N1—Au—Cl1	173.09 (14)	O1—C6—C5	112.7 (5)
Cl2—Au—Cl1	92.64 (7)	O2—C6—C5	104.5 (5)
C1—N1—C5	120.3 (6)	O1—C6—C7	107.2 (5)
C1—N1—Au	123.0 (4)	O2—C6—C7	113.1 (5)
C5—N1—Au	116.7 (4)	C5—C6—C7	105.7 (5)
C11—N2—C7	120.8 (6)	N2—C7—C8	120.5 (6)
C11—N2—Au	120.5 (5)	N2—C7—C6	116.2 (5)
C7—N2—Au	118.3 (4)	C8—C7—C6	123.1 (6)
N1—C1—C2	121.9 (6)	C9—C8—C7	117.8 (7)
C1—C2—C3	118.8 (6)	C10—C9—C8	120.6 (7)
C4—C3—C2	119.5 (6)	C9—C10—C11	119.9 (6)
C5—C4—C3	119.4 (7)	N2—C11—C10	120.3 (7)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1′···Cl3^{i}	0.84 (7)	2.34 (7)	3.077 (7)	147 (5)
O2—H2′···Cl3^{ii}	0.72 (8)	2.39 (8)	3.072 (6)	160 (8)

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

Although the dpk ligand was present in sufficient quantity during the synthesis of (II) for the 1:2 complex to form, elemental analysis suggested the crystals were those of the 1:1 complex. Further examination of this species revealed that the monoclinic unit cell was not the same as that reported earlier (Annibale *et al.*, 1981) since the *b* axis was not of similar length. The structure for (I) was solved by the heavy-atom method from which the position of the metal atom was determined to be on a center of inversion. The remaining non-H atoms were found from subsequent Fourier maps. The structure of (II) was solved by direct methods. For compound (I), H atoms were placed at calculated positions and thereafter allowed to ride on their parent atom, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O)$ [*SHELXL*93 (Sheldrick, 1993) defaults; C—H 0.93 and O—H 0.82 Å]. H atoms on water molecules were not located. For compound (II), all aromatic H atoms were placed at calculated positions and thereafter allowed to ride on their parent atom, with $U_{iso}(H) = 1.2U_{eq}(C)$ (*SHELXL*93 default; C—H 0.93 Å). The hydroxyl H atoms were refined without constraints.

Data collection: *SHELXTL-Plus* (Sheldrick, 1991) for (I); *P3/P4-PC Diffractometer Program* (Siemens, 1991) for (II). Cell refinement: *SHELXTL-Plus* for (I); *P3/P4-PC Diffractometer Program* for (II). For both compounds, data reduction: *SHELXTL-Plus*. Program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990) for (I); *SHELXTL-Plus* for (II). Program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993) for (I); *SHELXTL-Plus* for (II). Molecular graphics: *ORTEX* (McArdle, 1995) for (I); *SHELXTL-Plus* for (II). Software used to prepare material for publication: *SHELXS*86 for (I); *SHELXTL-Plus* for (II).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1220). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(π-allyl-6,7-dihydrohimachalene)-α,α-dichlorodipalladium†

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Abstract

Treatment of *trans*-6,7-dihydrohimachalene [(1*R*,2*R*,7*R*)-2,6,6,9-tetramethylbicyclo[5.4.0]deca-8-ene] with palladium(II) chloride gives bis(chloro)-bridged cyclopalladated dimers, $[Pd_2Cl_2(C_{15}H_{25})_2]$, with high regio- and stereoselectivity. The molecule displays crystallographic twofold symmetry and adopts a butterfly shape (the Pd_2Cl_2 unit is the 'body' and the organic ligands are the 'wings'). The methyl group on the asymmetric C atom points to the side in which the Pd_2Cl_2 unit is placed.

Comment

Organic synthesis *via* (π-allyl)palladium complexes has attracted much attention in recent years (Tsuji, 1980; Trost & Verhoeven, 1982). Pd^{II} salts provide activation of the allylic position of an olefin, thus forming the basis for a variety of allylic alkylation reactions (Backvall & Vergberg, 1988; Milstein, 1982). Recently, we have shown that this formation in monoterpenic series occurs

