Organometallics **1997,** *16,* 5064−5075

Bis-Chelated Palladium(II) Complexes with Nitrogen-Donor Chelating Ligands Are Efficient Catalyst Precursors for the CO/Styrene Copolymerization Reaction

Barbara Milani,* Anna Anzilutti, Lidia Vicentini, Andrea Sessanta o Santi,
Ennio Zangrando, Silvano Geremia, and Giovanni Mestroni

*Department of Chemical Sciences, University of Trieste, Via Licio Giorgieri 1,
34127 Trieste, Italy*

Received May 13, 1997[⊗]

A series of dicationic bis-chelated palladium(II) complexes $[Pd(N\text{-}N)_2][X]_2$ (N-N = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and their substituted derivatives; $X = PF_6^-$, BF_4^-, OTf^-, OTs^-) has been synthesized and completely characterized both in the solid state and in solution. The synthetic procedure involves a simple *one-pot* reaction between $Pd(MeCOO)_2$ and [(N-N)H][X]. These compounds are very active precatalysts for the CO/styrene copolymerization yielding perfectly alternating polyketones. The crystal structures of some complexes of the series provide evidence that a distorsion from the ideal square planar geometry toward a *twist* conformation occurs. In DMSO solution, one of the two nitrogen-donor ligands is involved in a dissociative equilibrium yielding a monochelated complex with two *cis* coordination sites available for the copolymerization catalytic process. The catalytically active species is very stable in 2,2,2-trifluoroethanol, where its activity was found unaltered for at least 48 h of reaction without apparent decomposition to palladium metal. The addition of 1,4-benzoquinone (BQ) to the catalytic system has a strong influence on the yield and, above all, on the molecular weight of polyketones. The zerovalent palladium complexes [Pd(N-N)(BQ)], which might be formed during the copolymerization process, have been synthesized and characterized. The crystal structure of [Pd(bipy)(BQ)] shows that benzoquinone acts as a mono-olefinic ligand to Pd. In the presence of protons, the Pd(0) complexes are readily oxidized to Pd(II) with the reduction of benzoquinone to hydroquinone. When [(N-N)H][X] is used as the source of protons, the resulting Pd(II) species is the precatalyst and can immediately re-enter the catalytic cycle.

Introduction

Since the pioneering papers of Sen,[1] the co- and terpolymerization reactions of carbon monoxide and olefins yielding perfectly alternating polyketones have become a very attractive field of research and there has been an increasing number of reports on this subject appearing in the current literature.[2] The industrial interest in these new materials is witnessed by the announcement by Shell of the incoming commercial availability of Carilon, a CO/ethylene/propylene polyketone.[3]

Several Pd(II) systems, either prepared *in situ* or involving presynthesized complexes, have been reported to homogeneously catalyze this class of reaction. The *in situ* systems, widely investigated by Drent,[4−6] are composed of a palladium(II) salt, a diphosphine (P-P) or dinitrogen (N-N) chelating ancillary ligand, a Brønsted acid as the cocatalyst, methanol as the solvent, and, frequently, an oxidant, such as 1,4-benzoquinone. In the case of the CO/ethylene copolymerization, the highest yields in polyketones were obtained in methanol with $Pd(MeCOO)_2$ or $Pd(CF_3COO)_2$, 1,3-bis(diphenylphosphino)propane (dppp), and triflic or *p*-toluenesulfonic acid as the cocatalyst.[4] In the catalytic systems based on preformed complexes, the palladium compounds always bear at least one molecule of diphosphine or dinitrogen chelating ligand in the coordination sphere. The other two coordination sites can be occupied either by anionic or neutral ligands. In general, their produc-

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

(1) (a) Sen, A.; Lai, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 3520. (b) Lai, T. W.; Sen, A. *Organometallics* **1984**, *3*, 866.

(2) (a) Bronco, S.; Consiglio, G.; Di Benedetto, S.; Fehr, M.; Spindler, F.; Togni, A. *Helv. Chim. Acta* **1995**, *78*, 883. (b) Amevor, E.; Bronco, S.; Consiglio, G.; Di Benedetto, S. *Macromol. Symp.* **1995**, *89*, 443. (c) Nozaki, K.; Sato, N.; Takaya, H. *J. Am. Chem. Soc.* **1995**, *117*, 9911. (d) Amevor, E.; Bürli, R.; Consiglio, G. *J. Organomet. Chem.* **1995**, 81. (e) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455. (f) Kacker, S.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 10591. (g) Jiang, Z.; Boyer, M. T.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 7037. (h) Markies, B. A.; Kruis, D.; Rietveld, M. H. P.; Verkerk, K. A. N.; Boesma, J.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 5263. (i) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137. (j) Bartolini, S.; Carfagna, C.; Musco, A. *Macromol. Rapid Commun.* **1995**, *16*, 9. (k) Forbes, M. D. E.; Rubern, S. R.; Nachtigallova, D.; Jordan, K. D.; Barborak, J. C. *J. Am. Chem. Soc.* **1995**, *117*, 3946. (l) Benetollo, F.; Bertani, R.; Bombieri, G.; Toniolo, L. *Inorg. Chim. Acta* **1995**, *233*, 5. (m) Valli, V. L. K.; Alper, H. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1715. (n) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (o) Brückner, S.; De Rosa, C.; Corradini, P.; Porzio, W.; Musco, A. *Macromolecules* **1996**, *29*, 1535. (p) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 2213. (q) Koide, Y.; Barron, A. R. *Macromolecules* **1996**, *29*, 1110. (r) Sperrle, M.; Aeby, A.; Consiglio, G.; Pfaltz, A. *Helv. Chim. Acta* **1996**, *79*, 1387. (s) Koster, R. A.; Birk, R. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (2), 525.

(3) (a) Alperwicz, N. *Chem. Week* **1995**, (Jan 25), 22. (b) Medema, D.; Noordam, A. *Chem. Mag.* **1995**, 127.

(4) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235.

(5) Representative examples: Drent, E. *E.* Pat. Appl. No. 229408, 1986. Drent, E. U.S. Patent No. 4778279, 1988.

(6) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.

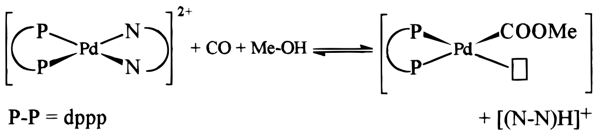
S0276-7333(97)00395-6 CCC: $14.00

tivity was found to be lower than that of comparable *in situ* systems.[7,8]

An important relationship between the nature of the chelating ligand and the olefinic comonomer was found in the early studies on these systems. Diphosphine ligands are required to achieve high yields in the copolymerization of aliphatic α-olefins.[6] On the contrary, a catalytic system modified by nitrogen-donor chelating ligands is required to prepare the CO/styrene copolymer.[2j,9,10] The catalytic systems based on diphosphine ligands catalyze the selective carbonylation of styrene to (*E*)-1,5-diphenylpent-1-en-3-one instead of its copolymerization.[9a,b]

Moreover, with α-olefins problems related to the control of the regio- and stereoselectivity of polyketones arise.[11−15] Particular attention has been dedicated to the stereochemistry of the insertion of styrene into the growing chain of the corresponding copolymer. Achiral N-donor ligands led to syndiotactic copolymers,[9c,d,14a] while chiral ligands with C_2 symmetry yielded isotactic copolymers.[2i,j] A stereoblock CO/styrene copolymer was obtained using a preformed complex with the chiral ligand followed by addition of the achiral ligand in the catalytic system.[15] Very recently, complexes containing a phosphino(dihydrooxazole) ligand were reported to give alternating CO/styrene copolymer either with a highly isotactic or with an essentially complete atactic microstructure, depending on the symmetry of the ligand.[2r] However, in all cases, the productivity is rather low, less than 500 g of CP/g of Pd (CP = copolymer) and also the molecular weight of the polyketone is not high enough to have useful properties.[2s] The mechanistic aspects of these copolymerization reactions are also of great interest.[2n,16] The active species is generally believed to be a monochelated cation.

For some years, we have been involved in the study of the CO/ethylene[17−19] and CO/styrene[14] copolymerizations promoted by different kinds of Pd(II) complexes, such as $[Pd(dppp)(N\text{-}N)][X]_2$ and $[Pd(N\text{-}N)(CF_3COO)_2]$. In particular, we found that with the bis-chelated precursors $[Pd(dppp)(N\text{-}N)][PF_6]_2$, formation of the active species involves production of $[(N\text{-}N)H][PF_6]$ (eq 1), which is believed to have an important role in the catalytic cycle.[18]



(1)

In this paper, we report the synthesis and characterization, both in the solid state and in solution, of the new compounds $[(N\text{-}N)H][X]$ (N-N = bipy, 4,4′-dimethyl-2,2′-bipyridine (Me_2-bipy), phen, 4,7-dimethyl-1,10-phenanthroline (Me_2-phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4-phen); $X = PF_6^-$, BF_4^-, *p*-toluenesulfonate (OTs^-), triflate (OTf^-)) and a preliminary investigation on their role in the chemistry of these palladium systems. A very facile and convenient procedure[19] for the synthesis of the corresponding $[Pd(N\text{-}N)_2][X]_2$ complexes, based on the use of $[(N\text{-}N)H][X]$, is also described, together with some results concerning their catalytic activity in the CO/styrene copolymerization reaction.

The role of 1,4-benzoquinone (BQ) in these catalytic systems is also investigated by studying the chemical behavior of Pd(0) complexes of the general formula [Pd(N-N)(BQ)] with 1,4-benzoquinone in the coordination sphere.

Experimental Section

General Comments. Commercial $Pd(NO_3)_2 \cdot 2H_2O$, $PdCl_2$, and $Pd(CF_3COO)_2$ were purchased from Aldrich and used as received. The bidentate nitrogen-donor chelating ligands (Aldrich) and analytical grade solvents (Baker) were used without further purification for synthetic and spectroscopic purposes. The methanol (Fluka) used for the catalytic reactions was purified by distillation from magnesium and iodine; the acetone for synthetic use was dried on Drierite overnight and stored under inert atmosphere; the 2,2,2-trifluoroethanol (Aldrich) for the catalytic reactions was used as received without any purification. Carbon monoxide (CP grade, 99.9%) was supplied by SIAD.

IR spectra were recorded on a Perkin-Elmer 983G spectrometer as Nujol mulls or KBr pellets (when indicated). ^1H NMR spectra of the complexes were recorded at 400 MHz on a Jeol EX 400 spectrometer operating in Fourier-transform mode, with tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were recorded on a Jeol EX 400 spectrometer at 100.5 MHz in 1,1,1,3,3,3-hexafluoro-isopropyl alcohol (HFIP) with a small amount of $CDCl_3$ for locking purposes and TMS as the internal standard. Limiting viscosity numbers (η) were measured in *m*-cresol at 100 °C in a standard capillary viscosity measuring device. The palladium residue present in the polyketones was determined by atomic absorption spectroscopy.

