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New palladacyclopentadiene complexes containing an N,P-donor setting. Crystal structure of [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)]

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Abstract

The synthesis of palladacyclopentadiene derivatives with the mixed-donor bidentate ligands *o*-Ph_2**P**C_6H_4–CH=NR (N ^ P) has been achieved. The new complexes of general formula [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=NR)] [R = Me (**1**), Et (**2**), ^{i}Pr (**3**), ^{t}Bu (**4**), NH–Me (**5**)] have been prepared by reaction between the precursor [Pd{C_4(COOMe)$_4$}]$_n$ and the corresponding iminophosphine. The polymer complex [Pd{C_4(COOMe)$_4$}]$_n$ also reacts with pyridazine ($C_4H_4N_2$) to give the insoluble dinuclear complex [Pd{C_4(COOMe)$_4$}(μ-$C_4H_4N_2$)]$_2$ (**6**), which has been successfully employed as precursor in the synthesis of pyridazine-based palladacyclopentadiene complexes. The reaction of **6** with tertiary phosphines yielded complexes containing an N,P-donor setting of formula [Pd{C_4(COOMe)$_4$}($C_4H_4N_2$)(L)] (L = PPh_3 (**7**), PPh_2Me (**8**), P(*p*-$MeOC_6H_4$)$_3$ (**9**), P(*p*-FC_6H_4)$_3$ (**10**)). The new complexes were characterized by partial elemental analyses and spectroscopic methods (IR, ^{1}H, ^{19}F and ^{31}P NMR). The molecular structure of complex **3** has been determined by a single-crystal diffraction study, showing that the iminophosphine acts as chelating ligand with coordination around the palladium atom slightly distorted from the square-planar geometry.

Keywords: Crystal structures; Palladium complexes; Metallocyclic complexes; Iminophosphine complexes

1. Introduction

The chemistry of metallacycles has received growing interest during recent years, as a result of their involvement in catalytic processes and their applications in organic synthesis [1–3]. The cycloaddition of two unsaturated fragments to a metal unit is one of the most useful methods of metallacycle synthesis, since it gives access to relatively complex structures starting from small unsaturated molecules [1]. Particularly, the oxidative cycloaddition of acetylenic esters such as dimethylacetylenedicarboxylate (dmad) to a Ni, Pd and Pt has received much attention [4,5], due in part to its involvement in different oligomerization and co-oligomerization catalytic reactions [6], and also because of the interesting behaviour as precursors in organometallic chemistry of the compounds formed. Thus, the polymer complex, palladacyclopentadiene, [Pd(C_4R_4)]$_n$ (R = COOMe), formed in the reaction of dmad with Pd(dba)$_2$ (dba = dibenzylidenacetone) reacts with a wide range of donor ligands to give soluble discrete molecules [4,5,7,8]. To date, just a few crystal structures of palladacyclopentadiene compounds are known [9]. Other features recently studied are their use as catalysts in the metathesis of enynes [10,11], dimerization of allenyl ketones [12], conversion of alkynes to conjugated dienes [9], and co-cyclotrimerizations of acetylenes with other acetylenes, alkenes and allenes [13–15].

On the other hand, there has been a recent surge of interest in the chemistry of polydentate ligands with both hard and soft donor atoms [16–22]. The metal complexes with N and P donor atoms display a variety

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of coordination modes well beyond those of P–P or N–N ligands [23]. Furthermore, these ligands show a particular behaviour binding soft metal centres such as Pd(II) and Pt(II) that make their complexes good precursors in catalytic processes [24–31]. Thus, it has been found that some complexes with N–P ligands are suitable for palladium-catalyzed allylic alkylation [32], oligomerization of olefins [33,34], homogeneous hydrogenation of double and triple C–C bonds [35] and co-polymerization of CO/olefins [36–38]. Among the most widely studied ligands with these characteristics are the pyridylphosphines and the iminophosphines that we present in this work, from which palladium complexes have been profusely reported [28–30,38–43]. In this sense, we have described in recent work the syntheses of some organometallic derivatives containing iminophosphine ligands, either with an *ortho*-metallated palladium(II) backbone [44] or pentafluorophenyl derivatives of nickel(II) [45] and palladium(II) [46].

Recently, new pyridazine complexes and their use as convenient precursors in organometallic synthesis have been reported [47].Other studies that make pyridazine complexes interesting to us have focused on the ability of this ligand to undergo metallotropic shifts between the two equivalent contiguous N-donor atoms [48,49]. This paper deals with the synthesis of new palladacyclopentadiene complexes containing an N,P-donor setting, made up either of iminophosphine ligands or by means of a pyridazine–tertiary phosphine set.

