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mer-Trichloro[2-(phenylamino)pyridinato]-oxotungsten(VI)

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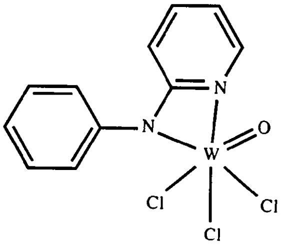
Abstract

mer-Trichloro(oxo)[2-(phenylamino)pyridinato-*N*,*N'*]-tungsten, $[WCl_3(O)(C_{11}H_9N_2)]$, is formed when tungsten(VI) oxotetrachloride and 2-(phenylamino)pyridine are heated in toluene under reflux. The ligand precursor loses an amino proton and forms a four-membered chelate ring with an N—W—N angle of 61.0(4)°. The monomeric complex displays a distorted octahedral coordination at tungsten.

Comment

Only a few aminopyridine complexes have been structurally characterized. Most closely related to the present compound, (I), is bis[2-(methylamino)pyridinato](tetramethylethylenediamine)vanadium, (II), which has a very similar aminopyridinato bonding pattern to that found here (Edema, Gambarotta, Meetsma, Spek & Veldman, 1991). The known aminopyridinato derivatives of tungsten, however, are quite different to the title compound. Tungsten(IV) chloride and 2-(phenylamino)-pyridine have been found to form tetrakis(phenylaminopyridinato)ditungsten(II) when sodium amalgam is used as a reducing agent with the lithium salt of the ligand precursor (Chakravarty, Cotton & Shamshoum, 1984). 2-Amino-6-methylpyridine has also been used as a ligand precursor for quadruply bonded dichromium, dimolybdenum and ditungsten complexes (Cotton, Niswander & Sekutowski, 1978). The only monomeric aminopyridine tungsten complex known previously is bis(2-aminopyridine)tris(3,5-dimethylpyrazoyl)-boratonitrosyltungsten, where 2-aminopyridine is monodentate and the heterocyclic N atom is uncoordinated (Obaidi, Hamor, Jones, McCleverty & Paxton, 1987).



(I)

The monomeric title complex has a symmetrically bidentate 2-(phenylamino)pyridinato group, with W—N distances of 1.983 (8) Å for the amido bond (W1—N7) and 2.298 (11) Å for the pyridine (py) donor bond (W1—N1). These bond lengths seem to be typical for tungsten(VI) complexes; in trichlorotris(diethylamido)-tungsten, the W—N(amido) distances are 1.913 (5)–1.938 (5) Å (Dietz, Allured & Dubois, 1993) and in dichlorobis(phenylimido)bipyridinetungsten, W—N(py) bond lengths of 2.315 (9) and 2.319 (8) Å occur (Clark, Nielson & Richard, 1988).

In the title complex, the W═O distance is 1.683 (10) Å and the W—Cl distances are between

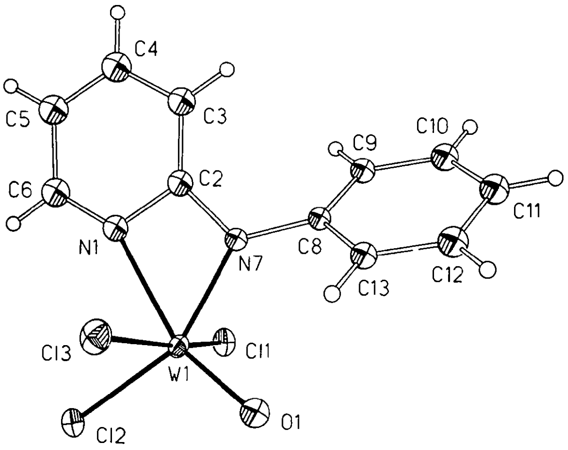


Fig. 1. The molecular structure of the title molecule with ellipsoids drawn at the 30% probability level.

2.321 (3) and 2.371 (3) Å. These values are comparable to those found in [W{(*R*)-$C_6H_4CH(Me)N(Me)NMe_2$}-Cl_3(=O)], where the W=O distances are 1.662 (7) and 1.678 (8) Å, and the W—Cl distances between 2.307 (4) and 2.334 (4) Å (van der Schaaf, Boersma, Kooijman, Spek & van Koten, 1993).

