CROATICA CHEMICA ACTA CCACAA **74** (4) 851–865 (2001)

ISSN-0011-1643
CCA-2772

Original Scientific Paper

Structural Aspects of Palladium Systems Used as Catalyst Precursors in CO/olefins co- and ter-Polymerisation Reactions

*Barbara Milani, Giovanni Mestroni, and Ennio Zangrando**

Dipartimento di Scienze Chimiche, Università di Trieste,
Via L. Giorgieri 1, I-34127 Trieste, Italy

Received February 23, 2001; revised April 9, 2001; accepted April 12, 2001

The synthesis and characterisation of three palladium complexes, involved in the homogeneous catalysis towards the CO-olefins co- and ter-polymerisation reactions, are reported. The [Pd (dpk$\cdot$CH$_3$OH) (CF$_3$CO$_2$)$_2$] (**1**), (dpk = di(2-pyridyl) ketone) and [Pd (dppp)(bipy)] [B(C$_6$F$_5$)$_4$]$_2$ (**2**), (bipy = 2,2'-bipyridine, dppp = 1,3-bis(diphenylphosphino)propane) compounds are examples of a neutral complex and of a dicationic mixed-ligands one, respectively. The catalytic activity of type **2** complexes was reported to be strongly dependent on the nature of the anion, and the tetra(perfluorophenyl) borate salt represents the best choice to date for the CO/aliphatic olefins copolymerisation. In both structures, the metal has a square planar coordination and the structural aspects of these complexes are discussed in comparison with their catalytic properties. The crystal structure of [Pd(bipy)(naphthoquinone)] (**3**), which is a putative intermediate of the catalytic cycle, is also reported.

Key words: palladium, crystal structure, polyketone, chelating ligand, copolymerisation.

INTRODUCTION

The discovery by Drent in 1983 (Refs. 1,2) that *in situ* Pd^{II} catalytic systems modified by diphosphine ligands produce high molecular weight

---

* Author to whom correspondence should be addressed. (E-mail: zangrando@univ.trieste.it)

CO/ethylene polyketones at high rates resulted in a fast development of research in this field, both by industry and academy.[3]

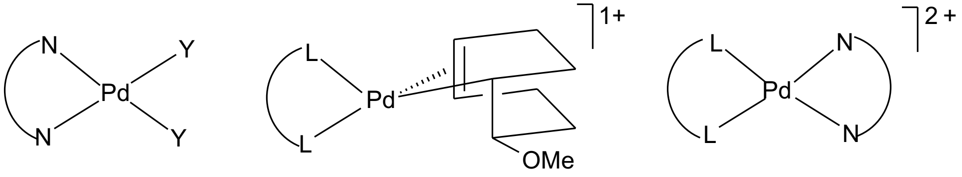
The CO/olefin co- and ter-polymerisation reactions yield perfectly alternating polyketones (Eq. (1)), one of which has become commercially available under the trade mark of Carilon®.[4]

$$n\mathrm{CO} + n\mathrm{CHR{=}CH_2} \xrightarrow{\text{catalyst}} -(\mathrm{C(O)CH(R)CH_2})_n- \tag{1}$$

R = H, Me, Ph.

This reaction is homogeneously catalysed by palladium(II) salts-based systems modified by bidentate phosphorus- or nitrogen-donor chelating ligands (P-P or N-N). The reactions are usually performed in methanol; different cocatalysts (*e.g.* Brønsted acids) and/or co-reagents (*e.g.* organic oxidants) may be required, depending on whether *in situ* catalytic systems or preformed complexes are being used. Early studies showed that there is a close relationship between the nature of the olefin co-monomer and the ancillary ligand. Catalytic systems based on diphosphine ligands, such as 1,3-bis(diphenylphosphino)propane (dppp), are required to achieve high yields in the copolymerisation of CO with aliphatic α-olefins.[2] On the other hand, Consiglio *et al.* reported that nitrogen-donor ligands are necessary in order to promote the copolymerisation of CO with aromatic olefins.[5] Quite recently, it was found that the same reaction is also performed by phosphino-phosphito ligands[6] or hybrid P-N ligands.[7]

Since 1991, we have been investigating the copolymerisation reaction using palladium(II) preformed complexes with both phosphorus- and nitrogen-donor ligands.[8] We mainly investigated three different series of complexes (Scheme 1): *i* neutral compounds $[\mathrm{Pd(N\text{-}N)Y_2}]$, characterised by the presence of one molecule of bidentate nitrogen ligand and two anions, such as acetate, trifluoroacetate, tosilate (OTs) and triflate (OTf);[9] *ii* monocationic derivatives $[\mathrm{Pd(L\text{-}L)(C_8H_{12}OCH_3)}][\mathrm{X}]$ (where L-L is a diphosphine or a nitrogen ligand, $\mathrm{C_8H_{12}OCH_3}$ is the cyclooctenylmethoxy group, and X is a non-coordinating anion, chosen among $\mathrm{PF_6^-}$, $\mathrm{BF_4^-}$, $\mathrm{BPh_4^-}$, OTf, $\mathrm{SbF_6^-}$, $\mathrm{B(3,5\text{-}(CF_3)_2C_6H_3)_4^-}$);[10] *iii* dicationic compounds $[\mathrm{Pd(L\text{-}L)(N\text{-}N)}][\mathrm{X}]_2$, which have two molecules of chelating ligand bound to the same palladium centre. These two molecules can be either different or equal; in the first case, one molecule is dppp and the other is an N-N ligand, yielding the so-called mixed-ligand complexes,[11] while in the other case both ligands are nitrogen-donor molecules.[12] The N-donor ligands were mainly chosen among 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) and their commercially available substituted derivatives.



