N3—Ru1—N4	79.6 (3)	N9—Ru2—N10	80.1 (3)
N3—Ru1—N5	173.4 (3)	N9—Ru2—N11	96.3 (2)
N3—Ru1—N6	95.9 (3)	N9—Ru2—N12	174.5 (3)
N4—Ru1—N6	89.0 (3)	N10—Ru2—N11	90.5 (3)
N4—Ru1—N5	95.1 (3)	N10—Ru2—N12	95.8 (3)
N5—Ru1—N6	79.9 (2)	N11—Ru2—N12	80.0 (2)

H atoms were placed at geometrically idealized coordinates for all expected locations. In the case of methyl C atoms, the torsion angle was set so as to maximize the sum of the electron density at the three calculated positions. The coordinates of all H atoms were then allowed to 'ride' on those of the attached C atoms, with isotropic displacement parameters fixed at 1.2 times (1.5 for methyl) the equivalent isotropic displacement parameters of their attached C atoms. In the final refinement cycles, the U^{ij} values of the C301 and C302 atoms (belonging to the diethyl ether solvate molecule) were constrained to be equal. Polar axis restraints were generated by the method of Flack & Schwarzenbach (1988). During the course of the cell determination, an initial tetragonal unit cell with $a = 17.89$ and $c = 12.79$ Å was obtained. Subsequent location of a sufficiently large number of strong reflections gave the larger tetragonal unit cell with $a = 25.372$ (1) and $c = 12.726$ (2) Å. Solution of the structure using the larger unit cell gave two independent molecules in the asymmetric unit in which the two cations are pseudosymmetrically related by a screw axis, as can be seen in the unit-cell packing diagram (Fig. 2). However, only 92 of 125 heavy atoms map fairly closely to their 'symmetry equivalents', indicating that no symmetry has been ignored in describing the overall structure and that the larger cell is required. Furthermore, refinement of the structure with the smaller unit cell resulted in a poorer structure with regard to both displacement parameters and the constancy of bond distances and angles. These factors were especially apparent during treatment of the anions and solvent molecules.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

This work was supported by the Robert A. Welch Foundation (No. Y-1301) and the Donors of The Petroleum Research Fund administered by the American Chemical Society. We also thank Johnson Matthey for a generous loan of ruthenium.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1256). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Barton, J. K., Goldberg, J. M., Kumar, C. V. & Turro, N. J. (1986). *J. Am. Chem. Soc.* **108**, 2081–2088.

Burstall, F. H. (1936). *J. Chem. Soc.* pp. 173–175.

Dwyer, F. P. & Gyarfas, E. C. (1947). *Proc. R. Soc. N. S. Wales*, **80**, 212–214.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.

Fox, M. A. & Channon, M. (1988). Editors. *Photoinduced Electron Transfer*. Amsterdam: Elsevier.

Gillard, R. D. & Hill, R. E. E. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1217–1236.

Hiort, C., Lincoln, P. & Nordén, B. (1993). *J. Am. Chem. Soc.* **115**, 3448–3454.

Lincoln, P., Broo, A. & Nordén, B. (1996). *J. Am. Chem. Soc.* **118**, 2644–2653.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Rillema, D. P., Jones, D. S. & Levy, H. A. (1979). *J. Chem. Soc. Dalton Trans.* pp. 849–851.

Seddon, E. A. & Seddon, K. R. (1984). In *The Chemistry of Ruthenium*, edited by R. J. H. Clark. Amsterdam: Elsevier.

Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). C**53**, 707–710

Bis(di-2-pyridylmethanediol-*N*,*N*′)-palladium(II) Dichloride Tetrahydrate and Dichloro(di-2-pyridylmethanediol-*N*,*N*′)-gold(III) Chloride

SHAUN O. SOMMERER,[a] ALAN J. JIRCITANO,[b] BARRY L. WESTCOTT,[b] KHALIL A. ABBOUD[c] AND JEANETTE A. KRAUSE BAUER[d]

[a]Department of Physical Sciences, Barry University, 11300 NE 2nd Avenue, Miami Shores, Florida 33161-6695, USA, [b]Division of Science, The Pennsylvania State University at Erie, The Behrend College, Station Road, Erie, Pennsylvania 16563-1200, USA, [c]Department of Chemistry, The University of Florida, Gainesville, Florida 32611-2046, USA, and [d]University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221-0172, USA. E-mail: sommerer@buaxp1.barry.edu

