Isomerization of $RuCl_2(Cyttp)$ ($Cyttp = C_6H_5P(CH_2CH_2CH_2P(C_6H_{11})_2)_2$) in solution

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Abstract

The structure of $RuCl_2(Cyttp)$ ($Cyttp = C_6H_5P(CH_2CH_2CH_2P(C_6H_{11})_2)_2$) in solution is very dependent on the polarity and coordination ability of the solvents. In non-polar solvents such as benzene, *mer*-$RuCl_2(Cyttp)$ and *fac*-$RuCl_2(Cyttp)$ are present in about equal quantity. In halogenated solvents (such as dichloromethane, chloroform, $CDCl_2CDCl_2$), three isomers are present: *fac*-$RuCl_2(Cyttp)$ (predominant), $[Ru_2Cl_3(Cyttp)_2]Cl$ (minor) and *mer*-$RuCl_2(Cyttp)$ (trace). In other polar solvents such as CD_3COOD and CD_3NO_2 the ionic dinuclear complex $[Ru_2Cl_3(Cyttp)_2]Cl$ is the major species along with *fac*-$RuCl_2(Cyttp)$. In methanol, only $[Ru_2Cl_3(Cyttp)_2]Cl$ is present. Acetonitrile complexes are formed when $RuCl_2(Cyttp)$ is treated with acetonitrile. The X-ray structure of *fac*-$RuCl_2(Cyttp)$ has been determined in space group $P2_1/n$ with cell parameters $a = 11.912(4)$, $b = 11.953(2)$, $c = 31.303(8)$ Å, $\beta = 94.32(2)°$, $V = 4444$ Å^3, $Z = 4$, $R = 0.042$ and $R_w = 0.050$ for the 4985 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 439 variables.

Introduction

The green complex *mer*-$RuCl_2(Cyttp)$ is a valuable starting material for ruthenium hydride and organometallic compounds containing Cyttp [1]. It has been reported to be prepared by the substitution reaction of $RuCl_2(PPh_3)_3$ with Cyttp and purified by column chromatography [2]. We have reinvestigated this reaction and found that other compounds are also produced. Further studies have shown that these new compounds are in fact the isomers of $RuCl_2(Cyttp)$ and the distribution of these isomers changes depending on the solvent. We herein report these interesting observations and the structures of the isomers.

Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk techniques unless stated otherwise. Solvents were all reagent grade and were distilled under argon from appropriate drying agents prior to use. Solutions were transferred by use of syringes that were flushed with argon before use. Minute traces of oxygen and water were removed from commercially available argon by passing the gas through two columns packed with hot (180 °C) BASF active copper catalyst and Drierite, respectively.

Reagent-grade chemicals were used as purchased from Aldrich Chemical Company Inc. unless stated otherwise. Ruthenium trichloride hydrate was loaned from Johnson Matthey Inc. $RuCl_2(PPh_3)_3$ [3] and $RuCl_2(DMSO)_4$ [4] were prepared as described in the literature. Cyttp [5] and *mer*-$RuCl_2(Cyttp)$ [2] were prepared by modified literature methods.

A Bruker AM-250 spectrometer was used to obtain proton (250.13 MHz) and ^{13}C NMR spectra in 5 mm tubes. Residual solvent proton or ^{13}C resonances were used as internal standards for the ^1H or ^{13}C NMR spectra. Phosphorus NMR spectra were collected on Bruker AM-250 (101.25 MHz) and Bruker AM-500 (202.46 MHz) spectrometers. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. The ^{31}P NMR data for $RuCl_2(Cyttp)$ and related compounds are listed in Table 1. Conductivity data were obtained on approximately 10^{-3} M solutions with a Lab-Line unbreakable-type conductivity cell Cat. No. 11200.

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TABLE 1. ^{31}P NMR data for $RuCl_2$(Cyttp) and related compounds[a]

Compound	δP_1	δP_2	δP_3	$J(P_1P_2)$	$J(P_1P_3)$	$J(P_2P_3)$	Solvent
mer-$RuCl_2$(Cyttp)	78.2(t)	14.7(d)		38.6			C_6D_6
fac-$RuCl_2$(Cyttp)	38.3(t)	60.8(br)	26.7(br)	50.3	50.3		CD_2Cl_2
	42.5(dd)	59.6(dd)	29.4(dd)	62.0	40.5	27.5	CD_2Cl_2[b]
	34.9(t)	45.2(br)		46.8			$CDCl_2CDCl_2$[c]
mer-$RuCl_2$(MeCN)(Cyttp)	27.8(t)	3.5(d)		34.8			CD_2Cl_2
fac-[RuCl(MeCN)$_2$(Cyttp)]Cl	20.7(t)	26.9(br)	19.4(br)	[d]	[d]	[d]	CD_3CN
	20.6	27.0	19.2	41	36	25	CD_3CN[e]
$[Ru_2Cl_3$(Cyttp)$_2]Cl$[f]	36.8(dd)	26.7(dd)	17.5(dd)	50.4	27.1	43.1	CD_2Cl_2
	35.9(dd)	27.2(dd)	19.1(dd)	48.5	26.3	44.3	
	35.1(dd)	27.9(dd)	19.2(dd)	48.9	27.1	42.8	

[a]Chemical shifts are in ppm with respect to external 85% H_3PO_4 (δ 0.0); positive values are downfield; coupling constants are in Hz. P_1 is the central phosphorus atom of the triphosphine; P_2 and P_3 are the two terminal phosphorus atoms of the triphosphine unless otherwise stated. br = broad, d = doublet, t = triplet. Spectra were obtained at room temperature unless otherwise stated. [b]At 230 K. [c]At 383 K. [d]Not assigned. [e]At 273 K. [f]Chemical shifts are not assigned to specific nuclei.

