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Synthesis and Characterization of Ruthenium Acetate Complexes Containing Triphosphines

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A series of ruthenium(II) acetate complexes were synthesized and characterized by $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR and IR spectroscopy. Treatment of $RuCl_2$(Cyttp) (Cyttp = $PhP(CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2)_2$) with 1 equiv of AgO_2CMe at room temperature gives *mer*-$RuCl(O_2CMe)$(Cyttp) and with excess NaO_2CMe in refluxing methanol produces *fac*-$RuCl(O_2CMe)$(Cyttp). *fac*-$RuCl(O_2CMe)$(ttp) (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$) was isolated when $(RuCl_2(ttp))_x$ was treated either with 1 equiv of AgO_2CMe at room temperature or with excess NaO_2CMe in refluxing methanol. Reaction of $(RuCl_2(ttp))_x$ with excess AgO_2CMe at room temperature gives *fac*-$Ru(O_2CMe)_2$(ttp). The structure of *fac*-$RuCl(O_2CMe)$(Cyttp) was determined by X-ray diffraction. *fac*-$RuCl(O_2CMe)$(Cyttp)·CH_3OH crystallized in the space group $P2_1/c$ with cell parameters a = 17.534 (6) Å, b = 10.371 (4) Å, c = 22.983 (8) Å, β = 92.35 (3)°, V = 4175.7 (20) Å^3, and Z = 4 and with $R(F)$ = 0.038 and $R_w(F)$ = 0.040.

Introduction

Carboxylato platinum-metal complexes have attracted much attention due to the variety of their structures and extensive chemistry.[2] Ruthenium acetate complexes also display various catalytic properties.[3-11] A large number of ruthenium carboxylate complexes have been synthesized, and most of the known mononuclear acetate complexes are PPh_3 complexes.[12] The chelating triphosphine ligands $PhP(CH_2CH_2CH_2PR_2)_2$ (R = Ph, ttp; R = Cy, Cyttp) offer several advantages over monodentate phosphines containing similar phosphino groups, such as more control of the coordination number and stereochemistry of the resulting complexes, increased basicity at the metal centers, and slower intra- and intermolecular exchange processes.[13,14] Several platinum-metal complexes of ttp and Cyttp are catalytically active in the hydrogenation of olefins.[13] It is likely that ruthenium carboxylate complexes of ttp and Cyttp might also display some interesting structural, chemical, and catalytic properties, as do their monophosphine analogues. We herein report the synthesis and characterization of a series ruthenium acetate complexes containing Cyttp and ttp.

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenk techniques, unless stated otherwise. Solvents were all reagent grade and were distilled over argon from appropriate drying agents prior to use. Solutions were transferred by use of syringes that were flushed with argon before use.

Reagent grade chemicals were used as purchased from Aldrich Chemical Co., Inc., unless stated otherwise. Sodium acetate was purchased from Mallinckrodt Inc. Ruthenium trichloride hydrate was loaned from Johnson Matthey Inc. $RuCl_2(PPh_3)_3$[15] and $RuCl_2$(Cyttp)[16] were prepared as described in the literature. Cyttp[17] and $(RuCl_2(ttp))_x$[18] were prepared by modified literature methods.

Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrometer from 4000 to 200 cm^{-1}, as pressed KBr pellets. Spectra were calibrated against the sharp 1601-cm^{-1} peak of polystyrene film. A Bruker AM-250 spectrometer was used to obtain proton (250.13 MHz), phosphorus-31 (101.25 MHz), and carbon-13 (62.9 MHz) NMR spectra in 5-mm tubes. Residual solvent proton or carbon-13 resonances were used as internal standards for the ^1H and ^{13}C NMR spectra. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. $^{31}P\{^1H\}$ NMR and selected ^1H NMR data are collected in Table I, and selected $^{13}C\{^1H\}$ NMR data are presented in Table II. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Az.

$(RuCl_2(ttp))_x$. A mixture of 1.50 g of $RuCl_2(PPh_3)_3$ (1.56 mmol) and 11.8 mL of 0.145 M ttp/benzene solution (1.71 mmol) in 30 mL of acetone was refluxed for 45 min to give a yellow-reddish solid. After the reaction mixture was cooled to room temperature, the solid was collected on a filter frit, washed with acetone, and dried under vacuum overnight. Yield: 0.97 g, 86%.

fac-$RuCl(O_2CMe)$(ttp). Method 1 (from NaO_2CMe). A mixture of 0.20 g of $(RuCl_2(ttp))_x$ (0.27 mmol) and 0.30 g of NaO_2CMe·$3H_2O$ (2.2 mmol) in 30 mL of MeOH was refluxed for 1 h to give a light yellow solid. After the reaction mixture was cooled to room temperature, the solid was collected by filtration, washed with MeOH, H_2O, and MeOH, and dried under vacuum overnight. Yield: 0.18 g, 87%. IR (KBr): $\nu(O_2C)$ 1540 cm^{-1}. Anal. Calcd for $C_{38}H_{40}ClO_2P_3Ru$: C, 60.20; H, 5.32; Cl, 4.68. Found: C, 59.50; H, 5.38; Cl, 5.43.

