Synthesis and Characterization of Monochelated Carboxylatopalladium(II) Complexes with Nitrogen-donor Chelating Ligands. Crystal Structures of Diacetato(1,10-phenanthroline)- and Diacetato(2,9-dimethyl-1,10-phenanthroline)-palladium(II)†

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Two series of monochelated carboxylatopalladium(II) complexes of general formula $[Pd(L-L)(MeCO_2)_2]$ and $[Pd(L-L)(CF_3CO_2)_2]$ [L–L = 1,10-phenanthroline (phen), 2,2′-bipyridine and their substituted derivatives) have been prepared and characterized. The chemical behaviour of the complexes in solution has been studied in different solvents mainly by means of ^1H NMR experiments. These showed that, unlike the acetato complexes, the trifluoroacetato derivatives undergo partial dissociation of the anionic ligand in Me_2SO solution at room temperature. A similar behaviour was also observed for the acetato complexes in CD_3OD. The signals of the $H^{2,9}$ protons in the phenanthroline series, and those of $H^{6,6'}$ in the bipyridine one, are excellent probes for the evaluation of the environment of the palladium atom. The crystal structures of $[Pd(phen)(MeCO_2)_2]$, $[Pd(2,9\text{-dmphen})(MeCO_2)_2]\cdot 0.40CH_2Cl_2$ and $[Pd(2,9\text{-dmphen})(MeCO_2)_2]\cdot 0.25CHCl_3$ (2,9-dmphen = 2,9-dimethyl-1,10-phenanthroline) have been determined. The co-ordination geometry around palladium is square planar in all the structures, but significant deviations from the idealized geometry occur in the last two in order to relieve the interligand contacts. These monochelated carboxylatopalladium(II) complexes are active catalysts in carbon monoxide–olefin copolymerization. Some preliminary results on their catalytic activity are also reported.

Palladium(II) compounds with nitrogen-donor chelating ligands (L–L), such as 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy) and their substituted derivatives, have proved to possess catalytic properties in several homogeneous processes. Examples are the interchange reaction between a vinyl ether and an alcohol,[1] hydration of nitriles to amides,[2] synthesis of alkylaromatic cyclic compounds involving C–C bond formation processes,[3] oxidation of benzene to phenol by molecular oxygen,[4] reductive carbonylation of nitroaromatic compounds[5] and carbon monoxide–olefin copolymerization to yield perfectly alternating polyketones.[6–10]

Since the first paper of Lai and Sen[11] in 1984, the latter reaction has assumed increasing commercial interest, as demonstrated by the great number of papers published in the last 2 years.[6–21] This is due to the low cost of the monomers and, above all, to the unusual properties of the polyketones obtained, which can be used as starting materials for the preparation of other types of functionalized polymers. The catalytic systems used for the CO–olefin copolymerization are typically formed '*in situ*' by palladium(II) salts $[Pd(MeCO_2)_2]$ or $[Pd(CF_3CO_2)_2]$ with a bidentate phosphorus- or nitrogen-donor chelating ligand, a suitable acid as cocatalyst and, frequently, an oxidant such as benzoquinone; methanol is usually the solvent of choice.[6,9] The catalytic system involving the bis(phosphine) ligands was reported to be the most active for the CO–C_2H_4 copolymerization while in the case of CO–styrene and CO–bicyclo[2.2.1]hept-2-ene the highest catalytic activity was obtained with the nitrogen-donor chelating ligands.[8] The most recent reports on the subject concern the development of catalytic systems which do not require cocatalysts. For instance, the complex $[Pd(phen)(p\text{-}MeC_6H_4SO_3)_2]$ was found to be a good catalyst for the chemo-, regio- and stereo-selective carbon monoxide–styrene copolymerization,[8,22] and $[Pd(L-L)(Me)(NCMe)][BR_4]$ (R = aryl) catalyse the CO–4-*tert*-butylstyrene copolymerization in chlorobenzene without any acid cocatalyst and any oxidant, yielding living alternating copolymers.[10] We found that complexes of general formula $[Pd(L-L)_2][PF_6]_2$ have a high catalytic activity in CO–olefin copolymerization, without any acid cocatalyst.[7]

Our interest in these promising catalytic systems caused us to undertake a detailed investigation of the chemistry of palladium complexes with nitrogen-donor chelating ligands. In this paper we address the synthesis and characterization of the monochelated carboxylato derivatives of general formula $[Pd(L-L)(MeCO_2)_2]$ and $[Pd(L-L)(CF_3CO_2)_2]$[L–L = bipy, 4,4′-dimethyl-2,2′-bipyridine (dmbipy), phen, 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen), 4,7-diphenyl-1,10-phenanthroline (dpphen), 4,7-dimethyl-1,10-phenanthroline (4,7-dmphen), or 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen)]. Although $[Pd(phen)(MeCO_2)_2]$ and $[Pd(bipy)(MeCO_2)_2]$ have been known for a long time,[1,23] their characterization was rather unsatisfactory. We found an alternative method for the synthesis of monochelated acetatopalladium(II) derivatives, as well as a method to prepare the corresponding trifluoroacetato compounds. These carboxylato derivatives can be used as precursors in the synthesis of other Pd(L–L) compounds, such as the bis(chelated) ones, and as catalysts in CO–olefin copolymerization. Some preliminary results on the CO–styrene copolymerization are also reported.

The structural study of Pd(L–L) complexes, initiated with the bis(chelated) derivatives $[Pd(bipy)_2][PF_6]_2$, $[Pd(phen)_2]$-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

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

$[PF_6]_2$ and $[Pd(tmphen)_2][PF_6]_2{\cdot}2bipy$,[24] is now extended to the monochelated derivatives $[Pd(phen)(MeCO_2)_2]$ and $[Pd(2,9\text{-}dmphen)(MeCO_2)_2]$.

Experimental

Starting Materials.—The compounds $[Pd(MeCO_2)_2]$ and $[Pd(CF_3CO_2)_2]$ were obtained from Aldrich and used as received. Nitrogen chelating ligands (Aldrich) and analytical grade solvents (Baker) were used without further purification for synthetic and spectroscopic purposes. Methanol (C. Erba) for catalytic reactions was purified by distillation from magnesium and iodine; styrene was freshly distilled over $LiAlH_4$; carbon monoxide (CP grade, 99.9%) was supplied by SIAD.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 983G spectrometer as Nujol mulls between CsI plates covered with polystyrene film.[25] Proton NMR of the carboxylato complexes were recorded at 400 MHz on a JEOL EX 400 spectrometer operating in the Fourier-transform mode, with tetramethylsilane ($SiMe_4$) as internal standard, ^{19}F NMR spectra at room temperature on a 200 MHz Bruker spectrometer, with $CFCl_3$ as internal standard, and ^{13}C NMR spectra of the copolymer on a Bruker 300 MHz spectrometer in $(CF_3)_2CHOH$ with a small amount of $CDCl_3$ for locking purposes and $SiMe_4$ as internal standard. Limiting viscosity numbers were measured in *m*-cresol at 100 °C in a standard capillary device. Conductivity measurements were carried out at 25.0 °C on a Beckman RC-18A conductivity bridge equipped with a fill-type cell and thermostatted with a Julabo F40 thermostat bath.

Synthesis of the Complexes.—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).

$[Pd(L\text{–}L)(MeCO_2)_2]$ **1**–**7**. The complexes $[Pd(phen)(MeCO_2)_2]$ and $[Pd(bipy)(MeCO_2)_2]$ were prepared either according to the literature procedure[1,23] or to the following new method, used also for all the other derivatives. The compound $[Pd(MeCO_2)_2]$ (4.4 mmol, 1 g) was dissolved at room temperature in acetone (90 cm^3). After 30 min the solution was filtered over fine paper and a few drops of glacial acetic acid were added to prevent formation of dimers. The compound L–L (5.28 mmol, Pd : L–L = 1 : 1.2) was added as a solid to the red solution. In a few minutes the product began to precipitate as a yellow solid and after 30 min it was filtered off, washed with cold acetone and vacuum dried. Average yield 70%.

