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Bis(chelated) palladium(II) complexes with a diphosphine and a dinitrogen ligand: very efficient catalyst precursors in the co- and ter-polymerisation of CO and olefins†

Barbara Milani,*[a] **Lidia Vicentini,**[a] **Anna Sommazzi,**[b] **Fabio Garbassi,**[b] **Elisabetta Chiarparin,**[a] **Ennio Zangrando**[a] **and Giovanni Mestroni**[a]

[a] *Dipartimento di Scienze Chimiche, Università di Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy*
[b] *Istituto Guido Donegani – ENICHEM, Via G. Fauser 4, 28100 Novara, Italy*

A new series of palladium(II) complexes of general formula [Pd(dppp)(L–L)][PF$_6$]$_2$ has been synthesised and characterised [dppp = Ph$_2$P(CH$_2$)$_3$PPh$_2$, L–L = 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine, phenanthroline or 3,4,7,8-tetramethyl-1,10-phenanthroline]. The crystal structure of [Pd(dppp)(bipy)][PF$_6$]$_2$ has been determined. The chemical behaviour of the complexes in solution has been studied by NMR spectroscopy. Depending on the nature of the solvent, the chemical environment of palladium in solution can be either the same as in the solid state or different. Whereas in CD$_2$Cl$_2$ the co-ordination sphere remains intact, partial dissociation of the nitrogen ligand occurs in co-ordinating solvents. The complexes were found to be very active catalyst precursors in the CO–olefin co- and ter-polymerisation reactions. Detailed investigation of their catalytic activity allowed the catalyst precursor to be considered as the result of the assembly of different parts, each with a well defined role. In particular, the dissociated N-donor modulates the proton concentration, thus affecting the length of the polymeric chain.

Carbon monoxide–olefins co- and ter-polymerisation reactions, yielding perfectly alternating polyketones, are of great interest, as demonstrated by the number of patents[1,2] and papers[3,4] published in recent years. The commercial availability of the CO–ethylene–propylene terpolymer with the name of Carilon® has been announced by Shell.[5]

The catalytic systems are based on palladium(II) salts with phosphorus- or nitrogen-donor chelating ligands, either as *in situ* systems[6] or as preformed complexes,[7] with a Brønsted acid as cocatalyst and, frequently, an oxidant such as 1,4-benzoquinone. When aliphatic olefins, in particular ethylene, are involved, catalytic systems based on diphosphines give higher yields of polyketones than those with dinitrogen ligands.[2a,6] For some years we have been involved in the investigation of palladium(II) complexes with nitrogen-donor chelating ligands as potential catalyst precursors in the CO–olefins copolymerisation.[2,8] We mainly focused on two different kinds of complexes: neutral monochelated compounds of general formula [Pd(L–L)(RCO$_2$)$_2$] [L–L = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) and their substituted derivatives; R = Me or CF$_3$] and dicationic bis(chelate) complexes of formula [Pd(L–L)(L′–L′)][X]$_2$ with L–L either equal or different to L′–L′, X = PF$_6^-$, CF$_3$CO$_2^-$ or MeCO$_2^-$. The monochelated compounds are very active in CO–styrene copolymerisation under mild conditions.[8] The bis(chelated) ones also catalyse CO–ethylene copolymerisation under more drastic conditions.[2a] In both cases no acid cocatalyst is required. Preliminary results on the carbon monoxide–ethylene copolymerisation catalysed by [Pd(L–L)(L′–L′)][PF$_6$]$_2$ complexes allowed us to recognise some important features of the catalytic system:[9] (*i*) the anion should be non-esterifiable and non-co-ordinating; (*ii*) the active species is very likely a monochelated one, therefore an equilibrium involving the dissociation of at least one of the two chelating ligands has to occur in solution; (*iii*) the other nitrogen chelating ligand is important to increase the stability of the catalyst toward decomposition to palladium metal.

Based on these considerations and the strong *trans* effect of the phosphine ligands and the lability of the Pd–N bond,[10] we synthesized a new class of palladium(II) complexes of general formula [Pd(dppp)(L–L)][PF$_6$]$_2$ [dppp = 1,3-bis(diphenylphosphino)propane; L–L = bipy **1**, 4,4′-dimethyl-2,2′-bipyridine (dmbipy) **2**, phen **3** or 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) **4**], with a diphosphine and a dinitrogen chelating ligand co-ordinated to the same palladium atom. In this paper we report the synthesis and characterisation of the new complexes together with their catalytic activity in CO–ethylene and CO–ethylene–propylene polymerisation reactions.

