Synthesis, characterization, and reactivity of a ruthenium(II) N,N',N''-tris(2-pyridyl)phosphine complex. X-ray analysis of RuCl₂(PPh₃)(Ppy₃) (py = 2-pyridyl)

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Abstract: Reaction of RuCl₂(PPh₃)₃ with Ppy₃ (py = 2-pyridyl) in benzene produced the *N*,*N'*,*N''*-Ppy₃ complex RuCl₂(PPh₃)(Ppy₃) **1**. Crystals of RuCl₂(PPh₃)(Ppy₃)·2CH₂Cl₂ (C₃₅H₃₁Cl₆N₃P₂Ru) are monoclinic, a = 17.269(2), b = 10.797(1), c = 20.604(1) Å, $\beta = 107.461(6)^\circ$, Z = 4, space group *P*2₁/*c*. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to R = 0.039 and $R_w = 0.035$ for 4184 reflections with $I \ge 3\sigma(I)$. Complex **1** reacts in MeOH or benzene with two-electron donors (L) to give the chloride-substituted, [RuCl(L)(PPh₃)(Ppy₃)]PF₆, or the triphenylphosphine-substituted products, RuCl₂(L)(Ppy₃), (L = CO, MeCN, PhCN), respectively. [RuCl(MeOH)(PPh₃)(Ppy₃)]BPh₄ was also isolated. The non-coordinated phosphorus atom in **1** was oxidized to form RuCl₂(PPh₃)(OPpy₃).

Key words: ruthenium, pyridylphosphines, crystal structure

Résumé : La réaction du RuCl₂(PPh₃)₃ avec de la Ppy₃ (py = 2-pyridyle) dans le benzène conduit à la formation du complexe N,N',N''-Ppy₃ du RuCl₂(PPh₃)(Ppy₃) **1**. Les cristaux du RuCl₂(PPh₃)(Ppy₃)·2CH₂Cl₂ (C₃₅H₃₁Cl₆N₃P₂Ru) sont monocliniques, groupe d'espace $P2_1/c$, avec a = 17,269(2), b = 10,797(1), et c = 20,604(1) Å, $\beta = 107,461(6)^{\circ} Z = 4$. On a résolu la structure par la méthode de Patterson et on l'a affinée par les méthodes des moindres carrés (matrice complète) jusqu'à des valeurs de R = 0,039 et $R_w = 0,035$ pour 4184 réflexions avec $I \ge 3\sigma(I)$. Dans du MeOH ou du benzène, le complexe **1** réagit avec des donneurs à deux électrons (L) pour fournir respectivement des produits substitués par le chlore, [RuCl(L)(PPh₃)(Ppy₃)]PF₆, ou des produits substitués par la triphénylphosphine, RuCl₂(L)(Ppy₃), (L = CO, MeCN, PhCN). On a aussi isolé le [RuCl(MeOH)(PPh₃)(Ppy₃)]BPh₄. On a oxydé l'atome de phosphore non coordiné du produit **1** pour former du RuCl₂(PPh₃)(OPpy₃).

Mots clés : ruthénium, pyridylphosphines, structure cristalline.

[Traduit par la rédaction]

Introduction

The N,N',N''-coordination mode of tris(2-pyridyl)phosphine (Ppy₃, py = 2-pyridyl), where the ligand binds to the metal centre via the three pyridyl nitrogens, has been observed with a variety of transition metals. All, except one, are cationic sandwich complexes containing two N,N',N''-Ppy₃ ligands and are of the general formula $[M(Ppy_3)_2]^{2+}$ (M = Mn, Co, Ni, Cu, Zn, Ru) (1–3). The X-ray crystal structures of the zinc (2) and the ruthenium (3) complexes have been determined and confirm the N,N',N''-coordination mode. Rarer are the half-sandwich complexes containing only one N,N',N''-Ppy₃ ligand, the only example (prior to this work) being Zn(Ppy₃)(NO₃)₂ (2). In this case, the complex is neutral and contains both a monodentate

Received February 2, 1996.

This paper is dedicated to Professor Howard C. Clark in recognition of his contributions to Canadian chemistry.

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¹ Author to whom correspondence may be addressed. Telephone: (604) 822-6645. Fax: (604) 822-2847. and a bidentate nitrate ligand. Thus, the N,N',N''-coordination mode has generally been observed in sandwich complexes of the first-row transition metals.

This paper reports on the synthesis, characterization, and reactivity of the N, N', N''-Ppy₃, half-sandwich complex RuCl₂(PPh₃)(Ppy₃) 1. In MeOH, one of the chloro ligands in 1 is labile, and this led to the investigation of some chloride-substitution reactions with neutral two-electron donors. Alternatively, the triphenylphosphine ligand in 1 can be replaced by carrying out the substitution reactions in benzene. This reactivity is similar to that of the well-known RuCl(PPh₃)₂(Cp) complex (Cp = η^5 -cyclopentadienyl), which also contains a facial six-electron donor ligand (4). Our interest in 2pyridylphosphine complexes stems from their potential as homogeneous catalysts in aqueous media (5). This present paper focuses on complex 1, which turned out to be water insoluble. Related complexes such as $[RuCl(PPh_3)(Ppy_3)_2]Cl$, which contains chelated P,N-coordinated Ppy₃ ligands, are water soluble and will be discussed elsewhere (6).

Experimental

All manipulations were carried out under Ar using standard Schlenk techniques. Solvents (Fisher or BDH) were dried and distilled under N_2 prior to use. MeCN and PhCN were dried

over CaH₂ for 24 h prior to fractional distillation, and stored under argon in the dark. NH_4PF_6 (Aldrich), $NaBPh_4$ (Aldrich), and m-ClC₆H₄C(O)OOH (*m*-CPBA) (Aldrich, 80–85% Tech. grade) were used as supplied. RuCl₂(PPh₃)₃ (7) and Ppy₃ (8) were prepared according to published procedures.

NMR spectra were recorded at room temperature (r.t.) on a Varian XL-300 MHz (300 MHz for ¹H; 121.4 MHz for ³¹P) spectrometer. 'H chemical shifts were recorded using the residual proton of the solvent as internal standard. All ³¹P chemical shifts were referenced to external 85% H_3PO_4 , by setting the chemical shift for P(OMe)₃ (Aldrich) at 141.00 ppm (relative to 85% H₃PO₄) in the appropriate solvent (9). Infrared spectra were recorded on a Mattson Genesis Series FTIR spectrometer as Nujol mulls between KBr plates or as KBr pellets. UV-visible spectra were recorded on a Hewlett-Packard-8452A diode array spectrometer. Solid state visible spectra were recorded by dissolving a small amount of complex in either MeOH or CH₂Cl₂ and placing the solution on a glass plate (UV cutoff 300 nm) and allowing the solvent to evaporate so that a thin amorphous film was left behind. The thin film was then placed in the beam of the spectrometer and the spectrum recorded. Conductivity measurements were made at 25°C using a model RCM151B Serfass conductance bridge (A. H. Thomas Co. Ltd.) connected to a 3403 cell from the Yellow Springs Instrument Company. The cell constant was determined by measuring the resistance of an aqueous solution of KCl (0.0100 M, $\sigma = 0.001 413 \text{ ohm}^{-1} \text{ cm}^{-1} \text{ at } 25^{\circ}\text{C}$) (10). Solutions of $\sim 1 \times 10^{-3}$ M in CH₃NO₂ or MeOH were made just prior to use. Elemental analyses were performed by Mr. P. Borda of this department.

