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Synthesis of optically active cyclopalladated complexes of primary benzylamine derivatives, (*R*)-(−)-2-phenylglycine methyl ester and (±)-1-phenylethylamine

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Cyclopalladation of optically active α-monosubstituted primary benzylamines such as **2**-phenylglycine methyl ester and 1-phenylethylamine has been studied. Palladium(II) acetate reacted with (*R*)-2-phenylglycine methyl ester hydrochloride to give the chloro-bridged dinuclear cyclopalladated complex (*R*,*R*)-[{Pd(μ-Cl)($C_6H_4CHCO_2MeNH_2$)}$_2$] **1**, whereas with (*R*)- or (*S*)-1-phenylethylamine palladium(II) acetate afforded the acetato-bridged dinuclear cyclopalladated complex (*R*,*R*)- or (*S*,*S*)-[{Pd(μ-O_2CMe)($C_6H_4CHMeNH_2$)}$_2$] from which the chloro-bridged dinuclear complex (*R*,*R*)- or (*S*,*S*)-[{Pd(μ-Cl)($C_6H_4CHMeNH_2$)}$_2$] was obtained by metathetical reaction with sodium chloride. Complexes **1** and [{Pd(μ-Cl)($C_6H_4CHMeNH_2$)}$_2$] were converted into mononucler cyclopalladated complexes (*R*)-[PdCl($C_6H_4CHCO_2MeNH_2$)(dmpy)], (*R*)-[PdCl($C_6H_4CHCO_2MeNH_2$)(PPh_3)] and (*R*)- or (*S*)-[PdCl($C_6H_4CHMeNH_2$)(dmpy)], by the bridge-splitting reactions with 3,5-dimethylpyridine (dmpy) and triphenylphosphine. The crystal structure of (*R*)-[PdCl($C_6H_4CHCO_2MeNH_2$)(PPh_3)] has been determined. A short contact between the amino group and carbonyl group probably represents a hydrogen bond.

Cyclometallation represents a facile method for the activation of aromatic rings,[1] and application of the resulting cyclometallated complexes to organic synthesis has been developed in terms of regiospecific introduction of functional groups.[2] Recently, optically active cyclopalladated complexes have received much attention in areas concerning the resolution of mono- or bi-dentate chiral ligands[3] and asymmetric Diels–Alder reactions.[4] Until now, easily available optically active cyclopalladated complexes have been limited to the complexes derived from chiral *N*,*N*-dimethyl-1-phenylethylamine,[5] *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine,[6] (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine[7] and (*S*)-1-(4-nitrophenyl)ethylamine.[8]

In 1984, Ryabov *et al.*[9] reported that palladium(II) acetate gave optically active cyclopalladated complexes with (*R*)-*N*,*N*-dimethyl-2-phenylglycine ethyl ester, a tertiary benzylamine derivative, but not with (*R*)-2-phenylglycine methyl ester, a primary benzylamine derivative. However, the former complex has not been generally used as a optically active cyclopalladated complex probably owing to the commercial non-availability of the amine. Recently we and others have reported that primary benzylamine can be cyclopalladated: (*i*) by treating palladium(II) acetate with the amine or its hydrochloride,[8,10] (*ii*) by treating [$PdCl_2$(amine)$_2$] with $AgClO_4$[7] or (*iii*) by decomposition of complexes [{Pd(O_2CMe)$_2$(amine)}$_2$].[11] This finding prompted us to investigate the cyclopalladation of commercially available and low-priced chiral α-monosubstituted primary benzylamines. Here, we describe successful cyclopalladation of (*R*)-(−)-2-phenylglycine methyl ester and (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine by palladium(II) acetate, and also a structural analysis of [PdCl($C_6H_4CHCO_2MeNH_2$)(PPh_3)], a cyclopalladated complex of (*R*)-(−)-2-phenylglycine methyl ester.

