

## Cyclometallated compounds. XV.<sup>1</sup> A tetranuclear acetate-bridged cyclo-palladated molecular box

Brendan J. O'Keefe and Peter J. Steel\*

 Department of Chemistry, University of Canterbury, Christchurch, New Zealand  
 Correspondence e-mail: p.steel@chem.canterbury.ac.nz

Received 31 May 2000

Accepted 24 August 2000

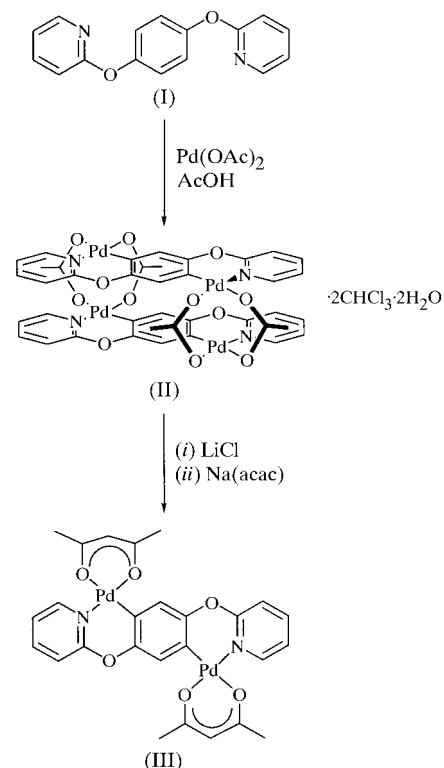
The title complex, tetra- $\mu$ -acetato- $O:O'$ -bis{[ $\mu$ -1,4-bis-(2-pyridyloxy)phenylene- $N,C^2:N',C^6$ ]dipalladium(II)} bis(trichloromethane) dihydrate,  $[\text{Pd}_4(\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_4] \cdot 2\text{CHCl}_3 \cdot 2\text{H}_2\text{O}$ , the product of the reaction of 1,4-bis(2-pyridyloxy)benzene with palladium acetate, is shown to be a tetranuclear, rather than a polymeric, species. It crystallizes about a centre of inversion and has two doubly cyclo-palladated ligands bridged by four acetate groups. The cyclopalladated ligand is far from planar in the complex and has the central benzene rings  $\pi$ -stacked. The chelate rings exist in shallow boat conformations.

### Comment

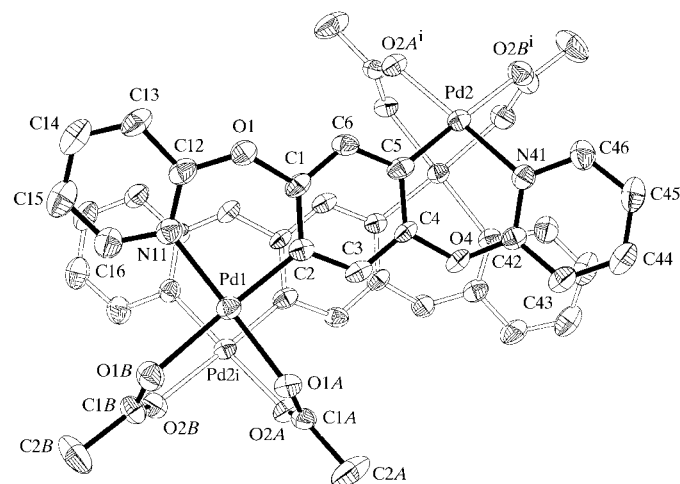
We have been interested for some time in the preparation of doubly cyclopalladated compounds (O'Keefe & Steel, 1999), particularly examples involving the double cyclopalladation of a single benzene ring (Caygill & Steel, 1990; Phillips & Steel, 1991; Hartshorn & Steel, 1998). Recently, we reported the cyclopalladation chemistry of all three isomers of bis(2-pyridyloxy)benzene (De Geest *et al.*, 1999). We described therein the preparation of the dinuclear complex (III), which, due to its insolubility in common NMR solvents, we were only able to characterize by elemental analysis and mass spectroscopy. This complex was prepared (see Scheme) by reaction of 1,4-bis(2-pyridyloxy)benzene (I), with palladium acetate to give an intermediate, (II), which was converted to the corresponding chloride by metathesis and thereafter to the acetylacetonate complex, (III). The nature of the initially formed product, (II), was a subject of doubt. Related acetate-bridged species have generally been considered to be polymeric in nature (Lydon & Rourke, 1997; Vicente *et al.*, 1997), but we proposed that (II) is a tetranuclear species, based on our previous determination of the structure of the product of the reaction of palladium acetate with 1,4-bis(benzothiazol-2-yl)benzene (O'Keefe & Steel, 1998). To resolve this ambiguity,