Syntheses. Elemental analyses (C, H, N) performed by Dr.Cebulec (Dipartimento di Scienze Chimiche, Trieste, Italy), were in perfect agreement with the proposed stoichiometry (Tables 1 and 2).

Compounds [(N-N)H][X] (1−12). The synthesis of compounds of the general formula [(N-N)H][X] can be performed

---

[7] Chien, C. W.; Zhao, A. X. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2735.

[8] Jiang, Z.; Sen, A. *Macromolecules* **1994**, *27*, 7215.

[9] (a) Barsacchi, M.; Consiglio, G.; Medici, L.; Petrucci, G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 989. (b) Pisano, C.; Mezzetti, A.; Consiglio, G. *Organometallics* **1992**, *11*, 20. (c) Barsacchi, M.; Batistini, A.; Consiglio, G.; Suter, U. W. *Macromolecules* **1992**, *25*, 3604. (d) Corradini, P.; De Rosa, C.; Panunzi, A.; Petrucci, G.; Pino, P. *Chimia* **1990**, *44*, 52.

[10] (a) Brookhart, M.; Rix, F. C.; De Simone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894. (b) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641.

[11] (a) Batistini, A.; Consiglio, G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31* (3), 303. (b) Batistini, A.; Consiglio, G. *Organometallics* **1992**, *11*, 1766.

[12] Chien, J. C. W.; Zhao, A. X.; Xu, F. *Polym. Bull.* **1992**, *28*, 315.

[13] Wong, P. K.; van Doorn, J. A.; Drent, E.; Sudmljer, O.; Stil, H. A. *Ind. Eng. Chem. Res.* **1993**, *32*, 986.

[14] (a) Milani, B.; Alessio, E.; Mestroni, G.; Sommazzi, A.; Garbassi, F.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1994**, 1903. (b) Milani, B.; Alessio, E.; Mestroni, G.; Zangrando, E.; Randaccio, L.; Consiglio, G. *J. Chem. Soc., Dalton Trans.* **1996**, 1021.

[15] Brookhart, M.; Wagner, M. L. *J. Am. Chem. Soc.* **1996**, *118*, 7219.

[16] Rülke, R. E.; Kaasjager, V. E.; Kliphuis, D.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K.; Goubitz, K. *Organometallics* **1996**, *15*, 668 and references therein.

[17] (a) Sommazzi, A.; Garbassi, F.; Mestroni, G.; Milani, B. U.S. Patent No. 5,310,871, 1994. (b) Milani, B. Ph.D. Thesis, University of Trieste, 1991−94.

[18] Milani, B.; Vicentini, L.; Sommazzi, A.; Garbassi, F.; Chiarparin, E.; Zangrando, E.; Mestroni, G. *J. Chem. Soc., Dalton Trans.* **1996**, 3139.

[19] Sommazzi, A.; Garbassi, F.; Mestroni, G.; Milani, B.; Vicentini, L. Eur. Pat. No. 96117237.6-2102, 1996.

[20] Bontempi, A.; Alessio, E.; Chanos, G.; Mestroni, G. *J. Mol. Catal.* **1987**, *42*, 67.

Table 1. Elemental Analyses for the Compounds [(N-N)H][X][a]

compounds	% C	% H	% N
[(bipy)H][PF_6] (**1**)	39.6 (39.7)	2.98 (3.00)	9.26 (9.27)
[(Me_2-bipy)H][PF_6] (**2**)	43.7 (43.6)	3.93 (3.97)	8.50 (8.48)
[(phen)H][PF_6] (**3**)	44.1 (44.2)	2.77 (2.78)	8.65 (8.60)
[(Me_2-phen)H][PF_6]·H_2O (**4**)	45.6 (45.2)	3.92 (4.06)	7.60 (7.53)
[(Me_4-phen)H][PF_6] (**5**)	50.2 (50.3)	4.50 (4.48)	7.35 (7.33)
[(Ph_2-phen)H][PF_6] (**6**)	60.5 (60.3)	3.60 (3.58)	5.90 (5.86)
[(bipy)H][BF_4] (**7**)	49.0 (49.2)	3.67 (3.72)	11.40 (11.48)
[(phen)H][BF_4] (**8**)	53.5 (53.8)	3.30 (3.38)	10.40 (10.45)
[(bipy)H_2][OTf]$_2$ (**9**)	32.7 (31.6)	2.18 (2.21)	6.43 (6.14)
[(phen)H][OTf] (**10**)	46.6 (47.3)	2.57 (2.75)	8.23 (8.48)
[(bipy)H_2][OTs]$_2$ (**11**)	57.3 (57.6)	4.78 (4.83)	5.61 (5.60)
[(phen)H][OTs]·H_2O (**12**)	61.5 (61.6)	4.89 (4.90)	7.50 (7.56)

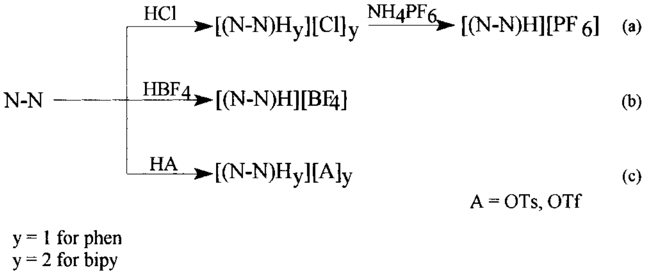
[a] Calculated values are reported in parentheses.

Table 2. Elemental Analyses for the Complexes [Pd(N-N)$_2$][X]$_2$[a]

compounds	% C	% H	% N
[Pd(bipy)$_2$][PF_6]$_2$ (**13**)	33.7 (33.9)	2.20 (2.28)	7.93 (7.91)
[Pd(Me_2-bipy)$_2$][PF_6]$_2$ (**14**)	37.8 (37.7)	3.15 (3.16)	7.30 (7.33)
[Pd(phen)$_2$][PF_6]$_2$ (**15**)	38.2 (38.1)	2.10 (2.13)	7.46 (7.40)
[Pd(Me_2-phen)$_2$][PF_6]$_2$ (**16**)	40.8 (41.4)	2.90 (2.98)	6.80 (6.89)
[Pd(Me_4-phen)$_2$][PF_6]$_2$ (**17**)	45.1 (44.2)	3.66 (3.71)	6.39 (6.45)
[Pd(Ph_2-phen)$_2$][PF_6]$_2$ (**18**)	54.7 (54.3)	3.44 (3.04)	5.61 (5.28)
[Pd(bipy)$_2$][BF_4]$_2$ (**19**)	40.5 (40.6)	2.67 (2.72)	9.50 (9.46)
[Pd(phen)$_2$][BF_4]$_2$ (**20**)	44.5 (45.0)	2.53 (2.52)	8.67 (8.75)
[Pd(bipy)$_2$][OTf]$_2$ (**21**)	37.0 (36.9)	2.11 (2.25)	7.72 (7.81)
[Pd(phen)$_2$][OTf]$_2$ (**22**)	40.4 (40.8)	1.99 (2.11)	7.17 (7.32)
[Pd(bipy)$_2$][OTs]$_2$·2H_2O (**23**)	50.2 (51.2)	4.29 (4.30)	6.92 (7.03)
[Pd(phen)$_2$][OTs]$_2$·2H_2O (**24**)	54.5 (54.0)	4.16 (4.05)	6.78 (6.63)

[a] Calculated values are reported in parentheses.

Scheme 1. Synthesis of the Protonated Nitrogen Compounds [(N-N)H][X]



according to the following procedures, depending on the nature of X^- (Scheme 1):

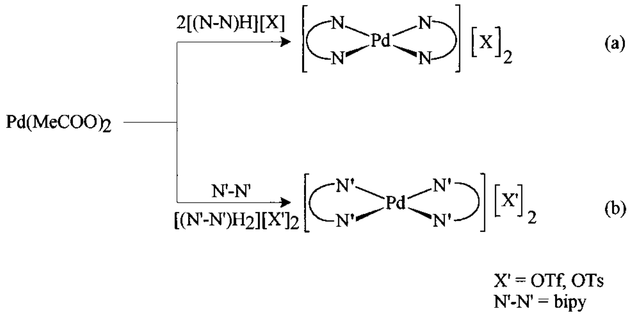
[(N-N)H][PF_6] 1−6. The dinitrogen ligand N-N (13 mmol) was dissolved in methanol (100 mL) at room temperature. Water (20 mL), HCl (aqueous solution 37%; 2 mL), and NH_4PF_6 (19 mmol; N-N:PF_6^- = 1:1.5) were added in this order to the colorless solution. Concentration to approximately half of the original volume induced precipitation of the product as a white solid. The solid was removed by filtration, washed with water, and dried under vacuum. Average yield: 85%.

Single crystals of [(phen)H][PF_6] suitable for X-ray analysis precipitated directly from reaction mixture. Crystals of [(bipy)H][PF_6] were obtained by dissolving 0.1 g of the compound (0.3 mmol) in 25 mL of methanol. The filtered solution was put in a porcelain evaporating dish, and 6 mL of diethyl ether was added. The beaker was covered with parafilm, and after 1 week at room temperature suitable crystals were obtained.

[(N-N)H][BF_4] 7−8. The compounds were synthesized using a procedure similar to that reported for the corresponding hexafluorophosphate derivatives, replacing NH_4PF_6 with HBF_4 (aqueous solution, 60%; N-N:HBF_4 = 1:2) and without the addition of water. Average yield: 60%.

[(N-N)H$_x$][OTf]$_x$ (*x* = 2 (9), 1 (10). The N-N ligand (1.0 mmol) was dissolved in acetone (5 mL) at room temperature, and triflic acid was added (0.2 mL for **9**, bipy:OTfH = 1:2.3; 0.1 mL for **10**, phen:OTfH = 1:1). The product precipitated as a white solid upon addition of diethyl ether. The mixture was stirred for 15 min at room temperature, and then the solid was removed by filtration, washed with diethyl ether, and dried under vacuum. Average yield: 85%.

Scheme 2. Synthesis of the Bis-Chelated Palladium(II) Complexes [Pd(N-N)$_2$][X]$_2$



[(N-N)H$_x$][OTs]$_x$ (*x* = 2 (11), 1 (12). The N-N ligand (1.0 mmol) was dissolved in acetone (20 mL) at room temperature, and *p*-toluenesulfonic acid was added (0.40 g for **11**, bipy:OTsH = 1:2; 0.20 g for **12**, phen:OTsH = 1:1). The product readily precipitated as a white solid. After the mixture was stirred for 15 min at room temperature, the solid was filtered off, washed with acetone, and dried under vacuum. Yield: 75%.

