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COMPLEXES OF FUNCTIONAL PHOSPHINES

IX *. PALLADIUM AND RHODIUM COMPLEXES WITH $[R_2PCH_2CO_2]^-$ (R = Ph, c-C_6H_{11}) LIGANDS. CRYSTAL AND MOLECULAR STRUCTURE OF $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH_2C(O)O\}]$

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Summary

The complexes $[(\eta^5\text{-}C_5Me_5)RhCl\{Ph_2PCH_2C(O)O\}]$ (1), $[o\text{-}C_6H_4CH_2NMe_2)\text{-}Pd\{Ph_2PCH_2C(O)O\}]$ (2), $[(C_{10}H_8N)Pd\{Ph_2PCH_2C(O)O\}]$ (3), $[(o\text{-}C_6H_4CH_2\text{-}NMe_2)Pd\{Cy_2PCH_2C(O)O\}]$ (4), and $[cis\text{-}Pd\{Ph_2PCH_2C(O)O\}_2]$ (5), in which the carboxylate ligand $R_2PCH_2COO^-$ (R = Ph, Cy) behaves as a (*P*,*O*) chelate have been prepared: e.g. by the reaction of Ph_2PCH_2COONa with the appropriate chloro complex. Complexes **2** and **4** may also be obtained by treatment of $[(o\text{-}C_6H_4CH_2\text{-}NMe_2)Pd\{R_2PCHC(O)OEt\}]$ with H_2O. Complex **2** has been studied by X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/n$ with *a* 8.774(9), *b* 17.823(3), *c* 13.969(14) Å, β 97.37(5), *V* 2166.6(6) $Å^3$ and $Z = 4$. The structure was solved and refined to $R = 0.023$ and $R_w = 0.032$. The palladium is complexed by two chelating ligands whose bite angles are 83.3(1)° for PPdO and 82.7(2)° for NPdC. The methylene carbon atoms induce a non-planar geometry within these ligands, with C(13) and C(17) displaced 0.395(4) and 0.353(4) Å, respectively, from the least-squares planes defined by each metallocycle.

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* For part VIII see ref. 1.

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Introduction

It is well known that the properties of transition metal complexes containing PR_3 (R = alkyl, phenyl) ligands may be profoundly modified by the introduction of a donor oxygen atom into one of the substituents of the tertiary phosphine [2]. In some cases the oxygen atom is capable of interacting with the transition metal, thus stabilizing the metal centre by chelation [3,4]; in others, this interaction does not occur in the ground state but can stabilize a polar transition state. Such anchimeric assistance has been observed by Miller and Shaw [5] in the oxidative addition reactions of *trans*-$[Ir(Cl)CO(Me_2PC_6H_4OMe\text{-}2)_2]$. It is also notable that a number of complexes containing chelating (P,O) ligands have been shown to be very good hydrogenation [6] and polymerisation catalysts [7]. In this paper we describe the synthesis and characterization of new palladium and rhodium complexes containing the ligand diphenyl- (or dicyclohexyl-)-phosphino acetate ($R_2PCH_2COO^-$), and present the crystal structure of $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH_2C(O)O\}]$.

Experimental

Reagents and physical measurements

Experiments were carried out under dry argon. Solvents were dried and distilled prior to use. Elemental analyses were performed by the Service Central de Microanalyses du CNRS. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin–Elmer 398 spectrophotometer as KBr pellets. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 200 and 81 MHz respectively on a Bruker WP 200 SY instrument. ^1H and ^{31}P chemical shifts are given relative to external $(CH_3)_4Si$ and H_3PO_4, respectively; positive sign denotes a shift downfield from the reference. Mass spectra were measured on a Thompson THN 208 mass spectrometer, CI, CH_4, 70 eV, 8 kV by R. Hubert (Université Louis Pasteur). Ph_2PCH_2COONa and $Cy_2PCH_2C(O)OEt$ [8], $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ [9], $[(o\text{-}C_6H_4CH_2NMe_2)Pd(\mu\text{-}Cl)]_2$ [10], $\{(C_{10}H_8N)Pd(\mu\text{-}Cl)]_2$ [11], $[(o\text{-}C_6H_4CH_2NMe_2)Pd(Ph_2PCHC(O)OEt]$ [4,12] and $[PdCl_2(PhCN)_2]$ [13] were prepared according to literature methods. $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Cy_2PCHC(O)OEt\}]$ was prepared in nearly quantitative yield by treating $[(o\text{-}C_6H_4CH_2NMe_2)PdCl\{Cy_2PCH_2C(O)OEt\}]$ with NaH in THF. The solution was filtered and evaporated to dryness in vacuo to leave the product as a hygroscopic powder.

