Synthesis and Structure of a Palladium(II) Chloride Complex with 2-(2-Methyl-3-phenyl-isoxazolidin-5-yl)-pyridine

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The 1:1 complex of palladium(II) chloride with 2-(2-methyl-3-phenyl-isoxazolidin-5-yl)-pyridine (L) has been prepared and studied by means of elemental analysis, ^{1}H NMR spectroscopy and X-ray diffraction (monoclinic, space group $P2_1/n$ with parameters: $a = 8.141(2)$, $b = 9.750(2)$, $c = 20.691(6)$ Å, $\beta = 95.62(3)^\circ$, $V = 1634.4(7)$ Å^3, $Z = 4$; $R1 = 0.054$ and $wR2 = 0.144$ for 3352 unique reflections). A square-planar coordination polyhedron has been established for the palladium atom both in acetone solution and in the solid state. The organic ligand is coordinated to metal in a bidentate manner *via* nitrogen atoms of the pyridine substituent (Pd-N(2) 2.125(3) Å) and the isoxazolidine heterocycle (Pd-N(1) 2.102(3) Å). The other two coordination positions of palladium are occupied by chlorine atoms (Pd-Cl(1) 2.321(1) and Pd-Cl(2) 2.333(1) Å). The six-membered chelate ring formed by Pd, N(2), C(4), C(1), O(1) and N(1) possesses a "twist-tub" conformation. The isoxazolidine cycle has an envelope conformation with an equatorial orientation of the methyl group.

Introduction

Isoxazolidine derivatives attract considerable attention as intermediates in organic synthesis [1]. Moreover, these substances display a wide spectrum of biological activity including pesticide, herbicide and anti-cancer properties [2 - 4].

Isoxazolidines are also interesting ligands in coordination chemistry. The presence of neigbouring σ-donor heteroatoms (N-O) enables one to prepare complexes with several types of coordination.

3,5-Disubstituted isoxazolidines are characterized by the presence of stereocenters and a five-membered kinetically labile ring which cause the existence of stereoisomers and conformers. The coordination of a 5-(2-pyridyl) substituted isoxazolidine to a metal ion, especially with participation of the isoxazolidine heteroatoms in N,N- or N,O-chelating manners, may stabilize one of the conformers of the isoxazolidine ring.

Although there are several reports on X-ray studies of arene and carbonyl complexes of Cr and W with isoxazolidines [5 - 7], these investigations did not illustrate how the coordination may have an influence on the relative stability of the isoxazolidine compounds. This report is the first attempt regarding this topic.

I II

To establish the peculiarities of isoxazolidine ring coordination to "soft" Pirson acids we have studied the palladium(II) dichloride complex with 2-(2-methyl-3-phenyl-isoxazolidin-5-yl)-pyridine as a ligand.

Experimental

Preparation of ligand and palladium complex

The starting materials for the synthesis of 2-(2-methyl-3-phenyl-isoxazolidin-5-yl)-pyridine (L) were commercially available benzaldehyde, N-methylhydroxylamine hydrochloride and 2-vinylpyridine. The N-methyl-C-phenylnitrone was prepared as described [8] (m. p. 84-85°C). The ligand L has been obtained by standard 1,3-dipolar reaction of N-methyl-C-phenylnitrone with

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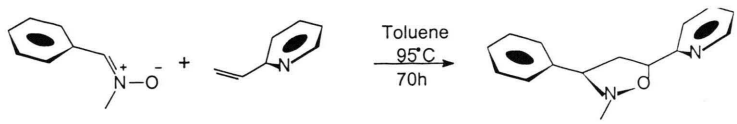

Table 1. Crystallographic data for $[Pd(L)Cl_2]$.

Formula	$C_{15}H_{16}Cl_2N_2OPd$
Formula weight	417.60
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	8.141(2)
b [Å]	9.750(2)
c [Å]	20.691(6)
β [°]	95.62(3)
U [Å^3]	1634.4(7)
Z	4
D_{calc} [g cm^{-3}]	1.697
μ(Mo-Kα) [cm^{-1}]	18.93
F(000)	832
Data collection	
$2\theta_{max}$ [°]	60.1
Index ranges	$0 \leq h \leq 15$, $0 \leq k \leq 13$, $-29 \leq l \leq 29$
Reflections collected	5353
Unique data	4726
R_{int}	0.055
Structure refinement	
Data used [I > 2σ(I)]	3352
Parameters refined	208
Data to parameters ratio	16.12
$R1$	0.054
R_w	0.130
GOF on F^2	0.986
Largest peak in final difference map [e Å^{-3}]	1.11

Table 2. Selected bond lengths (Å) and angles (°) for structure of $[Pd(L)Cl_2]$.

