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New palladium (substituted 1,10-phenanthroline) bis(methoxycarbonyl) complexes [Pd(L–L)(CO_2CH_3)$_2$]: preparation and structural features

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Abstract

New complexes of general formula Pd(L–L)(CO_2CH_3)$_2$ (L–L = 1,10-phenanthroline **1**; 2,9-dimethyl-1,10-phenanthroline **2**; 4,7-dimethyl-1,10-phenanthroline **3**; 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline **4**, 3,4,7,8-tetramethyl-1,10-phenanthroline **5**; and 4,7-diphenyl-1,10-phenanthroline **6**) were prepared either by exchange reaction between Pd(bipyridine)(CO_2CH_3)$_2$ **7** and the appropriate free ligand or by reacting Pd(L–L)Cl_2 suspended in MeOH under carbon monoxide, at room temperature, in the presence of a base. The structure of **1** was determined ab initio from X-ray powder diffraction data by using a simulated annealing technique and refined by the Rietveld method. **1** crystallizes in the orthorhombic *Pbca* space group with cell parameters $a = 8.0787(4)$, $b = 16.2797(8)$, $c = 22.843(1)$ Å and $Z = 8$.

Keywords: Palladium; Phenanthrolines; Alkoxycarbonyl; Carbonylation; X-ray structure

1. Introduction

Transition metal alkoxycarbonyl derivatives have been recognized as key intermediates in many relevant homogeneous catalytic processes involving alkanols and carbon monoxide [1]. The synthesis of carbonates and oxalates [2], the hydrocarboalkoxylation of alkenes [3] and alkynes [4,5] to the respective saturated and unsaturated esters, the copolymerization of alkenes with CO [6] appear to involve alkoxycarbonyl metal intermediates.

Due to their versatility, the alkoxycarbonyl complexes of transition metals have been studied extensively. The methoxycarbonyl iridium complex Ir(PPh_3)$_2$(CO_2CH_3)(CO)$_2$ was prepared by nucleophilic attack of the methoxide group on the carbonyl ligand in Ir(PPh_3)$_2$(CO)(OCH_3) [7]. Analogously, the ethoxycarbonyl complex [Ni(np_3)(CO_2Et)$_2$]BPh_4 [8] (np_3 = tris(2-diphenylphosphinoethyl)amine) was synthesized by ethoxide ion attack on Ni(np_3)(CO), while Ni(pnp)(CO_2CH_3)$_2$ [9], (pnp = 2,6-bis(diphenylphosphinomethyl)pyridine) was obtained from Ni(pnp)Cl_2 and amines under CO in methanol.

Platinum alkoxycarbonyl complexes have been prepared by reacting Pt(L–L)Cl_2, where L–L are phosphorous chelating ligands, such as dppe (dppe = 1,2-bis(diphenylphospinoethane) [10], pnp and also dppf ligands (dppf = 1,1′-bis(diphenylphosphino)ferrocene) [11] with CO in methanol, in the presence of a base.

Similarly, palladium bis(alkoxycarbonyl) complexes Pd(CO_2R)$_2$(PPh_3)$_2$ [12] were synthesized by carbonylation of PdCl_2(PPh_3)$_2$ suspended in MeOH with carbon monoxide, in the presence of an amine, whereas Pd-Cl(CO_2R)(PPh_3)$_2$ was prepared from PdCl_2(PPh_3)$_2$ under CO for a shorter reaction time [13] or by oxidative addition of an alkyl chloroformate to a Pd(0) complex, such as Pd(PPh_3)$_4$ [14]. The acetato(carbomethoxy) complex Pd(OAc)(CO_2CH_3)(PPh_3)$_2$ was analogously

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Table 1
Preparation of $Pd(L–L)(CO_2CH_3)_2$ by exchange reaction[a] or by sodium methoxide and or by potassium carbonate based procedures

Compound	Procedure			Colour
	Exchange Yield (%)	MeONa/CO Yield (%)	K_2CO_3/CO Yield (%)	
1	77	83	80	Yellow
2	0	71	0	Yellow
3	57	84	37	Yellow
4	0	70	20	Yellow
5	53	70	18	Light yellow
6	85	86	67	Yellow
7	—	83	55	Light green