$[(\eta^5\text{-}C_5Me_5)RhCl\{Ph_2PCH_2C(O)O\}]$ (1)

0.213 g (0.8 mmol) of solid Ph_2PCH_2COONa was added to a solution of 0.247 g (0.4 mmol) of $[(\eta^5\text{-}C_5Me_5)Rh(Cl)(\mu\text{-}Cl)]_2$ in MeOH (20 ml). After 12 h stirring, the suspension was filtered and the filtrate was evaporated to dryness in vacuo to leave an orange powder, which was recrystallized from dichloromethane/pentane: yield 0.363 g (88%); m.p. 237°C dec. Anal. Found: C, 55.63; H, 5.28. $C_{24}H_{27}ClO_2PRh$ calcd.: C, 55.78; H, 5.27%. IR (KBr): $\nu(C{=}O)$ 1642(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.57 (d, 15H, C_5Me_5, $^3J(RhH)$ 14 Hz), 3.22 and 3.47 (ABXY pattern (X = P, Y = Rh), 2H, PCH_2, $^2J(H_AH_B)$ 16.0 Hz, $^2J(H_AP)$ 12.7 Hz, $^2J(H_BP)$ 10.3 Hz, $^3J(H_ARh)$ 0.9 Hz, $^2J(H_BRh) \simeq 0$ Hz), 7.2–7.7 ppm (10H, aromatic H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.9 ppm (d, $^1J(RhP)$ 134 Hz). Mass spectrum (CI): m/e 517 ($M^+ + 1$, 50%), 481 ($M^+ + 1 - HCl$).

[(o-$C_6H_4CH_2NMe_2$)Pd{$Ph_2PCH_2C(O)O$}] (2)

To a stirred solution of [(*o*-$C_6H_4CH_2NMe_2$)Pd(μ-Cl)]$_2$ (0.226 g, 0.5 mmol) in CH_2Cl_2 (10 ml) was added solid Ph_2PCH_2COONa (0.307 g, 1.15 mmol). After 12 h stirring, the white suspension was filtered to remove NaCl, the yellow filtrate was concentrated to ca. 10 ml, and pentane was added. Storage at -20°C gave white air stable crystals of **2**: yield 0.440 g (91%); m.p. 205°C. Anal. Found: C, 56.94; H, 4.87. $C_{23}H_{24}NO_2PPd$ calcd.: C, 57.10; H, 5.00%. IR (KBr): ν(C=O) 1635(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.87 (d, 6H, $N(CH_3)_2$, ^4J(PH) 2.5 Hz), 3.47 (d, 2H, PCH_2, ^2J(PH) 11.1 Hz), 3.98 (d, 2H, NCH_2, ^4J(PH) 1.8 Hz), 6.4–7.6 (14H, aromatic H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.3 (s) ppm.