(*Received 17 July 1996; accepted 2 January 1997*)

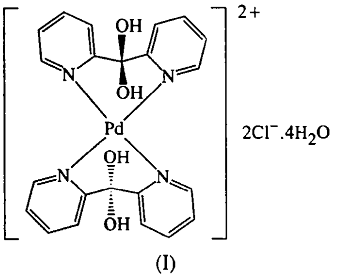
Abstract

Structural analyses of $[Pd(C_{11}H_{10}N_2O_2)_2]Cl_2.4H_2O$, (I), and $[Au(C_{11}H_{10}N_2O_2)Cl_2]Cl$, (II), revealed that both metals are in square-planar coordination environments. The Pd atom in (I) is coordinated equatorially by four N-atom donors and has two long-range Pd$\cdots$O interactions which lead to approximate pseudo-octahedral geometry. The Au complex achieves a coordination number of four with two N and two Cl donors, however, a weak long-range intramolecular axial interaction accounts for the fifth coordination site to make the species pseudo-square pyramidal.

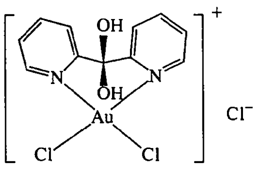
Acta Crystallographica Section C
ISSN 0108-2701 © 1997

Comment

Structural analyses of the title complexes, (I) and (II), were motivated by our continued interest in the behavior of di-2-pyridyl ketone (dpk) when combined with transition metals that are not normally stabilized by an octahedral coordination sphere.



(I)



(II)

The crystals of (I) were found to consist of a [Pd{dpk-(OH)$_2$}$_2$]$^{2+}$ complex cation, Cl^- anions and water molecules which are nearly isostructural with those in the previously reported [Pt{dpk-(OH)$_2$}$_2$]Cl_2.$4H_2O$ complex (Sommerer & Abboud, 1993). The difference between the structures is the positions of the Cl1 and O*W*2 atoms in the present structure which correspond to those of O(*W*2) and Cl(1), respectively, in [Pt{dpk-(OH)$_2$}$_2$]Cl_2.$4H_2O$. The Pd atom in the title compound is located on an inversion center, has the usual square-planar coordination and is involved in two long-range interactions at the approximate octahedral sites of the metal, with the O1 atom of one hydroxyl group [Pd···O1 2.816 (2) Å]. This is shorter than observed in [Pt{dpk-(OH)$_2$}$_2$]Cl_2.$4H_2O$, where the Pt···O(1) distance is 2.940 (6) Å, but is in excellent agreement with the Pd···O contact [2.824 (6) Å] reported for the [Pd^{II}Cl_2{dpk-(OH)$_2$}] complex (Annibale *et al.*, 1981). We observe the axial contacts leading to pseudo-octahedral geometry to be much longer than those usually considered as bonding interactions (*ca* 2.05 Å), though it is shorter than normal non-bonded distances (*ca* 3.6 Å). An angle of 27.9 (1)° is formed between the Pd···O1 vector and the normal of the coordination plane, which together with the Pd—N1 and Pd—N2 distances of 2.020 (3) and 2.022 (3) Å, respectively, are also in agreement (Annibale *et al.*, 1981). Finally, the O*W*2 atom is hydrogen bonded to HO1 and HO2, the details of which are given in Table 2.

The crystals of (II) were found to consist of [Au{dpk-(OH)$_2$}Cl_2]$^+$ and Cl^- counterions. The geometry of the [Au{dpk-(OH)$_2$}]$^{2+}$ cation is square planar and identical to that reported previously by Annibale *et al.* (1981). However, $Cl3^-$ (*i.e.* the counterion) is directly involved in a long-range interaction with the Au cation [Au···Cl3 3.229 (2) Å] and is also hydrogen bonded to both H1′ and H2′, the details of which are in Table 4. The long-range Au···Cl3 contact leads to a pseudo-square-pyramidal geometry for the Au atom and the combined intramolecular interactions join the cation/anion units into infinite extended chains.