Bone or glass spatulas, instead of steel spatulas, are recommended for handling these compounds, to avoid complexation of iron.

Complexes [Pd(N-N)$_2$][X]$_2$ (13−24). The complexes can be synthesized either from Pd(NO_3)$_2$·2H_2O or $PdCl_2$[20] or from Pd(MeCOO)$_2$ following this new method (Scheme 2):

[Pd(N-N)$_2$][PF_6]$_2$ 13−18. Pd(MeCOO)$_2$ (1.0 mmol) was dissolved in acetone (25 mL) at room temperature. After 30 min, [(N-N)H][PF_6] (3 mmol; Pd:[(N-N)H][PF_6] = 1:3) was added as a solid to the filtered red solution. The product readily precipitated as a yellow solid. After 30 min, it was removed by filtration, washed with acetone and vacuum dried. Average yield: 85%.

[Pd(N-N)$_2$][BF_4]$_2$ 19−20. A procedure similar to that reported above for [Pd(N-N)$_2$][PF_6]$_2$ was used, with the addition of [(N-N)H][BF_4] (Pd:[(N-N)H][BF_4] = 1:2.2) instead of [(N-N)H][PF_6]. The product readily precipitated as a yellow solid. After 30 min, it was removed by filtration, washed with acetone, and vacuum dried. Average yield: 75%. Single crystals for X-ray analysis of compounds **19** and **20** were obtained with the double-layer method. The compound (0.2 g, 0.3 mmol) was dissolved at room temperature in 5 mL of dimethyl sulfoxide. Methanol (4 mL) was stratified on the filtered orange solution. After 2 days, suitable crystals were obtained.

[Pd(bipy)$_2$][A]$_2$ (A = OTf$^-$ (21), OTs$^-$ (23)). Pd(MeCOO)$_2$ (1.0 mmol) was dissolved in methanol (15 mL) at room temperature. After 15 min bipy (1.0 mmol) was added to the filtered red solution, which turned to yellow. [(bipy)H_2][A]$_2$ (1.0 mmol) was then added as a solid. The product precipitated as a yellow solid, upon addition of some drops of diethyl ether. After 30 min, it was removed by filtration, washed with cold methanol, and vacuum dried. Yield: 80%.

[Pd(phen)$_2$][A]$_2$ (A = OTf$^-$ (22), OTs$^-$ (24)). Pd(MeCOO)$_2$ (1.0 mmol) was dissolved at room temperature in acetone (25 mL) for **22** or in methanol (15 mL) for **24**. After 30 min, [(phen)H][A] was added (2.0 mmol) to the filtered red solution and the color of the solution turned to yellow, and after 5 min, the product precipitated as a yellow solid. After 30 min, it was removed by filtration, washed with cold methanol, and vacuum dried. Average yield: 75%.

Pd_2(DBA)$_3$·$CHCl_3$ (DBA = *trans,trans*-dibenzylideneacetone). The compound was synthesized either according

Table 3. Summary of Crystal Data and Structure Refinement Details for 1, 3, 19, 20, and 26

	1	**3**	**19**	**20**	**26**
formula	$C_{10}H_9PF_6N_2$	$C_{12}H_9PF_6N_2$	$PdF_8N_4C_{20}B_2H_{16}$	$PdF_8N_4C_{24}B_2H_{16}$	$C_{16}H_{12}PdO_2N_2$
fw	302.16	326.18	592.39	640.43	370.69
cryst syst	monoclinic	triclinic	triclinic	orthorhombic	orthorhombic
space group (No.)	*Pc* (7)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$C222_1$ (20)	*Pnma* (62)
a/Å	6.1758(4)	6.482(1)	7.792(2)	16.064(2)	8.490(3)
b/Å	13.120(3)	8.003(2)	10.178(3)	19.886(2)	9.805(2)
c/Å	7.255(4)	12.802(4)	14.308(4)	14.558(2)	16.340(6)
α/deg		85.29(2)	75.44(2)		
β/deg	100.74(3)	88.57(2)	79.26(2)		
γ/deg		72.35(2)	78.68(2)		
U/Å^3	577.5(5)	630.7(3)	1065.6(5)	4651(1)	1360.2(7)
D_c/g cm^{-3}	1.74	1.72	1.85	1.83	1.81
Z	2	2	2	8	4
μ (Mo Kα)/cm^{-1}	2.96	2.77	9.43	8.71	13.50
F(000)	304	328	584	2528	736
cryst size/mm	0.20 × 0.10 × 0.30	0.20 × 0.25 × 0.40	0.45 × 0.30 × 0.50	0.10 × 0.20 × 0.25	0.50 × 0.60 × 0.15
$2\theta_{max}$/deg	60	56	56	56	60
octants collected	$\pm h,+k,+l$	$\pm h,\pm k,+l$	$\pm h,\pm k,+l$	$+h,+k,+l$	$+h,+k,+l$
no. of reflns collec.	1877	3180	5331	3098	2279
% transm. min,max			56.2, 99.9	97.6, 99.9	56.9, 98.9
no. of indep reflns	824 ($I > 3\sigma$)	1193 ($I > 2\sigma$)	4406 ($I > 3\sigma$)	1764 ($I > 3\sigma$)	1642 ($I > 3\sigma$)
no. of params	120	190	317	143	97
R (Fo)	0.052	0.052	0.043	0.064	0.031
R_w (F_o)	0.046 ($w = 1$)	0.055 ($w = 1/\sigma^2(F_o)$)	0.050 ($w = 1$)	0.066 ($w = 1$)	0.035 ($w = 1$)
goodness of fit	1.67	1.29	1.30	1.68	1.34
residuals/e Å^{-3}	0.60, −0.74	0.50, −0.12	0.78,-0.72	1.27, −0.72	0.54, −0.83

to the published procedure[21] or following this new method: $Pd(MeCOO)_2$ (1.1 mmol) was added to a solution of DBA (3.6 mmol) and MeCOONa (6.6 mmol) in methanol (30 mL) at 50 °C. The temperature was decreased to 40 °C, and immediately a deep violet solid, formulated as $Pd(DBA)_2$, precipitated. The mixture was stirred for 4 h at 40 °C, and then the solid was removed by filtration, washed with water, cold acetone, and vacuum dried. The raw material (0.63 g) was dissolved in refluxing $CHCl_3$ (25 mL). The dark red solution was filtered over fine paper, and the product precipitated upon addition of diethyl ether (45 mL). The solid was removed by filtration, washed with cold diethyl ether, and vacuum dried. Yield: 64%. Anal. Calcd for $C_{51}H_{42}O_3Pd_2\cdot CHCl_3$: C, 60.3; H, 4.19. Found: C, 60.1; H, 4.07. IR (KBr): 1610 (vs, ν(C=O)), 1572 (m, ν(C=C)) cm^{-1}.

[Pd(N-N)(BQ)] (N-N = phen (25) bipy (26)). $Pd_2(DBA)_3\cdot CHCl_3$ (0.4 mmol) was suspended in anhydrous acetone (20 mL) under inert atmosphere. The dinitrogen ligand (Pd:N-N = 1:1.2) and 1,4-benzoquinone (Pd:BQ = 1:1.7) were added as solids. After 5 min, the color of the suspension turned to brown-red. The suspension was filtered off, washed with cold acetone, and vacuum dried. Average yield: 86%. Anal. Calcd for $C_{18}H_{12}N_2O_2Pd$ (**25**): C, 54.8; H, 3.06; N, 7.10. Found: C, 54.0; H, 3.04; N, 7.03. Anal. Calcd for $C_{16}H_{12}N_2O_2Pd$ (**26**): C, 51.8; H, 3.26; N, 7.56. Found: C, 51.5; H, 3.15; N, 7.41. IR (KBr) for **25**: ν_{CO} 1606 cm^{-1}. IR (KBr) for **26**: ν_{CO} 1606 cm^{-1}. ^{1}H NMR ($CDCl_3$) for **25**: δ 8.90 (dd, 2H, $H^{2,9}$), 8.47 (dd, 2H, $H^{4,7}$), 7.95 (s, 2H, $H^{5,6}$), 7.83 (q, 2H, $H^{3,8}$), 5.77 (b, 4H, BQ) ppm. ^{1}H NMR for **26**: δ 8.54 (d, 2H, $H^{6,6'}$), 8.10 (d, 2H, $H^{3,3'}$), 8.01 (t, 2H, $H^{4,4'}$), 7.53 (t, 2H, $H^{5,5'}$), 5.69 (b, 4H, BQ) ppm. Single crystals of **26** suitable for X-ray analysis were obtained with the double-layer method by dissolving 0.2 g of compound (0.5 mmol) in a minimal amount of $CHCl_3$. The same volume of diethyl ether was stratified on the filtered red solution. The crystals were obtained overnight.

X-ray Analysis. X-ray Structure Determination of 1, 3, 19, 20, and 26. Details of crystal parameters, data collection, and refinements are summarized in Table 3. Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and Mo Kα radiation (λ = 0.7107 Å). The intensities of three standard reflections measured during the data collections did not show any decay for any of the compounds.

Correction for Lorentz and polarization effects were applied. An empirical absorption correction, based on a ψ-scan, was applied to the Pd complexes but not to the structures of protonated ligands **1** and **3**.

All the structures were determined by conventional Patterson methods followed by Fourier methods. The final refinements of **1** and **20** were carried out with isotropic thermal parameters of the carbon atoms and BF_4^- groups (when present), since the crystal quality did not allow for collection of a sufficient number of reflections at high values of θ. Hydrogen atoms at calculated positions (C−H bond distance 0.95 Å) were introduced in the final cycles of refinements as fixed contributions ($B = 1.3B_{eq}$ of their bonded atom). The final weighting scheme was $1/(F_o)^2$ for compound **19** and unity for **1, 3, 20**, and **26**. An attempt to evaluate the absolute configuration of compounds **1** and **20** did not produce satisfactory results. Atomic scattering factors and anomalous dispersion parameters were taken from ref 22. All calculations were carried out on a Micro-VAX2000 computer using the MolEN Enraf-Nonius system of programs.[23]

Catalysis. CO/C$_2$H$_4$ Copolymerization Reactions. The copolymerization reactions were carried out in a stainless-steel autoclave (2 L) by introducing, in order, the catalyst, the methanol, and the oxidant (BQ). The reactor was then pressurized with the mixture of monomers to the required pressure. The vessel was heated to the proper temperature, and the polymerization was carried out isothermally maintaining a constant pressure level by a continuous feed of monomers. After 5 h, the autoclave was cooled to room temperature, the residual pressure discharged, and the polymer removed by filtration, washed with methanol, and vacuum dried.

