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Note

Cyclopalladated *p*-azoxyanisole complexes. Synthesis and structure of {[bis(2-phenylpyridine)]-[4′-(methoxyphenyl-*NNO*-azoxy-N^2)-4-methoxyphenyl-2-ato]-palladium(II)}(tetrafluoroborate)

S. Armentano, G. De Munno, M. Ghedini* and S. Morrone

Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (Cs) (Italy)

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Abstract

Two molecules of Ph-Py (2-phenylpyridine) react with the solvate complex [(Azoxy-1)Pd(MeCN)$_2$][BF$_4$] to give the mononuclear cyclopalladated derivative [(Azoxy-1)Pd(Ph-Py)$_2$][BF$_4$] (**1**). The X-ray crystal structure of complex **1** is reported. Crystals were triclinic $P\bar{1}$ space group, with $a=11.714(2)$, $b=12.894(2)$, $c=13.331(2)$ Å, $\beta=78.74(2)$, $\gamma=66.32(2)°$ and $Z=2$. The structure was refined to $R=0.054$.

Key words: Crystal structures; Palladium complexes; Cyclopalladate complexes; Azoxybenzene complexes

Introduction

Cyclopalladation of appropriate molecules displaying liquid crystalline properties is a suitable synthetic procedure for the preparation of organometallic palladium mesogens [1]. Following such an approach a number of thermotropic cyclopalladated azoxybenzene compounds have been obtained [2, 3]. However, with reference to the cyclopalladation process, as several data are available for other substrates, little is known about azoxybenzenes [4]. Therefore we have been motivated to undertake extensive investigations on such a topic.

In particular, in a previous paper we reported on neutral, mononuclear cyclopalladated complexes obtained from *p*-azoxyanisole (thereafter H[Azoxy-1]) and substituted *N*-(phenyl)-2-salicylideneimines [5]. Herein we describe the synthesis and crystal structure determination of the ionic H[Azoxy-1] derivative [(Azoxy-1)Pd(Ph-Py)$_2$][BF$_4$] (**1**) where Ph-Py stands for 2-phenylpyridine.

Experimental

Preparation of compounds

The starting material [(Azoxy-1)Pd(MeCN)$_2$][BF$_4$] was prepared following the procedures previously reported [5].

[(Azoxy-1)Pd(Ph-Py)$_2$][BF$_4$] (1)

In a typical preparation, to a suspension of [(Azoxy-1)Pd(MeCN)$_2$][BF$_4$] (200 mg, 0.37 mmol) in absolute ethanol (10 ml), 2-phenylpyridine, Ph-Py (0.011 ml, 0.75 mmol) was added. The resulting yellow mixture was stirred at room temperature for 24 h. The orange precipitate which formed after that time was filtered off and dried under vacuum. Yield 85%. *Anal.* Found: C, 56.60; H, 3.85; N, 7.27. Calc. for $C_{36}H_{31}N_4BF_4O_3Pd$: C, 56.82; H, 4.10; N, 7.36%.

X-ray data collection and refinement

Orange crystals suitable for X-ray analysis were obtained from an ethanolic solution.

Diffraction data were collected on a Siemens R3m/V automatic four-circle diffractometer, using graphite-monochromated Mo Kα radiation. Crystal data for $C_{36}H_{33}BF_4N_4O_4Pd$: $M=778.9$, $a=11.714(2)$, $b=12.894(2)$, $c=13.331(2)$ Å, $\alpha=77.49(2)$, $\beta=78.74(2)$, $\gamma=66.32(2)°$, $V=1787.0(5)$ Å^3, $Z=2$, $D_{calc}=1.448$ g cm^{-3}, $F(000)=792$, Mo Kα radiation ($\lambda=0.71073$); μ(Mo Kα) $=5.84$ cm^{-1}, triclinic, space group $P\bar{1}$. A crystal of $0.23\times0.18\times0.31$ mm was used to collect 7445 reflections in the range $3.0<2\theta<52°$. Only 5271 independent reflections were observed ($I>3\sigma(I)$).

All data were corrected for Lorentz and polarization effects, absorption and extinction corrections being ignored. The structure was solved by standard Patterson methods and subsequently completed by Fourier recycling. All atoms, except the boron, fluorine and water oxygen atoms, were refined anisotropically. Because of the disorder the BF_4^- ion was treated as a rigid group with isotropic temperature factors. All hydrogen atoms were set in calculated positions and refined as riding atoms. A common thermal parameter was assigned to all hydrogen atoms. The final R value was 0.054, $R_w=0.060$ (weighting scheme $w=1.0000/[\sigma^2(F_o)+0.0044F_o^2]$), $S=1.07$.

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*Author to whom correspondence should be addressed.

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Solutions and refinements were performed with the SHELXTL-PLUS system [6]. The final geometrical calculations were carried out with the PARST program [7]. The graphical manipulations were performed using the XP utility of the SHELXTL-PLUS system. See also 'Supplementary material'.

Results and discussion

The molecular structure of **1** consists of the complex cation $[(Azoxy\text{-}1)Pd(Ph\text{-}Py)]^+$ (shown in Fig. 1) and a BF_4^- anion crystallized with a water molecule in the triclinic system. Selected bond distances and angles are listed in Table 1.