Preparation of RuCl₂(PPh₃)(Ppy₃), 1

Benzene (30 mL) was added to a mixture of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.48 g, 0.50 mmol) and Ppy₃ (0.13 g, 0.50 mmol). The resulting red solution was refluxed for 7 h in which time a dark red precipitate formed. After the volume was reduced in half, hexanes (40 mL) were added to complete precipitation. The red precipitate was filtered, washed with hexanes (3 × 10 mL) to remove any residual PPh₃, and dried under vacuum (0.32 g, 92%). Anal. calcd. for C₃₃H₂₇Cl₂N₃P₂Ru: C 56.66, H 3.89, N 6.01; found: C 56.65, H 3.89, N 5.96%.

Single crystals for an X-ray diffraction study were grown by Et_2O diffusion into a CH_2Cl_2 solution of the complex. The crystals isolated contained two CH_2Cl_2 solvates.

Preparation of [RuCl(MeOH)(PPh₃)(Ppy₃)]BPh₄, 2

NaBPh₄ (0.022 g, 0.064 mmol) was added to a clear orange solution of **1** (0.042 g, 0.060 mmol) in MeOH (30 mL). After being stirred for 0.5 h, the solution volume was reduced (to \sim 10 mL) under vacuum during which time an orange precipitate formed. The mixture was stirred for a further 0.5 h and then the precipitate was filtered off and washed with MeOH (2 \times 1 mL) and dried under vacuum (24 h), (0.033 g, 54%). Anal. calcd. for C₅₈H₅₁BClN₃OP₂Ru: C 68.61, H 5.06, N 4.14; found: C 67.85, H 4.94, N 4.21%.

Preparation of [RuCl(CO)(PPh₃)(Ppy₃)]PF₆, 3

To a degassed solution of 1 (0.13 g, 0.19 mmol) and NH_4PF_6 (0.032 g, 0.20 mmol) in MeOH (6 mL), CO gas (1 atm (101.3 kPa)) was added, and the mixture was heated at 65°C for 2 h. The initial red suspension formed a clear yellow solution,

which was pumped to dryness and the residue dissolved in acetone (5 mL). The resulting turbid, orange solution was filtered through Celite $545^{(0)}$ along with acetone washings (15 mL). The clear filtrate was pumped to dryness and MeOH added (1 mL) to form a yellow precipitate, which was filtered off and dried under vacuum (0.12 g, 75%). Anal. calcd. for $C_{34}H_{27}ClF_6N_3OP_3Ru$: C 48.79, H 3.48, N 5.02; found: C 48.65; H, 3.38; N, 4.96%.

Preparation of [RuCl(MeCN)(PPh₃)(Ppy₃)]PF₆, 4

To a suspension of 1 (0.085 g, 0.121 mmol) and NH_4PF_6 (0.020 g, 0.122 mmol) in MeOH (4 mL) was added a solution of MeCN in MeOH (1 mL, made by mixing 0.05 mL of MeCN in 5 mL of MeOH) and the resulting mixture refluxed for 10 min. The orange solution was pumped to dryness and the residue dissolved in acetone (5 mL) and filtered through Celite $545^{\text{(B)}}$. The volume was reduced (to ~3 mL) and ether (40 mL) added to form a yellow precipitate. The product was collected by filtration, washed with ether (3 × 5 mL), and dried under vacuum (0.084 g, 82%). Anal. calcd. for $C_{35}H_{30}ClF_6N_4P_3Ru$: C 49.45, H 3.56, N 6.59; found: C 49.58, H 3.64, N 6.73%.

Preparation of [RuCl(PhCN)(PPh₃)(Ppy₃)]PF₆, 5

To a red suspension of 1 (0.098 g, 0.14 mmol) and NH_4PF_6 (0.023 g, 0.14 mmol) in MeOH (10 mL) was added PhCN (0.05 mL) with a syringe. The resulting mixture was refluxed for 15 min during which time an orange solution formed. The MeOH was removed under vacuum and the residue dissolved in acetone (50 mL) and filtered through Celite 545[®]. The filtrate was concentrated (~5 mL) and Et₂O (30 mL) added. The yellow precipitate was filtered off and dried under vacuum (0.091 g, 71%). Anal. calcd. for C₄₀H₃₂ClF₆N₄P₃Ru: C 52.67, H 3.53, N 6.14; found: C 52.80, H 3.55, N 5.96%.

Preparation of RuCl₂(CO)(Ppy₃), 6

To a red suspension of 1 (0.13 g, 0.19 mmol) in C_6H_6 (10 mL) was added CO gas (1 atm). The suspension was refluxed for 42 h in which time an orange-brown suspension developed. Hexanes (30 mL) were added to further precipitation and the precipitate collected by filtration. The product was reprecipitated from CH₂Cl₂ (15 mL) by Et₂O (20 mL), filtered, and dried in vacuo (0.05 g, 56%). Anal. calcd. for $C_{16}H_{12}Cl_2N_3OPRu$: C 41.31, H 2.60, N 9.03; found: C 41.05, H 2.64, N 8.91%.

Preparation of RuCl₂(MeCN)(Ppy₃), 7

To a red suspension of 1 (0.13 g, 0.18 mmol) in C_6H_6 (10 mL) was added MeCN (1 mL, 19 mmol). The suspension was refluxed for 17 h. After the mixture was cooled to room temperature, the red precipitate was filtered off, washed with C_6H_6 (4 × 5 mL), and dried in vacuo (24 h), (0.06 g, 68%). Anal. calcd. for $C_{17}H_{15}Cl_2N_4PRu \cdot 1/6C_6H_6$: C 44.00, H 3.28, N 11.40; found: C 44.15, H 3.46, N 11.04%. The $1/6C_6H_6$ solvate was confirmed in the ¹H NMR (CDCl₃) spectrum at 7.36 ppm (s). Attempts to remove the solvate by heating (78°C, 24 h) under vacuum caused decomposition of the complex.