CO/Ph−CH=CH$_2$ Copolymerization Reactions. These reactions were carried out in a stainless-steel autoclave (150 mL), equipped with a Teflon liner, magnetic stirrer, heating mantle, and temperature controller. The complex $[Pd(bipy)_2][PF_6]_2$, 1,4-benzoquinone, styrene, and the solvent were placed in the autoclave, which was then pressurized to the proper pressure with CO and heated to the appropriate temperature. After cooling and releasing the residual gas, methanol (200

---

[21] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

[22] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[23] *MolEN, An Interactive Structure Determination Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

mL) was added. The copolymer was removed by filtration, washed with methanol, and vacuum dried.

Results and Discussion

Synthesis and Characterization of [(N-N)H][X] (1−12). The first examples of monoprotonated bipyridinium cations, [(bipy)H][ClO_4]^{24} and [(bipy)H][Fe(bipy)$_3$]-[ClO_4]$_4$,^{25} were reported in the late 1970s. In subsequent papers,$^{26-29}$ the monoprotonated bipyridinium cation was mainly used as a counterion to favor the growth of single crystals of coordination compounds suitable for X-ray analysis.

To the best of our knowledge, a complete series of protonated ligands with simple counterions [(N-N)H]-[X] (**1**−**12**) have never been reported. These compounds were isolated in high yield as white, pure microcrystalline solids by a procedure, which takes advantage of their low solubility in a proper solvent mixture, which depends on the chelating ligand and on the anion (Scheme 1).

Acidification with aqueous HCl of a solution of the chelating nitrogen ligand in a 5/1 mixture of methanol/water, followed by addition of NH_4PF_6, led to the precipitation of the hexafluorophosphate derivatives **1**−**6** (Scheme 1a). Addition of diethyl ether instead of NH_4PF_6 allowed the isolation of the intermediate product, which is [(N-N)H_2][Cl]$_2$ for the bipyridine ligands and [(N-N)H][Cl] for the phenanthroline ones.

The other compounds **7**−**12** were directly isolated on addition of a slight excess of the corresponding acid to a solution of the chelating nitrogen ligand: in methanol for $X = BF_4^-$ (**7** and **8**, Scheme 1b) and in acetone for $X = OTf^-$ (**9** and **10**) and OTs^- (**11** and **12**, Scheme 1c). The sulfonic derivatives of bipy precipitated as diprotonated compounds.

Care should be taken to avoid prolonged contact of solutions of **1**−**12** with glassware. When recrystallization of [(bipy)H][PF_6] was performed in glass beakers, the extraction of Si from glass occurred and crystals of [bipySiF_4] were isolated.^{30}

Figures 1 and 2 depict the ORTEP drawings^{31} with atom numbering scheme of the compounds **1** and **3**, respectively. Bond lengths and angles appear in the normal range, even though the structure of **1** is less precise. The bond angles at N2 (119.7(9)° and 115.1(4)° in **1** and **3**, respectively) agree with those observed previously for heterocycle rings without any extra annular attachment at N atom, while angles at protonated N1 are larger (126.8(9)° in **1** and 123.1(4)° in **3**). The torsion angle N1−C5−C6−N2 is 18(2)° and 4.5(6)° in **1** and **3**, respectively, implying a *cis* conformation. Correspondingly, the dihedral angle between the pyridine mean planes is 13.0(6)° and 3(1)°. A stable planar conformation was predicted for the *cis* [(bipy)H]$^+$ form in the gas phase, while the *trans* form has an interplanar angle of 26°,^{32} and the *cis*−*trans* equilibrium in [(bipy)H]$^+$ can be shifted toward the *cis* cation in the presence of a suitable coordination center. Therefore, the present data agree with other [(bipy)H]$^+$ structural results which indicate that the *cis* conformation is the one commonly found in the solid state, where the absolute value of the N−C−C−N torsion angle ranges from 0.0° to 18.0°.^{33}

The characterization in solution was done by ^1H NMR spectroscopy (Table 4). All spectra have four resonances, indicating the equivalence of the two halves of

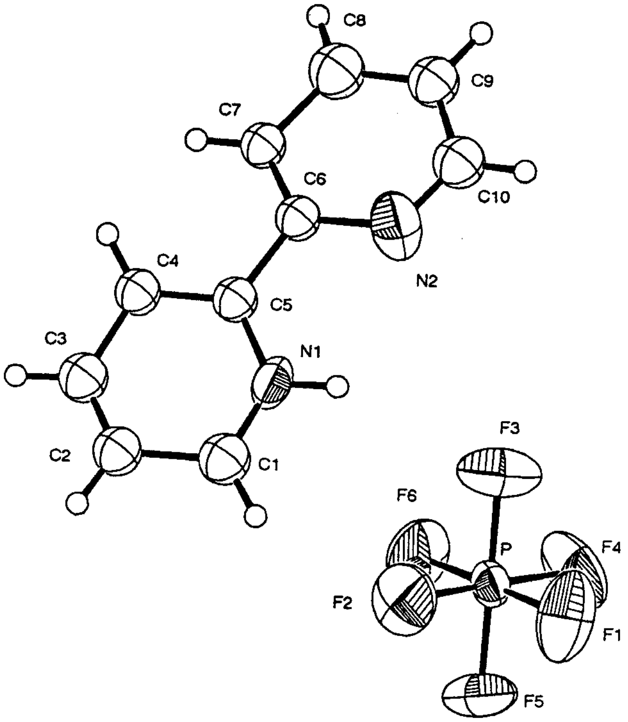


Figure 1. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme of [(bipy)H][PF_6].

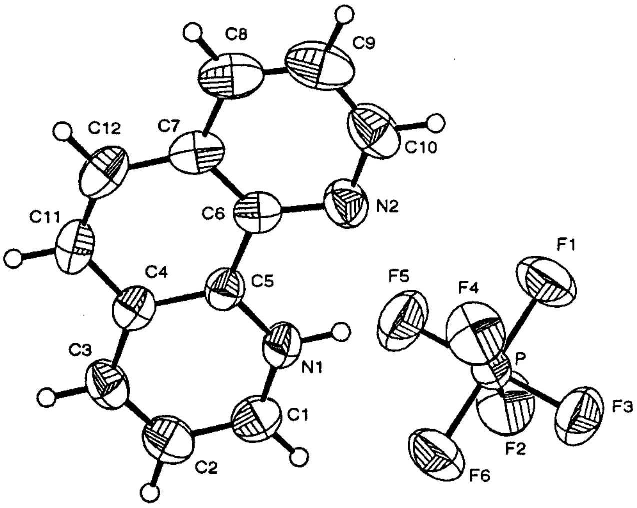


Figure 2. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme of [(phen)H][PF_6].

---

[24] Lipkowski, J.; Sgarabotto, P.; Andreetti, G. D. *Cryst. Struct. Comm.* **1976**, *5*, 931.

[25] Figgis, B. N.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 57.

[26] Stomberg, R.; Szentivanyi, H. *Acta Chem. Scand.* **1984**, *A38*, 121.

[27] Fuller, D. J.; Kepert, D. L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1987**, *40*, 2097.

[28] Roodt, A.; Leipoldt, J. G.; Deustch, E. A.; Sullivan, J. C. *Inorg. Chem.* **1992**, *31*, 1080.

[29] Decurtins, S.; Schmalle, H. W.; Schneuwly, P.; Oswald, H. R. *Inorg. Chem.* **1993**, *32*, 1888.

[30] Adley, A. D.; Bird, P. H.; Fraser, A. R.; Onyszchuk, M. *Inorg. Chem.* **1972**, *11*, 1402.

[31] Johnson, C. K.; ORTEP. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

[32] Howard, S. T. *J. Am. Chem. Soc.* **1996**, *118*, 10269.

[33] Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G., *J. Chem. Info. Comput. Sci.* **1991,** *31*, 187.

Table 4. ^{1}H NMR Data of Compounds [(N-N)H][X] and of the Corresponding Complexes $[Pd(N\text{-}N)_2][X]_2$[a]

compound	$H^{6,6'}$	$H^{5,5'}$	$H^{4,4'}$	$H^{3,3'}$
bipy	8.69 (d)	7.46 (dt)	7.95 (dt)	8.39 (d)
1	8.80 (d)	7.69 (t)	8.21 (t)	8.53 (d)
7	8.79 (d)	7.68 (dt)	8.19 (t)	8.53 (d)
9	8.85 (b)	7.81 (b)	8.34 (b)	8.61 (b)
11[b]	8.83 (d)	7.75 (t)	8.28 (t)	8.58 (d)
13	8.82 (d)	7.97 (t)	8.54 (t)	8.75 (d)
19	8.82 (d)	7.98 (t)	8.55 (t)	8.75 (d)
21	8.83 (d)	7.98 (t)	8.55 (t)	8.76 (d)
23[c]	8.81 (d)	7.98 (t)	8.54 (t)	8.75 (d)
Me_2-bipy	8.53 (d)	7.28 (dd)		8.23 (s)
2	8.70 (d)	7.65 (d)		8.48 (s)
14	8.63 (d)	7.80 (d)		8.62 (s)
compound	$H^{2,9}$	$H^{3,8}$	$H^{4,7}$	$H^{5,6}$
phen	9.11 (dd)	7.79 (q)	8.50 (dd)	8.00 (s)
3	9.30 (d)	8.20 (q)	9.04 (d)	8.35 (s)
8	9.30 (dd)	8.21 (q)	9.05 (dd)	8.36 (s)
10	9.31 (d)	8.23 (q)	9.07 (d)	8.37 (s)
12[d]	9.31 (d)	8.22 (q)	9.06 (d)	8.36 (s)
15	9.39 (d)	8.33 (q)	9.20 (d)	8.47 (s)
20	9.41 (d)	8.34 (q)	9.21 (d)	8.48 (s)
22	9.39 (b)	8.34 (b)	9.20 (d)	8.48 (s)
24[e]	9.38 (d)	8.32 (q)	9.19 (d)	8.46 (s)
Me_2-phen	8.94 (d)	7.61 (d)		8.16 (s)
4	9.15 (d)	8.08 (d)		8.46 (s)
16	9.10 (d)	7.91 (d)		8.40 (s)
Me_4-phen	8.83 (s)			8.16 (s)
5	9.08 (s)			8.47 (s)
17	9.05 (s)			8.48 (s)
Ph_2-phen	9.18 (d)	7.74 (d)	7.60 (m)[f]	7.86 (s)
6	9.35 (d)	8.15 (d)	7.69 (m)[f]	8.14 (d)
19[g]				

[a] In 10 mM DMSO-d_6 at room temperature; region of aromatic protons. [b] 7.47 (d), 7.11 (d), 2.29 (s) protons of OTs^-. [c] 7.45 (d), 7.08 (d), 2.27 (s) protons of OTs^-. [d] 7.47 (d), 7.11 (d), 2.29 (s) protons of OTs^-. [e] 7.42 (d), 7.05 (d), 2.24 (s) protons of OTs^-. [f] Protons of phenyl groups in 4,7 position. [g] Not soluble in DMSO-d_6 at 10 mM concentration at room temperature. s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

the protonated dinitrogen ligand. Assignments were made as previously reported.[14] All signals are shifted downfield with respect to the resonances of the unprotonated ligands, in agreement with the deshielding effect due to the presence of the N−H bond. No variation in the chemical shift was observed when the spectra were measured either at different concentrations of $[(N\text{-}N)H]^+$ or after the addition of a very small amount of CF_3COOH.

