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Preparation and Structural Characterization of a Pentacoordinate Ru(II) Complex, $RuCl_2(Ph_2PCH_2SiMe_3)_3$

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Abstract

The compound $RuCl_2(Ph_2PCH_2SiMe_3)_3$ was obtained from the reaction of ruthenium trichloride with diphenyl(trimethylsilylmethyl)phosphine. It crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with the following cell dimensions: $a = 18.289(2)$, $b = 10.517(2)$, $c = 26.410(7)$ Å, $\beta = 93.56(3)°$, $V = 5070(4)$ Å^3 and $Z = 4$. The molecular structure was determined by a single crystal X-ray study. The complex has a square pyramidal geometry with two *trans* phosphines and two *trans* chloride atoms in the base of the pyramid and a phosphine at the apex.

Introduction

Five-coordination complexes of ruthenium are still relatively rare [1]. The square pyramidal *versus* octahedral geometry around the Ru(II) center is preferred with bulky phosphines, such as triphenylphosphine, as ligands. The structure of $RuCl_2(Ph_3P)_3$ was reported many years ago [2]. The ruthenium atom is surrounded by two *trans* chlorides, two *trans* phosphorus and an apical phosphorus atom in a square pyramidal geometry. This arrangement minimizes steric repulsions of the bulky phosphine ligands. Bressan and Rigo [3] reported two cationic species $RuX(PP)_2^+$ (where X = Cl, Br and PP is $Ph_2P(CH_2)_2PPh_2$) as their PF_6^- salts. On the basis of the spectroscopic evidence these were formulated as having a square pyramidal arrangement of ligands, but no direct structural evidence was presented.

In the present study we have examined and structurally characterized a new five-coordinate ruthenium(II) complex possessing square pyramidal geometry.

Experimental

Materials

Ruthenium trichloride, hydrate was purchased from Aldrich Chemical Company. Diphenyl(trimethylsilylmethyl)phosphine, $Ph_2PCH_2SiMe_3$ was prepared by a modification of a literature procedure [4], a brief description of which is given below.

Synthesis of $Ph_2PCH_2SiMe_3$

Lithium diphenylphosphide was prepared from $(C_6H_5)_2PCl$ and Li wire in THF. When $(C_6H_5)_2PLi$ was formed, as indicated by a deep red color and the disappearance of the lithium wire, a solution of $(CH_3)_3SiCH_2Cl$ in THF was added dropwise with stirring and cooling (−10 °C). THF was then evaporated and the residue fractionally distilled. The purity of the phosphine was checked by ^{1}H NMR.

Preparation of $RuCl_2(Ph_2PCH_2SiMe_3)_3$

Ruthenium trichloride, $RuCl_3 \cdot 3H_2O$, 0.5 g (2 mmol) was dissolved in 15 ml of MeOH and excess phosphine (2.0 g) was added. The reaction mixture was boiled for 5 min, cooled and left for slow evaporation. A crop of green crystals was formed. They were filtered, washed with cold methanol, ether and finally dried. The yield was 0.7 g (37%). UV (dichloromethane solution); $\lambda_{max} = 722$ nm ($\epsilon = 1000$ M^{-1} cm^{-1}), $\lambda_{max} = 375$ nm ($\epsilon = 2300$ M^{-1} cm^{-1}). IR, nujol mull, ν(Ru–Cl) = 320 cm^{-1}. The color of the solution changes upon standing, which might indicate fluctional behavior as observed for $RuCl_2(Ph_3P)_3$ [5]. The electronic and infrared spectra were recorded with Cary 17D and Perkin-Elmer 785 spectrophotometers, respectively.

X-ray Crystallographic Procedures

A single crystal, obtained as described in the 'Experimental' was mounted on a tip of a glass fibre. Axial lengths and Laue symmetry were confirmed by axial photographs. Accurate cell dimensions were obtained by a least-squares fit of 25 carefully centered reflections in the range $20 < 2\theta < 30°$. Intensity data was collected on a CAD-4 autodiffractometer equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Lorentz and polarization factors were included, but no absorption correction was applied. The calculations were done on a depart-

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TABLE I. Crystal Data for $RuCl_2(Ph_2PCH_2SiMe_3)_3$

Formula	$RuCl_2P_3Si_3C_{48}H_{63}$
Formula weight	989.19
Space group	$P2_1/c$
Systematic absences	$0k0$: $k \neq 2n$; $h0l$: $l \neq 2n$;
a (Å)	18.289(2)
b (Å)	10.517(2)
c (Å)	26.410(7)
α (°)	90.0
β (°)	93.56(3)
γ (°)	90.0
V (Å^3)	5070(4)
Z	4
D_{calc} (g/cm^3)	1.296
Crystal size (mm)	0.15 × 0.1 × 0.5
μ(Mo Kα) (cm^{-1})	6.021
Data collection instrument	CAD-4
Radiation (monochromated in incident beam	Mo Kα (λ_α = 0.71073 Å)
Orientation reflections, number, range (2θ)	25, $20° < 2\theta < 30°$
Temperature (°C)	24
Scan method	ω
Data collection range, 2θ (°)	4, 45°
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6617, 4027
No. parameters refined	514
R[a]	0.0527
R_w[b]	0.0726
Quality-of-fit indicator[c]	1.82
Largest shift/e.s.d., final cycle	0.62
Largest peak (e/Å^3)	0.50

