Addressing the Poly- to Oligo-ketone Selectivity in Styrene Carbonylation Catalyzed by Palladium/bpy Complexes. Effect of the 6-Alkyl Substitution

ARTICLE *in* ORGANOMETALLICS · OCTOBER 2010

Impact Factor: 4.13 · DOI: 10.1021/om100585x

DOI: 10.1021/om100585x

ORGANOMETALLICS
Article

Addressing the Poly- to Oligo-ketone Selectivity in Styrene Carbonylation Catalyzed by Palladium/bpy Complexes. Effect of the 6-Alkyl Substitution

Angela D'Amora,[†,§] Lidia Fanfoni,[†] Daniela Cozzula,[‡] Nicol Guidolin,[†] Ennio Zangrando,[†] Fulvia Felluga,[†] Serafino Gladiali,[‡] Fabio Benedetti,[†] and Barbara Milani*[,†]

[†]*Dipartimento di Scienze Chimiche, Università di Trieste, Via Licio Giorgieri 1, 34127 Trieste, Italy, and* [‡]*Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy.* [§]*Current address: Università di Napoli Federico II, Dipartimento di Chimica Paolo Corradini, Via Cintia, 80126 Napoli, Italy*

Received June 15, 2010

Two series of organometallic Pd complexes, namely, (i) $[Pd(CH_3)(CH_3CN)(N-N')][PF_6]$ and (ii) $[Pd(CH_3)(N-N')_2][PF_6]$, with a range of 6-alkyl-substituted-2,2′-bipyridine ligands, including the new 6-(1-methoxyethyl)-2,2′-bipyridine, in both racemic and enantiopure form, and 2-(methoxymethyl)-6-(1*H*-1,2,3-triazol-1-yl)pyridine, have been studied. 6-(1-Methoxyethyl)-2,2′-bipyridine was synthesized both in racemic and in the opposite homochiral enantiomeric forms by two stereocomplementary chemoenzymatic procedures. The characterization of the new complexes, both in solid state and in solution, provides evidence for the formation of a unique isomer featuring the methyl ligand *trans* to the Pd−N bond of the substituted pyridine ring. For the complex with the bpy ligand having the *sec*-butyl substituent a cyclometalation reaction with the release of methane occurs, leading the substituted bpy to act as a terdentate N−N′−C ligand. Complexes of series ii feature one chelate N−N′ ligand, while the other one is coordinated to Pd in a monodentate fashion. In solution a fluxional process that makes equivalent the two N−N′ ligands is present, and the static ^{1}H NMR spectra correspond to an averaged structure where palladium is a stereogenic center. All these complexes behave as catalysts for styrene carbonylation, yielding CO/styrene oligoketones, which are optically active when catalysts containing chiral, enantiomerically pure, ligands are applied. For both series of complexes the reactivity with labeled CO has been investigated, leading to the formation of the corresponding Pd−acetyl species, with that for complexes of series ii featuring both N−N′ molecules bonded to the same metal center.

Introduction

During the last two decades, considerable interest has been focused on the synthesis of perfectly alternating, carbon monoxide/alkene copolymers.[1−9] This reaction is homogeneously catalyzed by Pd(II) complexes containing a wide array of bidentate ligands including bidentate phosphine donors, bidentate nitrogen donors, hybrid phosphorus−nitrogen systems, and phosphino-phosphite ligands. A variety of reaction conditions have been employed: CO pressure from 1 to 40 bar, temperatures from 30 to 90 °C, and solvent variations including alcohols, dichloromethane, chlorobenzene, water, ionic liquids, and supercritical CO_2. The addition of co-reagents, such as 1,4-benzoquinone (BQ), or cocatalysts, such as Bronsted acids, is often beneficial. The choice of the best reaction conditions depends both on the nature of the palladium complex used as precatalyst and on the nature of the alkene used as co-monomer.

It is well known that diphosphine ligands are the ligands of choice when aliphatic alkenes are the comonomers; *o*-methoxy-modified 1,3-bis(diphenylphosphino)propane (bdompp) was applied for the industrial production of Carilon, the CO/ethylene/propylene terpolymer.[10] By variation of the bdompp ligand, in particular by using the sulfonated derivative, 1,3-bis(di(2-methoxy-5-sulfonatophenyl)phosphino)propane (bdompp-S), and under properly modified reaction conditions, it was possible to shift the selectivity of the reaction from terpolymers to oligomers with M_w values between 1500 and 5000. This product was exploited at the commercial level

*Corresponding author. Phone: 0039 040 5583956. Fax: 0039 040 5583903. E-mail: milaniba@units.it.

(1) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520–3522.
(2) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866–870.
(3) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235–251.
(4) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663–681.
(5) Bianchini, C.; Meli, A. *Coord. Chem. Rev.* **2002**, *225*, 35–66.
(6) Nakano, K.; Kosaka, N.; Hiyama, T.; Nozaki, K. *Dalton Trans.* **2003**, 4039–4050.
(7) Durand, J.; Milani, B. *Coord. Chem. Rev.* **2006**, *250* (3−4), 542–560.
(8) García Suárez, E. J.; Godard, C.; Ruiz, A.; Claver, C. *Eur. J. Inorg. Chem.* **2007**, *2007* (18), 2582–2593.
(9) Anselment, T. M. J.; Vagin, S. I.; Rieger, B. *Dalton Trans.* **2008**, 4537–4548.
(10) Alperwicz, N. *Chem. Week* **1995**, 127.
(11) Drent, E.; Keijsper, J. J. US Patent 5225523, 1993.

 Published on Web 09/29/2010

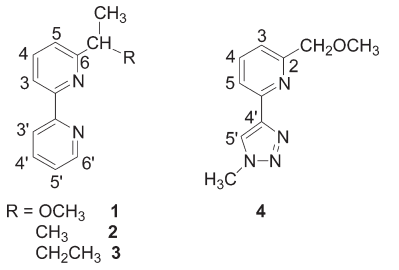
under the trademark of Carilite Oligomer.[11−13] Thanks to the chemical reactivity of the ketonic function, Carilite Oligomers can be cured in different ways, leading to Carilite and Cariverse resins, which have found various applications, i.e., as glues for wood composites and as electronic packaging, respectively.

When carbon monoxide is copolymerized with an aromatic alkene, like styrene or substituted styrenes, the best performing catalytic systems are based on palladium complexes with bidentate nitrogen-donor ligands.[7] The presence of substituents on the ligand has a remarkable effect on the catalyst performance and on the properties of the synthesized macromolecules.[14−16] In particular, when the position adjacent to both nitrogen donors is substituted, like in 2,9-dimethyl-1,10-phenanthroline,[17] the relevant palladium complexes are inactive in the CO/vinyl arene copolymerization, reasonably due to the steric hindrance generated by the two methyl substituents. Even the Pd complexes with 2,2′-bipyridines substituted on only one of the two *ortho* positions with respect to the N donor, 6-R-2,2′-bipyridine (R = Me, Et, ^{i}Pr),[18] are apparently inactive for the copolymerization reaction.

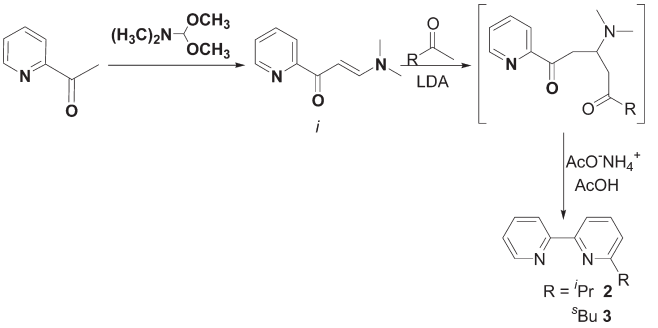
While there is extensive literature on the synthesis of polyketones from carbon monoxide and aromatic alkenes, few data have been reported on the synthesis of the corresponding oligomers. Low molecular weight compounds, such as dimethyl 2-phenylbutanedioate, dimethyl 2,5-diphenyl-4-oxo-pimelate, and 2-oxoglutarates, can be prepared from CO and styrene by using Pd−phenanthroline or Pd−diphosphine complexes in the presence of a large excess of 1,4-benzoquinone (BQ)[19,20] or under high CO pressure (350 bar).[21]

Aiming at investigating in more detail the effect of a monosubstitution of the carbon adjacent to the N donor, a few 6-alkyl-substituted-2,2′-bipyridines, comprising the new 6-(1-methoxyethyl)-2,2′-bipyridine (**1**), in both racemic and enantiopure form, the known 6-isopropyl-2,2′-bipyridine (**2**), *rac*-6-*sec*-butyl-2,2′-bipyridine (**3**), and the new 2-(methoxymethyl)-6-(1*H*-1,2,3-triazol-1-yl)pyridine (**4**) (Chart 1), have been screened as supporting ligands for monocationc Pd(II) complexes. These ligands were chosen with the aim to shed light on (a) the effect of different alkyl substituents in the ligand (as for **2** and **3**); (b) the possible occurrence of hemilabile coordination of a weak donor (as the oxygen for **1**); and (c) the influence of a nitrogen donor other than pyridine in the chelating arm (as for **4**).

Chart 1. The Studied 6-Alkyl-Substituted-2,2′-bipyridines 1−3, the Triazole Derivative 4, and Their Numbering Scheme



Scheme 1. Synthetic Pathway for Ligands 2 and 3



The catalytic behavior of these derivatives in styrene carbonylation has been analyzed in detail, together with some mechanistic investigation on the reactivity of these complexes with carbon monoxide.

Results and Discussion

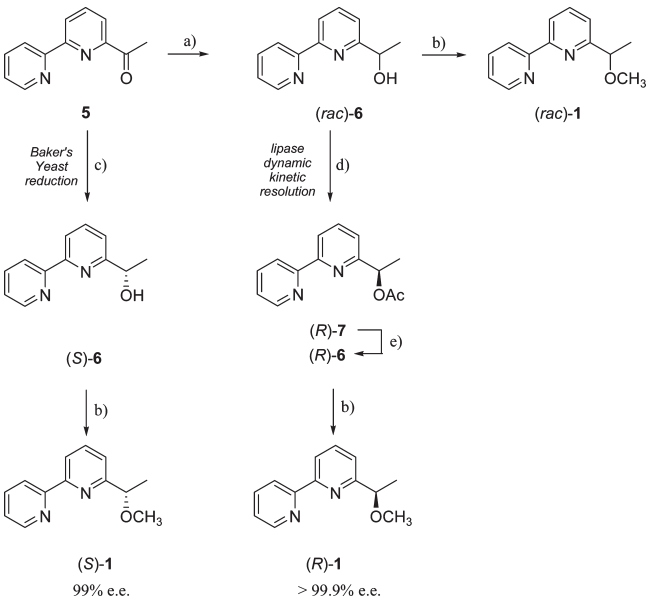
Synthesis and Characterization of Ligands 1−4. Ligands **2** and **3** are known compounds that were synthesized previously through low-yielding multistep procedures.[22,23] For this work, their preparation has been more conveniently accomplished by adapting a more expedient and better yielding methodology utilized for the preparation of alkyl-substituted terpyridines.[24]

Compounds **1** and **4** are reported here for the first time. Ligand *rac*-**1** was synthesized from ketone **5**,[25] by reduction to the corresponding carbinol **6** followed by methylation with CH_3I and NaH (Scheme 2).

The homochiral (*R*)-**1** and (*S*)-**1** were obtained by different chemoenzymatic methods. Enantiomerically pure (*S*)-**6** was synthesized from **5** by asymmetric reduction with Baker's yeast (*Saccharomyces cerevisiae*).[26−29] The reduction was performed under fermenting conditions (37 °C, saccharose, phosphate buffer, pH 7.4), reaching 93% conversion in 48 h.