i *ii* *iii*

Scheme 1

The most intriguing results concerning the catalytic activity were obtained with the complexes of the third series. In particular, the mixed-ligand complexes were found to be very active for the CO/ethylene and the CO/ethylene/propylene polymerisations, reaching productivities higher than those reported for the *in situ* system.[11] These complexes were more deeply investigated by Bianchini *et al.* and the effect of different P-P ligands was evaluated.[13] On the other hand, with the bischelated derivatives $[Pd(N\text{-}N)_2][PF_6]_2$ a detailed analysis of the CO/styrene copolymerisation was done, giving an insight into the parameters which affect the stability of the catalytic system. Actually, one of the main problems related to the latter reaction was the instability of the active species, which decomposed to palladium metal during the copolymerisation and CO/styrene polyketones were never obtained in high yield and with a molecular weight as high as required for industrial applications.[14] We found that changing the solvent from methanol to 2,2,2-trifluoroethanol (TFE) resulted in a strong increase of productivity without apparent decomposition of metal.[12b] In the literature, the oxidant, usually 1,4-benzoquinone, was claimed to be an essential component of the catalytic systems based on N-donor ligands, operating in methanol.[2] Thanks to the high stability of the active species generated by the $[Pd(N\text{-}N)_2][PF_6]_2$ precursors in trifluoroethanol, the CO/styrene copolymerisation can be carried out in the absence of the oxidant, and polyketones with a molecular weight up to 80000 were easily obtained.[12a]

The relationship between structure and reactivity is one of the main goals of modern chemistry.[15] For this purpose we prepared single crystals, suitable for X-ray analysis, of more than one exponent of the three series of complexes, allowing a comparison of their structural parameters.

In this paper, we report the crystal structure of three different complexes, viz. $[Pd(dpk\cdot CH_3OH)(CF_3CO_2)_2]$ (**1**) (dpk = di(2-pyridyl) ketone), $[Pd(dppp)(bipy)][B(C_6F_5)_4]_2$ (**2**) and [Pd(bipy)(NQ)] (**3**) (NQ = naphthoquinone), together with their implication for the copolymerisation reaction.

EXPERIMENTAL

General Comments

[Pd(CH_3CO_2)$_2$] was obtained from Johnson Matthey and used as received, as well as P- and N-donor ligands (Aldrich) and the analytical grade solvents (Baker). Methanol (Merck) for catalytic reactions was purified by distillation from magnesium and iodine; acetone (C. Erba) for synthetic use was dried on Drierite overnight and stored under an inert atmosphere. Carbon monoxide (CP grade, 99.9%) was supplied by SIAD.

Syntheses of Complexes

*[Pd(dpk·CH_3OH)(CF_3CO_2)$_2$] (**1**)*

The complex was synthesised according to the general procedure reported for compounds [Pd(N-N)(CF_3CO_2)$_2$].[9a]

[Pd(CH_3CO_2)$_2$] (0.5 g, 2.2 mmol) is dissolved in acetone (40 mL) at room temperature. After 30 minutes, di(2-pyridyl) ketone (0.48 g, 2.6 mmol; Pd : dpk = 1 : 1.2) is added to the filtered red solution. The product immediately precipitates as a yellow solid, which, after 30 minutes, is filtered off, washed with cold acetone and vacuum dried. Yield: 90%.

[Pd(dpk·CH_3OH)(CH_3CO_2)$_2$] (0.5 g, 1.2 mmol) is dissolved in methanol (20 mL) at room temperature. An excess of CF_3COOH (2.5 mL) is added to the yellow solution. After 30 minutes, the solution is concentrated and the solid precipitates as single crystals upon addition of diethyl ether, overnight at 4 °C. Yield: 80%.

Anal. Calcd. for $C_{16}H_{12}F_6N_2O_6Pd$: C 35.02, H 2.20, N 5.11%; found: C 34.85, H 2.15, N 5.07%.

*[Pd(dppp)(bipy)][B(C_6F_5)$_4$]$_2$ (**2**)*

The complex was synthesised following the procedure reported in the patent literature,[16] starting from [Pd(dppp)(CF_3CO_2)$_2$].[11]

[Pd(dppp)(CF_3CO_2)$_2$] (0.1 g, 0.13 mmol) is suspended in methanol (10 mL) and bipy (0.03 g, 0.16 mmol) is added, yielding a yellow solution. To this solution, *N*,*N*-dimethylanilinio tetra(perfluorophenyl)borate is added (0.24 g; Pd : B(C_6F_5)$_4$ = 1 : 2.2). After 20 minutes, water is added dropwise (2 mL) under stirring, at room temperature, and the final product precipitates as a white solid, which is filtered off, washed with water and vacuum dried. Yield: 90%.

Anal. Calcd. for $C_{85}H_{34}B_2F_{40}N_2P_2Pd$: C 50.21, H 1.69, N 1.38%; found: C 50.20, H 1.57, N 1.36%.