Preparation of RuCl₂(PhCN)(Ppy₃), 8

To a red suspension of 1 (0.18 g, 0.25 mmol) in C_6H_6 (10 mL) was added PhCN (1 mL, 11 mmol). The suspension was refluxed for 4 h, then stirred for a further 16 h at room temperature. Hexanes (30 mL) were added and the red precipitate

Compound	RuCl.(PPh.)(Pnv.)·2CH.Cl.
Formula	$C_1H_1C_1N_2P_1R_1$
fw	869 39
Crystal system	Monoclinic
Space group	P2 Ic
a Å	17269(2)
h Å	10.797(1)
с Å	20.604(1)
ß °	107 461(6)
$V Å^3$	3664 6(6)
Z	4
$\rho_{\rm outc}$, g/cm ³	1.576
F(000)	1752
$\mu(Mo K_{\alpha}), cm^{-1}$	9.83
Crystal size, mm	$0.15 \times 0.18 \times 0.25$
Transmission factors (relative)	0.96-1.00
Scan type	ω–2θ
Scan range, deg in ω	$1.00 + 0.35 \tan \theta$
Scan speed, deg/min	16 (up to 8 rescans)
Data collected	$+h, +k, \pm l$
$2\theta_{max}$, deg	55
Crystal decay, %	19.0
Total reflections	9154
Total unique reflections	8870
R _{merge}	0.049
Reflections with $I \ge 3\sigma(F^2)$	4184
No. of variables	424
R	0.039
R_w	0.035
gof	1.78
Max Δ/σ (final cycle)	0.0003
Residual density e/Å ³	-0.64 to 0.72

"Temperature 294 K, Rigaku AFC6S diffractometer, Mo K_{α} ($\lambda = 0.71069$ Å) radiation, graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count, function minimized $\Sigma w(|F_0| - |F_e|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma ||F_0| - |F_e||/\Sigma |F_o|$, $R_w = (\Sigma w(|F_0| - |F_e|)^2/\Sigma w|F_0|^2)^{1/2}$, and gof = $[\Sigma w(|F_0| - |F_e|)^2/(m-n)]^{1/2}$. Values given for R, R_w , and gof are based on those reflections with $I \ge 3\sigma(I)$.

collected by filtration. This product was reprecipitated from CH_2Cl_2 (5 mL) with Et_2O (50 mL) and dried under vacuum (78°C, 16 h), (0.12 g, 88%). Anal. calcd. for $C_{22}H_{17}Cl_2N_4PRu$: C 48.90, H 3.17, N 10.37; found: C 48.87, H 3.50, N 10.09%.

Preparation of RuCl₂(PPh₃)(OPpy₃), 9

A solution of 1 (0.21 g, 0.29 mmol) with excess *m*-CPBA (0.11 g, 0.51 mmol based on 80% purity) in CHCl₃ (25 mL) was stirred for 24 h. Hexanes (160 mL) were added and the resulting brown precipitate filtered. The brown precipitate was redissolved in CHCl₃ (5 mL), and hexanes (10 mL) added to form a light brown precipitate that was removed by filtration and discarded. Hexanes (150 mL) were added to the red filtrate causing formation of an orange-red precipitate that was collected and dried under vacuum (78°C, 48 h), (0.15 g, 52%). Anal. calcd. for $C_{33}H_{27}Cl_2N_3OP_2Ru$: C 55.39, H 3.80, N 5.87; found: C 55.14, H 3.80, N 6.06%.

X-ray crystallographic analysis of RuCl₂(PPh₃)(Ppy₃)·2CH₂Cl₂

Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least squares on $2 \sin \theta/\lambda$ values for 25 reflections with $2\theta = 20.1^{\circ}-29.4^{\circ}$. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, decayed linearly by 19%. The data were processed,² for Lorentz and polarization effects, decay, and absorption (semi-empirical, absed on azimuthal scans).

The structure was solved by the Patterson method. The asymmetric unit contains one molecule of the metal complex and two crystallographically independent dichloromethane molecules. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were fixed in calculated positions (C—H = 0.98 Å, $B_{\rm H}$ = 1.2 $B_{\rm bonded atom}$). No correction for secondary extinction was necessary. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International tables for X-ray crystallography (11). The largest peak on the final difference map (0.72 e Å⁻³) was located near the Ru atom. Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and selected bond angles appear in Tables 2-4, respectively. Hydrogen atom parameters, anisotropic thermal parameters, complete tables of bond lengths and angles, torsion angles, non-bonded contacts, and least-squares planes have been deposited as supplementary material.3

Results and discussion

Synthesis and characterization of $RuCl_2(PPh_3)(Ppy_3)$ 1 The synthesis and reactivity of 1 are summarized in Fig. 1 and characterization data for 1–9 are reported in Tables 5–8.

Complex 1 is readily made by reaction of equimolar amounts of RuCl₂(PPh₃)₃ and Ppy₃, and its crystal structure is shown in Fig. 2. The Ppy₃ ligand binds facially via the three pyridyl nitrogens, forming three six-membered rings, and the coordination sphere is completed by *cis* chlorides and a PPh₃. The geometry at Ru is close to octahedral with the angles ranging from 84.9(1)° to 94.9(1)°. The Ru(1)—N(3) bond, trans to the PPh₃, is slightly longer than the Ru(1)—N(1 and 2) bonds trans to Cl, (2.117(4) Å versus 2.075(4) Å and 2.090(4) Å, respectively). These values are similar to those reported for $[Ru(Ppy_3)_2][C_7H_7SO_3]_2$ (2.06(1)–2.09(1) Å) (3), which has two Ppy₃ ligands coordinated facially through the pyridyl nitrogens and is the only other ruthenium structure reported for a Ppy₃ ligand bound in this manner. The Ru(1)-Cl(1 and 2) bond lengths are identical and the Ru(1)—P(2) bond length is typical for that of a Ru(II) phosphine complex (12).

Bond lengths in the Ppy₃ ligand do not change upon coordi-

² teXsan: Crystal structure analysis package. Molecular Structure Corp. The Woodlands, Tex., 1985 and 1992.

³ Copies of material on deposit may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. Tables of hydrogen atom coordinates and bond lengths and angles involving hydrogen atoms have also been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.

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Table 2. Final atomic coordinates (fractional) and B_{eq} .