(12) Chang, B. T. A.; Dubois, D. A.; Fan, M.; Gelles, D. L.; Iyer, S. R.; Mohindra, S.; Tutunjian, P. N.; Wong, P. K.; Wright, W. J. In *CARIVERSE Resin: A thermally reversible network polymer for electronic application*, 49th Electronic Components and Technology Conference, 1999; **1999**; pp 49−55.
(13) Mul, W. P.; Dirkzwager, H.; Broekhuis, A. A.; Heeres, H. J.; Van der Linden, A. J.; Orpen, A. G. *Inorg. Chim. Acta* **2002**, *327*, 147–159.
(14) Bastero, A.; Claver, C.; Ruiz, A.; Castillon, S.; Daura, E.; Bo, C.; Zangrando, E. *Chem.—Eur. J.* **2004**, *10* (15), 3747–3760.
(15) Scarel, A.; Milani, B.; Zangrando, E.; Stener, M.; Furlan, S.; Fronzoni, G.; Mestroni, G.; Gladiali, S.; Carfagna, C.; Mosca, L. *Organometallics* **2004**, *23*, 5593–5605.
(16) Durand, J.; Zangrando, E.; Stener, M.; Fronzoni, G.; Carfagna, C.; Binotti, B.; Kamer, P. C. J.; Muller, C.; Caporali, M.; van Leeuwen, P. W. N. M.; Vogt, D.; Milani, B. *Chem.—Eur. J.* **2006**, *12*, 7639–7651.
(17) Milani, B.; Alessio, E.; Mestroni, G.; Sommazzi, A.; Garbassi, F.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1994**, 1903–1911.
(18) Stoccoro, S.; Alesso, G.; Cinellu, M. A.; Minghetti, G.; Zucca, A.; Bastero, A.; Claver, C.; Manassero, M. *J. Organomet. Chem.* **2002**, *664*, 77–84.
(19) Barsacchi, M.; Consiglio, G.; Medici, L.; Petrucci, G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 989–991.
(20) Consiglio, G.; Nefkens, S. C. A.; Pisano, C. *Inorg. Chim. Acta* **1994**, *220*, 273–281.
(21) Sperrle, M.; Consiglio, G. *J. Organomet. Chem.* **1996**, *506*, 177–180.
(22) Botteghi, C.; Chelucci, G.; Marchetti, M. *Synth. Commun.* **1982**, *12*, 25–33.
(23) Botteghi, C.; Caccia, G.; Chelucci, G.; Soccolini, F. *J. Org. Chem.* **1984**, *49*, 4290–4293.
(24) Chelucci, G. *Synth. Commun.* **1993**, *23*, 1987–1903.
(25) Constable, E. C.; Heirtzler, F.; Neuburger, M.; Zehnder, M. *J. Am. Chem. Soc.* **1997**, *119*, 5606–5617.
(26) Nakamura, K.; Matsuda, T. *Reduction of Ketones*; Wiley-VCH: Weinheim, 2002; Vol. *3*, pp 991−1047.
(27) Santaniello, E.; Ferraboschi, P.; Grisenti, P.; Manzocchi, A. *Chem. Rev.* **1992**, *92*, 1071–1140.
(28) Czuck, S.; Blanzer, B. I. *Chem. Rev.* **1991**, *91*, 49–97.
(29) Servi, S. *Synthesis* **1990**, 1–25.

Scheme 2. Synthetic Pathway for Ligands *rac*-1, (*R*)-1, and (*S*)-1[a]



[a] (a) $NaBH_4$, EtOH, rt, 99% yield; (b) NaH, CH_3I, THF, 0 °C, 99% yield; (c) baker's yeast, saccharose, phosphate buffer (pH 7.4), 37 °C, 75% yield; (d) *p*-chlorophenyl acetate, toluene, 70 °C, 2% $[Ru_2(CO)_4(\mu\text{-}H)(C_4Ph_4\text{-}COHOCC_4Ph_4]$, Novozyme 435, 75% yield; (e) K_2CO_3(aq), 99% yield.

As predicted from Prelog's rule, it afforded the *S*-configured carbinol,[30] in 99% ee and 75% chemical yield.

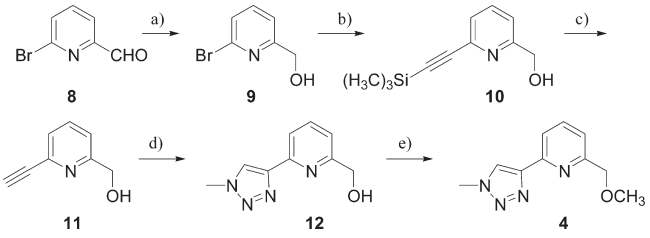
The antipode (*R*)-**6** was obtained according to the procedure developed for the resolution of chiral 1-heteroarylethanols[31,32] by lipase-catalyzed dynamic kinetic resolution of the racemate, using Novozyme (*Candida antarctica* lipase B (CAL-B), immobilized on polyacrylamide) and *p*-chlorophenylacetate as the acyl donor, in the presence of Shvo's complex as redox catalyst.

The reaction reached complete conversion in 48 h, giving the ester **7** of *R* configuration with excellent enantiomeric purity (ee > 99.9%) and in 70% yield after column chromatography. Mild hydrolysis (K_2CO_3(aq)) provided the corresponding enantiopure (*R*)-**6** in 70% overall yield from the racemic alcohol **6** (Scheme 2). The *R* configuration of this compound was confirmed by the sign of the optical rotation[33] and was in keeping with the well-known *R* enantiopreference of CAL-B.[34,35]

Methylation of the homochiral (*R*)-**6** and (*S*)-**6** gave the target ligands, (*R*)-**1** and (*S*)-**1**, in good isolated yield (68% and 74%, respectively).

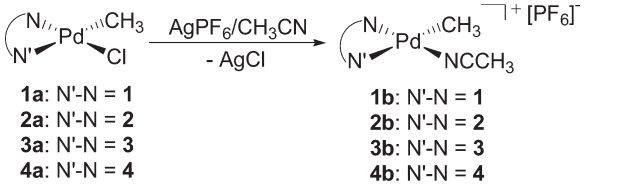
The synthesis of ligand **4** started from the commercially available bromo aldehyde **8** (Scheme 3). This was reduced by $NaBH_4$ to the alcohol **9**,[36] which by coupling with trimethylsilylacetylene was converted into the ethynyl derivative **10**.

Scheme 3. Synthetic Pathway for Ligand 4[a]



[a] (a) $NaBH_4$, EtOH, 99%; (b) trimethylsilylacetilene, $[Pd(PPh_3)_4]$ (cat.), CuI/NEt_3, 100%; (c) Bu_4NF 68%; (d) CH_3I, NaN_3, t-BuOH, H_2O, MW; 74%; (e) CH_3I, NaH, anhyd. THF, 0 °C, 100%.

Scheme 4. Synthetic Pathway for Monocationic Palladium Complexes 1b−4b



Desilylation by Bu_4NF in THF[37] gave the monosubstituted acetylene **11**. Microwave-assisted reaction of **11** with sodium azide and CH_3I in the presence of copper(I) catalyst afforded with complete regioselectivity the triazolylpyridine **12**.[38] Finally methylation of the OH gave the target ligand **4** in 50% overall yield from the starting aldehyde **8**.

Synthesis and Characterization of Pd Complexes $[Pd(CH_3)(CH_3CN)(N{-}N')][PF_6]$ 1b−4b (N−N′ = 1−4) and $[Pd(CH_3)(N{-}N')_2][PF_6]$ 1c−3c (N−N′ = 1−3). The synthesis of the monocationic Pd(II) complexes $[Pd(CH_3)(CH_3CN)(N{-}N')][PF_6]$ **1b−4b** was performed starting from $[Pd(CH_3COO)_2]$ according to the five-step procedure reported in the literature,[39−41] which involves a halogen abstraction reaction of the neutral derivatives $[Pd(CH_3)(Cl)(N{-}N')]$ **1a−4a** (N−N′ = **1−4**) as the last step (Scheme 4).

Single crystals suitable for X-ray analysis of the neutral derivatives *rac*-**1a** and **3a** were obtained upon addition of diethyl ether and *n*-hexane, respectively, to a dichloromethane solution of the complexes, at low temperature (Figure 1).

In both complexes the palladium ion attains the usual square-planar coordination geometry with bond lengths and angles within the typical range found for analogous Pd(II) complexes (Figure 1). In agreement with the *trans* influence of the Pd−CH_3 fragment, the Pd−N2 bond located *trans* to it is remarkably longer than the Pd−N1 one. In the two complexes the coordination plane forms a dihedral angle of ca. 18° with the mean plane through the bpy rings likely in order to avoid steric clashes with the alkyl groups. This aspect might be related to the fact that for both complexes the isomer detected in the unit cell is featured by the Pd−CH_3

(30) Prelog, V. *Pure Appl. Chem.* **1964**, *9*, 119–122.
(31) Felluga, F.; Baratta, W.; Fanfoni, L.; Pitacco, G.; Rigo, P.; Benedetti, F. *J. Org. Chem.* **2009**, *74*, 3547–3550.
(32) Persson, B. A.; Larsson, A. L. E.; Le Ray, M.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1999**, *121*, 1645–1650.
(33) Uenishi, J.; Hiraoka, T.; Hata, S.; Nishiwaki, K.; Yonemitsu, O. *J. Org. Chem.* **1998**, *63*, 2481–2487.
(34) Rotticci, D.; Hæffner, F.; Orrenius, C.; Norin, T.; Hult, K. *J. Mol. Catal. B: Enzym.* **1998**, *5*, 267–272.
(35) Chen, C.-S.; Fujimoto, Y.; Girdaukas, G.; Sih, C. J. *J. Am. Chem. Soc.* **1982**, *104*, 7294–7299.
(36) Landa, A.; Minkkila, A.; Blay, G.; Joergensen, K. A. *Chem.—Eur. J.* **2006**, *12*, 3472–3483.
(37) Bolm, C.; Ewald, M.; Felden, M.; Schlingloff, G. *Chem. Ber.* **1992**, *125*, 1169–1190.
(38) Appukkuttan, P.; Dehaen, W.; Fokin, V. V.; Van der Eycken, E. *Org. Lett.* **2004**, *6*, 4223–4225.
(39) Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; Van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769–5778.
(40) Groen, J. H.; Delis, J. G. P.; vanLeeuwen, P.; Vrieze, K. *Organometallics* **1997**, *16* (1), 68–77.
(41) Milani, B.; Marson, A.; Zangrando, E.; Mestroni, G.; Ernsting, J. M.; Elsevier, C. J. *Inorg. Chim. Acta* **2002**, *327*, 188–201.

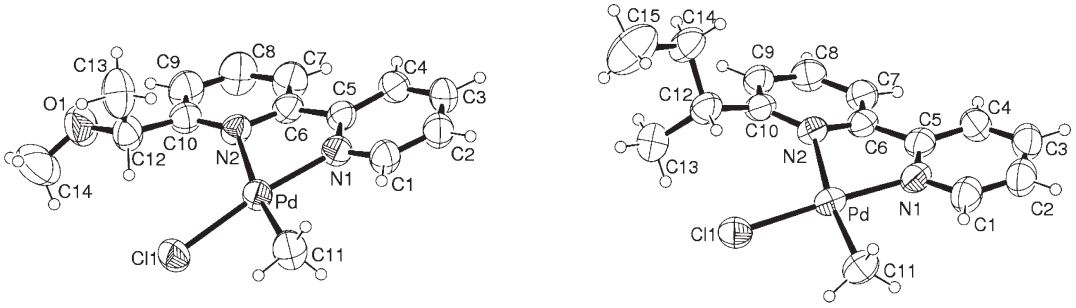


Figure 1. ORTEP drawing (thermal ellipsoids 35% probability level) of complexes *rac*-**1a** (a) and **3a** (b). Selected bond lengths [Å] and angles [deg]: for *rac*-**1a**, Pd−N(1) 2.051(3), Pd−N(2) 2.232(3), Pd−Cl(1) 2.3124(11), Pd−C(11) 2.028(4), N(1)−Pd−N(2) 78.51(13), N(1)−Pd−Cl(1) 171.96(9), N(2)−Pd−Cl(1) 103.07(9), C(11)−Pd−N(1) 92.79(18), C(11)−Pd−N(2) 171.22(17), C(11)−Pd−Cl(1) 85.38(14); **3a**, Pd−N(1) 2.055(6), Pd−N(2) 2.253(4), Pd−Cl(1) 2.304(2), Pd−C(11) 2.026(6), N(1)−Pd−N(2) 78.1(2), N(1)−Pd−Cl(1) 177.48(14), N(2)−Pd−Cl(1) 103.63(14), C(11)−Pd−N(1) 92.2(3), C(11)−Pd−N(2) 169.5(2), C(11)−Pd−Cl(1) 85.9(2).

bond *trans* to the substituted pyridine ring. The complexes were synthesized with the racemic ligand, and, as expected, both the enantiomers are present in the centrosymmetric unit cells. For complex *rac*-**1a**, the oxygen atom of the methoxyethyl substituent points far away from the palladium ion, almost coplanar with the pyridine ring (C9−C10−C12−O1 torsion angle of 10.9(6)°).

Both neutral and monocationic derivatives were fully characterized in solution by ^{1}H NMR spectroscopy.