$[Pd(L\text{–}L)(CF_3CO_2)_2]$ **8**–**14**. These complexes were synthesised by $MeCO_2^-$–$CF_3CO_2^-$ ligand exchange. The complex $[Pd(L\text{–}L)(MeCO_2)_2]$ (2.5 mmol) was dissolved at room temperature in methanol (80 cm^3). The yellow solution was filtered over fine paper and an excess of CF_3CO_2H added ($Pd:CF_3CO_2H = 1:27$). The product precipitated immediately as a deep yellow solid and after 30 min it was filtered off, washed with cold methanol and vacuum dried. Average yield 80%.

X-Ray Crystallographic Analyses.—Crystals suitable for X-ray investigation were obtained according to the above procedures, adopting the precaution of dissolving the ligand in the minimum amount of CH_2Cl_2 or $CHCl_3$ before addition.

Details of crystal parameters, data collection, and refinements are summarized in Table 2. Unit-cell dimensions were determined from Weissenberg and precession photographs, later refined by least-squares treatment of 25 reflections in the range θ 12–17° for all compounds. 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). Intensities of three standard reflections, measured during data collections, did not show any systematic variation for complex **1**. The intensity decreased by an average of 6.5 and 8.2% for **5a** and **5b**, respectively, and a linear correction was applied. Reflections having intensities $I \geqslant 3\sigma(I)$ were corrected for Lorentz-polarization factors and used in the subsequent refinement. An absorption correction was applied, based on empirical ψ-scan method, in all cases.

Table 1 Elemental analysis data for complexes **1**–**14** (calculated values in parentheses)

Complex	Analysis (%) C	H	N
1 $[Pd(phen)(MeCO_2)_2]$	47.0 (47.5)	3.40 (3.50)	7.00 (6.90)
2 $[Pd(tmphen)(MeCO_2)_2]$	51.3 (52.1)	4.75 (4.80)	6.00 (6.10)
3 $[Pd(4,7\text{-}dmphen)(MeCO_2)_2]$	48.7 (50.0)	4.45 (4.20)	5.75 (6.45)
4 $[Pd(dpphen)(MeCO_2)_2]$	60.8 (60.4)	3.90 (4.00)	5.10 (5.05)
5 $[Pd(2,9\text{-}dmphen)(MeCO_2)_2]$	46.5 (46.8)	4.15 (4.00)	5.95 (5.90)
6 $[Pd(bipy)(MeCO_2)_2]{\cdot}0.5CHCl_3$	37.9 (39.5)	3.20 (3.30)	6.45 (6.35)
7 $[Pd(dmbipy)(MeCO_2)_2]{\cdot}0.5CHCl_3$	41.7 (42.3)	3.85 (4.00)	6.00 (6.00)
8 $[Pd(phen)(CF_3CO_2)_2]$	37.7 (37.5)	1.40 (1.55)	5.70 (5.45)
9 $[Pd(tmphen)(CF_3CO_2)_2]$	42.0 (42.2)	2.65 (2.85)	4.85 (4.90)
10 $[Pd(4,7\text{-}dmphen)(CF_3CO_2)_2]$	39.6 (40.0)	2.20 (2.25)	5.40 (5.20)
11 $[Pd(dpphen)(CF_3CO_2)_2]$	50.0 (50.6)	2.25 (2.45)	4.15 (4.20)
12 $[Pd(2,9\text{-}dmphen)(CF_3CO_2)_2]$	39.8 (40.0)	2.10 (2.25)	5.15 (5.20)
13 $[Pd(bipy)(CF_3CO_2)_2]$	34.0 (34.4)	1.60 (1.65)	5.70 (5.75)
14 $[Pd(dmbipy)(CF_3CO_2)_2]$	37.0 (37.2)	2.25 (2.35)	5.20 (5.40)

All the structures were solved by conventional Patterson and Fourier methods and refined by full-matrix anisotropic least-squares methods. After anisotropic refinements, the calculated positions of hydrogen atoms all occurred in positive electron-density regions. The final cycles with the fixed hydrogen atom contributions ($B = 1.3B_{eq}$ of their bonded atom) converged to final R and R' values reported in Table 2. The final weighting scheme was $w = 1/\sigma(F_o)^2$ for complex **1** and $= 1/[\sigma(F_o)^2 + (0.02F_o)^2 + 1.0]$ for **5a** and **5b**.

For the isomorphous complexes **5a** and **5b** the analysis of the ΔF map revealed the presence of a molecule of CH_2Cl_2 (in **5a** with an occupancy factor of 0.40) and of a disordered molecule of $CHCl_3$ (in **5b**, occupancy factor = 0.25), with the central C atom lying on a two-fold axis. In **5a** and **5b** a peak was assigned to an oxygen atom of water with an occupancy of 0.30 and 0.50, respectively. The fractional occupancies were assigned on the basis of the respective electron-density peaks in the Fourier maps and were not refined.

Atomic scattering factors and anomalous dispersion parameters were taken from ref. 26. All calculations were carried out using the Enraf-Nonius SDP package[27] on a Micro VAX2000 computer. Final positional parameters of non-hydrogen atoms are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Copolymerization Reactions.—The copolymerizations were carried out in a 2 l stainless-steel autoclave with mechanical stirrer. After introduction of the catalytic solution, comprising the solvent (methanol), catalyst precursor, quinone and styrene, the reactor was pressurized with carbon monoxide and heated to the reaction temperature. During the reaction the pressure level was maintained by a continuous supply of carbon monoxide. After 10 h the autoclave was cooled to room temperature and vented. The copolymer was filtered off, washed several times with methanol and vacuum dried, to give a white, fine powder.

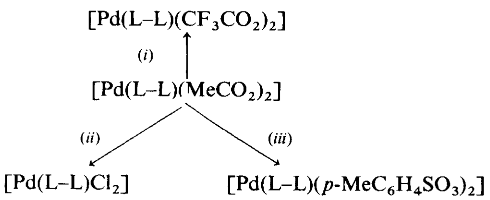
Results and Discussion

Synthesis of the Complexes.—The procedure reported in the literature for the synthesis of [Pd(phen)($MeCO_2$)$_2$] and [Pd(bipy)($MeCO_2$)$_2$] was based on the reaction between [Pd($MeCO_2$)$_2$] and L–L (phen or bipy) in benzene solution.[1,23] According to our new procedure, each complex of the series [Pd(L–L)($MeCO_2$)$_2$] could be more conveniently prepared by dissolution of [Pd($MeCO_2$)$_2$] in acetone followed by addition of the ligand as a solid. The product rapidly precipitated. The synthesis of the corresponding trifluoroacetato derivatives is reported here for the first time. A procedure similar to that used for the acetato compounds could not be used due to the very low solubility of the corresponding bis(chelated) complexes, [Pd(L–L)$_2$][CF_3CO_2]$_2$, which precipitated immediately from the reaction mixture of [Pd(CF_3CO_2)$_2$] and L–L. However, the lower solubility of [Pd(L–L)(CF_3CO_2)$_2$] compared to [Pd(L–L)($MeCO_2$)$_2$] allowed a ligand-exchange reaction to be carried out successfully in methanol. In fact, [Pd(L–L)(CF_3CO_2)$_2$] readily precipitated from a methanolic solution of [Pd(L–L)($MeCO_2$)$_2$] upon addition of an excess of trifluoroacetic acid.

Indeed, the acetate-exchange reaction can be considered as a general procedure for the synthesis of [Pd(L–L)L_2] (L = monoanionic ligand) complexes. Besides the trifluoroacetato derivatives, we also synthesized the chloride and toluene-*p*-sulfonato complexes in good yield (Scheme 1). This new general method is also more economic than those previously adopted, thanks to the low cost of the starting material [Pd($MeCO_2$)$_2$].