Synthesis and Characterization of the Complexes $[Pd(N\text{-}N)_2][X]_2$ (13−24). $[Pd(phen)_2][ClO_4]_2$[34a] and $[Pd(bipy)_2][ClO_4]_2$[34b] have been known for a long time. Their synthesis was based on the addition of a slight excess of the dinitrogen chelating ligand to a solution of Li_2PdCl_4, and precipitation of the product occurred upon addition of NH_4ClO_4.

The same procedure was used to obtain the hexafluorophosphate and tetrafluoroborate derivatives.[20] But the complexes obtained by this route invariably contained traces of chloride, whose amount varied in each preparation. Another synthetic approach, involving exchange of the nitrate anion with hexafluorophosphate in $Pd(NO_3)_2{\cdot}2H_2O$, was also used.[20]

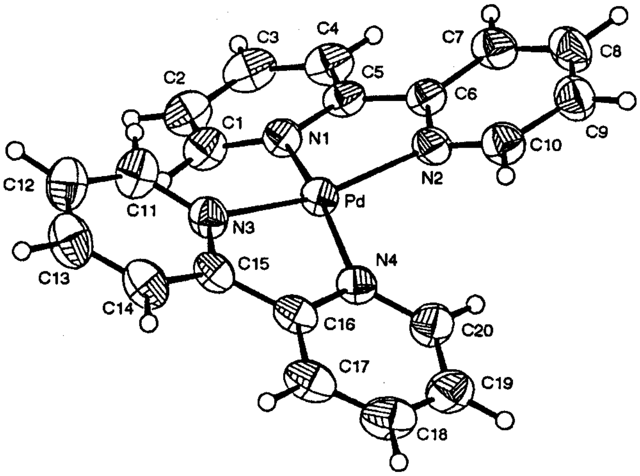


Figure 3. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme of the cation of $[Pd(bipy)_2]$-$[BF_4]_2$.

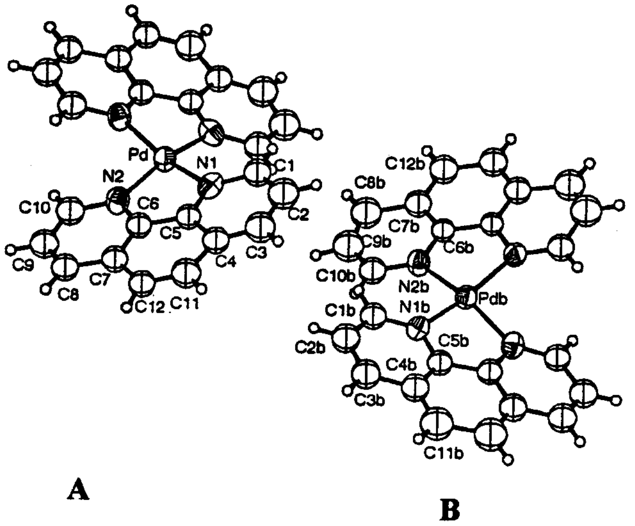


Figure 4. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme of the cations of $[Pd(phen)_2]$-$[BF_4]_2$.

Very recently, other rather complicated procedures have been reported for the synthesis of triflate and tetrafluoroborate derivatives.[35] Freshly prepared $[Pd(C_6H_5CN)_2Cl_2]$ (for bipy) and $[Pd(MeCN)_4][Y]_2$ (for phen) ($Y = OTf^-$, BF_4^-) were used as precursors.[35]

In this paper, we report a new simple *one-pot* reaction for the synthesis, in high yield and high purity, of the bis-chelated derivatives, $[Pd(N\text{-}N)_2][X]_2$, with different dinitrogen ligands and different anions.

Addition of 2 equiv of [(N-N)H][X] (Scheme 2a) or 1 equiv of bipy followed by 1 equiv of $[(bipy)H_2][X']_2$ ($X' = OTf^-$, OTs^-) (Scheme 2b) to an acetone solution of $Pd(MeCOO)_2$ led to the rapid precipitation of the product as a yellow microcrystalline solid.

The crystal structures of $[Pd(bipy)_2][PF_6]_2$ (**13**) and $[Pd(phen)_2][PF_6]_2$ (**15**) have been already reported by this group.[36] Figures 3 and 4 show a perspective view of the cations of $[Pd(bipy)_2][BF_4]_2$ (**19**) and $[Pd(phen)_2]$-$[BF_4]_2$ (**20**). In the latter, two crystallographically

---

(34) (a) Livingstone, S. E. *Chem. Abstr.* **1953**, 1526d. (b) Livingstone, S. E. *Chem. Abstr.* **1953**, 7932c.

(35) (a) Wehman, P.; Dol, G. C.; Moorman, E. R.; Kamer, P. C.; van Leeuwen, P. W. N. M.; Fraanje, J.; Gaubitz, K. *Organometallics* **1994**, *13*, 4856. (b) Wehman, P.; Kaasjager, V. E.; de Lange, W. G. J.; Hartl, F.; Kamer, P. C. J.; van Leeuwen, P. W. M. N. *Organometallics* **1995**, *14*, 3751.

(36) Geremia, S.; Randaccio, L.; Mestroni, G.; Milani, B. *J. Chem. Soc., Dalton Trans.* **1992**, 2117.

Table 5. Coordination Bond Lengths (Å) and Angles (deg) and Geometrical Parameters of Cations 19 and 20[a]

	19	**20** A	**20** B
Pd−N(1)	2.031(4)	2.02(1)	2.05(1)
Pd−N(2)	2.030(3)	2.01(1)	2.04(1)
Pd−N(3)	2.031(4)		
Pd−N(4)	2.029(3)		
N(1)−Pd−N(2)	80.3(1)	81.1(4)	99.3(4)
N(1)−Pd−N(3)	102.4(1)	101.1(5)[b]	82.1(5)[b]
N(1)−Pd−N(4)	164.3(2)	164.0(5)[c]	166.8(5)[c]
N(2)−Pd−N(3)	163.1(2)	101.3(4)[d]	82.3(4)[d]
N(2)−Pd−N(4)	101.8(1)		
N(3)−Pd−N(4)	80.2(1)		
PdN_2/PdN_2 α (°)	25.5(3)	24.7(3)	20.1(3)
N-N/N-N(°)	36.46(8)	29.66(9)	27.43(9)
PdN_2/N_2C_2 β (°)	1.0(5), 2.0(5)	0.4(5)	0.0(4), 0.6(4)
py/py γ (°)	8.7(6), 8.1(8)	1(1)	1(1), 3(2)
tetrahedral dist. N donors (Å)	±0.290(4)	±0.28(1)	±0.23(1)
Pd out-of-plane (Å)	0.010(1)	0.00	0.00

[a] Symmetry code: $i = -x, y, {}^1/_2 - z$ (**20** A); $i = x, -y, 1 - z$ (**20** B). [b] N(1)−Pd−N(1)^i. [c] N(1)−Pd−N(2)^i. [d] N(2)−Pd−N(2)^i.

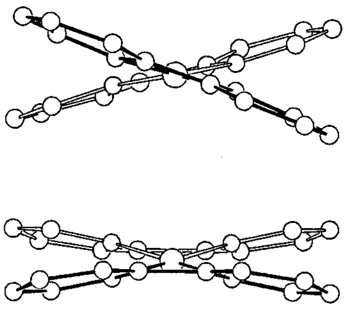


Figure 5. Side view of the *twist* conformation found in $[Pd(bipy)_2][BF_4]_2$ and $[Pd(phen)_2][BF_4]_2$ and of the *bow-step* conformation detected in $[Pd(bipy)_2][PF_6]_2$.

independent molecules A and B, having C_2 symmetry, were detected in the unit cell. The 2-fold axis passes through Pd and lays in the mean coordination plane in both molecules, relating the two N−N ligands in A and the two halves of each ligand in B.

The overall geometry of the bis-chelated compounds can be defined in terms of three interplanar angles: α, between the MN_2 planes; β, between the MN_2 and NCCN mean planes; γ, between the two pyridyl rings of bipy or between the two chemically equivalent moieties of phen.[14a,36] The calculated values for the complexes **19** and **20**, together with coordination bond lengths and angles, are reported in Table 5.

The coordination geometry of Pd in both of the cations is tetrahedrally distorted from square planar with a dihedral angle, α, of 25.5(3)° in **19** and of 24.7(3)° and 20.1(3)° in **20**. Consequently, the almost planar ligands alleviate their mutual steric interaction through a *twist* conformation. Alternatively, the crowding between the α-hydrogens of the two chelating ligands in this type of complex can be relieved through a *bow-step* arrangement. The angles β and γ describe the step deformation inside the N-ligand while α indicates the *twist* deformation between the ligands. Figure 5 sketches a side view of the *twist* arrangement found in complex **19** and of the *bow-step* one found in the corresponding PF_6^- salt (**13**).[36] Conformations similar to those observed in **19** and **13** were found in phen complexes **20** and **15**, respectively.

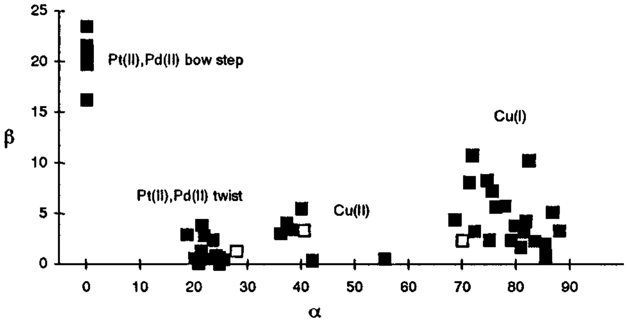


Figure 6. Scatter plot of β *vs* α angle in bis(chelated) tetracoordinated metal complexes. Empty squares indicate (from the right) the structures of Ag(II), Hg(II), and Ag(I).

