Cyclometalated Compounds. 10.[1] Preparation and Crystal Structure of a Nonpolymeric, Acetate-Bridged, Multiply Cyclopalladated Compound

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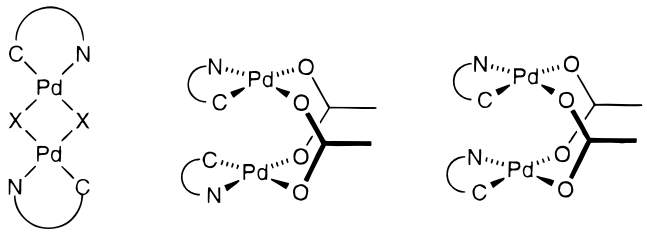
Summary: 1,4-Bis(benzothiazol-2-yl)benzene undergoes double cyclopalladation of the central benzene ring to form a nonpolymeric, acetate-bridged product that has been shown, by an X-ray crystal structure analysis, to be a topologically novel, counterhinged molecular box.

Introduction

Over the last three decades, cyclopalladated compounds[2] have found numerous applications in organic synthesis,[3] and, more recently, in material science[4] and as biologically active compounds.[5] Generally, such componds are prepared by reaction of an organic ligand with either palladium acetate or a tetrachloropalladate salt. In both cases, this results in the formation of bridged dimers **1**. As an extension of this work, double-



(**1**) (**2**) (**3**)

cyclopalladation reactions of certain ligands have been reported[6,7] and this usually results in the formation of insoluble bridged polymeric structures. To our knowledge, the only crystallographically characterized exception to this is the report of a bromo-bridged doubly cyclopalladated derivative of a substituted bis(*N*-benzylidene)-1,4-phenylenediamine, which has a planar dimeric structure.[8] However, acetate-bridged monopalladated dimers exist in a folded (hinged) arrangement, which can, in principle, exist as two geometrical isomers,[9] the anti isomer **2** with C_2 symmetry or the syn isomer **3** with C_s symmetry. In practice, the anti isomer **2** is usually obtained, and all crystallographically characterized acetate-bridged C,N-cyclopalladated dimers have this isomeric structure.[10,11] Because of this, and

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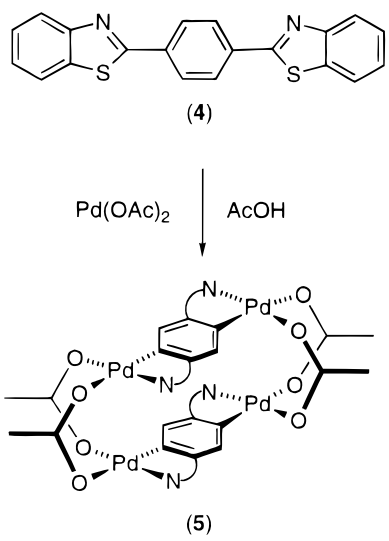
Scheme 1



the different topology between the planar-halide bridges and the folded-acetate bridges, it was difficult to envisage a nonpolymeric structure for a doubly cyclometalated compound from reaction with palladium acetate.[12]

We reasoned that it might be possible to prepare a nonpolymeric multiply metalated species by suitably organizing the requisite components utilizing $\pi-\pi$ stacking between planar aromatic compounds with appropriately located C,N donors. This might encourage formation of the syn isomer and allow for double capping by the palladium acetate bridges. One way to do this would involve double cyclopalladation of a single benzene ring, a phenomenon that is known, but rare.[7] We now report the successful realization of this objective by describing the preparation and X-ray crystal structure of a tetranuclear acetate-bridged product resulting from the double cyclopalladation of 1,4-bis(benzothiazol-2-yl)benzene (**4**; Scheme 1).