[($C_{10}H_8N$)Pd{$Ph_2PCH_2(C(O)O$}] (3)

To a stirred solution of [($C_{10}H_8N$)Pd(μ-Cl)]$_2$ (0.200 g, 0.35 mmol) in CH_2Cl_2 (20 ml) was added solid Ph_2PCH_2COONa (0.190 g, 0.72 mmol). After 12 h the white suspension was filtered and the yellow filtrate was concentrated to ca. 10 ml and pentane was added. Storage at -20°C gave **3** as a pale yellow powder: yield 0.293 g (85%); m.p. 175°C dec. Anal. Found: C, 58.30; H, 3.81. $C_{24}H_{20}NO_2PPd$ calcd.: C, 58.61; H, 4.10%. IR (KBr): ν(C=O) 1622(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.20 (d, 2H, CH_2Pd, ^3J(PH) 3.0 Hz), 3.58 (d, 2H, PCH_2, ^2J(PH) 11.4 Hz), 7.42–8.35 (16H, aromatic H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 16.5 (s) ppm.

[(o-$C_6H_4CH_2NMe_2$)Pd{$Cy_2PCH_2C(O)O$}] (4)

To a stirred suspension of [(*o*-$C_6H_4CH_2NMe_2$)Pd{$Cy_2PCHC(O)OC_2H_5$}] (0.262 g, 0.5 mmol) in THF (15 ml) was added 1 ml of water. After 1 h stirring, the yellow solution was filtered and the solvent was removed in vacuo. Recrystallisation from THF/pentane afforded white crystals of **4**: yield 0.248 g (90%), m.p. 150°C dec. Anal. Found: C, 55.51; H, 7.27. $C_{23}H_{36}NO_2PPd$ calcd.: C, 55.70; H, 7.32%. IR (KBr): ν(C=O) 1627(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.08–2.10 (22H, cyclohexyl H), 2.69 (d, 6H, $N(CH_3)_2$, ^4J(PH) 2.5 Hz), 2.69 (d, 2H, PCH_2, ^2J(PH) 10.1 Hz), 3.86 (d, 2H, NCH_2, ^4J(PH) 1.9 Hz), 6.74–7.07 (4H, aromatic H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 31.3 ppm.

[cis-Pd{$Ph_2PCH_2C(O)O$}$_2$] (5)

To a stirred solution of [$PdCl_2(PhCN)_2$] (0.383 g, 1 mmol) in CH_2Cl_2 (30 ml) was added a suspension of Ph_2PCH_2COONa (0.532 g, 2 mmol) in CH_2Cl_2 (10 ml). After 4 h the white suspension was filtered, the pale yellow solution was concentrated to ca. 10 ml, and pentane was added. Storage at -20°C afforded pale yellow crystals of **5**: yield 0.255 g (43%), m.p. 177°C. Anal. Found: C, 56.53; H, 3.94. $C_{28}H_{24}O_4P_2Pd$ calcd.: C, 56.73; H, 4.08%. IR (KBr): ν(C=O) 1640(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.57 (d, 4H, PCH_2, ^2J(PH) 12.6 Hz), 7.24–7.50 (20H, aromatic H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 13.2 (s) ppm.

X-ray data collection and structure determination of ***2***

Cell constants and other pertinent data are listed in Table 1. Precise lattice parameters were obtained by standard Enraf–Nonius least-squares methods using 25 carefully selected reflexions. Intensity data were collected on an automated four-circle diffractometer. No intensity decay was observed during the data collection period.

For all subsequent computations the Enraf–Nonius SDP package was used [14].

TABLE 1

CRYSTAL DATA AND DATA COLLECTION PARAMETERS OF $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH_2C(O)O\}]$ (2)

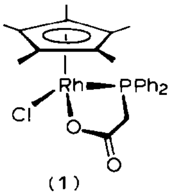
Formula	$PdNO_2PC_{23}H_{24}$
M_r	483.83
Crystal system	monoclinic
a, Å	8.774(9)
b, Å	17.823(3)
c, Å	13.969(14)
β deg	97.37(5)
V, Å^3	2166.6
Z	4
ρ calc.	1.493
Crystal dimension, mm	$0.22 \times 0.10 \times 0.08$
Space group	$P2_1/n$
$F(000)$	984
Diffractometer	Nonius CAD4
Radiation	Mo-K_α (graphite monochromator)
Linear abs coeff, cm^{-1}	9.40
Scan type	$\theta/2\theta$
Scan range, deg	$1+0.35\ \mathrm{tg}\theta$
θ limits, deg	1–23
no of data collected	3254
Unique data used	2157 ($I > 3\sigma(I)$)
R	0.023
R_w	0.032
Std error observn of unit weight	0.807
fudge factor	0.07

Intensities were corrected for Lorentz and polarization effects. Absorption corrections were omitted in view of the low linear absorption coefficient.