The Pd−N distances in complexes **19** and **20** are equal within their esd and are comparable with those found in $[Pd(N\text{-}N)_2][PF_6]_2$ complexes.[36]

The steric effects in bis(bipy) and bis(phen) metal complexes have been previously analyzed in terms of a simple van der Waals repulsion energy between the opposing α-hydrogen atoms in *rigid* chelates as a function of the *twist* angle.[37]

We performed a more detailed razionalization of the geometry in the solid state of this type of complex. The Cambridge Crystallographic Database[33] was searched for $[M(N\text{-}N)_2]^{n+}$ ($n = 1, 2$), and the values of angles α, β, and γ (mean values for the latters) were calculated for all the structures retrieved (43 hits, see Supporting Information). Figure 6 reports a scatter plot of β angles *vs* the dihedral angle α, which ranges from 0.0° (square planar coordination) to 70−90° (tetrahedrally coordinated Cu(I) complexes). Square planar Pt(II) and Pd(II) complexes were found grouped in two clusters: on the left, five structures with a *bow-step* conformation (α = 0°, β = 15−25°) and a more numerous group, which includes the data of **19** and **20**, with a *twist* arrangement (α = 18−27°, $\beta < 5°$). The more disperse data ($\beta \approx 10°$) on the right pertain to Cu(I) complexes of phenanthroline substituted in the 2,9-positions where, as expected, more severe distorsions are observed. A similar, but more disperse, scatter plot was obtained when γ is plotted *vs* α, indicating a correlation between the angles β and γ.

The analysis seems to suggest that *bow-step* arrangements in Pt and Pd complexes are stabilized in the solid state by stacking interactions between the nitrogen ligands[36] or between the nitrogen ligand and planar aromatic anions, such as picrate[38] or tetracyanoquinodimethane.[39] Nevertheless, this rationalization is unsatisfactory for $[Pd(bipy)_2][PF_6]_2$ which does not show any stacking interactions and where the metal exhibits weak interactions with the counterion (Pd---F distances of 3.02 Å). Therefore, the energy difference between the conformational isomers may be compensated by packing interactions (van der Waals and Coulombic).

The behavior of bis-chelated complexes in solution was studied by ^1H NMR spectroscopy in DMSO-d_6 (Table 4). The spectra of all of the complexes have four equally intense resonances in the region of the aromatic protons, indicating the equivalence both of the two

---

(37) Mc Kenzie, E. D. *Coord. Chem. Rev.* **1971**, *6*, 187.

(38) Maeda, S.; Nishida, Y.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2013.

(39) Dong, V.; Endres, H.; Keller, H. J.; Moroni, W.; Nöthe, D. *Acta Crystallogr.* **1977**, *B33*, 2428.

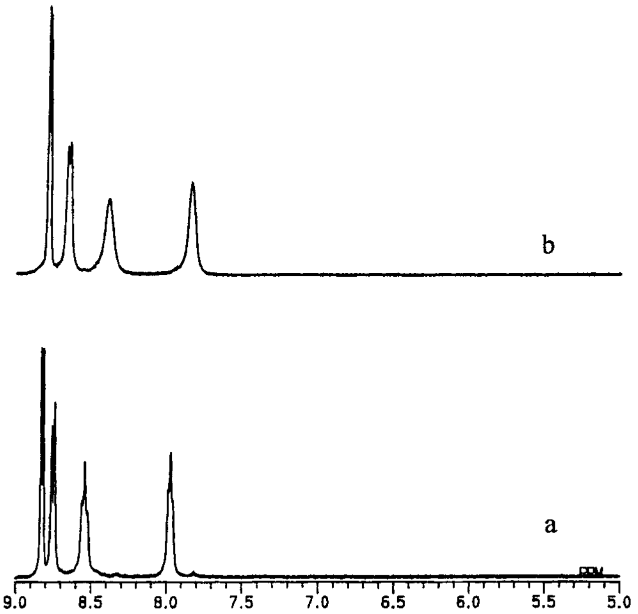
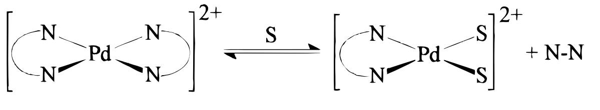


Figure 7. ^{1}H NMR spectra in DMSO-d_6 at room temperature of (a) $[Pd(bipy)_2][PF_6]_2$. (b) $[Pd(bipy)_2][PF_6]_2$ and 1 equiv of bipy. All 10 mM.

ligands bonded to palladium and of the two halves of each ligand. All signals are downfield-shifted with respect to those of the unbound ligand. The assignments were made as previously reported.[14]

At room temperature and at a 10 mM complex concentration, the resonances are rather broad; addition of free ligand causes further broadening and also a slight upfield shift of the resonances, whose chemical shifts become intermediate between those of the coordinated ligand and those of the free one (Figure 7). No signal due to the latter is present. This result establishes the presence of an exchange process between the free and bonded chelating nitrogen ligand (eq 2), whose rate is intermediate on the NMR time scale. By dissociation of the N-N molecule, the steric hindrance of the α hydrogens, shown in the solid state structures,[37] is completely relieved.



(2)

S = coordinating solvent

Copolymerization Reactions. The bis-chelated derivatives $[Pd(N-N)_2][X]_2$ were tested in the CO/olefin copolymerization reaction without any acid cocatalyst, yielding perfectly alternating polyketones whose characterization (elemental analyses, melting point, IR, ^{1}H and ^{13}C NMR spectra) is in agreement with the literature data.[14]

As already observed for the monochelated derivatives $[Pd(N-N)(R-COO)_2]$ (R = Me, CF_3),[14a] for the bis-chelated compounds $[Pd(N-N)_2][X]_2$ a strong influence of the anion on the productivity was also found. On going from hexafluorophosphate to trifluoroacetate and to acetate, a strong decrease of the catalytic activity was observed (Table 6a); indeed, in the case of the acetato derivative, the activity was almost negligible, due to the complete decomposition of the active species to palladium metal. The low activity of the carboxylato anions can be related to their coordination and esterification capabilities.[14a] The replacement of hexafluorophosphate with tetrafluoroborate also led to a strong decrease in the catalytic activity (Table 6b), and the same effect has been observed with the "mixed-ligand" complexes $[Pd(dppp)(bipy)][X]_2$ (X = PF_6^-, BF_4^-).[18] Van Leeuwen et al. also found that $[Pd(N\text{-}N)_2][OTf]_2$ complexes (*N-N* = 4,7-disubstituted-1,10-phenanthrolines) are usually less active than the corresponding BF_4^- salts in catalyzing the reductive carbonylation of nitroaromatic compounds to urethanes.[35b] An active participation of the anion was suggested as being responsible for this behavior,[35b] and this hypothesis was supported by a short Pd---O contact, in the solid state, of 2.922 Å in $[Pd(phen)_2][OTf]_2$.

Table 6. CO/C_2H_4 Copolymerization: Effect of the Anion

X	g of CP/g of Pd	η (dL/g)
(a) Catalyst Precursor: $[Pd(phen)_2][X]_2$[a]		
PF_6^-	2010	1.13
CF_3COO^-	880	0.10
$MeCOO^-$ [b]	20	n.d.
(b) Catalyst precursor: $[Pd(bipy)_2][X]_2$[c]		
PF_6^-	2292	1.42
BF_4^-	226	n.d.

[a] Reaction conditions: [Pd] = 1 × 10^{-3} M; [BQ] = 8 × 10^{-2} M; solvent, methanol, V = 500 mL; P_{tot} = 56 atm; T = 90 °C; time = 5 h. [b] $[Pd(phen)(MeCOO)_2]$ + phen. [c] Reaction conditions: [Pd] = 1.25 × 10^{-3} M; [BQ] = 0.1 M; solvent, methanol, V = 200 mL; P_{tot} = 56 atm; T = 70 °C; time = 5 h.

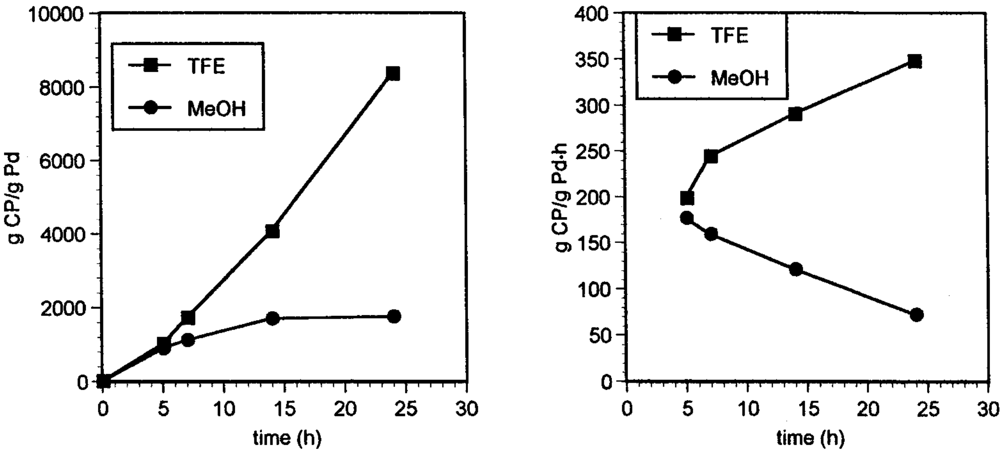
Careful analysis of the metal–anion interactions in the solid state shows that the BF_4^- anions approach the Pd ion, with the shortest Pd---F distances of 3.39 (**19**) and 3.50 Å (**20**), while in the hexafluorophosphate derivative **13,** this distance is 3.02 Å. Therefore, in this case, a correlation between the solid state results and the catalytic properties of the complexes gives contradictory results. The incomplete inertness of tetrafluoroborate in the reaction mixture[40] might be a better explanation for the lower catalytic activity of BF_4^- salts compared to PF_6^-.[41] On the basis of these considerations, the "ideal" anion should be noncoordinating and inert in the reaction mixture and hexafluorophosphate represents the best choice to date, not only for the productivity of the system, but also for the quality of the polymer. Indeed, with the PF_6^- compounds we obtained polyketones with a 10-fold greater η value compared to those produced with the corresponding CF_3COO^- salts.

Some preliminary results on the CO/styrene copolymerization had indicated $[Pd(bipy)_2][PF_6]_2$ as the most active compound among those tested.[17] Therefore, the present investigation was limited to this compound only. A change of the solvent from methanol to 2,2,2-trifluoroethanol (TFE) resulted in an increase of the productivity (from 650 g of CP/g of Pd in MeOH to 1134 g of CP/g of Pd in TFE). Moreover, the copolymer obtained in methanol was grey while that prepared in TFE was white, indicating that a negligible decomposition of the active species to palladium metal occurred. In TFE, the productivity was almost unaffected by the

---

(40) Beck, W.; Sinkel, K. *Chem. Rev.* **1988**, *88*, 1405.

