SYNTHESIS AND CRYSTAL STRUCTURE OF CARBONYLCHLOROBIS(TRIPHENYLPHOSPHINE)DITHIO-FORMATORUTHENIUM(II)TETRAHYDROFURAN [C42H39ClO2P2S2Ru]*

SARADA GOPINATHAN, I. R. UNNI and C. GOPINATHAN[†]

Inorganic Chemistry Division, National Chemical Laboratory, Pune 411 008, India

and

VEDAVATI G. PURANIK, S. S. TAVALE and T. N. GURU ROW

Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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Abstract—The title complex [RuCl(CO)(PPh₃)₂(S₂CH)](thf) has been prepared by the insertion of carbon disulphide into the Ru—H bond of [RuHClCO(PPh₃)₂(4-Vp)] followed by crystallization from a mixture of benzene and thf (4-Vp = 4-vinyl pyridine). Its structure has been determined by single crystal X-ray diffraction methods. The crystals are triclinic, space group PI, z = 2, a = 10.042(1), b = 11.216(1), c = 17.772(2) Å, $\alpha = 99.80(1)$, $\beta = 93.26(1)$ and $\gamma = 90.86(1)^{\circ}$. The structure, which has been refined to R = 0.078 for 4949 reflections, is a distorted octahedron.

Phosphine substitution in the complex RuHCl(CO) $(PPh_3)_3$ (I) has been reported to be carried out using phosphites, phosphonites and phosphinites.¹ Recently we reported the synthesis of monosubstitution products of the complex (I) using nitrogen heterocyclics.² The 4-vinylpyridine ruthenium(II) complex RuHCl(CO)(PPh₃)₂(4-Vp) (II) reacts with a variety of bidentate chelating ligands containing potential hydroxyl groups in the presence of a base to give chelated ruthenium complexes having O-O coordination with the elimination of chlorine and 4-vinyl pyridine.³ Activated olefins can readily be inserted into the Ru-H bond in the complex (II) to yield insertion products.⁴ We have extended this reaction by the synthesis of a dithioformate complex of Ru(II) using carbon disulphide.

EXPERIMENTAL

Reactions were carried out in a dry, oxygen-free nitrogen atmosphere, using dried, freshly distilled and degassed solvents. (a) Carbonylchlorohydridobis (triphenylphosphine) (4-vinylpyridine)ruthenium(II)

Freshly distilled 4-vinyl pyridine (0.84 g; 8 mmol)was added to a suspension of RuHCl(CO)(PPh₃)₃ (0.95 g; 1 mmol) in thf (50 cm³) in a Schlenk tube. The solution was stirred at 25° for 20 h to yield a white solid. This was filtered through a sintered disc, washed with thf and dried at 60° at 1 mm pressure, m.p. 199°C. Yield 0.62 g (78%). Found: C, 66.3; H, 4.9; P, 8.0. Calc. for C₄₄H₃₈ClNOP₂Ru: C, 66.4; H, 4.8; P, 7.8.

(b) Carbonylchlorobis (triphenylphosphine) dithioformatoruthenium(II)

To a suspension of RuHCl(CO)(PPh₃)₂(4-Vp) (0.20 g; 0.25 mmol) in benzene (25 cm³) was added carbon disulphide (5 cm³). The contents turned brown in 2 h and were kept at room temperature for 24 h. The yellow crystals separated were filtered and dried at 60°C at 1 mm pressure for 2 h. M.p. 223°C. Found: C, 59.5; H, 4.1; P, 8.0. Calc. for C₃₈H₃₁ClOP₂S₂Ru: C, 59.5; H, 4.1; P, 8.1. A portion of the product was crystallized from a benzene-

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[†] Author to whom correspondence should be addressed.

thf mixture (90:10, vol./vol.) to get crystals for X-ray studies.

(c) X-ray studies

A crystal of dimension $0.7 \times 0.35 \times 0.17$ mm was used for data collection. Formula weight 838.37, triclinic, $P\bar{1}$; a = 10.042(1), b = 11.216(1), c = 17.772(2) Å, $\alpha = 99.80(1)$, $\beta = 93.26(1)$, $\gamma = 90.96(1)^{\circ}$ and V = 1968.6 Å³; z = 2, density (by flotation) 1.412 g/cm³ (calc. 1.414 g/cm³), μ (Mo-K_a) = 6.76 cm⁻¹, F(000) = 860.

Intensity data were collected on an Enraf Nonius CAD 4F-11M diffractometer using the $\omega/2\theta$ scan technique with Mo-K_a ($\lambda = 0.7107$ Å, graphite monochromated) radiation. Cell dimensions were taken from 20 reflections ($32 \le 2\theta \le 39^\circ$). A total of 6438 reflections ($\theta < 23.5^\circ$) were collected with three standard reflections measured every 1000 s. The variations in these standard reflections were within 3%. A total of 4949 reflections with $|F_o| \le 3\sigma |F_o|$ were used in the final refinement of structural parameters. The structure was solved using a modified⁵ MULTAN 78⁶ package. The crystallographic numbering of the atoms is shown in Fig. 1.

