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Diacetato-κ^2O-bis[(*S*)-1-(4-fluorophenyl)ethylamine-κN]palladium(II) and di-μ-acetato-κ^4O:O'-bis{[(*S*)-2-(1-aminoethyl)-5-fluorophenyl-κ^2C^1,N]palladium(II)} benzene hemisolvate

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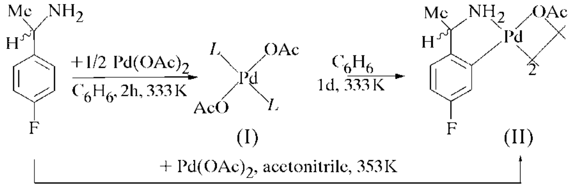
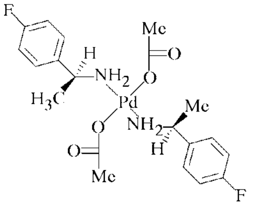
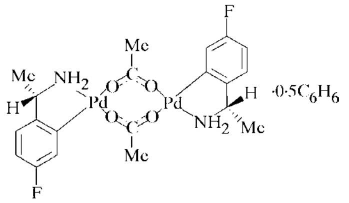
Complexes of the composition *trans*-[Pd(L)$_2$(OAc)$_2$] have been postulated as intermediates during cyclopalladation. The first structural characterization of such a precursor has now been achieved and its role in the reaction sequence has been established. Diacetato-κ^2O-bis[(*S*)-1-(4-fluorophenyl)ethylamine-κN]palladium(II), [Pd(O$_2$CMe)$_2$(4-FC$_6$H$_3$CHMeNH$_2$)$_2$] or [Pd(C$_2$H$_3$O$_2$)$_2$(C$_8$H$_{10}$FN)$_2$], (I), was obtained from palladium(II) acetate and (*S*)-NH$_2$CHMeC$_6$H$_3$F-4 in a 1:2 molar ratio. The intermediate was then reacted with additional palladium(II) acetate to give the acetate-bridged dinuclear complex di-μ-acetato-κ^4O:O'-bis{[(*S*)-2-(1-aminoethyl)-5-fluorophenyl-κ^2C^1,N]palladium(II)} benzene hemisolvate, [Pd(4-FC$_6$H$_3$CHMeNH$_2$)(μ-O$_2$CMe)]$_2$·0.5C$_6$H$_6$ or [Pd$_2$(C$_8$H$_9$FN)$_2$(C$_2$H$_3$O$_2$)$_2$]·0.5C$_6$H$_6$, (II).

Comment

The reaction of palladium(II) acetate and benzylamines under certain conditions results in the formation of a five-membered metallocycle, with the metal coordinated to both the amino N atom and the *ortho* C atom of the aromatic ring. Ryabov (1990) first postulated that this special case of orthometallation, often called cyclopalladation (Cope & Friedrich, 1968), proceeds *via* formation of an intermediate *trans*-bis(acetato)-bis(amine ligand) complex. Our interest in building blocks for quasi-racemic crystals (Englert *et al.*, 2000, 2002; Kalf *et al.*, 2002; Reemers & Englert, 2002) induced us to study this reaction. In this context, we have recently performed a structural study of this pathway for primary amines (Calmuschi & Englert, 2002), a relatively new class of substrates for cyclopalladation (Calmuschi *et al.*, 2004).




(I)


(II)

Vicente *et al.* (1997) infringed the historical second rule of Cope & Friedrich (1968) by cyclopalladating primary amines which even contained electron-withdrawing substituents on the aryl ring. They confirmed Ryabov's theory about the intermediate bis(ligand) complex and reported NMR data for this class of compounds. We have now achieved the isolation and structural characterization of the first *trans*-[Pd(L)$_2$-