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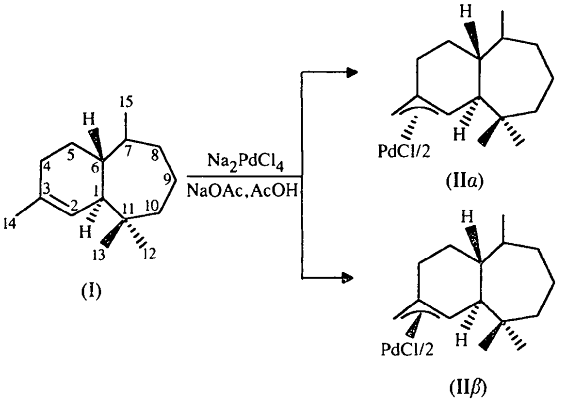
† Alternative name: di-μ-chloro-bis{[(8,9,15-η;1*R*,2*R*,7*R*)-2,6,6,9-tetramethylbicyclo[5.4.0]deca-8-ene]palladium}.

with high regio- and stereoselectivity (El Firdoussi *et al.*, 1992). This selectivity has also been established for a sesquiterpenic olefin, β-himachalene (Chiaroni, Riche, El Firdoussi, Benharref & Karim, 1993). In order to investigate the reactivity of the double bond in position 2,3 of *trans*-6,7-dihydrohimachalene, (I), prepared according to a previously described procedure (Joseph & Dew, 1968), we synthesized the title complex by mixing Na_2PdCl_4, $CuCl_2$ and NaOAc in acetic acid medium (yield 51%). Two isomers are possible according to the scheme below.



We have established the regiochemistry of the title complex by using high-resolution NMR spectroscopy. However, depending on the coordination of the palladium on the α or β face of the substrate, two stereoisomers could be obtained, *i.e.* (IIα) or (IIβ). X-ray diffraction of the complex revealed unambiguously that the Pd_2Cl_2 core is placed at the same face as the hydrogen at position C1 [structure (IIα)].

The structure consists of dimeric units as represented in Fig. 1. The two halves of the dimer are related by a crystallographic twofold axis. The two metal atoms are bridged by two Cl^- ions, the four atoms defining a very distorted square [torsion angle Cl′—Pd—Cl—Pd′ −36.1 (1)°, see also angles in Table 1]. The intermetallic distance is indicative of a weak but non-negligible metal–metal interaction.

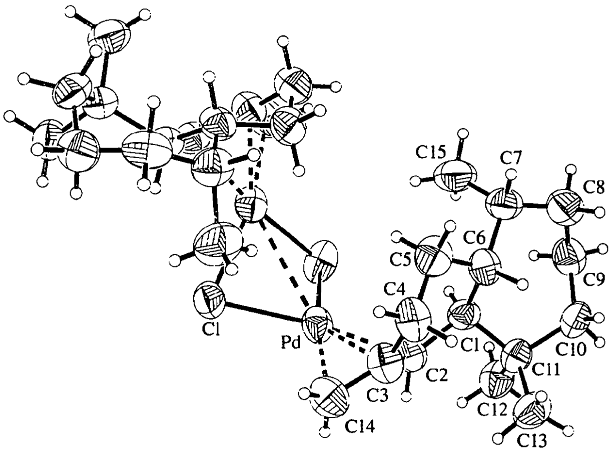


Fig. 1. View of the title compound, with the non-H atoms represented by 50% probability ellipsoids. The non-labelled half molecule is related to the other half by a twofold axis.

The coordination is completed by the carbanion resulting from the deprotonation of *trans*-6,7-dihydrohimachalene at the exocyclic methyl group at the six-membered ring (C14). Its absolute configuration, previously known from related natural products, is confirmed by the Flack parameter (Flack, 1983). The ligand binds in a η^3-allyl fashion through the C atoms at positions 2, 3 and 14. Analogous allyl organometallics of palladium with terpene derivatives have been described (Ammann *et al.*, 1992; Pregosin *et al.*, 1994) including one with β-himachalene (Chiaroni *et al.*, 1993), similar to that described in this paper, but with the ligand coordinated *via* C5—C6—C7 and the double bond preserved at C2—C3. The C···Pd distances are slightly shorter than those found in analogous compounds with the coordination sphere completed by a π-acceptor ligand (Cermak, Perera, Shaw & Thornton-Pett, 1996).

The geometry around the metal atom may be described as very distorted square planar (with the two Cl atoms plus C2 and C14 forming the square), with the bonds to C3 and to the other Pd atom lying well above the plane, their projections bisecting the Cl—Pd—Cl and C2—Pd—C14 angles. The allyl plane is, in this way, almost perpendicular to the average Pd_2Cl_2 plane [dihedral angle 89.3 (7)°]. Other $Pd_2Cl_2(allyl)_2$ dimers display analogous features but with a greater planarity of the Pd_2Cl_2 square, for example, it is perfectly planar in the compound described in Donovan, Hughes, Spara & Rheingold (1995).