<sup>1</sup> Part XIV: O'Keefe & Steel (1999).

we now report the X-ray crystal structure of (II), which we have since managed to crystallize by slow evaporation from a chloroform solution.



Complex (II) crystallizes in the monoclinic space group  $P2_1/c$ , the asymmetric unit containing one doubly palladated molecule of (I), two Pd atoms, two acetates, a molecule of chloroform disordered over three sites and a molecule of water disordered over two sites. The two cyclopalladated units are positioned about a centre of inversion with four acetates bridging the four Pd atoms, so that the molecular structure has the shape of a counter-hinged molecular box (Fig. 1).


**Figure 1**

A perspective view of (II) with the atom-labelling scheme. H atoms and solvate molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level; the symmetry code is as in Table 1.

The ligand acts as a doubly chelating *C,N*-donor bridging two Pd atoms through six-membered chelate rings. The benzene ring is dipalladated in a *para* arrangement, and thus the ligand adopts an *anti* conformation of the two pyridine rings with respect to the benzene ring. Unlike the situation in a structurally related tetranuclear complex (O'Keefe & Steel, 1998), the cyclopalladated ligand is far from planar. The planes of the pyridine rings are inclined to the benzene ring at angles of 30.1 (5) and 37.7 (5)° for the pyridines containing N11 and N41, respectively, with one ring being inclined above the plane of the benzene ring and the other below. This lack of planarity is due to flexibility provided by the O-atom spacer and the formation of six-membered chelate rings, rather than the five-membered rings of our earlier complex. The six-membered chelate rings have shallow boat conformations, with the Pd and O atoms lying out of the planes of the C and N atoms [Pd1 0.410 (6) and O1 0.288 (8) Å, and Pd2 0.821 (6) and O4 0.372 (8) Å].

All Pd–donor bond lengths are normal and show the usual lengthening of the bond *trans* to the *C*-donor (Churchill *et al.*, 1980; Navarro-Ranninger *et al.*, 1996). The geometry at each Pd atom is square planar and the Pd1··Pd2A separation is 2.918 (1) Å, which is considered non-bonding (Churchill *et al.*, 1980). The two central benzene rings, being related by a centre of inversion, are necessarily parallel and are separated by 3.21 (1) Å. These two rings are offset such that a bond of one ring sits over the centroid of the other ring and a significant  $\pi$ – $\pi$  interaction is indicated.

This structure determination confirms our earlier proposal (De Geest *et al.*, 1999) that (II) exists as a tetranuclear, rather than a polymeric, species, and suggests that other related compounds may also be so. It represents the first reported example of a crystal structure of a compound containing a doubly cyclopalladated benzene ring with six-membered *N,C*-chelate rings.

## Experimental

Complex (II) was prepared as previously described by De Geest *et al.* (1999). Crystals were obtained by slow evaporation of a chloroform solution.

### Crystal data

[Pd <sub>4</sub> (C <sub>16</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>4</sub> ] <sup>·-</sup> 2CHCl <sub>3</sub> ·2H <sub>2</sub> O	$D_x = 1.861 \text{ Mg m}^{-3}$
$M_r = 1461.06$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 6111 reflections
$a = 12.225 (5) \text{ \AA}$	$\theta = 2.15\text{--}26.36^\circ$
$b = 15.052 (5) \text{ \AA}$	$\mu = 1.735 \text{ mm}^{-1}$
$c = 14.135 (5) \text{ \AA}$	$T = 168 (2) \text{ K}$
$\beta = 91.797 (5)^\circ$	Plate, yellow
$V = 2599.7 (16) \text{ \AA}^3$	$0.38 \times 0.35 \times 0.04 \text{ mm}$
$Z = 2$	

