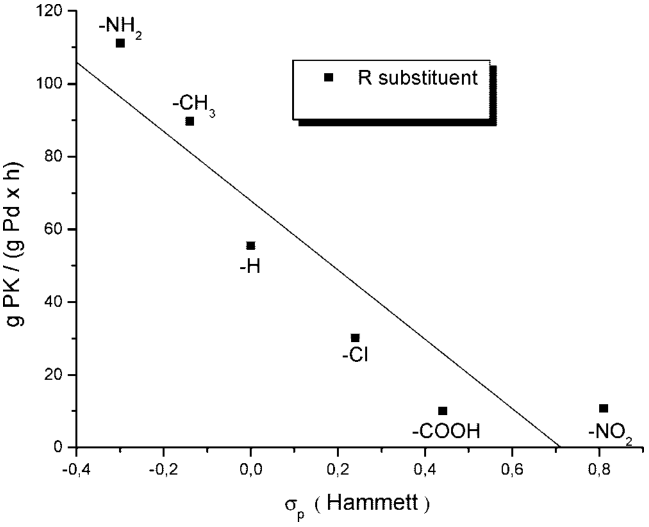


Figure 1. Influence of the electronic density of the R substituent (Hammett constants) on productivity (g of PK (g of Pd)$^{-1}$ h^{-1}).

Analysis by ^{1}H and ^{13}C NMR of the most soluble complex, **2a** (R = CH_3), shows twice the number of signals for protons $H^{2,2'}$, $H^{3,3'}$, and $H^{4,4'}$ (Scheme 3), indicating the presence of two coordination isomers in a ca. 1:1 ratio, owing to the unsymmetrical nature of the ligand.[15] For remote atoms (10, 12, and 13) only one signal is observed for each atom by ^{1}H NMR, while the signals of both isomers are observed by ^{13}C (see the Supporting Information for experimental details and characterization data). Although the cis/trans regioisomeric ratio of cationic palladium−methyl complexes should not influence the catalytic activity, it could, however, affect the stereoregularity of the reaction due to the different arrangements around the metal.

Table 1 summarizes the results of the experiments with complexes **1a–6a**, which were studied as CO/*tert*-butylstyrene (TBS) copolymerization precursors under mild conditions (1 bar of CO, room temperature, 24 h).[16] Under the studied conditions high productivities are obtained for complexes **1a–3a**, comparable to those of the most active palladium−methyl systems in the literature.[3] Notably we observed no decomposition to black palladium at the end of the polymerization runs.

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(5) Selected examples of [Pd(N-N)][X_2] catalysts: (a) Scarel, A.; Milani, B.; Zangrando, E.; Stener, M.; Furlan, S.; Fronzoni, G.; Mestroni, G.; Gladiali, S.; Carfagna, C.; Mosca, L. *Organometallics* **2004**, *23*, 1974. (b) Milani, B.; Scarel, A.; Mestroni, G.; Gladiali, S.; Taras, R.; Carfagna, C.; Mosca, L. *Organometallics* **2002**, *21*, 1323. (c) Milani, B.; Corso, G.; Mestroni, G.; Carfagna, C.; Formica, M.; Seraglia, R. *Organometallics* **2000**, *19*, 3435.

(6) Electronic effects can be crucial in this process: (a) Reference 3a. (b) Bastero, A.; Ruiz, A.; Claver, C.; Castillón, S.; Daura, E.; Bo, C.; Zangrando, E. *Chem. Eur. J.* **2004**, *10*, 3747. (c) Gambs, C.; Chaloupka, S.; Consiglio, G.; Togni, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2486.

(7) (a) Amouyal, E.; Homsi, A.; Chambron, J. C.; Sauvage, J. P. *J. Chem. Soc., Dalton Trans.* **1990**, 1841. (b) López, R.; Loeb, B.; Bossie, T.; Meyer, T. J. *Tetrahedron Lett.* **1996**, *37*, 5437. (c) Arancibia, A.; Concepción, J.; Daire, N.; Leiva, G.; Leiva, A. M.; Loeb, B.; del Rio, R.; Díaz, R.; Francois, A.; Valdivia, M. *J. Coord. Chem.* **2001**, *54*, 323.

(8) Phenanthroline (phen) and phen derivatives have shown superior performance as ligands in this reaction.[3a,5]

(9) See ref 2a, in particular Chapter 4, p 110 by Mul, W. P.; van der Made, A. W.; Smaardijk, A. A., Drent, E.

(10) Aguirre, P.; López, R.; Villagra, D.; Azocar-Guzman, I.; Pardey, A. J.; Moya, S. A. *Appl. Organomet. Chem.* **2003**, *17*, 36–41.

(11) Bergman, S. D.; Goldberg, I.; Carfagna, C.; Mosca, L.; Kol, M.; Milani, B. *Organometallics* **2006**, *25*, 6014.

(12) Brookhart, M.; Rix, F. C.; DeSimone, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 5894.

