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A coordination compound of (–)-ephedrine and palladium(II)

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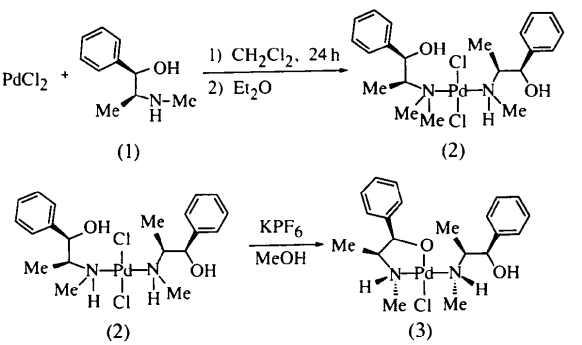
Abstract

The reaction of (–)-ephedrine with $PdCl_2$ in the presence of $NaPF_6$ leads to chloro[(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-ol-*N*][(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-olato-*N*,*O*]palladium(II), $[PdCl(C_{10}H_{14}NO)(C_{10}H_{15}NO)]$. The crystal structure determination shows two (–)-ephedrine [(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-ol] ligands, one as a chelating moiety and the other as a monodentate ligand in which only the N atom is coordinated to the Pd^{II} atom. An extensive hydrogen-bond network ensures the three-dimensional cohesion of the atomic arrangement.

Comment

Complexes of Pd^{II} are of interest both in radiopharmaceutical chemistry as β-emitters for radiotherapy applications (with ^{111}Pd) and in homogeneous catalysis. Ephedrine derivatives have aroused increasing interest as chiral ligands for catalytic enantioselective reactions (Mortezaei *et al.*, 1988), such as the asymmetric tautomerization of prochiral enols produced under Pd-induced domino reactions (Jamal Aboulhoda *et al.*, 1995) or the Pd-catalyzed enantioselective hydrogenation of α,β-unsaturated ketones (Thorey *et al.*, 1996). Very recently, complexes formed by the coordination of enantiopure β-amido alcohols to cationic η^3-allylpalladium units have been suggested by Bäckvall's group as the most important intermediates for the enantioselective 1,4-dialkoxylation of 1,3-dienes (Itami *et al.*, 1998), the chiral ligands being synthesized from β-amino alcohols and hydroquinone-type compounds (for the coordination of racemic β-amino alcohols to Pd^{II}, see Andrieu *et al.*, 1998). Although van Koten's group has already characterized alkoxopalladium(II) complexes derived from achiral amino alcohol ligands (Kapteijn *et al.*, 1997), little is known about the structure of their chiral counterparts. Therefore, a part of our work has concerned the complexation of (–)-ephedrine, (1), and palladium chloride and we present here the characterization of a new and unexpected Pd^{II} complex, namely chloro[(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-ol-*N*][(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-olato-*N*,*O*]palladium(II), (3), obtained under particular experimental conditions.



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

The reaction of $PdCl_2$ with two equivalents of (1) at room temperature leads to a new compound identified as (2) from IR and NMR spectroscopic and elemental analysis (see Scheme above). Crystallization of (2) under special conditions (see *Experimental*) led to compound (3), whose crystal presents characteristics suitable for X-ray analysis (see Scheme above).

The X-ray structure of (3) (Fig. 1) shows the unusual structure of this complex. One of the two amino alcohol ligands is selectively deprotonated to give an *N*,*O*-chelate, resulting in the expulsion of one chloride ligand, while the other amino alcohol ligand remains coordinated to Pd^{II} through the N atom. To our knowl-

edge, chiral amino alcohol–palladium complexes such as (2) and (3) have not been reported previously. The synthesis of (2) seems to be a trivial reaction, since the amines are strong ligands to electrophilic Pd^{II} (Andrieu *et al.*, 1998; Tsuji, 1995). In contrast, the formation of the palladacycle (3) was unexpected, especially under the experimental conditions used here.