2. Experimental

2.1. Materials and physical measurements

C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyzer. IR spectra were recorded on a Perkin–Elmer spectrophotometer 16F PC FT–IR, using Nujol mulls between polyethylene sheets. NMR data were recorded on a Bruker AC 200E (^{1}H) or a Varian Unity 300 (^{1}H, ^{19}F, ^{31}P) spectrometer. Mass spectrometric analyses were performed on a Fisons VG Autospec double-focusing spectrometer, operated in positive mode. Ions were produced by fast atom bombardment (FAB) with a beam of 25-Kev Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000.

The palladacyclopentadiene precursor was prepared by the published method [4]. The iminophosphine ligands were prepared according to reported procedures [25], and all the solvents were dried by standard methods before use.

2.2. Preparation of the complexes [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=NR)] [R = Me (**1**), Et (**2**), ^{i}Pr (**3**), ^{t}Bu (**4**), NH–Me (**5**)]

The complexes were obtained by treating [Pd{C_4(COOMe)$_4$}]$_n$ with the corresponding iminophosphine (molar ratio 1:1) in acetone according to the following general method. To an acetone (5 ml) solution of the precursor [Pd{C_4(COOMe)$_4$}]$_n$ (0.07 g, 0.18 mmol) was added the calculated amount of iminophosphine in acetone solution previously prepared. The reaction was stirred at room temperature for 30 min, and then the solvent was partially evaporated under reduced pressure. The addition of diethyl ether caused the formation of yellow solids, which were filtered off, washed with diethyl ether and air-dried. Yellow crystals of the compounds (**1**–**5**) were obtained in high yield by recrystallization from dichloromethane–diethyl ether.

[Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=NMe)] (**1**) was obtained in 84% yield. *Anal*. Calc. for $C_{32}H_{30}NO_8PPd$: C, 55.4; H, 4.4; N, 2.0. Found: C, 55.2; H, 4.4; N, 1.9%. IR (cm^{-1}): 1724, 1692 (C=O str), 1640 (C=N str). ^{1}H NMR ($CDCl_3$): 2.63 (s, 3H, Me), 2.80 (s, 3H, COOMe), 3.45 (s, 3H, COOMe), 3.53 (s, 3H, COOMe), 3.55 (s, 3H, COOMe), 6.78 (m, 1H, arom), 7.42–7.74 (m, 13H, arom), 8.32 (s, 1H, CH=N). ^{31}P NMR ($CDCl_3$): 28.1 (s). FAB MS (positive mode) *m*/*z*: 693 [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=NMe)]$^+$.

[Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=NEt)] (**2**) was obtained in 79% yield. *Anal*. Calc. for $C_{33}H_{32}NO_8PPd$: C, 56.0; H, 4.6; N, 2.0. Found: C, 55.7; H, 4.4; N, 2.2%. IR (cm^{-1}): 1722, 1694 (C=O str), 1640 (C=N str). ^{1}H NMR ($CDCl_3$): 1.00 (t, 3H, CH_3), 2.67 (s, 3H, COOMe), 3.48 (q-sh, 2H, CH_2), 3.53 (s, 6H, COOMe), 3.54 (s, 3H, COOMe), 6.70 (m, 1H, arom), 7.50–7.77 (m, 13H, arom), 8.42 (d, 1H, CH=N; $J_{PH} = 3.0$). ^{31}P NMR ($CDCl_3$): 27.3 (s). FAB MS (positive mode) *m*/*z*: 707 [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=NEt)]$^+$.

[Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**3**) was obtained in 80% yield. *Anal*. Calc. for $C_{34}H_{34}NO_8PPd$: C, 56.6; H, 4.7; N, 1.9. Found: C, 56.3; H, 4.8; N, 1.7%. IR (cm^{-1}): 1718, 1694 (C=O str), 1642 (C=N str). ^{1}H NMR ($CDCl_3$): 1.00 (s-br, 3H, CH_3), 1.22 (s-br, 3H, CH_3), 2.70 (s, 3H, COOMe), 3.52 (s, 3H, COOMe), 3.53 (s, 3H, COOMe), 3.54 (s, 3H, COOMe), 4.28 (m, 1H, CH), 6.67 (m, 1H, arom), 7.47–7.86 (m, 13H, arom), 8.44 (d, 1H, CH=N, $J_{PH} = 3.0$). ^{31}P NMR ($CDCl_3$): 30.9 (s). FAB MS (positive mode) *m*/*z*: 721 [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)]$^+$.

[Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=N^{t}Bu)] (**4**) was obtained in 72% yield. *Anal*. Calc. for $C_{35}H_{36}NO_8PPd$: C, 57.1; H, 4.9; N, 1.9. Found: C, 56.9; H, 4.6; N, 2.1%. IR (cm^{-1}): 1714, 1704 (C=O str), 1622 (C=N str). ^{1}H NMR ($CDCl_3$): 1.16 (s, 3H, CH_3); 1.22 (s-br, 6H, 2CH_3), 2.76 (s, 3H, COOMe), 3.49 (s, 3H, COOMe), 3,51 (s, 3H, COOMe), 3.54 (s, 3H, COOMe), 6.67 (m, 1H, arom), 7.40–7.80 (m, 13H, arom), 8.56 (d, 1H,

CH=N, $J_{PH} = 4.2$). ^{31}P NMR ($CDCl_3$): 28.1 (s). FAB MS (positive mode) m/z: 735 [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=N^{t}Bu)]$^+$.

[Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=NNHMe)] (**5**) was obtained in 74% yield. *Anal*. Calc. for $C_{32}H_{31}N_2O_8$PPd: C, 54.2; H, 4.4; N, 3.9. Found: C, 54.3; H, 4.7; N, 4.1%. IR (cm^{-1}): 1720, 1696 (C=O str), 1630 (C=N str). ^{1}H NMR ($CDCl_3$): 2.63 (s, 3H, COOMe), 2.76 (d, 3H, NMe), 3.52 (s, 3H, COOMe), 3.53 (s, 3H, COOMe), 3.54 (s, 3H, COOMe), 6.70 (m, 1H, arom), 7.04 (q, 1H, NH), 7.29–7.59 (m, 13H, arom), 8.50 (s, 1H, CH=N). ^{31}P NMR ($CDCl_3$): 28.1 (s). FAB MS (positive mode) m/z: 708 [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=NNHMe)]$^+$.

2.3. Preparation of the complex [Pd{C_4(COOMe)$_4$}-(μ-$C_4H_4N_2$)]$_2$($C_4H_4N_2$: pyridazine) (**6**)

Pyridazine (0.055 ml, 0.77 mmol) was added to an acetone solution (10 ml) of the precursor [Pd{C_4(COOMe)$_4$}]$_n$ (0.3 g, 0.77 mmol) and the reaction was stirred at room temperature for 30 min. The white solid precipitated after that time was filtered off, washed with acetone (2 ml) and diethyl ether (5 ml) and air-dried. Yield 85%. *Anal*. Calc. for $C_{32}H_{32}N_4O_{16}$Pd: C, 40.8; H, 3.4; N, 5.9. Found: C, 40.6; H, 3.4; N, 5.9%. IR (cm^{-1}): 1720, 1702 (C=O str), 1560 (pyz). FAB MS (positive mode) m/z: 911 [Pd{C_4(COOMe)$_3$(CO)}(μ-$C_4H_4N_2$)]$_2^+$, 884 [Pd{C_4(COOMe)$_3$}(μ-$C_4H_4N_2$)]$_2^+$ + 1, 884 [Pd$_2${C_4(COOMe)$_4$}$_2$($C_4H_4N_2$)]$^+$ + 2.

2.4. Preparation of the complexes [Pd{C_4(COOMe)$_4$}($C_4H_4N_2$)(L)] [L = PPh_3 (**7**), PPh_2Me (**8**), P(*p*-$MeOC_6H_4$)$_3$ (**9**), P(*p*-FC_6H_4)$_3$ (**10**)]

Compounds **7**–**10** were obtained by reacting stoichiometric amounts (molar ratio 1:2) of complex **6** (0.05 g, 0.053 mmol) and the corresponding phosphine (0.106 mmol) in 5 ml of acetone. After 30 min stirring at boiling temperature, the resulting solutions were concentrated under reduced pressure to half volume. The addition of diethyl ether caused precipitation of the new complexes, which were filtered off and recrystallized of CH_2Cl_2/diethyl ether.

[Pd{C_4(COOMe)$_4$}($C_4H_4N_2$)(PPh_3)] (**7**) was obtained in 70% yield. *Anal*. Calc. for $C_{34}H_{31}N_2O_8$PPd: C, 55.7; H, 4.3; N, 3.8. Found: C, 55.4; H, 4.1; N, 3.9%. IR (cm^{-1}): 1720, 1696 (C=O str), 1570 (pyz). ^{1}H NMR ($CDCl_3$): 2.43 (s, 3H, COOMe), 2.94 (s, 3H, COOMe), 3.48 (s, 3H, COOMe), 3.49 (s, 3H, COOMe), 7.27–7.55 (m, 18H, PPh_3 + pyz), 8.75 (m, 1H, pyz). ^{31}P NMR ($CDCl_3$): 27.9 (s). FAB MS (positive mode) m/z: 732 [Pd{C_4(COOMe)$_4$}($C_4H_4N_2$)(PPh_3)]$^+$.

