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(*R*)-Di-μ-acetato-κ^2*O*:*O*′-bis{[2-(1-aminoethyl)phenyl-κ^2*C*^{1},*N*]palladium(II)}, (*R*)-di-μ-chloro-bis{[2-(1-aminoethyl)phenyl-κ^2*C*^{1},*N*]palladium(II)} and [*SP*-4-4]-(*R*)-[2-(1-aminoethyl)phenyl-κ^2*C*^{1},*N*]chloro(pyridine-κ*N*)palladium(II)

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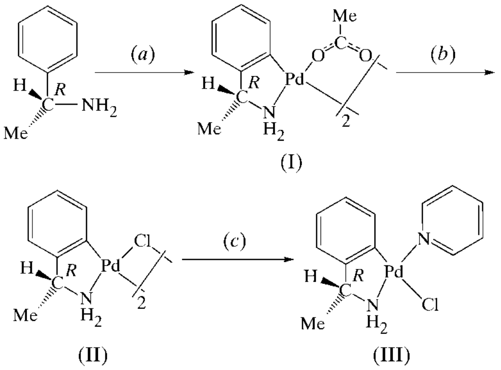
The title complexes, $[Pd_2(C_8H_{10}N)_2(C_2H_3O_2)_2]$, (I), $[Pd_2(C_8H_{10}N)_2Cl_2]$, (II), and $[Pd(C_8H_{10}N)Cl(C_5H_5N)]$, (III), respectively, have been prepared as intermediates and the final product of a cyclopalladation reaction sequence, and their structures studied by single-crystal X-ray diffraction. Complexes (I) and (II) represent the first structurally characterized dinuclear cyclopalladation products of primary amines. For (I) and (III), pseudosymmetry relates two independent molecules in the asymmetric unit.

Comment

We are interested in the cyclopalladation products of primary amines as building blocks for molecular crystals. Since the discovery of cyclopalladation by Cope & Friedrich (1968), preparative efforts and structural investigations have focused on complexes derived from tertiary amines. The work of Lewis *et al.* (1973), Dunina *et al.* (1984), Fuchita & Tsuchiya (1993), Fuchita *et al.* (1995, 1997), Vicente *et al.* (1993, 1997) and Albert *et al.* (1997) has shown that the reaction can, in principle, be extended to primary and secondary amines when appropriate reaction conditions and Pd^{II} sources are utilized.



(*a*) $Pd(OAc)_2/C_6H_6$, 323 K, 1 d
(*b*) NaCl/acetone–water (10:1)
(*c*) Pyridine/CH_2Cl_2

For primary amines, no complete structural study of the cyclopalladation pathway has been carried out to date. We decided to characterize both of the intermediates and the final product of the reaction sequence shown in the *Scheme* above, using single-crystal X-ray diffraction.

Starting from palladium(II) acetate and (*R*)-1-phenylethylamine, according to the method of Fuchita *et al.* (1997), steps (*a*) and (*b*) gave the dinuclear products (I) and (II), respectively. Bridging acetate and chloro ligands induce different overall conformations in these complexes. In (I), the planes of coordination around the Pd centres are stacked (Fig. 1), with a relatively short Pd$\cdots$Pd distance of 2.9 Å. Based on spectroscopic results, Fuchita and co-workers had correctly assigned the *anti* configuration to this acetate-bridged dimer.

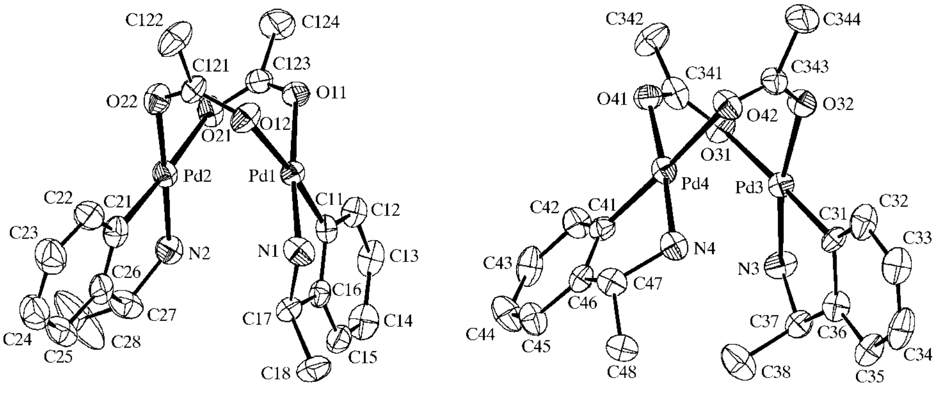


Figure 1
A view of the two symmetrically independent molecules of (I). Displacement ellipsoids are at the 30% probability level and H atoms have been omitted for clarity.