Because of the chelate-ring constraint, the N1—W1—N7 angle is acute [61.0 (4)°], being similar to the N—V—N angle [62.3 (2)°] in bis[2-(methylamino)-pyridinato](tetramethylethylenediamine)vanadium(II); the coordination of both donor N atoms is distorted for the same reason [*cf.* W1—N1—C2 90.1 (8) and W1—N1—C6 150.2 (8), and W1—N7—C2 103.4 (7) and W1—N7—C8 132.1 (8)°]. Despite this, the deviation of the W atom from the pyridine plane is only 0.08 (2) Å. The oxo group appears to require more space than the Cl atoms since all *cis*-Cl—W—O angles are greater than 90°, varying between 93.6 (3) and 108.5 (3)°.

Experimental

2-(Phenylamino)pyridine (4.10 g, 24.1 mmol) and tungsten(VI) oxotetrachloride (3.20 g, 9.38 mmol) were heated in toluene (50 ml) suspension for 90 min at 353 K. The solution was then filtered and evaporated to reduced volume (30 ml). Large black crystalline blocks with an average size of over 1 mm in each dimension were obtained at room temperature in 10 h. A portion of the crystals was transferred to perfluoro ether and the specimen was cut from a larger crystal. The crystal used for the X-ray measurements was mounted on a glass fiber using the oil-drop method (Kottke & Stalke, 1993). All reaction steps were carried out under an argon atmosphere using standard Schlenk techniques.

Crystal data

[$WCl_3(O)(C_{11}H_9N_2)$]
$M_r = 475.40$
Orthorhombic
$Pna2_1$
$a = 15.789 (13)$ Å
$b = 8.139 (10)$ Å
$c = 10.719 (7)$ Å
$V = 1377 (2)$ Å^3
$Z = 4$
$D_x = 2.293$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.0–17.5°$
$\mu = 8.956$ mm^{-1}
$T = 193 (1)$ K
Block
0.35 × 0.25 × 0.25 mm
Black

Data collection

Rigaku AFC-7*S* diffractometer
ω-2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.038$, $T_{max} = 0.106$
4364 measured reflections
1280 independent reflections

1171 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.095$
$\theta_{max} = 25°$
$h = -18 \rightarrow 18$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0295$
$wR(F^2) = 0.0753$
$S = 1.040$
1280 reflections
93 parameters
H atoms: riding with U(H) = $1.3U$(C)
$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.84$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.02 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}†
W1	0.33275 (3)	−0.01774 (4)	0.14631 (8)	0.0259 (2)
Cl1	0.3806 (2)	0.0947 (4)	−0.0451 (3)	0.0349 (7)
Cl2	0.2751 (2)	−0.2278 (4)	0.0240 (3)	0.0383 (8)
Cl3	0.2556 (3)	−0.1253 (4)	0.3116 (3)	0.0419 (8)
O1	0.4305 (7)	−0.0747 (10)	0.1915 (7)	0.037 (2)
N1	0.2164 (8)	0.1459 (11)	0.1125 (8)	0.031 (3)
C2	0.2538 (9)	0.2700 (12)	0.1770 (10)	0.030 (3)
C3	0.2143 (10)	0.4140 (15)	0.2003 (12)	0.036 (3)
C4	0.1348 (9)	0.4354 (14)	0.1500 (22)	0.044 (3)
C5	0.0953 (11)	0.3149 (16)	0.0846 (13)	0.042 (3)
C6	0.1408 (10)	0.1666 (16)	0.0668 (12)	0.038 (3)
N7	0.3317 (7)	0.2082 (10)	0.2154 (8)	0.022 (2)
C8	0.3950 (8)	0.3044 (12)	0.2701 (10)	0.023 (2)
C9	0.4153 (9)	0.4591 (13)	0.2263 (11)	0.029 (3)
C10	0.4821 (9)	0.5432 (15)	0.2751 (12)	0.034 (3)
C11	0.5312 (11)	0.4783 (14)	0.3719 (12)	0.037 (3)
C12	0.5109 (10)	0.3209 (14)	0.4167 (11)	0.037 (3)
C13	0.4441 (9)	0.2381 (13)	0.3653 (10)	0.029 (3)

† U_{iso} for O, N and C atoms.