For all complexes the coordination of N−N′ ligands to palladium resulted in a shift of the signals for all protons, while no signal due to the free ligand was present. For all complexes the number of signals and their integration confirm the coordination of the ligand in a nonsymmetric environment and indicate the presence in solution of only one species. The Pd−CH_3 resonance falls in the range 0.90−1.40 ppm, which are typical values for this signal in analogous complexes.[16]

For complexes **1a**−**3a** and **1b**−**3b**, NOE experiments performed upon irradiation of the $H^{6'}$ signal indicate the *cis* relationship between $H^{6'}$ and the Pd−CH_3 group, which consequently is *trans* to the more basic N-donor atom. This is in agreement with the solid-state structures. The Pd(II)-methyl complexes with nonsymmetric bidentate nitrogen-donor ligands reported in the literature feature the methyl group *trans* to the N atom with a lower Lewis basicity,[14,16,42−44] which is the opposite of our case. We have already observed the present geometry in analogous complexes with amine-imine ligands,[45] where, due to the *hard*−*soft* mismatch between Pd(II) and the sp^3 nitrogen, the resulting bond is weaker than the Pd−sp^2N bond, and the methyl group takes up the position *trans* to it. For the present complexes having both nitrogen atoms sp^2 hybridized, the preferential formation of the *trans* methyl isomer can be a consequence of the steric hindrance of the alkyl substituent in *ortho* position to the nitrogen donor.

Complexes **4a**,**b**, containing the triazole-derived ligand, could be dissolved only in DMSO, where at room temperature they showed broad signals in the ^{1}H NMR spectra. At 333 K the NMR spectra were consistent with the presence in solution of one single species, which could not be assigned to the *cis* or the *trans* geometry by NOE experiments. The observed broadening is indicative of a dynamic process in solution, reasonably due to the exchange between dimethylsulfoxide and one of the nitrogen donors of the chelating ligand. Similar processes have been noticed in Pd-bis-chelated complexes $[Pd(N-N)_2][PF_6]_2$ with N−N = 2,2′-bipyiridine or 1,10-phenanthroline ligands.[15,46]

Whereas complexes **1a**−**3a**, **1b**, and **2b** are stable in dichloromethane for days, at room temperature, complex **3b** evolves toward a new species shortly after dissolution, the conversion being completed in 5 h. This new species (isolated in 95% yield) has been fully characterized both in solution via NMR (see Supporting Information (SI), Figure 1S) and in the solid state by X-ray analysis and corresponds to the cyclometalated derivative **3b**′ (Figure 2a).

In **3b**′ the bpy acts as a terdentate ligand toward the palladium ion, through C11 of the *sec*-butyl group. The metal sits in the expected square-planar coordination geometry, the fourth position being occupied by acetonitrile. The six-membered ring shows a puckered conformation, where Pd, N1, C1, and C11 are essentially coplanar (max. deviation of 0.08 Å for N1), and C12 and C13 lie 0.35(2) and −0.53(2) Å below and above the best plane, respectively. The bond distances and angles (Figure 2) are comparable to those observed in the similar cyclopalladated complex obtained from 6-neopentyl-2,2′-bpy ligand.[47]

The NMR characterization of **3b**′ is in agreement with the solid-state structure: the Pd−CH_3 signal is missing, the multiplet of the CH_2 bonded to CH appears split into two well-separated multiplets, and two additional methylenic resonances (1.51 and 0.88 ppm) are present in place of the methyl of the *sec*-butyl substituent of **3b** at 0.89 ppm.

The cyclopalladation reaction results from the activation of the C−H bond at the methyl group of the *sec*-butyl substituent in the monocationic complex **3b** according to a

(42) Bastero, A.; Ruiz, A.; Claver, C.; Milani, B.; Zangrando, E. *Organometallics* **2002**, *21*, 5820–5829.
(43) Scarel, A.; Durand, J.; Franchi, D.; Zangrando, E.; Mestroni, G.; Milani, B.; Gladiali, S.; Carfagna, C.; Binotti, B.; Bronco, S.; Gragnoli, T. *J. Organomet. Chem.* **2005**, *690* (8), 2106–2120.
(44) Scarel, A.; Axet, M. R.; Amoroso, F.; Ragaini, F.; Elsevier, C. J.; Holuigue, A.; Carfagna, C.; Mosca, L.; Milani, B. *Organometallics* **2008**, *27*, 1486–1494.
(45) Axet, M. R.; Amoroso, F.; Bottari, G.; D'Amora, A.; Zangrando, E.; Faraone, F.; Drommi, D.; Saporita, M.; Carfagna, C.; Natanti, P.; Seraglia, R.; Milani, B. *Organometallics* **2009**, *28*, 4464–4474.
(46) Milani, B.; Anzilutti, A.; Vicentini, L.; Sessanta o Santi, A.; Zangrando, E.; Geremia, S.; Mestroni, G. *Organometallics* **1997**, *16*, 5064–5075.
(47) Zucca, A.; Cinellu, M. A.; Pinna, M. V.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. *Organometallics* **2000**, *19*, 4295–4304.

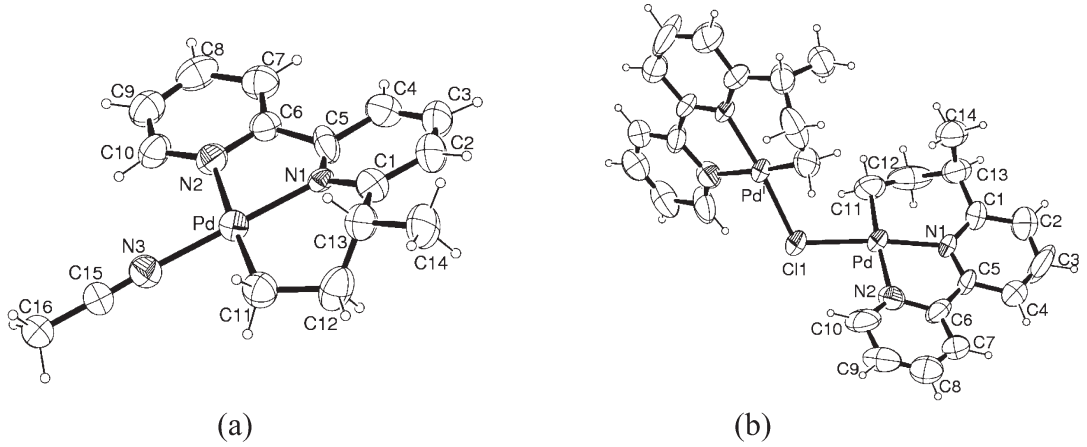


Figure 2. ORTEP drawing (thermal ellipsoids 20% probability level) of the cation of **3b′** (a) and of **3a′** (b) with atom labels of the crystallographic independent part. Selected bond lengths [Å] and angles [deg]: for **3b′**, Pd−N(1) 2.020(7), Pd−N(2) 2.134(9), Pd−N(3) 2.033(11), Pd−C(11) 2.022(12), N(1)−Pd−N(2) 79.4(3), N(1)−Pd−C(11) 97.8(4), C(11)−Pd−N(2) 176.3(4), N(1)−Pd−N(3) 175.7(3), N(3)−Pd−N(2) 97.3(4), C(11)−Pd−Cl(1) 85.38(14); for **3a′**, Pd−N(1) 1.999(9), Pd−N(2) 2.104(14), Pd−Cl(1) 2.337(3), Pd−C(11) 1.982(18), N(1)−Pd−N(2) 78.6(5), N(1)−Pd−Cl(1) 174.0(4), N(2)−Pd−Cl(1) 95.8(4), C(11)−Pd−N(1) 96.8(8), C(11)−Pd−N(2) 175.2(8), C(11)−Pd−Cl(1) 88.8(7).

first-order kinetic law (SI, Figure 2S). The transfer of this proton to the methyl bonded to palladium leads to the formation of methane, as demonstrated by NMR (eq 1).

$$\underset{\textbf{3b}}{[Pd(CH_3)(\textbf{3})(CH_3CN)][PF_6]} \xrightarrow[\text{r.t.}]{CH_2Cl_2} \underset{\textbf{3b'}}{[Pd(bpy\text{-}CH(CH_3)CH_2CH_2)(CH_3CN)][PF_6]} + CH_4 \quad (1)$$

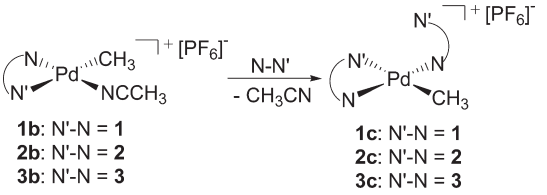
The cyclopalladation of 6-alkyl-substituted-bpy ligands proceeds easily from the cationic or neutral complexes where the bpy is coordinated as a bidentate chelating ligand, whenever it allows the formation of a five- or six-membered-ring metallacycle.[18,47−51] The cyclopalladation takes place even on the neutral complex **3a** in the absence of any coordinating solvent. However, in this case the reaction affords dinuclear chloride-bridged species **3a′** as the unique product (Figure 2b).

The X-ray analysis of **3a′** shows that the bpy acts as a terdentate ligand toward both the metal centers and that the two fragments are oriented almost orthogonally to each other, forming a dihedral angle of 82.3(4)° between the coordination mean planes. The geometry and the bond lengths Pd−N and Pd−C are similar to those of complex **3b′**, aside from the different accuracy.

The NMR characterization of **3a′** was performed in CD_2Cl_2 solution. At room temperature broad signals are observed that become sharper on decreasing the temperature, to 233 K. At this temperature a series of major signals confirming the solid-state structure is evident, plus an additional series of minor broad signals that were not clearly assigned (SI, Figure 3S).

3a′ can be easily transformed into **3b′** by treatment with $AgPF_6$ in the presence of acetonitrile.

Scheme 5. Synthetic Pathway for the Monocationic Palladium Complexes 1c−3c



By treatment with an excess of N−N′ ligand, the monocationic derivatives **1b−3b** release the coordinated acetonitrile, giving the complexes $[Pd(CH_3)(N{-}N')_2][PF_6]$ **1c−3c** (N−N′ = **1−3**), where one more unit of N−N′ ligand is coordinated to palladium (Scheme 5).[40,41,52,53]

Single crystals, suitable for X-ray analysis, of *rac*-**1c** and **3c** were obtained upon addition of diethyl ether to a CD_2Cl_2 solution of the complex (Figure 3).

The Pd atom exhibits a distorted square-planar coordination geometry with one bpy molecule acting as a monodentate and the other as a bidentate ligand, the fourth position being kept by the methyl group located *trans* to the substituted pyridine ring. As expected, the Pd−N2 bond distance is much longer than the Pd−N1.

The binding of the monodentate bpy ligand to Pd occurs at the unsubstituted pyridine nitrogen N3, the other nitrogen being at a distance from Pd of 2.656(4) and 2.760(4) Å in **1c** and **3c**, respectively. The metal is displaced from the mean plane of the four donors by 0.029(2) and 0.177(2) Å toward the apical N4, indicative of a weak interaction with that atom.

Although **1c** and **3c** appear similar at first sight, the coordinating atoms are almost coplanar with the chelating bpy in **1c** (9.6(2)°), while in **3c** the angle is much larger (25.18(9)°) (Figure 4). Moreover, the dihedral angle between the mean planes of the two bpy units is 86.13(9)° in **1c** and 67.99(9)° in **3c**. This implies a significant bending for the monocoordinated bpy in **3c**.

(48) Stoccoro, S.; Chelucci, G.; Cinellu, M. A.; Zucca, A.; Minghetti, G. *J. Organomet. Chem.* **1993**, *450*, C15–C16.
(49) Minghetti, G.; Cinellu, M. A.; Chelucci, G.; Gladiali, S.; F., D.; Manassero, M. *J. Organomet. Chem.* **1986**, *307*, 107–114.
(50) Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Sansoni, M. *Eur. J. Inorg. Chem.* **2002**, 3336–3346.
(51) Stoccoro, S.; Soro, B.; Minghetti, G.; Zucca, A.; Cinellu, M. A. *J. Organomet. Chem.* **2003**, *679*, 1–9.
(52) Garrone, R.; Romano, A. M.; Santi, R.; Millini, R. *Organometallics* **1998**, *17*, 4519–4522.
(53) Milani, B.; Corso, G.; Zangrando, E.; Randaccio, L.; Mestroni, G. *Eur. J. Inorg. Chem.* **1999**, 2085–2093.

