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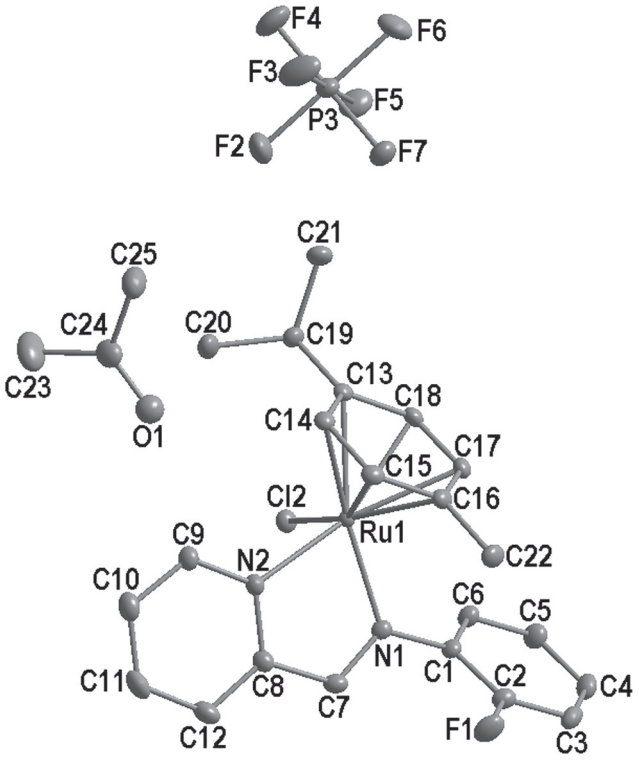
Crystal structure of chlorido-(η^6-*p*-cymene)-(*N*-(2-fluorophenyl)-1-(pyridin-2-yl)methanimine-κ^2*N*,*N*′)ruthenium(II) – acetone (1/1), $C_{22}H_{23}ClN_2F_7OPRu$



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Abstract

$C_{22}H_{23}ClN_2F_7OPRu$, monoclinic, $P2_1/c$ (no. 14), $a = 7.30480(10)$ Å, $b = 12.9540(3)$ Å, $c = 28.7076(6)$ Å, $\beta = 96.6990(10)°$, $V = 2697.95(9)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0196$, $wR_{ref}(F^2) = 0.0479$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Red block
Size:	$0.26 \times 0.23 \times 0.22$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.81 mm^{-1}
Diffractometer, scan mode:	Bruker Smart Apex-II, φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	101207, 6690, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6475
$N(param)_{refined}$:	346
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3]

Source of material

To a suspension of $[(\eta^6$-*p*-cymene)Ru(μ-Cl)I]$_2$ (0.2 mmol) in methanol (20 mL) was added the organic ligand (N-(2-fluorophenyl)-1-(pyridin-2-yl)methanimine; 0.42 mmol). The mixture was stirred at room temperature for 3 hours followed by the reduction in the volume of the solvent *in vacuo* to about (10 mL) before adding NH_4PF_6 (0.42 mmol). The mixture was then cooled in an ice bath while stirring for 2 hours leading to a precipitate, which was collected by filtration. The filtrate was washed with diethyl ether and dried *in vacuo*. Crystals were grown by the liquid diffusion method in which the solutions of the compounds in acetone were layered with hexane and left undisturbed for 2 days.