Experimental

Materials

The complex [Pd(MeCO$_2$)$_2$], dppp and the nitrogen donors were obtained from Aldrich and used as received. Analytical grade solvents (Baker) were used without further purification for synthetic and spectroscopic purposes. Methanol for catalytic reactions was supplied by Merck. Carbon monoxide, ethylene, propylene (purity >99%) were supplied by SIAD.

Physical measurements

The IR spectra were recorded on a Perkin-Elmer 983G spectrometer as Nujol mulls, proton NMR spectra of the complexes at 400 MHz on a JEOL EX 400 spectrometer operating in Fourier-transform mode, with tetramethylsilane (SiMe$_4$) as internal standard. Two-dimensional homonuclear correlated spectra were obtained with the automatic program of the instrument. The ^{31}P NMR spectra were recorded at 161.86 MHz on the JEOL EX 400 spectrometer with H$_3$PO$_4$ as external reference, ^{13}C NMR spectra of the polyketones on a Bruker 300 MHz spectrometer in 1,1,1,3,3,3-hexafluoropropan-2-ol with a small amount of CDCl$_3$ for locking purposes and SiMe$_4$ as internal standard. The limiting

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† *Non-SI unit employed:* atm = 101 325 Pa.

viscosity number (η) was measured in *m*-cresol at 100 °C in a standard capillary viscosity-measuring device.

Palladium present in the polyketone was determined by atomic absorption spectroscopy. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer 7 thermoanalysis system.

Synthesis of complexes

The complexes $[Pd(dppp)(CF_3CO_2)_2]$ and $[Pd(dppp)(MeCO_2)_2]$ were synthesised according to the procedure reported for the corresponding nitrogen complexes.[8a] Elemental analyses (C, H, N), performed by Dr. Cebulec (Dipartimento di Scienze Chimiche, Trieste, Italy), were in perfect agreement with the proposed stoichiometry (Table 1).

$[Pd(dppp)(L\text{–}L)][PF_6]_2$ 1–4. The complex $[Pd(dppp)(CF_3CO_2)_2]$ (1.5 mmol) was suspended in methanol (35 cm^3). The nitrogen donor was added to the white suspension (1.7 mmol, Pd : L–L = 1 : 1.2) and a yellow solution was obtained in a few minutes. The product precipitated immediately as a white microcrystalline solid upon addition of a solution of NH_4PF_6 in methanol (3 mmol, Pd : NH_4PF_6 = 1 : 3). After 30 min the solid was filtered off, washed with diethyl ether and vacuum dried. Average yield: 80%.

$[Pd(dppp)(bipy)][BF_4]_2$ 5. The synthetic procedure was the same as that for $[Pd(dppp)(L\text{–}L)][PF_6]_2$ except that an aqueous solution of HBF_4 (60%) (Pd : HBF_4 = 1 : 2.2) was added instead of NH_4PF_6 to the yellow solution. Yield: 90%. $\delta_H(CD_2Cl_2)$: 8.30 (2 H, d, $H^{3,3'}$), 8.08 (2 H, dt, $H^{4,4'}$), 7.90 (8 H, m, *o*-H), 7.62 (14 H, m, $H^{6,6'}$ + *m*- + *p*-H), 7.05 (2 H, dt, $H^{5,5'}$), 2.71 (4 H, m, PCH_2) and 2.28 (2 H, m, CH_2CH_2).

$[Pd(dppp)_2][PF_6]_2$ 6. The procedure was similar to that for $[Pd(dppp)(L\text{–}L)][PF_6]_2$, with the addition of dppp, instead of the nitrogen donor, to the white suspension of $[Pd(dppp)(CF_3CO_2)_2]$. Yield: 80%.

Crystallography

When complex **1** was recrystallised from CH_2Cl_2–Et_2O single crystals suitable for X-ray analysis were obtained.

Crystal data. $C_{37}H_{34}F_{12}N_2P_4Pd\cdot0.4CH_2Cl_2$, M = 964.97 (excluding CH_2Cl_2), light yellow, needle-shaped crystal (0.20 × 0.25 × 0.7 mm), space group *Pbca* (no. 61), a = 16.853(3), b = 16.155(3), c = 32.123(4) Å, U = 8746(2) Å^3, Z = 8, D_c = 1.52 g cm^{-3}, μ(Mo-Kα) = 7.0 cm^{-1}, $F(000)$ = 3872.

Unit-cell dimensions were determined from Weissenberg photographs, later refined by least-squares treatment of 25 reflections in the range θ 14–17°. A total of 10 513 reflections were collected [Enraf-Nonius CAD4 diffractometer, graphite monochromator, Mo-Kα radiation (λ = 0.7107 Å), room temperature, $2\theta_{max}$ = 56°], later corrected for Lorentz-polarisation effects and absorption (empirical ψ-scan method). Total decay of 10.6% over data collection, linear correction applied.