An Industrial Instruments Inc. conductivity bridge (model RC16B2) was used to determine the solution resistance at 1000 Hz. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

mer-$RuCl_2$(Cyttp), green isomer

A mixture of 3.61 g of Cyttp (6.08 mmol) and 5.50 g of $RuCl_2(PPh_3)_3$ (5.73 mmol) in *c.* 40 ml of acetone was stirred at room temperature for 30 min to give a bright green solid. The solid was then collected on a filter frit, washed with acetone and dried under vacuum overnight. Yield: 3.55 g, 81.6%. *Anal.* Calc. for $C_{36}H_{61}Cl_2P_3Ru$: C, 56.98; H, 8.10; Cl, 9.34; P, 12.25. Found: C, 56.73; H, 8.24; Cl, 9.24; P, 12.07%.

fac-$RuCl_2$(Cyttp), purple isomer

A mixture of 0.50 g of $RuCl_2(DMSO)_4$ (1.0 mmol) and 3.8 ml of 0.30 M Cyttp benzene solution (1.1 mmol) in 25 ml of acetone was refluxed for 45 min to give a purple solid. After the solution was cooled down to room temperature, the solid was collected by filtration, washed with acetone and dried under vacuum overnight. Yield: 0.52 g, 67%. *Anal.* Calc. for $C_{36}H_{61}Cl_2P_3Ru$: C, 56.98; H, 8.10; Cl, 9.34; P, 12.25. Found: C, 57.13; H, 8.28; Cl, 9.41; P, 12.12%.

$[Ru_2Cl_3$(Cyttp)$_2]Cl$

Method 1, from mer-$RuCl_2$(Cyttp)

A suspension of 0.20 g of *mer*-$RuCl_2$(Cyttp) (0.26 mmol) in 30 ml of MeOH was refluxed for several hours to give a reddish yellow solution. The volume of the reaction mixture was reduced to *c.* 8 ml, and the resulting solution was set in a freezer for two days to give yellow microcrystals. The solid was then collected on a filter frit, washed with small amount of ether and dried under vacuum overnight. Yield: 0.08 g, 40%. (The compound is soluble in MeOH, most of the compound is therefore left in solution.)

Method 2, from fac-$RuCl_2$(Cyttp)

The compound $[Ru_2Cl_3$(Cyttp)$_2]Cl$ is formed upon dissolution of the purple *fac*-$RuCl_2$(Cyttp) in MeOH (shaking for a few minutes).

$[Ru_2Cl_3$(Cyttp)$_2]BPh_4$

0.20 g of purple *fac*-$RuCl_2$(Cyttp) (0.26 mmol) was dissolved in 10 ml of MeOH to give a yellow solution. Then 0.10 g of $NaBPh_4$ (0.29 mmol) was added to the solution to give a light yellow solid. After stirring for 15 min the solid was collected on a filter frit, washed with H_2O and MeOH and dried under vacuum overnight. Yield: 0.22 g, 94%. *Anal.* Calc. for $C_{96}H_{142}BCl_3P_9Ru_2$: C, 64.01; H, 7.95; Cl, 5.91. Found: C, 63.83; H, 7.91; Cl, 6.03%.

mer-$RuCl_2$(MeCN)(Cyttp)

0.15 g of green compound *mer*-$RuCl_2$(Cyttp) (0.20 mmol) in 10 ml of MeCN was stirred at room temperature for 1 h to give a clear yellow solution. The liquids of the reaction mixture were then removed completely, and 10 ml of hexane was added to wash the greenish yellow residue. The greenish yellow solid was collected on a filter frit, washed with hexane and dried under vacuum. Yield: 0.13 g, 82%. *Anal.* Calc. for $C_{38}H_{64}Cl_2NP_3Ru$: C, 57.06; H, 8.07; Cl, 8.86; N, 1.75. Found: C, 57.03; H, 8.32; Cl, 8.60: N, 1.64%.

Reactions of fac-$RuCl_2$(Cyttp) with acetonitrile

(a) Dissolution of purple *fac*-$RuCl_2$(Cyttp) in CD_3CN in a NMR tube produced a colorless solution.

^{31}P NMR spectra were then collected on the solution (see 'Results').

(b) 0.15 g of purple compound *fac*-$RuCl_2$(Cyttp) (0.20 mmol) was dissolved in 10 ml of MeCN upon shaking to give a colorless solution. The ^{31}P NMR spectrum for the solution is identical to the one prepared by dissolving purple *fac*-$RuCl_2$(Cyttp) in CD_3CN. The liquid of the reaction mixture was then removed completely under vacuum to give a red residue. A ^{31}P NMR spectrum for the residue in CH_2Cl_2 was collected, which indicates that all the acetonitrile complex has converted into $RuCl_2$(Cyttp).

Interactions of $RuCl_2$(Cyttp) with other solvents

^{31}P NMR spectra of the solutions prepared by dissolving the purple solid *fac*-$RuCl_2$(Cyttp) in benzene, dichloromethane, $CDCl_2CDCl_2$, CD_3COOD, CD_3NO_2 and DMSO-d_6 were recorded.

