Synthesis and Crystal Structure of [RuCl₃{*N,N'*-bis(diphenylphosphino)-2,6-diaminopyridine}].3CH₃OH

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The title compound, [RuCl₃{*N,N'*-bis(diphenylphosphino)-2,6-diaminopyridine}].3CH₃OH (**1**·3CH₃OH), was synthesized and characterized by X-ray analysis. The compound crystallizes in a monoclinic system, and was characterized thus: *P*2₁/*n*, *a* = 13.224(9), *b* = 18.427(13), *c* = 14.745(10) Å, β = 90.409(13)°, *Z* = 4, *V* = 3593(4) Å³. The *R*1[*I* > 2σ(*I*)] and *wR*2 (all data) values are 0.0609 and 0.1626, respectively, for all 6622 independent reflections.

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The 2,6-diaminopyridine-based mixed-donor PNP ligands, developed by both the Haupt and Kirchner groups, are advantageous because the donor ability and the steric property can be easily modulated.^{1–3} Here, we report on the synthesis and X-ray crystal structure of an open-face ruthenium complex that is a potentially useful starting complex. The three chlorido ligands in the title compound, [RuCl₃{*N,N'*-bis(diphenylphosphino)-2,6-diaminopyridine}] (**1**), can thus be replaced by other ligands on demand to produce a wide variety of ruthenium complexes bearing the PNP ligand.

Crystal data are summarized in Table 1. A single crystal was mounted on a MicroMount™ (MiTeGen). Diffraction data were collected on a Rigaku Saturn 724 diffractometer. The data were integrated, scaled, sorted, and averaged using CrystalClear software. Absorption corrections were applied using the Coppens numerical method. The structure was solved using the SIR92 direct method, and refined using CRYSTALS on CrystalStructure 4.0. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on the calculated positions and refined as riding models.

Fig. 1 Chemical diagram of the title compound.

Complex **1** was synthesized as follows: To an orange solution of *trans*-[RuCl₂{*N,N'*-bis(diphenylphosphino)-2,6-diaminopyridine}(dimethylsulfoxide)]⁴ (100 mg, 0.137 mmol) in acetone (10 mL) was added concentrated aqueous HCl (3 mL). The solution was stirred for 14 h under air. After removal of the solvent *in vacuo*, the residue was dissolved in a mixture of methanol and acetone (2/1 v/v) to afford **1**·3CH₃OH as green crystals. Yield: 35 mg (38%). *m/z* = 685.1 (ESI-MS). Elemental analysis for C₃₂H₃₇Cl₃N₃O₃P₂Ru: calcd (%). C 49.21, H 4.76, N 5.38; found (%). C 48.98, H 4.72, N 5.48.

Kirchner *et al.* reported that the synthesis and characterization

Table 1 Crystal and experimental data

Chemical formula: C ₃₂ H ₃₇ Cl ₃ N ₃ O ₃ P ₂ Ru
Formula weight = 781.04
<i>T</i> = 123 K
Crystal system: monoclinic Space group: <i>P</i> 2 ₁ / <i>n</i>
<i>a</i> = 13.224(9) Å
<i>b</i> = 18.427(13) Å β = 90.409(13)°
<i>c</i> = 14.745(10) Å
<i>V</i> = 3593(4) Å ³ <i>Z</i> = 4
<i>D</i> _x = 1.444 g/cm ³
Radiation: Mo <i>K</i> _α (λ = 0.71075 Å)
μ(Mo <i>K</i> _α): 7.837 cm ⁻¹
Crystal size = 0.24 × 0.24 × 0.09 mm ³
No. of reflections collected = 18341
No. of independent reflections = 6622 <i>R</i> _{int} = 0.077
No. of observations (<i>I</i> > 2σ(<i>I</i>)): 3943
2θ _{max} = 51.5° with Mo <i>K</i> _α
Goodness-of-fit on <i>F</i> ² = 0.970
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]: <i>R</i> 1 = 0.0609
<i>R</i> indices (all data): <i>R</i> 1 = 0.1059 <i>wR</i> 2 = 0.1626
(Δσ) _{max} = 0.001
(Δρ) _{max} = 1.02 e Å ⁻³ (Δρ) _{min} = -0.65 e Å ⁻³
Measurement: Rigaku Saturn 724 Diffractometer
Data collection & cell refinement program: CrystalClear
Structure solving program: CrystalStructure 4.0
Structure determination: SIR 92
Refinement: full-matrix least squares against <i>F</i> ²
CCDC deposition number: 874861

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Fig. 2 ORTEP rendering of $[\text{RuCl}_3\{\text{N,N}'\text{-bis(diphenylphosphino)-2,6-diaminopyridine}\}]$ (**1**), showing 50% probability ellipsoids. All hydrogen atoms and solvent methanol molecules are omitted for clarity.

of a series of ruthenium(II) complexes having 2,6-diaminopyridine-based PNP ligands, but only one of them, *cis*- $[\text{RuCl}_2(\text{PNP-BIPOL})(\text{PPh}_3)]$ (**2**), [PNP-BIPOL = *N,N'*-bis(dibenzo[*d,f*][1,3,2]dioxaphosphine)-2,6-diaminopyridine] has been structurally characterized thus far.³ Osborn reported on the crystal structure of *trans*- $[\text{RuCl}_2(\text{PCNCP-Ph}_2)(\text{PPh}_3)]$ (**3**) where PCNCP-Ph₂ is 2,6-(diphenylphosphinomethyl)pyridine.⁵ The molecular structure of **1** with the atomic notation is depicted in Fig. 2. Selected bond lengths and angles are given in Table 2. The geometry around the ruthenium center exhibits a distorted octahedral with the meridional *N,N'*-bis(diphenylphosphino)-2,6-diaminopyridine ligand and three chlorine atoms. The Ru(1)–P(1) and Ru(1)–P(2) distances, (2.335(2) and 2.344(2) Å), are longer than those in **2** (2.257(3) and 2.272(3) Å), but shorter than those in **3** (2.4263(7) and 2.4122(7) Å). The Ru(1)–Cl(2) distance (2.368(2) Å) is shorter than that in **2** (2.431(3) Å) due to a stronger Ru(III)–Cl Coulombic interaction. The bond angle of Cl(1)–Ru(1)–Cl(3) (173.45(6)°) indicates that the chlorido ligands are bent away from the phenyl groups. These

Table 2 Selected bond distances (Å) and angles (°)

Ru(1)–Cl(1)	2.368(2)	Ru(1)–P(2)	2.344(2)
Ru(1)–Cl(2)	2.405(2)	Ru(1)–N(2)	2.070(5)
Ru(1)–Cl(3)	2.358(2)	P(1)–N(1)	1.691(6)
Ru(1)–P(1)	2.335(2)	P(2)–N(3)	1.703(5)
Cl(1)–Ru(1)–Cl(3)	173.45(6)	P(1)–Ru(1)–P(2)	164.89(7)
N(2)–Ru(1)–Cl(2)	177.78(14)		

considerations on bond distances and angles in **1** reveal that the molecule demands less steric hindrance than **2** and **3**, which have a PPh₃ ligand instead of chlorido.

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