The structure was solved by conventional Patterson and Fourier techniques and refined on F by full-matrix anisotropic least squares using 3710 reflections with $I \geqslant 3\sigma(I)$. The analysis of the ΔF map revealed a disordered CH_2Cl_2 (0.40 occupancy, on the basis of the respective electron-density peaks). The molecule was isotropically refined. After anisotropic refinements, the calculated positions of hydrogen atoms all occurred in positive electron-density regions. The final cycles with fixed H-atom contributions ($B = 1.3B_{eq}$ of their bonded atom), except those of the solvent molecule, converged to final R = 0.068, R' = 0.078 with unit weighting scheme. Goodness of fit 6.8, maximum positive and negative peaks in ΔF map 1.88 (close to CH_2Cl_2) and 0.49 e Å^{-3}, respectively.

Table 1 Analytical* data for complexes **1–6**

Complex	Analysis (%) C	H	N
1 $[Pd(dppp)(bipy)][PF_6]_2$	45.6 (46.05)	3.40 (3.55)	2.95 (2.90)
2 $[Pd(dppp)(dmbipy)][PF_6]_2$	46.4 (47.15)	3.75 (3.85)	3.00 (2.80)
3 $[Pd(dppp)(phen)][PF_6]_2$	47.1 (47.35)	3.35 (3.45)	2.90 (2.85)
4 $[Pd(dppp)(tmphen)][PF_6]_2$	49.1 (49.4)	3.70 (4.00)	3.10 (2.70)
5 $[Pd(dppp)(bipy)][BF_4]_2$	51.1 (52.3)	4.15 (4.05)	3.10 (3.30)
6 $[Pd(dppp)_2][PF_6]_2$	52.8 (53.1)	4.00 (4.30)	

* Required values are given in parentheses.

The quality of crystals together with their sensitivity to X-ray radiation, and the presence of the disordered CH_2Cl_2 molecule, did not allow a lower disagreement factor. Atomic scattering factors and anomalous dispersion parameters were taken from ref. 11. All calculations were carried out using the Enraf-Nonius SDP package[12] on a Micro VAX2000 computer.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/118.

Co- and ter-polymerisation reactions

The co- and ter-polymerisation reactions were carried out in a stainless-steel autoclave (2 dm^3) by introducing, in order, the catalyst, the required amount of methanol and, when needed, the oxidant. The reactor was then pressurised with the mixture of monomers to the required pressure. The vessel was heated to the desired temperature and the polymerisation carried out isothermally mantaining constant the pressure level by a continuous feed of monomer. After 5 h the autoclave was cooled to room temperature, the residual pressure discharged and the polymer formed filtered off, washed with methanol and vacuum dried.

CO–Styrene copolymerisation reaction

This reaction was carried out in a stainless-steel autoclave (150 cm^3), equipped with a Teflon liner, magnetic stirrer, heating mantle and temperature controller. The complex $[Pd(dppp)(bipy)][PF_6]_2$ (0.05 mmol), 1,4-benzoquinone (2 mmol), styrene (25 cm^3) and methanol (25 cm^3) were placed in the autoclave. The autoclave was pressurised to 35 atm with CO and heated to 70 °C for 5 h. After cooling and releasing the gas, methanol (200 cm^3) was added. No copolymer was formed.

Results and Discussion

Synthesis of complexes

The synthesis of the bis(chelated) mixed complexes **1–4** $[Pd(dppp)(L\text{–}L)][PF_6]_2$ is reported here for the first time. A slight excess of the dinitrogen donor is first added to a suspension of $[Pd(dppp)(CF_3CO_2)_2]$ in methanol, forming a yellow solution of $[Pd(dppp)(L\text{–}L)][CF_3CO_2]_2$. The product finally precipitates as a white solid upon addition of a slight excess of NH_4PF_6 [equations (1) and (2)]. The complex

$$[Pd(dppp)(CF_3CO_2)_2] + L\text{–}L \xrightarrow{MeOH} [Pd(dppp)(L\text{–}L)][CF_3CO_2]_2 \quad (1)$$

$$[Pd(dppp)(L\text{–}L)][CF_3CO_2]_2 + 2\,NH_4PF_6 \longrightarrow [Pd(dppp)(L\text{–}L)][PF_6]_2 + 2\,NH_4^+ + 2\,CF_3CO_2^- \quad (2)$$

$[\mathrm{Pd(dppp)(bipy)}][\mathrm{BF_4}]_2$ can be synthesised by the same procedure, adding aqueous $\mathrm{HBF_4}$ instead of $\mathrm{NH_4PF_6}$. On the contrary, addition of dppp to a suspension of $[\mathrm{Pd(L{-}L)(CF_3CO_2)_2}]$ in methanol led to a red solution which yielded a not well characterised solid upon addition of $\mathrm{NH_4PF_6}$. It was probably a mixture of the bis(chelated) $[\mathrm{Pd(dppp)_2}][\mathrm{PF_6}]_2$ and the mixed complex.