*[Pd(bipy)(NQ)] (**3**)*

The complex was synthesised following the method reported for the corresponding derivative with 1,4-benzoquinone.[12b]

[Pd_2(DBA)$_3$]·$CHCl_3$, DBA = *trans*, *trans*-dibenzylideneacetone (0.2 g, 0.2 mmol) was suspended in anhydrous acetone (10 mL) under an inert atmosphere. The bipy ligand (0.07 g; Pd : bipy = 1 : 1.2) and naphthoquinone (0.10 g; Pd : NQ = 1 : 1.7) were added as solids. After 10 minutes, the colour of the suspension turned to red. The suspension was filtered off, washed with cold acetone and vacuum dried. Yield: 90%. The compound was recrystallised by dissolving it in chloroform (0.10 g of **3** in 20 mL of chloroform). After filtration over fine paper and addition of diethyl ether, the solution was kept overnight at 4 °C yielding a microcrystalline solid, which was filtered off, washed with diethyl ether and vacuum dried.

Anal. Calcd. for $C_{20}H_{14}N_2O_2Pd$: C 57.09, H 3.35, N 6.66%; found: C 56.40, H 3.25, N 6.53%.

Structure Determination

Details of crystal parameters, data collection and refinements are summarized in Table I. Diffraction data were carried out at room temperature using the ω–2θ

TABLE I

Summary of crystal data and structure refinement details for **1**, **2**, and **3**

	1	**2**·CH_3OH	**3**
Empirical formula	$C_{16}H_{12}F_6N_2O_6Pd$	$C_{86}H_{38}B_2F_{40}N_2OP_2Pd$	$C_{20}H_{14}N_2O_2Pd$
Formula weight	548.68	2065.14	420.73
Crystal system	monoclinic	monoclinic	triclinic
Space group (No.)	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a / Å	7.994(1)	24.195(7)	8.297(1)
b / Å	23.144(2)	13.525(1)	9.431(2)
c / Å	10.366(2)	26.833(7)	11.194(1)
α / °			95.40(8)
β / °	96.17(1)	94.52(1)	100.36(6)
γ / °			110.47(8)
Volume /Å^3	1906.7(5)	8753(3)	795.4(2)
Z	4	4	2
D_{calc} /g cm^{-3}	1.911	1.567	1.757
μ Mo-Kα /cm^{-1}	1.069	0.381	1.182
F(000)	1080	4088	420
cryst size /mm	0.20 × 0.10 × 0.30	0.20 × 0.25 × 0.40	0.45 × 0.30 × 0.50
θ range	2.16 – 29.96	2.14 – 23.26	2.34 – 29.97
Octants collected	$\pm h$, $+k$, $+l$	$\pm h$, $+k$, $+l$	$\pm h$, $\pm k$, $+l$
Reflns collected	3871	12866	4854
Reflns unique	3487	12560	463
R_{int}	0.0607	0.0429	0.0215
No. of params	295	1206	226
Goodness of fit	1.047	1.111	1.128
R_1	0.0504	0.0569	0.0283
wR_2	0.0797	0.1676	0.0766
Residuals /e Å^{-3}	0.516, –0.699	1.288, –0.536	0.882, –0.545

scan technique on a CAD4 Enraf-Nonius single-crystal diffractometer equipped with a graphite monochromator and Mo–Kα radiation (λ = 0.7107 Å). Three standard reflections, measured at regular intervals throughout the data collection, showed no noticeable variation in intensity for any of the crystals. Intensity data were corrected for Lorentz-polarization effects and absorption using an empirical ψ-scan method. The structures were solved by the conventional Patterson and Fourier technique[17] and refined by the full-matrix anisotropic least-squares method.[18] All calculations were performed using the WinGX System, Ver 1.63.[19]

A difference Fourier synthesis revealed in **2** the presence of a methanol molecule disordered over two positions (site occupancy about 0.50 each). In **1**, the fluorine atoms of a CF_3 group are disordered over two positions (site occupancies of about 0.90 and 0.10). The final cycles with the fixed contribution of hydrogen atoms, except for those of the solvent molecule in **2**, converged to the final R_1 and wR_2 factors reported in Table I. Refined weighting schemes were $w = 1/[\sigma^2 (F_o^2) + (aP)^2 + bP]$, where a = 0.0157, 0.1187, and 0.0521, b = 0.0, 21.1304, and 0.0386 for compounds **1**, **2** and **3**, respectively, where $P = (\mathrm{Max}\ (F_o^2, 0) + 2F_c^2) / 3$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-157765 – 157767. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Monochelated Complexes

From a general point of view, the CO/olefin copolymerisation reactions can be carried out in two different experimental ways: at high pressure (up to 300 atm)[7,20] or at low pressure (from 1 up to 4 atm),[21] depending on the nature of the catalytic system.

Under the latter reaction conditions, the neutral monochelated carboxylato Pd^{II} complexes of the general formula $[Pd(N\text{-}N)Y_2]$ were used,[9] and among the different combinations of N-N ligands and anions tested, bipy and $CF_3CO_2^-$ was found to be the most successful.[9a]

During our continuous research aimed at designing more efficient catalysts, we have prepared and structurally characterised a neutral Pd^{II} complex with di(2-pyridyl) ketone. The general synthetic procedure for the $[Pd(N\text{-}N)(CF_3CO_2)_2]$ derivatives is based on an anion exchange reaction starting from the corresponding acetato species.[9a] When an excess of trifluoroacetic acid is added to a methanolic solution of $[Pd(dpk)(CH_3CO_2)_2]$, a yellow solid precipitates as single crystals useful for crystal structure determination.