Atom	x	у	z	B _{eq}
Ru(1)	0.20978(2)	0.25418(4)	0.23526(2)	2.33(1)
Cl(1)	0.14697(8)	0.23833(13)	0.32628(6)	3.44(5)
Cl(2)	0.25879(8)	0.46078(11)	0.27480(7)	3.41(5)
Cl(3)	0.83342(11)	0.1004(2)	0.42094(11)	8.1(1)
Cl(4)	0.67577(13)	0.2093(2)	0.38988(12)	10.2(1)
Cl(5)	0.9186(2)	0.1383(2)	0.1353(2)	14.4(2)
Cl(6)	0.7970(2)	0.0478(3)	0.01523(13)	14.9(2)
P(1)	0.11631(9)	0.20428(14)	0.06668(7)	3.63(6)
P(2)	0.32550(8)	0.14675(12)	0.30009(6)	2.41(5)
N(1)	0.2605(2)	0.2858(3)	0.1574(2)	2.5(2)
N(2)	0.1508(2)	0.0908(4)	0.1933(2)	2.5(2)
N(3)	0.1047(2)	0.3472(4)	0.1754(2)	2.9(2)
C(1)	0.2208(3)	0.2614(5)	0.0911(2)	3.1(2)
C(2)	0.2540(4)	0.2865(5)	0.0397(3)	4.1(3)
C(3)	0.3305(4)	0.3378(6)	0.0546(3)	4.9(3)
C(4)	0.3706(3)	0.3649(5)	0.1213(3)	3.9(3)
C(5)	0.3340(3)	0.3382(5)	0.1707(2)	3.2(2)
C(6)	0.1191(3)	0.0759(5)	0.1251(2)	3.0(2)
C(7)	0.0787(3)	-0.0309(5)	0.1251(2) 0.0967(3)	4.0(3)
C(8)	0.073(3)	-0.1260(5)	0.0307(3)	44(3)
C(0)	0.0075(3)	-0.1200(5)	0.1370(3)	3 9(3)
C(10)	0.0900(3) 0.1372(3)	-0.1094(3) -0.0015(5)	0.2070(3)	2.9(2)
C(10)	0.1372(3) 0.0710(3)	-0.0013(3)	0.2329(2) 0.1083(3)	2.9(2) 3.1(2)
C(12)	0.0719(3)	0.3224(3)	0.1003(3)	4.3(3)
C(12) C(13)	-0.0307(3)	0.3800(0) 0.4765(6)	0.0094(3)	4.3(3)
C(13)	-0.0307(3)	0.4703(0)	0.0982(3)	4.8(3)
C(14)	0.0024(4) 0.0604(3)	0.3024(3)	0.1034(3)	4.3(3)
C(15)	0.0094(3)	0.4300(3)	0.2020(3)	3.0(2)
C(10)	0.3932(3)	0.1074(4) 0.0442(5)	0.2300(2)	2.0(2)
C(17)	0.3030(3)	0.0443(5)	0.1890(3)	3.4(2)
C(18)	0.4130(4)	0.0110(5)	0.1504(3)	4.6(3)
C(19)	0.4943(4)	0.0416(6)	0.1717(3)	5.6(3)
C(20)	0.5255(4)	0.1068(7)	0.2303(3)	5.8(3)
C(21)	0.4763(3)	0.1412(5)	0.2694(3)	4.3(3)
C(22)	0.3107(3)	-0.0067(4)	0.3343(2)	2.6(2)
C(23)	0.3320(3)	-0.1180(5)	0.3111(3)	3.6(2)
C(24)	0.3189(4)	-0.2279(5)	0.3396(3)	4.5(3)
C(25)	0.2870(4)	-0.2290(6)	0.3929(3)	5.0(3)
C(26)	0.2649(3)	-0.1210(6)	0.4165(3)	4.5(3)
C(27)	0.2772(3)	-0.0089(5)	0.3874(2)	3.4(2)
C(28)	0.3938(3)	0.2088(5)	0.3810(2)	2.8(2)
C(29)	0.3773(3)	0.3182(5)	0.4079(3)	3.7(2)
C(30)	0.4287(4)	0.3606(5)	0.4700(3)	4.9(3)
C(31)	0.4958(4)	0.2927(6)	0.5039(3)	5.0(3)
C(32)	0.5123(4)	0.1807(6)	0.4793(3)	4.5(3)
C(33)	0.4608(3)	0.1397(5)	0.4180(3)	3.9(2)
C(34)	0.7551(4)	0.1747(7)	0.3602(3)	7.0(4)
C(35)	0.8545(5)	0.0185(7)	0.0999(4)	8.8(5)

 ${}^{a}B_{eq} = (8/3)\pi^{2}\Sigma\Sigma U_{ij}a^{*}{}_{i}a^{*}{}_{j}(\mathbf{a}_{i}\cdot\mathbf{a}_{j}).$

nation when compared to data for the free ligand (13), but bond angles do change somewhat. The C(1)-P(1)-C(6) angle (between the two py groups *trans* to Cl) increases slightly to 104.2(2)°, while the C(1)-P(1)-C(11) and C(11)-P(1)-C(6) angles decrease to 98.8(2)°, as compared to an average of 101.9° in the free ligand (13). These angles in 1 are similar to those found in [Ru(Ppy₃)₂][C₇H₇SO₃]₂ (100.9(8)°, 99.6(8)°, and 99.6(7)°) (3). The solution structure of 1 in CDCl₃ is consistent with the X-ray structure. The ³¹P{¹H} NMR spectrum contains two singlets (Table 5), the result of two uncoupled phosphorus nuclei. The low-field signal is assigned to the PPh₃, while the high-field signal is assigned to the Ppy₃ ligand, the assignments being based on the coordination chemical shift Δ values of 47.7 and 5.56 ppm for the PPh₃ and the Ppy₃ ligands, respectively (14–16). The small Δ value for the Ppy₃ ligand is

Bond	3ond Length		Length
Ru(1)Cl(1)Ru(1)Cl(2)Ru(1)P(2)Ru(1)P(2)	2.438(1)	P(2)—C(16)	1.845(5)
	2.438(1)	P(2)—C(22)	1.848(5)
	2.350(1)	P(2)—C(28)	1.854(5)
$ \begin{array}{l} \text{Ru}(1) - N(1) \\ \text{Ru}(1) - N(2) \\ \text{Ru}(1) - N(3) \\ \text{P}(1) - C(1) \end{array} $	2.075(4)	N(1) - C(1)	1.357(5)
	2.090(4)	N(1) - C(5)	1.341(6)
	2.117(4)	N(2) - C(6)	1.356(6)
	1.829(5)	N(2) - C(10)	1.352(6)
P(1) - C(6)	1.827(5)	$\frac{N(2)-C(10)}{N(3)-C(11)}$	1.354(6)
P(1) - C(11)	1.829(5)		1.346(6)

Table 4. Selected bond angles (deg) with estimated standard deviations in parentheses.

Bonds	Angle(deg)	Bonds	Angle(deg)
Cl(1)-Ru(1)-Cl(2)	89.84(5)	C(16)-P(2)-C(22)	101.1(2)
Cl(1)-Ru(1)-P(2)	91.54(5)	C(16)-P(2)-C(28)	103.6(2)
Cl(1)-Ru(1)-N(1)	174.4(1)	C(22)-P(2)-C(28)	96.0(2)
Cl(1)-Ru(1)-N(2)	89.1(1)	Ru(1)-N(1)-C(1)	122.9(3)
Cl(1)-Ru(1)-N(3)	88.9(1)	Ru(1)-N(1)-C(5)	120.3(3)
Cl(2)-Ru(1)-P(2)	96.37(5)	C(1)-N(1)-C(5)	116.7(4)
Cl(2)-Ru(1)-N(1)	85.6(1)	Ru(1)-N(2)-C(6)	121.6(3)
Cl(2)-Ru(1)-N(2)	171.0(1)	Ru(1)-N(2)-C(10)	121.6(3)
Cl(2)-Ru(1)-N(3)	84.9(1)	C(6)-N(2)-C(10)	116.7(4)
P(2)-Ru(1)-N(1)	92.1(1)	Ru(1)-N(3)-C(11)	121.6(3)
P(2)-Ru(1)-N(2)	92.6(1)	Ru(1)-N(3)-C(15)	120.7(4)
P(2)-Ru(1)-N(3)	178.6(1)	C(11)-N(3)-C(15)	117.6(4)
N(1)-Ru(1)-N(2)	94.9(1)	P(1)-C(1)-N(1)	120.1(3)
N(1)-Ru(1)-N(3)	87.6(1)	P(1)-C(1)-C(2)	117.3(4)
N(2)-Ru(1)-N(3)	86.2(2)	N(1)-C(1)-C(2)	122.4(5)
C(1)-P(1)-C(6)	104.2(2)	P(1)-C(6)-N(2)	121.0(4)
C(1)-P(1)-C(11)	98.8(2)	P(1)-C(6)-C(7)	116.4(4)
C(6)-P(1)-C(11)	98.8(2)	N(2)-C(6)-C(7)	122.2(5)
Ru(1)-P(2)-C(16)	112.6(2)	P(1)-C(11)-N(3)	120.7(4)
Ru(1)-P(2)-C(22)	117.9(2)	P(1)-C(11)-C(12)	118.4(4)
Ru(1)-P(2)-C(28)	122.4(2)	N(3)-C(11)-C(12)	120.9(5)