Conditions: 20 h at room temperature.
[a] Reaction exchange carried out between $Pd(bipy)(CO_2CH_3)_2$ **7** and the corresponding free ligand (for further details see experimental section).

prepared by treating $Pd(OAc)_2(PPh_3)_2$ under CO [15]. Although palladium complexes with nitrogen chelating ligands are very common, only a few examples of palladium bis-(methoxycarbonyl) complexes $Pd(bipy)(CO_2CH_3)_2$, bearing a bipyridine (bipy) ligand are known [16,17].

We now report the synthesis and spectroscopic characterization of bis(methoxycarbonyl) palladium (II) complexes $Pd(L–L)(CO_2CH_3)_2$, bearing substituted 1,10-phenanthrolines (L–L) as ligand, and the crystal structure of **1**, determined ab initio from X-ray powder diffraction data by using a simulated annealing technique.

2. Results and discussion

2.1. Synthesis of $Pd(L–L)(CO_2CH_3)_2$

Complexes $Pd(L–L)(CO_2CH_3)_2$ were prepared in good yield by ligand exchange reaction of complex $Pd(bipy)(CO_2CH_3)_2$ **7** with the appropriate free ligand (Eq. (1)):

$$\mathbf{7} + (L–L) \rightarrow Pd(L–L)(CO_2CH_3)_2 + bipy \quad (1)$$

or by reaction of $Pd(L–L)Cl_2$ with a base, such as sodium methoxide or potassium carbonate, in 1:2.2 molar ratio, in the presence of the free ligand (10% weight in respect to $Pd(L–L)Cl_2$) under carbon monoxide at room temperature (Table 1).

The most effective procedure to synthesize the palladium complexes uses sodium methoxide, as the base, yields being higher than those obtained by exchange reaction or with potassium carbonate.

The preparation of complex **2** failed both by ligand exchange and by using potassium carbonate as base. Moreover, the ligand exchange always failed when the ligand bore substituents in both 2 and 9 positions, independently from their steric hindrance, as in the case of complexes **2** and **4**. Furthermore, all the attempts to isolate the $Pd(L–L)(CO_2CH_3)_2$ complex, where L–L is 2,9-diphenyl-1,10-phenanthroline, were unsuccessful probably due to the bulky substituents in 2 and 9 positions. The synthesis of palladium bis(methoxycarbonyl) complexes by ligand exchange was unprecedented.

Added free nitrogen ligand has the effect to increase the complexes stability during the carbonylation reactions; indeed, the yield in complex **1** was 83% against 72% without added free 1,10-phenanthroline. Moreover, the added ligand allows us to obtain $Pd(bipy)(CO_2CH_3)_2$ **7** with a yield of 86% in respect to the 62% reported by Hanson and coworkers [16].

The compounds obtained were characterized by analytical, mass, IR and ^{1}H-NMR spectroscopy (Table 2), showing a perfect agreement with the proposed structure.

IR spectra showed adsorption bands in the regions 1680–1590 cm^{-1} and 1100 – 1030 cm^{-1}, assigned to $\nu_{C=O}$ and ν_{C-O} asymmetric and symmetric stretching, respectively. The double adsorptions for both $\nu_{C=O}$ and ν_{C-O} asymmetric and symmetric stretching, were ascribed to conformational *cis* and *trans* isomers [13]. No correlations were found between the carbonyl stretching adsorptions and the ligand pK_a values [18].