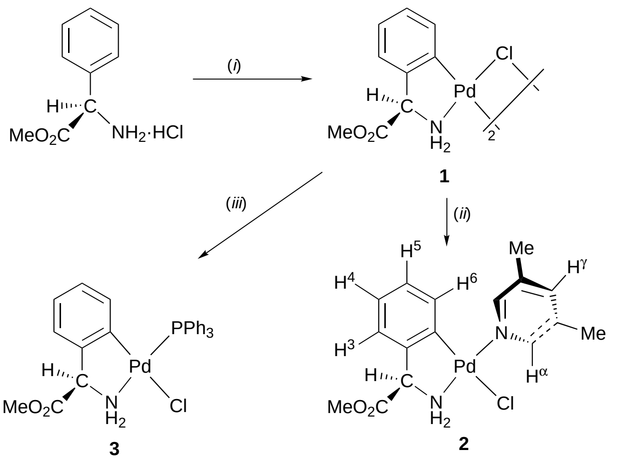
Results and Discussion

The ^{1}H NMR and optical rotation data of the complexes obtained in this study are summarized in Table 1.

Cyclopalladation of (*R*)-(−)-2-phenylglycine methyl ester

In 1995, Vicente *et al.*[8] first reported that the reaction of palladium(II) acetate with the hydrochloride salt of 1-(4-nitrophenyl)ethylamine produced the chloro-bridged dinuclear cyclopalladated complex [{Pd(μ-Cl)(4-$O_2NC_6H_3CHMeNH_2$)}$_2$], whereas the reaction with free 1-(4-nitrophenyl)ethylamine formed the acetato-bridged dinuclear cyclopalladated complex [{Pd(μ-O_2CMe)(4-$O_2NC_6H_3CHMeNH_2$)}$_2$].

We found that palladium(II) acetate did not yield a cyclopalladated complex with (*R*)-(−)-2-phenylglycine in benzene at 70 °C. However, using the above-mentioned method [*i.e.* acetone as solvent and the hydrochloride of the amine methyl ester (*R*)-(−)-$C_6H_5CHCO_2MeNH_3Cl$], a chloro-bridged dinuclear cyclopalladated complex (*R*,*R*)-[{Pd(μ-Cl)($C_6H_4CHCO_2MeNH_2$)}$_2$] **1** was obtained in 58% yield based on the palladium(II) acetate used. This complex reacted with 3,5-dimethylpyridine (dmpy) or triphenylphosphine to give the corresponding mononuclear cyclopalladated complexes, [PdCl($C_6H_4CHCO_2MeNH_2$)(dmpy)] **2** and [PdCl($C_6H_4CHCO_2MeNH_2$)(PPh_3)] **3**, respectively (Scheme 1). In the ^{1}H NMR spectrum of **2** aromatic protons appeared as four signals at δ 6.10, 6.84, 7.02 and 7.15, while that of **1** showed complicated aromatic resonances. The observation of the four separate signals, caused by the ring-current effect of the adjacent pyridine ring, confirmed the cyclopalladated structure of the (*R*)-(−)-2-phenylglycine methyl ester. Our successful isolation of **1** may imply that the use of Vicente's method involving the hydrochloride salt as amine source instead of the free amine provides a general method for direct synthesis of chloro-bridged cyclopalladated complexes. However, other attempts to prepare six-membered cyclopalladated complexes by reactions between palladium(II) acetate and hydrochloride salts of (*S*)-(+)-phenylalanine ester, $C_6H_5CH_2CHCO_2RNH_3Cl$ (R = Me or Et), carried out in refluxing acetone or butanone ended in failure. These results are consistent with the previous observation that six-membered palladacycles are much more difficult to obtain