consistent with its noncoordination. ³¹P{¹H} NMR data for other N,N',N''-coordinated Ppy₃ complexes have not been reported. As well, the ¹H NMR (CDCl₃) spectrum (Table 6) shows multiple peaks in the phenyl region and is consistent with the complex containing two equivalent (*trans* to Cl) and one inequivalent (*trans* to PPh₃) pyridyl rings. For example, the H6 protons (H adjacent to N in the 2-pyridyl group) give rise to two signals with an integration ratio of 2:1. (That the H6 proton occurs at the most downfield position has been established by others (17, 18).) Thus, the solid state structure of 1 is maintained in CDCl₃. However, when 1 is dissolved in MeOH the complex dissociates a chloride (described below).

The synthesis and structure of 1 are similar to those of other Ru(II) complexes containing a facially coordinated six-electron donor ligand. Three examples are RuCl₂(PPh₃)([9]aneS₃) (19), RuCl(PPh₃)₂(Cp) (4), and RuCl(PPh₃)₂(Tp) (20) (where [9]aneS₃ = 1,4,7-trithiacyclononane, and Tp = hydrotris(pyrazol-1-yl)borate). The remainder of the coordination spheres is completed by PPh₃ and Cl ligands, relative numbers of each

RuCl₂(PPh₃)(OPpy₃) 9

Fig. 1. Synthesis of compounds. Conditions: (i) Δ , C₆H₆, 7 h; (ii) MeOH, 1 h; (iii) MeOH, 65°C; L = CO, 2 h; L = MeCN, 10 min; L = PhCN, 15 min; (iv) Δ , C₆H₆; L = CO, 42 h; L = MeCN, 17 h; L = PhCN, 4 h, and 16 h at r.t.; (v) CDCl₃, r.t.; 1 atm O₂ 12 d, or *m*-CPBA, 24 h.

$$\begin{aligned} & \text{RuCl}_{2}(\text{PPh}_{3})_{3} + \text{Ppy}_{3} \underbrace{(i)}_{2 \text{ PPh}_{3}} \text{RuCl}_{2}(\text{PPh}_{3})(\text{Ppy}_{3}) \\ & 1 \end{aligned}$$

$$\begin{aligned} & \text{RuCl}_{2}(\text{PPh}_{3})(\text{Ppy}_{3}) + \text{MeOH} \underbrace{=}_{\text{[RuCl}(\text{MeOH})(\text{PPh}_{3})(\text{Ppy}_{3})]^{*} + \text{Cl}^{*} \\ & 1 \end{aligned}$$

$$\begin{aligned} & \text{RuCl}_{2}(\text{PPh}_{3})(\text{Ppy}_{3}) + \text{NaBPh}_{4} \underbrace{(ii)}_{NaCl} + \text{RuCl}_{2}(\text{MeOH})(\text{PPh}_{3})(\text{Ppy}_{3})]\text{BPh}_{4} \\ & 1 \end{aligned}$$

$$\begin{aligned} & \text{RuCl}_{2}(\text{PPh}_{3})(\text{Ppy}_{3}) + \text{L} + \text{NH}_{4}\text{PF}_{6} \underbrace{(iii)}_{NH_{4}\text{Cl}} + \frac{(\text{III})}{\text{L} = \text{CO}, 3} \\ & \text{L} = \text{MeCN}, 4 \\ & \text{L} = \text{PhCN}, 5 \end{aligned}$$

$$\begin{aligned} & \text{RuCl}_{2}(\text{PPh}_{3})(\text{Ppy}_{3}) + \text{xs L} \underbrace{(iv)}_{\text{PPh}_{3}} + \frac{(\text{RuCl}_{2}(\text{L})(\text{Ppy}_{3})}{\text{L} = \text{CO}, 6} \\ & \text{L} = \text{MeCN}, 7 \\ & \text{L} = \text{PhCN}, 8 \end{aligned}$$

$$\end{aligned}$$

Fig. 2. Perspective view of the RuCl₂(PPh₃)(Ppy₃) molecule; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

RuCl₂(PPh₃)(Ppy₃)

1



depending on the charge of the facial ligand. Finally, all of the complexes have been synthesized by PPh₃ ligand displacement from $RuCl_2(PPh_3)_3$, although this is not the most convenient method for $RuCl(PPh_3)_2(Cp)$ (4).

Table 5.	³¹ P{'H}	NMR	chemical	shifts	for	N,N',N''	-coordin	nated
tris(2-pyri	idyl)pho	sphine	complexe	es.				

Complex	Solvent	Ppy ₃ " (ppm)	PPh ₃ " (ppm)
$RuCl_{2}(L)(Ppy_{1})$			
$L = PPh_3, 1$	CDCl ₃	4.81	42.3
L = CO, 6	CDCl ₃	2.36	_
L = MeCN, 7	CDCl ₃	7.71	_
L = PhCN, 8	CDCl ₃	7.38	
$[RuCl(L)(PPh_3)(Ppy_3)]X$			
$L = CO; X = Cl^{b}$	CD ₃ OD	0.69	36.6
$L = CO; X = PF_{6}, 3^{c}$	CDCl ₃	-0.81	36.7
, i i i i i i i i i i i i i i i i i i i	CD ₃ OD	0.69	36.6
$L = MeCN; X = PF_{6}, 4$	CDCl ₃	2.32	41.4
$L = PhCN; X = PF_6, 5$	Acetone- d_6	3.57	42.8
-	CD_2Cl_2	2.18	41.2
RuCl ₂ (PPh ₃)(OPpy ₃), 9	CDCl ₃	3.56 ^d	40.4

"Singlet; shifts for free Ppy $_3$ and PPh $_3$ in CDCl $_3$ are -0.74 and -5.42 ppm, respectively.

"In situ.

For the PF₆ salts (3–5), the ${}^{31}P{}^{1}H{}$ septet for the anion was seen at δ -143 to -145 with ${}^{1}J_{PF}$ = 708–713 Hz.

^dOPpy₃.

Dissociation of chloride from 1

The molar conductivity of **1** is reported in Table 7. In CH₃NO₂, complex **1** is essentially a nonconductor, while in MeOH the conductivity approaches that expected for a 1:1 conductor. The solvents have comparable dielectric constants (ε = 38.6 for CH₃NO₂, and 32.6 for MeOH (25)), but the higher donor number of MeOH (20.0 vs. 2.7 (25)) leads to the formation of an ionic complex containing a coordinated MeOH (Fig. 1). The complex was isolated as [RuCl(MeOH)(PPh₃)(Ppy₃)]-BPh₄, **2**, but no NMR data could be recorded because of low solubility. Unfortunately the C analysis for **2** is 0.76% low, but two bands in the IR spectrum can be assigned to a coordinated MeOH: ν_{OH} at 3207 cm⁻¹ and ν_{OC} at 1001 cm⁻¹. For neat MeOH the corresponding bands appear at 3342 and 1033 cm⁻¹, respectively (26); the shifts are consistent with MeOH coordination.