Results and Discussion

Since 2-arylbenzothiazoles readily undergo monocyclopalladation reactions,[10,13] one of the substrates we examined for possible double palladation was 1,4-bis(benzothiazol-2-yl)benzene (**4**), which is readily available from condensation of terephthalic acid with 2-aminothiophenol.[14] Reaction of **4** with 2 equiv of palladium acetate gave a brick red solid (**5**) that showed some solubility in chloroform and dichloromethane, suggestive of a nonpolymeric complex. The ^{1}H NMR spectrum of **5** showed equivalent benzothiazole rings, a two-proton singlet (6.84 ppm) for the central benzene ring, and two acetate singlets (2.52, 2.32 ppm). The infrared spectrum of **5** showed characteristic bands due to bridging acetato ligands at 1420 and 1574 cm^{-1}, while the FAB mass spectrum showed a highest mass (M^+) cluster of peaks centered around 1346 amu, along with more intense peaks around 1287 amu, corresponding to $[M - OAc]^+$. Each of these clusters showed an isotopic distribution in good agreement with that calculated for the constituent elements within the formulation $M = [(L-H_2)_2Pd_4(OAc)_4]$. All of these spectral features suggested a doubly cyclopalladated, dimeric structure for **5**. To determine the exact structure of this compound, we turned to X-ray crystallography.

X-ray-quality crystals of **5** proved extremely elusive. For example, although small plates were obtained by recrystallization from dichloromethane, these underwent spontaneous decomposition upon removal from the mother liquor or failed to diffract sufficiently to provide an acceptable data set. After many attempts at recrystallization from various solvents, suitable crystals were finally obtained by crystallization from bromobenzene. The cyclopalladated compound **5** crystallizes in the monoclinic space group $P2_1/c$ and contains one doubly cyclopalladated ligand and half of a disordered bromobenzene solvate in the asymmetric unit. Each of these lies about a center of inversion, such that the molecular structure of **5** consists of two doubly cyclopalladated ligands, with the four palladium atoms bridged by four acetate groups, thus forming a topologically novel, counterhinged molecular box (Figure 1).

The ligand **4** acts as a doubly chelating C,N donor bridging two palladium atoms; coordination to the palladium through nitrogen rather than sulfur was confirmed by refinement of the atom identities and is in accord with that previously observed for the cyclopalladation of 2-phenylbenzothiazole.[10,13] The central benzene ring is dipalladated in a para arrangement, rather than the alternative ortho-dipalladated possibility. As a consequence, the ligand adopts an anti conformation of the two benzothiazole rings with respect to the benzene ring. The ligand is approximately planar (mean deviation from plane 0.098(8) Å), with Pd2 slightly out of this plane (0.234(6) Å) and Pd1 displaced significantly from the plane (0.560(6) Å). All palladium−donor bond lengths are normal (see Table 1).[10,11] The geometry at each palladium is approximately square planar (see Table 1), the largest deviations being associated with the C−Pd−N chelate rings. The Pd1−Pd2A distance is 2.881(1) Å, which is nonbonding. The planes of the two central benzene rings, being related by a center of inversion, are necessarily parallel and are separated by 3.418(9) Å. We believe that this $\pi-\pi$ stacking interaction contributes to the preference for dimer over polymer formation.

Since the completion of this work, papers have appeared describing 1,4-dipalladated benzene rings within a series of Schiff bases derived from terephthalaldehyde, along with their liquid crystalline properties.[15] The products formed from reaction with palladium acetate were represented as polymeric species. Given the structural similarity of these compounds, we believe that our own results suggest that these might, in fact, possess tetranuclear dimeric structures.

(12) As pointed out by a reviewer, reaction of 1,3-bis(1-methylbenzimidazol-2-yl)benzene with palladium acetate results in a trinuclear cyclopalladated product. However, in this case the ligand is only monopalladated and has a pendant nitrogen donor that acts as a bridge to another palladium, with the acetate ligand being monodentate; see: Ruttimann, S.; Bernardinelli, G.; Williams, A. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 392. A tetranuclear structure has been proposed, but not structurally characterized, for the double cyclopalladation of a diimine of isophthalaldehyde.[7c]