Scheme 1 (*i*) $Pd(O_2CMe)_2$; (*ii*) dmpy; (*iii*) PPh_3

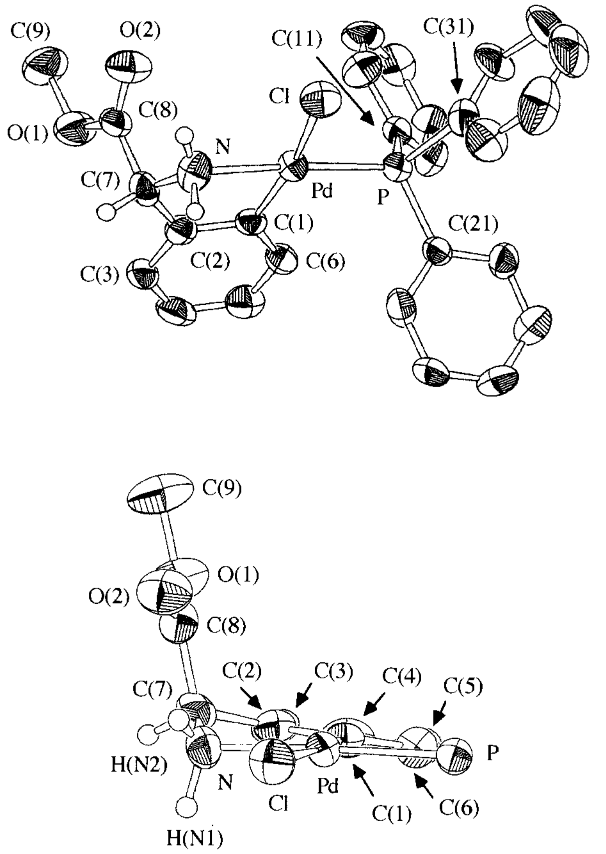
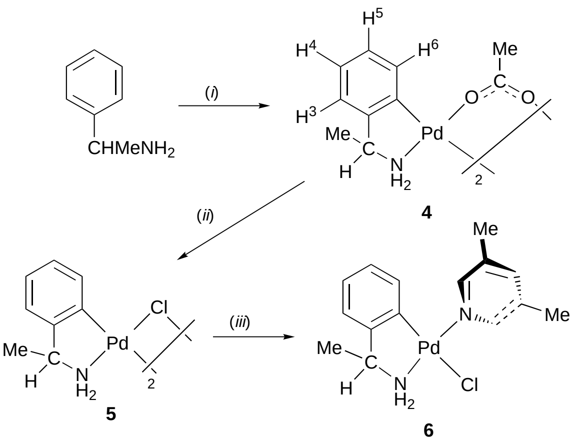


Fig. 1 Molecular structure of $[PdCl(C_6H_4CHCO_2MeNH_2)(PPh_3)]$ **3**

than five-membered ones.[1] However, during the revision of this paper, it was reported that 2-phenylethylamine can be ortho-metallated by treating it with palladium(II) acetate or by decomposition of the complex $[\{Pd(O_2CMe)_2(amine)\}_2]$ in spite of the six-membered ring that is formed.[11]

The molecular structure of complex **3** was established by an X-ray analysis. The ORTEP[12] drawings with the numbering scheme used are shown in Fig. 1, selected bond lengths and angles in Table 2. The co-ordination around palladium atom is essentially square planar and the maximum deviation from the mean plane composed of Pd, Cl, P, N and C(1) is 0.079(9) Å at N. The five-membered pallaldacycle is not planar but has an envelope structure with the nitrogen atom 0.399 Å out of the plane defined by the remaining four atoms. The dihedral angle between the phenyl ring and the palladacycle is 9.0°, while the methoxycarbonyl group stands nearly upright toward the palladium co-ordination plane (Fig. 1). The Pd–Cl bond length of 2.373(2) Å is similar to those observed elsewhere [2.382(3),[13] 2.399(3)[14] and 2.377(1) Å[15]] and slightly longer than the sum of the covalent radii (2.30 Å), consistent with the *trans* influence of the C atom. The bit angle of the chelate ring C(1)–Pd–N is 81.8(3)°. An intermolecular hydrogen bond N–H(N1)···O(2) ($\frac{1}{2} - x$, $-y$, $\frac{1}{2} + z$) is observed, with N···O 2.86(1), H···O 1.85(8) Å and N–H···O 169(7)°.