The very similar UV-visible spectra of 1 in CH₂Cl₂ and in the solid state (Table 8) imply that the solution structure of 1 in CH₂Cl₂ is the same as that in the solid state (i.e., of the neutral RuCl₂(PPh₃)(Ppy₃)). The lower wavelength maxima observed in MeOH are partially attributed to the formation of the coordinated MeOH complex 2. The spectrum of 2 in CH₂Cl₂, shows a λ_{max} at 414 nm, essentially the same as the 416 nm λ_{max} observed for 1 in MeOH, but the other λ_{max} for 2 (at 368 nm) corresponds to that seen for 1 in CH₂Cl₂. "Solvent effects" on the spectra are clearly important, and this is also evident when addition of a large excess of LiCl (even upto ~10 M) to an MeOH sample of 1 resulted in a change in the 416 nm maximum, to 422 nm, and not the 434 nm position seen for 1 in CH₂Cl₂.

Other ruthenium(II) phosphine complexes containing coordinated MeOH have been reported: the five-coordinate $RuCl_2(PMA)(PPh_3)$ (PMA = *o*-diphenylphosphino-*N*,*N*dimethylaniline) reversibly binds MeOH in benzene, as determined by 1H NMR spectroscopy (27); the isolated $Ru(H)_2(CO)(PPh_3)_2(MeOH)$ has been characterized by IR and **Fig. 3.** Structures of N,N',N''-tris(2-pyridyl)phosphine complexes. (L = PPh₃, 1; L = CO, 3, 6; L = MeCN, 4, 7; L = PhCN, 5, 8).



NMR spectroscopies (28); and $Ru(O_2CCF_3)_2(MeOH)$ -(CO)(PPh₃)₂ has been characterized by X-ray analysis (29). More closely related, the ionic behaviour observed for 1 parallels that of $RuCl(PPh_3)_2(Cp)$, which is a non-electrolyte in acetone but dissociates appreciably in MeOH (22). Haines and Du Preez isolated the complex [Ru(MeOH)(PPh_3)_2(Cp)]BPh_4, which they identified by NMR and IR spectroscopy, although no actual data were presented. As here, the product was not obtained analytically pure. Nevertheless, the ability of RuCl(PPh_3)_2(Cp) to dissociate chloride in MeOH has led to a variety of chloride exchange reactions for the Cp complex (4), and similar reactivity is seen with 1.

Chloride-substitution reactions

The chloride-substitution reactions are summarized in Fig. 1.

When 1 was heated in CD₃OD under 1 atm CO gas, the initially red suspension changed into a clear yellow solution; the in situ ³¹P{¹H} NMR spectrum contained two singlets attributed to the species [RuCl(CO)(PPh₃)(Ppy₃)]Cl. However, on a synthetic scale, attempts to isolate this salt always resulted in the formation of an oil. A similar reaction carried out in the presence of NH₄PF₆, however, did allow for isolation of [RuCl(CO)-(PPh₃)(Ppy₃)]PF₆ **3** as an analytically pure yellow salt.

The ³¹P{¹H} NMR (CD₃OD) spectrum of **3** matched that of the in situ species and consisted of two singlets for two uncoupled phosphorus nuclei. The IR spectrum contained a single CO stretch and the compound was a 1:1 conductor in nitromethane. The H6 protons of the Ppy₃ ligand gave rise to three signals in the ¹H NMR spectrum indicating the inequivalence of the three pyridyl groups. These data are consistent with the structure given in Fig. 3, which shows the compound as a racemate.

There is a solvent dependence for the formation of 3. In ace-

Complex	Solvent	δ , ppm (peak ^{<i>a</i>} , no. of H, assignment ^{<i>b</i>})
RuCl ₂ (L)(Ppy ₃)		
$L = PPh_3, 1$	CDCl ₃	6.15(m,2H,Ppy ₃);7.17(m,9H, <i>m-p</i> -PPh ₃);7.29(m,2H,Ppy ₃);7.43(m,1H,Ppy ₃);7.59(m,6H, <i>o</i> -PPh ₃);7.68(m,1H,Ppy ₃);7.93(m,3H,Ppy ₃);8.52(p-d,2H,H6-Ppy ₃);10.22(p-d,1H,H6-Ppy ₃)
L = CO, 6	CDCl ₃	7.30(m,2H,Ppy ₃);7.61(m,1H,Ppy ₃);7.77(m,2H,Ppy ₃);7.90(m,1H,Ppy ₃);8.14(m,3H,Ppy ₃); 9.47(p-d,2H,H6-Ppy ₃);9.98(p-d,1H,H6-Ppy ₃)
L = MeCN, 7	CDCl ₃	2.67(s,3H,MeCN);7.20(m,3H,Ppy ₃);7.62(m,3H,Ppy ₃);8.03(m,3H,Ppy ₃); 9.69(p-d,2H,H6-Ppy ₃); 9.90(p-d,1H,H6-Ppy ₃)
L = PhCN, 8	CDCl ₃	7.17-7.75(m's,11H,Ppy ₃ ,PhCN);8.08(m,3H,Ppy ₃);9.65(p-d,2H,H6-Ppy ₃); 9.96(p-d,1H,H6-Ppy ₃)
[RuCl(L)(PPh ₃)(Ppy ₃)]PF ₆	
L = CO, 3	CDCl ₃	6.56(m,1H,Ppy ₃);6.74(m,1H,Ppy ₃);7.33(m,12H, <i>o-m</i> -PPh ₃);7.45(m,3H, <i>p</i> -PPh ₃); 7.54(m,1H,Ppy ₃);7.84(m,2H,Ppy ₃);7.95(m,2H,Ppy ₃);8.26(m,1H,Ppy ₃);8.49(m,3H,Ppy ₃); 9.56(p-d,1H,H6-Ppy ₃)
	CD ₃ OD	6.66(m,1H,Ppy ₃);6.85(m,1H,Ppy ₃);7.27(m,12H, <i>o-m</i> -PPh ₃);7.42(m,3H, <i>p</i> -PPh ₃); 7.58(m,1H,Ppy ₃);7.62(m,1H,Ppy ₃);7.75(m,1H,Ppy ₃);7.92(m,1H,Ppy ₃);7.98(m,1H,Ppy ₃); 8.15(p-d,1H,H6-Ppy ₃);8.27(m,1H,Ppy ₃);8.36(m,1H,Ppy ₃);8.48(p-d,1H,H6-Ppy ₃); 9.47(p-d,1H,H6-Ppy ₃)
L = MeCN, 4	CDCl ₃	2.21(s,3H,MeCN);6.53(m,1H,Ppy ₃);6.93(m,1H,Ppy ₃);7.36(m,15H,PPh ₃);7.51(m,1H,Ppy ₃); 7.60(m,2H,Ppy ₃);7.87(m,1H,Ppy ₃);8.20(m,3H,Ppy ₃);8.31(p-d,1H,H6-Ppy ₃); 8.50(p-d,1H,H6-Ppy ₁); 9.61(p-d,1H,H6-Ppy ₂)
L = PhCN, 5	Acetone-d ₆	6.80(m,1H,Ppy ₃);6.94(m,1H,Ppy ₃);7.30–7.65(m's,20H);7.70–7.89(m's,3H);7.93 (m,1H,Ppy ₃); 8.13(m,1H,Ppy ₃);8.39-8.55(m's,3H);8.60(p-d,1H,H6-Ppy ₃); 9.88(p-d,1H,H6-Ppy ₃)
RuCl ₂ (PPh ₃)(OP	ру ₃) 9	
	CDCl ₃	6.35(m,2H,Ppy ₃);7.14–7.33(m's,9H);7.49–7.62 (m's,9H);7.89(m,1H,Ppy ₃);8.15(m,3H); 8.45 (p-d,2H,H6-Ppy ₃);10.13(p-d,1H,H6-Ppy ₃)