Method 2 (from AgO_2CMe). To a suspension of 0.0227 g of AgO_2CMe (0.136 mmol) in 15 mL of MeOH were added 0.1000 g of $(RuCl_2(ttp))_x$ (0.1361 mmol) and 10 mL of benzene. The resulting mixture was stirred at room temperature for 3 h to give a light yellow solution and a gray precipitate. The solvents of the reaction mixture were removed completely, and the residue was extracted with 25 mL of CH_2Cl_2. The CH_2Cl_2 solution was separated from the solid by passing the mixture through a filter frit containing ca. 4 cm of Celite. The solvent of the filtration was removed completely, and 10 mL of MeOH was added to give a light yellow solid. The solid was collected by filtration, washed with MeOH, and dried under vacuum overnight. Yield: 0.07 g, 70%. The spectroscopic data for the product are identical to those for *fac*-$RuCl(O_2CMe)$(ttp) prepared by method 1.

fac-$RuCl(O_2CMe)$(Cyttp). A mixture of 0.20 g of $RuCl_2$(Cyttp) (0.26 mmol) and 0.30 g of NaO_2CMe·$3H_2O$ (2.2 mmol) in 30 mL of MeOH was refluxed for 1 h to give a yellow solution. The volume of the solution was reduced to ca. 10 mL, and the resulting mixture was set in a freezer for several days to give a yellow crystalline solid. The crystalline solid was collected by filtration, washed with MeOH, and dried under vacuum overnight. Yield: 0.10 g, 49% (the compound is soluble in MeOH). X-ray-quality crystals were obtained by slowly evaporating solvents from saturated solutions of *fac*-$RuCl(O_2CMe)$(Cyttp) or *mer*-

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Table I. $^{31}P\{^1H\}$ and Selected ^1H NMR Data for the Ruthenium Acetate Complexes[a]

compd	^{31}P NMR $\delta(P_1)$	$\delta(P_2)$	$\delta(P_3)$	$J(P_1P_2)$	$J(P_2P_3)$	$J(P_1P_2)$	^1H NMR δ(Me)
mer-RuCl(O_2CMe)(Cyttp)	45.7	10.5	10.5	38.8	38.8	0	1.75
fac-RuCl(O_2CMe)(Cyttp)	39.2	35.8	35.8	47.4	47.4	0	1.82
	39.7	36.9	34.6	45.0	50.5	25.5[b]	
fac-RuCl(O_2CMe)(ttp)	40.4	36.7	34.2	53.5	42.2	29.2	1.45
fac-Ru(O_2CMe)$_2$(ttp)	40.1	38.0	38.0	51.4	51.4	0	1.70
	40.5	38.8	36.2	53.5	42.9	31.6[c]	1.81, 1.62[d]

[a] Spectra were obtained at 303 K in dichloromethane solution except where indicated; ^{31}P 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; P_2 and P_3 are the two terminal phosphorus atoms in the triphosphine ligand. [b] At 240 K. [c] At 210 K. [d] δ(Ru–H) = −22.4 ppm (dt; J(PH) = 38.2, 20.8 Hz).

Table II. Selected ^{13}C NMR Data for the Ruthenium Acetate Complexes[a]

compd	$\delta(O_2C)$	δ(Me)	δ(P–CH)[b]
mer-RuCl(O_2CMe)(Cyttp)	183.5	24.2	37.3 t (8.9), 36.3 t (8.0)
fac-RuCl(O_2CMe)(Cyttp)[c]	185.8	25.4	43.5 d (18.0), 41.4 d (22.8) 39.6 d (16.9), 36.7 d (20.6)
fac-RuCl(O_2CMe)(ttp)	184.9	24.2	
fac-Ru(O_2CMe)$_2$(ttp)	182	25.3	

[a] The spectra were obtained in CD_2Cl_2 except where indicated. ^{13}C chemical shifts are in ppm with respect to Me_4Si (δ 0.0). [b] Signal of the ipso carbon atoms of the cyclohexyl groups attached to the terminal phosphorus atoms. d = doublet; t = triplet. The values in parentheses are coupling constants $|^1J(PC) + {}^3J(PC)|$ in Hz. [c] In C_6D_6.

RuCl(O_2CMe)(Cyttp) in CH_2Cl_2/MeOH with a stream of argon. IR (KBr): $\nu(O_2C)$ 1535 cm^{-1}. Anal. Calcd for $C_{38}H_{64}ClO_2P_3Ru$: C, 58.34; H, 8.25; Cl, 4.53. Found: C, 58.34; H, 8.30; Cl 4.69.

***mer*-RuCl(O_2CMe)(Cyttp).** A mixture of 0.0440 g of AgO_2CMe (0.263 mmol) and 0.2000 g of $RuCl_2$(Cyttp) (0.2634 mmol) in 10 mL of CH_2Cl_2 and 30 mL of MeOH was stirred at room temperature for 30 min to give a pink solution and a gray solid. The gray solid (AgCl) was removed by filtration through a filter frit containing ca. 4 cm of Celite. The solvents of the filtrate were removed completely, and ca. 10 mL of MeOH was added to give a light pink solid. The pink solid was collected by filtration, washed with MeOH, and dried under vacuum overnight. Yield: 0.17 g, 73%. IR (KBr): $\nu(O_2C)$ 1530 cm^{-1}. Anal. Calcd for $C_{38}H_{64}ClO_2P_3Ru$: C, 58.34; H, 8.25; Cl, 4.53. Found: C, 58.30; H, 8.08; Cl 4.47.