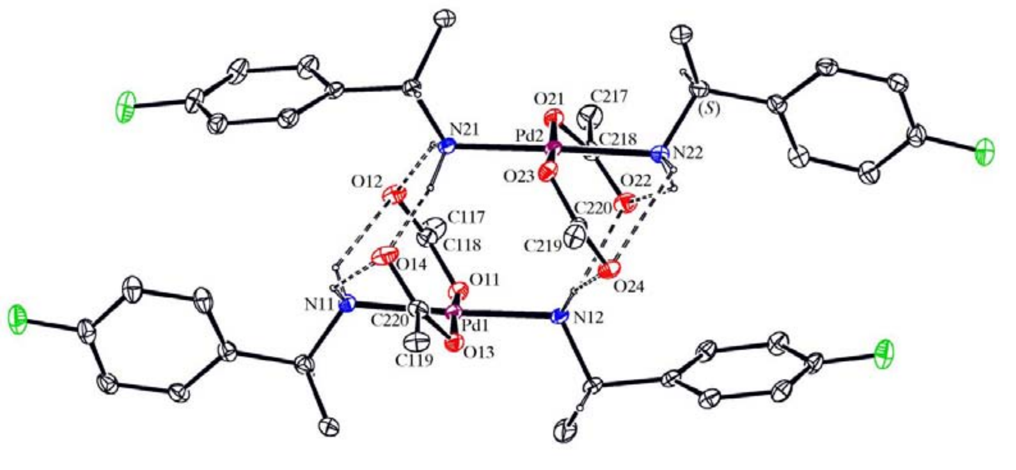


Figure 1
A view of the two independent molecules in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and selected H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines.

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(OAc)$_2$] precursor complex: the reaction between palladium(II) acetate and (*S*)-1-(4-fluorophenyl)ethylamine in a 1:2 molar ratio gives [Pd(O$_2$CMe)$_2$(4-FC$_6$H$_3$CHMeNH$_2$)$_2$], (I). The reaction pathway is shown in the scheme above.

To the best of our knowledge, only one other Pd^{II} compound containing terminal acetate ligands and primary amines has been reported to date. That dinuclear complex represents a second intermediate in the cyclopalladation pathway and was separated and fully characterized by Vicente *et al.* (1997).

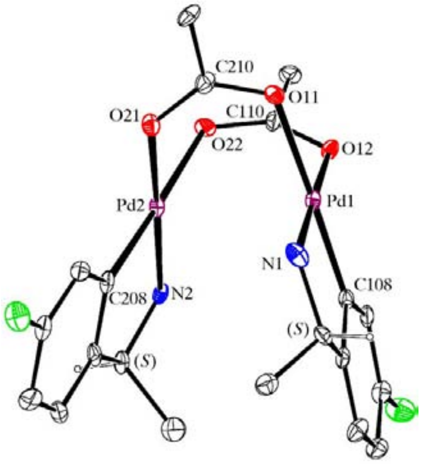

Figure 2
A view of the molecule of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and selected H atoms are shown as small spheres of arbitrary radii. The benzene solvent molecule has been omitted for clarity.

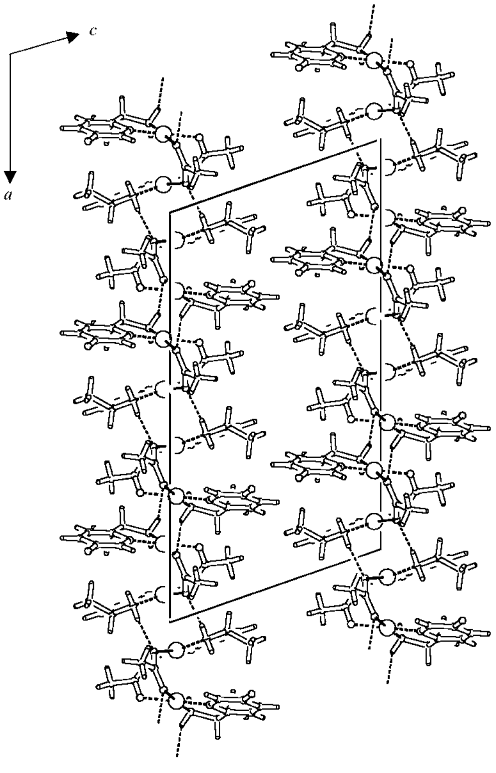

Figure 3
A view of the hydrogen-bonding interactions in (II).