[a] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$

mental VAX-780 computer with a SDP package software. Monitoring of three intense reflections showed no decay in intensity during the data collection. The position of the ruthenium atom was found from the direct methods, MULTAN; positions of the remaining non-hydrogen atoms were found by alternating least-squares cycles and difference Fourier maps. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included. In the final cycle 4027 data with $F_o^2 > 3\sigma(F_o^2)$ were used to refine 514 parameters to give $R = 0.0527$ and $R_w = 0.0726$. Final difference Fourier map was featureless with a largest peak of 0.6 e/Å^3. Relevant crystallographic data are summarized in Table I. Positional parameters and isotropic-equivalent displacement parameters are given in Table II.

TABLE II. Positional Parameters and Isotropic-equivalent Displacement Parameters for $RuCl_2(Ph_2PCH_2SiMe_3)_3$[a]

Atom	x	y	z	B (Å^2)
Ru	0.74145(4)	0.24398(7)	0.37654(3)	2.88(1)
Cl(1)	0.6521(1)	0.3971(2)	0.34642(9)	3.73(5)
Cl(2)	0.8211(1)	0.0647(2)	0.3878(1)	4.35(6)
P(1)	0.6454(1)	0.1074(2)	0.39977(9)	3.13(5)
P(2)	0.7571(1)	0.3441(2)	0.44999(9)	3.06(5)
P(3)	0.8317(1)	0.3473(3)	0.33220(9)	3.43(5)
Si(1)	0.5017(2)	0.1622(3)	0.3227(1)	4.22(7)
Si(2)	0.6543(1)	0.5010(3)	0.5302(1)	3.86(6)
Si(3)	0.8591(2)	0.5714(3)	0.2494(1)	4.79(7)
C(1)	0.5501(5)	0.163(1)	0.3889(3)	3.8(2)
C(2)	0.5573(6)	0.180(1)	0.2657(4)	5.9(3)
C(3)	0.4368(7)	0.301(1)	0.3262(5)	8.8(4)
C(4)	0.4511(6)	0.009(1)	0.3124(4)	5.7(3)
C(5)	0.6695(5)	0.3818(9)	0.4766(3)	3.7(2)
C(6)	0.7387(5)	0.580(1)	0.5600(4)	4.9(3)
C(7)	0.5917(6)	0.630(1)	0.5019(5)	6.5(3)
C(8)	0.6075(6)	0.411(1)	0.5798(4)	5.7(3)
C(9)	0.8131(5)	0.5070(9)	0.3064(4)	4.4(2)
C(10)	0.8977(8)	0.736(1)	0.2684(5)	8.4(4)
C(11)	0.7884(7)	0.589(1)	0.1967(5)	7.7(4)
C(12)	0.9352(6)	0.471(1)	0.2253(4)	6.1(3)
C(20)	0.6499(5)	0.0513(8)	0.4659(3)	3.3(2)
C(21)	0.7105(5)	−0.0186(9)	0.4829(3)	4.3(2)
C(22)	0.7182(6)	−0.060(1)	0.5332(4)	5.4(3)
C(23)	0.6641(5)	−0.033(1)	0.5668(4)	5.4(3)
C(24)	0.6047(6)	0.037(1)	0.5509(4)	5.8(3)
C(25)	0.5953(5)	0.079(1)	0.4992(4)	4.7(2)
C(30)	0.6444(5)	−0.0446(9)	0.3657(3)	3.6(2)
C(31)	0.6796(5)	−0.058(1)	0.3218(3)	4.1(2)
C(32)	0.6769(6)	−0.173(1)	0.2947(4)	5.4(3)
C(33)	0.6376(6)	−0.274(1)	0.3123(4)	5.5(3)
C(34)	0.6000(6)	−0.2640(9)	0.3557(4)	5.4(3)
C(35)	0.6036(5)	−0.149(1)	0.3833(4)	4.5(2)
C(40)	0.8125(5)	0.2610(9)	0.5002(3)	3.8(2)
C(41)	0.8798(5)	0.216(1)	0.4888(4)	4.5(2)
C(42)	0.9266(6)	0.157(1)	0.5269(4)	5.8(3)
C(43)	0.9013(7)	0.146(1)	0.5750(4)	6.7(3)
C(44)	0.8332(7)	0.189(1)	0.5874(4)	6.1(3)
C(45)	0.7875(6)	0.247(1)	0.5490(3)	4.8(2)
C(50)	0.8041(5)	0.4993(9)	0.4480(3)	3.1(2)
C(51)	0.8722(5)	0.521(1)	0.4700(4)	4.2(2)
C(52)	0.9028(6)	0.644(1)	0.4677(4)	5.4(3)
C(53)	0.8645(5)	0.745(1)	0.4419(4)	4.6(2)
C(54)	0.7964(5)	0.7179(9)	0.4194(4)	4.5(2)
C(55)	0.7651(5)	0.5976(9)	0.4216(3)	3.7(2)
C(60)	0.8222(5)	0.2442(9)	0.2760(3)	3.7(2)
C(61)	0.8743(6)	0.162(1)	0.2601(4)	6.0(3)
C(62)	0.8576(7)	0.079(1)	0.2193(4)	7.6(4)
C(63)	0.7943(8)	0.080(1)	0.1940(4)	7.7(4)
C(64)	0.7365(7)	0.159(1)	0.2094(4)	7.8(4)
C(65)	0.7527(6)	0.245(1)	0.2515(3)	6.0(3)
C(70)	0.9286(5)	0.347(1)	0.3550(3)	4.4(2)
C(71)	0.9624(6)	0.468(1)	0.3645(4)	6.1(3)
C(72)	1.0337(7)	0.470(1)	0.3863(5)	8.1(4)
C(73)	1.0714(6)	0.356(2)	0.3961(4)	8.8(4)
C(74)	1.0366(6)	0.236(1)	0.3870(4)	7.1(3)
C(75)	0.9661(5)	0.232(1)	0.3658(4)	5.4(3)