Pd(1)-N(1)	2.102(3)	N(1)-C(15)	1.497(5)
Pd(1)-N(2)	2.125(3)	N(1)-C(3)	1.518(5)
Pd(1)-Cl(1)	2.321(1)	C(1)-C(4)	1.523(5)
Pd(1)-Cl(2)	2.333(1)	C(1)-C(2)	1.561(6)
O(1)-C(1)	1.452(5)	C(2)-C(3)	1.545(6)
O(1)-N(1)	1.465(4)		
N(1)-Pd(1)-N(2)	92.2(1)	O(1)-N(1)-Pd(1)	110.4(2)
N(1)-Pd(1)-Cl(1)	88.7(1)	C(15)-N(1)-Pd(1)	112.2(2)
N(2)-Pd(1)-Cl(1)	173.6(1)	C(3)-N(1)-Pd(1)	109.6(2)
N(1)-Pd(1)-Cl(2)	174.86(8)	C(8)-N(2)-C(4)	117.4(3)
N(2)-Pd(1)-Cl(2)	92.4(1)	C(8)-N(2)-Pd(1)	120.6(3)
Cl(1)-Pd(1)-Cl(2)	87.10(4)	C(4)-N(2)-Pd(1)	121.7(2)
C(1)-O(1)-N(1)	105.0(3)	O(1)-C(1)-C(4)	108.6(3)
O(1)-N(1)-C(15)	104.0(3)	O(1)-C(1)-C(2)	105.0(3)
O(1)-N(1)-C(3)	102.5(3)	C(3)-C(2)-C(1)	104.5(3)
C(15)-N(1)-C(3)	117.5(3)	N(1)-C(3)-C(2)	100.7(3)

freshly distilled 2-vinylpyridine (bp 80-82°C/29 mm) [8] according to scheme above.

The mixture of products was separated by means of column chromatography on silica gel with acetone-chloroform (1:3) as an eluent. The yield of L (oil) was ~65%.

The palladium complex has been synthesized from commercial $Na_2[PdCl_4]$ in accordance with scheme:

$$Na_2[PdCl_4] + L \rightarrow [Pd(L)Cl_2] + 2NaCl$$

L (0.163 g, 0.68 mmol) dissolved in 5 ml of warm methanol was added dropwise to a mechanically stirred solution of Na_2PdCl_4 (0.200 g, 0.68 mmol) in 6 ml of methanol. The yellow solution was stirred at r.t. for 1 h. The yellow precipitate was filtered and recrystallized from acetone-chloroform (1:1). The yellow residue was dried additionally *in vacuo* at ~ 50°C. The yield of palladium complex was 0.200 g (~70%). It is readily soluble in chloroform, dichloromethane, acetone, acetonitrile and practically insoluble in hexane. Analysis for $[Pd(L)Cl_2]$: $C_{15}H_{16}Cl_2N_2OPd$ (Mr = 417.60): Calcd C 43.14, H 3.86, N 6.71. Found C 43.6, H 3.9, N 6.6%.

The IR spectrum of liquid L as thin film between KBr discs was recorded on a UR-10 (Carl Zeiss, Jena) spectrometer (400-4000 cm^{-1}).

^{1}H NMR spectra of the ligand ($CDCl_3$) and the complex (acetone-d_6) were obtained on a Bruker WP-100 (100.1 Hz) at 293 K using tetramethylsilane (TMS) as an internal standard.

Crystal structure determination

All crystallographic measurements were made at 293 K using a four circle Siemens P3/PC automated diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ 0.71073 Å). An orange prismatic single crystal of the demensions 0.5×0.1×0.1 mm was used.

The structure was solved by direct methods by using the SHELXTL-PLUS set of programs [9]. H atoms were placed at calculated positions and refined isotropically. The structure was established by full-matrix least-square calculations with an anisotropic approximation for all non-hydrogen atoms to an $R1$ value of 0.054 ($wR2$= 0.144, 3352 reflections, F > 4σ(F), S = 0.986). Table 1 lists details of cell parameters, data acquisition and structure