Solid-state Studies.—The solid-state infrared spectra of the complexes allowed the carbon–oxygen stretching frequencies to be correlated with the nature of the carboxylate co-ordination.[25] Both in the acetato and in the trifluoroacetato series the asymmetric carbon–oxygen stretching frequency [$\nu_{asym}(CO_2)$] increased compared to that of the free carboxylate ion, while the symmetric stretching frequency [$\nu_{sym}(CO_2)$] correspondingly decreased. Owing to these shifts, the separation between the two carbon–oxygen frequencies ($\Delta\nu$) was considerably larger for the complexes than for the free anion (more than 200 cm^{-1} for the acetato derivatives, and more than 260 cm^{-1} for the trifluoroacetato ones; see Table 4) suggesting a unidentate (end-on) co-ordination of the carboxylate anion. Such a mode would remove the equivalence of the two oxygen atoms and generate a pseudo-ester configuration (see below).

The X-ray analysis of [Pd(phen)($MeCO_2$)$_2$] **1** and of [Pd(2,9-dmphen)($MeCO_2$)$_2$] **5** confirmed the unidentate end-on co-ordination of acetate. Moreover, for the 2,9-dmphen derivative two structures **5a** and **5b** were determined having different solvents of crystallization. Some relevant geometrical parameters for **1**, **5a** and **5b** are given in Table 5. The ORTEP[28] drawings of the molecules of **1** and of **5b** are given in Figs. 1 and 2, respectively.



Scheme 1 (*i*) CF_3CO_2H; (*ii*) HCl; (*iii*) *p*-$MeC_6H_4SO_3H$

The molecule of complex **1** is essentially planar with short Pd–N bond lengths of 2.002(3) and 2.018(3) Å and Pd–O distances of 2.017(3) and 1.999(3) Å. The Pd atom lies essentially in the O_2N_2 co-ordination mean plane, the atoms of which are coplanar within ± 0.015 Å. The (phen)PdO_2 moiety is essentially planar (see below). The $MeCO_2^-$ groups are oriented in such a way that one is above and the other below the co-ordination plane (Fig. 1), nearly perpendicular to it.

The geometries of the molecules of complexes **5a** and **5b** are very similar as reported in Table 5. The Pd–N distances are significantly longer (*ca.* 0.02 Å), than those found in **1** while the Pd–O distances [1.989(5)–2.000(5) Å] do not differ from those found in **1**. The Pd atom is significantly displaced out of the co-ordination plane towards O(4) of one $MeCO_2^-$ ligand, by 0.155(1) Å in **5a** and 0.152(1) Å in **5b** (Fig. 2). The O_2N_2 atoms are coplanar within ±0.05 **5a** and ±0.04 Å **5b**. The (2,9-dmphen)PdO_2 unit, in both **5a** and **5b**, deviates noticeably from planarity as shown by the side view of molecule **5b** in Fig. 3. The two $MeCO_2^-$ groups are oriented in a way similar to that found in **1**. As noted above, the C–O(1) and C–O(3) distances, in both **1** and **5**, are about 0.08 Å longer than C–O(2) and C–O(4) distances, consistent with a pseudo-ester configuration of the acetate ligands.

The overall geometry of bis(chelated) compounds [M(L–L)$_2$]$^{2+}$ has been defined in terms of three interplanar angles:[24] α, β and γ, represented in Fig. 4(*a*) and 4(*b*). The same angles may be used for monochelated derivatives [Pd(L–L)L_2] [Fig. 4(*c*)]. The values of these angles for **1**, **5a**, **5b** and for other similar species, containing phen or variously substituted phen ligands, are reported in Table 6, together with the corresponding Pd–N distances. For bis(chelated) [M(L–L)$_2$]$^{2+}$

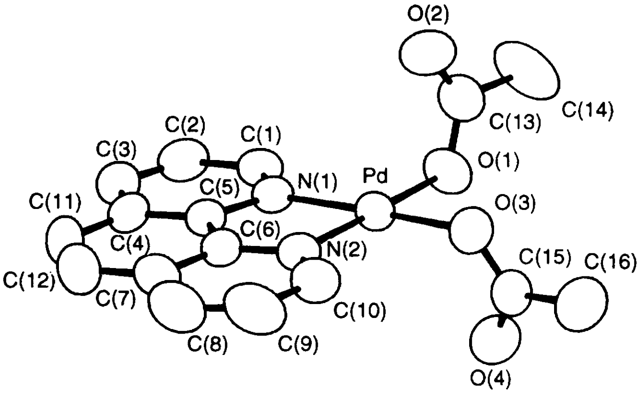


Fig. 1 An ORTEP drawing (50% probability thermal ellipsoids) and labelling scheme for non-hydrogen atoms of complex **1**

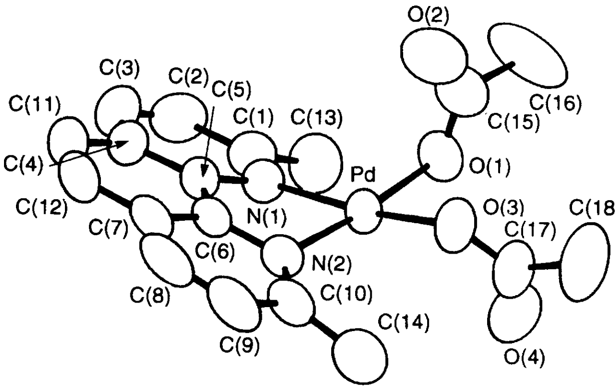


Fig. 2 An ORTEP drawing (50% probability thermal ellipsoids) and labelling scheme for non-hydrogen atoms of complex **5b**. The same scheme applies also to **5a**

species (M = Pd or Pt)[24,29,35] the crowding between the two ligands is relieved in either one of the two ways sketched in Fig. 4(*a*) (twist conformation) and 4(*b*) (bow-step conformation) as described in ref. 24. Data of Table 6 show that for L ligands with small-sized X donor atoms (O or N) and L–L ligands not substituted in 2,9 positions, as in **1**, [Pd(phen)(NCO)$_2$][30] and in [Pd(dpphen)(tcbq)][30] (tcbq = tetrachloro-*o*-benzoquinone) the angles α, β and γ have values close to zero, leading to an approximately planar conformation of the (L–L)PdX$_2$ unit. Correspondingly, short Pd–N distances in the range 2.002–2.016 Å are observed. Upon increasing the size of the X donor atom, as in [Pd(dpphen)Cl$_2$],[31] small deviations of the (L–L)PdX$_2$ unit from planarity occur [Fig. 4(*c*)], with Pd–N distances slightly lengthened, ranging from 2.031 to 2.041 Å. The distortion increases further in complexes with 2,9-substituted phen and L ligands with small-sized X donor atoms, as in **5a** and **5b**, leading to bow-bent conformations with β 32.1 and 31.0° and γ 10.6 and 9.6°, respectively, and to Pd–N distances in the range 2.023–2.036 Å, longer than those observed in **1**. Correspondingly, a displacement of Pd from the co-ordination plane occurs (see above) with α 12.5° in **5a** and 12.1° in **5b**. Therefore the α angle in bow-bent conformations is related to a pyramidal distortion of the N$_2$PdX$_2$ unit [Fig. 4(*c*)], rather than to a tetrahedral distortion observed in the twist conformation [Fig. 4(*a*)]. This effect is more enhanced in [Pd(L–L)Cl$_2$][32] {L–L = 2,9-bis[2,2-di(methoxycarbonyl)-ethyl]-1,10-phenanthroline} where an increase in the Pd–N distances to 2.064 Å is also observed. On the other hand, the presence of *trans*-influencing ligands, as in [Pd(2,9-dmphen)-(NO$_2$)$_2$],[34] induces a lengthening of the Pd–N distances to 2.09 Å which attenuates the steric hindrance between the L–L and NO$_2$ ligands, reducing the distorsion of the molecule. An even more pronounced lengthening of the Pd–N bond is observed in the case of a strong *trans*-influencing ligand such as methyl in [Pd(2,9-dmphen)Me(Cl)],[33] where the Pd–N bond *trans* to methyl is 2.230(4) Å compared to that *trans* to Cl [2.067(4) Å]. This distorted L–L co-ordination does not remove the steric interaction between the anionic ligands and the methyl groups of 2,9-dmphen, as indicated by the α and β values (Table 6). This molecule dissymmetry might have