Scheme 2 (*i*) $Pd(O_2CMe)_2$; (*ii*) NaCl; (*iii*) dmpy

Cyclopalladation of (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine

(*R*)-(+)-1-Phenylethylamine reacted with palladium(II) acetate to give the acetato-bridged dinuclear cyclopalladated complex (*R*,*R*)-$[\{Pd(\mu\text{-}O_2CMe)(C_6H_4CHMeNH_2)\}_2]$ (*R*,*R*)-**4** (Scheme 2). Similarly (*S*)-(−)-1-phenylethylamine afforded the enantiomer of (*R*,*R*)-**4**, (*S*,*S*)-$[\{Pd(\mu\text{-}O_2CMe)(C_6H_4CHMeNH_2)\}_2]$ (*S*,*S*)-**4**. Both (*R*,*R*)-**4** and (*S*,*S*)-**4** were converted into the corresponding chloro-bridged analogues, (*R*,*R*)- and (*S*,*S*)-$[\{Pd(\mu\text{-}Cl)(C_6H_4CHMeNH_2)\}_2]$ (*R*,*R*)- and (*S*,*S*)-**5**, respectively, by the reaction with sodium chloride. Moreover, (*R*,*R*)- and (*S*,*S*)-**5** reacted with dmpy to give the mononuclear cyclopalladated complexes (*R*,*R*)- and (*S*,*S*)-$[PdCl(C_6H_4CHMeNH_2)(dmpy)]$ (*R*)- and (*S*)-**6**, respectively. Related complexes have been reported.[7]

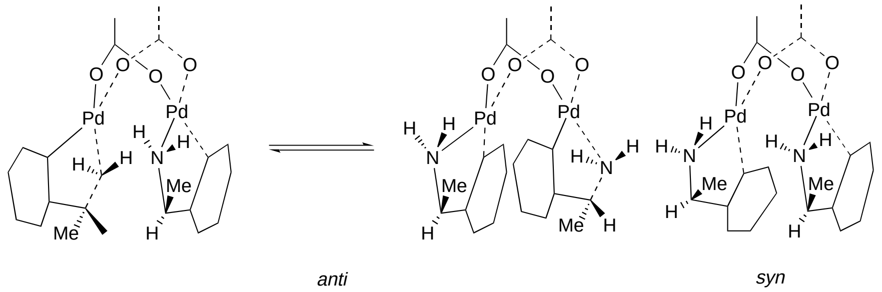
Complexes **4** exhibited two strong bands at 1560 and 1405 cm^{-1} in their IR spectra attributable to the bridging acetato ligands,[16] and showed dynamic behaviour in their ^1H NMR spectra. At 50 °C the acetato-methyl protons resonated as one singlet at δ 1.84, indicating that **4** have the *anti* not the *syn* configuration (Scheme 3). Concerning the CH, CMe and NH protons, they were observed as broad signals at δ 1.0 and 3.0–5.3. At 35 °C the former signal changed into two broad signals at δ 0.75 and 1.2, while the latter separated into broad signals at δ 3.05, 3.4, 4.2 and 5.0. Finally at −60 °C the low-temperature limiting spectrum was observed. At −60 °C ^1H–^1H correlation spectroscopy (COSY) revealed the presence of two isomers in **4**: one exhibited signals at δ 0.59 (2.4 H, Me), 1.77 (2.4 H, O_2CMe), 3.0–3.1 (0.67 H, NH), 4.15 (0.8 H, CH) and 5.55 (0.67 H, NH), the other signals at δ 1.19 (3.6 H, Me), 1.82 (3.6 H, O_2CMe), 3.0–3.1 (1.2 H, CH), 3.75 (1.33 H, NH) and 4.6 (1.33 H, NH). Considering that the two co-ordination planes in an acetato-bridged dinuclear complex are combined by two mutually *cis* μ-acetate ligands with a dihedral angle of 24°,[17] **4** was expected to have two isomers **4**-o and **4**-i as shown in Scheme 3 and the dynamic behaviour of the ^1H NMR spectra is attributable to the inversion of the acetato bridges. The major and minor isomers of **4** were assigned to **4**-o and **4**-i, respectively, considering the anisotropic shielding of the methyl signal (δ 0.59) caused by the benzene ring situated just over the benzylic carbon.