The crystal analysis reveals addition of one molecule of methanol to the carbonyl group of di(2-pyridyl) ketone, and the resulting complex is better formulated as [Pd(dpk·CH_3OH)(CF_3CO_2)$_2$] (**1**). Indeed, when the di(2-pyridyl) ketone is coordinated to a number of metal ions, its carbonyl group easily undergoes addition of various nucleophiles, including methanol, which is the solvent often used in the copolymerisation reactions, leading to the corresponding condensation product.[22] Moreover, addition of chiral alcohol might open the possibility of synthesising isotactic CO-styrene polyketone.

Crystals of **1** consist of neutral molecules in which the palladium attains the usual square planar coordination being bound to two trifluoroacetate anions and to the nitrogen atoms of the chelating dpk·CH_3OH ligand. A view of the complex with the atom labeling scheme is given in Figure 1, and a selection of bond lengths and angles are reported in Table II. The Pd-N bond lengths are 1.993(5) and 1.994(5) Å, comparable with those reported in [Pd(phen)(CH_3CO_2)$_2$],[9a] but shorter than those found in the [Pd(N-N)$_2$]$^{2+}$ complexes.[23] The trifluoroacetate groups assume a unidentate end-on coordination, both oriented to the same side of the N_2O_2 plane, and the Pd-O distances, of 2.015(4) and 2.031(5) Å, fall in the range of those reported for the [Pd(N-N)(CF_3CO_2)$_2$] complexes where N-N is an atropisomeric bidentate nitrogen ligand.[9b] The dpk·CH_3OH has the six membered chelating ring in a boat conformation, with a dihedral angle between the pyridyl rings of

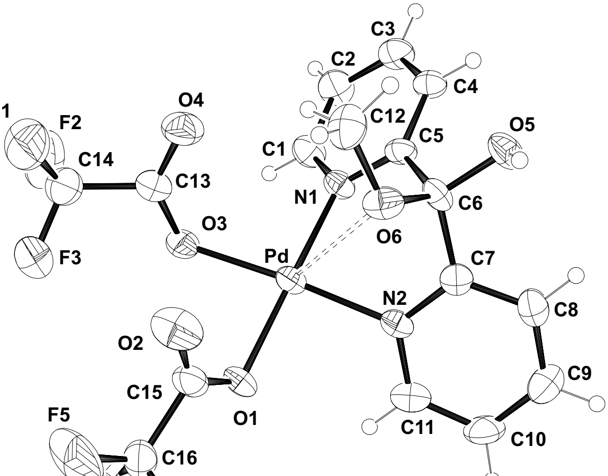


Figure 1. ORTEP view and atom numbering scheme (40% thermal ellipsoids) of compound **1**. Of the disordered F(4–6) fluorines, only atoms at higher occupancy are shown.

TABLE II

Selected bond lengths / Å and angles / ° for compounds **1**, **2** and **3**

Bond lengths / Å		Bond angles / °	
		Compound 1	
Pd-N(1)	1.993(5)	N(1)-Pd-N(2)	88.6(2)
Pd-N(2)	1.994(5)	O(1)-Pd-O(3)	85.1(2)
Pd-O(1)	2.015(4)	N(1)-Pd-O(1)	177.1(2)
Pd-O(3)	2.031(5)	N(2)-Pd-O(1)	91.6(2)
Pd···O(6)	2.945(5)	N(1)-Pd-O(3)	94.6(2)
		N(2)-Pd-O(3)	175.8(2)
		Compound 2	
Pd-N(1)	2.125(5)	N(2)-Pd-N(1)	78.4(2)
Pd-N(2)	2.111(6)	P(2)-Pd-P(1)	87.30(7)
Pd-P(1)	2.272(2)	N(1)-Pd-P(1)	98.96(16)
Pd-P(2)	2.262(2)	N(1)-Pd-P(2)	167.85(16)
		N(2)-Pd-P(1)	170.73(16)
		N(2)-Pd-P(2)	96.95(16)
		Compound 3	
Pd-N(1)	2.118(3)	N(2)-Pd-N(1)	77.33(12)
Pd-N(2)	2.114(2)	C(11)-Pd-C(12)	39.95(13)
Pd-C(11)	2.070(4)	C(11)-Pd-N(1)	163.15(10)
Pd-C(12)	2.088(3)	C(12)-Pd-N(1)	123.20(12)
C(11)-C(12)	1.421(4)	C(11)-Pd-N(2)	119.39(13)
		C(12)-Pd-N(2)	158.48(11)

56.4(2)°. This allows a very favourable coordination angle of 88.6(2)° (compared to the value of that of bipy ligands in **2** and **3** of *ca.* 77.5°) and a short contact between the metal and the methoxy oxygen O(6) of 2.945(5) Å. This distance, comparable to those of 2.824(6) Å (Ref. 24) and 2.940(6) Å (Ref. 25) found in Pd complexes containing a dpk-diol ligand, is shorter than expected for normal non-bonded ones (3.6 Å), thus indicative of a Pd---O weak interaction. The metal, in fact, becomes slightly displaced by 0.050(3) Å from the coordination plane towards the oxygen at a *pseudo*-apical position.