Complex (I) crystallizes in the monoclinic space group $P2_1$. The asymmetric unit contains two molecules of quite similar conformation, with the acetate groups and the H atoms of the amine N atom directed to the same face of the coordination plane (Fig. 1). The symmetrically independent molecules approach each other in a face-to-face fashion, hence interacting *via* two pairs of hydrogen bridges, each pair between an amine NH$_2$ donor and uncoordinated acetate O atoms as acceptors. This conformation is probably stabilized by the intermolecular interactions and is therefore limited to the solid state. Table 2 gives geometric information for the hydrogen bonds in (I).

In terms of intramolecular geometry, complex (I) may best be compared with bis(acetato-*O*)bis(diethylamine-*N*)-palladium(II). This mononuclear square-planar Pd^{II} complex, with two monodentate acetate and two secondary amine ligands coordinated to the metal in a *trans* geometry (Kravtsova *et al.*, 1996), exhibits metal–ligand distances similar to those observed in (I). Due to the different hydrogen-bond donor–acceptor balance, this kind of interaction is limited to just one intramolecular hydrogen bond in the asymmetric unit of the centrosymmetric complex.

Further reaction of (I) with palladium(II) acetate results in the formation of [{Pd(4-FC$_6$H$_3$CHMeNH$_2$)$_2$(μ-O$_2$CMe)], (II), thus proving the role of (I) as the primary intermediate in cyclopalladation. The orthometallated complex (II) crystallizes from benzene with 0.5 equivalents of solvent; the benzene molecules occupy the twofold axes in space group *C*2. The geometry of this acetate dimer corresponds to the inner isomer, with both methyl groups attached at the chiral atom pointing towards each other (Fig. 2). The Pd$\cdots$Pd distance is 2.8733 (10) Å, slightly shorter than in the dinuclear complex of the unsubstituted amine ligand (Calmuschi & Englert, 2002). A two-dimensional network of hydrogen bonds in the *ab* plane is formed in (II) (Fig. 3). Table 4 gives details of the intermolecular hydrogen bonds. Complexes (I) and (II) both exhibit rather weak non-classical intermolecular hydrogen bonds.

Experimental

Pd(OAc)$_2$ and (*S*)-NH$_2$CHMeC$_6$H$_3$F-4 were stirred in benzene in a molar ratio of 1:2 at room temperature for 2 h. The resulting mixture was filtered and the filtrate concentrated *in vacuo*. Addition of hexane afforded green–yellow crystals of the mononuclear intermediate complex (I) (yield 89%). This product underwent further reaction with an additional equivalent of Pd(OAc)$_2$ in benzene at 333 K for 1 d. The mixture was filtered and concentrated and the product, (II), was precipitated with hexane (yield 93%). Single crystals suitable for X-ray structure determination were obtained from solutions in a 1:1 benzene–hexane mixture. Alternatively, complex (II) may be obtained by reaction of equimolar amounts of Pd(OAc)$_2$ and (*S*)-NH$_2$CHMeC$_6$H$_3$F-4 in refluxing acetonitrile for a period of 4 h.

Compound (I)

Crystal data

$[Pd(C_2H_3O_2)_2(C_8H_{10}FN)_2]$
$M_r = 502.83$
Monoclinic, $P2_1$
$a = 10.589$ (2) Å
$b = 17.537$ (3) Å
$c = 11.686$ (2) Å
$\beta = 100.954$ (3)°
$V = 2130.6$ (7) Å^3
$Z = 4$
$D_x = 1.568$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8096 reflections
$\theta = 1.8–28.4°$
$\mu = 0.92$ mm^{-1}
$T = 110$ (2) K
Irregular, yellow
0.80 × 0.70 × 0.60 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.500$, $T_{max} = 0.577$
29 128 measured reflections

10 628 independent reflections
10 531 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 28.4°$
$h = -14 \rightarrow 14$
$k = -23 \rightarrow 23$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.061$
$S = 1.06$
10 628 reflections
531 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Absolute structure: Flack (1983), with 5132 Friedel pairs
Flack parameter = −0.017 (11)