Ru(O_2CMe)$_2$(ttp). A mixture of 0.2000 g of $(RuCl_2(ttp))_x$ (0.2722 mmol) and 0.1000 g of AgO_2CMe (0.5988 mmol) in 20 mL of CH_2Cl_2 and 20 mL of MeOH was stirred at room temperature for 2 h. The gray precipitate (AgCl) was removed by filtration through a filter frit containing ca. 4 cm of Celite to give a yellow solution. The solvents of the filtrate were removed completely, and 20 mL of ether was added to the residue. The resulting mixture was set in a freezer for several days to give a yellow crystalline solid. The yellow crystalline solid was collected by filtration, washed with Et_2O, and dried under vacuum overnight. Yield: 0.12 g, 56% (the compound is slightly soluble in Et_2O and MeOH). IR (KBr): $\nu(O_2C)$ 1610, 1525 cm^{-1}. Anal. Calcd for $C_{40}H_{43}O_4P_3Ru$: C, 61.46; H, 5.54; Cl, 0. Found: C, 61.46; H, 5.32; Cl, 0.

RuH(O_2CMe)(Cyttp). A mixture of 0.20 g of $RuCl_2$(Cyttp) (0.26 mmol) and 0.30 g of $NaO_2CMe{\cdot}3H_2O$ (2.2 mmol) in 30 mL of MeOH was refluxed under hydrogen for 5 h to give a yellow solution. The reaction mixture was then cooled to room temperature, and the volume of the reaction mixture was reduced to 6 mL to give a yellow solid. The solid was collected on a filter frit, washed with MeOH, and dried under vacuum overnight. Yield: 0.15 g, 76%.

X-ray Data Collection for *fac*-RuCl(O_2CMe)(Cyttp)·CH_3OH. Crystal, data collection, and refinement parameters are collected in Table III. A yellow crystal was mounted on a glass fiber with epoxy cement. The unit cell parameters were obtained from the least-squares fit of 25 reflections ($20° \le 2\theta \le 25°$). Preliminary photographic characterization showed $2/m$ Laue symmetry and the systematic absences in the diffraction data ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) uniquely established the space group as $P2_1/c$. No absorption correction was applied (low μ, well-shaped crystal, $T_{max}/T_{min} = 1.022$).

Structure Solution and Refinement. The structure was solved by an interpreted Patterson map which located the Ru atom. The remaining non-hydrogen atoms were located through subsequent least-squares and difference Fourier cycles. All hydrogen atoms were included as idealized isotropic contributions (d(CH) = 0.960 Å; U = 1.2U(for attached C)), and phenyl rings were fixed as rigid planar hexagons (d(CC) = 1.345 Å). All non-hydrogen atoms were refined with anisotropic parameters. The unit cell also contains a molecule of CH_3OH.

Table III. Crystallographic Data for *fac*-RuCl(O_2CMe)(Cyttp)·CH_3OH

formula: $C_{38}H_{64}ClO_2P_3Ru{\cdot}CH_3OH$	space group: $P2_1/c$
fw = 814.38	λ = 0.71073 Å (Mo Kα)
a = 17.534 (6) Å	T = 296 K
b = 10.371 (4) Å	ρ_{calcd} = 1.295 g cm^{-3}
c = 22.983 (8) Å	μ = 5.73 cm^{-1}
β = 92.35 (3)°	$R(F)^a$ = 0.038
V = 4175.7 (26) Å^3	$R_w(F)^b$ = 0.040
Z = 4	

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

Final atomic coordinates and selected bond lengths and bond angles are presented in Tables IV and V, respectively. All computer programs and the sources of the scattering factors are contained in the SHELXTL (5.1) program library (G. Sheldrick, Nicolet Corp., Madison, WI).

Results

The preparation reactions of the ruthenium acetate complexes are summarized in Scheme I.

Treatment of $RuCl_2$(Cyttp) with excess sodium acetate in refluxing methanol for 1 h produces *fac*-RuCl(O_2CMe)(Cyttp). However, when $RuCl_2$(Cyttp) is treated with 1 equivalent of silver acetate in MeOH/CH_2Cl_2 at room temperature for ca. 30 min, *mer*-RuCl(O_2CMe)(Cyttp) is produced. In fact, the compound *mer*-RuCl(O_2CMe)(Cyttp) is the kinetic product for the latter reaction. Thus, *mer*-RuCl(O_2CMe)(Cyttp) in CH_2Cl_2/MeOH solution isomerizes completely into *fac*-RuCl(O_2CMe)(Cyttp) in several days. The presence of the polar solvent MeOH is necessary for the isomerization, since no isomerization occurred in pure benzene or dichloromethane. The facial isomer *fac*-RuCl(O_2CMe)(Cyttp) is thermodynamically more stable than the meridional isomer *mer*-RuCl(O_2CMe)(Cyttp), probably owing to the strong trans interaction of the two PCy_2 groups in the meridional isomer. Similar isomerization has been observed previously; for example, the kinetically favored complex *trans*-$RuCl_2$(dppm)$_2$ isomerizes into the thermodynamically more stable and electronically more favorable complex *cis*-$RuCl_2$(dppm)$_2$ on heating to minimize trans phosphine interactions.[19] Since isomerization occurs only in the presence of the polar solvent MeOH, it is likely that the intermediate is probably an ionic species such as [Ru(O_2CMe)(Cyttp)]Cl, formed by dissociation of chloride.