[Pd{C_4(COOMe)$_4$}($C_4H_4N_2$)(PPh_2Me)] (**8**) was obtained in 67% yield. *Anal*. Calc. for $C_{29}H_{29}N_2O_8$PPd: C, 51.9; H, 4.4; N, 4.2. Found: C, 51.46; H, 4.6; N, 4.6%. IR (cm^{-1}): 1714, 1702 (C=O str), 1572 (pyz). ^{1}H NMR ($CDCl_3$): 2.15 (d, 3H, PPh_2Me, $J_{PH} = 8.4$), 2.77 (s, 3H, COOMe), 2.94 (s, 3H, COOMe), 3.48 (s, 3H, COOMe), 3.50 (s, 3H, COOMe), 7.24–7.42 (m, 11H, PPh_2Me + pyz), 7.51 (m, 2H, pyz), 8.81 (m, 1H, pyz). ^{31}P NMR ($CDCl_3$): 9.4 (s). FAB MS (positive mode) m/z: 670 [Pd{C_4(COOMe)$_4$}($C_4H_4N_2$)(PPh_2Me)]$^+$.

[Pd{C_4(COOMe)$_4$}($C_4H_4N_2$){P(*p*-$MeOC_6H_4$)$_3$}] (**9**) was obtained in 76% yield. *Anal*. Calc. for $C_{37}H_{37}N_2O_{11}$PPd: C, 54.0; H, 4.5; N, 3.4. Found: C, 53.9; H, 4.7; N, 3.7%. IR (cm^{-1}): 1732, 1704 (C=O str), 1568 (pyz). ^{1}H NMR ($CDCl_3$): 2.58 (s, 3H, COOMe), 3.07 (s, 3H, COOMe), 3.60 (s, 6H, COOMe), 3.78 (s, 9H, P(*p*-$MeOC_6H_4$)$_3$), 7.26–7.43 (m, 15H, P(*p*-$MeOC_6H_4$)$_3$ + pyz), 8.67 (m, 1H, pyz). ^{31}P NMR ($CDCl_3$): 27.9 (s). FAB MS (positive mode) m/z: 822 [Pd{C_4(COOMe)$_4$}($C_4H_4N_2$){P(*p*-$MeOC_6H_4$)$_3$}]$^+$.

[Pd{C_4(COOMe)$_4$}($C_4H_4N_2$){P(*p*-FC_6H_4)$_3$}] (**10**) was obtained in 77% yield. *Anal*. Calc. for $C_{34}H_{28}F_3N_2O_8$PPd: C, 51.9; H, 3.6; N, 3.6. Found: C, 51.8; H, 3.9; N, 3.4%. IR (cm^{-1}): 1734, 1702 (C=O str), 1568 (pyz). ^{1}H NMR ($CDCl_3$): 2.57 (s, 3H, COOMe), 2.98 (s, 3H, COOMe), 3.51 (s-br, 6H, COOMe), 7.14 (m, 6H, P(*p*-FC_6H_4)$_3$), 7.52–7.62 (m, 9H, P(*p*-FC_6H_4)$_3$ + pyz), 8.85 (m, 1H, pyz). ^{31}P NMR ($CDCl_3$): 27.9 (s). FAB MS (positive mode) m/z: 786 [Pd{C_4(COOMe)$_4$}-($C_4H_4N_2$){P(*p*-FC_6H_4)$_3$}]$^+$.

2.5. Crystal structure determination of [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**3**)

X-ray diffraction experiment was carried out on a Siemens P4 diffractometer at −100 °C. The crystallographic data are shown in Table 1. Data were collected using a single crystal of dimensions 0.4 × 0.3 × 0.2 mm. Accurate cell parameters were determined by least-squares fitting of 55 reflections. The scan method was ω with the range of *hkl* ($-13 \le h \le 4$, $-16 \le k \le 16$, $-24 \le l \le 24$ corresponding to $2\Theta_{max} = 50°$. Two molecules were found in the asymmetrical unit, the structure was solved by the Patterson method and refined anisotropically on F^2 [50]. Hydrogen atoms were introduced in calculated positions. The final R factor was 0.0366 $R_w = 0.0754$ where $w = 1[\sigma^2(F_o^2) + (0.0380P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$ over 7958 observed reflections [$I > 2\sigma(I)$].