Crystallographic analysis of fac-$RuCl_2$(Cyttp)·2DMSO

The X-ray quality crystals were obtained by slowly evaporating solvents from a saturated solution of $RuCl_2$(Cyttp) in CH_2Cl_2/DMSO. Crystals of this compound are purple–brown in color and fairly clear. The crystal used for data collection was covered with a thin layer of epoxy as a precaution against decomposition in air. The crystal system is monoclinic with systematic absences $0k0$, $k=2n+1$ and $h0l$, $h+l=2n+1$, which uniquely determine the space group as $P2_1/n$. The cell constants $a=11.912(4)$, $b=11.953(2)$, $c=31.303(8)$ Å and $\beta=94.32(2)°$ were determined at room temperature on a Rigaku AFC5 diffractometer by a least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 23 to 28° with Mo Kα radiation.

Data was measured by the ω scan method. Six standard reflections were measured after every 150 reflections and indicated that the crystal was stable during data collection. The data were corrected for Lorentz and polarization effects; no correction for absorption was made. All calculations were done with the TEXSAN package [6] of crystallographic programs.

The position of the ruthenium atom was located on a Patterson map. This atom was then used as a phasing model in the DIRDIF procedure [7] and most of the remainder of the ruthenium complex was located on the electron density map. Missing atoms were found using standard Fourier methods. There are two solvent molecules of DMSO per asymmetric unit incorporated into the lattice. One of these DMSO molecules is disordered and a model was developed which assigned alternate sites for the sulfur and oxygen atoms. Hence the occupancy factors for S(2) and O(2) were determined to be 0.75 and those for the alternate sites, S(3) and O(3), were then set at 0.25 each. This disordered molecule was kept at the isotropic level for all the least-squares refinements.

After a cycle of anisotropic refinement of the ruthenium complex, the hydrogen atoms were included in the model as fixed contributions in their calculated positions with C–H = 0.98 Å. No hydrogen atoms were added to the methyl carbon atoms of the DMSO molecules. The final refinement cycle gave agreement indices of $R=0.042$ and $R_w=0.050$ for the 4985 intensities with $F_o^2>3\sigma(F_o^2)$ and the 439 variables (anisotropic non-hydrogen atoms of the ruthenium complex and one DMSO molecule, the disordered DMSO molecule, isotropic and all hydrogen atoms fixed). The maximum and minimum peak height in the final difference electron density map are 0.60 and -0.74 e/Å^3. Scattering factors for neutral atoms were used and are from the usual sources: the non-hydrogen atoms and anomalous dispersion terms from ref. 8a, for the hydrogen atoms from ref. 8b. Further crystallographic details are given in Table 2. Final atomic coordinates and se-

TABLE 2. Crystallographic details for *fac*-$RuCl_2$(Cyttp)·2DMSO

Formula	$C_{40}H_{73}Cl_2O_2P_3S_2Ru$
Formula weight	915.03
Space group	$P2_1/n$
a (Å)	11.912(4)
b (Å)	11.953(2)
c (Å)	31.303(8)
β (°)	94.32(2)
V (Å^3)	4444
Z	4
D_{calc} (g/cm^3)	1.37
Crystal size (mm)	0.12×0.26×0.38
Radiation	Mo Kα with graphite monochromator
Linear absorption coefficient (cm^{-1})	6.96
Temperature	ambient
Scan type	ω
2θ limits (°)	$4\leqslant 2\theta\leqslant 50$
Scan speed	8°/min in ω with a total of 8 scans/ref.
Scan range	$(1.05+0.35\tan\theta)°$ in ω
Data collection	$+h$, $+k$, $\pm l$
No. unique data	8289
No. unique data with $F_o^2>3\sigma(F_o^2)$	4985
Final no. variables	439
$R(F)$[a]	0.042
$R_w(F)$[b]	0.050
Goodness of fit	1.43

[a] $R(F)=\Sigma\|\|F_o\|-|F_c\|\|/\Sigma|F_o|$. [b] $R_w(F)=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w=1/\sigma^2(F_o)$.

lected bond lengths and bond angles are presented in Tables 3 and 4, respectively.

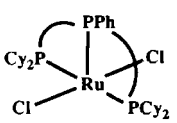
Results

Preparation and structures of monomeric $RuCl_2(Cyttp)$

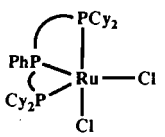
Treatment of $RuCl_2(PPh_3)_3$ in toluene or benzene with Cyttp produced a mixture of the green isomer *mer*-$RuCl_2$(Cyttp) and the purple isomer *fac*-$RuCl_2$(Cyttp). The purple isomer is slightly soluble in acetone and thus could be removed by washing the crude solid with acetone to give a bright green solid. The yield of the green solid prepared this way is very dependent on the reaction time, a longer reaction time would result in lower yield. In fact, the most convenient method for preparation of the green compound is to treat $RuCl_2(PPh_3)_3$ with Cyttp in acetone at room temperature. The reaction is completed in less than 30 min and only the green compound precipitates out. A small amount of purple compound was also formed in the reaction but usually remained in the filtrate.