Table 2
Analytical, mass and IR data of $Pd(L–L)(CO_2CH_3)_2$ complexes in nujol mull

Compound	Analytical data calc. (found) (%)			*m/e*	p*K*a	$\nu_{C=O}$ (cm^{-1})	ν_{C-O} (cm^{-1})
	C	H	N	(FAB)			
1	47.52 (47.60)	3.46 (3.40)	6.93 (7.01)	404	4.86	1665–1645	1100–1050
2	50.00 (50.02)	4.17 (4.13)	6.48 (6.51)	432	6.17	1680–1650	1070–1030
3	50.00 (50.07)	4.17 (4.19)	6.48 (6.45)	432	5.94	1640–1625	1080–1040
4	60.00 (59.80)	4.64 (4.56)	5.00 (5.10)	560	—	1675–1640	1080–1045
5	26.08 (25.59)	5.65 (5.70)	6.08 (6.10)	464	6.31	1640–1600	1090–1050
6	58.64 (58.70)	4.13 (4.20)	5.26 (5.31)	532	4.84	1670–1640	1080–1030
7	44.20 (44.31)	3.68 (3.62)	7.36 (7.42)	380	4.44	1650–1620	1070–1020
8	44.21 (4435)	2.89 (2.93)	7.36 (7.25)	380	—	1670	1030

Table 3
^{1}H-NMR[a] data for compounds **1**–**6**

Compound	δ (H_2)	δ (H_3)	δ (H_4)	δ (H_5)δ	δ (H_6)	δ (H_7)	δ (H_8)	δ (H_9)	δ (H-COOMe)	δ ($H_{Subst.}$)
1	8.90 (dd)	7.68 (dd)	8.41(dd)	7.86(s)	7.86(s)	8.41 (dd)	7.68 (dd)	8.90 (dd)	3.77 (s)	—
2	—	7.53 (d)	8.24 (d)	7.79 (s)	7.79 (s)	8.24 (d)	7.53 (d)	—	3.70 (s)	2.86 (s, CH_3)
3	8.72 (d)	7.52 (d)	—	8.10 (s)	8.10 (s)	—	7.52 (d)	8.72 (d)	3.63 (s)	2.80 (s, CH_3)
4	—	7.80 (s)	—	7.45 (s)	7.45 (s)	—	7.80 (s)	—	3.70 (s)	2.90 (s, CH_3) 7.5–7.6 (m, Ph)
5	8.70 (s)	—	—	8.10 (s)	8.10 (s)	—	—	8.70 (s)	3.70 (s)	2.70 (s, CH_3) 2.50 (s, CH_3)
6	9.14 (d)	7.80 (d)	—	7.99 (s)	7.99 (s)	—	7.80 (d)	9.14 (d)	3.71 (s)	7.5–7.6 (m, Ph)
8	9.25 (dd)	8.6 (m)	7.8 (m)	7.98 (s)	7.98 (s)	7.83 (m)	8.6–8.7 (m)	8.87 (dd)	3.86 (s)	—

Spectra were recorded immediately after dissolution.
s, singlet; d, doublet; dd, double doublet; m, multiplet.
[a] Spectra were recorded in CD_2Cl_2. δ (^{1}H) values in ppm from TMS as internal standard.

The ^{1}H-NMR analysis (Table 3) were consistent with the formation of Pd(L–L)(CO_2CH_3)$_2$, showing singlets in the 3–4 ppm region due to the methoxy group protons; the spectra were obtained in CD_2Cl_2, since in $CDCl_3$ the methoxycarbonyl groups react in a few minutes with the catalytic action of HCl, usually contained in trace amounts in chloroform, affording Pd(phen)Cl(CO_2CH_3) **8** in 70% yield (Eq. (2)) ([11]a):

$$\mathbf{1} + HCl \rightarrow Pd(phen)Cl(CO_2CH_3) + CO + MeOH \quad (2)$$

Compound Pd(phen)Cl(CO_2CH_3) **8** was characterized by ^{1}H-NMR (Table 3), it showed the methyl singlet of the methoxycarbonyl group shifted from 3.77 to 3.86 ppm (Table 3); moreover, the two protons in position 2 and 9 gave two signals (H_2 at 9.25 ppm and H_9 at 8.87 ppm).