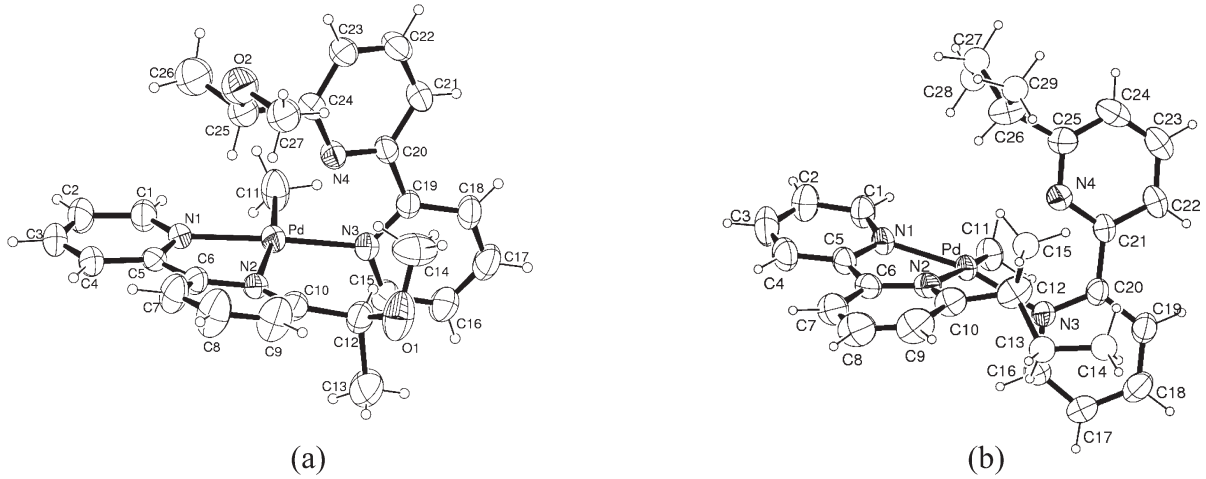


Figure 3. ORTEP drawing (thermal ellipsoids 35% probability level) of the complex cations of *rac*-**1c** (a) (for clarity only one of the disordered 1-methoxyethyl groups at C24 is shown) and of **3c** (b) (carbon atoms of the *sec*-butyl group at C12 and C26 are drawn with a fixed radius due to the high thermal motion). Selected bond lengths [Å] and angles [deg]: for *rac*-**1c**, Pd−N(1) 2.055(4), Pd−N(2) 2.247(4), Pd−N(3) 2.087(4), Pd−C(11) 2.026(5), Pd---N(4) 2.656(4), N(1)−Pd−N(2) 78.10(15), N(3)−Pd---N(4) 70.32(15), C(11)−Pd−N(1) 92.91(19), C(11)−Pd−N(2) 170.39(18), C(11)−Pd−N(3) 82.73(18), C(11)−Pd---N(4) 94.9(2), N(1)−Pd−N(3) 172.31(16), N(1)−Pd---N(4) 116.53(14), N(3)−Pd−N(2) 106.58(14), N(2)−Pd---N(4) 86.21(12); for **3c**, Pd−N(1) 2.041(4), Pd−N(2) 2.195(3), Pd−N(3) 2.083(3), Pd−C(11) 2.033(4), Pd---N(4) 2.760(4), N(1)−Pd−N(2) 78.97(15), N(3)−Pd---N(4) 67.98(12), C(11)−Pd−N(1) 93.53(18), C(11)−Pd−N(2) 171.22(17), C(11)−Pd−N(3) 84.23(18), C(11)−Pd---N(4) 84.60(17), N(1)−Pd−N(3) 165.79(14), N(1)−Pd---N(4) 125.88(12), N(3)−Pd−N(2) 101.92(14), N(2)−Pd---N(4) 103.46(13).

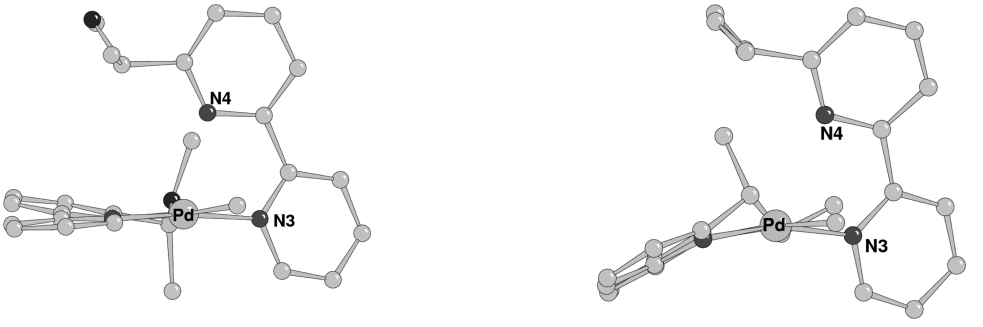


Figure 4. View along the N1−N2 vector in **1c** (left) and **3c** (right) indicating the distortions observed in the solid state.

Chiral recognition occurs in the case of **3c** where the *sec*-butyl groups in the independent molecule in the unit cell have the same configuration. On the contrary, the 1-methoxyethyl group of the monocoordinated bpy was found disordered over two positions corresponding to the different configurations (*R,S*) of the stereogenic center (occupancy 50% each) in **1c**.

In the literature there are few other examples of palladium−organometallic complexes with two molecules of bidentate nitrogen ligands, one of which acts as monodentate $[Pd(N-N)_2(L)][X]$ (with N−N = Ar-BIAN, phen, and its derivatives; L = CH_3, CH_2NO_2; X = triflate, PF_6^-).[40,41,52,53] The available crystal structures of these complexes show that the Pd---N interaction, involving the nitrogen donor of the uncoordinated ring, has a length in between 2.562 and 2.760 Å. The relative distance found in the crystal structure of *rac*-**1c** and **3c** falls in this range.

The NMR spectra of the $[Pd(N-N)_2(L)][X]$ complexes reported thus far point out the presence of a fluxional process, which makes equivalent both the molecules of the N−N ligand and both halves of each of them.[40,41,53]

The ^{1}H NMR spectrum of the 6-isopropyl complex **2c** shows that in solution is present only one single compound, which has the two bpy units equivalent in the palladium coordination sphere and the methyl groups of the isopropyl substituent diastereotopic (SI, Figure 4S). These data clearly indicate that a dynamic process equilibrating the two N−N′ ligand molecules is occurring and that at the same time a stereogenic element is built up in the structure of the complex.

In the ^{1}H NMR spectrum of (*R*)-**1c** two signals for the Pd−CH_3 group and two sets of resonances for the protons of the N−N′ ligands are observed (Figure 5a). The number of signals and their relative integration indicate the presence in solution of two species in the ratio of 1.7:1, having two equivalent molecules of bpy. ROESY experiments indicate that these two species are in exchange at a slow rate on the NMR time scale, at room temperature.

The ^{1}H NMR spectrum of (*rac*)-**1c** shows a duplication of the signals with respect to (*R*)-**1c** (Figure 5c), and the same pattern of resonances is observed for complex **3c**, having *rac*-6-*sec*-butyl-2,2′-bipyridine coordinated to palladium (SI, Figure 5S).

To assess the NMR evidence, it is reasonable to assume that the coordination geometry at the Pd center moves from distorted square planar to trigonal bipyramid, having the CH_3 bonded to Pd and the N atoms of the two substituted

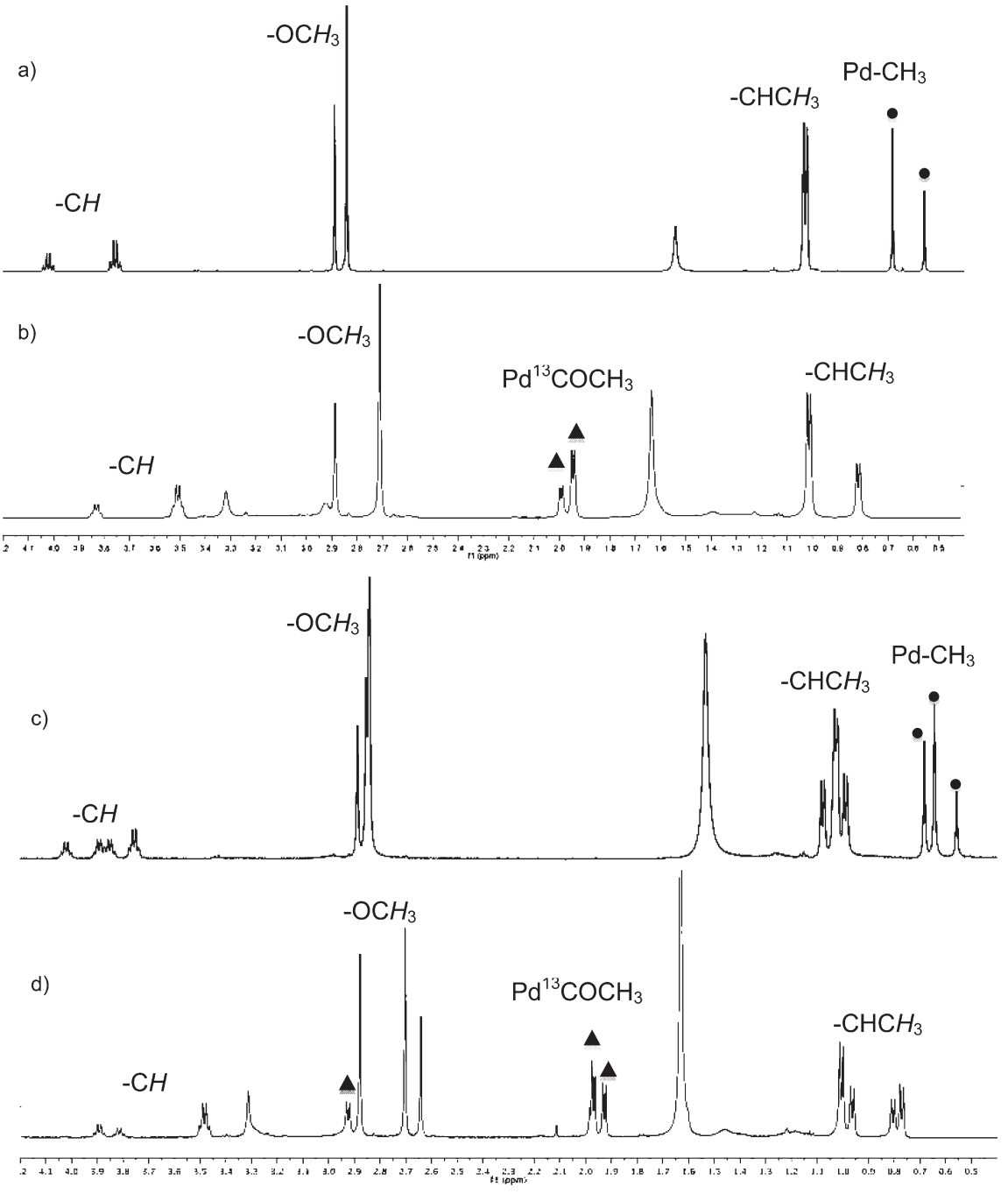


Figure 5. ^{1}H NMR spectra, in CD_2Cl_2 solution, at room temperature, of (a) (*R*)-**1c**; (b) (*R*)-**1c** + ^{13}CO; (c) (*rac*)-**1c**; (d) (*rac*)-**1c** + ^{13}CO. Region of aliphatic protons.

pyridine rings in equatorial positions and the N donors of the unsubstituted rings in the axial sites (Figure 6). In this geometry the palladium is stereogenic, and this accounts for the presence of diastereoisomers in solution with different configurations at the metal center (i.e., in the case of (*R*)-**1c** they are *R,R,*Δ_{Pd} and *R,R,*Λ_{Pd}). Since palladium, in the absence of any particularly demanding steric hindrance, has an exclusive preference for the square-planar geometry, the proposed pentacoordinated species represents an averaged structure between two limiting square-planar complexes, interconverting into one another by a dynamic phenomenon. This process proceeds with retention of the stereochemical integrity and inversion of the configuration at the Pd stereocenter. Notably, if the exchange of the N donors occurs through a Berry pseudorotation, this is accompanied as well by inversion of configuration as observed.

Alternatively this NMR behavior might be the consequence of the hindered rotation around the Pd−N bond of the η^1-bonded bpy ligand in a square-planar complex, the trigonal bipyramid being the limiting structure evolving from the square-planar geometry through the formation of an additional Pd−N bond.[58] The NMR data collected do not allow making a choice between these two possibilities.

