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Crystal structure of η^6 -*p*-cymene-iodido-(*N*-isopropyl-1-(pyridin-2-yl)methanimine- κ^2 *N,N'*)ruthenium(II) hexafluorophosphate(V), $C_{19}H_{26}IN_2F_6Ru$

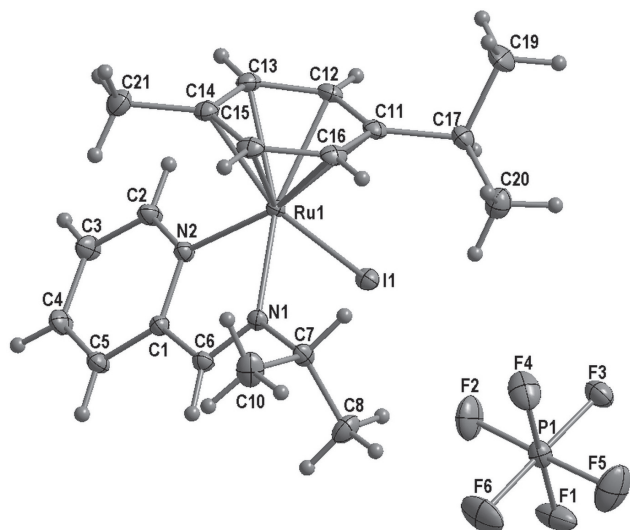


Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.20 × 0.17 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.18 mm ⁻¹
Diffractometer, scan mode:	Bruker Smart Apex-II, φ and ω
θ_{\max} , completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	17004, 5626, 0.015
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5236
$N(\text{param})_{\text{refined}}$:	271
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3]

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Abstract

$C_{19}H_{26}IN_2F_6Ru$, triclinic, $P\bar{1}$ (no. 2), $a = 9.240(2)$ Å, $b = 10.019(3)$ Å, $c = 12.689(3)$ Å, $\alpha = 78.921^\circ$, $\beta = 81.596(10)^\circ$, $\gamma = 83.654^\circ$, $V = 1136.30(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0174$, $wR_{\text{ref}}(F^2) = 0.0440$, $T = 173$ K.

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The asymmetric unit of the salt-type title 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.

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Source of material

To a suspension of $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}I)]_2$ (0.2 mmol) in methanol (20 mL) was added the ligand (0.42 mmol). The mixture was stirred at room temperature for 3 h followed by reduction of the solvent volume *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 h 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 by layering a solution of the compound in acetone with hexane and left undisturbed for 2 days. Orange crystals, yield = 80%, m.p. 150 °C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆). δ [ppm] 9.51 (d, $J_{\text{HH}} = 5.4$ Hz, 1H, Py); 8.80 (s, 1H, CH=N); 8.23–8.21 (m, 1H, Py); 8.15 (d, $J_{\text{HH}} = 7.2$ Hz, 1H, Py); 7.80 (s, 1H, Py); 6.26 (d, $J_{\text{HH}} = 6.26$ Hz, 1H, (p-cyAr)); 6.18 (d, $J_{\text{HH}} = 6.10$ Hz, 1H(p-cyAr)); 5.94 (d, $J_{\text{HH}} = 6.10$ Hz, 1H, (p-cyAr)), 5.89 (d, $J_{\text{HH}} = 6.30$ Hz, 1H, (p-cyAr)), 4.88 (sep, 1H, CH) 2.63 (m, 1H, CH (Me)₂); 2.16 (s, 3H, (Me)); 1.59 (d, $J_{\text{HH}} = 6.80$ Hz, 3H, (Me)); 1.41 (d, $J_{\text{HH}} = 6.64$ Hz, 3H, (Me)) (0.95 (d, $J_{\text{HH}} = 6.88$ Hz, 3H, (Me)). ¹³C NMR (400 MHz, DMSO-*d*₆). δ [ppm] 165.3 (CH=N), 155.7 (Py), 155.5 (Py); 139.8 (Py); 128.8 (Py); 128.2 (Py); 104.2 (Ar); 103.4 (Ar); 87.6 (Ar); 84.5 (Ar); 65.5 (CH); 30.5 (Me); 23.8 (Me); 22.3 (Me); 22.1 (Me); 21.30 (Me); 18.4 (Me). IR (solid state): ν (C=N) 1622.1 cm⁻¹. MS (ESI, M/Z): 520.98 [$C_{19}H_{26}IN_2Ru$]⁺.

Experimental details

Crystal evaluation and data collection were done on a Bruker Smart APEX2 diffractometer equipped with an Oxford