The exocyclic C15 methyl group and the metal atom are placed at the same face of the organic moiety. The seven-membered ring displays a twisted conformation, with C1 and C9 placed at one side (the C15–Pd side) and C6 and C10 lying on the other side of the plane defined by atoms C7, C8 and C11. The whole molecule adopts a butterfly shape, with its wings (the organic ligands) folded to the opposite side of the Cl atoms. The packing of the crystal displays only normal van der Waals contacts.

Experimental

The compound was synthesized from *trans*-6,7-dihydrohimachalene following a known procedure (Trost, Strege, Weber, Fullerton & Dietsche, 1978) for synthesizing π-allyl–palladium compounds from olefins.

Crystal data

$[Pd_2Cl_2(C_{15}H_{25})_2]$
$M_r = 694.40$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Tetragonal
$P4_12_12$
$a = 8.9054\,(13)$ Å
$c = 37.978\,(8)$ Å
$V = 3011.9\,(9)$ Å^3
$Z = 4$
$D_x = 1.531$ Mg m^{-3}
D_m not measured

Cell parameters from 34 reflections
$\theta = 15.1$–$19.8°$
$\mu = 1.388$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.6 × 0.4 × 0.2 mm
Orange–yellow

Data collection

Stoe–Siemens Stadi-4 diffractometer
ω scans
Absorption correction: ψ scans (Sheldrick, 1994)
$T_{\min} = 0.389$, $T_{\max} = 0.758$
8888 measured reflections
4393 independent reflections
2707 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0069$
$\theta_{\max} = 30.01°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 53$
3 standard reflections
frequency: 120 min
intensity decay: 26.5%

Refinement

Refinement on F^2
$R(F) = 0.0738$
$wR(F^2) = 0.1530$
$S = 1.130$
4392 reflections
168 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 8P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.025$ e Å^{-3}
$\Delta\rho_{\min} = -0.416$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = $-0.15\,(11)$

Table 1. *Selected geometric parameters (Å, °)*

Pd—C14	2.112 (12)	Pd—Cl$^{\rm i}$	2.423 (3)
Pd—C3	2.138 (10)	Pd—Pd$^{\rm i}$	3.100 (2)
Pd—C2	2.141 (9)	C2—C3	1.425 (13)
Pd—Cl	2.412 (3)	C3—C14	1.381 (15)
C14—Pd—C3	37.9 (4)	C2—Pd—Cl$^{\rm i}$	101.1 (3)
C14—Pd—C2	68.6 (4)	Cl—Pd—Cl$^{\rm i}$	88.01 (11)
C3—Pd—C2	38.9 (3)	Pd—Cl—Pd$^{\rm i}$	79.73 (8)
C14—Pd—Cl	102.4 (3)	C3—C2—C1	125.0 (8)
C3—Pd—Cl	132.7 (3)	C14—C3—C2	117.3 (9)
C2—Pd—Cl	170.9 (3)	C14—C3—C4	123.3 (9)
C14—Pd—Cl$^{\rm i}$	167.3 (3)	C2—C3—C4	117.8 (8)
C3—Pd—Cl$^{\rm i}$	135.9 (3)		

Symmetry code: (i) $-y, -x, \frac{1}{2} - z$.

H atoms were idealized, except for those of the allyl group (H2, H141 and H142), which were refined with the C2—H2, C14—H141 and C14—H142 distances restrained to be the same, and the C3—C14—H141 and C3—C14—H142 angles also restrained to be the same. Isotropic displacement parameters for H atoms were fixed at 1.2 times the equivalent isotropic displacement parameters of their parent C atom. The high R value is associated with data collection at high angle (to 60° in 2θ); there is still significant intensity at such high angles.

Data collection: *STADI4* (Stoe & Cie, 1995*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1995*b*). Program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *XL* in *SHELXTL*. Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *XL* in *SHELXTL*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Five-Coordinated Monomer of Chloro[*N*,*N'*-(di-2-hydroxy-1-naphthylidene)-1,2-diaminobenzene]iron(III)

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Abstract

In the dioxane solvate of the title complex, chloro{2,2'-[*o*-phenylenebis(nitrilomethylidyne)]dinaphtholato-*N*,*N'*,*O*,*O'*}iron(III), $[FeCl(C_{28}H_{18}N_2O_2)].C_4H_8O_2$, the