Styrene Carbonylation Reaction. The monocationic complexes **1b**−**4b** have been tested as precatalysts in the CO/styrene alternate insertion by carrying out the reaction under conditions typical for the production of the relevant

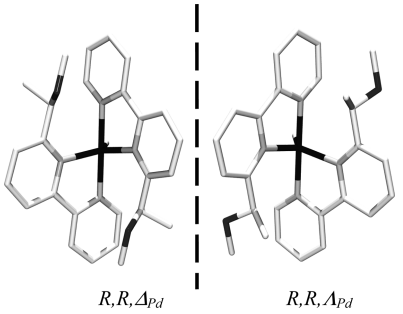
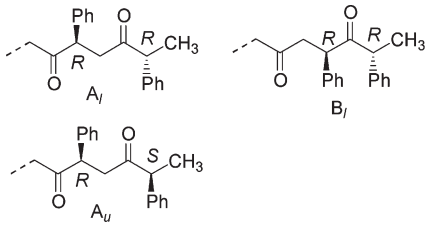


Figure 6. Computer modeling of the two diastereoisomeric palladium complexes.

Chart 2. Observed CO/Styrene Oligomer End Groups[a]



[a] In all cases the other termination of the oligoketone chain is the vinyl group Ph−CH═CH−.

copolymer (2,2,2-trifluoroethanol (TFE), T = 30 °C, 1 bar of CO, [BQ]/[Pd] = 40, [styrene]/[Pd] = 6800).

In no case were high molecular weight polymers obtained. The reaction product consisted of a yellow-orange oil that was characterized by ESI-MS and ^{1}H NMR spectroscopy (SI, Figures 6S and 7S). The mass analysis indicates for the product a mixture of low molecular weight molecules ($M_w \approx$ 368−896), characterized as a mixture of oligoketones with a number of repetitive units (132 Da each) ranging from 1 to 5.

This attribution finds support in the ^{1}H NMR spectrum that shows three peaks due to vinylic protons at 6.97, 6.73, and 6.41 ppm and a number of partially overlapping sharp signals for the methynic and methylenic protons, in the range 1.35−1.55 ppm, which are not easy to clear. In spite of the complicated pattern, a comparison with literature data[54,55] allows us to recognize two doublets at 1.50 and 1.48 ppm as diagnostic for the *l* (like) and *u* (unlike) stereoisomers of one end group (A, 2,5-diphenylpentyl-3-one end group), whereas the doublet at 1.40 ppm can be confidently attributed to the *l* diastereoisomer of the regioisomeric terminal group B (2,4-diphenylpentyl-3-one) (Chart 2, Figure 7a).

Although all the tested complexes (**1b**−**4b**) are active catalysts for the CO/styrene oligomerization reaction, the catalyst productivity is strongly affected by the structure of the ligand. The cationic complex with the triazole ligand (**4b**) is the least productive catalyst, while *rac*-**1b** is the most active one, reaching a productivity of almost 200 g PK/g Pd (grams of oligoketones per gram of palladium) (Table 1). In each case no decomposition to Pd metal is observed.

These results point out the remarkable influence exerted by the presence of a substituent on the C atom adjacent to the N donor of one of the two pyridine rings of the bpy ligands.

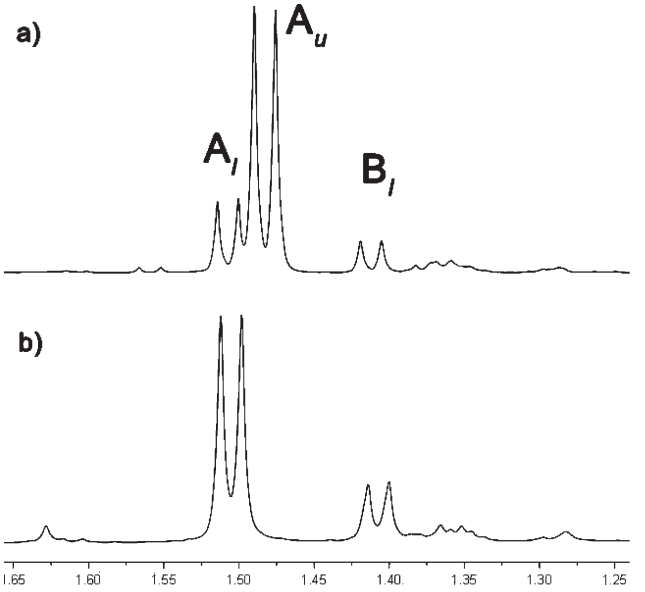


Figure 7. ^{1}H NMR spectra in $CDCl_3$: signals of the methyl group of the end groups of oligoketones obtained with (a) *rac*-**1b** and (b) *rac*-**1b** + *rac*-**1**.

Table 1. CO/Styrene Oligomerization: Effect of the Ligand Nature (precatalyst: [Pd(CH$_3$)(CH$_3$CN)(N−N′)][PF$_6$], 1b−4b)[a]

run	N−N′	yield (mg)	g PK/g Pd	A/B (%)	A_l (%)	A_u (%)
1	*rac*-**1**	254	185	63/37	40	60
2	**2**	187	136	75/25	>99	
3	**3**	155	113	75/25	>99	
4	**4**	103	79	88/12	80	20

[a] Reaction conditions: $n_{Pd} = 1.27 \times 10^{-5}$ mol, styrene V = 10 mL, TFE V = 20 mL, P_{CO} = 1 bar, [BQ]/[Pd] = 40, T = 30 °C, t = 24 h, [styrene]/[Pd] = 6800.

The presence of such a group promotes the switch of the selectivity of the carbonylation reaction from polyketones of different molecular weights, as obtained with unsubstituted bpy ligands,[46] toward the synthesis of oligoketones. We may speculate that this outcome is a consequence of the steric congestion generated by the presence of the alkyl substituent in close proximity to the catalytic center. At CO pressures as low as 1 bar, the β-elimination process that leads to the termination of the growing chain competes more and more favorably with the insertion reaction that supports the propagation of the chain.

Whereas the nature of the N−N′ ligand does not affect the number of repetitive units inserted into the oligoketone chain, it influences the regioisomeric and the diasteroisomeric distribution of the end groups. With all the tested precatalysts, the oligomer with the 2,5-diphenyl-3-one end group is the prevailing regioisomer. The A to B ratio depends on the substituent on the pyridine ring, being the lowest for *rac*-**1** and the highest for **4**. The ratio between the two diasteroisomers, A_l and A_u, is also related to the nature of the substituent on the pyridine ring, and the precatalysts containing ligands **2** and **3** give the A_l diasteroisomer exclusively (Table 1).

A modest but non-negligible effect of the configuration of the chiral ligand was observed in the oligomerization reactions catalyzed by **1b** (Table 2, runs 1−3). While in all cases there is a preference for the A regioisomer, the productivity, the diastereoselectivity, and the A/B ratio depend on

(54) Aeby, A.; Gsponer, A.; Sperrle, M.; Consiglio, G. *J. Organomet. Chem.* **2000**, *603*, 122–127.
(55) Sperrle, M.; Aeby, A.; Consiglio, G.; Pfaltz, A. *Helv. Chim. Acta* **1996**, *79*, 1387–1392.

the configuration of the ligand, the racemate being less selective than the enantiopure derivatives (Table 2). In the presence of 0.5 equivalents (with respect to Pd) of free ligand, whichever its configuration, the diastereoselectivity undergoes a major change resulting in the exclusive formation of the oligoketone with the A_l end group only (Table 2, runs 4−6, Figure 7b). This is accompanied by a slight decrease of the productivity, while the A/B ratio remains almost unaffected.

CD analysis points out that the oligoketones prepared with the enantiopure catalysts (*S*)- and (*R*)-**1b** in the presence of the corresponding free ligand both display optical activity, although the relevant CD curves are not specular (SI, Figure 8S). This fact combined with the ^{1}H NMR data (Table 2) indicates that a high diastereoface discrimination takes place for the insertion of the first two styrene units but that in the following insertions there is a decay of efficiency in the stereorecognition process. This fact supports the view that the stereochemistry dictated by the original chiral array at the catalytic center is contrasted by the chirality of the growing oligoketone chain, which becomes more and more influential in addressing the choice of the diastereoface for the incoming monomer. Similar conclusions have been reported in the literature for Pd catalysts based on phosphino- and pyridine-oxazoline ligands.[54]

These results suggest as well that different catalytic species may be generated whether or not some free ligand is added to the complex *rac*-, (*S*)-, or (*R*)-**1b**. Moreover, it seems reasonable to assume that this catalytic species should contain two molecules of N−N′ ligand bound to the same Pd center, possibly in the arrangement of complexes **1c**−**3c**. In addition, the productivity, the A/B ratio, and the diastereoselectivity do not change on varying the free ligand to Pd ratio from 0.25:1 to 1:1 (Table 2, runs 4, 7, 8), thus suggesting that only a small amount of the initial Pd complex is transformed into the active species.

To optimize the reaction conditions, a series of experiments has been carried out with precatalyst *rac*-**1b** varying some reaction parameters.

1,4-Benzoquinone is recognized as an essential component of the catalytic system. Indeed, when the oxidant is not present, formation of inactive palladium black takes place in 2 h and no product is isolated after 24 h (Table 3). The productivity of the catalytic system increases on increasing the [BQ]/[Pd] ratio, and no formation of palladium metal is evident by using an excess of BQ, the amount of which has no influence on the oligomer distribution.

Table 2. CO/Styrene Oligomerization: Effect of the Ligand Chirality and of the N−N′/Pd Ratio[a]

run	precat.	yield (mg)	g PK/g Pd	A/B (%)	A_l (%)	A_u (%)
1	*rac*-**1b**	254	185	63/37	40	60
2	(*S*)-**1b**	267	194	90/10	25	75
3	(*R*)-**1b**	211	153	75/25	75	25
4[b]	*rac*-**1b** + *rac*-**1**	203	150	64/36	> 99	
5[b]	(*S*)-**1b** + (*S*)-**1**	145	105	79/21	> 99	
6[b]	(*R*)-**1b** + (*R*)-**1**	129	94	69/31	> 99	
7[c]	*rac*-**1b** + *rac*-**1**	207	151	63/37	> 99	
8[d]	*rac*-**1b** + *rac*-**1**	202	149	62/38	> 99	

[a] Reaction conditions, see Table 1. [b] [free ligand]/[Pd] = 0.5:1. [c] [free ligand]/[Pd] = 1:1. [d] [free ligand]/[Pd] = 0.25:1.

Table 3. CO/Styrene Oligomerization: Effect of [BQ]/[Pd] (precatalyst: [Pd(CH_3)(CH_3CN)(*rac*-1**)][PF_6])**[a]

[BQ]/[Pd]	yield (mg)	g PK/g Pd
0	0	0
5	75	55
20	186	135
40	254	185

[a] Reaction conditions: see Table 1.

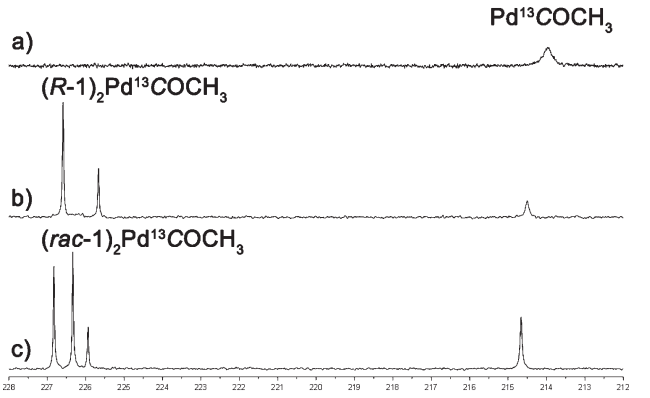
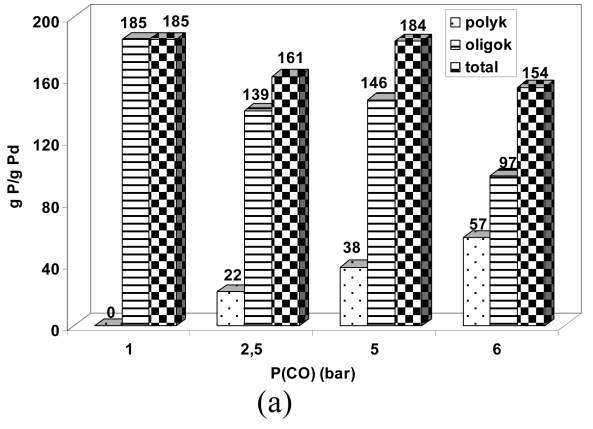


Figure 9. ^{13}C NMR spectra, in CD_2Cl_2 solution, of (a) (*R*)-**1b** + ^{13}CO (*T* = 298 K); (b) (*R*)-**1c** + ^{13}CO (*T* = 263 K); (c) (*rac*)-**1c** + ^{13}CO (*T* = 253 K). Region of carbonyl.