2.2. Reactivity of Pd(L–L)(COOMe)$_2$

When heated at 50°C for 8 hrs in methanol, complex **1** reacted with two equivalents of phenanthrolinium hexafluophasphate phenHPF$_6$, an acid bearing a non-coordinating anion, prepared according to the literature [19], to yield Pd(phen)$_2$(PF$_6$)$_2$ **9** (Eq. (3)):

$$\mathbf{1} + 2phenHPF_6 \rightarrow Pd(phen)_2(PF_6)_2 + 2CO\uparrow + 2MeOH + phen \quad (3)$$

Four equivalents of the acid were needed, however, to displace the reaction to right, as shown by the change of the suspension colour from yellow to pink. The reaction residue was washed several times with diethyl ether, to eliminate the phenanthroline still present. The ^{1}H-NMR spectrum (in CD_3CN) of the solid residue showed adsorptions attributable to a single species. These results are attributable to a dynamic equilibrium between all the species present in solution, as brought about by the comparison with the ^{1}H-NMR spectrum of the mixture of complex Pd(phen)$_2$(PF$_6$)$_2$ **9**, prepared according to the literature [20], together with one equivalent of the phenanthroline ligand and two equivalents of the acid phenHPF$_6$, which showed the same resonance patterns of a mixture in 1:1:2 molar ratio of **9**:phen:phenHPF$_6$.

The alkoxycarbonyl palladium complex **1**, suspended in methanol/water (10/1 v/v) at 65°C, decomposes to black Pd(0), with a concomitant formation of free phenanthroline.

2.3. Crystal structure of **1**

Since all attempts to grow crystal of **1** suitable for single crystal X-ray analysis failed, the crystal structure determination was performed ab initio by using the simulated annealing technique and refined by the Rietveld method (see Section 3). The complexity of the molecule imposed the use of constraints during the refinement, performed by defining four rigid bodies (the Pd atom, the phen ligand and the two methoxycarbonyl groups) with fixed geometry but free to rototranslate with respect to a defined pivot atom. In spite of the hard constraints imposed, the refinement led to an excellent reproduction of the experimental XRD pattern, as demonstrated by the low residual error index factors reported in Table 4, together with the main crystallographic data.

Fractional atomic coordinates for non-H atoms and the main geometrical features of **1** are reported in Tables 5 and 6, respectively. It must be pointed out that estimated S.D. values reported in Tables 5 and 6 are surely underestimated as a consequence of the rigid-body refinement scheme adopted. In fact, this approach allows the accurate determination of the location and orientation of the different groups with known geometry and is generally used to reduce the number of

Table 4
Data collection and crystallographic data for 1

Formula	$C_{16}H_{14}N_2O_4Pd$
Molecular weight	404.70
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	8.0787(4)
b (Å)	16.2797(8)
c (Å)	22.843(1)
V (Å^3)	3004.3(2)
$D_{calc.}$ (mg m^{-3})	1.7894
Radiation	Cu–K$_\alpha$ ($\lambda = 1.54178$ Å)
Linear absorption coefficient μ (cm^{-1})	104.03
Sample	Yellow-brown powder
Diffractometer	Siemens D500
Scan type	θ/θ
2θ range (°)	5–80
Step size (°2θ)	0.03
Accumulation time (s/step)	10
Number of steps	2501
Number of reflections	910
R_p	0.068
R_{wp}	0.088
Atomic scattering factors	Int. Tables of Crystallography Vol. IV

parameters to be refined when the diffraction data do not contain sufficient information for treating them (in other words, when the ratio reflections/parameters is low). The refinement with the rigid-body approximation then leads to a sufficiently accurate determination