The square planar coordination around the palladium(II) ion involves the cyclometalated [Azoxy-1] fragment and two N-bonded Ph-Py molecules. With reference to the C(9), N(1), N(3) and N(4) mean coordination plane, Pd is 0.022(1) Å above it. The Pd–N(1) and Pd–C(9) lengths, 2.029(5) and 1.968(5) Å, respectively, as well as the structural features of both the C(9)–Pd–N(1)–N(2)–C(8) metallacycle and the orthometalated phenyl ring, compare well with those previously reported [5] for [(Azoxy-1)Pd(L)] (HL=*N*-(phenyl)-2-salicylideneimine) (**2**). The N(2)–O(2) distances, 1.225(8) Å, and 1.258(3) Å in **2** [5], are also similar and a little shorter than in the unmetalated H[Azoxy-1] molecule (1.279(4) Å) [8], probably the effect of metal coordination.

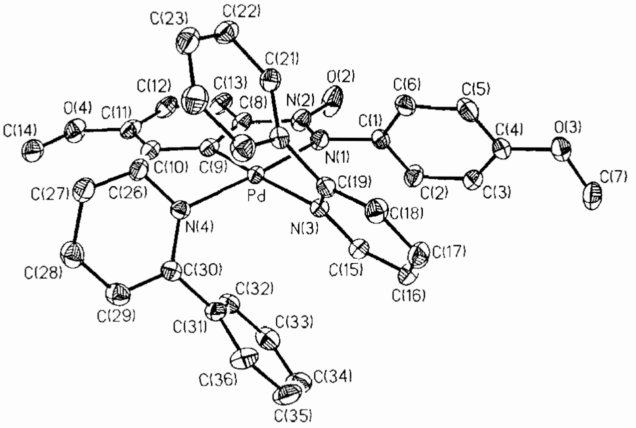

Fig. 1. View of the cation of $[(Azoxy\text{-}1)Pd(Ph\text{-}Py)][BF_4]$ (1), with the atomic numbering scheme. Thermal ellipsoids are plotted at the 20% probability level. Hydrogen atoms are omitted for clarity

TABLE 1. Selected bond distances (Å) and angles (°) for $PdC_{36}H_{33}BF_4N_4O_4$ with e.s.d.s. in parentheses

Bond lengths			
Pd–N(1)	2.029(5)	Pd–N(3)	2.141(4)
Pd–N(4)	2.058(5)	Pd–C(9)	1.968(5)
O(2)–N(2)	1.225(8)	N(1)–N(2)	1.312(7)
N(2)–C(8)	1.432(8)	C(8)–C(9)	1.393(9)
Bond angles			
N(1)–Pd–N(3)	92.9(2)	N(1)–Pd–N(4)	174.3(2)
N(3)–Pd–N(4)	92.8(2)	N(1)–Pd–C(9)	81.0(2)
N(3)–Pd–C(9)	173.3(2)	N(4)–Pd–C(9)	93.3(2)
Pd–N(1)–N(2)	115.1(4)	Pd–N(1)–C(1)	127.4(4)
N(2)–N(1)–C(1)	117.3(5)	O(2)–N(2)–N(1)	123.5(5)
O(2)–N(2)–C(8)	122.1(5)	N(1)–N(2)–C(8)	114.4(5)
N(2)–C(8)–C(9)	116.6(5)	N(2)–C(8)–C(13)	119.4(6)
C(9)–C(8)–C(13)	124.0(6)	Pd–C(9)–C(8)	112.8(4)
Pd–C(9)–C(10)	131.0(5)	C(8)–C(9)–C(10)	116.2(5)
Pd–N(3)–C(15)	115.9(4)	Pd–N(3)–C(19)	125.1(3)
C(15)–N(3)–C(19)	118.9(5)	Pd–N(4)–C(26)	118.2(5)
Pd–N(4)–C(30)	123.0(3)	C(26)–N(4)–C(30)	118.5(5)

In contrast, the dihedral angle between the Pd, N(1), N(2), C(8), C(9) and C(1), C(2), C(3), C(4), C(5), C(6) planes, 69.8(2)° in **1** and 52.2(1)° in **2**, is quite different.

The two Ph-Py molecules, coordinated through the pyridine nitrogen atoms, form inequivalent Pd–N bonds (Pd–N(3)=2.141(4), Pd–N(4)=2.058(5) Å) as expected for the stronger *trans* influence exerted by a Pd–C(phenyl) σ bond [9]. The coordination geometry displayed by the bulky Ph-Py ligands is determined by the steric hindrance. Thus with reference to the coordination plane, each pyridine ring is tilted by 64.4(2) and 70.8(2)°, for Ph-Py bearing the N(3) and N(4) atom, respectively, and forms dihedral angles of about 55° with the pertinent phenyl rings located above and below the palladium atom. Such a configuration gives Pd···H–C(19) and Pd···H–C(30) contacts (for hydrogen atoms in calculated positions) at about 2.90 Å. Therefore the monodentate Ph-Py ligands adopt a coordination geometry like benzo[*h*] quinoline (bquin) in the $[Pd(dmp)(bquin)(H_2O)][BF_4]$ complex (dmp=2-(dimethylaminomethyl)phenyl) which shows the Pd···H–C(10) contact at 2.09 Å [10].

The BF_4^- anions and the water molecules are involved in van der Waals contacts with hydrogen atoms (i.e. $F(2)\text{---}H(6^{i})=2.41(1)$ Å, $i=x-1, y, z$; $F(2)\text{---}H(14A^{i})=2.520$ Å, $i=-x+1, -y+1, -z$; $O(1)\text{---}H(16^{i})=2.660$ Å, $i=x-1, y+1, z$).

Supplementary material

Details of experimental procedures are available from the authors on request.

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