Treatment of $RuCl_2(DMSO)_4$ with Cyttp in refluxing acetone, however, gave a purple solid which consists of predominantly the purple isomer *fac*-$RuCl_2$(Cyttp). This is in contrast with the substitution reactions of $RuCl_2(DMSO)_4$ with other chelating tridentate ligands; for example, $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ was isolated when triphos ($MeC(CH_2PPh_2)_3$) was used [9]; $RuCl_2(etp)(DMSO)_2$ was the product when etp ($PhP(CH_2CH_2PPh_2)_2$) was used [10]; the reaction of L ($L=PhCH_2N(CH_2CH_2PPh_2)_2$) with $RuCl_2(DMSO)_4$ produced $[RuCl(DMSO)_2(L)]Cl$ [11].

The spectroscopic data for the green isomer suggest that it is a meridional square-pyramidal complex with the central phosphorus atom occupying the apical position as shown below. In its ^{13}C NMR spectrum in benzene, the resonances for the cyclohexyl ipso carbon atoms appear as virtual triplets at 38.0 (t, $J(PC)=9.4$Hz) and 34.7 (t, $J(PC)=9.9$ Hz) ppm; thus the triphosphine must be meridional around ruthenium so that the terminal phosphorus atoms are *trans* to each other [12]. Consistent with this arrangement, its ^{31}P NMR spectrum in benzene shows a doublet at 14.7 ppm for the terminal PCy_2 groups and a triplet at 78.2 ppm ($J(PP)=38.6$ Hz) for the central phosphorus atom. Thus, the central phosphorus atom is significantly deshielded compared with the terminal ones. Such a ^{31}P NMR pattern has been observed for several similar meridional



green isomer



purple isomer

TABLE 3. Final positional parameters and B_{eq} values for the non-hydrogen atoms of $RuCl_2$(Cyttp)·2DMSO[a]

Atom	x	y	z	B_{eq}
Ru	0.32667(3)	0.02728(3)	0.12379(1)	2.22(2)
CL1	0.3275(1)	−0.1023(1)	0.06295(4)	3.68(6)
CL2	0.2608(2)	−0.1344(1)	0.16025(5)	6.1(1)
S1	0.0415(2)	0.0843(2)	0.43781(7)	5.7(1)
S2	0.4614(3)	0.0993(3)	0.4536(1)	6.95(7)
S3	0.4856(7)	0.0657(7)	0.4268(2)	5.1(1)
P1	0.2932(1)	0.1278(1)	0.18443(4)	2.47(5)
P2	0.2548(1)	0.1599(1)	0.08072(4)	2.63(6)
P3	0.4995(1)	0.0881(1)	0.10763(4)	2.66(6)
O1	0.0185(5)	−0.0379(4)	0.4377(2)	8.0(3)
O2	0.4088(8)	0.0132(8)	0.4289(3)	8.7(2)
O3	0.395(1)	0.013(1)	0.4602(5)	4.0(3)
C1	0.2892(5)	0.2811(4)	0.1794(2)	3.1(2)
C2	0.2178(5)	0.3271(4)	0.1418(2)	3.3(2)
C3	0.2630(4)	0.3053(4)	0.0983(2)	3.0(2)
C4	0.3088(5)	0.1702(5)	0.0277(2)	3.4(3)
C5	0.4357(5)	0.1917(5)	0.0287(2)	3.5(3)
C6	0.5085(5)	0.1005(5)	0.0497(2)	3.3(2)
C7	0.3963(4)	0.1035(5)	0.2317(2)	2.9(2)
C8	0.4222(5)	0.2038(5)	0.2616(2)	3.8(3)
C9	0.5206(6)	0.1766(6)	0.2941(2)	4.9(3)
C10	0.5010(5)	0.0699(6)	0.3183(2)	4.9(3)
C11	0.4745(5)	−0.0274(6)	0.2885(2)	4.4(3)
C12	0.3743(5)	−0.0014(5)	0.2573(2)	3.5(3)
C13	0.1565(4)	0.0918(5)	0.2060(2)	3.1(2)
C14	0.0563(5)	0.0849(6)	0.1729(2)	4.3(3)
C15	−0.0467(5)	0.0363(7)	0.1926(2)	5.5(4)
C16	−0.0770(6)	0.0992(7)	0.2311(3)	5.9(4)
C17	0.0226(6)	0.1088(7)	0.2636(2)	5.5(4)
C18	0.1235(5)	0.1597(6)	0.2439(2)	4.3(3)
C19	0.1041(4)	0.1381(5)	0.0655(2)	3.1(2)
C20	0.0319(5)	0.2266(6)	0.0560(2)	4.9(3)
C21	−0.0813(6)	0.2076(7)	0.0424(3)	5.7(4)
C22	−0.1199(5)	0.1009(7)	0.0392(2)	4.9(3)
C23	−0.0517(5)	0.0127(6)	0.0495(2)	5.3(4)
C24	0.0605(5)	0.0315(5)	0.0627(2)	4.2(3)
C25	0.5693(4)	0.2216(5)	0.1265(2)	3.3(2)
C26	0.6720(5)	0.2560(6)	0.1024(2)	4.8(3)
C27	0.7176(6)	0.3698(7)	0.1176(3)	6.5(4)
C28	0.7452(6)	0.3744(6)	0.1652(3)	6.0(4)
C29	0.6467(7)	0.3393(7)	0.1884(2)	6.3(4)
C30	0.6041(6)	0.2250(6)	0.1737(2)	4.8(3)
C31	0.6076(4)	−0.0213(5)	0.1242(2)	3.4(2)
C32	0.5865(5)	−0.0752(5)	0.1662(2)	4.6(3)
C33	0.6768(6)	−0.1608(6)	0.1803(2)	5.1(3)
C34	0.6892(2)	−0.2464(6)	0.1462(3)	6.1(4)
C35	0.7145(7)	−0.1931(7)	0.1050(3)	6.7(4)
C36	0.6250(6)	−0.1079(6)	0.0903(2)	5.5(4)
C37	0.1223(7)	0.1082(6)	0.3940(2)	6.4(4)
C38	0.1465(7)	0.1084(6)	0.4788(2)	6.1(4)
C39	0.6113(8)	0.0835(8)	0.4524(3)	8.2(2)
C40	0.4429(8)	0.2222(8)	0.4224(3)	7.6(2)