Unlike the diphosphine ligands,[26] no systematic study of the bite angle of N-N chelating ligands has been reported. However, the value of the N-Pd-N bite angle (88.6(2)°) found in the Pd-dpk·CH_3OH compound, very close to 90°, prompted us to test it in the CO/styrene copolymerisation reaction.

When compound [Pd(dpk·CH_3OH)(CF_3CO_2)$_2$] was used as precatalyst under the typical reaction conditions applied for the [Pd(bipy)(CF_3CO_2)$_2$] complex,[9b] no polyketone formation was observed and a complete decomposition to palladium metal was recorded after 15 minutes of reaction. Therefore, despite the likely favourable bite angle, compound **1**, under the applied conditions, is totally unstable and no further investigation in this field was done.

Bischelated Complexes

The mixed-ligand complexes $[Pd(dppp)(N\text{-}N)]^{2+}$ were tested as catalyst precursors in the CO/ethylene copolymerisation and CO/ethylene/propylene terpolymerisation.

Influence of the nature of the nitrogen-donor chelating ligand on the activity has reported.[11] A remarkable decrease in the yield of the copolymer with increasing the coordinating ability of the nitrogen-donor ligand was observed, and, as reported for the monochelated derivatives, higher activity was achieved with bipy.

The catalytic activity was also strongly dependent on the nature of the counterions. Replacement of PF_6^- with BF_4^- led to a strong decrease in catalytic activity, which was even more pronounced with the trifluoroacetato and acetato anions, since the latter possess coordination and esterification capabilities.[11] The same strong influence of the anion was also observed in the CO/styrene copolymerisation with the bischelated complexes $[Pd(bipy)_2]\,[X]_2$ and $[Pd(phen)_2][X]_2$ (X = PF_6^- or BF_4^-).[12b]

Now, we have extended the series of mixed-ligand complexes to $B(C_6F_5)_4^-$, another non-coordinating anion.[16] Single crystals of $[Pd(dppp)(bipy)]\,[B(C_6F_5)_4]_2$ (**2**) were easily obtained by the synthetic mixture.

The structure of the Pd complex cation of **2** is depicted in Figure 2. The structure displays a conformation very similar to that of the PF_6^- salt[11] with the metal in a square planar coordination geometry slightly tetrahedrally distorted, the N and P donors being displaced by ± 0.20 and ± 0.17 Å, respectively, from the coordination mean plane. The Pd-N bond distances of 2.125(5) and 2.111(6) Å (Table II) are similar within their e.s.d.'s. and slightly longer than those detected in bischelated bipy derivatives,[23] being affected by the trans influence of the dppp. The pyridines of the bipy ligand are slightly tilted at a torsion angle N(1)-C(5)-C(6)-N(2) of 8.0°. The Pd-P bond lengths are 2.272(2) and 2.262(2) Å, and a steric strain in the diphosphine ligand is evident on considering the large deviations from ideality of

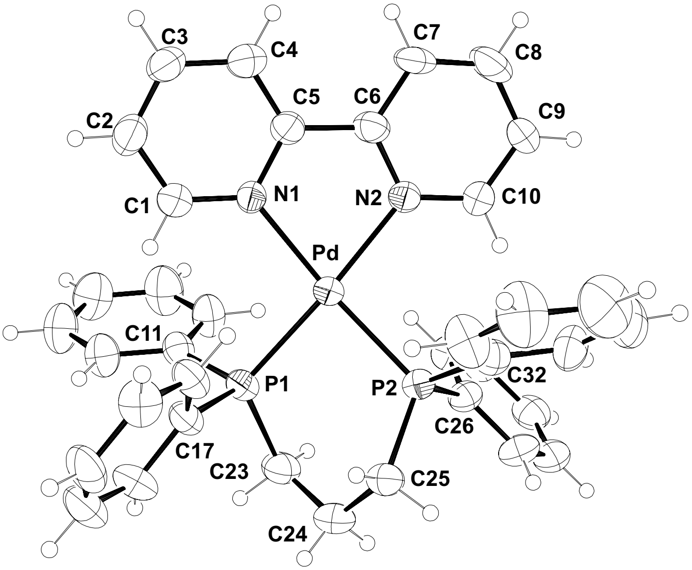


Figure 2. ORTEP drawing and atom numbering scheme (40% thermal ellipsoids) of the complex cation of **2**.

the bond angles in the alkyl chain, which fall in the range from 114.8(6) to 117.1(6)°.