The crystal structure was solved by using MULTAN [15] and refined by full matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in their calculated positions in the structure factor calculations but not refined (C–H 0.95 Å; B_H 4.0 Å^2). The final difference map showed no significant maxima. Refinement results are given in Table 1. Final positional parameters and their estimated standard deviations are given in Table 2. Anisotropic thermal parameters for all non-hydrogen atoms and lists of observed and calculated structures factors are available on request (from D.G.).

Results and discussion

Reaction of two equivalents of Ph_2PCH_2COONa with $[Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ yielded the orange complex $[(\eta^5\text{-}C_5Me_5)Rh(Cl)\{Ph_2PCH_2C(O)O\}]$ (**1**) (see eq. 1). Its

$[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ + 2 Ph_2PCH_2COONa ⟶  (1)

(1)

TABLE 2

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR [(o-$C_6H_4CH_2NMe_2$)Pd{$Ph_2PCH_2C(O)O$}] (2)

Atom	x	y	z	B (Å^2) [a]
Pd	0.69517(3)	0.03016(1)	0.36452(2)	2.594(5)
P	0.8001(1)	−0.07197(5)	0.30913(6)	2.74(2)
O(1)	0.7863(3)	−0.0138(1)	0.5000(2)	3.53(5)
O(2)	0.9121(4)	−0.1053(2)	0.5827(2)	5.73(8)
N	0.6003(3)	0.1256(2)	0.4264(2)	3.08(6)
C(1)	0.9227(4)	−0.0673(2)	0.2135(3)	3.09(8)
C(2)	1.0409(5)	−0.0153(3)	0.2229(3)	4.8(1)
C(3)	1.1390(5)	−0.0117(3)	0.1523(4)	6.3(1)
C(4)	1.1164(6)	−0.0573(3)	0.0734(3)	6.7(1)
C(5)	0.9991(6)	−0.1080(3)	0.0643(3)	6.0(1)
C(6)	0.9024(5)	−0.1135(2)	0.1338(3)	4.49(9)
C(7)	0.6673(4)	−0.1492(2)	0.2804(3)	3.24(8)
C(8)	0.7012(5)	−0.2222(2)	0.3100(4)	5.3(1)
C(9)	0.5965(6)	−0.2786(2)	0.2868(4)	6.5(1)
C(10)	0.4593(5)	−0.2649(3)	0.2343(4)	6.2(1)
C(11)	0.4219(6)	−0.1926(3)	0.2065(4)	7.2(1)
C(12)	0.5234(6)	−0.1350(3)	0.2300(3)	5.4(1)
C(13)	0.9312(4)	−0.0993(2)	0.4152(3)	3.60(8)
C(14)	0.8724(4)	−0.0724(2)	0.5072(3)	3.50(8)
C(15)	0.5613(5)	0.1132(3)	0.5250(3)	4.8(1)
C(16)	0.7140(5)	0.1864(2)	0.4296(3)	4.03(9)
C(17)	0.4615(4)	0.1462(2)	0.3589(3)	4.26(9)
C(18)	0.4919(4)	0.1329(2)	0.2574(3)	3.58(8)
C(19)	0.5948(4)	0.0753(2)	0.2421(3)	3.02(7)
C(20)	0.6150(5)	0.0592(2)	0.1467(3)	4.07(9)
C(21)	0.5370(5)	0.0992(3)	0.0698(3)	4.9(1)
C(22)	0.4407(5)	0.1567(3)	0.0871(3)	5.4(1)
C(23)	0.4168(5)	0.1739(3)	0.1802(3)	4.6(1)

[a] The values for these anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3\ [a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab\cos\gamma B_{1,2} + ac\cos\beta B_{1,3} + bc\cos\alpha B_{2,3}]$.