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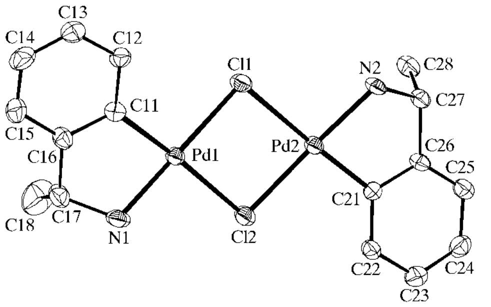

Figure 2
A view of the molecule of (II). Displacement ellipsoids are at the 30% probability level and H atoms have been omitted for clarity.

In contrast with the rather compact molecular shape of (I), the chloro complex, (II), is essentially flat (Fig. 2). The best planes through the two Pd centres and their coordinating atoms subtend a dihedral angle of 5.9 (2)°. Complexes (I) and (II) represent the first examples of structurally characterized dinuclear intermediates in the cyclopalladation of primary amines.

For the final reaction product, (III) (Fig. 3), five X-ray structure determinations involving cyclopalladated complexes of primary amines have been published to date (Dunina *et al.*, 1999; Vicente *et al.*, 1993; Fedorov *et al.*, 1997; Fuchita *et al.*, 1997). The groups of Vicente and Jones (Vicente *et al.*, 1993) have described both a neutral compound and a cationic complex derived from the same chiral ligand, 1-phenylethylamine, used in our preparations.

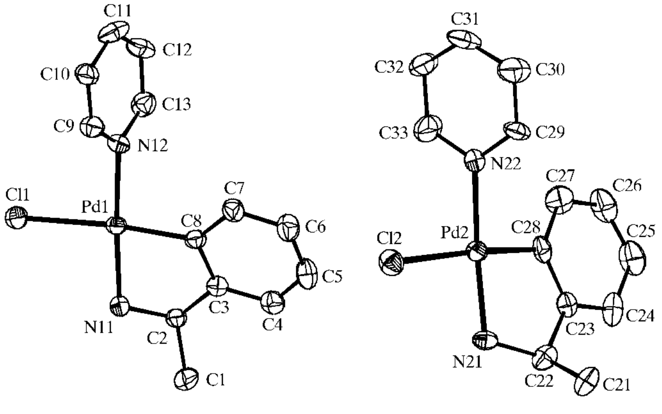

Figure 3
A view of the two symmetrically independent molecules of (III). Displacement ellipsoids are at the 30% probability level and H atoms have been omitted for clarity.

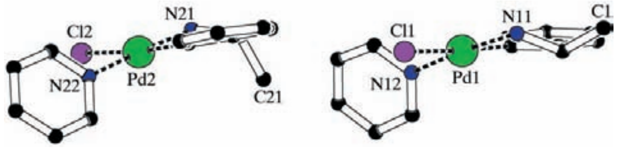

Figure 4
The pseudo-glide plane in (III). The pseudo-reflection is in the view direction and the pseudo-translation is to the right.

Experimental

The series of compounds (I)–(III) was prepared according to the procedure of Fuchita *et al.* (1997). (*R*)-(+)-1-Phenylethylamine was reacted with palladium(II) acetate to give the acetate-bridged dinuclear cyclopalladated complex (I) (see *Scheme*), which was converted to the corresponding chloro-bridged analogue, (II), by reaction with sodium chloride. The chloro-bridged dinuclear complex was then cleaved with pyridine to give the mononuclear cyclopalladated complex, (III). Yields of up to 90% for the dinuclear intermediates, (I) and (II), and of 75% for the mononuclear complex, (III), were obtained. Complexes (II) and (III) crystallized as elongated plates and needles, respectively.