In both isomers of RuCl(O_2CMe)(Cyttp), the acetate ligand is bidentate, as inferred from their infrared spectra. The $\nu(OCO)_{asym}$ frequencies are observed at 1530 cm^{-1} for *mer*-RuCl(O_2CMe)(Cyttp) and 1535 cm^{-1} for *fac*-RuCl(O_2CMe)(Cyttp). For comparison, the $\nu(OCO)_{asym}$ frequencies for monodentate acetate groups are observed at 1613 and 1596 cm^{-1} in Ru(O_2CMe)$_2$(CO)$_2$(PPh_3)$_2$[20] and 1630 cm^{-1} in Ru(O_2CMe)$_2$(CO)(PPh_3)$_2$;[21] those for chelate acetate groups are observed at

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Table IV. Final Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for *fac*-RuCl(O_2CMe)(Cyttp)·CH_3OH

	x	y	z	U[a]
Ru	2171.2 (2)	369.1 (4)	1975.9 (1)	27.7 (1)
P(1)	1792.8 (6)	360 (1)	1005.7 (5)	30.8 (4)
P(2)	1020.3 (6)	−345 (1)	2229.7 (5)	32.5 (4)
P(3)	2749.7 (6)	−1627 (1)	2117.7 (5)	32.5 (4)
Cl	1660.6 (7)	2611 (1)	1977.5 (5)	46.1 (4)
O(1)	3289 (2)	1319 (3)	1888 (1)	41 (1)
O(2)	2819 (2)	1161 (3)	2750 (1)	43 (1)
C(1)	1843 (3)	−1000 (4)	475 (2)	32 (1)
C(2)	1500 (3)	−2269 (5)	670 (2)	47 (2)
C(3)	1685 (3)	−3360 (5)	247 (2)	58 (2)
C(4)	1411 (3)	−3054 (5)	−375 (2)	64 (2)
C(5)	1734 (3)	−1764 (5)	−560 (2)	59 (2)
C(6)	1549 (3)	−686 (5)	−141 (2)	49 (2)
C(7)	2417 (2)	1620 (4)	687 (2)	35 (2)
C(8)	3172 (3)	1078 (5)	491 (2)	45 (2)
C(9)	3738 (3)	2152 (5)	370 (3)	60 (2)
C(10)	3404 (3)	3097 (5)	−80 (3)	63 (2)
C(11)	2636 (3)	3609 (5)	103 (3)	58 (2)
C(12)	2066 (3)	2545 (5)	233 (2)	50 (2)
C(13)	812 (2)	951 (5)	869 (2)	39 (2)
C(14)	195 (2)	174 (5)	1156 (2)	44 (2)
C(15)	192 (2)	321 (5)	1818 (2)	42 (2)
C(16)	78 (3)	−434 (5)	3205 (2)	49 (2)
C(17)	−143 (3)	−76 (5)	3753 (2)	56 (2)
C(18)	276 (3)	806 (5)	4068 (2)	55 (2)
C(19)	921 (3)	1329 (6)	3847 (2)	55 (2)
C(20)	1152 (3)	965 (5)	3302 (2)	47 (2)
C(21)	737 (3)	65 (5)	2972 (2)	38 (2)
C(22)	816 (2)	−2072 (5)	2193 (2)	37 (2)
C(23)	1401 (3)	−2898 (5)	2519 (2)	46 (2)
C(24)	2147 (3)	−3063 (5)	2218 (2)	44 (2)
C(25)	3368 (2)	−1629 (5)	2799 (2)	41 (2)
C(26)	2908 (3)	−1436 (6)	3351 (2)	48 (2)
C(27)	3435 (3)	−1166 (7)	3876 (2)	69 (2)
C(28)	3998 (3)	−2266 (8)	3995 (3)	84 (3)
C(29)	4441 (3)	−2536 (8)	3451 (2)	78 (3)
C(30)	3908 (3)	−2789 (6)	2908 (2)	56 (2)
C(31)	3396 (2)	−2137 (5)	1522 (2)	39 (2)
C(32)	3544 (3)	−3590 (5)	1440 (2)	54 (2)
C(33)	3981 (3)	−3829 (6)	889 (3)	66 (2)
C(34)	4719 (3)	−3085 (7)	893 (3)	73 (3)
C(35)	4588 (3)	−1653 (6)	983 (3)	64 (2)
C(36)	4142 (3)	−1388 (5)	1527 (2)	48 (2)
C(37)	3319 (3)	1600 (5)	2421 (2)	45 (2)
C(38)	3944 (3)	2446 (8)	2662 (3)	90 (3)
So	7543 (6)	8820 (11)	1450 (4)	236 (6)
Sc	7714 (8)	9283 (7)	1918 (5)	254 (10)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Bond Lengths and Angles for *fac*-RuCl(O_2CMe)(Cyttp)·CH_3OH[a]