The catalytic activity of [Pd(dppp)(bipy)][$B(C_6F_5)_4]_2$ was patented and the results are now reported in Table III.[16] Thus far, the highest catalytic activity was reported for the hexafluorophosphate derivative, its replacement with the tetra(perfluorophenyl)borate one resulting in a further increase of productivity. The effect of the anion is particularly evident at a low catalyst concentration (Table III). Regardless of the presence of the oxidant, the activity of the system with the $B(C_6F_5)_4^-$ anion is double that of the PF_6^- and a productivity of 55 kg CP/g Pd can be achieved. Compound **2** is also a very good catalyst precursor for the CO/ethylene/propylene terpolymerisation reaction, reaching a productivity of 24 kg TP/g Pd.[16]

A tentative rationalisation of the dependence of the catalytic activity on the nature of the anion can be based on the analysis of the metal-anion distances in solid state. In the [Pd(dppp)(bipy][$PF_6]_2$ derivative, the shortest Pd---F distance is 3.44 Å, while in the $B(C_6F_5)_4^-$ derivative it is 4.16 Å, thus indicating a weak Pd---F interaction in the former compound. An analogous trend was found in the [Pd(phen)$_2$][X]$_2$ complexes, where the corresponding distances are 4.07 Å for the PF_6^- derivative and 3.52 Å for the BF_4^- one.[12b,23] Therefore, these results suggest that the higher is the metal-anion distance in solid state, the higher is the catalytic activity of the compound. However,

TABLE III

CO/ethylene copolymerisation reaction: effect of the anion catalyst precursor $[Pd(dppp)(bipy)][X]_2$

X	BQ	kg CP/g Pd	η	Amount of Pd
	mmol		dl g^{-1}	ppm[a]
PF_6^-	4	25	1.02	17
PF_6^-	0	20	1.00	18
$B(C_6F_5)_4^-$	4	55	1.10	15
$B(C_6F_5)_4^-$	0	41	1.05	16

Reaction conditions: n_{Pd} = 0.05 mmol; solvent methanol V = 1.2 L; P_{tot} = 56 atm; T = 80 °C; time = 5 h.

[a] Palladium contained in the product.

a similar inspection of the $[Pd(bipy)_2][X]_2$ complexes revealed an opposite trend: the derivative with the highest activity ($X = PF_6^-$) has the shortest distance (Pd---F 3.02 Å with respect to 3.39 Å when $X = BF_4^-$). These data indicate that correlation between the catalytic properties and the interionic interactions in solid state appears unsatisfactory, since crystal packing plays a crucial role in the solid state through van der Waals and coulombic interactions.

With the aim to determine the relative cation-anion position in solution, we investigated the interionic structure, by means of $^{19}F\{^1H\}$ HOESY and ^1H NOESY NMR experiments, of a series of Pd^{II} complexes of $[Pd(C_8H_{12}OCH_3)(bipy)][X]$ type. [10] The counterion, regardless of its nature, was located above and below the bipy plane shifted toward the ring *trans* to the σ-bond of the η^1,η^2-cyclooctenyl derivative. In this type of complexes, the productivity of the CO/styrene copolymer increased as the interionic interactions, in solution, decreased and the $B(3,5-(CF_3)_2C_6H_3)_4^-$ anion, for which a very low concentration of intimate ion pair was detected, showed to be the most efficient. In the future, this analysis will be applied also to $B(C_6F_5)_4^-$.

Pd^0 *Intermediate*

It is well known that the productivity of the Pd-catalysed CO/olefin copolymerisation reaction can be enhanced upon addition to the reaction mixture of an organic oxidant, from the family of quinones. The presence of the oxidant is of high importance for the catalytic systems based on N-donor ligands.[2] It has a strong influence on both the productivity of the system and the molecular weight of the produced polyketones.

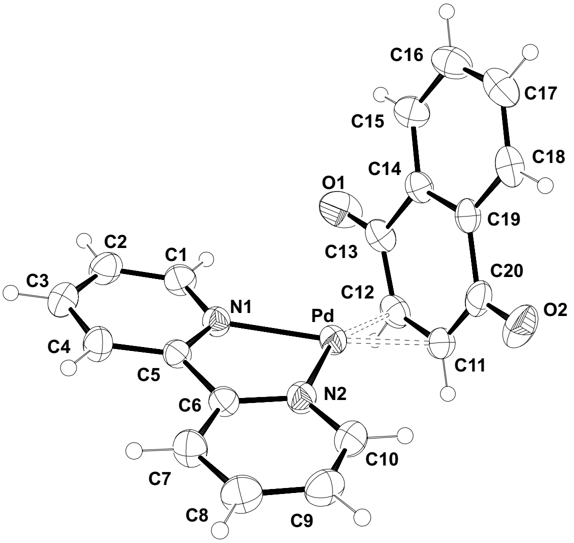


Figure 3. ORTEP view and atom numbering scheme (40% thermal ellipsoids) of compound **3**.

Among the different quinones tested, the most interesting results were obtained with 1,4-benzoquinone (BQ) and naphthoquinone (NQ).[27]

In the reaction pathway of the CO/olefin copolymerisation, one of the termination steps involves a palladium-hydride species [Pd(L-L)(H)(solv)]$^+$, which can dissociate the hydrogen as a proton, leading to a Pd^0 intermediate. The latter can be reoxidized to palladium(II) by an oxidant, such as benzoquinone or naphthoquinone. The intermediate with the quinone bound to palladium(0) has always been postulated,[2] but neither detected nor trapped. We studied the chemical behaviour in solution of compounds [Pd(N-N)(BQ)] by treating them with the corresponding protonated salt [(N-N)H][PF$_6$]. The result was a rapid oxidation of Pd^0 to Pd^{II} with the concomitant reduction of benzoquinone to hydroquinone.[12b] Moreover, the resulting Pd^{II} species corresponds exactly to the catalyst precursors and can immediately re-enter the catalytic cycle.