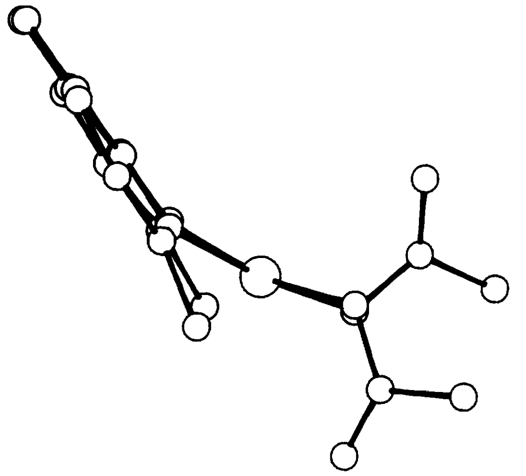


Fig. 3 Perspective view of the cation **5b**, showing the bending of the 2,9-dmphen ligand with respect to the palladium co-ordination plane

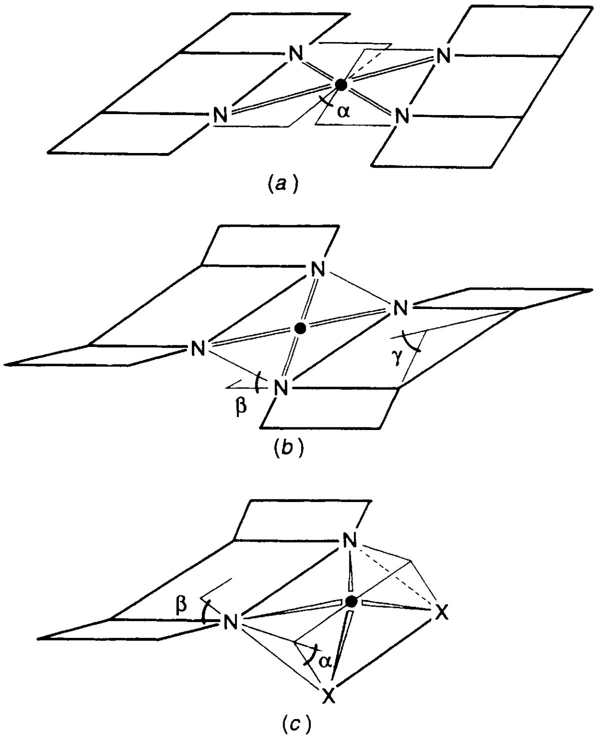


Fig. 4 Conformational geometries of [Pd(L–L)$_2$]$^{2+}$ cations (*a*) and (*b*) and of the (L–L)PdX$_2$ unit (*c*)

Table 2 Crystallographic data and details of refinements for compounds **1**, **5a** and **5b** *

	1	**5a**	**5b**
Formula	$C_{16}H_{14}N_2O_4Pd$	$C_{18}H_{18}N_2O_4Pd\cdot 0.40CH_2Cl_2\cdot 0.30H_2O$	$C_{18}H_{18}N_2O_4Pd\cdot 0.25CHCl_3\cdot 0.50H_2O$
M	404.7	455.2	471.6
Crystal size/mm	0.4 × 0.3 × 0.6	0.5 × 0.4 × 0.4	0.3 × 0.3 × 0.8
a/Å	22.594(8)	18.657(6)	19.275(7)
b/Å	9.519(1)	18.321(4)	18.204(6)
c/Å	15.419(5)	13.534(4)	13.572(5)
β/°	113.55(1)	119.93(1)	121.79(1)
U/Å^3	3040(1)	4009(2)	4048(2)
D_c/g cm^{-3}	1.77	1.51	1.55
μ (Mo-Kα)/cm^{-1}	12.2	10.7	10.3
F(000)	1616	1835	1900
$2\theta_{max}$/°	60	56	56
No. data measured	3462	5169	5231
Maximum, minimum transmission (%)	99.9, 91.2	99.9, 87.4	99.9, 69.8
No. unique data with $I \geqslant 3\sigma(I)$	1835	2612	2997
No. of parameters	208	250	268
R	0.029	0.052	0.055
R′	0.036	0.056	0.066

* Details in common = monoclinic, space group *C*2/*c*; *Z* = 8.

Table 3 Fractional atomic coordinates and their estimated standard deviations (e.s.d.s)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **1**							
Pd	0.126 97(2)	0.175 32(3)	0.156 52(2)	C(6)	0.104 3(2)	−0.109 9(4)	0.105 2(2)
O(1)	0.097 5(2)	0.361 7(3)	0.187 3(2)	C(7)	0.110 8(2)	−0.249 9(4)	0.077 7(2)
O(2)	0.129 2(2)	0.292 6(3)	0.334 4(2)	C(8)	0.168 0(3)	−0.284 0(5)	0.069 7(3)
O(3)	0.212 0(2)	0.260 7(3)	0.175 3(2)	C(9)	0.216 2(3)	−0.187 4(5)	0.090 2(3)
O(4)	0.168 1(2)	0.353 1(3)	0.032 3(2)	C(10)	0.206 7(2)	−0.051 0(5)	0.117 0(3)
N(1)	0.045 6(1)	0.071 4(3)	0.137 0(2)	C(11)	0.002 9(3)	−0.298 6(4)	0.065 3(3)
N(2)	0.152 4(2)	−0.013 8(3)	0.123 2(2)	C(12)	0.058 0(3)	−0.341 1(4)	0.059 4(3)
C(1)	−0.008 0(2)	0.115 5(4)	0.141 4(2)	C(13)	0.109 1(2)	0.381 2(5)	0.274 2(3)
C(2)	−0.062 8(2)	0.030 4(5)	0.123 9(2)	C(14)	0.098 2(3)	0.528 0(5)	0.299 4(3)
C(3)	−0.060 1(2)	−0.106 6(5)	0.099 6(2)	C(15)	0.214 2(2)	0.333 0(4)	0.106 0(3)
C(4)	−0.004 4(2)	−0.158 0(4)	0.093 0(2)	C(16)	0.278 7(2)	0.392 1(6)	0.124 2(3)
C(5)	0.047 0(2)	−0.066 9(4)	0.111 9(2)				
Complex **5a**							
Pd	0.182 07(3)	0.124 34(3)	0.093 09(4)	C(8)	−0.004 9(5)	−0.057 9(5)	−0.135 6(5)
O(1)	0.234 5(3)	0.204 2(3)	0.206 9(4)	C(9)	0.074 9(5)	−0.077 9(5)	−0.078 2(6)
O(2)	0.151 4(4)	0.176 9(4)	0.273 7(6)	C(10)	0.138 2(5)	−0.026 0(4)	−0.021 4(5)
O(3)	0.253 6(3)	0.056 9(3)	0.220 9(4)	C(11)	−0.121 0(4)	0.119 3(6)	−0.226 3(6)
O(4)	0.365 9(3)	0.088 0(3)	0.216 4(5)	C(12)	−0.107 7(4)	0.047 7(6)	−0.214 3(6)
N(1)	0.090 4(3)	0.185 7(3)	−0.030 8(4)	C(13)	0.156 3(6)	0.306 0(4)	0.010 1(7)
N(2)	0.118 4(3)	0.043 7(3)	−0.018 7(4)	C(14)	0.224 7(5)	−0.048 0(5)	0.033 8(7)
C(1)	0.082 6(5)	0.257 9(4)	−0.047 4(6)	C(15)	0.209 3(5)	0.209 9(5)	0.275 9(7)
C(2)	0.004 7(5)	0.287 4(5)	−0.120 7(7)	C(16)	0.254 9(7)	0.265 7(7)	0.368 9(9)
C(3)	−0.062 7(5)	0.244 4(6)	−0.178 1(7)	C(17)	0.330 0(5)	0.056 2(5)	0.259 3(7)
C(4)	−0.055 4(4)	0.168 9(5)	−0.166 5(6)	C(18)	0.378 9(7)	0.011 8(7)	0.368(1)
C(5)	0.023 5(4)	0.142 5(4)	−0.092 9(5)	C(19)[a]	0	0.272(2)	0.25
C(6)	0.038 1(4)	0.066 1(4)	−0.083 7(5)	C1[b]	0.021 6(9)	0.322 4(9)	0.359(1)
C(7)	−0.026 3(4)	0.017 2(5)	−0.145 4(5)	O(5)[c]	0.480(2)	0.018(1)	0.195(3)
Complex **5b**							
Pd	0.181 48(3)	0.121 36(3)	0.091 54(4)	C(9)	0.069 9(5)	−0.081 9(5)	−0.0808(6)
O(1)	0.238 0(3)	0.200 9(3)	0.207 6(4)	C(10)	0.132 3(5)	−0.029 7(5)	−0.023 7(6)
O(2)	0.168 9(4)	0.168 1(4)	0.290 0(5)	C(11)	−0.122 0(4)	0.117 3(7)	−0.228 8(6)
O(3)	0.254 6(3)	0.052 3(3)	0.219 3(4)	C(12)	−0.109 9(5)	0.044 4(7)	−0.218 3(6)
O(4)	0.364 6(3)	0.084 6(4)	0.215 2(5)	C(13)	0.154 7(6)	0.304 6(5)	0.008 8(8)
N(1)	0.089 6(3)	0.184 3(3)	−0.032 5(4)	C(14)	0.218 4(6)	−0.053 0(5)	0.028 9(8)
N(2)	0.115 0(3)	0.039 8(3)	−0.021 0(4)	C(15)	0.221 5(5)	0.202 7(5)	0.286 3(7)
C(1)	0.082 0(5)	0.256 6(5)	−0.049 0(6)	C(16)	0.273 1(7)	0.257 1(7)	0.380 8(9)
C(2)	0.003 0(5)	0.286 6(6)	−0.123 4(7)	C(17)	0.331 8(5)	0.053 7(5)	0.258 4(7)
C(3)	−0.065 0(5)	0.243 1(7)	−0.181 2(7)	C(18)	0.380 4(7)	0.008 6(7)	0.369(1)
C(4)	−0.056 2(4)	0.167 6(6)	−0.169 4(6)	C(19)[d]	0	0.346(2)	0.25
C(5)	0.021 4(4)	0.140 3(5)	−0.096 5(5)	C1(1)[d]	0.014(1)	0.311(1)	0.149(1)
C(6)	0.035 2(4)	0.063 0(5)	−0.087 2(5)	C1(2)[d]	−0.057(1)	0.296(1)	0.259(2)
C(7)	−0.029 4(4)	0.014 5(5)	−0.148 7(5)	C1(3)[d]	0.083(1)	0.365(1)	0.365(2)
C(8)	−0.009 3(5)	−0.060 7(5)	−0.138 2(6)	O(5)[e]	0.479(1)	0.020(1)	0.194(2)