The ^1H NMR spectrum of complex **5**, in spite of the low solubility in $CDCl_3$, showed four well separated signals due to the *o*-phenylene protons in the cyclopalladated moiety

Table 1 Selected spectroscopic properties of complexes **1**–**6**

	^1H NMR spectra[a]					
	Cyclopalladated moiety					
Complex	C_6H_4 moiety	CH	Me	NH	Others	α_{589}[b]/°
1 (*R*,*R*)-[{Pd(μ-Cl)-($C_6H_4CHCO_2MeNH_2$)}$_2$]	6.9–7.2 (8 H, m)	4.9 (2 H, br)	3.85 (6 H, s)	4.7 (4 H, br)		—[c]
2 (*R*)-[PdCl($C_6H_4CHCO_2MeNH_2$)-(dmpy)]	6.10 (1 H, dd, H^6)[d] 6.84 (1 H, t, H^5)[f] 7.15 (1 H, d, H^3)[f] 7.02 (1 H, dt, H^4)[d]	5.03 (1 H, t)[e]	3.87 (3 H, s)	4.65 (2 H, br) 7.40 (1 H, s, H^γ) 8.44 (2 H, s, H^α)	2.26 (3 H, s, Me)	+83.8
3 (*R*)-[PdCl($C_6H_4CHCO_2MeNH_2$)-(PPh_3)]	6.4–6.5 (2 H, m, H^6, H^5) 6.86 (1 H, t, H^4)[g] 7.09 (1 H, t, H^3)[g]	5.13 (1 H, t)[e]	3.90 (3 H, s)	4.2 (1 H, br) 4.65 (1 H, br)	7.3–7.8 (15 H, m, Ph)	+33.0
4[h] (*R*,*R*)- and (*S*,*S*)-[{Pd(μ-O_2CMe)-($C_6H_4CHMeNH_2$)}$_2$]	6.52 (2 H, d, H^3 or H^6)[i] 6.7–6.9 (6 H, m, H^4–H^6 or H^3, H^5 and H^6)	3.0–3.1 (1.2 H, c)[j,k] 4.15 (0.8 H, c)[l]	0.59 (2.4 H, d)[l,m] 1.19 (3.6 H, d)[k,m]	3.0–3.1 (0.67 H, br)[j,l] 3.75 (1.33 H, br)[k] 4.6 (1.33 H, br)[k] 5.55 (0.67 H, br)[l]	1.77(3.6H,s,Me)[k] 1.82(2.4H,s,Me)[l]	—[c]
5 (*R*,*R*)- and (*S*,*S*)-[{Pd(μ-Cl)-($C_6H_4CHMeNH_2$)}$_2$]	6.69 (1 H, d, H^6)[i] 6.88 (1 H, t, H^4)[i] 6.97 (1 H, t, H^5)[i] 7.22 (1 H, d, H^3)[i]	4.3 (1 H, br s)	1.55[n]	3.2 (1 H, br) 4.0 (1 H, br)		—[c]
6 (*R*)- and (*S*)-[PdCl(C_6H_4-$CHMeNH_2$)(dmpy)]	6.15 (1 H, dd, H^6)[o] 6.8–6.9 (2 H, c, H^3 and H^5) 7.01 (1 H, dt, H^4)[o]	4.43 (1 H, sxt)[f]	1.64 (3 H, d)[p]	3.35 (1 H, br) 4.3 (1 H, br)	2.29 (3 H, s, Me) 7.41 (1 H, s, H^γ) 8.511 (1 H, s, H^α) 8.505 (2 H, s, H^α)	−20.3[q] +25.4[r]