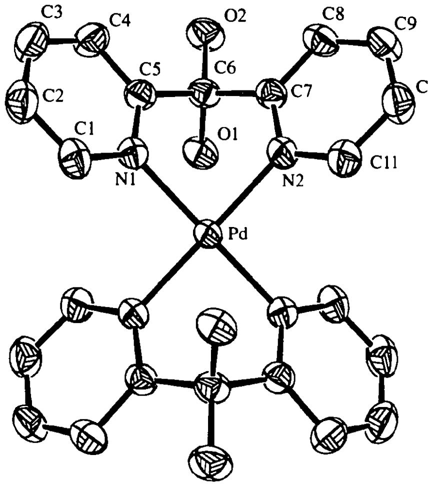


Fig. 1. Displacement ellipsoid drawing of compound (I), with ellipsoids drawn at the 50% probability level.

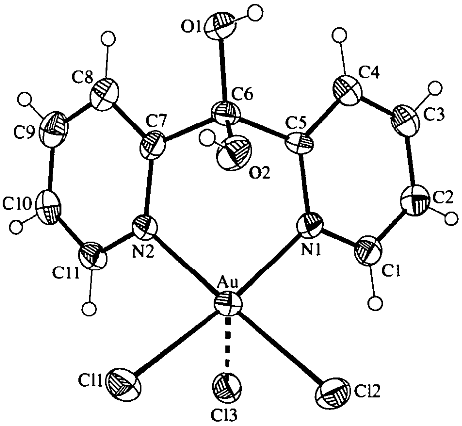


Fig. 2. Displacement ellipsoid drawing of compound (II), with ellipsoids drawn at the 50% probability level.

Experimental

For the preparation of compound (I), potassium tetrachloropalladate(II) was combined with dpk in a 1:2 stoichiometric ratio in 75 ml of H_2O. The resulting solution was filtered and slow evaporation of the clear filtrate gave clear pale-yellow crystals suitable for X-ray diffraction studies. For the preparation of compound (II), gold(III) chloride was combined with dpk in a 1:2 stoichiometric ratio in 75 ml of H_2O. The resulting mixture was filtered and slow evaporation of the clear filtrate gave clear dark-yellow crystals suitable for X-ray diffraction studies.

Compound (I)

Crystal data

$[Pd(C_{11}H_{10}N_2O_2)_2]Cl_2.4H_2O$
$M_r = 653.78$
Monoclinic
$C2/c$
$a = 14.814\,(3)$ Å
$b = 12.372\,(2)$ Å
$c = 14.306\,(2)$ Å
$\beta = 91.080\,(10)°$
$V = 2621.5\,(8)$ Å^3
$Z = 4$
$D_x = 1.656$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 20$–$22°$
$\mu = 0.965$ mm^{-1}
$T = 293\,(2)$ K
Rod
$0.55 \times 0.40 \times 0.25$ mm
Light yellow

Data collection

Nicolet *P*3 diffractometer
θ–2θ scans
Absorption correction: analytical
$T_{\min} = 0.230$, $T_{\max} = 0.277$
3041 measured reflections
3041 independent reflections
2545 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 27.56°$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 18$
3 standard reflections every 300 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0364$
$wR(F^2) = 0.1206$
$S = 1.054$
3041 reflections
171 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 4.5639P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.032$ e Å^{-3}
$\Delta\rho_{\min} = -0.814$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pd—N1	2.020 (3)	C2—C3	1.371 (6)
Pd—N2	2.022 (3)	C3—C4	1.385 (5)
O1—C6	1.401 (4)	C4—C5	1.387 (4)
O2—C6	1.385 (3)	C5—C6	1.530 (4)
N1—C5	1.342 (4)	C6—C7	1.529 (4)
N1—C1	1.352 (4)	C7—C8	1.392 (4)
N2—C11	1.348 (4)	C8—C9	1.379 (5)
N2—C7	1.354 (4)	C9—C10	1.378 (6)
C1—C2	1.379 (5)	C10—C11	1.387 (4)
N1—Pd—N2^{i}	92.98 (10)	N1—C5—C6	116.7 (3)
N1—Pd—N2	87.02 (10)	C4—C5—C6	122.1 (3)
C6—O1—HO1	109.5 (2)	O2—C6—O1	112.2 (3)
C6—O2—HO2	109.5 (2)	O2—C6—C7	106.7 (2)
C5—N1—C1	119.7 (3)	O1—C6—C7	110.5 (3)
C5—N1—Pd	119.1 (2)	O2—C6—C5	111.7 (3)
C1—N1—Pd	121.2 (2)	O1—C6—C5	106.6 (2)
C11—N2—C7	119.5 (3)	C7—C6—C5	109.3 (2)
C11—N2—Pd	121.4 (2)	N2—C7—C8	120.9 (3)
C7—N2—Pd	119.1 (2)	N2—C7—C6	116.2 (2)
N1—C1—C2	121.3 (3)	C8—C7—C6	122.9 (3)
C3—C2—C1	119.3 (3)	C9—C8—C7	119.1 (3)
C2—C3—C4	119.6 (3)	C10—C9—C8	120.0 (3)
C5—C4—C3	118.9 (3)	C9—C10—C11	118.7 (3)
N1—C5—C4	121.2 (3)	N2—C11—C10	121.7 (3)