[a] Site occupancy 0.20. [b] Site occupancy 0.40. [c] Site occupancy 0.30. [d] Site occupancy 0.25. [e] Site occupancy 0.50.

significance in catalysis. The copolymerization catalytic cycle of the monochelated carboxylato complexes involves co-ordination of an alkyl group to the palladium atom.

Solution Studies.—The chemical behaviour of these complexes in solution might give helpful information on their catalytic behaviour. This investigation was done mainly by ^1H NMR experiments and, owing to solubility reasons, was carried out in two distinct solvents for the two series, $CDCl_3$ for acetato compounds and $(CD_3)_2SO$ for trifluoroacetato derivatives. Only the bipy derivatives allowed direct comparison in the same solvent [$(CD_3)_2SO$]. Some selected results in CD_3OD will be also reported.

The spectra of both series of complexes share some common features: the number of signals, equal to half the number of chemically equivalent groups, suggests equivalence of the two halves of the complex; all resonances are shifted relative to those of the free L–L, and no signal due to the latter is present (except in CD_3OD).

In the case of acetato derivatives (Table 7) the signals of the protons which lie closer to the nitrogen atoms, that is $H^{2,9}$ in the phenanthroline series and $H^{6,6'}$ in the bipyridine series, are shifted upfield (about 0.50–0.60 ppm) compared to free L–L. With the exception of the signal of $H^{3,3'}$ in the bipyridine ligands, all the other signals are shifted downfield relative to free L–L. Despite the opposite shifts, the resonances of $H^{2,9}$ and $H^{6,6'}$ when present are the most downfield ones in the phen and bipy series, respectively. The only exception is the dmbipy derivative.

In the trifluoroacetato derivatives (Table 8) the upfield shift of the $H^{2,9}$ and $H^{6,6'}$ signals is even greater than for the acetato compounds, so that in this case they are not the most downfield resonances.

Assignment of the aromatic signals based only on their multiplicity and on selective decoupling experiments was not always unambiguous and some nuclear Overhauser effect (NOE) experiments were required. In the case of [Pd(phen)$(MeCO_2)_2$] the doublet corresponding to $H^{4,7}$ could be unambiguously distinguished from that of $H^{2,9}$ on the basis of its positive NOE with the singlet of $H^{5,6}$. A similar experiment was performed for the corresponding trifluoroacetato derivative. The assignments of $H^{2,9}$ and $H^{5,6}$ for the tmphen acetate complex were based upon analogies in the chemical shifts with the other derivatives of the series. In the dpphen acetate complex the phenyl substituents gave two multiplets accounting for six and four protons, respectively. The downfield multiplet was attributed to the *o*- and *p*-protons, which, owing to the conjugated system, should be more affected by co-ordination. The other multiplet, almost unshifted compared to that of free L–L, should be due to the protons in the *meta* position.

While for the acetato series all the signals are sharp at room temperature, for the trifluoroacetato derivatives the resonances of $H^{2,9}$ or $H^{6,6'}$ when present are very broad and the fine structure of other signals is also not very well resolved. On the other hand, the signals of $[Pd(bipy)(MeCO_2)_2]$ in the same solvent $[(CD_3)_2SO]$ are very sharp, suggesting that the broadening must be connected with the presence of $CF_3CO_2^-$. The signals of each trifluoroacetato complex became better resolved upon increasing the temperature [Fig. 5(*a*)]. A similar effect was observed also upon addition of $Na(O_2CCF_3)$ to a solution of the complex. For example, in the case of $[Pd(phen)(CF_3CO_2)_2]$ the doublet structure of the $H^{2,9}$ signal became evident at a $Na(O_2CCF_3)$: Pd ratio of 100 : 1 [Fig. 5(*b*)]. This behaviour suggests the establishment of an equilibrium, involving the dissociation of $CF_3CO_2^-$, between at least two species with co-ordinated L–L (Scheme 2).

The difference between the acetato and trifluoroacetato series is in agreement with $CF_3CO_2^-$ being a weaker σ-donor ligand than $MeCO_2^-$. According to the temperature dependence of the NMR spectra, the exchange rate between dissociated and undissociated species is intermediate on the NMR time-scale at room temperature. The enhanced resolution of the spectra observed by increasing the temperature can be attributed to an increase in the equilibrium rate, while that observed upon addition of sodium trifluoroacetate is due to a shift of the equilibrium towards the undissociated species.

The partial dissociation of $CF_3CO_2^-$ in Me_2SO solution was also suggested by the molar conductivity of $[Pd(L\text{-}L)(CF_3CO_2)_2]$ complexes (≈33 Ω^{-1} cm^2 mol^{-1}), compared to the negligible conductivity of $[Pd(bipy)(MeCO_2)_2]$ in the same solvent.