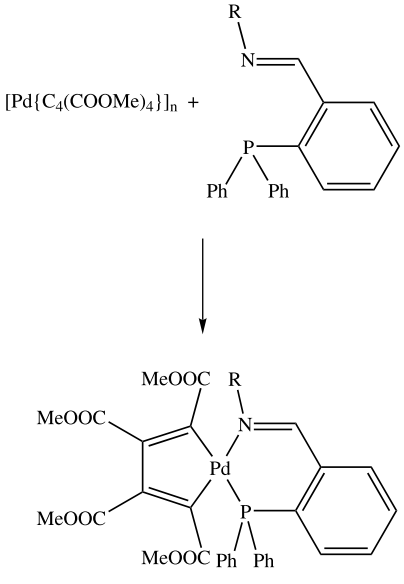
3. Results and discussion

3.1. Iminophosphine complexes

In acetone, [Pd{C_4(COOMe)$_4$}]$_n$, reacts with iminophosphines (molar ratio 1:1) under mild conditions to

Table 1
Crystal data and structure refinement for [Pd{C_4(COOMe)$_4$}(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)]

Empirical formula	$C_{34}H_{34}NO_8PPd$
Formula weight	721.99
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.8930(10)
b (Å)	13.8110(10)
c (Å)	20.235(2)
α (°)	82.918(6)
β (°)	88.618(8)
γ (°)	79.864(8)
V (Å^3)	3246.8(5)
Z	4
D_{calc} (Mg m^{-3})	1.477
Absorption coefficient (mm^{-1})	0.673
F(000)	1480
Crystal size (mm)	0.20 × 0.30 × 0.40
θ Range for data collection (°)	3.02–25.00
Index ranges	$-13 \le h \le 4$, $-16 \le k \le 16$, $-24 \le l \le 24$
Reflections collected	16 613
Independent reflections	11 401 [$R_{int} = 0.0402$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11 401/0/811
Goodness-of-fit on F^2	0.888
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0366$, $wR_2 = 0.0754$
R indices (all data)	$R_1 = 0.0632$, $wR_2 = 0.0819$
Largest difference peak and hole (e Å^{-3})	0.563 and −0.716



R : Me(**1**), Et(**2**), ^{i}Pr (**3**), ^{t}Bu (**4**), HNMe (**5**)

Scheme 1.

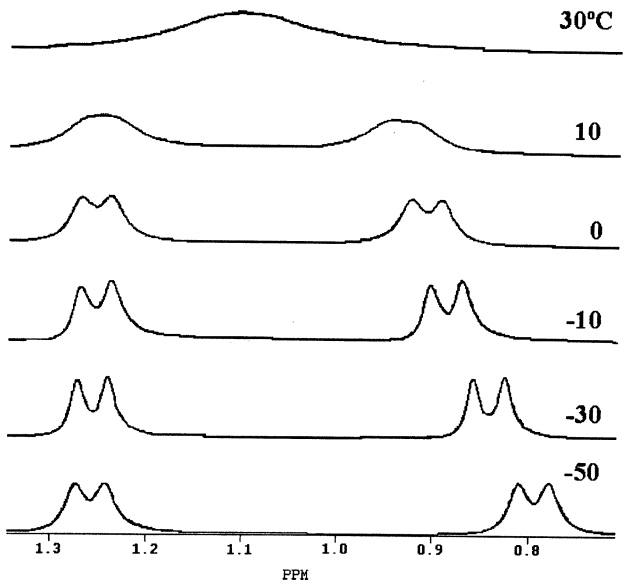


Fig. 1. Variable-temperature ^{1}H NMR spectrum of **3** (methyl groups of the isopropyl fragment).

give the corresponding neutral square-planar complexes [Pd{C_4(COOMe)$_4$}(N^P)] shown in Scheme 1.

The new palladium complexes **1**–**5** are air-stable, yellow solids that show negligible molar conductance. The IR spectra of these complexes show two very strong bands [ν(CO)] at 1705 ± 20 cm^{-1} characteristic of the carboxylate groups [4] and a band in the 1650–1600 cm^{-1} region attributed to the C=N stretching vibration of the iminophosphine, shifted to lower frequencies than in the free ligands [44].