Orange, yield 85%, **m.p.** 150 °C (decomp.). **^{1}H NMR** (400 MHZ, DMSO-d$_6$): δ [ppm] 9.58 (d, $J_{HH} = 5.4$ Hz, 1H, Py); 8.90 (s, 1H, CH=N); 8.35 (M, 1H, Py); 8.28 (m, 1H, Py); 7.90 (m, 3H, Py); 7.51(t, 2H, p-cyAr); 6.18 (d, $J_{HH} = 6.10$ Hz, 1H(p-cyAr)); 5.94 (d, $J_{HH} = 6.10$ Hz, 1H, (p-cyAr)); 2.57 (sep, 1H, CH) 2.63 (m, 1H, CH (Me)2); 2.16 (s, 3H, (Me)); 1.01 (d, $J_{HH} = 6.64$ Hz, 3H, (Me) (0. 95 (d, $J_{HH} = 6.88$ Hz, 3H, (Me). **^{13}C NMR** (400 MHZ, DMSO-d6): δ [ppm] 168.07 (CH=N), 159.9 (Py), 155.5 (Py); 148.12 (Py); 139.94 (Py); 130.10 (py); 128.2 (Py); 124.80 (Ar); 124.70 (Ar); 116.60 (Ar); 105.2 (Ar); 103.4 (Ar); 86.6 (Ar); 86.1 (Ar); 85.0 (Ar); 84.8 (Ar); 30.5 (Me); 21.8 (Me); 18.4 (Me). **IR**

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
C23	0.1629(3)	0.3209(2)	0.44231(7)	0.0428(5)
H23A	0.2809	0.2871	0.4392	0.064*
H23B	0.1788	0.3960	0.4417	0.064*
H23C	0.0718	0.2999	0.4162	0.064*
C24	0.0973(2)	0.28990(13)	0.48774(6)	0.0255(3)
C25	−0.0875(2)	0.33045(16)	0.49642(6)	0.0326(4)
H25A	−0.1840	0.2937	0.4764	0.049*
H25B	−0.0945	0.4043	0.4891	0.049*
H25C	−0.1049	0.3199	0.5294	0.049*
O1	0.1869(2)	0.23504(12)	0.51589(5)	0.0443(4)
C1	0.96435(18)	0.17810(10)	0.72779(5)	0.0135(2)
C2	0.97641(19)	0.09853(11)	0.76040(5)	0.0164(3)
C3	1.06889(19)	0.10925(12)	0.80501(5)	0.0189(3)
H3	1.0734	0.0541	0.8269	0.023*
C4	1.1548(2)	0.20259(12)	0.81690(5)	0.0204(3)
H4	1.2220	0.2111	0.8470	0.024*
C5	1.1435(2)	0.28396(12)	0.78505(5)	0.0199(3)
H5	1.2024	0.3477	0.7936	0.024*
C6	1.04645(19)	0.27232(11)	0.74080(5)	0.0162(3)
H6	1.0361	0.3286	0.7194	0.019*
C7	0.91593(18)	0.09242(11)	0.65526(5)	0.0162(3)
H7	1.0073	0.0434	0.6665	0.019*
C8	0.82373(18)	0.08754(11)	0.60784(5)	0.0152(2)
C9	0.60555(19)	0.16595(11)	0.55441(5)	0.0174(3)
H9	0.5139	0.2173	0.5471	0.021*
C10	0.6446(2)	0.09750(12)	0.51947(5)	0.0215(3)
H10	0.5810	0.1029	0.4888	0.026*
C11	0.7762(2)	0.02170(12)	0.52974(5)	0.0232(3)
H11	0.8036	−0.0259	0.5063	0.028*
C12	0.8677(2)	0.01627(12)	0.57480(5)	0.0213(3)
H12	0.9586	−0.0352	0.5829	0.026*
C13	0.45898(18)	0.39326(10)	0.64335(5)	0.0138(2)
C14	0.36734(18)	0.30125(11)	0.62899(5)	0.0145(2)
H14	0.2978	0.2977	0.5989	0.017*
C15	0.37743(18)	0.21297(11)	0.65902(5)	0.0149(2)
H15	0.3187	0.1506	0.6481	0.018*
C16	0.47334(19)	0.21686(11)	0.70469(5)	0.0152(3)
C17	0.56286(19)	0.31154(11)	0.71980(5)	0.0153(3)
H17	0.6264	0.3166	0.7505	0.018*
C18	0.55750(18)	0.39651(10)	0.68971(5)	0.0146(2)
H18	0.6205	0.4579	0.7001	0.017*
C19	0.45954(19)	0.48809(11)	0.61267(5)	0.0160(3)
H19	0.5773	0.5260	0.6220	0.019*
C20	0.4495(2)	0.46452(12)	0.56042(5)	0.0253(3)
H20A	0.4505	0.5293	0.5428	0.038*
H20B	0.5560	0.4225	0.5545	0.038*
H20C	0.3357	0.4266	0.5503	0.038*
C21	0.3006(2)	0.55837(11)	0.62313(5)	0.0221(3)
H21A	0.2989	0.6204	0.6035	0.033*
H21B	0.1835	0.5214	0.6163	0.033*
H21C	0.3177	0.5784	0.6563	0.033*
C22	0.4856(2)	0.12441(11)	0.73640(5)	0.0197(3)
H22A	0.3730	0.1192	0.7518	0.030*
H22B	0.5923	0.1317	0.7603	0.030*
H22C	0.4996	0.0619	0.7179	0.030*
F1	0.89194(13)	0.00775(7)	0.74847(3)	0.02501(19)
F2	0.49083(18)	0.82957(10)	0.59316(4)	0.0432(3)
F3	0.19196(16)	0.83020(8)	0.60659(4)	0.0407(3)
F4	0.33518(16)	0.98103(8)	0.59499(4)	0.0376(3)
F5	0.55918(13)	0.94162(8)	0.65351(4)	0.0299(2)
F6	0.26128(14)	0.94113(8)	0.66716(4)	0.0333(2)
F7	0.41625(14)	0.79047(7)	0.66533(3)	0.0264(2)
P3	0.37645(5)	0.88512(3)	0.63004(2)	0.01883(8)
Cl2	0.89479(4)	0.36426(3)	0.62383(2)	0.01570(6)
Ru1	0.65734(2)	0.26281(2)	0.65280(2)	0.01010(3)
N1	0.86875(15)	0.16607(9)	0.68160(4)	0.0128(2)
N2	0.69313(15)	0.16166(9)	0.59806(4)	0.0136(2)

