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Communications

Very Stable Palladium(II)−(N−N) Catalysts for the Synthesis of High-Molecular-Weight CO/Styrene Polyketones

Barbara Milani,* Alessandro Scarel, and Giovanni Mestroni

Dipartimento di Scienze Chimiche, Università degli Studi di Trieste, Via Licio Giorgieri 1, 34127 Trieste, Italy

Serafino Gladiali and Rossana Taras

Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy

Carla Carfagna and Luca Mosca

Istituto di Scienze Chimiche, Università di Urbino, Piazza Rinascimento 6, 61029 Urbino, Italy

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*Summary: A dicationic (N−N) bis-chelated Pd(II) complex containing the 3-alkyl-substituted 1,10-phenanthroline **1** as the unique ligand provides exceptionally high productivities in CO/styrene copolymerization, giving a polymer of unprecedentedly high molecular weight.*

Following Drent's discovery that Pd(II)−diphosphine complexes are very efficient catalysts for the CO/ethylene copolymerization,[1] in the last 10 years much interest has been paid to the behavior of olefins other than ethylene. In the copolymerization of CO with aromatic olefins, Consiglio found that, while chelating diphosphines such as 1,3-bis(diphenylphosphino)propane lead only to monocarbonylated products, bidentate N-donor ligands afford polyketones with high selectivity.[2] More recently, the same copolymerization has been performed in the presence of bidentate phosphino−phosphito[3] or P−N-heterodonor ligands.[4] In both these cases, however, the catalytic activities are much lower than those typical of the N−N ligands.

In recent papers on CO/styrene copolymerization by $[Pd(N-N)_2][PF_6]_2$ precatalysts, we have shown that a change of the reaction medium from methanol to 2,2,2-trifluoroethanol (TFE)[5] allows for this reaction to pro-

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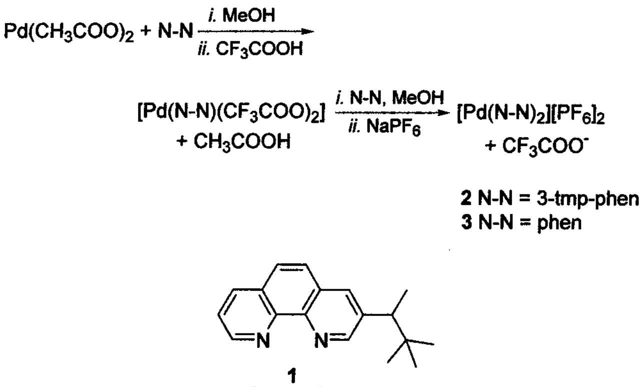
Scheme 1



1
3-tmp-phen

ceed, even in the absence of 1,4-benzoquinone.[5a] This additive was claimed to be essential for a Pd complex based on N-donor ligands to be catalitically active.[1a] Under our conditions the $[Pd(phen)_2]^{2+}$ catalyst was more stable than the $[Pd(bipy)_2]^{2+}$ derivative and afforded a polyketone with a molecular weight (M_w) higher than 80 000. End-group analysis of this polymer revealed that β-hydrogen elimination is the only effective chain-end process.[5a]

Substituted phenanthrolines have been used in this process with modest positive (5-methyl and nitro) or negative (3,4,7,8-tetramethyl) effects.[6] Therefore, pursuing our interest in this area, we have turned our attention to dicationic Pd(II) complexes derived from 3-alkyl-substituted phenanthrolines. These ligands have been previously exploited by us in the Rh-catalyzed asymmetric H-transfer reduction of prochiral ketones,[7] where the best results were obtained with (*S*)-3-(1,2,2-trimethylpropyl)-1,10-phenanthroline (3-tmp-phen, **1**).[8] The dicationic bis-chelated Pd(II) compound $[Pd(3\text{-tmp-phen})_2][PF_6]_2$ (**2**) was synthesized from the racemic ligand, through a two-step procedure[9] (Scheme 1), and its behavior in copolymerization reactions was checked against $[Pd(phen)_2][PF_6]_2$ (**3**).

The CO/styrene copolymerization tests were run in trifluoroethanol, at 50 °C, under 40 atm of CO pressure. No other cocatalyst or coreagent was added to the reaction mixture.[10] At a styrene/**2** ratio of 48 000, both the productivity and M_w of the syndiotactic polyketone produced were almost doubled with respect to those of the product obtained with the unsubstituted phen catalyst **3** (2.7 kg of CP/g of Pd vs 1.5 kg of CP/g of Pd (kg of CP/g of Pd = kilograms of copolymer per gram of palladium); M_w = 206 000 vs 108 000 after 24 h of reaction[11]). Moreover, no decomposition to palladium metal was observed.