The ^{1}H NMR spectra show the corresponding aromatic signals of the neutral ligands, with a typical iminic singlet or doublet resonance in the 8–8.5 ppm region, depending on the strength of the coupling to the phosphorus atom [25]. The most characteristic chemical shifts of the compounds are the ones that correspond to the methoxycarbonyl groups, which act as a probe for the compounds' geometry, i.e. symmetric complexes show two signals and asymmetric show four resonances [9]. The signals of one of the pairs of methoxycarbonyl groups (β-positions relative to palladium) are relatively insensitive to the nature of donor atoms in *trans*, and occurred in the asymmetric iminophosphine complexes as two resonance signals between 3.5 and 3.6 ppm. The higher field resonances are then due to the methoxycarbonyl on the α-carbons, and the magnitude of the shift is roughly related to the donor atom placed in *trans* position [4]. Thus, the methoxycarbonyl group *trans* to iminic nitrogen (between 3.45 and 3.52 ppm) occurred to higher field that the methoxycarbonyl *trans* to phosphorus (between 2.70 and 2.80 ppm). An outstanding feature was found in ^{1}H NMR spectrum of complex **3**. It exhibited two broad signals for the methyl groups of the isopropyl fragment at room temperature, suggesting

hindered rotation of the $(CH_3)_2CH$-substituent around the N–C bond. Fig. 1 shows the spectra of complex **3** as a function of temperature. At 0 °C and lower temperatures the rotation is sufficiently sluggish to make the methyl groups distinguishable by their chemical shifts, and two 1:1 doublet resonances are observed. As the temperature is raised the signals broaden and finally coalescence in one resonance at 30 °C.

The ^{31}P NMR spectra of the new iminophosphine complexes consist of singlets with chemical shifts in the range observed for related organometallic Pd(II) compounds [44,46].

The proposed formulae of the new complexes are also confirmed by FAB mass spectrometry. The positive FAB MS data of the complexes with the m/z values for the observed fragments are listed in Table 2. The spectra of **1**–**5** show the peaks of the molecular ion $[Pd\{C_4(COOMe)_4\}(N\,\hat{}\,P)]^+$ and additional peaks to $[Pd\{C_4(COOMe)_3(CO)\}(N\,\hat{}\,P)]^+$ $(M^+ - MeO)$, $[Pd\{C_4(COOMe)_3\}(N\,\hat{}\,P)]^+$ $(M^+ - COOMe)$ and $[Pd(N\,\hat{}\,P)]^+$ $(M^+ - \{C_4(COOMe)_4\})$.

The crystal structure of **3** is shown in Fig. 2, and selected bond and angles are presented in Table 3. The coordination around palladium is tetrahedrically distorted from the ideal square-planar geometry, with a mean angle (for the two molecules in the asymmetrical