[a] $B_{eq}=(8/3)\pi^2\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

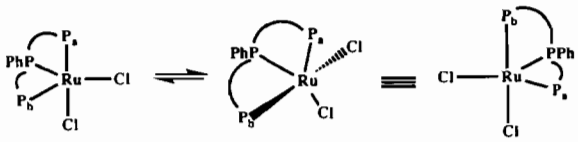
TABLE 4. Selected bond lengths and angles for *fac*-$RuCl_2(Cyttp)\cdot 2DMSO$[a]

Bond lengths (Å)			
Ru–P(1)	2.306(1)	Ru–P(2)	2.212(2)
Ru–P(3)	2.276(2)	Ru–Cl(1)	2.455(1)
Ru–Cl(2)	2.406(2)		
Bond angles (°)			
P(1)–Ru–P(2)	92.60(5)	P(1)–Ru–P(3)	103.41(5)
P(1)–Ru–Cl(1)	167.97(5)	P(1)–Ru–Cl(2)	86.86(6)
P(2)–Ru–P(3)	87.18(6)	P(2)–Ru–Cl(1)	90.19(5)
P(2)–Ru–Cl(2)	137.73(7)	P(3)–Ru–Cl(1)	88.40(5)
P(3)–Ru–Cl(2)	134.90(7)	Cl(1)–Ru–Cl(2)	83.22(6)

[a]e.s.d.s in the least significant figure are given in parentheses.

square pyramidal complexes with an apical phosphine, such as $RuCl_2(PR_3)_3$ ($PR_3 = PPh_3$, $PEtPh_2$) [13], $RuCl_2(PPh_3)(L_2)$ (L_2 = dppb, dppp) [14] and $Ru_2Cl_4(diop)_3$ [15]. For example, the resonance for the apical PPh_3 appeared at 75.0 ppm and the basal PPh_3 at 23.3 ppm in $RuCl_2(PPh_3)_3$ [13] and the apical PPh_2 at 72.9 ppm and the basal PPh_3 and PPh_2 at 19.6 and 34.3 ppm, respectively, in $RuCl_2(PPh_3)(dppp)$ [14]. Interestingly some of these complexes, for example $Ru_2Cl_4(diop)_3$ [15] and $RuCl_2(PEtPh_2)_3$ [13], are also green.

The purple isomer is fluxional in solution and adopts a TBP structure with one chloride and one of the terminal phosphorus atom occupying the axial positions (see above). This has been confirmed by X-ray diffraction and is consistent with the ^{31}P NMR parameters in solution. In the room temperature ^{31}P NMR spectrum in CD_2Cl_2 a triplet at 38.3 ppm ($J(PP) = 50.3$ Hz) and two broad signals at 60.8 and 26.7 ppm were observed for the purple isomer *fac*-$RuCl_2(Cyttp)$. When the temperature is lowered below 260 K, three doublet of doublets signals were observed for the purple isomer. Thus the triphosphine must be facial around ruthenium. The variable temperature ^{31}P NMR spectra for $RuCl_2(Cyttp)$ in the temperature range 303–403 K were collected in $CDCl_2CDCl_2$ solution. The spectra show that as the temperature is increased above 333 K, the two broad signals observed at room temperature at *c.* 24 and *c.* 67 ppm disappeared, and a new broad signal at *c.* 45 ppm appeared when the temperature is above 373 K. The triplet at 34.8 ppm remains unchanged in the temperature range 303–403 K. This implies that the fluxionality is caused by the chemical exchange process involving the two terminal PCy_2 groups. The most likely mechanism for the chemical exchange process is shown in the eqn. below, which involves Bailar rotations. Thus P_a and P_b are inequivalent at low temperature since one is in an apical position, while the other is in an equatorial



position. However, an average of the ^{31}P chemical shift for the PCy_2 groups is observed at high temperature owing to the fast exchange process.

Description of the structure of fac-$RuCl_2(Cyttp)\cdot 2DMSO$

The molecular structure of fac-$RuCl_2(Cyttp)$ is shown in Fig. 1. The overall geometry around ruthenium is approximately trigonal bipyramidal. The triphosphine occupies the facial positions. The Ru–P and Ru–Cl bond lengths are normal compared with literature values [16]. It is interesting to note the Ru–Cl(1) bond (*trans* to P(1), 2.455(1) Å) is significantly longer than the bond Ru–Cl(2) (2.406(2) Å), presumably due to the *trans* influence of P(1). This is the first X-ray diffraction characterized compound containing a facial Cyttp ligand.