Full-matrix least squares refinement⁷ of scale, positional, anisotropic thermal parameters for Ru, S, P and Cl atoms, and isotropic thermal parameters for the rest of the non-hydrogen atoms (hydrogen atoms were geometrically fixed and were not refined) gave an R value of 0.078. A final difference Fourier map was featureless. Atomic scattering factors used were from the International Tables for Xray Crystallography.⁸ Lists of observed and calculated structure factors, final positional and equivalent temperature factors for all non-hydrogen atoms, atomic coordinates for hydrogen atoms and anisotropic thermal parameters have been deposited with the Editor. Atomic coordinates have also been submitted to the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The complex [RuHCl(CO)(PPh₃)₂(4-Vp)] reacts with carbon disulphide in benzene at an ambient temperature to yield the insertion product as an airstable yellow crystalline solid with the elimination of 4-vinyl pyridine. Upon crystallization from benzene-thf mixture, one molecule of tetrahydrofuran is retained in the crystal as seen by X-ray diffraction studies but it can be removed by heating the crystals at 60°C at 1 mm pressure. The thf-free sample was used for spectral studies. This yellow product shows IR absorption bands in the carbonyl region at 1945 cm⁻¹ characteristic of a terminal carbonyl group. The bands at 1235 and 930 cm⁻¹ are attributable to δ (HCS) and v_{as} (CS₂) respectively, which suggest the presence of a chelated dithio ligand.^{9,10}

¹H NMR spectrum comprises of a triplet at δ 11.88, ⁴J(PH) ~ 8 Hz due to the coupling of dithioformate proton (S₂CH) with *trans* phosphorus nuclei.

Crystal structure of [C₄₂H₃₉ClO₂P₂S₂Ru]

A perspective view of the molecule is given in Fig. 2. Table 1 gives interatomic bond distances and bond angles along with e.s.d.'s in parentheses. The molecule has a distorted octahedral coordination around the ruthenium atom. The two sulphur atoms are cis with respect to each other which enables chelation with the metal atom, thereby closing a four membered ring. The two triphenylphosphine groups are also *cis* to each other while the carbonyl group is *trans* to the chlorine atom. The bite angle of the dithioformate group is 70.5° and is nearly equal to that in bis(dithioformato)-(71°).11 bis(triphcnylphosphine)ruthenium(II) There is a delocalization in the HCS₂ ligand [C(1)-S(1) = C(1)-S(2) = 1.67(1) Å]. Similar delocalization is found in the rhenium complex¹² $Re(CO)_2(HCS_2)_2(PPh_3)_2$, in $Pd(S_2CPh)_2$ and its nickel analogue.13



Fig. 1.



Synthesis and structure of carbonylchlorobis(triphenylphosphine)dithioformatoruthenium(II)tetrahydrofuran 1861

Bond lengths (Å)	
Ru—Cl	2.421(3)
Ru—S(1)	2.447(2)
Ru—S(2)	2.427(2)
Ru—P(1)	2.396(2)
Ru—P(2)	2.398(2)
Ru—C(2)	2.064(17)
S(1)—C(1)	1.670(14)
S(2)—C(1)	1.667(14)
C(2)O(1)	0.755(21)
Bond angles (°)	
Cl - Ru - S(1)	85.2(1)
Cl—Ru—S(2)	87.8(1)
Cl - Ru - P(1)	94.5(1)
Cl-Ru-P(2)	89.9(1)
Cl—Ru—C(2)	172.2(5)
S(1)— Ru — $S(2)$	70.5(1)
S(1)— Ru — $P(1)$	93.1(1)
S(1)— Ru — $P(2)$	160.6(1)
S(1)RuC(2)	87.2(5)
S(2)— Ru — $P(1)$	163.3(1)
S(2)—Ru—P(2)	90.6(1)
S(2)—Ru—C(2)	87.9(5)
P(1)— Ru — $P(2)$	105.9(1)
P(1)— Ru — $C(2)$	87.8(5)
P(2)— Ru — $C(2)$	96.7(5)
Ru - S(1) - C(1)	86.9(5)
Ru - S(2) - C(1)	87.6(5)
S(1)—C(1)—S(2)	115.0(10)

Table 1. Some selected bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses

The distances of all coordinating atoms are normal. However, the C(2)—O(1) is too short (0.76 Å). A strikingly similar value is seen in the structure of *trans*-carbonylbis (triphenylphosphine) rhodium (I) chloride.¹⁴ The difference Fourier map does not indicate any disorder in this region and also the temperature factor associated with this oxygen atom is normal. The crystal structure has a molecule of tetrahydrofuran (thf) of crystallization and there are no significant interactions of this moiety with the structure. The thermal vibrations associated with the thf molecule are large; however the bond lengths and the bond angles are about normal. The crystal structure is stabilized by van der Waal's interactions.

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