(41) (a) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G.; Terenzi, S. *Organometallics* **1996**, *15*, 4349. (b) Macchioni, A.; Bellachioma, G.; Gramlich, V.; Rüegger, H.; Terenzi, S.; Venanzi, L. M. *Organometallics* **1997**, *16*, 2139.



(a) (b)

Figure 8. CO/styrene copolymerization: effect of solvent. Catalyst precursor: [Pd(bipy)$_2$][PF$_6$]$_2$. Reaction conditions: see Table 8. Plots of (a) productivity *vs* reaction time, (b) reaction rate *vs* reaction time.

Table 7. CO/Styrene Copolymerization: Effect of Temperature. Catalyst Precursor: [Pd(bipy)$_2$][PF$_6$]$_2$[a]

T (°C)	t (h)	g of CP	g of CP/ g of Pd	g of CP/ g of Pd·h	Pd (ppm)	η (dL/g)
70	5	1.63(w)	2836	567	127	0.23
75	5	2.32(w)	4037	807	102	0.17
80	5	2.91(w)	5064	1013	52	0.12
60	7	1.09(w)	1897	271	n.d.	0.27
65	7	1.60(w)	2784	398	n.d.	n.d.
70	7	2.36(w)	4107	587	60	0.25
75	7	3.15(w)	5481	784	49	0.17
80	7	4.56(w)	7935	1134	44	0.14

[a] Reaction conditions: $n_{\mathrm{Pd}} = 0.54 \times 10^{-2}$ mmol; $n_{\mathrm{BQ}} = 0.348$ mmol; *V* (styrene) = 30 mL; *V* (TFE solvent) = 20 mL; *V* (2,2′-dimethoxypropane (DMP)) = 0.5 mL; $P_{\mathrm{CO}} = 40$ atm.

Table 8. CO/Styrene Copolymerization: Effect of Reaction Time. Catalyst Precursor: [Pd(bipy)$_2$][PF$_6$]$_2$[a]

[styr]/[Pd]	time (h)	g of CP	g of CP/g of Pd	η (dL/g)
48 000	7	1.09(w)	1897	0.27
48 000	14	2.33(w)	4054	0.32
48 000	24	4.80(w)	8354	0.35
96 000[b]	14	1.44(w)	5012	0.32
96 000[b]	24	1.74(w)	6056	0.32
96 000[b]	48	4.88(w)	17 367	0.36[c]

[a] Reaction conditions: see Table 7, *T* = 60 °C. [b] $n_{\mathrm{Pd}} = 0.27 \times 10^{-2}$ mmol. [c] Pd = 32 ppm.

catalyst concentration and values as high as 1.1 kg of CP/g of Pd at a [styr]/[Pd] ratio of 48 000 were obtained. Despite the increase in productivity, the η value is still low (0.21 dL/g) and the amount of palladium residue is quite high (154 ppm). To improve this catalytic system the effect of different parameters was analyzed.

The temperature plays an important role both on the activity of the system and on the quality of polyketones produced (Table 7). An increase of the temperature resulted in a remarkable increase of the activity, and at 80 °C the productivity was almost four times higher than that at 60 °C (Table 7). The copolymer was white and contained a low amount of palladium. However, the temperature had a negative effect on the molecular weight of the polymer: the η value decreased on increasing the temperature (Table 7). As high molecular weight polymers are needed for useful applications,[2s] we decided to work at 60 °C and, in order to increase the yield, the reaction time was prolonged. The effect of the reaction time was examined at two different catalyst concentrations, which correspond to a [styr]/[Pd] ratio of 48 000 and 96 000, respectively. The reactions were carried out for 1 or 2 days, respectively, and 5 g of copolymer was recovered in both cases at the end. At the [styr]/[Pd] ratio of 96 000, this yield corresponds to a productivity of 17.4 kg of CP/g of Pd, with minor decompostion of the catalytic species (Table 8). The copolymer had an η value of 0.36 dL/g and contained 32 ppm of Pd only. This result represents the first example of the production of CO/styrene copolymer in high yield, with the highest molecular weight and the lowest amount of palladium to date.

At 60 °C, the difference between methanol and TFE was investigated in details. As reported in Figure 8, although after 5 h the yields of copolymer in the two solvents were comparable, for longer reaction times the yield in 2,2,2-trifluoroethanol became increasingly higher than that in methanol. The plot of productivity *vs* the reaction time shows an asymptotic behavior in methanol, and after 14 h the active species was deactivated and the copolymer was grey (Figure 8a). In TFE, the productivity increased on extending the reaction time and the catalyst was still active after 24 h: a productivity of 8.3 kg of CP/g of Pd was obtained for this reaction time and negligible decomposition to metal was observed. Moreover, while in methanol the reaction rate decreased with time, in TFE it increased (Figure 8b). These trends indicate that the difference between the two solvents might be related to the catalyst lifetime. It is straightforward to note that the stability of the catalyst is greatly enhanced in trifluoroethanol with respect to methanol.

The productivity was also influenced by the pressure of carbon monoxide (Table 9) and it increased on decreasing the CO pressure, confirming the inhibiting effect of CO already observed by Brookhart[2n] and this group.[14b] At an initial pressure of 10 atm, measured at room temperature, a productivity of at least 15 kg of CP/g of Pd was achieved. The drop of CO pressure during the reaction, due to the impossibility of providing a continuous feed of CO, might have prevented the system from even higher yields and might also be responsible for the low η values observed (Table 9).

Table 9. CO/Styrene Copolymerization: Effect of CO Pressure. Catalyst Precursor: $[Pd(bipy)_2][PF_6]_2$[a]

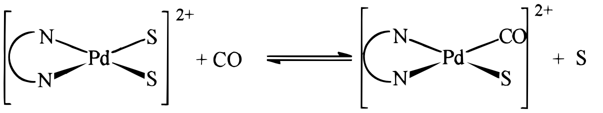
P_{CO} (atm)[b]	g of CP	g of CP/ g of Pd	g of CP/ g of Pd·h	η (dL/g)
40	2.33(w)	4054	290	0.32
20	3.36(w)	5847	418	0.43
10[c]	>584(w)	>10 162	>726	0.32
10[c,d]	>4.35(w)	>15 139	>1081	n.d.

[a] Reaction conditions: see Table 7; T = 60 °C; t = 14 h. [b] measured at room temperature. [c] $P_{CO} = 0$ after 14 h. [d] $n_{Pd} = 0.27 \times 10^{-2}$ mmol; [styr]/[Pd] = 96 000.

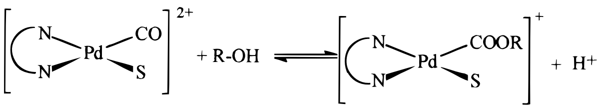
All of these experiments were conducted with the addition of 1,4-benzoquinone, which has been reported to be essential in high amounts for achieving high productivities.[2s,6] We found that only a small excess of the oxidant with respect to palladium is required to have high yields of polyketones ([BQ]/[Pd] = 5) (Table 10), but the most important result concerns the effect of the amount of benzoquinone on the molecular weight of polyketones. We found that this parameter greatly increases by decreasing the BQ concentration. Indeed, the copolymer obtained with a [BQ]/[Pd] ratio of 5 has the remarkably high η value of 0.64 dL/g, which represents the first case of a CO/styrene copolymer with such a high molecular weight. It cannot be excluded that with a further improvement of the catalytic system, copolymers with an η value close to 1 dL/g might be produced.

The copolymerization reaction mechanism has been extensively discussed by several scientists, such as Drent,[4,6] Brookhart,[2i,n] Vrieze,[16] Sen,[42] and Consiglio.[11b] It is generally accepted that the catalytic cycle is comprised of three parts: the initiation, propagation, and termination steps. The propagation steps are recognized to be the same in all of the copolymerization processes and consist of subsequent alternating migratory insertions of an alkyl group to CO and of an acyl group to olefin, which have been studied by NMR spectroscopy by Brookhart[2i,n] and Vrieze.[16] Instead, the initiation and termination steps are different depending on the nature of the olefinic comonomer.

For our system, we propose that the initiation steps consist of three different equilibria. First (eq 2), the dissociation of one molecule of the nitrogen ligand from palladium generates a monochelated species with two avalaible coordination sites in a *cis* configuration. The affinity of palladium for CO is known;[6] therefore, the coordination of carbon monoxide is likely to happen on this species (eq 3), followed by the interaction with alcohol and the subsequent formation of the monocationic carboalkoxy derivative and one proton (eq 4).



(3)



(4)

This carbomethoxy intermediate may be considered as the real active species. The proton can react with the free N-N molecule according to equilibrium 5, yielding the monoprotonated ligand. This equilibrium is impor-

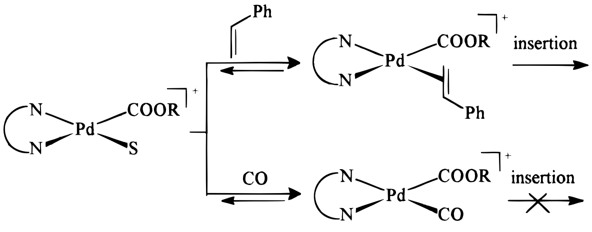
Table 10. CO/Styrene Copolymerization: Effect of 1,4-Benzoquinone. Catalyst Precursor: $[Pd(bipy)_2][PF_6]_2$[a]

BQ (mmol)	[BQ]/[Pd]	g of CP	g of CP/g of Pd	η (dL/g)
0.348	64	2.33(w)	4054	0.32
0.108	20	2.15(w)	3741	n.d.
0.054	10	2.18(w)	3793	n.d.
0.027	5	2.58(w)	4490	0.64

[a] Reaction conditions: see Table 7, T = 60 °C; t = 14 h.

$$\text{N-N} + H^+ \rightleftharpoons [(\text{N-N})H]^+ \qquad (5)$$

tant for control of the proton concentration during the copolymerization process and it might contribute to increase the concentration of the carboalkoxy intermediate. Coordination of styrene to the monocationic active species, followed by insertion, will lead to the propagation of the polymeric chain (eq 6a). On the contrary, coordination of carbon monoxide leads to a carbonyl carbomethoxy intermediate, which, due to the unfavorable thermodynamics of the double carbonylation reaction,[43] cannot proceed further (eq 6b). This

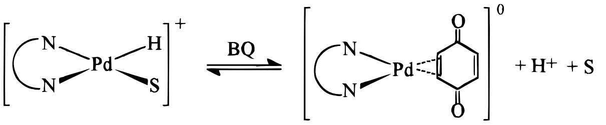


(6a)
(6b)

monocarbonyl carbomethoxy species has been isolated and structurally characterized by Brookhart, who demonstrated that this is the resting state of the catalytic cycle.[2i]

Drent reported that in the CO/styrene copolymerization the termination steps always produce a hydride species, which can either be reoxidized to palladium(II) by the oxidant or decompose to palladium metal.[6] The termination steps can be a β-hydrogen elimination or an alcoholysis, which requires the nucleophilic attack of the alcohol to the metal center. The higher productivity, observed by us, in TFE with respect to methanol might be due in part to the lower nucleophilicity of TFE compared to MeOH.