Interaction of $RuCl_2(Cyttp)$ with solvents

The solution structures of $RuCl_2(Cyttp)$ are very dependent on solvents as indicated by its solution ^{31}P NMR spectra. The ^{31}P NMR spectra *in* C_6D_6 and CD_2Cl_2 are shown in Figs. 2 and 3, respectively.

An equilibrium was attained between the green isomer *mer*-$RuCl_2(Cyttp)$ and the purple isomer *fac*-$RuCl_2(Cyttp)$ in benzene solution. When the green

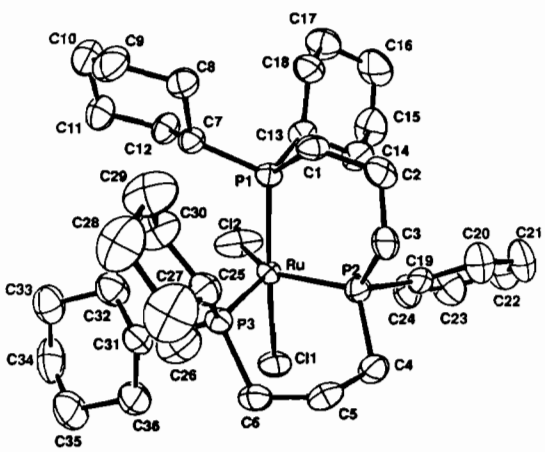


Fig. 1. The molecular structure of *fac*-$RuCl_2(Cyttp)\cdot 2DMSO$. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids have been drawn at the 50% probability level.

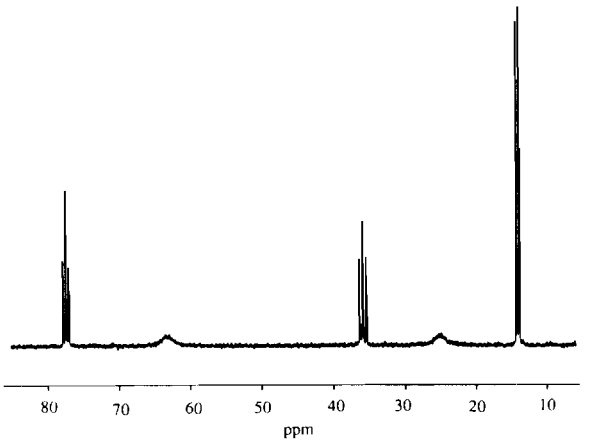


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(Cyttp)$ in benzene at 101.25 MHz.

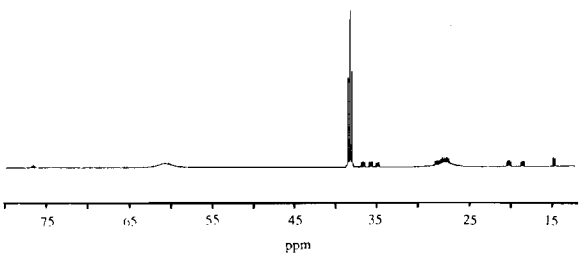


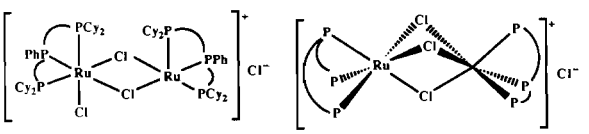
Fig. 3. $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2(Cyttp)$ in dichloromethane at 202.46 MHz.

solid isolated from acetone was dissolved in benzene, the initial solution consisted of predominantly the green isomer and a trace amount of the purple isomer. After *c.* 24 h at room temperature, the benzene solution consisted of almost equal amounts of the green isomer and the purple isomer. When the purple solid isolated from the reaction of $RuCl_2(DMSO)_4$ with Cyttp was dissolved in benzene, the initial solution consisted predominantly of the purple isomer and a trace amount of the green isomer. After several hours, the composition of the solution was the same as the one prepared from the green isomer after storage at room temperature for a day.

The dichloride complex $RuCl_2(Cyttp)$ ionizes in MeOH. The purple solid dissolves in MeOH upon shaking for a few min at room temperature to give a yellow solution. At room temperature, the green solid is insoluble in MeOH, but dissolves in refluxing MeOH to give a yellow solution. The ^{31}P NMR spectra of the yellow solutions obtained from the green and purple solids are identical and in fact are very complicated. The ^{31}P NMR data suggest that there are three sets of phosphorus atoms with about equal intensity, and each set consists of three different phosphorus atoms, which might imply that the MeOH solution of $RuCl_2(Cyttp)$ contains three slightly different ruthenium centers with facial Cyttp.

Other experiments suggest that the species in MeOH can be best described as $[Ru_2Cl_3(Cyttp)_2]Cl$. Treatment of the yellow solution of '$RuCl_2(Cyttp)$' with excess or one equivalent of $NaBPh_4$ yielded $[Ru_2Cl_3(Cyttp)_2]BPh_4$, which has been confirmed by elemental analyses. The compound $[Ru_2Cl_3(Cyttp)_2]BPh_4$ displays an almost identical ^{31}P NMR spectrum in dichloromethane to that of the yellow methanol solution of '$RuCl_2(Cyttp)$'. In addition, the FAB mass spectrum of $RuCl_2(Cyttp)$ in MeOH shows parent ion peaks around 1481, as required for $[Ru_2Cl_3(Cyttp)_2]^+$. The molar conductance was measured to be 71.4 ohm^{-1} cm^2 mol^{-1} for the solution prepared by dissolving 0.0379 g of purple solid $RuCl_2(Cyttp)$ in 25.0 ml of MeOH (1.00×10^{-3} M assuming $[Ru_2Cl_3(Cyttp)_2]Cl$). This value is close to that observed for a 1:1 electrolyte in MeOH (general range 80–115 ohm^{-1} cm^2 mol^{-1}) [17].