[a] Measured in $CDCl_3$ at 23 °C unless noted elsewhere; δ in ppm relative to internal $SiMe_4$; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, sxt = sextet, m = multiplet, c = complex, br = broad. [b] In CH_2Cl_2 at 25 °C; *c* = 0.4 g per 100 cm^3. [c] Not measured owing to the low solubility. [d] $^3J_{HH} = 7.6$, $^4J_{HH} = 1.5$ Hz. [e] $^3J_{HH} = 5.9$ Hz. [f] $^3J_{HH} = 7.6$ Hz. [g] $^3J_{HH} = 7.8$ Hz. [h] In $(CD_3)_2CO$. [i] $^3J_{HH} = 7.5$ Hz. [j] Overlapping with NH protons. [k] Due to **4**-*o* isomer. [l] Due to **4**-*i* isomer. [m] $^3J_{HH} = 6.3$ Hz. [n] Overlapping with H_2O signal. [o] $^3J_{HH} = 7.8$, $^4J_{HH} = 1.0$ Hz. [p] $^3J_{HH} = 6.4$ Hz. [q] (*R*) Isomer. [r] (*S*) Isomer.



(*R*,*R*)-4-o **(*R*,*R*)-4-i**

Scheme 3 The *anti* and *syn* configurations of complex **4**, and **4**-o and **4**-i isomers (o and i refer to outer and inner methyl groups respectively) depicted using the *R*,*R* isomer as a representative

(Table 1). In the ^1H spectrum of **6**, one of the aromatic protons, H^6, appeared at a considerably higher field at δ 6.15 owing to the magnetic anisotropy of the pyridine ring, co-ordinated nearly perpendicularly to the square-planar palladium(II) plane.[18]

In conclusion, using Vicente's previously reported method we have performed the first synthesis of chiral cyclopalladated 2-phenylglycine methyl ester derivatives and also established a method for the preparation of chiral cyclopalladated 1-phenylethylamine derivatives.

Experimental

General

The IR spectra were measured on a Hitachi 295 spectrophotometer, ^1H NMR spectra on a JEOL JNM-GX-270 spectrometer using tetramethylsilane as an internal standard. Melting points were determined on a Yanaco MP-500D micro melting-point apparatus and are uncorrected. Optical rotations were measured with a JASCO model DIP-370 digital polarimeter on the specified solution in 1 dm cells at 25 °C.

Palladium(II) acetate was prepared according to the procedures of Wilkinson and co-workers.[19] Other reagents were obtained commercially and used without purification.

Syntheses

(*R*,*R*)-[{Pd(μ-Cl)($C_6H_4CHCO_2MeNH_2$)}$_2$] 1. (*R*)-(−)-2-Phenylglycine methyl ester hydrochloride (0.944 g, 4.68 mmol) was added to a stirred solution of palladium(II) acetate (1.000 g, 4.45 mmol) in acetone (100 cm^3). The resulting dark orange solution was heated under reflux for 20 h and then filtered. The filtrate was concentrated then diluted with hexane to give yellow microcrystals of complex **1** (0.791 g, 58%), m.p. 188–191 °C (decomp.) (Found: C, 35.45; H, 3.35; N, 4.5. $C_{18}H_{20}Cl_2N_2O_4Pd_2$ requires C, 35.3; H, 3.3; N, 4.6%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1725 (CO), 3265, 3195 (NH).