During our investigations we studied the crystal structure of [Pd(bipy)(BQ)]. The monofunctional nature of benzoquinone was determined, in contrast to that previously proposed, where both the olefinic π bonds were supposedly employed in the coordination.[28] 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 the free benzoquinone, in agreement with the coordination through the olefinic π bond rather than through the oxygen atoms.

The molecular structure of [Pd(bipy)(NQ)], presently reported (Figure 3), shows the naphthoquinone coordinated to the Pd through the olefinic π bond whose distance of 1.421(4) Å indicates a largely single bond character. The chelating bipy is coordinated to the metal centre with a mean value of 2.116(3) Å for the Pd-N distances, while the Pd-C bond distances are 2.070(4), 2.088(3) Å. The dihedral angle formed by the best fit planes through the quinone moiety and the coordination plane is 87.2(1)°. None of these structural features differ from those detected in the previously reported BQ derivative,[12b] and the monofunctional nature of naphthoquinone, in comparison with benzoquinone, has no evident effect on the productivity of the system.

CONCLUSIONS

The design of an efficient catalyst requires a good understanding of the role of each of the components, while the metal-ligand interactions and their electronic properties mainly determine the catalytic capability of the system. On the other hand, other components of the catalytic system, such as the solvent, the co-catalyst and the co-reagents, also play an active and evident role.

As regards the dpk ligand, even though complex $[Pd(dpk \cdot CH_3OH)(CF_3CO_2)_2]$ in methanol is completely inactive due to its fast decomposition to metal, it should be tested in aprotic solvents such as dichloromethane, in analogy to the palladium-bis-oxazoline derivatives,[21b] and further investigations will be done.

For the mixed-ligand complexes $[Pd(dppp)(N\text{-}N)][X]_2$, the $B(C_6F_5)_4^-$ anion, which represents the best choice so far, will be extended also to the $[Pd(N\text{-}N)_2][X]_2$ compounds with the purpose to evaluate its influence on both the productivity and molecular weight of the CO/styrene copolymerisation and CO/ethylene/styrene terpolymerisation reaction. In the latter reaction, the effect of the naphthoquinone will be also studied in more detail.

Acknowledgments. – This work was supported by Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST 60%; Rome) and PRIN (Grant No. 9903153427).

REFERENCES

1. (a) E. Drent, *Eur. Patent Appl.* **121** (1984) 965. (b) E. Drent, J. A. M. van Broekhoven, and M. J. Doyle, *J. Organomet. Chem.* **417** (1991) 235–251.
2. E. Drent and P. H. M. Budzelaar, *Chem. Rev.* **96** (1996) 663–681.
3. (a) W. P. Mul, H. Oosterbeek, G. A. Beitel, G.-J. Kramer, and E. Drent, *Angew. Chem., Int. Ed. Engl.* **39** (2000) 1848–1851. (b) B. Sesto and G. Consiglio, *Chem.*

Commun. (2000) 1011–1012. (c) C. Gambs, S. Chaloupka, G. Consiglio, and A. Togni, *Angew. Chem., Int. Ed. Engl.* **39** (2000) 2486–2488. (d) J. G. Knight, S. Doherty, A. Harryman, E. G. Robins, M. Betham, G. R. Eastham, R. P. Tooze, M. R. J. Elsegood, P. Champkin, and W. Clegg, *Organometallics* **19** (2000) 4957–4967. (e) J.-C. Yuan and S.-J. Lu, *J. Polym. Science: Part A: Polym. Chem.* **38** (2000) 2919–2924. (f) S. Kacker, J. A. Sissano, and D. N. Schulz, *J. Polym. Science: Part A: Polym. Chem.* **38** (2000) 752–757. (g) G. P. Suranna, P. Mastrorilli, C. F. Nobile, and W. Keim, *Inorg. Chim. Acta* **305** (2000) 151–156. (h) K. Nozaki, N. Kosaka, S. Muguruma, and T. Hiyama, *Macromolecules* **33** (2000) 5340–5346.