Characterisation in the solid state

The infrared spectra of complexes **1**–**4** present, besides the bands of the diphosphorus and the dinitrogen ligand,[13] those, strong and broad, of the hexafluorophosphate anion (ν_{str} 835, ν_{bend} 559 $\mathrm{cm^{-1}}$).[14]

An ORTEP drawing of the cation of complex **1** is depicted in Fig. 1 and relevant geometrical parameters are reported in Table 2. The Pd atom has a square-planar co-ordination through the bipyridine and diphosphine ligands, the metal being slightly displaced by 0.04 Å from the $\mathrm{P_2N_2}$ mean plane, the atoms of which are coplanar within ±0.21 Å. The Pd–P distances have the same value [2.261(3) and 2.262(3) Å], slightly longer than those found in $[\mathrm{PdCl_2(dppp)}]$ [2.247(2) Å][15] and in $[\mathrm{Pd(NCS)_2(dppp)}]$ [2.241(1) Å].[16] The Pd–N distances [2.117(9) and 2.128(9) Å], effected by the *trans* influence of the dppp, are significantly longer, although less accurate, than those reported for bis(chelated) bipy derivatives [mean 2.036(2) Å][17] and in monochelated $[\mathrm{Pd(phen)(MeCO_2)_2}]$ [mean 2.010(3) Å].[8a] The angle between the two pyridine rings is 7.7°.

Since the co-ordination to the Pd atom requires a considerable eclipsing of bonds, steric strain is evidenced in the diphosphine ligand on considering the large deviation from ideality of the bond angles in the alkyl chain (Table 2) and the displacements of the two P donors from the $\mathrm{PdN_2}$ plane, −0.33 and +0.50 Å for P(1) and P(2), respectively. Similar geometrical features were also observed in $[\mathrm{PdCl_2(dppp)}]$.[15]

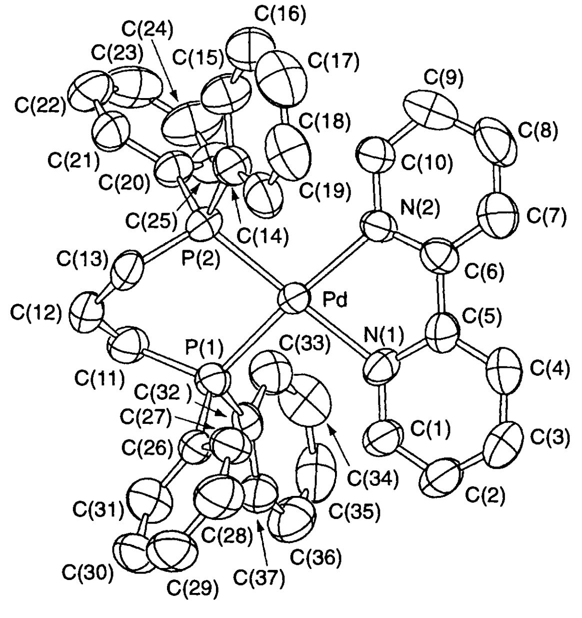


Fig. 1 An ORTEP drawing and the atom numbering scheme of the cation of complex **1** with 50% probability thermal ellipsoids

Table 2 Selected bond distances (Å) and angles (°) of complex **1**

Pd–P(1)	2.262(3)	Pd–N(1)	2.117(9)
Pd–P(2)	2.261(3)	Pd–N(2)	2.128(9)
P(1)–Pd–P(2)	87.4(1)	N(1)–Pd–N(2)	77.5(4)
P(1)–Pd–N(1)	97.8(3)	P(1)–C(11)–C(12)	113.5(9)
P(1)–Pd–N(2)	170.3(3)	C(11)–C(12)–C(13)	118(1)
P(2)–Pd–N(1)	166.8(3)	C(12)–C(13)–P(2)	114.8(9)
P(2)–Pd–N(2)	99.1(3)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Characterisation in solution

The chemical behaviour of complexes **1**–**4** in solution was investigated by ^{1}H NMR spectroscopy (Table 3). Proton NMR spectra recorded in $\mathrm{CD_2Cl_2}$ at room temperature show some common features: all resonances are sharp and shifted with respect to those of the free ligands; no signal due to the latter is present. The protons of co-ordinated 1,3-bis(diphenylphosphino)propane give a similar pattern for all complexes: two multiplets at high field for the propylenic bridge (δ 2.71–2.25), integrating for four and two protons respectively, and two multiplets at low field for the aromatic rings, integrating for eight and twelve protons respectively.