(solid state): γ (C=N) 1610.1 cm^{-1}. **MS** (ESI, M/Z): 471.0580 $[C_{19}H_{26}ClN_2Ru]^+$.

Experimental details

Crystal evaluation and data collection were done on a Bruker Smart APEX2 diffractometer with an Oxford Cryostream low temperature apparatus operating at 100(1) K. The structure was solved by the direct method using the SHELXS [2] program and refined. All hydrogen atoms were placed in idealized positions and refined in riding models with U_{iso} assigned the values of 1.2 times those of their parent atoms and the distances of C—H were constrained to 0.93 Å for all the aromatic H atoms, 0.96 Å for methyl hydrogens and 0.98 Å for methine hydrogen. The visual crystal structure information was performed using ORTEP-3 [3].

Comment

Arene ruthenium half-sandwich compounds belong to a well established family of robust organometallic complexes [4–9]. There is a continued interest in arene ruthenium systems due to their potential as catalysts in a wide range of organic reactions [4–9], promising anticancer and antimicrobial properties [10, 11] and their DNA binding ability [12]. This contribution is a part of our continuing interest in half-sandwich ruthenium(II) complexes with *N*,*N*′-bidentate ligands [5–12].

In the asymmetric unit there is one cationic ruthenium complex featuring the "pseudo-octahedral three-legged piano stool" structures, one hexafluorophosphate anion and an acetone solvent molecule. The ruthenium centre is coordinated to the *N*,*N*′-bidentate ligand through the N atom of the pyridine and the N atom of the imine bond and a chlorido ligand at the base of the stool and the *p*-cymene ring at the apex of the stool [5–12]. The Ru—N bond lengths of the complex are 2.0835(14) and 2.0858(14) Å and these value are comparable to those reported for other arene ruthenium complexes with *N*,*N*′ donor ligands [5–12]. The N—Ru—N bond angle is 76.63(4)°. The N—Ru—Cl bond angles are 86.26(3) and

85.63(3)°. These values are in agreement to those reported for related compounds [5–16].

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