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

Pd1—O11	2.0192 (15)	O13—C120	1.289 (2)
Pd1—O13	2.0271 (14)	O23—C220	1.298 (2)
Pd1—N12	2.0409 (16)	O21—C218	1.299 (2)
Pd1—N11	2.0652 (16)	O11—C118	1.299 (2)
Pd2—O23	2.0144 (14)	O12—C118	1.233 (2)
Pd2—O21	2.0155 (14)	O24—C220	1.235 (2)
Pd2—N21	2.0507 (16)	O22—C218	1.237 (3)
Pd2—N22	2.0575 (17)	O14—C120	1.243 (3)
O11—Pd1—O13	174.33 (6)	O23—Pd2—O21	174.96 (6)
O11—Pd1—N12	89.55 (6)	O23—Pd2—N21	89.13 (6)
O13—Pd1—N12	87.67 (6)	O21—Pd2—N21	87.98 (6)
O11—Pd1—N11	91.22 (6)	O23—Pd2—N22	91.23 (6)
O13—Pd1—N11	91.83 (6)	O21—Pd2—N22	91.77 (7)
N12—Pd1—N11	176.65 (7)	N21—Pd2—N22	178.36 (7)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*A*···O14	0.95	2.11	2.867 (2)	136
N11—H11*B*···O12	0.95	2.15	2.896 (2)	134
N12—H12*A*···O22	0.95	2.16	3.029 (2)	151
N12—H12*B*···O24	0.95	2.01	2.923 (2)	161
N21—H21*A*···O12	0.95	2.17	3.040 (2)	151
N21—H21*B*···O14	0.95	2.05	2.956 (2)	160
N22—H22*A*···O24	0.95	2.41	2.930 (2)	114
N22—H22*B*···O22	0.95	2.25	2.892 (2)	124

Compound (II)

Crystal data

$[Pd_2(C_8H_9FN)_2(C_2H_3O_2)_2]\cdot 0.5C_6H_6$
$M_r = 646.27$
Monoclinic, $C2$
$a = 22.504$ (5) Å
$b = 9.1632$ (19) Å
$c = 12.279$ (3) Å
$\beta = 109.131$ (4)°
$V = 2392.2$ (9) Å^3
$Z = 4$

$D_x = 1.794$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8096 reflections
$\theta = 1.9–28.4°$
$\mu = 1.55$ mm^{-1}
$T = 110$ (2) K
Rod, yellow
0.64 × 0.10 × 0.03 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.437$, $T_{max} = 0.955$
12 301 measured reflections

5876 independent reflections
5354 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 28.3°$
$h = -30 \rightarrow 30$
$k = -11 \rightarrow 12$
$l = -16 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.070$
$S = 1.01$
5876 reflections
303 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.80$ e Å^{-3}
Absolute structure: Flack (1983), with 2732 Friedel pairs
Flack parameter = −0.09 (3)

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

Pd1—C108	1.965 (5)	Pd2—O21	2.072 (3)
Pd1—N1	2.020 (4)	Pd2—O22	2.172 (3)
Pd1—O12	2.065 (3)	Pd2—Pd2^{i}	3.1494 (9)
Pd1—O11	2.139 (3)	O11—C210	1.259 (5)
Pd1—Pd2	2.8717 (7)	O21—C210	1.259 (5)
Pd2—C208	1.944 (4)	O22—C110	1.265 (5)
Pd2—N2	2.042 (4)	O12—C110	1.272 (5)
C108—Pd1—N1	83.00 (18)	C208—Pd2—N2	82.62 (18)
C108—Pd1—O12	94.32 (17)	C208—Pd2—O21	94.42 (17)
N1—Pd1—O12	177.14 (14)	N2—Pd2—O21	177.03 (14)
C108—Pd1—O11	175.70 (19)	C208—Pd2—O22	173.12 (16)
N1—Pd1—O11	92.76 (15)	N2—Pd2—O22	92.04 (13)
O12—Pd1—O11	89.90 (13)	O21—Pd2—O22	90.93 (13)

Symmetry code: (i) $2 - x, y, 2 - z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O12^{i}	0.95	2.06	2.947 (5)	155
N2—H2*A*···O22^{ii}	0.95	2.02	2.877 (5)	149

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, 2 - z$; (ii) $2 - x, y, 2 - z$.

H atoms were introduced in idealized positions (C—H = 0.98 Å and N—H = 0.95 Å) and refined as riding.

For both compounds, 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: DN1048). Services for accessing these data are described at the back of the journal.

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