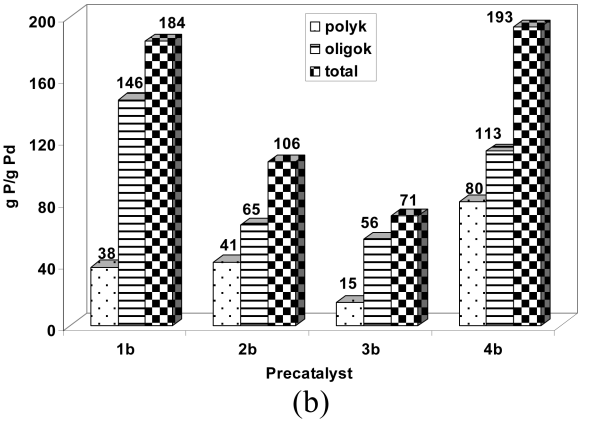
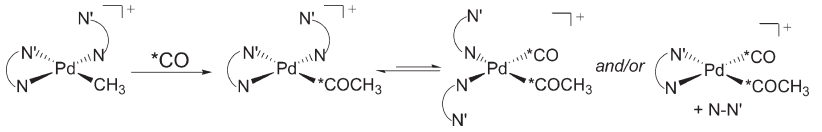
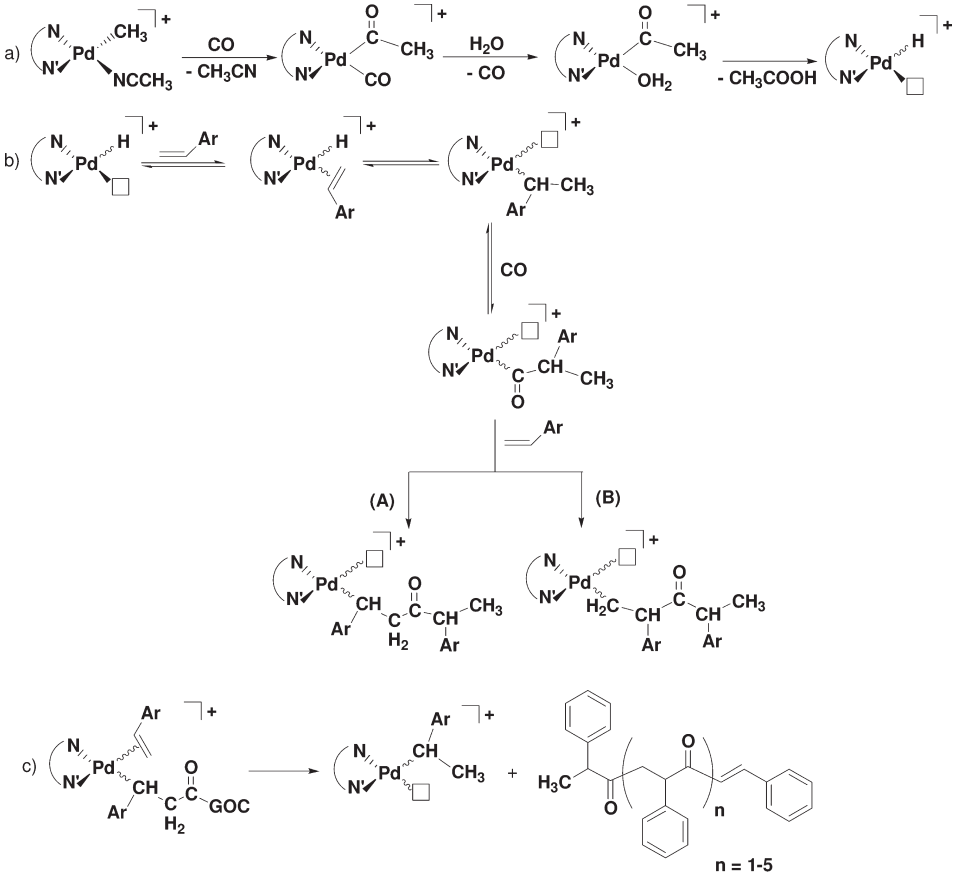


Figure 8. CO/styrene oligomerization. (a) Effect of CO pressure. Precatalyst: *rac*-**1b**. Reaction conditions: $n_{Pd} = 3.19 \times 10^{-6}$ mol, styrene *V* = 2.5 mL, TFE *V* = 5 mL, [BQ]/[Pd] = 40, *T* = 30 °C, *t* = 24 h, [styrene]/[Pd] = 6800. (b) Effect of precatalyst. Reaction conditions: $n_{Pd} = 3.19 \times 10^{-6}$ mol, styrene *V* = 2.5 mL, TFE *V* = 5 mL, P_{CO} = 5 bar, [BQ]/[Pd] = 40, *T* = 30 °C, *t* = 24 h, [styrene]/[Pd] = 6800. g P/g Pd = grams of product per gram of palladium; polyk = polyketone; oligok = oligoketone.

Scheme 6. Reactivity with Carbon Monoxide of Complexes 1c−3c



Scheme 7. Proposed Reaction Mechanism for Complexes 1b−4b: (a) Activation Step; (b) Insertion of the First Two Repetitive Units; (c) Termination Step



The effect of benzoquinone is remarkable and apparently different from that exerted in the CO/styrene copolymerization in alcoholic media, since no ester end groups are observed at the end of the oligoketone chains.[19−21,46] The available catalytic data do not allow making any speculation and/or hypothesis on the role played by benzoquinone in this specific catalytic system.

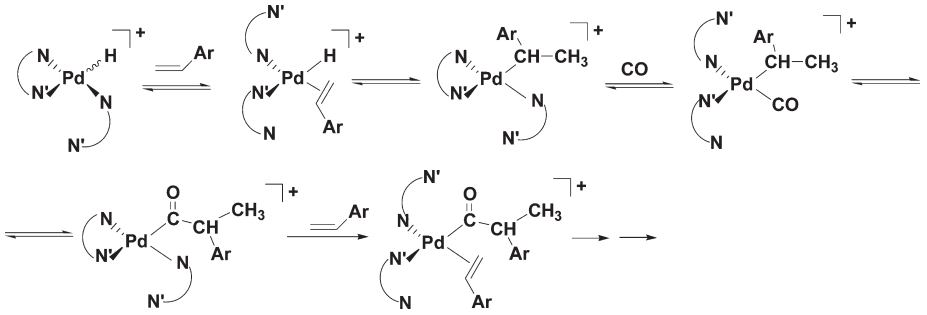
Longer reaction times, from 8 to 48 h, result in a remarkable increase in the productivity (SI, Figure 9S). This does not follow from a comparable increase in the number of repetitive units inserted into the oligomer chain, but rather from the fact that the catalyst does not show any evident decomposition to palladium metal and is still active after 48 h.

The effect of CO pressure was evaluated with precatalyst *rac*-**1b** by using a Tinyclave glass reactor (Figure 8a). Increasing the CO pressure from 1 to 6 bar resulted in the formation of a higher amount of polyketone with the contemporary decrease of the oligoketones, while the whole productivity remains almost unchanged. When the behavior of complexes **2b**−**4b** was inspected at 5 bar, the trend of the total productivity was found analogous to that of the oligomerization reaction (Table 1) for the bpy ligands, while the triazole-containing complex turned out to be the most productive catalyst (Figure 8b).

Reactivity of Complexes [Pd(CH$_3$)(CH$_3$CN)(N−N′)][PF$_6$] 1b, 2b and [Pd(CH$_3$)(N−N′)$_2$][PF$_6$] 1c−3c (N−N′ = 1−3) with Carbon Monoxide. For both series of complexes, **1b/2b** and **1c**−**3c**, the reactivity with ^{13}CO was studied by *in situ* ^{1}H and ^{13}C NMR spectroscopy, by bubbling carbon monoxide for 5 min into a 10 mM solution of the complex, at 298 K. In some cases the spectra were recorded at 263 or 253 K, to ensure sharp signals.

For complexes **1b** and **2b**, having one molecule of N−N′ coordinated to palladium, in the ^{1}H NMR spectrum recorded after 10 min from the treatment with ^{13}CO, the signal of the Pd−CH$_3$ fragment disappears, being replaced by a doublet around 2.90 ppm. The singlet of free acetonitrile is present, while no signal due to the free ligand (**1**, **2**) is observed. In the carbonyl region of the ^{13}C NMR spectrum the two signals around 214 and 170−174 ppm are assigned to the carbonyl group of the Pd−acetyl fragment and to the CO bonded to Pd, respectively (Figure 9a). On the basis of these data and in agreement with the literature,[41,42,45] it is reasonable to assume that the species resulting from the carbonylation reaction is the

Scheme 8. Proposed Reaction Mechanism for Complexes 1c−3c: The First Steps



Pd-acetyl-carbonyl derivative $[Pd(COCH_3)(CO)(N{-}N')][PF_6]$ (N−N′ = **1**, **2**). No information about its geometry was obtained.

When the same experiment was performed on complexes **1c−3c**, having two molecules of N−N′ bonded to palladium, the ^{1}H NMR spectra recorded after 10 min do not show any signal of the precursor nor any signal due to the free N−N′ ligand. It is straightforward to note that for complex (*R*)-**1c** the two singlets of the Pd−CH_3 fragment of the two diastereoisomers are replaced by two new doublets in the range 2.0−1.9 ppm (Figure 5b) and that when *rac*-**1c** is reacted with ^{13}CO the three singlets of Pd−CH_3 transformed into three doublets (Figure 5d). The carbonyl region of the related ^{13}C NMR spectra shows the signal around 215 ppm plus two or three additional resonances at lower field (225−228 ppm), depending on if the complex with the pure enantiomer or the racemic form of the ligand is used (Figure 9b and c). Analogous variations are observed in the NMR of **3c** after reaction with the labeled CO. Finally, in the case of complex **2c**, with the isopropyl substituent on bpy, the diastereoisomeric nature of the CH_3 of the substituent is preserved even after the reaction with CO.

These NMR data indicate that complexes **1c−3c** easily react at room temperature with carbon monoxide, leading to the Pd−acetyl species $[Pd(COCH_3)(N{-}N')_2][PF_6]$ with both N−N′ molecules coordinated to palladium. This species is in equilibrium with the Pd-acetyl-carbonyl derivative, where apparently both N−N′ molecules are coordinated to the same Pd center, most likely in a monodentate fashion (Scheme 6).

On the basis of the NMR studies and of the oligomers end-group distribution, the following hypothesis for the mechanism of the oligomerization reaction is proposed (Scheme 7). The catalytically active species is a Pd−H intermediate that might be formed from the precatalyst via the insertion of carbon monoxide into the Pd−CH_3 bond, followed by the nucleophilic attack of water (present in traces both in CO and in TFE) on the Pd−acetyl intermediate (Scheme 7a). Migratory insertion of styrene on the Pd−hydride occurs with a secondary regiochemistry, and the resulting Pd−alkyl fragment reacts with CO to form the Pd−acyl intermediate. On this species the coordination of styrene takes place, followed by its migratory insertion according to a non-regiospecific reaction, since primary regiochemistry is also observed in the insertion (Scheme 7b). Growing of the oligomer chain proceeds up to a maximum of five repetitive units, and then β-hydrogen elimination takes place according to the monomer-assisted mechanism,[56] leading to the oligomer with a vinyl termination and to the Pd−alkyl species that can start a new catalytic cycle (Scheme 7c). The concomitant formation of polyketone observed when the reaction is carried out at higher CO pressure is in keeping with this mechanism: CO occupies the fourth coordination site required for the β-hydrogen elimination to take place, thus favoring the growth of the polymeric chain over its termination.

When the catalytic reaction is carried out in the presence of a slight excess of free ligand with respect to palladium, an analogous catalytic cycle can be envisaged with the difference that both N−N′ molecules are always bonded to the metal center. In some steps one molecule can act as a bidentate ligand and the other as a monodentate ligand, whereas in the steps where two *cis* coordination sites are required for the reaction to occur, both N−N′ molecules might be monocoordinated (Scheme 8). This hypothesis is supported by the observed reactivity of complexes **1c−3c** with carbon monoxide and by recent literature reports, where the presence of monodentate phenanthroline ligands in Pd-catalyzed carbonylation reactions has been observed.[57]

Conclusions

In this work a series of a few 6-alkyl-substituted-2,2′-bipyridines, N−N′, has been synthesized and their coordination chemistry to palladium investigated, isolating two classes of complexes: (i) $[Pd(CH_3)(CH_3CN)(N{-}N')][PF_6]$ and (ii) $[Pd(CH_3)(N{-}N')_2][PF_6]$. In contrast with literature data on similar Pd complexes with nonsymmetric nitrogen ligands, the present compounds feature a Pd−methyl fragment *trans* to the Pd−N bond, where the N atom belongs to the substituted pyridine ring, likely for steric reasons. In complexes of series ii one N−N′ molecule shows the expected chelating behavior, whereas the other behaves as monodentate. However, in solution an averaged situation is established and the ^{1}H NMR spectra are consistent with a complex where the palladium ion is a stereogenic center.