At least two hypotheses can be advanced for the nature of the dissociated species: the co-ordination position set free by $CF_3CO_2^-$ might either be replaced by Me_2SO or by the

$$\begin{tikzcd}[\mathrm{Pd(L\text{-}L)(CF_3CO_2)_2}] \arrow[d, shift left, "-\mathrm{CF_3CO_2^-}"] \\ \mathrm{[Pd(L\text{-}L)(CF_3CO_2)]^+/[Pd(L\text{-}L)(CF_3CO_2)(Me_2SO)]^+} \arrow[u, shift left]\end{tikzcd}$$

Scheme 2

Table 4 Infrared absorption data (cm^{-1}) for $[Pd(L\text{-}L)(RCO_2)_2]$ (R = Me or CF_3) complexes

Complex	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\Delta\nu$
1	1619	1375	244
4	1624	1373	251
3	1625	1380	245
2	1630	1377	255
5	1630	1369	261
6	1625	1377	248
7	1619	1315	304
8	1714	1403	311
11	1716	1400	316
10	1720	1405	315
9	1723	1402	321
12	1700	1402	298
13	1710	1405	305
14	1710	1410	300
$Na(O_2CMe)$*	1578	1414	164
$Na(O_2CCF_3)$*	1680	1457	223

* Assumed ionic, included for comparison.

Table 5 Selected bond lengths (Å) and angles (°) of compounds **1**, **5a** and **5b**

	1	**5a**	**5b**
Pd–N(1)	2.002(3)	2.035(5)	2.036(5)
Pd–N(2)	2.018(3)	2.023(5)	2.029(5)
Pd–O(1)	2.017(3)	1.991(5)	1.989(5)
Pd–O(3)	1.999(3)	1.999(5)	2.000(5)
O(1)–C(13)	1.271(5)	—	—
O(2)–C(13)	1.201(5)	—	—
O(3)–C(15)	1.288(5)	—	—
O(4)–C(15)	1.211(4)	—	—
O(1)–C(15)	—	1.24(1)	1.27(1)
O(2)–C(15)	—	1.23(1)	1.22(1)
O(3)–C(17)	—	1.25(1)	1.29(1)
O(4)–C(17)	—	1.23(1)	1.20(1)
N(1)–Pd–N(2)	81.9(1)	81.3(2)	82.0(2)
N(1)–Pd–O(1)	95.8(1)	96.8(2)	96.9(2)
N(1)–Pd–O(3)	174.4(1)	168.1(3)	168.5(3)
N(2)–Pd–O(1)	177.5(1)	173.6(3)	173.7(3)
N(2)–Pd–O(3)	92.6(1)	94.9(2)	94.0(2)
O(1)–Pd–O(3)	89.8(1)	85.8(2)	85.9(2)
Pd–N(1)–C(1)	130.3(3)	131.4(4)	131.8(4)
Pd–N(1)–C(5)	113.1(3)	108.8(4)	108.5(5)
Pd–N(2)–C(6)	111.5(3)	107.9(5)	108.3(5)
Pd–N(2)–C(10)	128.8(3)	130.7(4)	131.1(4)
C(1)–N(1)–C(5)	116.5(3)	118.9(5)	118.9(6)
C(6)–N(2)–C(10)	119.7(3)	119.9(5)	119.2(6)

Table 6 Geometrical parameters defining the conformations of bis- and mono-chelated palladium complexes containing phen or substituted phen ligands

Complex	Ref.	Pd–N/Å		α/°	β/°	γ/°	Conformation
$[Pd(phen)_2][ClO_4]_2$	29	2.042	2.059	18.7	9.8	3.0	Twist
$[Pd(tmphen)_2][PF_6]_2$	24	2.032	2.042	21.3	10.7	4.3	Twist
$[Pd(phen)_2][PF_6]_2$	24	2.050		0.0	16.2	13.4	Bow-step
$[Pd(phen)(MeCO_2)_2]$ **1**		2.002	2.018	1.3	0.7	1.9	Planar
$[Pd(phen)(NCO)_2]$	30	2.002	2.016	1.1	3.5	4.0	Planar
[Pd(dpphen)(tcbq)]	30	2.004	2.016	1.6	1.1	1.6	Planar
$[Pd(dpphen)Cl_2]$	31	2.031	2.036	3.4	6.2	5.1	≈Planar
		2.032	2.041	3.7	8.3	6.9	≈Planar
$[Pd(2,9\text{-}dmphen)(MeCO_2)_2]$ **5a**		2.023	2.035	12.5	32.1	10.6	Bow-bent
5b		2.028	2.036	12.1	31.0	9.6	Bow-bent
$[Pd(L\text{-}L)Cl_2]$*	32	2.053	2.064	14.0	39.5	15.7	Bow-bent
[Pd(2,9-dmphen)Me(Cl)]	33	2.230	2.067	15.3	36.7	13.0	Bow-bent
$[Pd(2,9\text{-}dmphen)(NO_2)_2]$	34	2.091	2.092	7.1	3.3	4.0	≈Planar

* L–L = 2,9-Bis[2,2-di(methoxycarbonyl)ethyl]-1,10-phenanthroline.

Table 7 Proton NMR spectral data of $[Pd(L-L)(MeCO_2)_2]$ complexes compared to free L–L in $CDCl_3$ at room temperature: region of aromatic protons

Complex or L–L	δ (L–L/protons)[a] $H^{2,9}$	$H^{3,8}$	$H^{4,7}$	$H^{5,6}$
phen	9.20(dd)	7.65(q)	8.27(dd)	7.82(s)
1	8.63(dd)	7.81(q)	8.57(dd)	7.99(s)
tmphen	8.93(s)			8.04(s)
2	8.30(s)			8.09(s)
4,7-dmphen	9.05(d)	7.46(d)		8.04(s)
3	8.45(d)	7.60(d)		8.12(s)
dpphen	9.23(d)	7.60(d)	7.53(m)[b]	7.86(s)
4	8.70(d)	7.76(d)	7.53(m)[b] 7.61(m)[b]	8.00(s)
2,9-dmphen		7.50(d)	8.13(d)	7.71(s)
5		7.47(d)	8.33(d)	7.84(s)
	$H^{6,6'}$	$H^{3,3'}$	$H^{4,4'}$	$H^{5,5'}$
bipy	8.69(d)	8.40(d)	7.83(dt)	7.32(dt)
6	8.28(dd)	8.24(d)	8.11(dt)	7.45(dt)
dmbipy	8.54(d)	8.22(s)		7.14(dd)
7	8.01(d)	8.11(s)		7.19(dd)

[a] s = Singlet, d = doublet, q = quartet, m = multiplet, dd = double doublet, dt = double triplet. [b] Protons of phenyls in 4 and 7 positions.

Table 8 Proton NMR spectral data of $[Pd(L-L)(CF_3CO_2)_2]$ complexes compared to free L–L in $(CD_3)_2SO$ at room temperature: region of aromatic protons[a]

Complex or L–L	δ (L–L/protons) $H^{2,9}$	$H^{3,8}$	$H^{4,7}$	$H^{5,6}$
phen	9.11(dd)	7.79(q)	8.50(dd)	8.00(s)
8[a]	8.43(br)	8.14(q)	9.03(dd)	8.30(s)
tmphen	8.83(s)			8.16(s)
9	8.00(br)			8.35(s)
4,7-dmphen	8.94(d)	7.61(d)		8.16(s)
10	8.20(br)	7.96(d)		8.36(s)
dpphen	9.18(d)	7.74(d)	7.60(m)[b]	7.86(s)
11[a]	8.51(d)	8.09(d)	7.65(m)[b]	8.07(s)
2,9-dmphen		7.62(d)	8.34(d)	7.86(s)
12		7.85(d)	8.81(d)	8.18(s)
	$H^{6,6'}$	$H^{3,3'}$	$H^{4,4'}$	$H^{5,5'}$
bipy	8.69(m)	8.39(m)	7.95(m)	7.46(m)
13	8.09(br)	8.61(d)	8.44(dt)	7.85(dt)
dmbipy	8.53(d)	8.23(s)		7.28(dd)
14	7.90(br)	8.47(s)		7.66(dd)

[a] Chemical shift values measured at 125 °C; signals at 25 °C were too broad for assignment. [b] Protons of phenyls in 4 and 7 positions.

remaining trifluoroacetate, which would bind as a chelate. The ^{19}F NMR spectra, in $(CD_3)_2SO$ solution at room temperature, were not helpful in determining the nature of the dissociated species since only one sharp signal was observed.