The ^{31}P NMR spectra of all complexes present a resonance at a lower field compared to that of free dppp (Table 3). The number of resonances in the ^{1}H and ^{31}P NMR spectra suggests that each complex maintains the same symmetry as in the solid state. The ^{1}H NMR signals of the nitrogen ligands were assigned mainly on the basis of correlation spectroscopy (COSY) and, when required, nuclear Overhauser effect (NOE) experiments. Some of these signals can be overlapped by the signals of the aromatic protons of dppp.

Even though the very low solubility of complexes **1**–**4** in methanol prevented NMR investigation in this solvent used in the catalytic reactions, in other polar, co-ordinating solvents such as $\mathrm{Me_2SO}$ a different behaviour was observed compared to that in $\mathrm{CD_2Cl_2}$. In the spectra of $[\mathrm{Pd(dppp)(L{-}L)}][\mathrm{PF_6}]_2$ (L–L = bipy or dmbipy) in $\mathrm{(CD_3)_2SO}$ at room temperature the signals of the free nitrogen ligand are present, besides those of the co-ordinated one. On the contrary, in the spectrum of complexes **3** and **4** the signals of the phenanthroline ligands are broad and no signal due to free phen can be observed. A further broadening of these peaks was induced both by raising the temperature and by addition of free N-donor. These results indicate the presence of a dissociation of the nitrogen ligand from the bis(chelated) mixed-ligand complex yielding a monochelated species **7** [equation (3), solv = $\mathrm{(CD_3)_2SO}$].

$$[\mathrm{Pd(dppp)(L{-}L)}][\mathrm{PF_6}]_2 \overset{\mathrm{solv}}{\rightleftharpoons} \underset{\mathbf{7}}{[\mathrm{Pd(dppp)(solv)_2}][\mathrm{PF_6}]_2} + \mathrm{L{-}L} \quad (3)$$

Depending on the nature of the chelating ligand, the dissociation rate, at room temperature, can be slow (**1**, **2**) or relatively fast (**3**, **4**) on the NMR time-scale. For $[\mathrm{Pd(dppp)(bipy)}][\mathrm{PF_6}]_2$ and $[\mathrm{Pd(dppp)(dmbipy)}][\mathrm{PF_6}]_2$, 20 and 10% dissociation can be estimated.

In agreement with the ^{1}H NMR spectra, the ^{31}P NMR spectra in $\mathrm{(CD_3)_2SO}$ of both complexes **1** and **2** present two peaks of different intensities. While the major peak depends on the nature of L–L (δ 17.2 for **1** and 18.2 for **2**), the minor resonance has the same chemical shift (δ 17.9) in both spectra, indicating the same dissociated species **7** is formed from both complexes. The ^{31}P NMR spectra of **3** and **4** present only one peak (δ 17.9 and 16.7).

Polymerisation reactions

The mixed-ligand complexes $[\mathrm{Pd(dppp)(L{-}L)}][\mathrm{PF_6}]_2$ were tested as catalyst precursors in the CO–ethylene copolymerisation and CO–ethylene–propylene terpolymerisation [equation (4), R = H or Me]. The influence of the nature of the nitrogen-donor chelating ligand on the catalytic activity is reported in Table 4; a remarkable decrease in the yield of the copolymer with increasing co-ordinating ability of the nitrogen-donor

Table 3 Proton and ^{31}P NMR data for complexes **1**–**4** compared to those of free L–L and dppp in CD_2Cl_2 at room temperature: region of aromatic protons