4. (a) N. Alperwicz, *Chem. Week* (1995) January 25th, 22. (b) D. Medema and A. Noordam, *Chem. Magazine* (1995) 127–130.
5. M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci, and U. W. Suter, *Angew. Chem., Int. Ed. Engl*. **30** (1991) 989–991.
6. K. Nozaki, N. Sato, and H. Takaya, *J. Am. Chem. Soc*. **117** (1995) 9911–9912.
7. (a) M. Sperrle, A. Aeby, G. Consiglio, and A. Pfaltz, *Helv. Chim. Acta* **79** (1996) 1387–1392. (b) A. Aeby, A. Gsponer, and G. Consiglio *J. Am. Chem. Soc*. **120** (1998) 11000–11001.
8. A. Sommazzi, F. Garbassi, G. Mestroni, and B. Milani, It. Patent, N. MI91/A 002929 (1991).
9. (a) B. Milani, E. Alessio, G. Mestroni, A. Sommazzi, F. Garbassi, E. Zangrando, N. Bresciani-Pahor, and L. Randaccio, *J. Chem. Soc., Dalton Trans*. (1994) 1903–1911. (b) B. Milani, E. Alessio, G. Mestroni, E. Zangrando, L. Randaccio, and G. Consiglio, *J. Chem. Soc., Dalton Trans*. (1996) 1021–1029.
10. (a) A. Macchioni, G. Bellachioma, G. Cardaci, M. Travaglia C. Zuccaccia, B. Milani, G. Corso, E. Zangrando, G. Mestroni, C. Carfagna, and M. Formica, *Organometallics* **18** (1999) 3061–3069. (b) B. Milani, F. Paronetto, and E. Zangrando, *J. Chem. Soc., Dalton Trans*. (2000) 3055–3057.
11. B. Milani, L. Vicentini, A. Sommazzi, F. Garbassi, E. Chiarparin, E. Zangrando, and G. Mestroni, *J. Chem. Soc., Dalton Trans*. (1996) 3139–3144.
12. (a) B. Milani, G. Corso, G. Mestroni, C. Carfagna, M. Formica, and R. Seraglia, *Organometallics* **19** (2000) 3435–3441. (b) B. Milani, A. Anzilutti, L. Vicentini, A. Sessanta o Santi, E. Zangrando, S. Geremia, and G. Mestroni, *Organometallics* **16** (1997) 5064–5075.
13. C. Bianchini, H. M. Lee, P. Barbaro, A. Meli, S. Moneti, and F. Vizza, *New J. Chem*. **23** (1999) 929–938.
14. R. A. Koster and R. H. Birk, *Polym. Prepr.* (Am. Chem. Soc., Div. Polym. Chem.) **37** (1996) 525–526.
15. H.-B. Bürgi and V. Shklover, in: H.-B. Bürgi and J. D. Dunitz (Eds.), *Structure Correlation*, Vol. 1, VCH, Weinheim, 1994, p 303.
16. A. Sommazzi, F. Garbassi, G. Mestroni, and B. Milani, Eur. Patent Appl. N. 97104955.6–2102 (1997); *Chem. Abs.* P346797q (1997).
17. G. M. Sheldrick, SHELXS-86, Program for structure solution, *Acta Crystallogr., Sect. A* **46** (1990) 467–473.
18. G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement, University of Göttingen, Germany, 1997.
19. L. J. Farrugia, *J. Appl. Cryst.* **32** (1999) 837–838.
20. A. Aeby and G. Consiglio, *Inorg. Chim. Acta* **296** (1999) 45–51.
21. (a) M. Brookhart, F. C. Rix, J. M. De Simone, and J. C. Barborak, *J. Am. Chem. Soc.* **114** (1992) 5894–5895. (b) M. Brookhart, M. I. Wagner, G. G. A. Balavoine,

and H. A. Haddou, *J. Am. Chem. Soc.* **116** (1994) 3641–3642. (c) M. Brookhart and M. I. Wagner, *J. Am. Chem. Soc.* **118** (1996) 7219–7220.
22. (a) R. R. Osborne and W. R. Mc Whinnie, *J. Chem. Soc*. (1967) 2075–2078. (b) M. C. Feller and R. Robson, *Aust. J. Chem*. **21** (1968) 2919–2927. (c) M. C. Feller and R. Robson, *Aust. J. Chem*. **23** (1970) 1997–2003.
23. S. Geremia, L. Randaccio, G. Mestroni, and B. Milani, *J. Chem. Soc., Dalton Trans*. (1992) 2117–2118.
24. G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. B. Cingi, A. M. M. Lanfredi, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans*. (1981) 2280–2289, and refs. therein.
25. S. O. Sommerer, A. J. Jircitano, B. L. Westcott, K. A. Abboud, and J. A. K. Bauer, *Acta Crystallogr., Sect. C* **53** (1997) 707–710.
26. P. W. N. M. van Leeuwen, P. C. Y. Kamer, J. N. H. Reek, and P. Dierkes, *Chem. Rev.* **100** (2000) 2741–2769.
27. (a) E. Drent, Eur. Patent Appl. N. 229,408 (1987). (b) J. A. M. Broekhoven and E. Drent, Eur. Patent Appl. N. 235,865 (1987). (c) A. W. de Jong and J. J. Keijsper, Eur. Patent Appl. N. 486,103 (1992).
28. T. Ukai, H. Kuwazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organomet. Chem.* **65** (1974) 253–266.

SAŽETAK

Strukturne značajke prekursora katalizatora na bazi paladija u co- i ter-polimerizacijskim reakcijama CO s otapalima

Barbara Milani, Giovanni Mestroni i Ennio Zangrando

Opisana je sinteza, svojstva i kristalna struktura triju kompleksa paladija, koji se primjenjuju kao homogeni katalizatori u co- i ter-polimerizacijskim reakcijama CO s otapalima. Razmotrena su svojstva neutralnog kompleksa [Pd(dpk·CH_3OH)(CF_3CO_2)$_2$] (**1**), (dpk = di(2-piridil) keton) i dikationskog kompleksa s dva različita liganda [Pd(dpp)(bipy)][B(C_6F_5)$_4$]$_2$ (**2**), (bipy = 2,2'-bipiridin, dpp = 1,3-bis(difenilfosfin)propan). Utvrđeno je da katalitička aktivnost kompleksa **2** bitno ovisi o prirodi aniona. Najefikasnijom u toj skupini katalizatora pokazala se tetra(perfluorfenil)boratna sol. Potanko je razmotrena ovisnost katalitičkih svojstava pripravljenih kompleksa o strukturi. Također opisana je kristalna struktura [Pd]bipy(naftokinona)] (**3**) za koji se pretpostavlja da je međuprodukt u katalitičkom ciklusu.