Table 6. ¹H NMR chemical shifts for N, N', N''-coordinated tris(2-pyridyl)phosphine complexes at room temperature.

"s = singlet; m = multiplet; m's = more than one multiplet; p-d = pseudo-doublet(multiplet).

^bAssignments to specific ligands are made where possible; o = ortho-H; m = meta-H; p = para-H, of Ph groups; H6 = pyridyl-H, adjacent to N of Ppy₃ ligand.

	IR stretch (cm ⁻¹)	$\Lambda_{\rm M}$ (CH ₃ NO ₂ , 25°C) ^b		
Complex L	$\operatorname{RuCl}_2(L)(\operatorname{Ppy}_3)$	RuCl(L)(PPh ₃)(Cp)	$(ohm^{-1} mol^{-1} cm^{2})$ RuCl ₂ (L)(Ppy ₃)	
PPh ₃ , 1			9.9; 67.4 ^c	
CO, 6	$v_{co} = 1942$ (s)	$v_{\rm CO} = 1958 \ (21)^d$		
MeCN, 7	$v_{\rm CN} = 2270 \ ({\rm w})$			
PhCN, 8	$v_{CN} = 2224 (m)$	_		
L	$[\operatorname{RuCl}(L)(\operatorname{PPh}_3)(\operatorname{Ppy}_3)]^+$	$[\operatorname{Ru}(L)(\operatorname{PPh}_3)_2(\operatorname{Cp})]^+$	$[RuCl(L)(PPh_3)(Ppy_3)]^+$	
MeOH, 2	$v_{OH} = 3207 \text{ (s)}, v_{OC} = 1001(\text{s})$	_		
CO, 3	$v_{c0} = 1979$ (s)	$v_{co} = 1981$ (22)	80.4	
MeCN, 4	$v_{\rm CN} = 2274 \ ({\rm w})$	$v_{CN} = 2265$ (23)	79.3	
PhCN, 5	$v_{CN} = 2232 \text{ (m)}$	$v_{\rm CN} = 2228 \ (23)$	79.3	

Table 7. Some infrared and conductivity data for N, N', N''-coordinated tris(2-pyridyl)phosphine complexes and analogous Cp complexes.

"s = strong; m = medium; w = weak.

^bAccepted ranges (ohm⁻¹ mol⁻¹ cm²) for 1:1 conductors: in CH₃NO₂ (75-90); in MeOH (80–115) (24).

'In MeOH. Calculated using the molecular weight for RuCl₂(PPh₃)(Ppy₃) (699.52 g mol⁻¹). If calculated with the

molecular weight of [RuCl(MeOH)(PPh₃)(Ppy₃)]Cl (731.56 g mol⁻¹) the molar conductivity is 64.4.

^dAppropriate reference appears in parentheses for the Cp complexes.

tone, the reaction at room temperature was slow (11 d) and a mixture of mainly 3 and some $RuCl_2(CO)(Ppy_3)$ 6 (see below) was obtained. The minor product is formed via displacement of the PPh₃ of 1. In MeOH, the formation of the cationic

MeOH intermediate allows for a more efficient mechanism for the formation of **3**.

Use of a procedure similar to that described above for 3 allowed for isolation of the nitrile complexes

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Table 8. UV-visible data for N, N', N''-coordinated tris(2-pyridyl)phosphine complexes.

Complex	Solvent		$\lambda_{max} \ (\epsilon_{max} \times 10^{-3}) \ nm \ (M^{-1} \ cm^{-1})$	
RuCl ₂ (L)(Ppy ₃)				
$L = PPh_3$, 1	CH_2Cl_2	270(20.5)	368(6.40)	434(7.60)
	MeOH	264(20.0)	350(6.00)	416(7.90)
	Solid State ^a		368	438
	Solid State ^b	_	368	438
L = CO, 6	CH ₂ Cl ₂	270(15.6)	350(5.96)	434(3.05)
	MeOH	264(8.92)	338(3.10)	400(1.92)
L = MeCN, 7	CH_2Cl_2	_	386(7.92)	428(9.31) ^c
	MeOH		372(7.67)	$418(8.63)^d$
L = PhCN, 8	CH_2Cl_2	268(24.8)	374(12.0)	434(13.9)
	MeOH	260(22.2)	356(9.10)	414(11.3)
$[RuCl(MeOH)(PPh_3)(Ppy_3)]BPh_4$, 2	CH_2Cl_2		$368(-4.84)^{e}$	414(~5.59) ^e
[RuCl(L)(PPh ₃)(Ppy ₃)]PF ₆				
L = CO, 3	CH ₂ Cl ₂	270(18.0)	366(3.07)	
	MeOH	266(19.0)	352(3.20)	
L = MeCN, 4	CH ₂ Cl ₂	262(18.9)	336(5.88)	386(7.54) ^f
L = PhCN, 5	CH ₂ Cl ₂	260(19.1)	324 (10.6)	386(9.61) ^g
$RuCl_2(PPh_3)(OPpy_3), 9$	CH_2Cl_2	262(18.5)	362(6.90)	430(7.35)
	MeOH	262(17.8)	346(6.59)	412(7.50)

"Amorphous film made from a CH₂Cl₂ solution.

^bFilm made from a MeOH solution.

Shoulder at 466 nm ($\epsilon = 6540$).

^dShoulder at 450 nm ($\varepsilon = 6630$).

^cComplex not analytically pure. ^fShoulder at 424 nm ($\varepsilon = 5570$).