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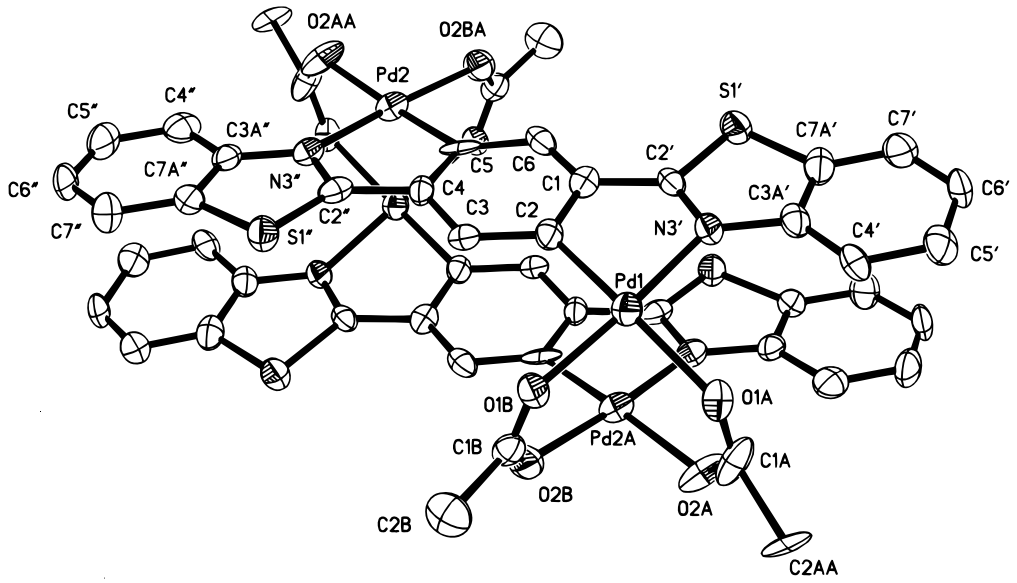

Figure 1. Perspective view and atom labeling of the X-ray structure of **5**. The hydrogen atoms, one contributor of the disordered acetate methyl group, and the disordered bromobenzene solvate are omitted for clarity.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 5

Pd1−C2	1.953(6)	Pd2−C5	1.991(6)
Pd1−N3′	2.026(5)	Pd2−N3″	2.048(5)
Pd1−O1B	2.047(4)	Pd2−O2B[a]	2.062(4)
Pd1−O1A	2.135(4)	Pd2−O2A[a]	2.148(4)
Pd1−Pd2[a]	2.8810(7)		
C1−C2	1.408(8)	C1−C6	1.402(8)
C2−C3	1.383(8)	C3−C4	1.415(8)
C4−C5	1.395(8)	C5−C6	1.388(9)
C1−C2′	1.450(8)	C4−C2″	1.447(9)
O1A−C1A	1.249(8)	C1A−O2A	1.273(8)
O1B−C1B	1.231(7)	C1B−O2B	1.265(7)
C2−Pd1−N3′	81.3(2)	C5−Pd2−N3″	80.9(2)
C2−Pd1−O1B	94.2(2)	C5−Pd2−O2B[a]	93.0(2)
N3′-Pd1-O1B	175.0(2)	N3″-Pd2−O2B[a]	173.8(2)
C2−Pd1−O1A	175.2(2)	C5−Pd2−O2A[a]	176.4(2)
N3′-Pd1-O1A	98.0(2)	N3″-Pd2−O2A[a]	99.0(2)
O1B−Pd1−O1A	86.3(2)	O2B[a]-Pd2−O2A[a]	87.0(2)
C6−C1−C2	123.8(6)	C6−C1−C2′	125.5(6)
C2−C1−C2′	110.7(5)	C3−C2−C1	116.7(6)
C3−C2−Pd1	127.1(5)	C1−C2−Pd1	115.7(5)
C2−C3−C4	120.1(6)	C5−C4−C3	121.9(6)
C5−C4−C2″	114.2(6)	C3−C4−C2″	123.8(6)
C6−C5−C4	118.5(6)	C6−C5−Pd2	127.4(5)
C4−C5−Pd2	114.1(5)	C5−C6−C1	118.5(6)
C2′−N3′−C3A′	112.3(5)	C2′−N3′-Pd1	111.5(4)
C3A′−N3′-Pd1	135.5(5)	C2″-N3″-C3A″	110.6(6)
C2″-N3″-Pd2	113.6(5)	C3A″-N3″-Pd2	135.7(4)
C1A−O1A-Pd1	118.0(4)	O1A−C1A−O2A	126.8(6)
C1A−O2A-Pd2[a]	132.1(5)	C1B−O1B−Pd1	123.5(4)
O1B−C1B−O2B	128.1(6)	C1B−O2B−Pd2[a]	125.1(5)

[a] Symmetry transformation used to generate equivalent atoms: $1-x, 1-y, 1-z$.