Complexes of class i generate active catalysts for styrene carbonylation, yielding perfectly alternating CO/styrene oligoketones, thus indicating that the introduction of a substituent in *ortho* position with respect to the N donor of one of the two pyridine rings of the N−N′ ligands remarkably affects the selectivity of the reaction that is directed toward the synthesis of low molecular weight molecules. With unsubstituted bpy, polyketones of different molecular weights are the products.[46] The selectivity of the reaction is also

(56) Rix, F. C.; Rachita, M. J.; Wagner, M. I.; Brookhart, M.; Milani, B.; Barborak, J. C. *Dalton Trans.* **2009**, 8977–8992.

(57) Ragaini, F.; Gasperini, M.; Cenini, S.; Arnera, L.; Caselli, A.; Macchi, P.; Casati, N. *Chem.—Eur. J.* **2009**, *15*, 8064–8077.

(58) We thank one of the referees for suggesting this alternative.

influenced by the CO pressure, and concomitant formation of copolymer occurs when the reaction is carried out at a CO pressure of at least 2 bar.

The characterization of the end groups of the produced oligoketones provides evidence that, beside the fragments originated from the usual secondary insertion of styrene into the Pd−acyl bond, alkyl groups deriving from the insertion of styrene with a primary regiochemistry are also formed. In addition, when the carbonylation reaction is carried out with the catalyst containing the chiral, enantiomerically pure ligand, in the presence of an excess of free ligand, optically active oligoketones are produced with a complete diastereorecognition for the insertion of the first two styrene units.

Finally, the study of the reactivity of both classes of complexes with ^{13}CO indicates the formation of the corresponding Pd−acetyl species, $[Pd(COCH_3)(CO)(N-N')][PF_6]$ and $[Pd(COCH_3)(N-N')_2][PF_6]$, the latter having both N−N′ molecules coordinated to palladium.

Experimental Section

General Considerations. $[Pd(OAc)_2]$ was a gift from Engelhard Italia and was used as received. 2,2,2-Trifluoroethanol (TFE) (Aldrich) and the analytical grade solvents (Fluka) were used without further purification for synthetic, spectroscopic, and catalytic purposes. Dichloromethane used for the synthesis of complexes was purified through distillation over CaH_2 under an inert atmosphere and used freshly distilled. Carbon monoxide (CP grade 99.9%) was supplied by SIAD. ^1H and ^{13}C NMR spectra of ligands were recorded at 400 MHz on a JEOL EX 400 spectrometer; ^1H and ^{13}C NMR spectra of complexes and of their reactivity with ^{13}CO were recorded at 500 MHz on a Varian 500 spectrometer; the resonances were referenced to the solvent peak versus TMS ($CDCl_3$ at δ 7.26, CD_2Cl_2 at δ 5.32, and dmso-d_6 at 2.50 δ). ^{13}C NMR spectra of oligoketones were recorded in $CDCl_3$ at 125.68 MHz and referenced at δ 77.0 on a Varian 500 spectrometer.

Synthesis of Ligands 2 and 3. These ligands were prepared by a procedure reported in the literature for the preparation of alkyl-substituted terpyridines.[24]

A solution of 6-acetylpyridine (1 g; 8.25 mmol) and *N*,*N*-dimethylformamide dimethyl acetal (2.25 g; 17.44 mmol) in toluene (5 mL) was refluxed while methanol was gradually removed by slow distillation. The reaction was heated until no more methanol was distilled (ca. 12 h). The toluene was removed under reduced pressure to give ***i*** as a dark green oil (1.43 g; 98% yield). The ^1H NMR of the crude shows that the product is more than 95% pure. It is used as such in the next step. ^1H NMR (300 MHz, $CDCl_3$): δ 8.64 (d, J = 6 Hz, 1H, $H^{6'}$), 8.16 (d, J = 7.8 Hz, 1H, $H^{3'}$), 7.94 (d, J = 13 Hz, 1H, $CHN(CH_3)_2$), 7.80 (td, J = 10.1 Hz, 6.3 Hz, 1H, $H^{5'}$), 7.36 (m, 1H, $H^{4'}$), 6.47 (d, J = 12 Hz, 1H, $CHCHN(CH_3)_2$).

Compound ***i*** (1.37 g; 8.11 mmol) was added to a solution of the enolate of the appropriate methyl ketone, previously prepared by the reaction of the substrate with one equivalent of LDA in anhydrous THF (25 mL). The solution was allowed to stir for 20 h at room temperature. Then solid ammonium acetate (6.23 g; mmol 80.95) and acetic acid (12 mL) were added. The resulting mixture was refluxed while THF and acetic acid were slowly distilled off in the course of 3 h. The residue was taken up with CH_2Cl_2 and washed with 10% K_2CO_3(aq), and the organic phase dried (Na_2SO_4). The solvent was removed under vacuum, and the product was distilled under reduced pressure to give the pure product as a pale yellow oil.

2: 57% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 1.35 (d, J = 7 Hz, 6H, $-CH_3$), 2.88 (m, 1H, $CH(CH_3)_2$), 7.15 (d, J = 6.2 Hz, 1H, H^3), 7.30 (m, 1H, $H^{4'}$), 7.71 (t, J = 12 Hz, 8.6 Hz, 1H, H^4), 7.80 (td, J = 6 Hz, 0.3 Hz, 1H, $H^{5'}$), 8.20 (d, J = 9 Hz, 1H, H^5), 8.50 (d, J = 6 Hz, 1H, $H^{3'}$), 8.67 (d, J = 6 Hz, 1H, $H^{6'}$). ^{13}C NMR (75.6 MHz): δ 22.43 (q, $CHCH_3$), 35.54 (d, $CHCH_3$), 117.81 (d, $C^{3'}$), 120.40 (d, C^5), 121.17 (d, $C^{5'}$), 123.96 (d, C^3), 137.16 (d, $C^{4'}$), 137.60 (d, C^4), 149.17 (d, C^2), 154 (d, $C^{2'}$), 155 (d, C^6), 166 (d, $C^{6'}$). ESI-MS: m/z 183 ($M + H^+$), 198 ($M + Na^+$).

3: 50% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, 3H, J = 13.8 Hz, 9 Hz, $CHCH_3$); 1.35 (d, 3H, J = 9 Hz, $CHCH_3$), 1.67 (m, 1H, $CHCH_2CH_3$), 1.85 (m, 1H, $CHCH_2CH_3$), 2.88 (m, 1H, $CHCH_2CH_3$), 7.15 (d, J = 6.2 Hz, 1H, H^3), 7.29 (m, 1H, $H^{4'}$), 7.72 (t, J = 12.6 Hz, 6.8 Hz, 1H, H^4), 7.83 (td, J = 12.9 Hz, 6 Hz, 1H, $H^{5'}$), 8.19 (d, J = 9 Hz, 1H, H^5), 8.49 (d, J = 6 Hz, 1H, $H^{3'}$), 8.68 (d, J = 6 Hz, 1H, $H^{6'}$).

Synthesis of Ligands 1 and 4. 6-Acetyl-2,2′-bipyridine 5. It was synthesized following the procedures reported in the literature.[25] Spectroscopic and analytical data were in agreement with those reported.

***rac*-1-(2,2′-Bipyridin-6-yl)ethanol 6.** $NaBH_4$ (190 mg, 5 mmol) was added portionwise, at room temperature, to an ethanol solution of **5** (1.00 g, 5 mmol). The mixture was stirred for 2 h (TLC); the solvent was evaporated under reduced pressure, and the residue was washed with a saturated solution of NH_4Cl and extracted with CH_2Cl_2. The organic phase was dried on anhydrous Na_2SO_4 and evaporated to give the racemic alcohol **6** in 99% yield, which was used without further purification. Spectroscopic and analytical data were in agreement with those reported.[33]

***rac*-6-(1-Methoxyethyl)-2,2′-bipyridine 1.** NaH (60% dispersion in mineral oil, 5 mmol) was put in a three-neck flask under an Ar atmosphere and washed two times with freshly distilled THF; then the suspension was cooled to 0 °C. A solution of the alcohol **6** (0.5 g, 2.5 mmol) in THF and CH_3I (5 mmol) were subsequently added, and the mixture was stirred at 0 °C for 5 h (TLC CH_2Cl_2/CH_3OH, 9:1). The reaction was quenched with saturated NH_4Cl, and the product extracted three times with CH_2Cl_2. The collected organic phases were dried on Na_2SO_4 and evaporated to get pure 6-(1-methoxyethyl)-2,2′-bipyridine (*rac*-(**1**), *R*-(**1**), and *S*-(**1**)) in 80% average yield. IR (neat): 3061, 2978, 2929, 2822, 1581, 1564, 1118 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.53 (d, J = 6.8 Hz, 3H, $CHCH_3$), 3.36 (s, 3H, OCH_3), 4.53 (q, J = 6.8 Hz, 1H, $CHCH_3$), 7.29 (m, 1H, $H^{5'}$), 7.44 (d, J = 7.6 Hz, 1H, H^5), 7.8 (td, J = 7.6 Hz, 2 Hz, 1H, $H^{4'}$), 7.83 (t, J = 8 Hz, 1H, H^4), 8.28 (dd, J = 7.6 Hz, 0.8 Hz, 1H, $H^{3'}$), 8.44 (d, J = 8 Hz, 1H, H^3), 8.63 (dm, J = 4.8 Hz, 1H, $H^{6'}$). ^{13}C NMR (100.1 MHz, $CDCl_3$): δ 22.2 (q, $CHCH_3$), 56.9 (q, OCH_3), 80.9 (d, $CHCH_3$), 119.6 (d, C^3), 119.8 (d, C^5), 121.3 (d, $C^{3'}$), 123.7 (d, $C^{5'}$), 136.9 (d, $C^{4'}$), 137.7 (d, C^4), 149.2 (d, $C^{6'}$), 155.4 (s, $C^{2'}$), 156.3 (s, C^2), 162.7 (d, C^6). ESI-MS: m/z 215 ($M + H^+$), 237 ($M + Na^+$).

(*R*)-(+)-1-(2,2′-Bipyridin-6-yl)ethylacetate 7. Catalyst $[Ru_2(CO)_4(\mu\text{-}H)(C_4Ph_4\text{-}COHOCC_4Ph_4)]$ (0.044 mg, 0.04 mmol) and Novozyme 435 (60 mg) were suspended in toluene, under argon. A degassed solution of the racemic alcohol **6** (2 mmol) and 4-chlorophenyl acetate (1.02 g, 6 mmol) in toluene (5 mL) was transferred to this suspension, and the mixture was stirred under argon, at 70 °C, for 48 h until complete conversion (GC). The enzyme was filtered off, and the reaction mixture was separated on silica (petroleum ether/ethyl acetate as eluent) to yield (*R*)-**7** (70%). ee > 99.9% (by HRCGC), $[\alpha]_D$ +89.0 (*c* 0.5, $CHCl_3$) [lit. $[\alpha]_D$ +85.0 (*c* 1.87, $CHCl_3$)]. Spectroscopic and analytical data were in agreement with those reported.[33]

(*R*)-(−)-1-(2,2′-Bipyridin-6-yl)ethanol 6. The acetate **7** (1.4 mmol) was hydrolyzed with K_2CO_3 (193 mg, 1.4 mmol) in methanol/water (1:1) at room temperature, following the reaction with TLC. Methanol was evaporated under reduced pressure, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were extracted with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Chromatography on silica (CH_2Cl_2/ethyl acetate as eluent) gave the pure *R*-alcohol in 99% yield. ee > 99.9% (by chiral HRGC), $[\alpha]_D$ −21.3 (*c* 0.6, $CHCl_3$) [lit. for *S*-**6**: $[\alpha]_D$ +26.0 (*c* 1.62, $CHCl_3$)].[33]

(*S*)-(+)-1-(2,2′-Bipyridin-6-yl)ethanol 6. Saccharose (56 g) was added to a stirred suspension of dry baker's yeast (56 g) in phosphate buffer (0.1 M, pH 7.4). The mixture was preincubated for 30 min at 37 °C, and 6-acetyl-2,2′-bipyridine (0.7 g, 3.6 mmol) was added at room temperature. The reaction was monitored by HRGC, and after 2 days the broth was extracted with ether. The organic phase was dried and evaporated to give a residue, which was chromatographed on an SiO_2 column (petroleum ether/ethyl acetate as eluent), giving 75% yield at 93% conversion. ee = 99% (by HRCGC). $[\alpha]_D$ +21.7 (*c* 0.35, $CHCl_3$) [lit. $[\alpha]_D$ +26.0 (*c* 1.62, $CHCl_3$)].[33]

(*R*)- and (*S*)-6-(1-Methoxyethyl)-2,2′-bipyridine 1 were prepared following the procedure described above; (*R*)-(+)-(6-(1-methoxyethyl)-2,2′-bipyridine: ee > 99.9% (by HRCGC). $[\alpha]_D$ +106.5 (*c* 0.6, $CHCl_3$); (*S*)-(−)-(6-(1-methoxyethyl)-2,2′-bipyridine: ee = 99% (by HRCGC). $[\alpha]_D$ −103.5 (*c* 0.4, $CHCl_3$).