Table 5
Fractional atomic coordinates of non-H atoms for **1**

	x	y	z	B_{iso} (Å^2)
Pd(1)	0.2100(3)	−0.0898(2)	0.1514(2)	0.36
N(2)	0.0838(10)	−0.1920(6)	0.1867(3)	0.54
C(3)	−0.0002(10)	−0.2565(6)	0.1594(3)	0.74
C(4)	−0.0813(10)	−0.3156(6)	0.1930(3)	0.74
C(5)	−0.0787(10)	−0.3102(6)	0.2542(3)	0.74
C(6)	0.0054(10)	−0.2456(6)	0.2815(3)	0.74
C(7)	0.0866(10)	−0.1865(6)	0.2478(3)	0.74
C(8)	0.0082(10)	−0.2403(6)	0.3426(3)	0.74
C(9)	0.0922(10)	−0.1758(6)	0.3699(3)	0.74
C(10)	0.1733(10)	−0.1168(6)	0.3361(3)	0.74
C(11)	0.1705(10)	−0.1222(6)	0.2751(3)	0.74
C(12)	0.2573(10)	−0.0523(6)	0.3634(3)	0.74
C(13)	0.3383(10)	0.0067(6)	0.3298(3)	0.74
C(14)	0.3357(10)	0.0014(6)	0.2686(3)	0.74
N(15)	0.2516(10)	−0.0631(6)	0.2412(3)	0.54
C(16)	0.1659(15)	−0.1261(7)	0.0701(6)	0.74
O(17)	0.0522(15)	−0.0838(7)	0.0382(6)	0.81
O(18)	0.2398(15)	−0.1815(7)	0.0428(6)	0.81
C(19)	0.0310(15)	−0.1225(7)	−0.0174(6)	0.74
C(20)	0.3107(13)	0.0154(7)	0.1247(4)	0.74
O(21)	0.2862(13)	0.0824(7)	0.1479(4)	0.81
O(22)	0.4102(13)	0.0174(7)	0.0768(4)	0.81
C(23)	0.4804(13)	0.0975(7)	0.0707(4)	0.74

Table 6
Selected bond lengths (Å) and angles (°) for **1**

Pd(1)–N(2)	2.111(9)	Pd(1)–N(15)	2.124(8)
Pd(1)–C(16)	1.981(14)	Pd(1)–C(20)	1.992(12)
C(16)–Pd(1)–C(20)	92.5(5)	N(15)–Pd(1)–C(20)	93.2(4)
N(15)–Pd(1)–C(16)	174.3(5)	N(2)–Pd(1)–C(20)	172.6(4)
N(2)–Pd(1)–C(16)	92.1(4)	N(2)–Pd(1)–N(15)	82.5(3)
Pd(1)–N(2)–C(7)	108.8(6)	Pd(1)–N(2)–C(3)	131.0(5)
Pd(1)–N(15)–C(14)	131.5(6)	Pd(1)–N(15)–C(11)	108.7(5)
Pd(1)–C(16)–O(18)	126.7(10)	Pd(1)–C(16)–O(17)	118.2(9)
Pd(1)–C(20)–O(22)	120.6(8)	Pd(1)–C(20)–O(21)	124.4(8)

of the location and orientation of the different groups, but does not give any possibilities to refine the internal geometry of the rigid-bodies determining the possible distortions of the groups. To do that, the refinement of the positions of the individual non-H atom failed, probably because of the exessive numbers of parameters involved in the refinement. In any case, the results obtained is, in our opinion, very satisfactory demostrating that is it possible to solve and refine the structure of relatively complex molecules from X-ray diffraction data.

The molecular structure, with the atom labelling scheme adopted, is shown in Fig. 1. As expected, the Pd(phen)$(CO_2CH_3)_2$ complex displays a square planar coordination (Pd is 0.044(3) Å from the plane through N(2), N(15), C(15) and C(20)). The methoxycarbonyl groups are crystallographically inequivalent, so that the possible internal symmetry of the molecule, observed in the structure of the analogous complex with bipyridine [17], is lost. The Pd(1)–C(16) and Pd(1)–C(20) bond length are not significantly different within the standard uncertainty and are very close to the analogous bond observed in Pd(bipy)$(CO_2CH_3)_2$ (1.989(9) Å) [17]. The same is true for the Pd(1)–N(2) and Pd(1)–N(15) bonds (Table 6)