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.34230(19)	0.25218(17)	0.70043(14)	0.0138(3)
C2	0.3932(2)	0.02407(18)	0.77376(15)	0.0182(3)
H2	0.4523	-0.0454	0.8139	0.022*
C3	0.2694(2)	-0.01053(19)	0.73865(16)	0.0202(4)
H3	0.2457	-0.1027	0.7535	0.024*
C4	0.1804(2)	0.0900(2)	0.68173(16)	0.0201(4)
H4	0.0967	0.0675	0.6555	0.024*
C5	0.2159(2)	0.22430(19)	0.66384(15)	0.0175(3)
H5	0.1551	0.2958	0.6273	0.021*
C6	0.39037(19)	0.38808(17)	0.68729(14)	0.0146(3)
H6	0.3355	0.4662	0.6532	0.017*
C7	0.5638(2)	0.53641(17)	0.71118(14)	0.0156(3)
H7	0.6556	0.5258	0.7462	0.019*
C8	0.4519(2)	0.6296(2)	0.76871(18)	0.0253(4)
H8A	0.4888	0.7196	0.7595	0.038*
H8B	0.3593	0.6387	0.7378	0.038*
H8C	0.4352	0.5905	0.8460	0.038*
C10	0.6023(2)	0.5951(2)	0.59182(16)	0.0253(4)
H10A	0.6371	0.6857	0.5844	0.038*
H10B	0.6796	0.5348	0.5593	0.038*
H10C	0.5149	0.6025	0.5549	0.038*
C11	0.81503(18)	0.21185(18)	0.88233(15)	0.0158(3)
C12	0.76943(19)	0.07682(18)	0.89261(15)	0.0160(3)
H12	0.7500	0.0231	0.9626	0.019*
C13	0.75308(19)	0.02281(18)	0.80155(15)	0.0167(3)
H13	0.7274	-0.0683	0.8107	0.020*
C14	0.77435(19)	0.10265(19)	0.69490(15)	0.0176(3)
C15	0.81764(19)	0.23640(19)	0.68479(15)	0.0178(3)
H15	0.8322	0.2921	0.6152	0.021*
C16	0.83962(18)	0.28840(19)	0.77760(15)	0.0167(3)
H16	0.8718	0.3773	0.7683	0.020*
C17	0.8355(2)	0.26487(19)	0.98273(15)	0.0191(4)
H17	0.7565	0.2309	1.0413	0.023*
C19	0.9831(3)	0.2031(3)	1.0193(2)	0.0391(6)
H19A	0.9973	0.2369	1.0843	0.059*
H19B	0.9839	0.1034	1.0357	0.059*
H19C	1.0626	0.2296	0.9614	0.059*
C20	0.8230(2)	0.4203(2)	0.96849(17)	0.0264(4)
H20A	0.8374	0.4472	1.0363	0.040*
H20B	0.8982	0.4568	0.9106	0.040*
H20C	0.7255	0.4566	0.9495	0.040*
C21	0.7496(2)	0.0468(2)	0.59780(16)	0.0243(4)
H21A	0.7204	-0.0466	0.6210	0.036*
H21B	0.6717	0.1042	0.5619	0.036*
H21C	0.8405	0.0462	0.5472	0.036*
N1	0.51049(16)	0.39793(14)	0.72382(11)	0.0129(3)
N2	0.43209(16)	0.15269(15)	0.75287(12)	0.0135(3)
P1	-0.01712(5)	0.32867(5)	1.35346(4)	0.01770(9)
Ru1	0.61542(2)	0.21849(2)	0.79809(2)	0.01065(4)
I1	0.43390(2)	0.25309(2)	0.97949(2)	0.01582(4)
F1	-0.17631(14)	0.34985(15)	1.42094(10)	0.0367(3)
F2	-0.06014(17)	0.19179(15)	1.32491(12)	0.0408(3)
F3	0.04199(13)	0.24255(13)	1.46124(10)	0.0267(3)
F4	0.14242(14)	0.30624(16)	1.28689(11)	0.0358(3)
F5	0.0292(2)	0.46406(14)	1.38355(13)	0.0490(4)
F6	-0.07647(17)	0.41510(17)	1.24738(11)	0.0451(4)

Cryostream low temperature apparatus operating at 100(1) K. The structure was solved by direct method using the SHELXS [2] program and refined with SHELXL [2]. 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, 0.960 Å for methyl hydrogens and 0.98 Å for methine hydrogen. The visual crystal structure information was performed using ORTEP-3 [3].

Comment

Ruthenium half-sandwich complexes have found many applications as metallodrugs and as catalysts in various reactions [4, 5]. Biologically, ruthenium complexes have shown potential as anticancer agents [6, 7] and as antimicrobial agents [6]. In catalysis, ruthenium half-sandwich complexes have found applications in, oxidative transformations of alkanes [4], cleavage of double bonds [8], oxidation of alcohols [9] and in transfer hydrogen of ketones [10].

The title compound is part of our continuing studies of half-sandwich ruthenium(II) complexes [6–11]. The asymmetric unit contains one cationic ruthenium complex featuring a “pseudo-octahedral three-legged piano stool” structure and one counter anion (see the figure). In this arrangement, the ruthenium centre is coordinated to the *N,N'*-bidentate ligand, through the N atom of the pyridine moiety and the imine N atom, and one iodido ligand to form the base of the stool while the *p*-cymene ring acts as the apex of the stool [6–10]. In the complex, the Ru–N bond distances are 2.0714(14) and 2.0761(14) Å. This value is comparable to those reported for other arene ruthenium complexes with *N,N'* donor ligands [4–10]. The N–Ru–N bond angle is 76.99(6) while those of N–Ru–I are 84.44(4) and 83.95(4)°. These values are close to those reported for related compounds [6, 12]. All C–C, C–N and P–F bond length and angles are in the expected range [6–13].

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