	L–L protons[a]				dppp protons		
Complex/ligand	$H^{6,6'}$	$H^{5,5'}$	$H^{4,4'}$	$H^{3,3'}$	*o*	*m* + *p*	^{31}P
dppp					7.36 (m)	7.30 (m)	−17.6
bipy	8.65 (dd)	7.31 (dt)	7.82 (dt)	8.42 (dd)			
1	7.68 (m)[b]	7.07 (dt)	8.07 (dt)	8.26 (d)	7.98 (m)	7.68 (m)	17.9
dmbipy	8.48 (d)	7.13 (d)		8.26 (s)			
2	7.53 (m)	6.88 (d)		8.07 (s)	7.95 (m)	7.68 (m)	18.1
	$H^{2,9}$	$H^{3,8}$	$H^{4,7}$	$H^{5,6}$			
phen	9.13 (dd)	7.63 (q)	8.27 (dd)	7.82 (s)			
3	8.02 (m)[b]	7.40 (q)	8.58 (dd)	8.07 (s)	8.02 (m)	7.67 (m)	18.3
tmphen	8.86 (s)			8.06 (s)			
4	8.22 (s)			7.65 (m)[b]	7.93 (m)	7.65 (m)	15.3

[a] s = singlet, d = doublet, q = quartet, t = triplet, m = multiplet. [b] The multiplet is overlapped by the dppp signals.

$$n\,CO + n\,CH_2{=}CHR \xrightarrow{\text{catalyst}} -(COCHRCH_2)_n- \qquad (4)$$

ligand is evidenced (runs 1,2 and 3,4). The highest activity is obtained with 2,2′-bipyridine (Table 4, run 4). The complex $[Pd(dppp)(bipy)][PF_6]_2$ is indeed a very active catalyst precursor in the CO–ethylene copolymerisation without any acid cocatalyst and the yield of copolymer is doubled with respect to that of the *in situ* system (Table 4, runs 4 and 11). The complex remains active in the absence of the oxidant, even though a decrease in the yield of copolymer is observed (Table 4, run 5). Complex **1** is also remarkably more active than the corresponding monochelated derivatives $[Pd(dppp)(RCO_2)_2]$ (R = CF_3 or Me) (Table 4, runs 9 and 10). As observed for CO–styrene copolymerisation,[8a] the monochelated acetato derivative leads to a complete loss of catalytic activity together with catalyst decomposition to palladium metal.

The mixed-ligand complex **1** shows a higher productivity than the corresponding symmetrical bis(chelated) species $[Pd(dppp)_2][PF_6]_2$ (Table 4, run 8). This difference could be related to the different nature of the Pd–P and the Pd–N bonds.[10] Dissociation of one of the two molecules of dppp from the symmetrical bis(chelated) species is expected to be rather difficult, with a consequent reduction of the concentration of the monochelated active species. The higher lability of the nitrogen ligand with respect to the phosphorus one was confirmed by the NMR studies in $(CD_3)_2SO$ solution.

The replacement of PF_6^- with BF_4^- leads to a strong decrease in catalytic activity, regardless of the presence of the quinone (Table 4, runs 4,6 and 5,7). We had observed the same strong influence of the anion on the catalytic activity of the bis(chelated) complexes $[Pd(bipy)_2][X]_2$ (X = PF_6^- or BF_4^-) in CO–ethylene copolymerisation.[2c] This decrease in activity might be related to the incomplete inertness of tetrafluoroborate anion which can partially react with palladium in the reaction mixture.[18]

Complex **1** is also a very good catalyst precursor for the terpolymerisation reactions CO–ethylene–propylene and CO–ethylene–hex-1-ene without any acid cocatalyst and any oxidant (Table 5). Moreover, when **1** was used as catalyst precursor in the CO–styrene copolymerisation no copolymer was obtained. This confirms that the active species should be a monochelated diphosphine complex, which, in agreement with previous results,[7a,19] does not catalyse the CO–styrene copolymerisation.

On the basis of the above results we propose that the active species is formed by dissociation of the nitrogen-donor chelating ligand. The monochelated species can then react either with CO and MeOH yielding the methoxycarbonyl species, or with CO and water yielding the hydrido species [Scheme 1(*a*)]. In both cases the free L–L can react with the protons generated in the above reactions to give the weak acid $[H(L–L)][PF_6]$. This hypothesis reveals one of the main differences between the new complexes and the catalytic systems reported in the literature, where the formation of the active species led to strong acids[6] [Scheme 1(*b*)].

Polyketone characterisation

The co- and ter-polymers were characterised according to literature methods.[20] All those obtained with the new catalyst precursors are white powders of high crystallinity (35–50% as determined by X-ray diffraction) and decomposition of the catalyst precursors to palladium metal is not observed, even if a small amount of palladium is still present in the products (18–40 ppm) as determined by atomic absorption.