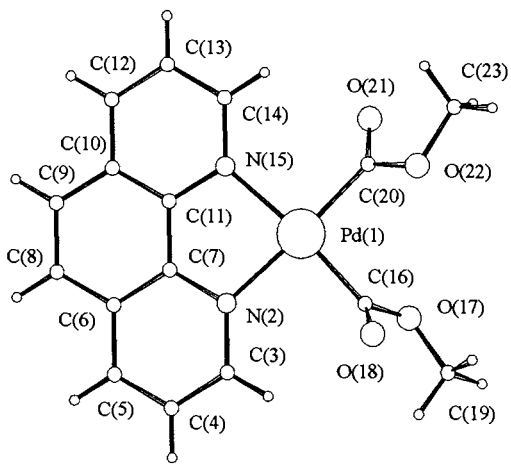

Fig. 1. Molecular structure of **1** with the atomic numbering scheme adopted.

3. Experimental section

3.1. General comments

All reactions were performed under argon atmosphere, using the Schlenk tube techniques. Methanol was distilled under argon from CaH_2 and stored on 4 Å molecular sieves. Sodium methoxide was prepared by reacting sodium metallic with anhydrous methanol. $Pd(L–L)Cl_2$ [21,22] and $PhenHPF_6$ were prepared according to the literature [19]. Phenanthrolines and $Pd(MeCN)_2Cl_2$ were obtained from Fluka and Aldrich, respectively, and used as received. Carbon monoxide was purchased from Rivoira.

^1H- and ^{13}C-NMR spectra were recorded on 200 MHz Brucker Electrospin AG 200 BZH Instrument, while IR spectra were recorded using a Perkin Elmer 1420 Instrument. FAB MS were recorded on a Finnigan MAT M scan Instrument, using *m*-nitrobenzylalcohol as a matrix.

3.2. Preparation of $Pd(phen)(CO_2CH_3)_2$ **1** by exchange reaction

Only the preparation of $Pd(phen)(CO_2CH_3)_2$ by exchange reaction is reported; the complexes **2**, **3**, **4**, **5**, **6** and **7** were prepared in an analogous manner. To a canary yellow solution of 0.2 g (0.526 mmol) of $Pd(bipy)(CO_2CH_3)_2$ in 25 cm^3 methanol were added 0.095 g (0.526 mmol) of phenanthroline under argon. The mixture was vigourously stirred for 20 h at room temperature. After this period, the solution changed to lemon yellow. The solid was filtered and washed with hexane until the bipyridine was completely removed, and, subsequentially, with diethylether, thus removing phenanthroline, eventually still present. The lemon yellow complex was dried under vacuum with a yield of 77%.

^{13}C-NMR (δ ppm, referenced to TMS) of **1:** 50.446; 125.26; 127.24; 129.47; 138.38; 145.19; 151.57; 187.61.

^{13}C-NMR (δ ppm, referenced to TMS) of **3:** 188.36; 151.09; 147.90; 145.17; 128.96; 125.78; 123.27; 50.29; 19.32.

^{13}C-NMR (δ ppm, referenced to TMS) of **6:** 50.15;125.37; 126.00; 128.23; 129.40; 129.93; 130.03; 136.64; 146.82; 151.53; 151.78; 187.96.

3.3. Preparation of $Pd(phen)(CO_2CH_3)_2$ **1** by the sodium methoxide procedure

We report only the preparation of $Pd(phen)(CO_2CH_3)_2$; the complexes **2**, **3**, **4**, **5**, **6** and **7** were similarly prepared. A 11.50 ml solution of sodium methoxide (0.55 M) in methanol (6.32 mmol) was added under argon to a suspension of 1.00 g of $Pd(phen)Cl_2$ (2.80 mmol) and 0.10 g of 1,10-phenanthroline (10% weight in respect to $Pd(phen)Cl_2$) in 25 cm^3 of methanol. The resulting suspension was stirred under CO for 20 h at room temperature. After this time, the solvent was distilled and methylene chloride added; the suspension was filtered on celite to remove the NaCl; then the solution distilled under reduced pressure and the solid dried in vacuo (yield = 83%).