Table 2. *Selected geometric parameters (Å, °)*

W1—O1	1.683 (10)	W1—Cl1	2.371 (3)
W1—N7	1.983 (8)	N1—C6	1.30 (2)
W1—N1	2.298 (11)	N1—C2	1.360 (15)
W1—Cl3	2.321 (3)	C2—N7	1.39 (2)
W1—Cl2	2.339 (3)	N7—C8	1.40 (2)
O1—W1—N7	98.9 (4)	N1—W1—Cl1	83.9 (3)
O1—W1—N1	159.8 (4)	Cl3—W1—Cl1	166.79 (14)
N7—W1—N1	61.0 (4)	Cl2—W1—Cl1	85.46 (12)
O1—W1—Cl3	99.1 (3)	C6—N1—W1	150.2 (8)
N7—W1—Cl3	93.5 (3)	C2—N1—W1	90.1 (8)
N1—W1—Cl3	85.4 (3)	N1—C2—N7	105.5 (9)
O1—W1—Cl2	108.5 (3)	C2—N7—C8	123.6 (9)
N7—W1—Cl2	152.1 (3)	C2—N7—W1	103.4 (7)
N1—W1—Cl2	91.4 (3)	C8—N7—W1	132.1 (8)
Cl3—W1—Cl2	87.02 (14)	C9—C8—N7	122.3 (11)
O1—W1—Cl1	93.6 (3)	C13—C8—N7	119.3 (9)
N7—W1—Cl1	88.2 (3)		

In the final refinement, anisotropic displacement parameters were refined only for W and Cl atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1278). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ruthenium(II) Complex Containing a New Hybrid Bidentate Phosphine–Thioether Ligand: $[(p\text{-Cymene})RuCl(Me_2PCH_2CH_2SMe)][BPh_4].0.5CH_2Cl_2$

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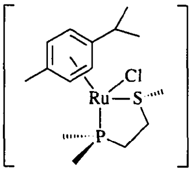
Abstract

In the title compound, chloro(η^6-*p*-cymene)[1-(dimethylphosphino-*P*)-2-(methylthio-*S*)ethane]ruthenium(II) tetraphenylborate hemidichloromethane solvate, $[RuCl(C_{10}H_{14})(C_5H_{13}PS)][B(C_6H_5)_4].0.5CH_2Cl_2$, the hybrid $Me_2PCH_2CH_2SMe$ ligand is bidentate (κ^2P,S), forming a five-membered chelate ring. The complex cation has two chiral centres, *i.e.* on the Ru and S atoms, and the relative configuration is *R**(Ru)*S**(S).

Comment

In the course of our research on transition-metal complexes containing hybrid bidentate or polydentate phosphine ligands, we prepared a new phosphine–thioether ligand, *i.e.* $Me_2PCH_2CH_2SMe$ (Suzuki, Morikawa & Kashiwabara, 1996). The most intriguing properties of this ligand are related to the presence on the P atom of sterically undemanding but strongly electron-donating methyl substituents and the potential it has to act as both a monodentate P-atom donor and as a bidentate chelating ligand (Kashiwabara & Taguchi, 1996). In order to reveal the molecular structure of a transition metal complex containing such a novel ligand, we prepared the title complex and carried out a diffraction analysis. The asymmetric unit contains a discrete complex cation, $[(p\text{-cymene})RuCl(Me_2PCH_2CH_2SMe)]^+$, (I), a BPh_4^- anion and half a CH_2Cl_2 molecule. The CH_2Cl_2 solvate molecule lies close to a crystallographic inversion centre and the C atom (C51) is positionally disordered.



(I)

In the complex cation, (I), $Me_2PCH_2CH_2SMe$ acts as a bidentate ligand to form a five-membered chelate ring with a bite angle of 83.86 (6)°, which is comparable to that found for $Me_2PCH_2CH_2PMe_2$ in ruthenium(II) complexes (Field, Hambley & Yau, 1994). It has a piano-stool structure with the *p*-cymene and Cl ligands completing the coordination sphere of the metal. There are two chiral centres, *i.e.* on the Ru and S atoms, and the absolute configuration at these centers is *R*(Ru)*S*(S) or *S*(Ru)*R*(S). This configuration is more sterically advantageous than the diastereomeric alternative of *R*(Ru)*R*(S) or *S*(Ru)*S*(S), which would give rise to severe steric repulsion between the *p*-cymene and S—Me groups. The Ru—P bond [2.312 (2) Å] is slightly shorter than that in the structurally related complex $[(p\text{-cymene})RuCl\{PPh(2\text{-}O\text{-}C_6H_3\text{-}6\text{-}OMe)[C_6H_3(OMe)_2\text{-}2,6]\}]$ [(II), 2.342 (3) Å; Yamamoto, Sato, Matsuo, Sudoh & Igoshi, 1996], which may reflect the steric demand and greater electron-donating power of the methyl substituents in (I). The Ru—Cl bond length [2.389 (2) Å] is comparable to those found in the related (II) and [(*p*-cymene)RuCl-