Bond Lengths (Å)					
Ru-P(1)	2.300 (1)	Ru-P(2)	2.249 (1)	Ru-P(3)	2.322 (1)
Ru-Cl	2.492 (1)	Ru-O(1)	2.210 (3)	Ru-O(2)	2.229 (3)
Ru-C(37)	2.561 (5)	O(1)-C(37)	1.257 (6)	O(2)-C(37)	1.267 (6)

Bond Angles (deg)			
P(1)-Ru-P(2)	91.4 (1)	P(1)-Ru-P(3)	103.9 (1)
P(1)-Ru-Cl	85.2 (1)	P(1)-Ru-O(1)	97.8 (1)
P(1)-Ru-O(2)	153.2 (1)	P(1)-Ru-C(37)	125.4 (1)
P(2)-Ru-P(3)	93.5 (1)	P(2)-Ru-Cl	88.9 (1)
P(2)-Ru-O(1)	168.2 (1)	P(2)-Ru-O(2)	110.3 (1)
P(2)-Ru-C(37)	139.4 (1)	P(3)-Ru-Cl	170.6 (1)
P(3)-Ru-O(1)	91.5 (1)	P(3)-Ru-O(2)	90.6 (1)
Cl-Ru-O(1)	84.5 (1)	Cl-Ru-O(2)	80.0 (1)
Cl-Ru-C(37)	79.1 (1)	O(1)-Ru-O(2)	58.9 (1)
O(1)-Ru-C(37)	29.4 (1)	O(2)-Ru-C(37)	29.7 (1)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

1526 cm^{-1} in $RuH(O_2CMe)(PPh_3)_3$ and 1528 cm^{-1} in $RuH(O_2CMe)(CO)(PPh_3)_2$.[21]

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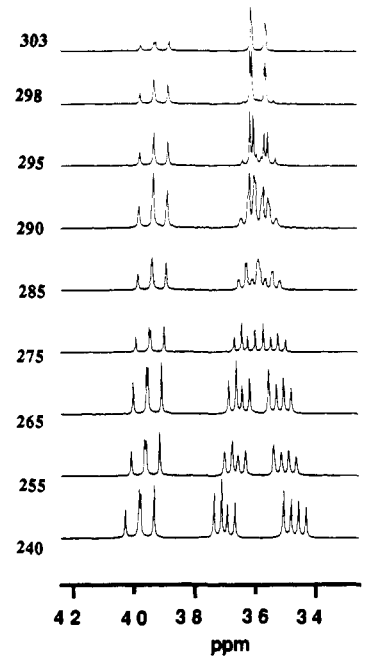
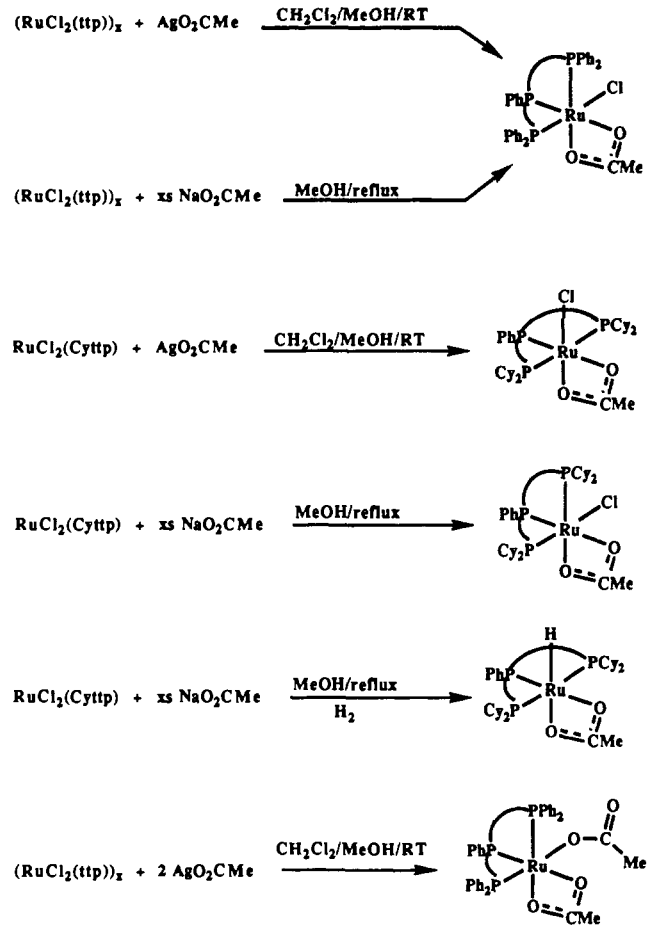


Figure 1. Variable-temperature (240–303 K) $^{31}P\{^1H\}$ NMR spectra of *fac*-RuCl(O_2CMe)(Cyttp) in CD_2Cl_2 at 101.25 MHz.