Compound (I)

Crystal data

$[Pd_2(C_8H_{10}N)_2(C_2H_3O_2)_2]$
M_r = 571.23
Monoclinic, $P2_1$
a = 10.423 (4) Å
b = 13.398 (5) Å
c = 15.861 (5) Å
β = 93.429 (9)°
V = 2210.9 (13) Å^3
Z = 4
D_x = 1.716 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 30 754 reflections
θ = 1.3–28.7°
μ = 1.65 mm^{-1}
T = 295 (2) K
Parallelepiped, yellow
0.12 × 0.05 × 0.05 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.826, $T_{\max}$ = 0.922
30 720 measured reflections
11 234 independent reflections
7251 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.092
$\theta_{\max}$ = 28.7°
$h = -13 \rightarrow 14$
$k = -18 \rightarrow 18$
$l = -21 \rightarrow 21$

Table 1
Selected geometric parameters (Å, °) for (I).

Pd1···Pd2	2.9059 (14)	Pd3—C31	1.979 (11)
Pd1—O11	2.071 (9)	Pd4—O41	2.074 (9)
Pd1—O12	2.172 (9)	Pd4—O42	2.193 (9)
Pd1—N1	2.033 (12)	Pd4—N4	2.078 (10)
Pd1—C11	1.962 (13)	Pd4—C41	1.966 (13)
Pd2—O21	2.196 (9)	C16—C17	1.555 (17)
Pd2—O22	2.112 (10)	C17—N1	1.550 (14)
Pd2—N2	2.041 (10)	C26—C27	1.57 (2)
Pd2—C21	1.968 (13)	C27—N2	1.553 (16)
Pd3···Pd4	2.9355 (14)	C36—C37	1.542 (17)
Pd3—O31	2.196 (9)	C37—N3	1.480 (14)
Pd3—O32	2.052 (8)	C46—C47	1.541 (15)
Pd3—N3	2.059 (10)	C47—N4	1.512 (14)
O11—Pd1—O12	88.7 (4)	O32—Pd3—O31	88.3 (4)
N1—Pd1—O11	174.0 (4)	N3—Pd3—O31	95.8 (4)
N1—Pd1—O12	94.7 (4)	N3—Pd3—O32	166.9 (4)
C11—Pd1—O11	94.4 (5)	C31—Pd3—O31	178.0 (4)
C11—Pd1—O12	173.6 (4)	C31—Pd3—O32	93.8 (4)
C11—Pd1—N1	82.7 (5)	C31—Pd3—N3	82.4 (4)
O22—Pd2—O21	89.9 (4)	O41—Pd4—O42	87.5 (4)
N2—Pd2—O21	93.7 (4)	N4—Pd4—O41	175.9 (4)
N2—Pd2—O22	176.5 (4)	N4—Pd4—O42	96.1 (3)
C21—Pd2—O21	172.9 (5)	C41—Pd4—O41	94.8 (4)
C21—Pd2—O22	93.5 (5)	C41—Pd4—O42	174.5 (4)
C21—Pd2—N2	82.9 (5)	C41—Pd4—N4	81.4 (4)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.177$
$S = 1.01$
11 234 reflections
513 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 1.0577P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.028$
$\Delta\rho_{\max} = 0.70$ e Å^{-3}
$\Delta\rho_{\min} = -1.27$ e Å^{-3}
Absolute structure: Flack (1983), 5363 Friedel pairs
Flack parameter = 0.01 (7)

Compound (II)

Crystal data

$[Pd_2(C_8H_{10}N)_2Cl_2]$
$M_r = 524.04$
Orthorhombic, $P2_12_12_1$
$a = 7.330$ (3) Å
$b = 10.819$ (4) Å
$c = 22.453$ (8) Å
$V = 1780.4$ (11) Å^3
$Z = 4$
$D_x = 1.955$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 302 reflections
$\theta = 1.8$–$28.2°$
$\mu = 2.32$ mm^{-1}
$T = 293$ (2) K
Elongated plate, light yellow
1.00 × 0.45 × 0.02 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.205$, $T_{\max} = 0.955$
24 210 measured reflections
4390 independent reflections
3782 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.088$
$\theta_{\max} = 28.2°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.109$
$S = 1.07$
4390 reflections
201 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.88$ e Å^{-3}
Absolute structure: Flack (1983), 1867 Friedel pairs
Flack parameter = 0.02 (6)

Table 2
Selected geometric parameters (Å, °) for (II).