The differences between the two phen ligands increase dramatically at a styrene-to-palladium ratio of 96 000. While the activity of $[Pd(phen)_2][PF_6]_2$ steadily decreases on prolonging the time, the productivity of the 3-tmp-phen-based catalyst increases linearly with time, reaching a value of 10.3 kg of CP/g of Pd after 96 h of reaction (Figure 1). This value represents the highest productivity ever obtained in this reaction in the absence of benzoquinone. Even after such a long time, the catalyst maintained its activity and no separation of palladium black was noticed on opening the autoclave.

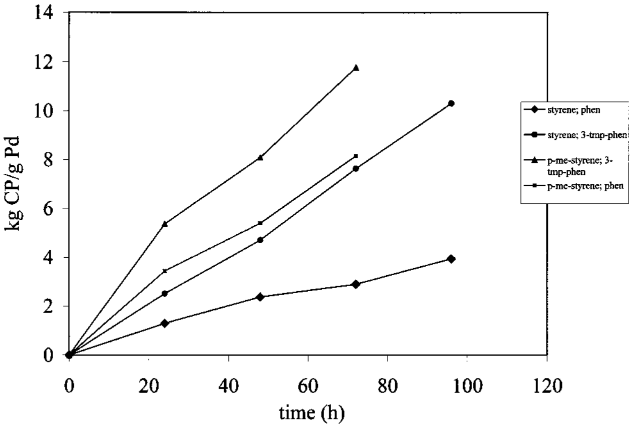


Figure 1. CO/aromatic olefin copolymerization: effect of time on productivity. The catalyst precursor was **2** or **3**. Reaction conditions: $n_{Pd} = 0.27 \times 10^{-5}$ mol; aromatic olefin V = 30 mL; solvent TFE V = 20 mL; T = 50 °C; p_{CO} = 40 atm.

Notably, with the new ligand, the higher the productivity, the higher the M_w of the polyketone. This increases steadily with the reaction time up to an M_w

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[8] (a) Gladiali, S.; Pinna, L.; Delogu, G.; De Martin, S.; Zassinovich, G.; Mestroni, G. *Tetrahedron: Asymmetry* **1990**, *1*, 635 and references therein. (b) For an improved synthetic procedure of **1**: Gladiali, S.; Chelucci, G.; Mudadu, M. S.; Gastaut, M. A.; Thummel, R. P. *J. Org. Chem.* **2001**, *66*, 400.

[9] Synthetic procedure. Synthesis of $[Pd(\mathbf{1})(CF_3COO)_2]$: 0.19 mmol of ligand **1** is added, at room temperature, to a methanolic solution of $Pd(CH_3COO)_2$ (0.16 mmol in 5 mL of CH_3OH). The solution becomes darker, and after complete dissolution of the ligand it is filtered over fine paper. An excess of CF_3COOH (0.35 mL) with respect to palladium is added, changing the color of the solution from red-brown to yellow. The product precipitates as a yellow solid upon concentration of the solution to half volume. It is removed by filtration, washed with cold methanol, and vacuum-dried. From the mother liquor a second fraction of the product is recovered upon addition of diethyl ether and after one night at 4 °C. Total yield: 55%. ^1H NMR in DMSO-d_6 at room temperature (400 MHz, referenced to the solvent peak versus TMS at δ 2.50): 9.03 (d, 1H, H^7, $J^{H7,8} = 4.15$ Hz), 8.92 (s, 1H, H^4), 8.5 (broad, $H^2 + H^9$), 8.28 (AB, 2H, $H^{5,6}$), 8.12 (dd, 1H, H^8, $J^{H8,9} = 2.68$ Hz), 3.05 (broad, CH), 1.36 (d, 3H, CH_3–CH, $^3J = 3.42$ Hz), 0.89 (s, 9H, $(CH_3)_3$–C). Synthesis of $[Pd(3\text{-tmp-phen})_2][PF_6]_2$ (**2**): 0.05 mmol of 3-(1,2,2-trimethylpropyl)-1,10-phenanthroline is added, at room temperature, to a methanolic suspension of $[Pd(3\text{-tmp-phen})(CF_3COO)_2]$ (0.06 mmol of complex in 2 mL of CH_3OH), yielding an orange-red solution. To this solution is added $NaPF_6$, dissolved in the minimum amount of methanol ($Pd:PF_6^- = 1:2.2$), giving the precipitation of the product as a yellow solid. After 15 min with stirring, at room temperature, the solid is removed by filtration, washed with cold methanol, and vacuum-dried. Yield: 65%. Anal. Found: C, 46.60; H, 4.33; N, 6.03. Calcd for $C_{36}H_{40}N_4F_{12}P_2Pd$: C, 46.74; H, 4.37; N, 6.06. ^1H NMR in acetone-d_6 at room temperature (400 MHz, referenced to the solvent peak versus TMS at δ 2.00): 9.44 (d, 2H, H^9, $J^{H8,9} = 2.44$ Hz), 9.23 (s, 2H, H^2), 9.18 (d, 2H, H^7, $J^{H7,8} = 4.15$ Hz), 9.11 (s, 2H, H^4), 8.45 (AB, 4H, $H^{5,6}$), 8.32 (dd, 2H, H^8), 3.27 (q, 2H, CH), 1.52 (d, 6H, CH_3–CH, $^3J = 3.66$ Hz), 0.99 (s, 18H, $(CH_3)_3$–C).