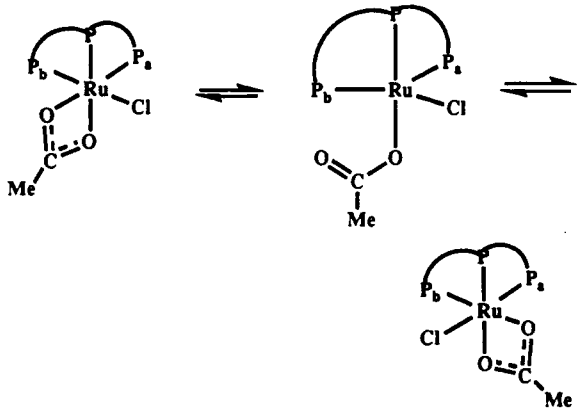
Scheme I. Preparation Reactions for the Ruthenium Acetate Complexes



The ^{31}P NMR spectrum of *fac*-RuCl(O_2CMe)(Cyttp) in benzene at room temperature shows three doublet of doublet resonances, indicating that the triphosphine Cyttp is facially bonded to ruthenium and the compound is stereochemically rigid on the NMR time scale at room temperature. Interestingly, the compound is fluxional at room temperature in dichloromethane,

as indicated by its ^{31}P NMR spectrum (Figure 1), which exhibits an AB_2 pattern with an apparent doublet at 35.8 ppm for the two terminal PCy_2 groups and an apparent triplet at 39.2 ppm (J(PP) = 47.4 Hz) for the central PPh group. As the temperature is lowered, the fluxionality slows and three doublet of doublet phosphorus resonances are observed. In the ^{31}P NMR spectrum of *fac*-$RuCl(O_2CMe)$(Cyttp) at 240 K in CD_2Cl_2, the resonance at 39.7 ppm is assigned to the unique central phosphorus atom of the triphosphine, since it corresponds to the triplet at room temperature. The resonances at 36.9 and 34.6 ppm are assigned to the PCy_2 group trans to the chloride and the one trans to the acetate ligand, respectively, by comparison with the trans influence of chloride and acetate ligands on phosphorus chemical shifts. For comparison, the resonance for the phosphine trans to X in Pt(X)(Me)(dppe) is observed at 42.0 ppm when X = Cl and 34.0 ppm when X = O_2CMe.[22] Similarly, the resonance for the central phosphorus atom trans to X in $[Pt(X)(ttp)]AsF_6$ is observed at −20.8 ppm when X = Cl and −29.8 ppm when X = O_2CMe.[23] The ^{31}P NMR parameters in benzene were assigned similarly. Although the ^{31}P NMR spectrum in CD_2Cl_2 changes with temperature, the ^1H NMR spectrum does not change significantly with temperature.

The line shapes of the variable-temperature ^{31}P NMR spectra suggest that the fluxionality is caused by the chemical-exchange process involving the two terminal PCy_2 groups as shown in eq 1. A similar mechanism has been proposed for rapid intramolecular exchange of mono- and bidentate carboxylate ligands.[21,24-26] Thus, three different phosphorus signals are observed at low temperature when the exchange rate is slow, while an average chemical shift for the two terminal PCy_2 groups is observed due to fast exchange at room temperature.

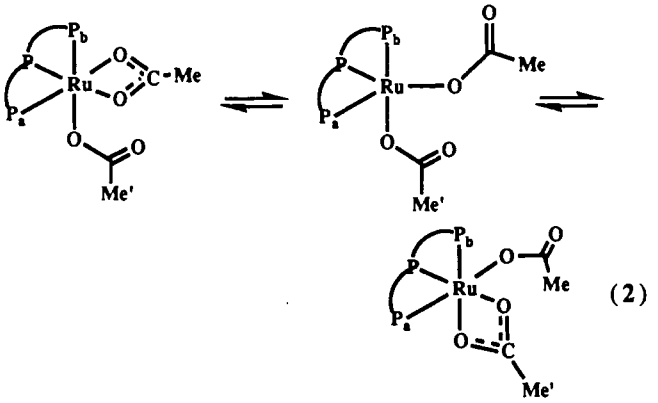


(1)

In contrast to case of *fac*-$RuCl(O_2CMe)$(Cyttp), no evidence of fluxionality is observed for the yellow isomers *mer*-$RuCl(O_2CMe)$(Cyttp) in both dichloromethane and benzene at room temperature. This observation is parallel to that for the two isomers of *fac*- and *mer*-$RuCl_2$(Cyttp).[16]