Pd1—Cl1	2.332 (2)	Pd2—Cl2	2.333 (2)
Pd1—Cl2	2.447 (2)	Pd2—N2	2.019 (5)
Pd1—N1	2.020 (6)	Pd2—C21	1.946 (7)
Pd1—C11	1.946 (8)	C17—N1	1.490 (10)
Pd2—Cl1	2.4781 (19)	C27—N2	1.505 (9)
Cl1—Pd1—Cl2	86.90 (7)	N2—Pd2—Cl2	177.97 (18)
N1—Pd1—Cl1	175.2 (2)	C21—Pd2—N2	81.9 (3)
N1—Pd1—Cl2	95.67 (19)	C21—Pd2—Cl1	177.4 (2)
C11—Pd1—N1	81.2 (3)	C21—Pd2—Cl2	96.1 (2)
C11—Pd1—Cl1	96.5 (2)	Pd1—Cl1—Pd2	92.98 (7)
C11—Pd1—Cl2	175.5 (2)	Pd2—Cl2—Pd1	93.74 (7)
Cl2—Pd2—Cl1	86.15 (7)	C17—N1—Pd1	110.7 (5)
N2—Pd2—Cl1	95.82 (17)	C27—N2—Pd2	112.7 (4)

Compound (III)

Crystal data

$[Pd(C_8H_{10}N)Cl(C_5H_5N)]$
$M_r = 341.12$
Tetragonal, $I4_1$
$a = 18.511$ (5) Å
$c = 15.698$ (6) Å
$V = 5379$ (3) Å^3
$Z = 16$
$D_x = 1.685$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37 267 reflections
$\theta = 1.6$–$28.5°$
$\mu = 1.56$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
1.05 × 0.08 × 0.03 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.292$, $T_{\max} = 0.955$
37 248 measured reflections
6731 independent reflections
5005 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.098$
$\theta_{\max} = 28.5°$
$h = -24 \rightarrow 24$
$k = -24 \rightarrow 24$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.110$
$S = 1.05$
6731 reflections
309 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}
Absolute structure: Flack (1983), 3230 Friedel pairs
Flack parameter = 0.01 (6)

Table 3
Selected geometric parameters (Å, °) for (III).

Pd1—Cl1	2.409 (3)	Pd2—Cl2	2.430 (3)
Pd1—N11	2.056 (7)	Pd2—N21	2.012 (7)
Pd1—N12	2.040 (7)	Pd2—N22	2.042 (8)
Pd1—C8	1.947 (10)	Pd2—C28	1.994 (10)
N11—C2	1.498 (10)	N21—C22	1.499 (11)
C2—C3	1.511 (12)	C22—C23	1.480 (14)
N11—Pd1—Cl1	93.9 (2)	N21—Pd2—Cl2	93.9 (2)
N12—Pd1—Cl1	89.6 (2)	N22—Pd2—Cl2	89.9 (2)
C8—Pd1—Cl1	174.4 (3)	C28—Pd2—Cl2	173.1 (3)
N12—Pd1—N11	175.0 (3)	N21—Pd2—N22	175.9 (3)
C8—Pd1—N11	81.2 (3)	C28—Pd2—N21	81.3 (4)
C8—Pd1—N12	95.5 (4)	C28—Pd2—N22	95.1 (4)
C2—N11—Pd1	110.2 (6)	C22—N21—Pd2	113.5 (6)

Complexes (I) and (III) crystallize with two molecules in the asymmetric unit. In both cases, the independent moieties are related by pseudosymmetry. We can exclude centrosymmetric space groups because enantiomerically pure ligands of known chirality were used for the synthesis and the absolute configuration of the ligands is reliably reproduced by the diffraction experiment. We note that, despite several systematic absence violations, the structure of (III) can apparently be solved in space group $I4_1/a$. Tentative refinement in this centrosymmetric supergroup results in an unreasonably anisotropic displacement parameter for the methyl C atom attached to the chiral centre, an artificially shortened C—C separation (*ca* 1.1 Å) associated with this group, and significantly higher residual electron density close to the methyl group (0.84 Å). Fig. 4 shows the pseudosymmetry between the independent molecules in (III). This model, although obviously inappropriate for (III), might well represent the hitherto unknown structure of the racemate. In the refinement of complexes (I)–(III), all H atoms were introduced in idealized positions, with C—H = 0.98 Å, and N—H = 0.98 Å for (I) and 0.95 Å for (II) and (III), and included as riding with $U_{\rm iso}({\rm H}) = 1.3U_{\rm eq}({\rm C,N})$.

For all three complexes, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1575). Services for accessing these data are described at the back of the journal.

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