In view of the complexity of the ^{31}P NMR spectrum of $[Ru_2Cl_3(Cyttp)_2]X$ (X = Cl, BPh_4), it is possible that there are several isomers present in solution. However, attempts to separate possible isomers failed. Thus, the true structures for $[Ru_2Cl_3(Cyttp)_2]Cl$ are not clear. To fit the ^{31}P NMR data, the following



A B

two dimers **A** and **B** are proposed as the possible species in solution which would give 9 different phosphorus resonances with about equal intensity if one assumes that the ratio of **A** to **B** is *c.* 2 to 1. The structure **A** has six chemically inequivalent phosphorus atoms and **B** has three. Dichloro- and trichloro-bridged ruthenium phosphine complexes are well known [18]. However there are many other possible structures. Thus X-ray diffraction is necessary to clarify the structures. Unfortunately attempts to obtain X-ray quality crystals of the species present in the MeOH solution of '$RuCl_2(Cyttp)$' failed.

The isolated purple solid, presumably *fac*-$RuCl_2(Cyttp)$, or the yellow solid, $[Ru_2Cl_3(Cyttp)_2]Cl$, dissolves in dichloromethane to give a deep red–brown solution. The solution contains predominantly *fac*-$RuCl_2(Cyttp)$, a small amount of $[Ru_2Cl_3(Cyttp)_2]Cl$ and a trace amount of *mer*-$RuCl_2(Cyttp)$, as indicated by its ^{31}P NMR spectrum (see Fig. 3). A similar solution was also obtained by dissolving the green solid (presumably *mer*-$RuCl_2(Cyttp)$) in dichloromethane and setting the

resulting solution at room temperature for *c.* 4 h, although initially the solution contains predominantly the green isomer *mer*-$RuCl_2$(Cyttp). The compositions of $RuCl_2$(Cyttp) in chloroform and $CDCl_2CDCl_2$ are similar to that in dichloromethane at room temperature except that the percentages of $[Ru_2Cl_3(Cyttp)_2]Cl$ are slightly higher in chloroform and $CDCl_2CDCl_2$.

In other polar solvents such as CD_3COOD and CD_3NO_2 at room temperature, the solutions consist predominantly of $[Ru_2Cl_3(Cyttp)_2]Cl$ along with the minor component *fac*-$RuCl_2$(Cyttp). The dichloride complex $RuCl_2$(Cyttp) is barely soluble in acetone and DMSO. In the solutions of the above two solvents, the major species is *fac*-$RuCl_2$(Cyttp).

The structures of $RuCl_2$(Cyttp) in solution are also dependent on temperature. For example, at room temperature (303 K) the $CDCl_2CDCl_2$ solution of $RuCl_2$(Cyttp) consists predominantly of *fac*-$RuCl_2$(Cyttp) and a small amount of $[Ru_2Cl_3(Cyttp)_2]Cl$; while at 403 K, the solution consists of *c.* 60% of *fac*-$RuCl_2$(Cyttp) and 40% of *mer*-$RuCl_2$(Cyttp). The process is reversible.

The dichloride complex $RuCl_2$(Cyttp) reacts with acetonitrile to form acetonitrile complexes. At room temperature, the green isomer reacted with CH_3CN to form *mer*-$RuCl_2$(MeCN)(Cyttp). A medium intensity band at 2260 cm^{-1} was observed for the $\nu(C{\equiv}N)$ frequency. In the ^{31}P NMR spectrum, the resonances for the central and two terminal phosphorus atoms were observed at 27.8 (t, $J(PP) = 34.8$ Hz) and 3.5 (d) ppm, respectively, implying that the triphosphine is meridional around ruthenium. The two chlorides are probably *trans* to each other as in *trans-mer*-$RuCl_2$(CO)(Cyttp) prepared by treatment of the green isomer *mer*-$RuCl_2$(Cyttp) with CO [2].

Dissolution of the purple isomer *fac*-$RuCl_2$(Cyttp) in CD_3CN produced a colorless solution, presumably due to the formation of the complex *fac*-[RuCl(MeCN)$_2$(Cyttp)]Cl as indicated by the ^{31}P NMR spectrum of the colorless solution. Consistent with the facial arrangement of the triphosphine Cyttp, the room temperature (303 K) ^{31}P NMR spectrum of *fac*-[RuCl(MeCN)$_2$(Cyttp)]Cl displayed a pseudo triplet at 20.7 ppm ($J(PP) = 38$ Hz) for the central PPh group and two broad peaks at 19.4 and 26.9 ppm for the two terminal PCy_2 groups. The broad nature of the signals for the two terminal PCy_2 groups at 303 K is probably caused by the chemical exchange process involving the two terminal PCy_2 groups. Thus, as the temperature is lowered below 283 K, the fluxional process is slowed down and three pseudo triplets were observed for the complex *fac*-[RuCl(MeCN)$_2$(Cyttp)]Cl, for example at 27.0, 20.6 and 19.2 ppm at 273 K. The molar conductance was measured to be 128 ohm^{-1} cm^2 mol^{-1} for the 1.00×10^{-3} M solution (prepared by dissolving 0.0190 g of purple solid $RuCl_2$(Cyttp) in 25.0 ml of MeCN). The value indicates that a monomeric 1:1 electrolytic compound was formed. For comparison, such values were reported to range from 120 to 160 ohm^{-1} cm^2 mol^{-1} for 10^{-3} M 1:1 electrolytes in MeCN [17]. An attempt to isolate the species failed, because the compound is unstable under vacuum (0.1 torr) losing MeCN to give $RuCl_2$(Cyttp). It is likely that the compounds such as *fac*-[RuCl(MeCN)$_2$(Cyttp)]X (X = PF_6, BPh_4) could be isolated, but we have not performed the experiment yet.