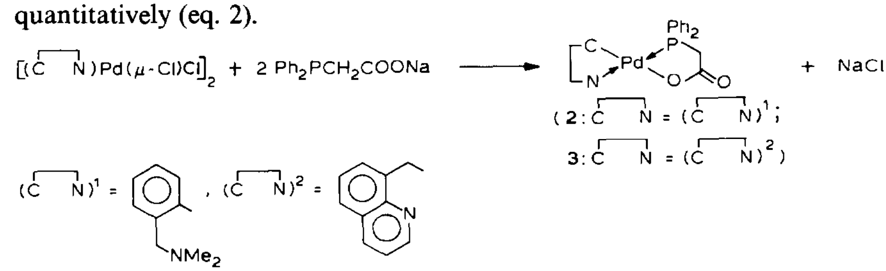
TABLE 3

SPECTROSCOPIC DATA OF SOME COMPLEXES CONTAINING CHELATING [$R_2PCH_2C(O)O]^-$ LIGANDS

		IR [a] ν(C=O)	^{1}H NMR [b] $\delta(PCH_2)$	^{1}H NMR [b] ^2J(PH)	$^{31}P\{^1H\}$ NMR [b] δ(P)	Ref.
[(η^5-C_5Me_5)RhCl{$Ph_2PCH_2C(O)O$}]	(1)	1642	3.22 [c] 3.47	12.6 10.3	27.9 [d]	this work
[(o-$C_6H_4CH_2NMe_2$)Pd{$Ph_2PCH_2C(O)O$}]	(2)	1635	3.47 [d]	11.1	19.3 [d]	this work
[($C_{10}H_8N$)Pd{$Ph_2PCH_2C(O)O$}]	(3)	1622	3.58 [d]	11.4	16.5	this work
[(o-$C_6H_4CH_2NMe_2$)Pd{$Cy_2PCH_2C(O)O$}]	(4)	1627	2.69 [c]	10.1	31.3 [c]	this work
[cis-Pd{$Ph_2PCH_2C(O)O$}$_2$]	(5)	1640	3.57 [c]	12.6	13.2 [c]	this work, 17
[(η^3-C_8H_{13})Ni{$Ph_2PCH_2C(O)O$}]		1580	1.37 [e]	0	−2.6 [e]	7

[a] cm^{-1} (KBr). [b] ^{1}H and ^{31}P NMR data in ppm relative to ext. Me_4Si or ext. H_3PO_4 (85%), respectively. Coupling constants in Hz. [c] In CD_2Cl_2. [d] In $CDCl_3$. [e] In C_6D_6.

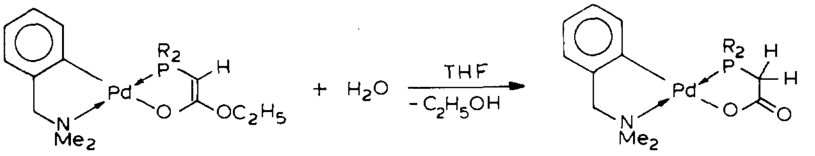
IR spectrum shows a typical ν(C=O) band at 1642 cm^{-1}. The presence in the ^{1}H NMR spectrum of an ABXY (X = P; Y = Rh) pattern for the two non equivalent PCH_2 protons (see Table 3) is accounted for by the chelating behaviour of the diphenylphosphinoacetate ligand. When Ph_2PCH_2COONa was treated with the cyclometallated complexes [(C N)Pd(μ-Cl)]$_2$ (CH N = dimethylbenzylamine $C_6H_5CH_2NMe$; 8-methylquinoline $C_{10}H_9N$), complexes **2** and **3** were formed quantitatively (eq. 2).