Table 2
FAB mass spectrometric data for the palladium(II) complexes

	Ions (m/z)
1	$[Pd\{C_4(COOMe)_4\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NMe)]^+$ (693)
	$[Pd\{C_4(COOMe)_3(CO)\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NMe)]^+$ (662)
	$[Pd\{C_4(COOMe)_3\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NMe)]^+$ (634)
	$[Pd(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NMe)]^+$ (409)
2	$[Pd\{C_4(COOMe)_4\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NEt)]^+$ (707)
	$[Pd\{C_4(COOMe)_3(CO_2)\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NEt)]^+$ (692)
	$[Pd\{C_4(COOMe)_3\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NEt)]^+$ (648)
	$[Pd(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NEt)]^+$ (423)
3	$[Pd\{C_4(COOMe)_4\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}N^iPr)]^+$ (721)
	$[Pd\{C_4(COOMe)_3(CO)\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}N^iPr)]^+$ (690)
	$[Pd\{C_4(COOMe)_3\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}N^iPr)]^+$ (662)
	$[Pd(o\text{-}Ph_2PC_6H_4\text{–}CH{=}N^iPr)]^+$ (437)
4	$[Pd\{C_4(COOMe)_4\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}N^tBu)]^+$ (735)
	$[Pd\{C_4(COOMe)_3(CO)\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}N^tBu)]^+$ (704)
	$[Pd\{C_4(COOMe)_3\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}N^tBu)]^+$ (676)
	$[Pd(o\text{-}Ph_2PC_6H_4\text{–}CH{=}N^tBu)]^+$ (451)
5	$[Pd\{C_4(COOMe)_4\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NNHMe)]^+$ (708)
	$[Pd\{C_4(COOMe)_3(CO)\}(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NNHMe)]^+$ (677)
	$[Pd(o\text{-}Ph_2PC_6H_4\text{–}CH{=}NNHMe)]^+$ (423)
6	$[Pd\{C_4(COOMe)_3(CO)\}(\mu\text{-}C_4H_4N_2)]_2^+$ (911)
	$[Pd\{C_4(COOMe)_3\}(\mu\text{-}C_4H_4N_2)]_2^+ + 1$ (884)
	$[Pd_2\{C_4(COOMe)_4\}_2(C_4H_4N_2)]^+ + 2$ (884)
	$[Pd_2\{C_4(COOMe)_3\}_2(C_4H_4N_2)]^+$ (803)
7	$[Pd\{C_4(COOMe)_4\}(C_4H_4N_2)(PPh_3)]^+$ (732)
	$[Pd\{C_4(COOMe)_4\}(PPh_3)]^+$ (652),
	$[Pd\{C_4(COOMe)_3(CO)\}(PPh_3)]^+$ (652),
	$[Pd\{C_4(COOMe)_3\}(PPh_3)]^+$ (593), $[Pd(PPh_3)]$ (368)
8	$[Pd\{C_4(COOMe)_4\}(C_4H_4N_2)(PMePh_2)]^+$ (670)
	$[Pd\{C_4(COOMe)_3(CO)\}(C_4H_4N_2)(PMePh_2)]^+$ (639)
	$[Pd\{C_4(COOMe)_4\}(PMePh_2)]^+$ (590),
	$[Pd\{C_4(COOMe)_3(CO)\}(PMePh_2)]^+$ (531),
	$[Pd\{C_4(COOMe)_3\}(PMePh_2)]^+$ (531), $[Pd(PMePh_2)]$ (368)
9	$[Pd\{C_4(COOMe)_4\}(C_4H_4N_2)\{P(p\text{-}MeO\text{–}C_6H_4)_3\}]^+$ (810)?
	$[Pd\{C_4(COOMe)_4\}\{P(p\text{-}MeO\text{–}C_6H_4)_3\}]^+$ (743),
	$[Pd\{P(p\text{-}MeO\text{–}C_6H_4)_3\}]^+$ (459)
10	$[Pd\{C_4(COOMe)_4\}(C_4H_4N_2)\{P(p\text{-}FC_6H_4)_3\}]^+$ (786)
	$[Pd\{C_4(COOMe)_3(CO)\}(C_4H_4N_2)\{P(p\text{-}FC_6H_4)_3\}]^+$ (755)
	$[Pd\{C_4(COOMe)_4\}\{P(p\text{-}FC_6H_4)_3\}]^+$ (706)
	$[Pd\{C_4(COOMe)_3(CO)\}\{P(p\text{-}FC_6H_4)_3\}]^+$ (675)
	$[Pd\{C_4(COOMe)_3\}\{P(p\text{-}FC_6H_4)_3\}]^+$ (647), $[Pd\{P(p\text{-}FC_6H_4)_3\}]^+$ (422)

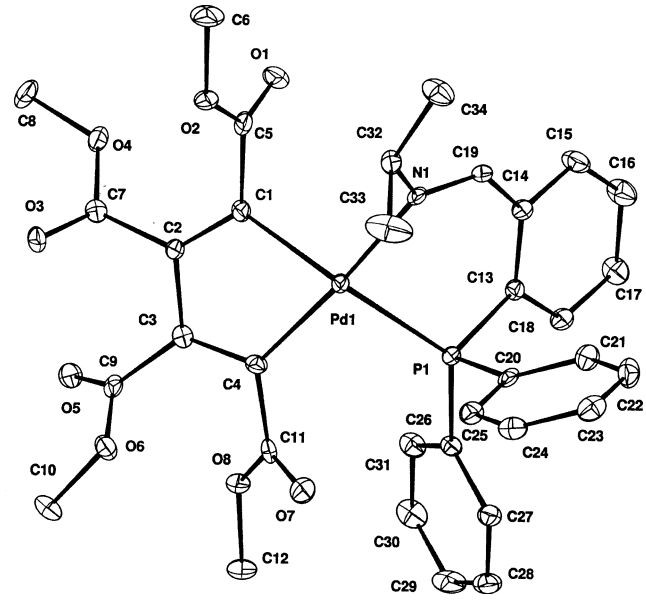


Fig. 2. ORTEP diagram of one of the two independent molecules present in the asymmetric unit of **3**.