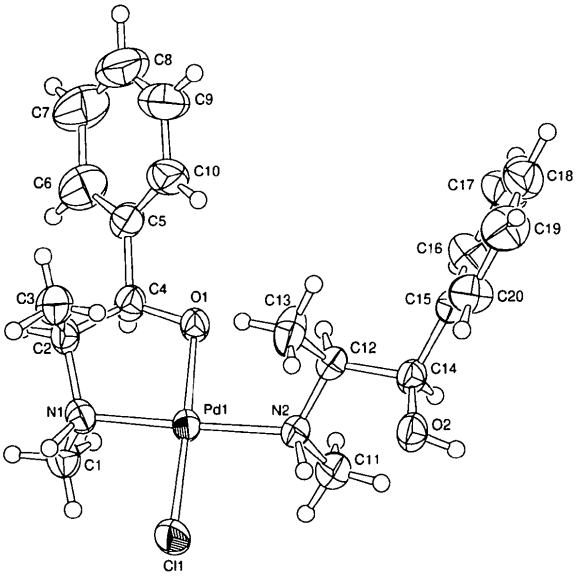


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of one of the two conformers of (3), showing the atom-numbering scheme and 45% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

From a structural point of view, one must emphasise two features of (3), namely, the coordination of the Pd atom and the hydrogen-bond network. The Pd atom has the usual square-planar coordination, formed here by one O, one Cl and two N atoms. This type of coordination is not exceptional, since 11 examples can be found (Cambridge Structural Database, 1999), but in only one of them are the two N atoms located in opposite corners of the coordination square as in (3). The main geometrical features of the PdN_2OCl group are reported in Table 1. This group is slightly distorted, but is nevertheless almost perfectly planar since the maximum displacement from the weighted least-squares plane (N1/N2/O1/Cl1) is 0.069 (3) Å, the Pd atom being just 0.029 (2) Å out of the plane and thus almost perfectly in it. All other bonding parameters (Table 1) fall in the range found in the literature (Allen *et al.*, 1987).

The crystal packing is controlled by a set of inter- and intramolecular contacts. The network thus formed includes an intramolecular bond (N2—H18···O2) and two intermolecular bonds (O2—H23···O1 and N1—H4···Cl1); geometrical details are given in Table 2. These last two bonds generate a very intricate three-dimensional network.

Experimental

All solvents were dried and distilled under argon before use. The reagents, substrate and catalysts were commercial materials. IR spectra were recorded on a Spectrafile IR™ *Plus* MIDAC (KBr pellets) and NMR spectra on an AC 250 Bruker instrument with $CDCl_3$ as the solvent. Elemental analyses were performed on a Perkin–Elmer 2400 instrument for CHN in Reims, or by the Service Central d'Analyse du CNRS in Lyon. Synthesis of $[PdCl_2(C_{10}H_{15}NO)_2]$, compound (2): (−)-ephedrine (0.56 g, 3.4 mmol) was added to a suspension of $PdCl_2$ (0.3 g, 1.7 mmol) in CH_2Cl_2 (30 ml). After stirring for 24 h, a yellow homogeneous solution was obtained. After evaporation of the solvent, an oil was obtained. This was treated with diethyl ether to afford a transparent yellow powder (0.82 g, 96% yield). Although many recrystallizations were attempted, we were unable to obtain crystals suitable for X-ray analysis. Spectroscopic analysis of (2): ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 0.82 (CH_3, J = 6.2 Hz), 2.45 (CH_3N), 2.78 (HCN, J = 3 Hz), 4.75 (HCO); ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 14.3 (CH_3), 34.0 ($CNCH_3$), 60.4 (CH_3N), 73.0 (COH), 128.1 (Ph), 127.0 (Ph), 126.1 (Ph); IR (cm^{-1}): 3470 (OH, *br*), 3297 (NH, sharp), 2974 (Ph), 1992 (Ph), 1936 (Ph), 1871 (Ph), 1846 (Ph), 750 (Ph), 750 (Ph), 2829 (CH_3). Elemental analysis for (2): $C_{20}H_{30}Cl_2N_2O_2Pd$ (507.4), calculated: C 47.31, H 5.96, N 5.52, Cl 13.96, Pd 20.95%; found: C 47.04, H 5.28, N 5.15, Cl 13.42, Pd 21.07%. Compound (3) was obtained when (2) was treated with two equivalents of KPF_6 in methanol at room temperature, followed by concentration of the solution. Compound (3) crystallized at 278 K and the crystals were collected by filtration and characterized by X-ray structure determination.