(2)

The *trans* N–Pd–P array in **2** can easily be deduced from the observation of ^4J(PH) coupling constants (^4J(P–NCH$_3$) 2.5 Hz, ^4J(P–NCH$_2$) 1.8 Hz). Other pertinent spectroscopic data for **2**, **3** and related known complexes with $R_2PCH_2COO^-$ ligands are presented in Table 3. Hydrolysis of palladium complexes containing chelating anionic phosphino-ester ligands of the type [$R_2PCHC(O)$-OC_2H_5]$^-$ can also give chelate complexes with phosphino acetato ligands (eq. 3).

(Continued on p. 409)



(3)

(**2**: R = Ph; **4**: R = c-C_6H_{11})

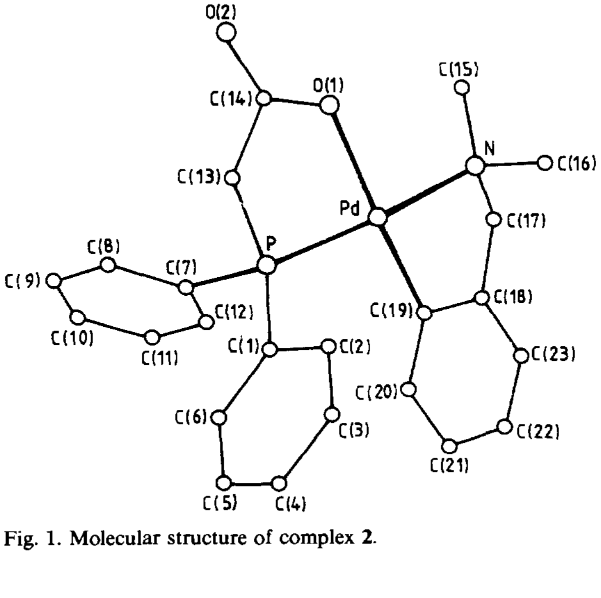


Fig. 1. Molecular structure of complex **2**.

TABLE 4

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (deg) IN $(o\text{-}\overline{C_6H_4CH_2NMe_2})\text{-}\overline{Pd\{Ph_2PCH_2C(O)O}\}$ (**2**)

Pd–P	2.218(1)	P–Pd–O(1)	83.3(1)
Pd–O(1)	2.105(3)	P–Pd–N	176.4(1)
Pd–N	2.121(3)	P–Pd–C(19)	100.9(1)
Pd–C(19)	1.986(4)	O(1)–Pd–N	93.2(1)
P–C(1)	1.819(4)	O(1)–Pd–C(19)	175.2(1)
P–C(7)	1.810(4)	N–Pd–C(19)	82.7(2)
P–C(13)	1.817(4)	Pd–P–C(1)	121.9(1)
O(1)–C(14)	1.282(5)	Pd–P–C(7)	114.5(1)
O(2)–C(14)	1.216(5)	Pd–P–C(13)	100.5(2)
N–C(15)	1.477(6)	Pd–O(1)–C(14)	121.5(3)
N–C(16)	1.466(5)	Pd–N–C(15)	114.1(3)
N–C(17)	1.483(6)	Pd–N–C(16)	107.6(3)
C(17)–C(18)	1.494(7)	Pd–N–C(17)	105.7(3)
C(13)–C(14)	1.520(6)	P–C(13)–C(14)	110.8(3)
mean C⋯C in		O(1)–C(14)–C(13)	116.8(3)
phenyl rings	1.371(8)	O(1)–C(14)–O(2)	123.9(4)
		N–C(17)–C(18)	109.3(4)
		C(17)–C(18)–C(19)	117.2(4)
		Pd–C(19)–C(18)	112.8(3)
		Pd–C(19)–C(20)	129.9(3)

TABLE 5

LEAST-SQUARES PLANES FOR $[(o\text{-}\overline{C_6H_4CH_2NMe_2)}\overline{Pd\{Ph_2PCH_2C(O)O}\}]$ (**2**)