Their alternating structure was confirmed by elemental analysis and NMR spectroscopy. The elemental analysis values correspond to a CO:olefin ratio of 1.0:1 [C, 64.2 (64.25); H, 7.20 (7.20); O, 28.6 (28.55)% for the copolymer]. The carbonyl group exhibits a characteristic IR band at about 1695 cm^{-1} (KBr). In the CO–ethylene–propylene terpolymer the propylene units are randomly distributed along the chain. Melting temperatures are high: 250–260 °C for the copolymer and 200–225 °C [C_3 = 10–5% (percentage of propylene present in the polymeric chain)] for the terpolymer. They are insoluble in many of the common organic solvents, but soluble in solvents having high polarity and acidity like *m*-cresol, *o*-chlorophenol and 1,1,1,3,3,3-hexafluoropropan-2-ol.

Thermogravimetric analyses (TGA) (Fig. 2) shows that the CO–ethylene copolymer is stable up to 250 °C with a residue of about 25% by weight at 600 °C. The corresponding DSC curve, (Fig. 3) exhibits a T_m at 252 °C (heating rate 20 °C min^{-1}) with ΔH_f = 142 J g^{-1}. After cooling to ambient temperature at 20 °C min^{-1} a second scan, also at a heating rate of 20 °C min^{-1}, produced a lowered melting transition at 242 °C.

All the co- and ter-polymers analysed present limiting viscosity numbers higher than 1.0 dl g^{-1}, *i.e.* their average molecular weight is relatively high. In the case of the CO–ethylene copolymer a dependence of the molecular weight on the nature of the nitrogen chelating ligand is observed (Table 4). This could be related to the basicity properties of the ligand. According to the proposed mechanism [Scheme 1(*a*)] the nitrogen ligand can act as a modulator of proton concentration and influence the chain-termination step.[6]

Conclusions

The new complexes were found to be very active in CO–olefin co- and ter-polymerisation reactions. The catalytic trends allowed us to consider the catalyst precursor as the result of

Table 4 CO–Ethylene copolymerisation: effect of the catalyst precursor

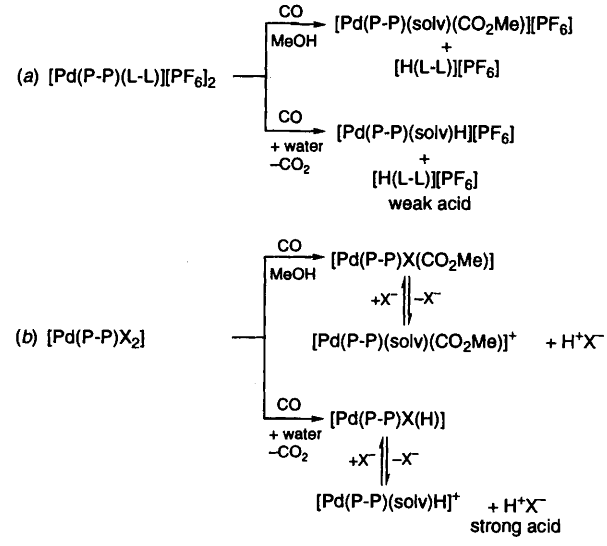
Run	Complex	1,4-Benzoquinone (mmol)	kg Copolymer per g Pd	η/dl g^{-1}	Amounts of Pd (ppm)[a]
1	$[Pd(dppp)(phen)][PF_6]_2$	8	11.2 (w)	2.13	n.d.
2	$[Pd(dppp)(tmphen)][PF_6]_2$	8	3.9 (w)	1.2	n.d.
3	$[Pd(dppp)(dmbipy)][PF_6]_2$	8	18.2 (w)	2.88	n.d.
4	$[Pd(dppp)(bipy)][PF_6]_2$	8	42.3 (w)	1.52	17.7
5	$[Pd(dppp)(bipy)][PF_6]_2$	0	23.0 (w)	1.66	18.0
6	$[Pd(dppp)(bipy)][BF_4]_2$	8	2.6 (w)	n.d.	n.d.
7	$[Pd(dppp)(bipy)][BF_4]_2$	0	1.3 (w)	n.d.	n.d.
8	$[Pd(dppp)_2][PF_6]_2$	8	3.5 (w)	n.d.	221.3
9	$[Pd(dppp)(CF_3CO_2)_2]$	8	17.1 (w)	0.74	40.4
10	$[Pd(dppp)(MeCO_2)_2]$	8	0.075 (b)	n.d.	n.d.
11	$[Pd(MeCO_2)_2]$ + dppp + CF_3CO_2H[b]	8	21.5 (w)	1.03	38.7

Reaction conditions: n_{Pd} = 0.1 mmol; solvent, methanol, V = 1200 cm^3; P_{tot} = 56 atm; T = 80 °C; time = 5 h. Product: w = white, b = black, n.d. = Not determined. [a] Palladium contained in the product. [b] Reactions conditions: n_{Pd} = 0.1 mmol, n_{dppp} = 0.1 mmol, $n_{CF_3CO_2H}$ = 2 mmol; solvent, methanol, V = 1200 cm^3; P_{tot} = 56 atm; T = 80 °C; time = 5 h.