[10] For the procedure of a typical copolymerization reaction, see ref 5a.

[11] The molecular weights (M_w) of copolymers and the molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography versus polystyrene standards. The analyses were recorded on a Knauer HPLC (K-501 Pump, K-2500 spectrophotometer) with a PLgel 5 μm 10^4 Å GPC column and chloroform as solvent (flow rate 0.6 mL/min). The CO/styrene copolymer was dissolved as follows: 3 mg of the sample was solubilized with 120 μL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and chloroform was added up to 10 mL while the CO/*p*-methylstyrene copolymer was directly soluble in chloroform. The statistical calculations were performed using the Bruker Chromstar software program.

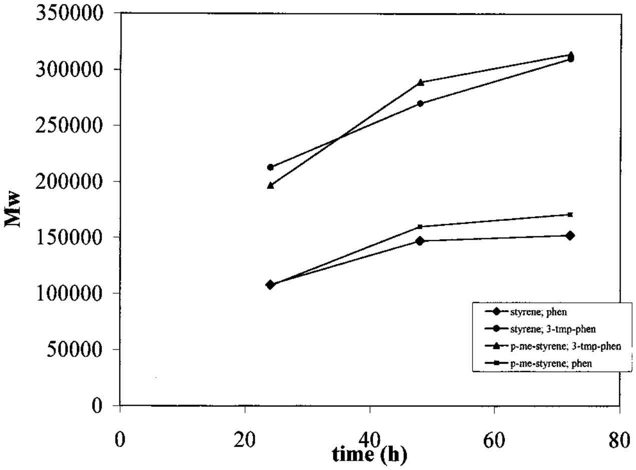

Figure 2. CO/aromatic olefin copolymerization: effect of time on molecular weight. The catalyst precursor was **2** or **3**. For the reaction conditions, see Figure 1.

value higher than 300 000. This is the highest M_w obtained thus far in this reaction and is about twice as high as the M_w of the polyketone obtained with the unsubstituted phen (Figure 2). The tacticity of the polyketone produced is basically the same as that of the copolymer obtained with the simple phen (82% of the syndiotactic triad and 9% each for the two eterotactic triads, determined on the basis of the C-ipso signals in the ^{13}C NMR spectra of the polyketones).

In the copolymerization of *p*-methylstyrene the productivity with both catalysts **2** and **3** was twice as high as those obtained with styrene, as a consequence of the modest increase of the electron density on the olefin bond (Figure 1). The M_w's of the resulting polyketones, however, were very similar to those of the CO/styrene products, indicating that the improvement in the yields was due to an increase in the number rather than the length of the polymeric chains.

These results demonstrate that the introduction of an alkyl substituent in a putatively innocent position of a phen ligand exerts a profound influence on the polymer chain growth in Pd-catalyzed CO/arylethene copolymerization. Positive consequences are as follows: (i) a very stable catalytic species is generated; (ii) exceptionally high productivity is reached; (iii) polyketones of unprecedentedly high M_w's are obtained.

A systematic investigation of the catalytic behavior of other 3-alkyl-substituted phenanthrolines is in progress, to understand which way the alkyl substitution in the phen ligand is able to retard the termination process in this polymerization.

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Supporting Information Available: Tables giving data for the CO/styrene copolymerization reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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