### Data collection

Siemens SMART CCD diffractometer	5261 independent reflections
Exposures over $0.5^\circ \varphi$ or $\omega$ rotation scans	3476 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Siemens, 1999)	$R_{\text{int}} = 0.089$
$T_{\text{min}} = 0.559$ , $T_{\text{max}} = 0.934$	$\theta_{\text{max}} = 26.36^\circ$
26 967 measured reflections	$h = -15 \rightarrow 15$
	$k = -18 \rightarrow 13$
	$l = -17 \rightarrow 17$

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

Pd1–C2	1.980 (7)	Pd2–C5	1.962 (7)
Pd1–N11	2.044 (6)	Pd2–N41	2.007 (5)
Pd1–O1A	2.052 (5)	Pd2–O2A <sup>i</sup>	2.067 (4)
Pd1–O1B	2.171 (5)	Pd2–O2B <sup>i</sup>	2.158 (5)
C2–Pd1–N11	89.3 (2)	N41–Pd2–O2B <sup>i</sup>	92.5 (2)
C2–Pd1–O1A	91.6 (2)	O2A <sup>i</sup> –Pd2–O2B <sup>i</sup>	88.71 (18)
N11–Pd1–O1A	176.6 (2)	C1–C2–Pd1	124.0 (5)
C2–Pd1–O1B	177.6 (2)	C3–C2–Pd1	121.2 (5)
N11–Pd1–O1B	92.9 (2)	C4–C5–Pd2	120.2 (5)
O1A–Pd1–O1B	86.22 (18)	C6–C5–Pd2	125.1 (5)
C5–Pd2–N41	86.4 (2)	C1A–O1A–Pd1	126.2 (4)
C5–Pd2–O2A <sup>i</sup>	92.5 (2)	C1A–O2A–Pd2 <sup>i</sup>	125.0 (4)
N41–Pd2–O2A <sup>i</sup>	178.8 (2)	C1B–O1B–Pd1	124.9 (4)
C5–Pd2–O2B <sup>i</sup>	178.1 (2)	C1B–O2B–Pd2 <sup>i</sup>	126.7 (5)

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

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0748P)^2 + 0.2065P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.134$	$(\Delta/\sigma)_{\text{max}} = 0.027$
$S = 1.028$	$\Delta\rho_{\text{max}} = 0.96 \text{ e \AA}^{-3}$
5261 reflections	$\Delta\rho_{\text{min}} = -0.95 \text{ e \AA}^{-3}$
404 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0010 (3)

Crystal decay was monitored by the measurement of duplicate reflections. The chloroform and water solvate molecules were disordered over three and two sites, respectively. The H atoms of the water solvate molecules were not located; other H atoms were placed in calculated positions and allowed to ride on their carrier C atoms. The disordered chloroform solvate molecules were restrained to have the same bond distances and angles.

Data collection: *SMART* (Siemens, 1999); cell refinement: *SAINT* (Siemens, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1153). Services for accessing these data are described at the back of the journal.

## References

- Caygill, G. B. & Steel, P. J. (1990). *J. Organomet. Chem.* **395**, 375–381.
- Churchill, M. R., Wasserman, H. J. & Young, G. J. (1980). *Inorg. Chem.* **19**, 762–770.
- De Geest, D. J., O'Keefe, B. J. & Steel, P. J. (1999). *J. Organomet. Chem.* **579**, 97–105.
- Hartshorn, C. M. & Steel, P. J. (1998). *Organometallics*, **17**, 3487–3496.
- Lydon, D. P. & Rourke, J. P. (1997). *J. Chem. Soc. Chem. Commun.* pp. 1741–1742.
- Navarro-Ranninger, C., Zamora, F., Martinez-Cruz, L. A., Isea, R. & Masager, J. R. (1996). *J. Organomet. Chem.* **518**, 29–36.
- O'Keefe, B. J. & Steel, P. J. (1998). *Organometallics*, **17**, 3621–3623.
- O'Keefe, B. J. & Steel, P. J. (1999). *Inorg. Chem. Commun.* **2**, 10–13, and references therein.
- Phillips, I. G. & Steel, P. J. (1991). *J. Organomet. Chem.* **410**, 247–255.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1999). *SMART* (Version 5.05), *SAINT* (Version 5.00) and *SADABS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Vicente, J., Abad, J.-A., Rink, B., Hernandez, F.-S. & Ramirez de Arellano, M. C. (1997). *Organometallics*, **16**, 5269–5282.