Experimental Section

General Considerations. ^{1}H NMR spectra were recorded on a Varian 300 Unity spectrometer with a 3 mm probe operating at 300 MHz. Infrared spectra were recorded with a Shimadzu FTIR-8201PC spectophotometer. Fast atom bombardment (FAB) mass spectra were recorded using a Kratos MS80RFA spectrometer; spectra were acquired in a nitrobenzyl alcohol matrix using an Iontech ZN1FW FAB gun operated at 8 KV and 2 mA. 1,4-Bis(benzothiazol-2-yl)benzene (**4**) was prepared according to the literature procedure.[14] Mp: 254−255 °C (lit.[14] mp 257−258 °C).

Preparation of Cyclopalladated Complex 5. A suspension of **4** (0.248 g, 0.72 mmol) and palladium acetate (0.324 g, 1.44 mmol) in acetic acid (10 mL) was heated at reflux for 5 h. The acetic acid was removed under reduced pressure. The brown residue was repeatedly extracted with hot dichloromethane to give an orange solution. The combined extracts were reduced to dryness in vacuo to give a brick red solid (**5**). Crude yield: 0.483 g, 95%. Mp: >300 °C. Crystals suitable for X-ray crystal structure analysis were grown from bromobenzene. Infrared spectrum: ν(C=O, acetate) 1420, 1574 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.82 (d, 4H, H4′ or H7′), 7.38 (d, 4H, H4′ or H7′), 7.03 (m, 8H, H5′, H6′), 6.84 (s, 4H, H3, H6), 2.52 (s, 6H, CH_3), 2.32 (s, 6H, CH_3). Anal. Calcd for $C_{48}H_{32}N_4O_8S_4Pd_4$: C, 42.81; H, 2.40; N, 4.16. Found: C, 42.15; H, 2.60; N, 4.36. Anal. Calcd for $C_{48}H_{32}N_4O_8S_4Pd_4{\cdot}C_6H_5Br$: C, 43.13; H, 2.48; N, 3.73. Found: C, 43.25; H, 2.47; N, 3.79.

Table 2. Selected Crystallographic Data for 5

$C_{48}H_{32}N_4O_8Pd_4S_4{\cdot}C_6H_5Br$	space group: $P2_1/c$
fw: 1503.6	$Z = 2$
$a = 9.8921(3)$ Å	$D_{exptl} = 1.997$ g cm^{-3}
$b = 21.9373(7)$ Å	$\lambda = 0.71073$ Å
$c = 11.7254(3)$ Å	$\mu = 2.444$ mm^{-1}
$\beta = 100.719(1)°$	$F(000) = 646$
$V = 2500.1(1)$ Å^3	$R^a = 0.0442$
$T = -132$ °C	$R_w{}^b = 0.0952$ (all 4367 data)

[a] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$ for 2840 data with $I > 2\sigma(I)$. [b] $R_w = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$.

X-ray Crystallography. Table 2 lists selected crystallographic data for **5**. Data were collected with a Siemens SMART CCD area detector on a red plate measuring 0.48 × 0.17 × 0.03 mm, using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å). A total of 11 738 reflections with $3.7° < 2\theta < 50.7°$ were collected. The structure was solved by direct methods and refined (all non-hydrogen atoms anisotropic) on F^2, using all 4367 independent data. C−H hydrogen atoms were included in calculated positions. The methyl group of one acetate ligand is disordered over two positions, while the bromobenzene molecule lies on a center of inversion, which necessitates its disorder over two orientations.

Supporting Information Available: Tables of information on data collection, structure solution, and refinement, atom coordinates, anisotropic displacement parameters, and all bond distances and angles for **5** (7 pages). Ordering information is given on any current masthead page.

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