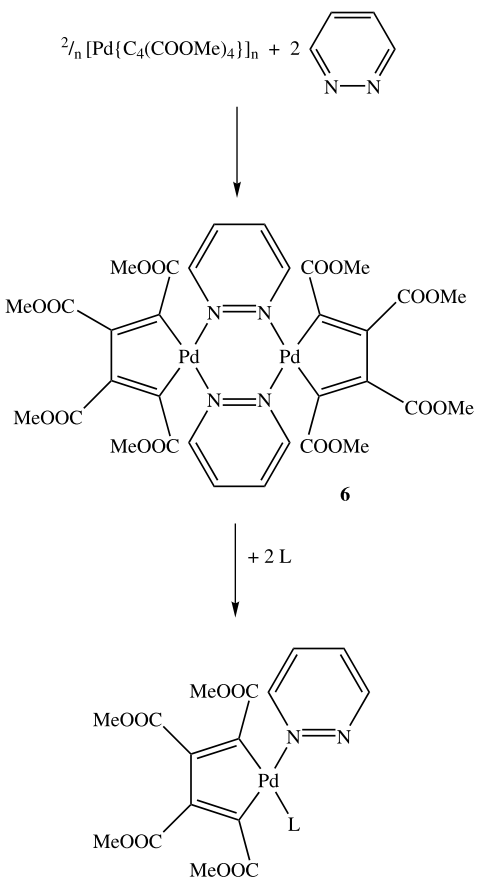
Table 3
Selected bond lengths (Å) and angles (°) for complex **3**

Pd(1)–C(4)	2.024(4)
Pd(1)–C(1)	2.084(4)
Pd(1)–N(1)	2.116(3)
Pd(1)–P(1)	2.2898(10)
C(4)–Pd(1)–C(1)	79.53(15)
C(4)–Pd(1)–N(1)	170.38(14)
C(1)–Pd(1)–N(1)	96.27(13)
C(4)–Pd(1)–P(1)	101.15(11)
C(1)–Pd(1)–P(1)	167.80(11)
N(1)–Pd(1)–P(1)	84.80(8)
Pd(2)–C(38)	2.029(4)
Pd(2)–C(35)	2.077(4)
Pd(2)–N(2)	2.113(3)
Pd(2)–P(2)	2.2914(10)
C(38)–Pd(2)–C(35)	79.43(15)
C(38)–Pd(2)–N(2)	170.38(14)
C(35)–Pd(2)–N(2)	95.44(13)
C(38)–Pd(2)–P(2)	101.51(11)
C(35)–Pd(2)–P(2)	169.37(11)
N(2)–Pd(2)–P(2)	85.04(9)

unit) between the C(1)–Pd–C(4) and N(1)–Pd–P(1) planes of 15.0(1)°, with the N and P atoms of the iminophosphine ligand lying in a different side in relation to the C(1)–Pd–C(4) plane (0.31 and 0.45 Å, respectively). Regarding the chelate rings, the palladacycle is plane, and the six-membered one of the iminophosphine adopts an envelope conformation similar to that described in other related complexes [44]. The COOMe groups are obviously planar and present an alternate conformation regarding the chelate ring. Thus, if one OMe lies in a side of the plane, then the next group has the O in this side. The mean angle between the COOMe and the chelate plane is 53.3(1)°. The only significant difference between the two molecules present in the asymmetric unit is the angle between the COOMe group on the C(2) atom and the chelate plane (38.3 and 46.5°, respectively).

3.2. Pyridazine complexes

The addition of pyridazine to a solution of the $[Pd\{C_4(COOMe)_4\}]_n$ in acetone (molar ratio 1:1) leads to the formation of the insoluble compound $[Pd\{C_4(COOMe)_4\}(\mu\text{-}C_4H_4N_2)]_2$ (**6**) (Scheme 2). When a Pd:ligand mol ratio of 1:2 was used, the same result was obtained. The IR spectrum of **6** shows the characteristic absorptions of methoxycarbonyl groups and a band around 1560 cm^{-1} attributed to the pyridazine ligand. The above-mentioned insolubility of the new compound prevented the acquisition of good-quality NMR spectra, although further evidence for its dinuclearity comes from the FAB MS spectrometry (Table 2). This complex reacts with tertiary phosphines (molar ratio 1:2) in acetone to give the soluble asymmetric complexes of general formula $[Pd\{C_4(COOMe)_4\}(C_4H_4N_2)(L)]$ (**7**–**10**). The presence of pyridazine in the mononuclear complexes is confirmed by ^1H NMR spectroscopy. The spectra show the characteristic signals of the methoxycarbonyl groups of the asymmetric complexes, and the resonance signals corresponding to the pyridazine ligand. The low field signal observed at $\delta \sim 8.7$ is assigned to the H6 atom of monodentate pyridazine [47]. The FAB MS data of the complexes are listed in Table 2. Spectra of the new compounds show a similar pattern of fragmentation which includes peaks of the molecular ions, $[Pd\{C_4(COOMe)_4\}(C_4H_4N_2)(L)]^+$, as well as the same behaviour concerning the $\{C_4(COOMe)_4\}$ ligand that was observed for iminophosphine complexes **1**–**5**.



Scheme 2.

4. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 163514. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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