It has been reported that treatment of $(RuCl_2(ttp))_x$ with excess sodium acetate in boiling THF produced *mer*-$RuCl(O_2CMe)$(ttp).[18] When the reaction is carried out in refluxing methanol, however, *fac*-$RuCl(O_2CMe)$(ttp) is isolated. The compound *fac*-$RuCl(O_2CMe)$(ttp) could also be prepared by treatment of $(RuCl_2(ttp))_x$ with 1 equiv of silver acetate in CH_2Cl_2/MeOH. This is in contrast to the reaction of $RuCl_2$(Cyttp) with 1 equiv of silver acetate, which produces *mer*-$RuCl(O_2CMe)$(Cyttp). The acetate group is also a chelate ligand in *fac*-$RuCl(O_2CMe)$(ttp), as indicated by the presence of an infrared band at 1540 cm^{-1}, characteristic of $\nu(OCO)_{asym}$ for chelate acetate ligands. The chemical shifts for the acetate group in the ^{13}C NMR spectrum are also comparable with those for $RuCl(O_2CMe)$(Cyttp). However, in the proton NMR spectrum, the chemical shift for the methyl protons (1.45 ppm) in *fac*-$RuCl(O_2CMe)$(ttp) is significantly smaller than that in *fac*-$RuCl(O_2CMe)$(Cyttp) (1.75 ppm). The difference is probably caused by the "ring current" effect of the phenyl rings on the terminal phosphorus atoms of ttp. Such a chemical shift difference has been observed in *fac*-$Ru(\eta^4\text{-}CH_2{=}CHCOMe)$(triphos) ($\delta$(Me) = 1.50 ppm, triphos = ttp; δ(Me) = 2.04 ppm, triphos = Cyttp).[27] The ^{31}P NMR spectrum of *fac*-$RuCl(O_2CMe)$(ttp) in CD_2Cl_2 or benzene shows three doublet of doublet resonances at room temperature, indicating that the triphosphine is facial around ruthenium and that the compound is rigid at room temperature, which is in contrast to the fluxional behavior of *fac*-$RuCl(O_2CMe)$(Cyttp) in dichloromethane.

Treatment of $(RuCl_2(ttp))_x$ with either 2 equiv or an excess of silver acetate yielded *fac*-$Ru(O_2CMe)_2$(ttp), which contains a monodentate and a chelate acetate ligand. In the infrared spectrum, the $\nu(OCO)_{asym}$ frequencies for monodentate and chelate acetate ligands were observed at 1610 and 1525 cm^{-1}, respectively. The compound is fluxional in both benzene and dichloromethane. Thus, in its ^1H NMR spectra in benzene or dichloromethane at room temperature, only one singlet at 1.70 ppm assignable to the O_2CMe protons was observed, indicating a rapid interchange between the monodentate and chelate acetate groups. The singlet at 1.70 ppm, assignable to O_2CMe, observed at room temperature in CD_2Cl_2 is separated into two peaks at ca. 1.8 and 1.6 ppm when the temperature is lowered below 240 K. The variable-temperature ^{31}P NMR spectra in CD_2Cl_2 are similar to those of *fac*-$RuCl(O_2CMe)$(Cyttp). The fluxionality is also reflected in its ^{13}C NMR spectrum in CD_2Cl_2 at room temperature, which shows a broad signal at ca. 182.0 ppm assignable to the carbonyl carbon atoms and a signal at 25.3 ppm assignable to the methyl carbon atoms of the acetate ligands. The stereochemistry of *fac*-$Ru(O_2CMe)_2$(ttp) at low temperature is similar to those of $Ru(O_2CR)_2(CO)(PPh_3)_2$ (R = CF_3,[24,26] Me[26]), $Ru(O_2CCF_3)_2(PF_3)(PPh_3)_2$,[25] and $Ru(O_2CCF_3)_2(PF_2NMe_2)_2(PPh_3)$.[25] These monophosphine ruthenium diacetate complexes are also fluxional at room temperature. The mechanisms for interchange of the PCy_2 groups and of the mono- and bidentate acetate ligands, shown in eq 2, are similar to those proposed for the diacetate ruthenium complexes of monophosphines.[24-26]



(2)

Prolonged refluxing of a mixture of $RuCl_2$(Cyttp) and sodium acetate in MeOH under a hydrogen atmosphere produces RuH(O_2CMe)(Cyttp). We have previously reported that the compound is also produced from the reaction of RuH_4(Cyttp) with vinyl acetate.[27]

Description of the Structure of *fac*-$RuCl(O_2CMe)$(Cyttp)·CH_3OH. The molecular structure of *fac*-$RuCl(O_2CMe)$(Cyttp) is shown in Figure 2. The ruthenium center has a distorted octahedral geometry with the triphosphine occupying facial positions and a chelate acetate group. The distortion from the octahedral structure arises from the small angle subtended by the

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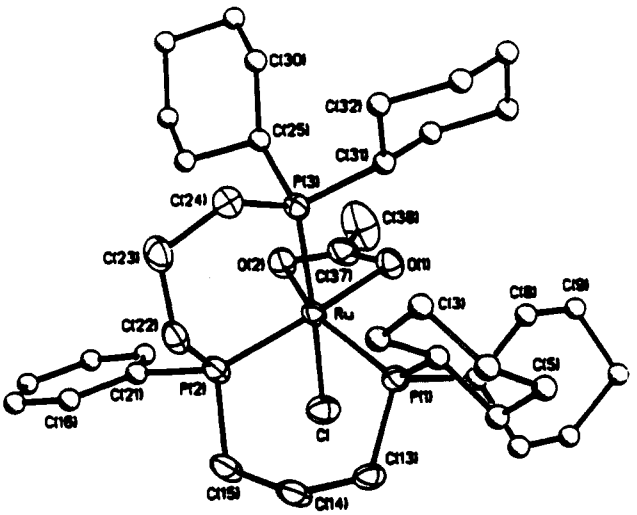