Symmetry code: (i) $-x, -y, 1-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—HO1···O*W*2	0.82	2.01	2.826 (3)	173
O2—HO2···O*W*2^{i}	0.82	2.06	2.865 (4)	167

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

Compound (II)

Crystal data

$[Au(C_{11}H_{10}N_2O_2)Cl_2]Cl$
$M_r = 505.53$
Monoclinic
$P2_1/n$
$a = 9.233\,(2)$ Å
$b = 12.271\,(3)$ Å
$c = 12.627\,(3)$ Å
$\beta = 95.58\,(3)°$
$V = 1423.8\,(5)$ Å^3
$Z = 4$
$D_x = 2.358$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 10$–$12°$
$\mu = 10.892$ mm^{-1}
$T = 293\,(2)$ K
Block
$0.34 \times 0.27 \times 0.23$ mm
Yellow

Data collection

Siemens *P*3 diffractometer
ω scans
Absorption correction: by integration
$T_{\min} = 0.057$, $T_{\max} = 0.166$
3455 measured reflections
3259 independent reflections
2720 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0638$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = -16 \rightarrow 16$
40 standard reflections every 100 reflections intensity decay: < 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0365$
$wR(F^2) = 0.0938$
$S = 1.008$
3259 reflections
181 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 3.458$ e Å^{-3}
$\Delta\rho_{\min} = -1.988$ e Å^{-3}
Extinction correction: *SHELXTL-Plus*
Extinction coefficient: 0.0042 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Au—N2	2.039 (5)	C1—C2	1.372 (9)
Au—N1	2.042 (5)	C2—C3	1.397 (9)
Au—Cl2	2.275 (2)	C3—C4	1.392 (10)
Au—Cl1	2.276 (2)	C4—C5	1.378 (9)
O1—C6	1.369 (8)	C5—C6	1.528 (8)
O2—C6	1.410 (8)	C6—C7	1.537 (9)
N1—C1	1.337 (8)	C7—C8	1.393 (9)
N1—C5	1.380 (7)	C8—C9	1.383 (10)
N2—C11	1.341 (9)	C9—C10	1.372 (10)
N2—C7	1.366 (8)	C10—C11	1.372 (9)
N2—Au—N1	86.0 (2)	C4—C5—N1	120.0 (6)
N2—Au—Cl2	176.0 (2)	C4—C5—C6	122.4 (6)
N1—Au—Cl2	91.1 (2)	N1—C5—C6	117.5 (5)
N2—Au—Cl1	90.6 (2)	O1—C6—O2	113.5 (5)

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).

This research was supported by a Cottrell College Science Award of Research Corporation, Tucson, Arizona, USA.

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.

References

Annibale, G., Canovese, L., Cattalini, L., Natile, G., Biagini-Cingi, M., Manotti-Lanfredi, A. & Tiripicchio, A. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2280–2287.

McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1991). *P3/P4-PC Diffractometer Program*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sommerer, S. O. & Abboud, K. A. (1993). *Acta Cryst.* C**49**, 1152–1154.

Acta Cryst. (1997). C**53**, 710–712

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

Larbi El Firdoussi,[a] Smaïl Allaoud,[a] Abdellah Karim,[a] Alejandro F. Barrero,[b] Miguel Quirós,[c] Yves Castanet[d] and André Mortreux[d]

[a]*Laboratoire de Chimie de Coordination, Faculté des Sciences Semlalia, Marrakech, Morocco,* [b]*Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain,* [c]*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain, and* [d]*Laboratoire de Catalyse Homogène et Hétérogène, UA CNRS, 402 Villeneuve d'Ascq, France. E-mail: mquiros@goliat.ugr.es*

(*Received 9 October 1996; accepted 16 December 1996*)

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

---

† 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}.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997