*Shoulder at 424 nm ($\varepsilon = 6330$)

 $[RuCl(L)(PPh_3)(Ppy_3)]PF_6$, where L = MeCN (4) or L = PhCN (5). The isolated complexes (Fig. 3) were characterized in the same manner as 3. Only one equivalent of MeCN was used to make 4. When excess or neat MeCN was used, the isolated product contained small amounts of impurities, as determined by ${}^{31}P{}^{1}H$ NMR. Similarly, when $RuCl_2(PPh_3)(Ppy_3)$ and one equivalent of NH₄PF₆ were refluxed in a mixture of PhCN and some acetone (needed to dissolve NH_4PF_6), the isolated product mixture contained 5 and a second product which showed a ³¹P{¹H} singlet at δ 6.30 (in acetone- d_6) or 5.05 (in CD₂Cl₂). This second product, also formed from refluxing RuCl₂(PhCN)(Ppy₃) 8 in MeOH with one equivalent of NH₄PF₆ and excess PhCN, is tentatively formulated as $[RuCl(PhCN)_2(Ppy_3)]PF_6$. The complex was not further characterized because of the presence of other minor impurities. Finally, when 1 is refluxed in neat PhCN without NH_4PF_6 , $RuCl_{2}(PhCN)(Ppy_{3})$ 8 is formed (see below).

In summary, the best route to chloride-substitution products of 1 is via reactions in MeOH, which allow for dissociation of chloride and disfavour substitution of PPh₃, which occurs in other solvents.

Triphenylphosphine-substitution reactions

By use of a nonpolar solvent such as benzene, the PPh₃ in 1 is readily displaced, the chemistry being similar to that of RuCl(PPh₃)₂(Cp), where the PPh₃ has been replaced by other phosphines, CO, and isocyanides, to name a few (4).

The refluxing of 1 in C_6H_6 under 1 atm CO gas gives two precipitated products, based on the ³¹P{¹H} NMR (CDCl₃) spectrum which contained two singlets at δ 2.36 (major) and

4.77 (minor). The complex RuCl₂(CO)(Ppy₃) **6** giving rise to the singlet at 2.36 ppm was separated as an orange solid by precipitation from CH₂Cl₂ with Et₂O, while the minor product was not characterized. The ¹H NMR (CDCl₃) spectrum of **6** contained two H6 signals integrating in a 2:1 ratio, and the NMR data and the single ν CO IR band are consistent with a structure analogous to that of RuCl₂(PPh₃)(Ppy₃) (Fig.3).

Similar reactions of 1 with MeCN and PhCN (Fig. 1) allowed for isolation of RuCl₂(MeCN)(Ppy₃) 7 and $RuCl_{2}(PhCN)(Ppy_{3})$ 8, respectively, with structures similar to that of the CO complex. These two complexes were isolated in slightly different manners. Complex 8 formed as a red precipitate during the reaction in benzene, the remainder of the product being precipitated by addition of hexanes. The product was then reprecipitated from CH_2Cl_2 with Et_2O to remove a C_6H_6 solvate that otherwise was not removed under vacuum. Finally, 8 was heated under vacuum to remove any remaining solvates, and an analytically pure product was produced. Complex 7 was isolated directly as a red precipitate from the C_6H_6 solution without the addition of hexanes and dried under vacuum for 24 h. The analysis of this complex was calculated including 1/6 mol of C₆H₆ solvate. The C₆H₆ solvate was confirmed by integration of the ¹H NMR (CDCl₃) spectrum. When 7 was heated in vacuum (78°C, 24 h) the complex partially decomposed, becoming red-brown in colour; the elemental analysis had a much lower nitrogen percentage, suggesting that MeCN was being lost.

A further factor perhaps assisting the substitution of the PPh₃ in 1 is that the complex is only slightly soluble in C_6H_6 , and thus the concentration of the substituting ligand is high,

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relative to that of 1. The longer reaction time required for the CO complex in comparison to the nitrile complexes (42 versus 17-20 h) is probably the result of the relatively low concentration of CO versus that of the nitriles.

There is a striking similarity between the carbonyl and nitrile stretches of the N,N',N''-Ppy₃ complexes and those of the analogous Cp complexes (see Table 7; no data could be found for the Cp analogues of 7 and 8). For example, the cationic carbonyl complexes produced by substitution of the chloride in 1, or in RuCl(PPh₃)₂(Cp), have essentially the same CO stretches, indicating that the electronic properties of the Ru centre, in terms of back-donation into the π orbital of the CO ligand, are the same. The implication is that the 14-electron fragments RuCl(Ppy₃) and Ru(PPh₃)(Cp) have similar electronic properties. Within either the Ppy₃ or Cp systems, the cationic complexes have the higher ν_{CO} or ν_{CN} values, consistent with the usual property of less π -back-donation from the Ru in the cationic systems.

Reaction of 1 with oxygen and m-CPBA

The in situ reaction of 1 with 1 atm O_2 gas in CDCl₃ was followed by ³¹P{¹H} NMR spectroscopy and, after 3 d at room temperature, signals for 1 and a new species were present in the spectrum. The new signals are for the complex $RuCl_2(PPh_3)$ - $(OPpy_3)$ 9 (see Fig. 3), which was synthesized independently using *m*-CPBA as the O-atom donor. In the O₂-system, after 12 d, 9 is the only species present along with a small peak for $OPPh_3$ ($\delta_P 29.6$). Thus, the free phosphorus of the Ppy₃ group in $RuCl_2(PPh_3)(Ppy_3)$ is oxidized to the phosphine oxide, indeed at a rate comparable to that of free Ppy_3 . The presence of $OPPh_3$ in the spectrum of the in situ reaction suggests that a second ruthenium product is being formed; this could be a paramagnetic ruthenium-oxo or -peroxo-type species (30) but, because of the relatively small amount of OPPh₃ formed, no attempts were made to isolate this other product. In the system of 9 from 1 using *m*-CPBA, the benzoic acid by-product was removed by selective precipitation with hexanes. Reaction of RuCl₂(PPh₃)₃ with $OPpy_3$ gave a complex mixture of products including 9.

Other complexes containing a coordinated OPpy₃ ligand have the general formula $[M(OPpy_3)_2][X]_2$ (M = Mn, Co, Ni, Cu, Zn, with $X = ClO_4(1)$; or M = Ru, with $X = PF_6(31)$), and have been synthesized directly using OPpy₃. The OPpy₃ ligands coordinate via the three pyridyl nitrogens and form octahedral complexes. Infrared data are not reported for the Ru complex, but the v_{PO} stretches for the first-row transition metal complexes range from 1231 to 1236 cm⁻¹; 9 gives a similar ν_{PO} stretch at 1235 cm⁻¹. These ν PO values are higher than that of the free $OPpy_3$ ligand, 1215 cm⁻¹ (1), the increase possibly resulting from the configuration imposed on the ligand upon coordination, or from an increase in $p\pi - d\pi$ bonding between the oxygen and phosphorus, caused by an increase in the electronegativity of the phosphorus, induced by the coordinating pyridyl groups (1). This is consistent with the general trend for phosphine oxides (OPR₃) which show an increase in the ν_{PO} wave numbers as R becomes more electronegative (ref. 25, p. 827).

A comparison of the UV-visible spectra of 9 with those of 1 (Table 8) shows that oxidation of the Ppy₃ ligand has only a small influence on the electronic environment at the metal centre, and imply that 9 also dissociates chloride in MeOH.

Acknowledgements

We thank the Natural Sciences and Engineering Research

Council of Canada for financial support (research grant for B.R.J. and postgraduate fellowship for R.P.S), and Johnson Matthey Ltd. and Colonial Metals Inc. for loans of RuCl₃3H₂O.

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