Figure 2. Molecular structure of *fac*-$RuCl(O_2CMe)(Cyttp)\cdot CH_3OH$. The solvent molecule and hydrogen atoms have been removed and the carbon atoms of the phenyl and cyclohexyl rings drawn as spheres with arbitrary radii for clarity. The thermal ellipsoids are drawn at the 40% probability level.

chelate acetate (58.9 (1)°). Such a small bite angle for the acetate ligand is normal and quite similar to those found in related ruthenium acetate complexes such as $RuH(O_2CMe)(PPh_3)_3$,[28] $Ru(O_2CMe)(p\text{-}MeC_6H_4NCH)(CO)(PPh_3)_2$,[29a] $[Ru(O_2CMe)(dppm)_2]BPh_4$,[29b] $[Ru(O_2CMe)(PMe_2Ph)_4]PF_6$,[29c] and $RuCl(O_2CMe)(CO)(PPh_3)_2$.[30] The acetate is coordinated in a symmetrical manner, as in analogous ruthenium complexes.[29b,c,30] The Ru–O bond distances (2.210 (3), 2.229 (3) Å) are in the range for reported values (e.g., 2.152 (6) and 2.144 (6) Å in $RuCl(O_2CMe)(CO)(PPh_3)_2$[30] and 2.173 (8) and 2.279 (8) Å in $Ru(O_2CMe)(p\text{-}MeC_6H_4NCH)(CO)(PPh_3)_2$[29a]). The Ru–P bond distances are very similar to those found in *fac*-$RuCl_2(Cyttp)$[16] and are in the range for the literature values.[31]

Discussion

It is interesting to note that *fac*-$RuCl(O_2CMe)(Cyttp)$ is more stable than *mer*-$RuCl(O_2CMe)(Cyttp)$, which gradually isomerizes into *fac*-$RuCl(O_2CMe)(Cyttp)$ in methanol, whereas *mer*-$RuH(O_2CMe)(Cyttp)$ is the only product of the reaction of $RuCl_2(Cyttp)$ with excess acetate in refluxing methanol under a hydrogen atmosphere. It appears that meridional complexes of Cyttp are usually favored due to steric interaction. Facial complexes could be more stable when there is a possibility that all the phosphorus atoms could be trans to weak trans-influence ligands to eliminate the trans phosphine interaction. The facial compound is more fluxional than the corresponding meridional isomer. For example, *fac*-$RuCl(O_2CMe)(Cyttp)$ and *fac*-$RuCl_2(Cyttp)$[16] are fluxional in dichloromethane at room temperature, whereas there is no evidence indicating that *mer*-$RuCl(O_2CMe)(Cyttp)$ and *mer*-$RuCl_2(Cyttp)$[16] are fluxional under similar conditions. The fluxionality is also dependent on solvents; for example, *fac*-$RuCl(O_2CMe)(Cyttp)$ is fluxional in dichloromethane but is rigid in benzene at room temperature. Complexes containing more than one carboxylate group are more fluxional than those with only one carboxylate group, as illustrated by the fluxional behavior of $Ru(O_2CMe)_2(ttp)$ and rigid behavior of $RuCl(O_2CMe)(ttp)$ in dichloromethane at room temperature.

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Supplementary Material Available: Tables of crystallographic details and complete bond distances, bond angles, anisotropic thermal parameters, and coordinates and U values for hydrogen atoms (6 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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A Fluxional Binuclear Nickel(I) Complex and Evidence for Reversible A-Frame Formation

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The synthesis, structure, and fluxionality of the unusual dinickel(I) complex $[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ (**1a**), dppm = $Ph_2PCH_2PPh_2$, are described. Complex **1a** is formed by reaction of nickel(0) with nickel(II), in particular by reaction of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ with $[NiCl_2(dppm)_2]$ or of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $NiCl_2\cdot 6H_2O$. The crystal structure of **1a**·CH_2Cl_2 was determined by X-ray crystallography. [Space group $P2_1/n$, a = 13.890 (1) Å, b = 18.011 (1) Å, c = 19.614 (1) Å, β = 99.809 (4)°, Z = 4. The structure is based on 6722 reflections with $I \geq 3\sigma(I)$ and $4° \leq 2\theta(\text{Mo K}\alpha) \leq 54°$; 614 variables were refined to convergence at R = 0.038 and R_w = 0.051.] The molecular structure of **1a** contains a Ni–Ni bond of 2.617 (1) Å, a semibridging carbonyl and a trans,cis arrangement of the dppm ligands. The stereochemistries of the two nickel centers are therefore different, one being roughly square planar and the other roughly trigonal bipyramidal. However, in solution, the NMR spectra suggest a more symmetrical "A-frame" structure, and the data are rationalized in terms of a very easy fluxionality involving exchange of carbonyl between the nickel centers. Theoretical studies lend support to this hypothesis.

Introduction

The structures of certain d^9–d^9 dimers of the nickel group may exist in two structural forms as typefied by **1**, **3**, and **2**, **4**, respectively, in which LL is the binucleating ligand dppm ($Ph_2PCH_2PPh_2$) or dpam ($Ph_2AsCH_2AsPh_2$).

In the complexes **2** and **4** and several related "A-frame" complexes, there is no metal–metal bonding and each metal atom has square planar stereochemistry.[2] However, in **1**, **3**, and related

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