[PdCl($C_6H_4CHCO_2MeNH_2$)L] (L = dmpy 2 or PPh_3 3). A clear solution was obtained immediately by adding dmpy (0.073 g, 0.68 mmol) to a suspension of complex **1** (0.200 g, 0.327 mmol) in dichloromethane (25 cm^3). After stirring for 5 h at room temperature the resulting mixture was filtered. The filtrate

Table 2 Selected bond lengths (Å) and angles (°) for complex **3**

Pd–C(1)	2.019(8)	C(7)–N	1.48(1)
Pd–N	2.089(8)	C(8)–O(1)	1.298(9)
Pd–P	2.243(2)	C(8)–O(2)	1.220(9)
Pd–Cl	2.373(2)	O(1)–C(9)	1.46(1)
C(1)–C(2)	1.40(1)	P–C(11)	1.812(1)
C(2)–C(7)	1.50(1)	P–C(21)	1.828(8)
C(7)–C(8)	1.51(1)	P–C(31)	1.832(8)
C(1)–Pd–N	81.8(3)	N–Pd–Cl	87.3(2)
Cl–Pd–P	95.85(8)	P–Pd–C(1)	95.0(2)
C(1)–Pd–Cl	169.1(2)	N–Pd–P	176.0(3)
Pd–C(1)–C(2)	113.2(6)	Pd–C(1)–C(6)	130.5(6)
C(6)–C(1)–C(2)	116.0(7)	C(1)–C(2)–C(7)	118.4(7)
C(1)–C(2)–C(3)	122.3(8)	C(3)–C(2)–C(7)	119.3(7)
C(2)–C(7)–N	107.7(6)	C(2)–C(7)–C(8)	112.7(7)
C(8)–C(7)–N	108.0(8)	C(7)–N–Pd	111.4(5)
C(7)–C(8)–O(1)	115.4(8)	C(7)–C(8)–O(2)	122.3(8)
O(1)–C(8)–O(2)	122.2(9)	C(8)–O(1)–C(9)	117.7(8)
C(11)–P–Pd	111.1(3)	C(21)–P–Pd	113.9(3)
C(31)–P–Pd	118.0(3)	C(11)–P–C(21)	109.8(4)
C(11)–P–C(21)	102.7(4)	C(21)–P–C(31)	100.4(4)

was concentrated then diluted with diethyl ether to give yellow microcrystals of **2** (0.218 g, 81%), m.p. 171–172 °C (decomp.) (Found: C, 46.25; H, 4.65; N, 6.7. $C_{16}H_{19}ClN_2O_2Pd$ requires C, 46.5; H, 4.65; N, 6.8%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1740 (CO), 3235, 3160 (NH). Complex **3** was prepared in the same way with PPh_3: yield 83%, m.p. 194–195 °C (decomp.) (Found: C, 57.3; H, 4.5; N, 2.4. $C_{27}H_{25}ClNO_2PPd$ requires C, 57.05; H, 4.45; N, 2.45%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1710 (CO), 3325, 3235 (NH).

(*R*,*R*)- and (*S*,*S*)-[{Pd(μ-O$_2$CMe)(C$_6$H$_4$CHMeNH$_2$)}$_2$] (*R*,*R*)- and (*S*,*S*)-4. (*R*)-(+)-1-Phenylethylamine (0.279 g, 2.45 mmol) and palladium(II) acetate (0.500 g, 2.23 mmol) were mixed in benzene (25 cm^3), and then heated at 50 °C for 20 h. The resulting mixture was filtered and the filtrate was concentrated. Addition of hexane afforded yellow crystals of the complex (*R*,*R*)-**4** (0.446 g, 70%), m.p. 165–167 °C (decomp.) (Found: C, 42.05; H, 4.6; N, 4.9. $C_{20}H_{26}N_2O_4Pd_2$ requires C, 41.6; H, 4.6; N, 4.8%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1560, 1405 (CO_2), 3245, 3200 (NH). Complex (*S*,*S*)-**4** was similarly prepared from (*S*)-(−)-1-phenylethylamine, yield 63%, m.p. 165–167 °C (decomp.) (Found: C, 42.1; H, 4.6; N, 4.85. $C_{20}H_{26}N_2O_4Pd_2$ requires C, 41.6; H, 4.6; N, 4.8%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1560, 1405 (CO_2), 3245, 3200 (NH).