In exchanging systems the peak shape depends on the equilibrium constant, on the exchange rate and on the frequency dispersion in the static spectrum of the nuclei undergoing exchange.[36] Since only 2,9- or 6,6'-protons give very broad signals, it can be concluded that the difference in frequency between the resonances of the dissociated and undissociated species must be rather large only for such protons.

The bandshape variations with the $CF_3CO_2^-$: Pd ratio and the temperature show that the resonance of the undissociated species (high $CF_3CO_2^-$: Pd ratio) is very close to that of the exchanging system at the fast-exchange limit. This behaviour is in agreement with the equilibrium being shifted toward the undissociated species.[36]

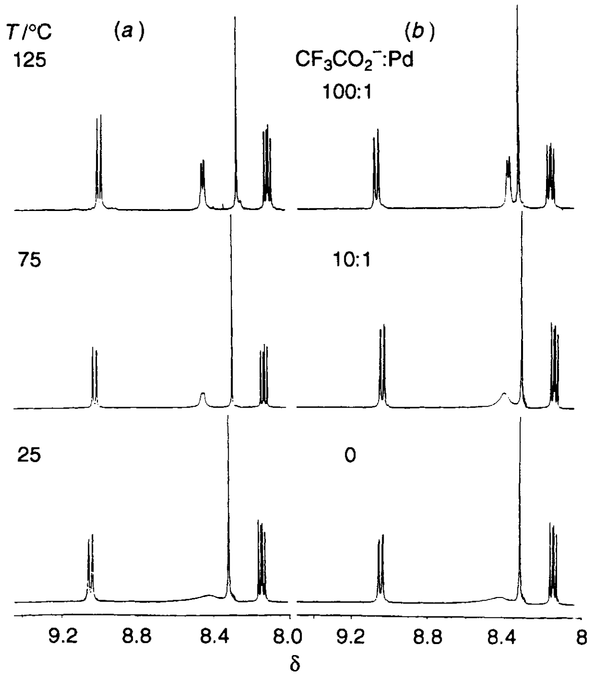


Fig. 5 Proton NMR spectra of $[Pd(phen)(CF_3CO_2)_2]$ in $(CD_3)_2SO$ at concentration 10 mmol dm^{-3}: (*a*) variation with temperature; (*b*) variation with $CF_3CO_2^-$: Pd ratio

Selected NMR experiments performed on $[Pd(phen)(MeCO_2)_2]$ and $[Pd(bipy)(CF_3CO_2)_2]$ showed that in methanol both complexes undergo partial dissociation of the anionic ligand, as indicated by the broadening of the signals and by the appearance of the signal of free carboxylate. From the intensity of the signal of the free anion, a 10% dissociation of acetate could be estimated. A low-temperature study, interrupted at −40 °C by solubility limits, showed a resolution enhancement of the signals of complex **1** and the appearance of minor peaks for co-ordinated phen. They are very broad and almost undetectable at room temperature, and might be attributed to at least one dissociated species. In the case of both **1** and **13**, the addition of the corresponding free anion induced the disappearance of the minor set of peaks and a better resolution of the major resonances. This behaviour is in good agreement with the hypothesis advanced for trifluoroacetato derivatives in Me_2SO solution.

Copolymerization Reactions.—We investigated the catalytic activity of the monochelated carboxylato complexes $[Pd(L-L)(RCO_2)_2]$ in the carbon monoxide–styrene copolymerization [equation (1)]. Methanol was used as solvent and 1,4-benzoquinone as oxidant. No acid cocatalyst was added. The reaction was carried out at low temperature (40 °C) and at a pressure of 40 atm of carbon monoxide.

$$n\mathrm{PhCH{=}CH_2} + n\mathrm{CO} \xrightarrow[\text{quinone, MeOH}]{\text{catalyst}} -(\mathrm{CO{-}CHPh{-}CH_2})_n- \qquad (1)$$

The resulting CO–styrene copolymer exhibits a polyketone structure, as demonstrated by the IR spectra in the solid state, and has a high melting point (270–280 °C). Despite being insoluble in most organic solvents, it is soluble in *m*-cresol and $(CF_3)_2CHOH$, which were used for measurements of the intrinsic viscosity and of NMR spectra, respectively. According to the ^{13}C NMR results, the copolymer has a regular structure with perfectly alternating CO and styrene units, in agreement also with the elemental analyses (Found: C, 81.35; H, 6.10. Calc.: C, 81.80; H, 6.10%). In accord with the literature on similar systems,[8,12,16,20] the spectra are consistent with a syn-

Table 9 Carbon monoxide–styrene copolymerization

(*a*) Effect of the catalyst precursor

Precursor	g copolymer per g Pd
[Pd(phen)(MeCO$_2$)$_2$]	4
[Pd(phen)(CF$_3$CO$_2$)$_2$]	300
[Pd(phen)$_2$][CF$_3$CO$_2$]$_2$	118
[Pd(phen)$_2$][PF$_6$]$_2$	140

(*b*) Effect of the quinone concentration *

Precursor	Amount of quinone/mmol	g copolymer per g Pd
[Pd(phen)$_2$][PF$_6$]$_2$	40	140
[Pd(phen)(CF$_3$CO$_2$)$_2$]	40	300
[Pd(phen)(CF$_3$CO$_2$)$_2$]	10	269
[Pd(phen)(CF$_3$CO$_2$)$_2$]	5	188
[Pd(phen)(CF$_3$CO$_2$)$_2$]	0	81

Reaction conditions: [Pd] = 1×10^{-3} mol dm^{-3}; P_{tot} = 40 atm; 40 °C; methanol solvent: V = 500 cm^3; 40 mmol quinone; 10 h. * Limiting viscosity number measured in *m*-cresol at 100 °C for [Pd(phen)(CF$_3$CO$_2$)$_2$]: 0.07 at 40 mmol quinone, 0.15 dl g^{-1} in the absence of quinone.

diotactic stereoregularity, and allowed us to recognize methoxycarbonyl and unsaturated groups as the major chain-end groups.[20] The chain length of the copolymer, measured as the number-average molecular weight (M_n), was evaluated by ^{13}C NMR spectroscopy as 5000–7000.

Catalytic activities are reported in Table 9; a remarkable dependence on the nature of the carboxylato anion was observed. The acetato derivatives showed a much lower catalytic activity than the corresponding trifluoroacetato ones [Table 9(*a*)]. This difference could be related to the ability of acetate and trifluoroacetate to undergo esterification and to their σ-donor power. Since acetate is more esterifiable than trifluoroacetate,[37] a greater amount of water is expected to be formed by the methanol esterification reaction with the acetato derivatives than with the trifluoroacetato ones. The presence of an excess of water might favour the reduction of the catalyst to inactive Pd^0.[21] A similar trend was found for the CO–ethylene copolymerization when [Pd(phen)$_2$][CF$_3$CO$_2$]$_2$ and [Pd(phen)$_2$][MeCO$_2$]$_2$ were used as catalyst precursors.[7] Moreover, it has been reported that, in order to achieve catalytic activity, the anion should have a weak or non-co-ordinating ability.[7,8] In agreement also with our NMR results in Me$_2$SO, trifluoroacetate is a weaker σ-donor ligand than is acetate.

Direct comparison with the corresponding bis(chelated) complex, [Pd(phen)$_2$][CF$_3$CO$_2$]$_2$, showed that, at 40 °C, the monochelated trifluoroacetato derivative was more active than the bis(chelated) one. Moreover, at this low temperature the monochelated compound had a catalytic activity higher than that of [Pd(phen)$_2$][PF$_6$]$_2$, the most active bis(chelated) catalyst for the CO–styrene copolymerization at 70 °C [Table 9(*a*)].