Plane no.	Atoms	Distance from plane, Å
1	Pd	0.001(1)
	O(1)	0.029(3)
	P	0.000(1)
	C(19)	−0.060(4)
	N	0.002(3)
2	Pd	−0.001(1)
	N	0.186(3)
	C(17)	−0.353(4)
	C(18)	0.016(4)
	C(19)	0.152(4)
3	Pd	0.001(1)
	P	−0.022(1)
	C(13)	0.395(4)
	C(14)	−0.047(4)
	O(1)	−0.115(3)

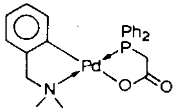
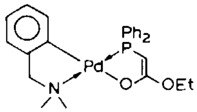
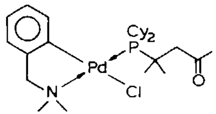
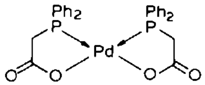
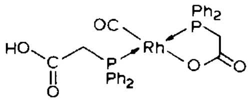
Dihedral angles between the planes 2–3: 5.6°

Equations of the planes of the form $Ax + By + Cz - D = 0$

Plane	A	B	C	D
1	0.8598	0.5074	−0.0582	4.6473
2	0.7890	0.6043	−0.1111	4.0495
3	0.8453	0.5263	−0.0926	4.4041

TABLE 6

SELECTED DATA OF SOME COMPLEXES CONTAINING THREE-ELECTRON DONOR C⌐N AND/OR P⌐O CHELATES

Complex	Chelate bite angle (deg)		Distances within the metallocycles (Å)				Ref.
	N⌐C	P⌐O	M–N	M–C	M–P	M–O	
 (2)	82.7(2)	83.3(1)	2.121(3)	1.986(4)	2.218(1)	2.105(3)	this work
	82.4(3)	83.8(1)	2.119(6)	1.973(7)	2.242(2)	2.117(5)	4
	81.7(2)		2.170(3)	2.030(4)	2.320(1)	–	19
 (5)		82.1(2) 82.8(1)			2.236(2) 2.234(2)	2.074(5) 2.078(5)	16
		81.4(2)			2.302(2)	2.064(6)	17

The latter reaction takes place very rapidly compared to those of eq. 1 or 2 in which chloride ions have to be displaced. The bis(P,O) chelate complex [*cis*-$Pd\{Ph_2PCH_2C(O)O\}_2$] (**5**) was prepared by treating $PdCl_2(PhCN)_2$ with two molar equivalents of Ph_2PCH_2COONa. Complexes with the $[Ph_2PCH_2COO]^-$ chelate may also be prepared by treating diphenylphosphinoacetic acid with the appropriate precursor compound [16,17]. In all the Pd complexes reported here the oxygen atom of the chelate ligand occupies the position *trans* with respect to the σ-bonded carbon of the cyclometallated ligand. This feature appears to be general for this class of complexes [4]. In all the complexes reported here the acetato function is bonded to only one metal centre, unlike the situation reported recently for the related propionato function in $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ complexes [18]. The structure of complex **2** was confirmed by an X-ray diffraction study.

Molecular structure of $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH_2C(O)O\}]$ *(2)*

An ORTEP view of **2** is shown in Fig. 1. Selected interatomic distances and angles are given in Table 4 and least-squares planes in Table 5. The coordination around the palladium may be regarded as planar, since the maximum deviation from the mean coordination plane, including Pd, is 0.060(4) Å (C(19)) (Table 5). The metal centre is complexed by two chelating ligands whose bite angles are 82.7(2)° for NPdC(19) and 83.3(1)° for PPdO(1). These values appear to be normal when compared to those for other complexes containing similar 3-electron $\overline{N\ \ C}$ and/or $\overline{P\ \ O}$ chelates, as can be seen from Table 6. Interatomic distances within the metallocycles are normal as compared with those in related molecules (see Table 6). None of the metallocycles in **2** is strictly planar (Table 5): in both rings, the CH_2 carbon atoms lie ca. 0.4 Å out of the mean plane in order to accomodate their sp^3 hybridization. (N–C(17)–C(18) 109.3(4)°, P–C(13)–C(14) 110.8(3)°).

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