The hydride species can dissociate the hydrogen atom as a proton, and the resulting Pd(0) species can bind the oxidant (eq 7). The intermediate with the benzoquinone bound to palladium has been always postulated,[6] but neither detected nor trapped. Therefore, to tentatively understand its role, we investigated the chemical behavior in solution of the Pd(0) compounds, [Pd(N-N)(BQ)], whose synthesis was performed by following either the procedure reported in literature[21] or,



(7)

---

[42] Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303.

[43] (a) Chen, J. T.; Sen A. *J. Am. Chem. Soc.* **1984**, *106*, 1506. (b) Sen, A.; Chen, J. T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148.

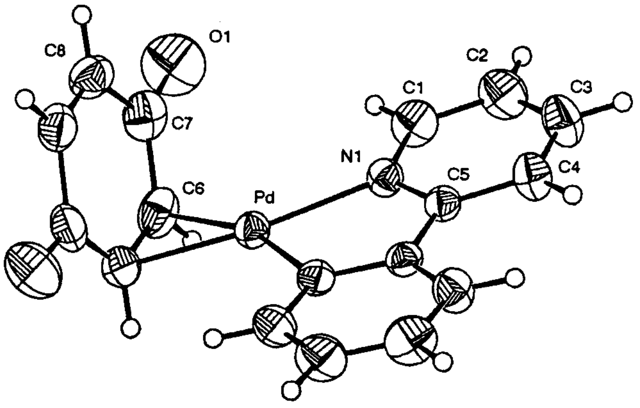


Figure 9. ORTEP drawing of [Pd(bipy)(BQ)]. Relevant coordination bond lengths (Å) and angles (deg): Pd−N(1) 2.119(3), Pd−C 2.083(4) Å, N(1)−Pd−N(1^i) 77.0(1), N(1)−Pd−C(6) 121.4(1), N(1)−Pd−C(6^i) 161.2(1), C(6)−Pd−C(6^i) 40.0(2). Atoms indicated by ^{i} are related by *x*, 0.5 −*y*, *z*.

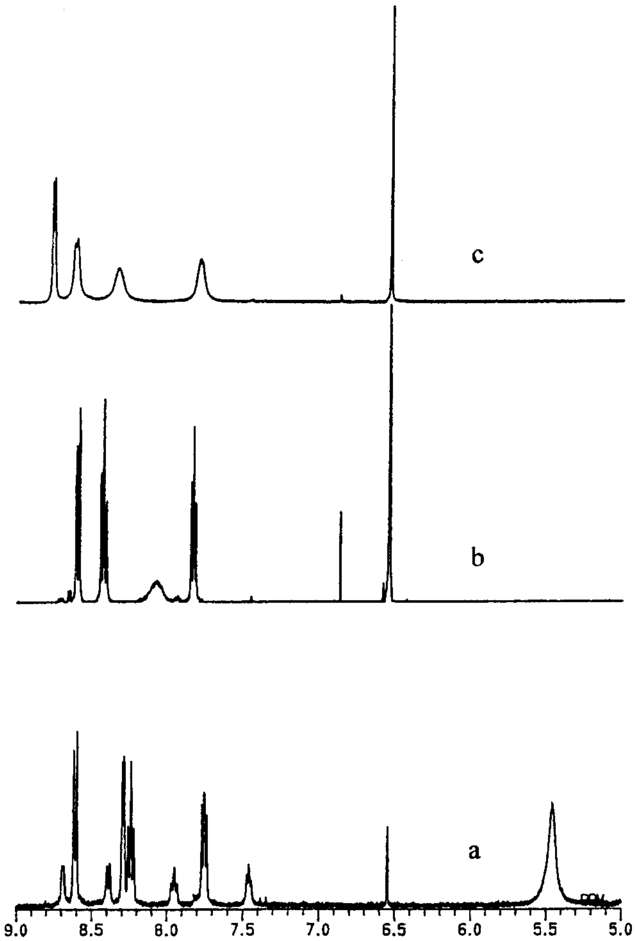


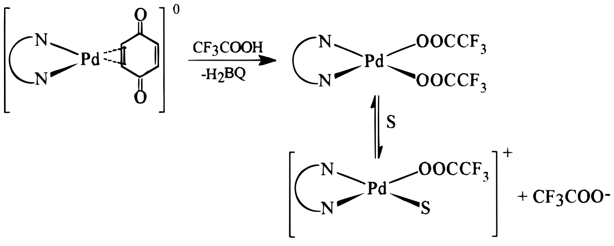
Figure 10. ^{1}H NMR spectra in DMSO-d_6 of (a) [Pd(bipy)(BQ)], (b) [Pd(bipy)(BQ)] and CF_3COOH, (c) [Pd(bipy)(BQ)] and 2 equiv of [(bipy)H][PF_6].

more conveniently, the simplified method described in this paper, starting from [Pd(MeCOO)$_2$]. These complexes were characterized both in the solid state and in solution (see Experimental Section). The infrared spectrum in the solid state has a strong CO stretching band at 1606 cm^{-1}, with a shift of 45 cm^{-1} to lower frequencies with respect to free benzoquinone. In agreement with literature data,[21] this value of $\Delta\nu$ is indicative of coordination of benzoquinone through the olefinic π bond, rather than through the oxygen atoms.

The X-ray structure determination (Figure 9) showed that benzoquinone binds as a mono-olefinic ligand to Pd; the coordinated olefinic bond length of 1.423(6) Å indicates a largely single-bond character. The dihedral angle between BQ and the coordination plane is 84.65(5)°. The monofunctional nature of benzoquinone contrasts with that previously proposed, where both of the olefinic π bonds were supposedly employed in the coordination to palladium,[21] while in agreement with the very recent results of Klein et al.[44]

The solution chemical behavior of [Pd(bipy)(BQ)] (**26**) was studied by ^{1}H NMR spectroscopy. The spectrum in $CDCl_3$ (red solution) has, besides the resonances of coordinated bipy, only one broad signal at 5.69 ppm for the four protons of benzoquinone. This result, in agreement with that reported for a similar platinum compound [Pt(PPh$_3$)$_2$(BQ)], suggests the occurrence of an equilibrium between the two fluxional isomers, which differs for the olefinic π bond coordinated to Pd.[45]

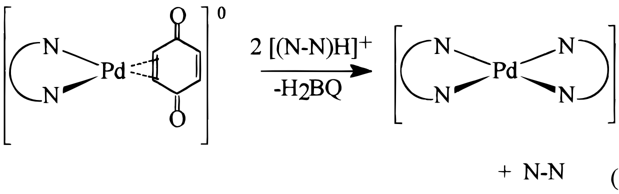
The ^{1}H NMR spectrum of **26** in DMSO-d_6 (red solution) shows, besides the main resonances of the complex, other minor peaks belonging to a coordinated bipy species, also including that of free hydroquinone at 6.54 ppm (Figure 10a). At the moment, no assignment has been made regarding this species. The color of this solution immediately turned to yellow upon addition of CF_3COOH. As shown by the ^{1}H NMR spectrum (Figure 10b), benzoquinone completely transformed into free hydroquinone while the bipy resonances correspond to those of [Pd(bipy)(CF_3COO)$_2$], eq 8.[14a]



(8)

H_2BQ = 1,4-Hydroquinone

The red solution of [Pd(bipy)(BQ)] in DMSO-d_6 also turned yellow upon addition of 2 equiv of [(bipy)H][PF_6]. Again, the ^{1}H NMR spectrum showed the resonances of free hydroquinone and no signal due to benzoquinone (Figure 10c). The bipy resonances are the same as those in the spectrum of [Pd(bipy)$_2$][PF_6]$_2$ plus 1 equiv of bipy (Figure 7b), eq 9.



(9)

Therefore, the benzoquinone Pd(0) complex, which might also form during the catalytic cycle, is readily oxidized to Pd(II) in the presence of protons with the concomitant reduction of benzoquinone to hydroquinone. Moreover, the resulting Pd(II) species corresponds exactly to the catalyst precursors and can immediately

---

[44] Klein, R. A.; Elsevier, C. J.; Hartl, F. *Organometallics* **1997**, *16*, 1284.

[45] Vagg, R. S. *Acta Crystallogr.* **1977**, *B33*, 3708.

re-enter into the catalytic cycle. In fact, when [Pd(bipy)(BQ)] was used as the precatalyst in the presence of 2 equiv of [(bipy)H][PF_6] and BQ, in such an amount that [BQ]/[Pd] = 5, under usual reaction conditions, in TFE, a productivity of 4194 g of CP/g of Pd (yield 2.41 g of CP) was obtained.

Conclusions

The analysis of the catalytic systems reported in this paper indicated that, to date, [Pd(bipy)$_2$][PF_6]$_2$, easily synthesized by a *one-pot* reaction, is the most efficient precatalyst for the CO/styrene copolymerization. High productivities of CO/styrene polyketone were achieved in 2,2,2-trifluoroethanol; the polymer has a good molecular weight and contains a low amount of palladium residue.

A putative intermediate of the catalytic cycle, [Pd(bipy)(BQ)], was synthesized and structurally characterized. Investigation of its solution chemistry verified that oxidation to the Pd(II) precursor occurs at room temperature in the presence of protons with concomitant reduction of BQ to hydroquinone.

In our catalytic system, proton concentration is controlled by the free nitrogen ligand. If the source of protons is the protonated chelating ligand, [(N-N)H]$^+$, oxidation of [Pd(N-N)(BQ)] leads to the formation of [Pd(N-N)$_2$]$^{2+}$ species, which corresponds to the catalyst precursor.

Acknowledgment. This work was supported by Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST 60%; Rome). Dr. A. Sommazzi (Istituto Guido Donegani—ENICHEM) is gratefully acknowledged for the CO/C_2H_4 copolymerization and for determination of the values of the limiting viscosity number as well as for those of palladium residue present in the copolymers. Prof. Maurice Brookhart (University of North Carolina, Chapel Hill) is gratefully acknowledged for helpful discussions. We thank Johnson Matthey for a generous loan of Pd(MeCOO)$_2$.

Supporting Information Available: Tables of crystal data, data collection parameters, and refinement, refined atomic coordinates and calculated H-atom coordinates, thermal parameters, and bond lengths and angles for **1**, **3**, **9**, **20**, and **26** and a table of CO/styrene copolymerization regarding the effect of solvent on the productivity of the catalytic system (24 pages). Ordering information is given on any current masthead page.

OM9703954