2-(Methoxymethyl)-6-(1*H*-1,2,3-triazol-1-yl)pyridine 4. (6-Bromopyridin-2-yl)methanol 9. It was prepared in quantitative yield by $NaBH_4$ reduction of 6-bromo-2-pyridinecarboxaldehyde.[36] Spectroscopical and analytical data were in accordance with the literature.

(6-((Trimethylsilyl)ethynyl)pyridin-2-yl)methanol 10. It was prepared following a literature method.[37] Trimethylsilylacetylene (1.11 mL, 8.0 mmol) was added to a stirred solution of **9** (376 mg, 2.0 mmol), $[Pd(PPh_3)_4]$ (48 mg, 0.08 mmol), and CuI (11 mg, 0.08 mmol) in 8 mL of triethylamine. The mixture, from which a white precipitate formed, was heated at 50 °C and then cooled at room temperature. The conversion into the product was complete in a few minutes (TLC with ethyl acetate, $KMnO_4$ rev.) After addition of ether, the solution was washed with aqueous NH_4Cl (sat.), dried over Na_2SO_4, and evaporated to give a crude product, which was used in the further step without purification. For analytical purposes, a pure sample of **10** was obtained by flash chromatography (eluent petroleum ether/ethyl acetate, 3:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.36 (s, 9H, Me_3Si), 4.57 (s, 2H, CH_2OH), 7.21 (d, ^3J = 7.7 Hz, H^5, 1H), 7.35 (d, ^3J = 7.7 Hz, H^3, 1H), 7.62 (t, ^3J = 7.7 Hz, H^4, 1H). ^{13}C NMR (100.1 MHz, $CDCl_3$): δ −0.4 (q, $SiMe_3$), 64.3 (t, CH_2OH), 95.1 (s, acetylenic C^2), 103.4 (s, acetylenic C^1), 120.0 (d, C^3 or C^5), 126.0 (C^5 or C^3) 136.7 (d, C^4), 141.8 (s, C^6), 159.9 (s, C^2). ESI-MS: 206.1 [MH+]. Anal. Calcd for $C_{11}H_{15}NOSi$: C, 64.34; H, 7.36; N, 6.82. Found: C, 64.35; H, 7.40; N, 6.85.

(6-Ethynylpyridin-2-yl)methanol 11. The crude **10** (410 mg, 2 mmol assuming a 100% yield in the previous step) was dissolved in THF. Then Bu_4N (1 M solution in THF, 3 mL, 3 mmol) was added at room temperature. After 10 min stirring, ether was added and the solution washed with water first, then with saturated NH_4Cl, and finally dried over Na_2SO_4 and evaporated to give an oily residue, which was purified on column chromatography (petroleum ether/ethyl acetate, 8:2): yield 78% after column chromatography (eluent petroleum ether/ethyl acetate, 1:1); crystalline product, mp 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 (s, 1H, CCH), 3.90 (broad, OH), 4.73 (s, 2H, CH_2OH), 7.29 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.64 (dd, *J* = 7.7 and 7.9 Hz, 1H). ^{13}C NMR (100.1 MHz, $CDCl_3$): δ 64.2 (t, CH_2OH), 77.4 (d, acetylenic C^2), 82.4 (s, acetylenic C^1), 120.4 (d, C^3 or C^5) 126.0 (d, C^5 or C^3), 136.9 (d, C^4), 141.0 (s, C^6), 160.2 (s, C^2). ESI-MS: 156.1 [M + Na^+]. Anal. Calcd for C_8H_7NO: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.23; H, 5.31; N, 10.49.

6-(1-Methyl-1*H*-1,2,3-triazol-4-yl)pyridin-2-yl)methanol 12. Acetylene **11** (0.146 g, 1.1 mmol), CH_3I (0.142 g, 1.0 mmol), and sodium azide (0.071 g, 1.1 mmol) were suspended in a 1:1 mixture of water and *tert*-BuOH (1 mL each) in a 10 mL glass vial equipped with a small magnetic stirring bar. CuI (0.1 g) was added, and the mixture was irradiated under MW for 10 min at 100 °C, using an irradiation power of 100 W. A yellow precipitate was filtered off, and the solution concentrated to dryness under vacuum, giving a residue from which compound **12** was obtained in a 74% yield after flash chromatography. White solid, mp > 200 °C. IR (Nujol): 3445 (broad), 3310 (sh), 3063, 1599, 1580 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.14 (s, 3H, CH_3N), 4.76 (s, 2H, CH_2OH), 4.82 (s, 1H, OH), 7.16 (d, ^3J = 7.9 Hz, 1H, H^3), 7.74 (t, *J* = 7.9 Hz, 1H, H^4), 8.01 (d, *J* = 7.9 Hz, 1H, H^5), 8.12 (s, 1H, $H^{5'}$). ^{13}C NMR (100.1 MHz): δ 36.8 (q, CH_3N), 63.9 (t, CH_2OH), 118.7 (d, C^5), 119.6 (d, C^3), 123.1 (d, $C^{5'}$), 137.6 (d, C^4), 148.1 (s), 148.9 (s), 158.7 (s). ESI-MS: 191.1 [M+], 214.1 [M + Na^+]. Anal. Calcd for $C_9H_{10}N_4O$: C, 56.83; H, 5.30; N, 29.46. Found: C, 56.80; H, 5.28; N, 29.50.

2-(Methoxymethyl)-6-(1-methyl-1*H*-1,2,3-triazol-4-yl)pyridine 4. A solution of alcohol **12** (191 mg, 1 mmol) in 2.5 mL of dry THF was dropwise added to suspension of NaH (44 mg, 60% in mineral oil, 1.1 mmol) in dry THF, at 0 °C. After 30 min CH_3I (142 mg, 62 μL, 1 mmol) was added at 0 °C from a septum, and the mixture was allowed to reach rt, then quenched with aqueous saturated NH_4Cl, extracted with diethyl ether, and dried (Na_2SO_4). Evaporation of the solvent left an oily residue, which was passed on a short SiO_2 column (ethyl acetate), to give quantitatively compound **4** as a white solid, mp 78−9 °C. IR (Nujol): 3147, 1604, 1578, 1116 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.42 (s, 3H, CH_3O), 4.11 (s, 3H, CH_3N), 4.58 (s, 2H, CH_2OMe), 7.32 (d, *J* = 7.7, 1H, H^3), 7.72 (t, *J* = 7.7, 1H, H^4), 7.98 (d, *J* = 7.7, 1H, H^5), 8.10 (s, 1H, $H^{5'}$). ^{13}C NMR (100.1 MHz, $CDCl_3$): δ 36.7 (q, CH_3N), 58.7 (CH_3O), 75.5 (t, CH_2OMe), 118.7 (d, C^5), 120.3 (d, C^3), 123.1 (d, $C^{5'}$), 137.3 (d, C^4), 148.6 (s), 149.6 (s), 158.1 (s). ESI-MS 227.0 [M + Na^+]. Anal. Calcd for $C_{10}H_{12}N_4O$: C, 58.81; H, 5.92; N, 27.43. Found: C, 58.78; H, 6.00; N, 27.50.

Oligomerization Reactions at Atmospheric CO Pressure. All experiments were carried out in a three-necked, thermostated, 75 mL glass reactor equipped with a magnetic stirrer and connected to a temperature controller. After establishment of the reaction temperature (30 °C), the precatalyst, 1,4-benzoquinone, the vinyl arene, and TFE were placed inside. CO was bubbled through the solution for 10 min; afterward a 4 L balloon filled with CO was connected to the reactor. The system was stirred at the same temperature for 24 h to give a yellow solution. The reaction mixture was then poured into methanol (100 mL) and stirred for 1 h at room temperature, and then the solvent was evaporated to obtain a yellow-orange oil. The product was dried under vacuum until constant weight was reached.

Oligo- and Polymerization Reactions at Higher CO Pressure. A 10 mL Büchi Tinyclave glass reactor was used for these reactions. The Tinyclave reactor was charged with 1,4-benzoquinone, the precatalyst, and TFE and was placed in an oil bath at 30 °C. Under a CO stream, the vinyl arene was added and the reactor was pressurized at the operating CO pressure. The mixture was stirred at the same temperature for 24 h. The reaction mixture was poured into methanol, and the insoluble copolymer was filtered off and dried under reduced pressure. The solution, containing oligomers, was concentrated to obtain a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): CO/styrene: δ 8.21−7.10 (aromatic protons), 6.97 (m, B_l 1H, Ph-*CH*=CH−), 6.73 (pst, A_l 1H, (Ph-*CH*=CH−), 6.41 (pst, A_u 1H, (Ph-*CH*=CH−), 4.55−3.81 (broad, CO-*CH*(Ph)−), 4.03 (m, A_l 1H, CH_3-*CH*(Ph)−), 3.91 (m, B_l 1H, CH_3-*CH*(Ph)−), 3.65 (m, A_u 1H, CH_3-*CH*(Ph)−), 3.53−2.57 (broad, −(Ph)CH-CH_2-CO−), 1.50 (d, A_l 3H, −(Ph)CH-CH_3), 1.48 (d, A_u 3H, −(Ph)CH-CH_3), 1.40 (d, B_l 3H, −(Ph)CH-CH_3). ^{13}C NMR (500 MHz, $CDCl_3$, 298 K): δ 209.10−208.17 (broad, CO) 136.19 (B_l Ph-*CH*=CH−), 135.38 (A_u Ph-*CH*=CH−), 128.47 (C_{arom}), 116.37 (A_l Ph-*CH*=CH−), 53.28−52.02 (CO-*CH*(Ph)−), 53.23 (B_l CH_3-*CH*(Ph)−), 52.42 (A_l CH_3-*CH*(Ph)−), 42.43 (A_u CH_3-*CH*(Ph)−), 44.26−42.32, 30.02, 29.47 (−(Ph)CH-CH_2-CO−), 21.29 (A_u −(Ph)CH-CH_3), 17.63 (A_l −(Ph)CH-CH_3), 17.18 (B_l −(Ph)CH-CH_3).

Acknowledgment. Collaborative research was carried out by S.G. and B.M. in the framework of the COST D40 project of EU. This work was supported by MIUR (PRIN No. 2007HMTJWP_002), by Regione Friuli Venezia Giulia. Engelhard Italia is gratefully acknowledged

for a generous gift of [Pd(AcO)$_2$]. Università di Trieste is acknowledged for a fellowship to A.D'A. Fondazione CRTrieste is also gratefully acknowledged for the generous donation to the Dipartimento di Scienze Chimiche of a Varian 500 NMR spectrometer. Fondazione Benefica "Kathleen Foreman Casali" is gratefully acknowledged for the generous donation of the Büchi Tinyclave glass reactor.

Supporting Information Available: Synthesis and characterization of Pd complexes **1a**−**4a**, **1b**−**4b**, **3a**′, **3b**′, and **1c**−**3c**. Reactivity of Pd complexes **1b**, **2b**, and **1c**−**3c** with ^{13}CO. X-ray structure determination and table of data collections and refinements. X-ray crystallographic data in CIF format for the structure determinations of *rac*-**1a**, **3a**, **3b**′, **3a**′, *rac*-**1c**, and **3c**. Plot of kinetics for the transformation of **3b** into **3b**′. ^{1}H NMR spectra of **3b**, **3b**′, **3a**′, **2c**, and **3c**. ESI-MS of a CO/styrene oligoketone. ^{1}H NMR of a CO/styrene polyketone and of an oligoketone. CD spectra of two oligoketones. Plot of productivity vs time. This material is available free of charge via the Internet at http://pubs.acs.org.