Discussion

The structure of $RuCl_2$(Cyttp) in solution is very dependent on the polarity and coordination ability of the solvents. In non-polar solvents such as benzene, *mer*-$RuCl_2$(Cyttp) and *fac*-$RuCl_2$(Cyttp) are present in about equal quantity. In halogenated solvents (such as dichloromethane, chloroform or $CDCl_2CDCl_2$), three isomers are present: *fac*-$RuCl_2$(Cyttp) (predominant), $[Ru_2Cl_3(Cyttp)_2]Cl$ (minor) and *mer*-$RuCl_2$(Cyttp) (trace). In other polar solvents such as CD_3COOD and CD_3NO_2, $[Ru_2Cl_3(Cyttp)_2]Cl$ is the major species along with *fac*-$RuCl_2$(Cyttp). In methanol, only $[Ru_2Cl_3(Cyttp)_2]Cl$ is present. Acetonitrile complexes are formed when $RuCl_2$(Cyttp) is treated with acetonitrile.

The green compound *mer*-$RuCl_2$(Cyttp) is the kinetic product for the reaction of $RuCl_2(PPh_3)_3$ with Cyttp in benzene or acetone, and is present in significant amount when reaching equilibrium in non-polar solvents such as benzene. The partial isomerization of the green isomer into the purple isomer in benzene is responsible for the varying yields for the green isomer in its preparation from the substitution reaction in benzene. The isomerization from the meridional complex to the facial complex is probably due to the *trans* influence of the terminal PCy_2 groups. The strong *trans* influence PCy_2 group prefers to be *trans* to a weak *trans* influence ligand (chloride). The facial geometry is electronically preferred for the triphosphine. Steric interaction, on the other hand, would favor a meridional arrangement of the triphosphine ligand around ruthenium. Thus a mixture of meridional and facial isomers is observed in benzene owing to the balance of electronic and steric factors. Isomerization of *trans*-$RuCl_2(dppm)_2$ into *cis*-$RuCl_2(dppm)_2$ to minimize *trans* phosphine interaction has been reported previously [19].

It is interesting to note that *fac*-$RuCl_2$(Cyttp) ionizes much more readily than *mer*-$RuCl_2$(Cyttp)

in MeOH. This is probably caused by the *trans* effect of the phosphorus ligand to labilize the *trans* chloride [20]. Formation of $[Ru_2Cl_3(Cyttp)_2]Cl$ by dissolving $RuCl_2(Cyttp)$ in polar solvents such as MeOH and $MeNO_2$ is not surprising since many haloruthenium(II) phosphine complexes of the formula $[Ru_2Cl_3(P)_6]Cl$ (P = monophosphines) could be synthesized by treatment of $RuCl_3 \cdot xH_2O$ with excess phosphines in refluxing alcohols [21], or by substitution reaction of $RuCl_2(PPh_3)_4$ or $RuCl_2(PPh_3)_3$ with phosphines in ethanol or dichloromethane [13].

The triphosphine complex $RuCl_2(Cyttp)$ displays slightly different solution behavior compared with its monophosphine or diphosphine analogs such as $RuCl_2(L)_3$ ($L = PPh_3$ [13, 22], $PEtPh_2$ [13]) and $RuCl_2(PPh_3)(dppb)$ [14]. For example, the square pyramidal complexes *mer*-$RuCl_2(L)_3$ ($L = PPh_3$ [13, 22], $PEtPh_2$ [13]) and *mer*-$RuCl_2(PPh_3)(dppb)$ [14] are fluxional at room temperature, whereas there is no evidence that *mer*-$RuCl_2(Cyttp)$ is. The slowing of intramolecular chemical exchange is caused by the presence of the chelating triphosphine. However, *fac*-$RuCl_2(Cyttp)$ is fluxional in solution at room temperature. The monophosphine complex $RuCl_2(PPh_3)_3$ [13, 22] dissociates one PPh_3 to give dichloro-bridged dimers, whereas the presence of the chelating triphosphine prevents this from occurring. In addition, no facial isomers were observed in the solutions of $RuCl_2(L)_3$ ($L = PPh_3$ [13, 22], $PEtPh_2$ [13]) or $RuCl_2(PPh_3)_2(dppb)$ [14].

Supplementary material

Tables (SUP-1-7) of complete bond distances (2 pages) and angles (3 pages), calculated positional parameters and *B* values for hydrogen atoms (1 page), torsion or conformation angles (4 pages), anisotropic thermal parameters for the non-hydrogen atoms (1 page), final thermal parameters for solvent atoms (1 page), and observed and calculated structure factors (34 pages) for *fac*-$RuCl_2(Cyttp) \cdot 2DMSO$ are available from the authors upon request.

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