Crystal and Molecular Structure of Thiocarbonylbis(triphenylphosphine)-rutheniumtri-μ-chloro-chlorobis(triphenylphosphine)ruthenium

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Crystals of the title compound, $CS(PPh_3)_2RuCl_3Ru(PPh_3)_2Cl$, are orthorhombic, space group $Pn2_1a$ with a = 21·53, b = 23·40, c = 14·20 Å. For 1258 independent reflections recorded on film, the final R was 0·115. Both ruthenium atoms have a distorted octahedral co-ordination, with the two octahedra sharing a common face defined by three chlorine atoms. The Ru • • • Ru distance is 3·35 Å. Two different molecular structures may exist in the crystal, differing in the relative positions of the thiocarbonyl and terminal chloro groups of the molecule.

THE synthesis and reactions of the title compound are given in the preceding paper.[1]

EXPERIMENTAL

From a series of reactions, red crystals were isolated with an apparent empirical formula of $C_{37}H_{30}Cl_2P_2RuS$. The sample from which the crystal was selected, however, differed substantially from the 4·3% sulphur required by that structure (Found: C, 60·7; H, 4·3; Cl, 9·4; P, 8·5; S, 2·3. $C_{73}H_{60}Cl_4P_4Ru_2S$ requires C, 61·0; H, 4·2; Cl, 9·9; P, 8·6; S, 2·2%).

Crystal Data.—$C_{73}H_{60}Cl_4P_4Ru_2S$, M = 1436. Dark red orthorhombic crystals, a = 21·53, b = 23·40, c = 14·20 Å, U = 7154 Å^3, D_m = 1·41 g cm^{-3}, D_c = 1·35 g cm^{-3}. Z = 4, $\mu(\text{Cu-}K_\alpha)$ = 63 cm^{-1}. The observed conditions of reflection ($0kl$, $k + l = 2n$; $h0l$ no conditions; $hk0$, $h = 2n$) indicate that the space group is $Pnma$ (No. 62) or $Pn2_1a$ (alternative setting of $Pna2_1$, No. 33).

Structure Determination.—The data were collected on multiple film packs by the equi-inclination Weissenberg technique for layers $0kl$—$15kl$. Intensities for 1258 reflections with $\sin\theta/\lambda \leqslant 0{\cdot}40$ Å^{-1} were estimated visually using a calibrated intensity strip. As it was impractical to collect cross layer data, the layers were scaled statistically, and the scale factors were allowed to vary individually in the isotropic cycles of least squares-refinement.

From the Patterson function, positions of the ruthenium atoms were deduced which were compatible with the centrosymmetric space group $Pnma$. A Fourier map phased by these positions gave plausible positions for all chlorine, sulphur, and phosphorus atoms. The weakest of three peaks in the special position (b) was assigned to the sulphur atom and the others to chlorine, while the strongest of three peaks in general positions was assumed to be chlorine and the others phosphorus. This partial structure was refined by full matrix least squares, and converged at R 0·30, giving the positional parameters listed in Table 1. Some of the temperature factors varied unrealistically, and it was impossible to locate phenyl rings in a difference map satisfactorily. In any case, the structure requires two pairs of *cis*-triphenylphosphine groups to eclipse one another.

TABLE 1

Fractional co-ordinates and thermal parameters of atoms determined in the centrosymmetric space group. The corresponding atoms in the final structure 1(a) are given in brackets

Atom	x	y	z	U/Å^2
Ru [Ru(1), Ru(2)]	0·0897	0·3217	0·2169	0·032
Cl [Cl(1)]	0·0075	1/4	0·2218	0·043
Cl [Cl(2)]	0·1430	1/4	0·3158	0·014
S [Cl(3)]	0·1257	1/4	0·0927	0·030
Cl [S(1), P(3)]	0·1956	0·3750	0·1809	0·097
P [P(1), Cl(4)]	0·0239	0·3653	0·0991	0·082
P [P(2), P(4)]	0·0660	0·3791	0·3451	0·043

The symmetry was relaxed to that of the non-centrosymmetric space group $Pn2_1a$. This made it possible to interchange one of the terminal chlorine atoms with a phosphorus atom, and the other with the presumed bridging sulphur atom. Several cycles of refinement of heavy atom positions and difference Fourier syntheses made it possible to locate all the phenyl rings. The origin was fixed by holding invariant the y-parameter of the two ruthenium atoms in turn. Further refinement of the structure, complete except for the carbon atom of the thiocarbonyl group, was carried out, constraining all the carbon atoms of the phenyl rings to shift as idealised planar groups with C–C = 1·39 Å, and a single isotropic temperature factor for all carbon atoms. Unit weights were used, and the series converged with R 0·12, the quantity minimised being $\Sigma(|F_o| - |F_c|)^2$. As there was no large variation for this function for ranges of $|F_o|$, no other weighting scheme was used.