3.4. Preparation of $Pd(phen)(CO_2CH_3)_2$ **1** by the potassium carbonate procedure

We report only the preparation of $Pd(phen)(CO_2CH_3)_2$; the complexes **2**, **3**, **4**, **5**, **6** and **7** were similarly prepared. To a suspension of 1.00 g of $Pd(phen)Cl_2$ (2.80 mmol) and 0.100 g of 1,10-phenanthroline (10% by weight in respect to $Pd(phen)Cl_2$) in 25 cm^3 of methanol was added under argon 0.8 g K_2CO_3 (5.79 mmol). The resulting suspension was stirred under CO for 20 h at room temperature. Work-up of complexes was analogous to the experiment carried out with sodium methoxide. The yield of **1** was 80%.

3.5. Preparation of $Pd(phen)(CO_2CH_3)Cl$ **8** by reaction of $Pd(phen)(CO_2CH_3)_2$ with $CHCl_3$

In a 50 cm^3 three necked round-bottom flask, a solution of 0.15 g of $Pd(phen)(CO_2CH_3)_2$ (0.37 mmol) in 25 cm^3 of chloroform was stirred under argon at room temperature for 20 h. After this time, the solvent was distilled and the residue washed with diethyl ether, and dried under vacuum, to obtain 0.10 g of pink solid (yield = 71%). ^1H-NMR (in CD_2Cl_2 δ referenced to TMS): 9.25 ppm (dd, 1H); 8.87 ppm (dd, 1H); 8.56 ppm (m, 2H); 7.98 ppm (s, 2H); 7.83 ppm (m, 2H); and 3.86 (s, 3H). ^{13}C-NMR (in CD_2Cl_2 δ referenced to TMS): 52.71; 125.69; 126.09;127.36; 127.88; 138.73;138.88; 149.91; 153.07; 187.57. IR (in nujol mull): 1670 and 1030 cm^{-1}. Mass spectrum (FAB): $m/e = 381$ (M + 1).

3.6. Reaction of $Pd(phen)(CO_2CH_3)_2$ with four equivalents of $PhenHPF_6$

In a 50 cm^3 three necked round-bottom flask, under argon and at room temperature, was stirred a suspension of 0.130 g $Pd(phen)(CO_2CH_3)_2$ (0.32 mmol) in 25 cm^3 methanol anhydrous; then, 0.210 g of $PhenHPF_6$ (0.64 mmol) were added. After 20 h, since the reaction mixture appeared unchanged, it was heated at 60°C and another two equivalents of acid $PhenHPF_6$ (0.21 g; 0.64 mmol) were added. After 8 h, the suspension changed to pink and the solid was filtered, washed with diethyl ether and dried in vacuum, thus obtaining 0.48 g of pink solid.

^1H-NMR of the pink residue (in CD_3CN δ referenced to TMS): 9.13 ppm (dd, 4H); 8.96 ppm (dd, 4H); 8.29 ppm (s, 4H); 8.14 ppm (m, 4H). ^1H-NMR ob-

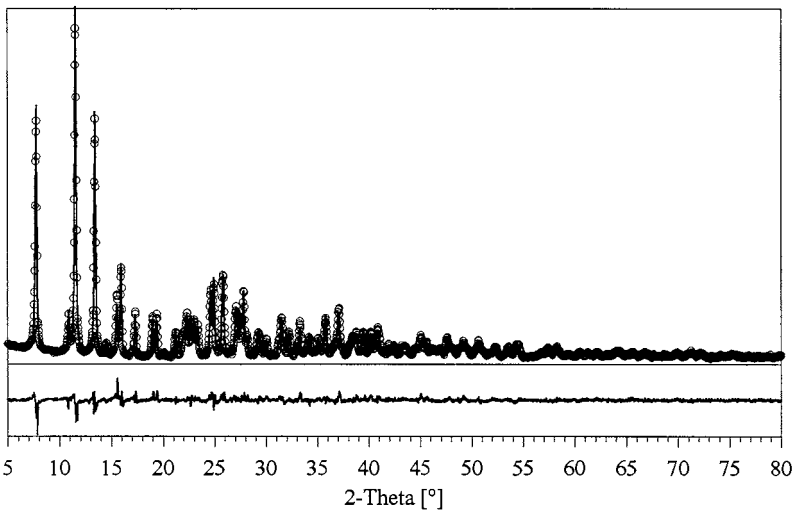

Fig. 2. Experimental (○), calculated (—) and difference (lower) XRD patterns for **1**.