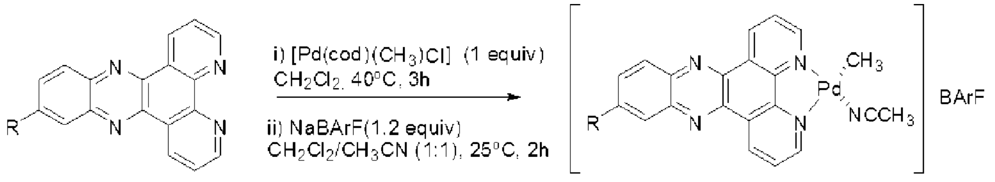
(13) NMR spectra were not informative, due to the low solubility of the products.

(14) Complexes **1a**−**6a** could be characterized by ^{1}H NMR, but their solubility was not sufficient to obtain good ^{13}C spectra, except for **2a**.

(15) Such mixtures of geometric isomers have reported for similar palladium−methyl complexes: (a) Leone, A.; Gischig, S.; Elsevier, C. J.; Consiglio, G. *J. Organomet. Chem.* **2007**, *692*, 2056. (b) Reference 3b. (c) Soro, B.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Zucca, A.; Bastero, A.; Claver, C. *J. Organomet. Chem.* **2004**, *689*, 1521.

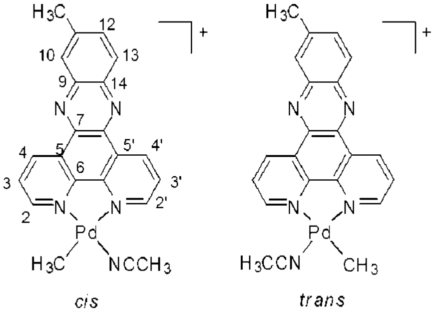
(16) *tert*-Butylstyrene instead of styrene is used to afford soluble alt-CO-*tert*-butylstyrene polyketones: Brookhart, M.; Rix, F. C.; DeSimone, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 5895–5897.

Scheme 2. Preparation of Palladium−Methyl Precursors 1a–6a



1-6 **1a-6a**

Scheme 3. Numbering Scheme of Ligands in the Cationic Palladium Complexes



When productivities are related to the electronic nature of the R substituent in the ligand, an increase in productivity is observed with increasing electron-donating character. As a way to evaluate the electronic effect of substituents on the reaction, the Hammet parameter (σ_p) for the R substituents are plotted against the productivities of the different complexes in Figure 1.[17] A correlation appears, the catalysts bearing electron-rich substituents (**1a** and **2a** with NH_2 and CH_3, respectively) being the most productive, in contrast to those having electron-deficient substituents which are an order of magnitude less active (**4a**, **5a**, and **6a** with Cl, COOH, and NO_2). The complex **3a**, with unmodified dppz, has an intermediate performance (entry 3) and notably behaves better than the related catalyst with phenanthroline as the chelating ligand,[3a] as recently reported for $[Pd(dppz)_2][X]_2$ complexes.[11] Therefore, it seems that the extended aromatic system indeed exerts a positive influence on the catalytic system stabilizing it.[18]

Molecular weights were determined by gel permeation chromatography against polystyrene standards. No clear relationship was found between the electronics of the dppz-R ligand and the molecular weight of the polymer (e.g., for **2a** ($R = CH_3$) $M_w = 4.3 \times 10^4$ and for **6a** ($R = NO_2$) $M_w = 4.6 \times 10^4$). This indicates that there is no influence of the ligand electronic effect on the relative rates of the chain transfer reaction vs the chain propagation reaction, probably due to the remote position of the substituents in the ligand. The highest molecular weight was obtained with the most active catalyst **1a** (Table 1, entry 1).

Narrow polydispersities of ca. 1.7–2 indicate single active species (see Figure S1 in the Supporting Information). Differential scanning calorimetry (DSC) measurements allowed us to determine the T_g value (ca. 152 °C), which is slightly lower for the polyketone obtained with catalyst **6a** (142 °C). No melting transitions were observed, as expected for amorphous polymers. The stereoregularity of the polymers was determined by ^{13}C NMR. Highly syndiotactic materials (97% of the *uu* triad) were obtained with all precursors, as expected for planar ligands.[1a]

In conclusion, we have reported the synthesis of cationic palladium−methyl complexes containing dppz-R ligands, which are highly active catalysts for CO/*tert*-butylstyrene copolymerization under mild conditions of pressure and temperature. Electronic modification of the dppz-R ligand at a position remote from the coordinated nitrogen atoms tunes the productivity of the palladium precursors. The most productive catalysts are those containing electron-rich substituents.

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Supporting Information Available: Text and a figure giving experimental details and characterization data for the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700524V

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(17) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

(18) Although activity measurements should be performed to state this point, the absence of black palladium at the end of the reaction seems to indicate the higher stability of these catalysts.