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[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as (4/3) $[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE III. Selected Bond Distances (Å) and Bond Angles (°) for $RuCl_2(Ph_2PCH_2SiMe_3)_3$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom 3	Angle
Ru	Cl(1)	2.395(2)	Cl(1)	Ru	Cl(2)	165.91(7)
Ru	Cl(2)	2.390(2)	Cl(1)	Ru	P(1)	89.54(6)
Ru	P(1)	2.379(2)	Cl(1)	Ru	P(2)	91.12(7)
Ru	P(2)	2.210(2)	Cl(1)	Ru	P(3)	90.55(7)
Ru	P(3)	2.348(2)	Cl(2)	Ru	P(1)	86.87(7)
P(1)	C(1)	1.843(7)	Cl(2)	Ru	P(2)	102.83(7)
P(1)	C(20)	1.840(7)	Cl(2)	Ru	P(3)	89.17(7)
P(1)	C(30)	1.833(7)	P(1)	Ru	P(2)	96.83(7)
P(2)	C(5)	1.832(7)	P(1)	Ru	P(3)	163.93(7)
P(2)	C(40)	1.839(7)	P(2)	Ru	P(3)	99.24(7)
P(2)	C(50)	1.847(7)	Ru	P(1)	C(1)	118.4(3)
P(3)	C(9)	1.836(8)	Ru	P(1)	C(20)	116.6(2)
P(3)	C(60)	1.837(7)	Ru	P(1)	C(30)	112.7(2)
P(3)	C(70)	1.836(7)	C(1)	P(1)	C(20)	103.6(3)
			C(1)	P(1)	C(30)	102.6(3)
			C(20)	P(1)	C(30)	100.6(3)
			Ru	P(2)	C(5)	111.8(2)
			Ru	P(2)	C(40)	116.2(3)
			Ru	P(2)	C(50)	115.5(2)
			C(5)	P(2)	C(40)	106.4(3)
			C(5)	P(2)	C(50)	103.8(3)
			C(40)	P(2)	C(50)	101.8(3)
			Ru	P(3)	C(9)	119.2(2)
			Ru	P(3)	C(60)	95.5(2)
			Ru	P(3)	C(70)	122.0(3)

Results and Discussion

The compound $RuCl_2(Ph_2PCH_2SiMe_3)_3$ was prepared by the reaction of $RuCl_3$ with excess phosphine. Ligand substitution is accompanied by the reduction to Ru(II). The preparation is analogous to that of $RuCl_2(Ph_3P)_3$, although yields are lower. This could be due to the fact that the reaction was conducted in air. We did not make any attempts to optimize the reaction conditions in order to get better yields.