Crystal data

$[PdCl(C_{10}H_{14}NO)(C_{10}H_{15}NO)]$
M_r = 471.31
Trigonal
$P3_121$
a = 10.734 (4) Å
c = 35.245 (6) Å
V = 3517 (1) Å^3
Z = 6
D_x = 1.335 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 10.2–11.9°
μ = 0.920 mm^{-1}
T = 293 K
Hexagonal prism
0.41 × 0.40 × 0.40 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.657, T_{max} = 0.692
7386 measured reflections
3917 independent reflections
2924 reflections with $I > 2\sigma(I)$

R_{int} = 0.023
θ_{max} = 29.95°
h = 0 → 13
k = 0 → 13
l = −49 → 41
2 standard reflections
every 120 reflections
intensity decay: 8.29%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.030$
$S = 1.748$
2924 reflections
235 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.00004|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pd1—Cl1	2.295 (1)	Pd1—N1	2.017 (3)
Pd1—O1	1.990 (2)	Pd1—N2	2.051 (2)
Cl1—Pd1—O1	176.24 (8)	O1—Pd1—N1	84.1 (1)
Cl1—Pd1—N1	94.65 (8)	O1—Pd1—N2	93.2 (1)
Cl1—Pd1—N2	88.16 (8)	N1—Pd1—N2	176.7 (1)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H23···O1^{i}	0.87	1.77	2.604 (3)	160
N1—H4···Cl1^{ii}	1.04	2.31	3.285 (3)	156
N2—H18···O2	0.95	2.41	2.776 (3)	103

Symmetry codes: (i) $y, x-1, 2-z$; (ii) $x-y, -y, \frac{5}{3}-z$.

All H atoms were located by difference Fourier syntheses.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1045). Services for accessing these data are described at the back of the journal.

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Di-μ-bromo-bis[bromo(η^6-*para*-cymene)-ruthenium(II)] benzene solvate and di-μ-iodo-bis[(η^6-*para*-cymene)iodo-ruthenium(II)] toluene solvate

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Abstract

The homologous title molecules, $[Ru_2Br_4(C_{10}H_{14})_2]\cdot C_6H_6$, (1), and $[Ru_2I_4(C_{10}H_{14})_2]\cdot C_7H_8$, (2), consist of arene–ruthenium moieties [Ru-to-ring distances of 1.655 (2) Å in (1) and 1.673 (3) Å in (2)] with a terminal halogen ligand [Ru—Br 2.548 (1) Å in (1) and Ru—I 2.726 (1) Å in (2)], held together by two symmetrical halogen bridges [Ru—Br 2.575 (1) Å in (1) and Ru—I 2.736 (1) Å in (2)]. The arene rings are planar and parallel to each other, and the terminal halogen ligands are coordinated to ruthenium *trans* with respect to each other. Both molecules possess C_i symmetry.

Comment

The title compounds, $(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)_2Ru_2(\mu\text{-}X)_2X_2$ [(1) X = Br; (2) X = I], were first obtained from the reaction of $[(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)_2Ru_2(\mu\text{-}OH)_3][BPh_4]$ with HBr and HI, respectively (Gould *et al.*, 1984), while the chloro analogue, $(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)_2Ru_2(Cl)_2\text{-}Cl_2$, was first reported as a product of the reaction of hydrated ruthenium(III) chloride with α-phellandrene (Bennett & Smith, 1974). The benzene complexes $(\eta^6\text{-}C_6H_6)_2Ru_2(\mu\text{-}X)_2X_2$ have been known for even longer (Zelonka & Baird, 1972), the chloro derivative having been reported first, erroneously as a polymer (Winkaus & Singer, 1967). Surprisingly, structural information is available only for chloro derivatives of the hexamethylbenzene, ethylbenzoate and trindane analogues, *i.e.* $(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}Cl)_2Cl_2$ (McCormick & Gleason, 1988), $(\eta^6\text{-}C_6H_6CO_2Et)_2Ru_2(\mu\text{-}Cl)_2Cl_2$ (Therrien *et al.*, 1998) and $(\eta\text{-}^6C_{15}H_8)_2Ru_2(\mu\text{-}Cl)_2Cl_2$ (Gupta *et al.*, 1997). As