We also analysed the dependence of the catalytic activity on the concentration of 1,4-benzoquinone. As previously reported, the oxidant plays an important role both in the activity and selectivity.[8,9,14,22] A loss of activity resulted when the quinone concentration was decreased [Table 9(*b*)]; it was marginal when the quinone amount was reduced from 40 to 10 mmol, but became relevant when the benzoquinone was further decreased. However, it should be noted that the catalytic system was still active in the absence of any 1,4-benzoquinone. The oxidant concentration affects also the intrinsic viscosity, and therefore the molecular weight, of the copolymer. In agreement with the literature,[8] an increase in the intrinsic viscosity was found upon lowering the benzoquinone concentration.

The influence of the nature of the nitrogen chelating ligand was also examined. A decrease in catalytic activity was observed on going from bipy to phen to tmphen (Table 10). This trend could be related to the electron-donor properties of the ligands, which increase in the same order. A complete loss of activity resulted when the complex with 2,9-dimethyl-1,10-phenanthroline was used as catalyst precursor (Table 10). This is probably due to the steric hindrance of the methyl groups in 2 and 9 positions.

Table 10 Carbon monoxide–styrene copolymerization: effect of the nitrogen ligand

L–L *	pK_a	g copolymer per g Pd
bipy	4.44	376
phen	4.86	300
tmphen	6.31	141
2,9-dmphen	6.17	0

For reaction conditions see Table 9. * Catalyst precursor: [Pd(L–L)(CF$_3$CO$_2$)$_2$].

Conclusion

Solution NMR studies suggest that, depending on the nature of the solvent, the Pd atom in the complexes described can either maintain the same co-ordination environment as in the solid state or partially dissociate the carboxylate ligand. In agreement with the different co-ordinating abilities of acetate and trifluoroacetate, dissociation of the latter is easier. When no dissociation occurs, the distortions observed in the solid state are very likely rapidly mediated in solution.

Comparison of the structures of monochelated [Pd(phen)(MeCO$_2$)$_2$] and bis(chelated) [Pd(phen)$_2$][PF$_6$]$_2$ complexes indicates that the Pd–N distance is longer in the latter (Table 6). This lengthening may be attributed not only to steric hindrance between H^{2,9} of the two molecules of phenanthroline co-ordinated to the same palladium atom, but also to the different nature of the Pd–N bond in mono- and bis-chelated complexes. In the dicationic bis(chelated) complexes the charge density on palladium is presumably lower than in the monochelated ones, implying a less-pronounced π-back donation contribution to the Pd–N bond. The lower charge density expected for this reason on the nitrogen atoms of the bis(chelated) compared to the monochelated complexes is in agreement with preliminary NMR results[38] which show that, while in the monochelated derivatives the signals of H^{2,9} or H$^{6,6'}$ are shifted upfield compared to free L–L, in the bis(chelated) derivatives they are shifted downfield. This confirms that the ^{1}H NMR signals of H^{2,9} in the phenanthroline series, and of H$^{6,6'}$ in the bipyridine series, are excellent probes for the evaluation of the co-ordination environment of the palladium atom. Their chemical shifts and bandshape are considerably different in the acetato and trifluoroacetato derivatives, as well as in the mono- and bis-chelated series.

The complexes described were found to be active in the CO–styrene copolymerization. Further studies on their catalytic behaviour in CO–olefin copolymerization are in progress.

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References

1 J. E. McKeon and P. Fitton, *Tetrahedron*, 1972, **28**, 233.

2 G. Villain, G. Constant, A. Gaset and Ph. Kalck, *J. Mol. Catal.*, 1980, **7**, 355.

3 M. Catellani and G. Chiusoli, *J. Organomet. Chem.*, 1992, **425**, 151.

4 T. Jintoku, K. Takaki, Y. Fujiwara, Y. Fuchita and K. Hiraki, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 438.

5 A. Bontempi, E. Alessio, G. Chanos and G. Mestroni, *J. Mol. Catal.*, 1987, **42**, 67.

6 E. Drent, *E. Pat. Appl.*, 229 408, 1986; *U.S. Pat.*, 4 778 279, 1988.

7 A. Sommazzi, F. Garbassi, G. Mestroni and B. Milani, *E. Pat.*, 93 200 331.2, 1993.

8 M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci and U. W. Suter, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 989.

9 E. Drent, J. A. M. van Broekhoven and M. J. Doyle, *J. Organomet. Chem.*, 1991, **417**, 235.

10 M. Brookhart, F. C. Rix, J. M. De Simone and J. C. Barborak, *J. Am. Chem. Soc.*, 1992, **114**, 5894.

11 T.-W. Lai and A. Sen, *Organometallics*, 1984, **3**, 866.

12 P. Corradini, C. De Rosa, A. Panunzi, G. Petrucci and P. Pino, *Chimia*, 1990, **44**, 52.

13 A. Batistini and G. Consiglio, *Organometallics*, 1992, **11**, 1766.

14 C. Pisano, S. C. A. Nefkens and G. Consiglio, *Organometallics*, 1992, **11**, 1975.

15 A. Batistini, G. Consiglio and U. W. Suter, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 303.

16 M. Barsacchi, A. Batistini, G. Consiglio and U. W. Suter, *Macromolecules*, 1992, **25**, 3604.

17 J. C. W. Chien, A. X. Zhao and F. Xu, *Polym. Bull.*, 1992, **28**, 315.

18 A. X. Zhao and J. C. W. Chien, *J. Polym. Sci., Part A, Polym. Chem.*, 1992, **30**, 2735.

19 A. Sen, *Acc. Chem. Res.*, 1993, **23**, 303.

20 V. Busico, P. Corradini, L. Landriani and M. Trifuoggi, *Makromol. Chem., Rapid Commun.*, 1993, **14**, 261.

21 P. K. Wong, J. A. van Doorn, E. Drent, O. Sudmeyer and H. A. Stil, *Ind. Eng. Chem. Res.*, 1993, **32**, 986.

22 C. Pisano, A. Mezzetti and G. Consiglio, *Organometallics*, 1992, **11**, 20.

23 T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

24 S. Geremia, L. Randaccio, G. Mestroni and B. Milani, *J. Chem. Soc., Dalton Trans.*, 1992, 2117.

25 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.

26 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

27 B. A. Frenz, Enraf-Nonius Structure Determination Package, College Station, TX, and Enraf-Nonius, Delft, 1980.

28 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

29 J. V. Rund and A. C. Hazell, *Acta Crystallogr., Sect. B*, 1980, **36**, 3103.

30 V. P. Zagorodnikov, T. S. Khodashova, M. N. Vargaftik, I. I. Moiseev and M. A. Porai-Koshits, *Koord. Khim.*, 1985, **11**, 95.

31 J. Anbei, C. Kruger and B. Pfeil, *Acta Crystallogr., Sect. C*, 1987, **43**, 2334.

32 F. R. Fronczek, I. Kahwa, S. Lu, G. R. Newkome, M. A. Ollino, W. D. Pitts, A. Sittattrakul, J. C. Wang and S. F. Watkins, *Acta Crystallogr., Sect. C*, 1988, **44**, 933.

33 V. De Felice, V. G. Albano, C. Castellari, M. E. Cucciolito and A. De Renzi, *J. Organomet. Chem.*, 1991, **403**, 269.

34 J. Fridrichsons, A. Mc L. Mathieson and L. F. Power, *J. Cryst. Mol. Struct.*, 1971, **1**, 333.

35 A. Hazell and A. Mukhopadhyay, *Acta Crystallogr., Sect. B*, 1980, **36**, 1647.

36 J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982.

37 E. K. Euranto, *The Chemistry of Carboxylic Acids and Esters*, ed. S. Patai, Interscience, New York, 1969, pp. 505–588.

38 B. Milani, unpublished work.

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