The structure consists of discrete monomers of $RuCl_2(Ph_2PCH_2SiMe_3)_3$. There are no unusual intermolecular contacts. The ruthenium atom resides on a general position in space group $P2_1/c$ ($Z = 4$) and therefore there are no crystallographic restrictions on the molecule. The geometry around the central Ru atom is best described as a distorted tetragonal pyramid. The Ru atom is displaced toward the center of the pyramid and is 0.309(1) Å above the base defined by Cl(1), P(3), Cl(2) and P(1). The four atoms in the base of the pyramid are not strictly planar. The two Cl atoms are bent toward the Ru atom, the two phosphorus atoms are pushed away from it. The displacements are on an average 0.18 Å from the least-squares plane. The empty octahedral site is blocked by the two bulky phosphines. Examination of the contacts around the ruthenium atom reveals that the C(2) carbon of the trimethylsilyl group is 4.376 Å away from it, a distance too large for any significant through-hydrogen interaction. A labelled ORTEP drawing of the molecule is presented in Fig. 1. Selected bond distances

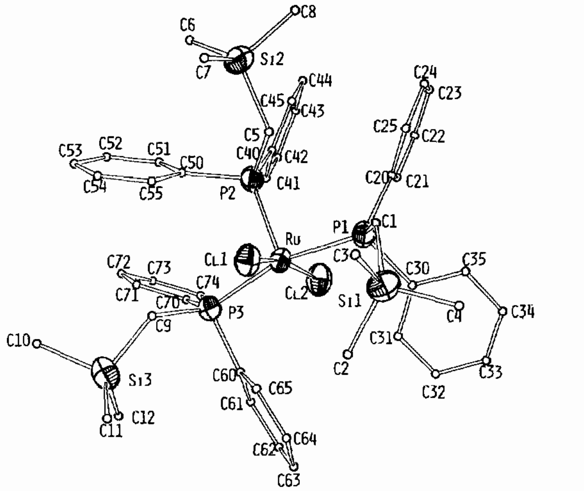

Fig. 1. ORTEP drawing of $RuCl_2(Ph_2PCH_2SiMe_3)_3$ at the 50% probability level. Phenyl and methyl carbons are represented as arbitrarily small circles for the sake of clarity. Atom labelling scheme is defined.

TABLE IV. Comparison of Selected Structural Data for Three Square Pyramidal Complexes

	$OsCl_2(Ph_3P)_3$[a]	$RuCl_2(Ph_3P)_3$[b]	$RuCl_2(Ph_2PCH_2SiMe_3)_3$[c]
M–X	2.383(2)	2.387(7)	2.395(2)
	2.399(2)	2.388(7)	2.390(2)
$M–P_B$[d]	2.410(2)	2.374(6)	2.379(2)
	2.366(2)	2.412(6)	2.348(2)
$M–P_A$[e]	2.235(2)	2.230(8)	2.210(2)
$P_B–M–P_B$	158.07(7)	156.4(2)	165.91(7)
Cl–M–Cl	160.65(8)	157.2(2)	163.93(7)

[a] Ref. 6. [b] Ref. 2. [c] This work. [d] P_B, phosphorus in the base of the pyramid. [e] P_A, apical phosphorus.

and angles are given in Table III. Ru–Cl distances are 2.395(2) and 2.390(2) Å; Ru–P distances in the base of the pyramid are 2.379(2) and 2.348(2) Å. The apical phosphorus–ruthenium bond is shortened to 2.210(2) Å (see Table IV). This effect has been noticed before for square pyramidal coordination. Because of the displacement of the Ru atom toward the center of the pyramid the angles in the base are smaller than 180°. The Cl(1)–Ru–Cl(2) angle is 165.91(7) Å, and the P(1)–Ru–P(3) angle is 163.93(7) Å. The structure with two *trans* chloride atoms is also supported by the IR evidence showing only one Ru–Cl band at 320 cm^{-1}.

This structure is very similar to the structures reported for $RuCl_2(Ph_3P)_3$ and $OsCl_2(Ph_3P)_3$ [2, 6]. Some important bond distances and angles for the three compounds are summarized in Table IV. Examination of the contents of Table IV shows a remarkable similarity of intramolecular distances and angles in all three of these molecules. The angles in the base of the pyramid are closer to 180° in our case indicating that the phosphine used is less sterically demanding than triphenylphosphine.

Supplementary Material

Full listings of bond distances and angles, anisotropic displacement parameters and calculated and observed structure factors (27 pages) may be obtained from author F.A.C.

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References

1 E. A. Seddon and K. R. Seddon, 'The Chemistry of Ruthenium', Elsevier, Amsterdam, 1984.
2 S. J. La Placa and J. A. Ibers, *Inorg. Chem., 4,* 778 (1965).
3 M. Bressau and P. Rigo, *Inorg. Chem., 14,* 2286 (1975).
4 B. E. Cooper and W. J. Owen, *J. Organomet. Chem., 21,* 329 (1970).
5 K. G. Caulton, *J. Am. Chem. Soc., 96,* 3005 (1974).
6 A. Chakravarty, F. A. Cotton, D. A. Tocher, *Acta Crystallogr., Sect. C, 41,* 698 (1985).