Table 5 CO–Ethylene–aliphatic olefin terpolymerisation. Catalyst precursor: $[Pd(dppp)(bipy)][PF_6]_2$

Second olefin	1,4-Benzoquinone (mmol)	kg Terpolymer per g Pd	η/dl g^{-1}
Hex-1-ene	8	31.8 (w)	2.63
Propylene	8	36.7 (w)	1.66
Propylene	0	14.8 (w)	1.43

Reaction conditions: n_{Pd} = 0.1 mmol; solvent, methanol, V = 1200 cm^3; amount of second olefin, 50 g; P_{tot} = 56 atm; T = 70 °C; time = 5 h.



Scheme 1 solv = solvent

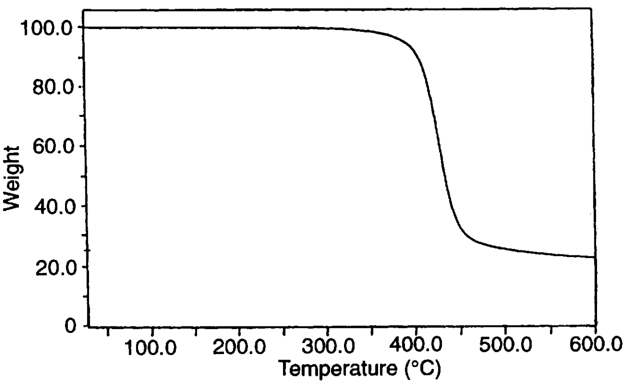


Fig. 2 The TGA curve of the CO–ethylene copolymer obtained with $[Pd(dppp)(bipy)][PF_6]_2$

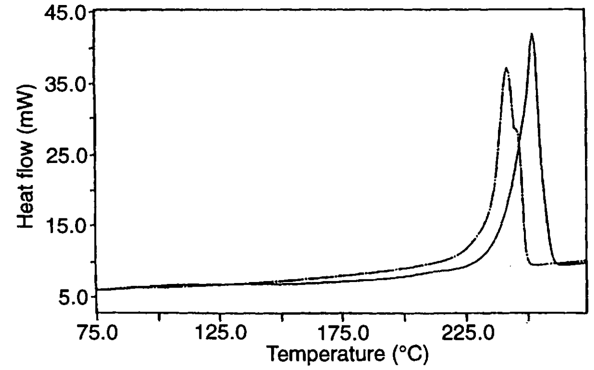
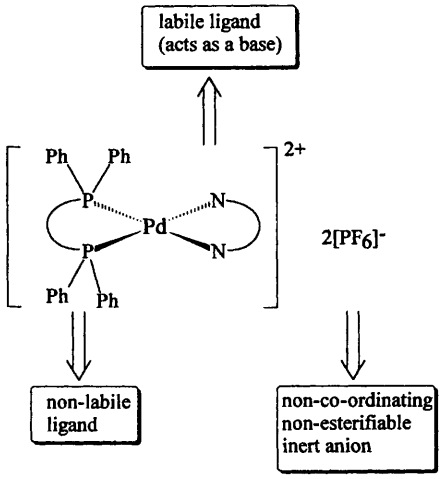


Fig. 3 The DSC curves of the CO–ethylene copolymer obtained with $[Pd(dppp)(bipy)][PF_6]_2$: ——, first scan; — · —, second scan



Scheme 2 Schematic drawing of the different components of the catalyst precursor

the assembly of different parts, each one with a well defined role (Scheme 2): (*i*) the anion has to be unreactive and hexafluorophosphate represents the best choice to date* (see above); (*ii*) the nitrogen ligand is labile and can dissociate to give the monochelated active species; (*iii*) once dissociated it can bind to protons, buffering their concentration and influencing the molecular weight of the polymers; (*iv*) dppp is the ancillary ligand which shows the highest specific catalytic activity in the CO–aliphatic olefin co- and ter-polymerisation reactions.

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* It should be noted that recent results in this field were obtained with BF_4^- derivatives,[4e,21] the activity of which might be enhanced by appropriate change of the anion.

Moreover, optically active co- and ter-polymers might be obtained by using a chiral diphosphine as ancillary ligand.

Acknowledgements

Financial support from Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST 60%; Rome) is gratefully aknowledged.

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Received 6th *February* 1996; *Paper* 6/00871B