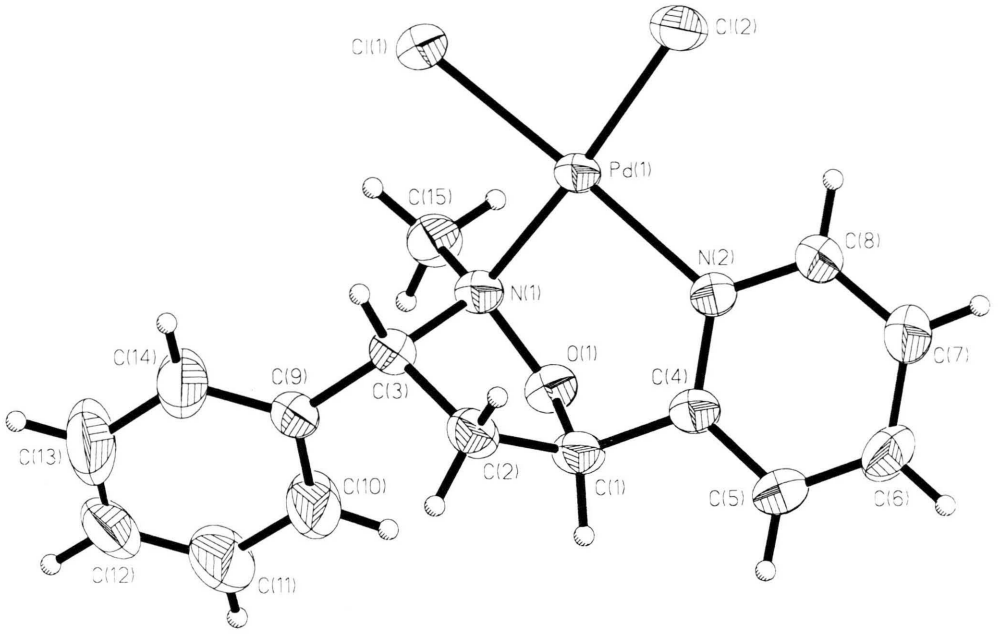

Fig.1. Molecular structure of [Pd{2-(2-methyl-3-phenyl-isoxazolidin-5-yl)-pyridine}Cl_2].

refinement. Selected geometric parameters of [Pd(L)Cl_2] are listed in Table 2. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Center and may be obtained by quoting the number CCDC 136771.

Results and Discussion

The IR spectrum of L shows characteristic strong absorptions at 2990 - 3095 (ν(C-H)) and 1500 - 1600 cm^{-1} (ν(C=C) of the aromatic groups) and at 2770-2915, 1335-1470 (ν(C-H) and δ(C-H) of the aliphatic groups).

In the ^{1}H NMR spectrum of L the signal of C^5H is located at δ 5.35 (dd). Thus the 1,3-dipolar reaction is highly regioselective and gives 3,5-disubstituted isoxazolidine [10].

The ^{1}H NMR spectrum of [Pd(L)Cl_2] shows some interesting features. The shifts of protons C^5H, C^3H, CH_3-N and α-pyridine groups were found at lower field as compared with the corresponding ^{1}H NMR shifts of isoxazolidine in L (ppm, δ: C^5H 5.35, C^3H 3.75, CH_3 2.69, α-py 8.57 for L; C^5H 6.00, C^3H 4.25, CH_3 2.87, α-py 9.50 for complex). Therefore, we concluded that the organic ligand was coordinated to the palladium atom in a bidentate manner *via* two nitrogen atoms. This was confirmed by the X-ray study.

Description of the structure

The [Pd(L)Cl_2] complex has a molecular array. The crystal lattice consists of the racemate of [Pd{(3R,5R)-2-(2-methyl-3-phenyl-isoxazolidin-5-(yl)-pyridine}Cl_2] and [Pd{(3S,5S)-2-(2-methyl-3-phenyl-isoxazolidin-5-(yl)-pyridine}Cl_2]. There is a short contact between neighbouring molecules for H(10)[C(10)]· · ·Cl(2) 2.82 Å (1.5-x, y-0.5, 0.5-z) (the sum of van-der-Waals radii being 3.06 Å). The palladium atom has a nearly square planar environment (torsion angle N(1)-Cl(1)- N(2)-Cl(2) - 7°). It is bonded to two nitrogen atoms of the ligand and two chlorine atoms. In contrast to X-ray data for related structures [11 - 14], the Pd-N(pyridine) bond is longer than (Pd-N (isoxazolidine nitrogen atom) (Pd-N(1) 2.102(3) Å, Pd-N(2) 2.125(3) Å)). An analogous pattern is observed when palladium is coordinated *via* the nitrogen atoms of pyridine and C=N azomethine groups [15 - 17].

The distances O(1)-N(1), N(1)-C(3), N(2)-C(8), N(2)-C(4) (1.465(4), 1.518(5), 1.354(5), 1.364(5) Å) are longer than their averages seen in organic molecules (1.438, 1.469, 1.337, 1.337 Å[18]) as a

result of the coordination of the nitrogen atoms to the metal atom. C(1)-C(2) (1.561(6) Å) and C(3)-C(9) (1.536(5) Å) are also longer than the averages found for related system (1.521 and 1.513 Å [18]).

The six-membered chelate ring formed by Pd, N(2), C(4), C(1), O(1), N(1) has a twist-tub conformation. The atoms O(1) and N(1) deviate by 1.15 and 0.59 Å, respectively, from the mean plane of the atoms PdN(2)C(4)C(1).

The isoxazolidine ring has an envelope conformation. The deviation of N(1) from the mean plane of atoms C(3)C(2)C(1)O(1) is 0.67 Å. The pyridine ring is almost coplanar to the C(1)-H(1) bond with a torsion angle H(1)-C(1)-C(4)-C(5) of 11.3°. The methyl group has equatorial orientation [torsion angle C(15)-N(1)-C(3)-C(2) 157.1(3)°], while the phenyl group is situated axially [torsion angle C(1)-C(2)-C(3)-C(9) 97.7(4)°].

Thus we may conclude that 5-(2-pyridyl)-substituted N-methyl isoxazolidines can act as N,N donor bidentate ligands for "soft" palladium(II) cation. The six-membered chelate ring stabilizes an envelope conformation of the isoxazolidine ring with an equatorial orientation of the methyl group.

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