(*R*,*R*)- and (*S*,*S*)-[{Pd(μ-Cl)(C$_6$H$_4$CHMeNH$_2$)}$_2$] (*R*,*R*)- and (*S*,*S*)-5. An acetone–water suspension (10 : 1, 22 cm^3) containing complex (*R*,*R*)-**4** (0.230 g, 0.403 mmol) and sodium chloride (0.094 g, 0.094 mmol) was stirred at room temperature for 1 d. The resulting mixture was evaporated to dryness and the residue extracted with dichloromethane. The extract was concentrated and diluted with hexane to give yellow crystals of (*R*,*R*)-**5** (0.190 g, 90%), m.p. 203–204 °C (decomp.) (Found: C, 36.9; H, 4.0; N, 5.2. $C_{16}H_{20}Cl_2N_2Pd$ requires C, 36.65; H, 3.85; N, 5.35%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3285, 3230 (NH). Complex (*S*,*S*)-**5** was similarly prepared from (*S*,*S*)-**4**, yield 80%, m.p. 203–204 °C (decomp.) (Found: C, 36.85; H, 4.05; N, 5.15. $C_{16}H_{20}Cl_2N_2Pd$ requires C, 36.65; H, 3.85; N, 5.35%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3285, 3230 (NH).

(*R*)- and (*S*)-[PdCl(C$_6$H$_4$CHMeNH$_2$)(dmpy)] (*R*)- and (*S*)-6. Addition of dmpy (0.045 g, 0.420 mmol) to a suspension of complex (*R*,*R*)-**5** (0.100 g, 0.191 mmol) in dichloromethane (15 cm^3) gave a clear solution immediately. After stirring overnight at room temperature, addition of hexane to the mixture yielded (*R*)-**6** (0.113 g, 80%), m.p. 188–190 °C (decomp.) (Found: C, 49.0; H, 5.4; N, 7.55. $C_{15}H_{19}ClN_2Pd$ requires C, 48.8; H, 5.2; N, 7.6%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3225, 3170 (NH). Complex (*S*)-**6** was similarly prepared from (*S*,*S*)-**5**, yield 79%, m.p. 191–192 °C (decomp.) (Found: C, 48.25; H, 5.2; N, 7.15. $C_{15}H_{19}ClN_2Pd$ requires C, 48.8; H, 5.2; N, 7.6%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3225, 3170 (NH).

X-Ray crystallography

Suitable crystals of [PdCl(C$_6$H$_4$CHCO$_2$MeNH$_2$)(PPh$_3$)] **3** were grown from dichloromethane and hexane.

Crystal data. $C_{27}H_{25}ClNO_2PPd$, $M = 568.33$, orthorhombic, space group $P2_12_12_1$, $a = 15.961(3)$, $b = 17.614(4)$, $c = 9.014(3)$ Å, $U = 2534.1(9)$ Å^3, $D_c = 1.490$ g cm^{-3}, $F(000) = 1152$, $Z = 4$, μ(Mo-Kα) = 9.25 cm^{-1}, Mo-Kα radiation, $\lambda = 0.710\ 69$ Å.

A yellow prismatic crystal having approximate dimensions of 0.15 × 0.20 × 0.25 mm was mounted on a glass fibre. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Mo-Kα radiation. Cell constants were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $20.10 < 2\theta < 24.96°$. The data were collected at a temperature of 20 + 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0°. A total of 3306 reflections was collected. During the data collection the intensities of three representative reflections were measured after every 150 and an absorption correction was applied (based on azimuthal scans of several reflections, transmission range 0.94–1.00). The observed data were corrected for Lorentz and polarization effects. All the calculations were performed using the TEXSAN software package.[20] The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were included in fixed positions. The final cycle of full-matrix least-squares refinement was based on 2166 observed reflections [$I > 3.00\sigma(I)$] and 310 variable parameters and converged (largest parameter was 0.00 times its e.s.d.) with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.039$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.033$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/534.

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