tained by dosing **9:** $PhenHPF_6$: Phen in a molar ratio of 1:2:1 (in CD_3CN δ referenced to TMS): 9.13 ppm (dd, 4H); 8.96 ppm (dd, 4H); 8.29 ppm (s, 4H); 8.14 ppm (m, 4H). IR (in nujol mull): 850 cm^{-1}. Mass spectrum of **9** (FAB) m/e 233. Calc. for $Pd(phen)_2^{++}$: 233.

3.7. Crystal structure of $Pd(phen)(CO_2CH_3)_2$ (1)

X-ray powder diffraction (XRD) data for **1** were collected at 298 K on a Siemens D500 diffractometer, operating in the θ/θ geometry, using Cu–K_α radiation ($\lambda = 1.54178$ Å). Step-scanning procedure, with a step size 0.03° 2θ and 20 s/step accumulation time, was applied over the 5–80° 2θ angular region. Indexing of the pattern was performed with the TREOR-5 program [23] by using the interplanar spacings of the first 50 peaks accurately determined with the routine FIT of the software package DIFFRAC-AT (Siemens). The pattern was fully indexed with an orthorhombic unit cell with dimensions: $a = 8.080(2)$, $b = 16.383(4)$, $c = 22.849(9)$ Å. Inspection of the reflections revealed the systematic extinctions consistent with the space groups *Pbca* (no. 61 International Tables for X-ray Crystallography), that on the basis of the computed crystal density, implies the existence of eight molecules of **1** per unit cell. The centrosymmetric *Pbca* space group was initially chosen on the basis of the computed crystal density for a unit cell containing eight molecules of **1**. The consistency of the indexing was checked with the EXTRA program [24] used for extracting the intensities of the reflections by the full-pattern deconvolution method. A Patterson map was computed from these data allowing the localization of the Pd atom; the successive Fourier and difference Fourier maps were however unsuccessful. For these reasons the solution of the structure was attempted by using the simulated annealing procedure recently applied by Ramprasad et al. for the solution of the structure of $Li_3[Co(CN)_5]\cdot 2DMF$ [25]. The calculations were performed with the Molecular_PD functionality within the Molecular Simulations CATALYSIS software package [26]. Firstly, the fragment Pd(phen) was placed at the center of the unit cell and randomly rototranslated according to a Metropolis Monte Carlo algorithm; at each step, the XRD pattern was simulated and compared with the experimental one. Once the best fit was obtained, two $-CO_2CH_3$ moieties were added to the Pd(phen) fragment to obtain a model of the complex with Pd atom in square planar coordination. Another run of simulated annealing was performed allowing the random rotation of the two methoxycarbonyl groups around the Pd–C bonds. The final model, with residual error index $R_{wp} = 0.21$ was then refined using a revised version [27] of the PREFIN Rietveld program [28]. We chose this package because it allows the refinement of diffraction data in the rigid bodies approximations and the adequate treatment of the peak asymmetry [25], affecting the reflections in the low angles region of the XRD pattern. The refinement involved the rototranslation of four rigid bodies: the Pd atom, the phen ligand and the two methoxycarbonyl moieties. The pseudo-Voigt peak profile function, with refinable gaussian character, was used and the breadth of the reflections as a function of the diffraction angle was modelled with the Caglioti, Paoletti and Ricci equation [29]. The instrumental background was defined by a linear interpolation of points with refinable intensity, while isotropic temperature factors were refined by grouping chemically similar atoms.

In spite of the hard constraints introduced, an excellent reproduction of the experimental XRD pattern was obtained (Fig. 2). It must be pointed out that all the attempts to improve the quality of the fit by refining the position of the each non-H atom failed, probably be-

cause of the excessive number of parameters involved in the refinement.

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