A difference Fourier map at this stage showed no significant extramolecular peaks, but did show peaks between the ruthenium atoms and both the terminal chlorine and sulphur atoms. Two structures were refined further, these differing only in the relative positions of the chloro and thiocarbonyl

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[1] T. A. Stephenson, E. S. Switkes, and P. W. Armit, preceding paper.

groups, and the carbon atom of the thiocarbonyl was now included. The ruthenium atoms were given anisotropic thermal parameters, and both structures converged at R 0·115. These structures are not crystallographically equivalent, and neither of them entirely removes the extra electron density in the difference Fourier map. Attempts at refining a disordered structure midway between the two were unsuccessful as the data do not resolve the two superimposed ligands. Hence, the heavy atom skeletons of both structures are shown in Figure 1(a) and (b), and an impression of the full structure, based on the first model, in Figure 2. Positional and thermal parameters for heavy atoms are given in Table 2, and positional parameters for the phenyl carbon atoms in Table 3. Derived distances and angles are

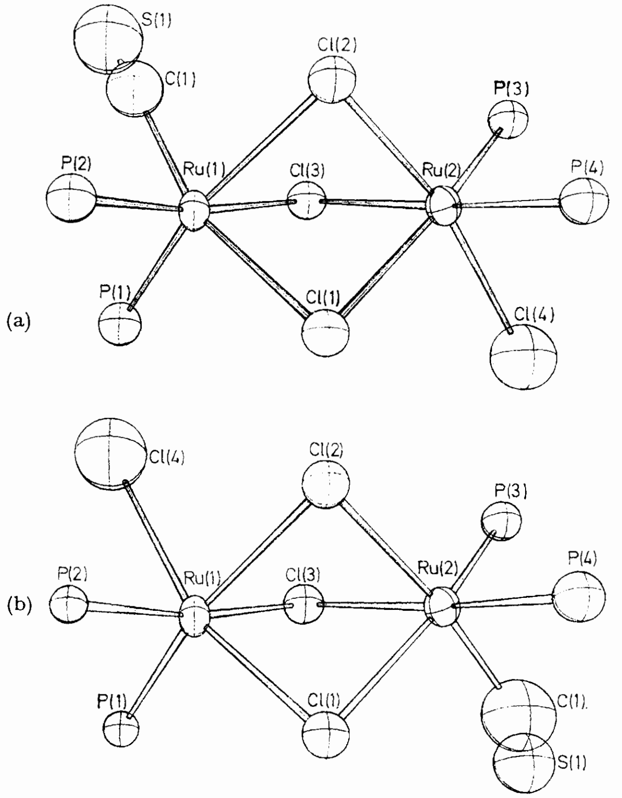

FIGURE 1 (a) Heavy atom skeleton, first set of co-ordinates; (b) heavy atom skeleton, second set of co-ordinates

TABLE 2

(A) Fractional co-ordinates and thermal parameters for structure as in Figure 1(a)

Atom	10^4x	10^4y	10^4z	$10^3U/Å^2$
Ru(1)	870 (3)	3181 (5)	2090 (4)	*
Ru(2)	933 (3)	1751 (5)	2190 (4)	*
Cl(1)	57 (66)	2468 (11)	2389 (11)	37 (5)
Cl(2)	1441 (7)	2477 (12)	3181 (10)	37 (5)
Cl(3)	1251 (6)	2440 (11)	987 (11)	36 (5)
Cl(4)	157 (12)	1134 (12)	1096 (18)	89(10)
S(1)	2158 (15)	3733 (13)	1835 (20)	106 (11)
P(1)	335 (10)	3607 (10)	907 (15)	41 (7)
P(2)	612 (10)	3815 (10)	3325 (15)	35 (8)
P(3)	1727 (10)	1215 (10)	1648 (15)	34 (7)
P(4)	631 (10)	1277 (10)	3555 (15)	31 (7)
C(1)	1700 (44)	3549 (40)	2104 (60)	64 (34)

* Anisotropic thermal parameters for Ru(1) and Ru(2).

Atom	$10^3U_{11}/$ $Å^2$	$10^3U_{22}/$ $Å^2$	$10^3U_{33}/$ $Å^2$	$10^3U_{23}/$ $Å^2$	$10^3U_{13}/$ $Å^2$	$10^3U_{12}/$ $Å^2$
Ru(1)	29 (6)	18 (4)	54 (6)	1 (4)	0 (4)	0 (4)
Ru(2)	31 (5)	27 (4)	23 (5)	7 (5)	1 (4)	−2 (4)

(B) Fractional co-ordinates and thermal parameters for structure as in Figure 1(b)

Atom	10^4x	10^4y	10^4z	$10^3U/Å^2$
Ru(1)	872 (3)	3204 (5)	2089 (4)	†
Ru(2)	930 (3)	1772 (5)	2190 (4)	†
Cl(1)	58 (6)	2478 (11)	2388 (11)	38 (5)
Cl(2)	1438 (7)	2497 (12)	3187 (11)	37 (5)
Cl(3)	1251 (7)	2457 (11)	986 (11)	36 (5)
Cl(4)	2096 (13)	3730 (13)	1870 (19)	114 (11)
S(1)	118 (14)	1125 (13)	1006 (23)	78 (11)
P(1)	339 (10)	3617 (10)	903 (15)	28 (7)
P(2)	615 (9)	3831 (9)	3327 (14)	20 (7)
P(3)	1710 (10)	1244 (10)	1669 (15)	34 (7)
P(4)	641 (10)	1293 (11)	3570 (16)	37 (8)
C(1)	340 (30)	1250 (30)	1590 (50)	105 (19)

† Anisotropic thermal parameters for Ru(1) and Ru(2).

Atom	$10^3U_{11}/$ $Å^2$	$10^3U_{22}/$ $Å^2$	$10^3U_{33}/$ $Å^2$	$10^3U_{23}/$ $Å^2$	$10^3U_{13}/$ $Å^2$	$10^3U_{12}/$ $Å^2$
Ru(1)	31 (6)	20 (4)	56 (6)	−0 (4)	0 (4)	−1 (4)
Ru(2)	35 (5)	28 (4)	26 (5)	10 (5)	2 (4)	−3 (4)

(Estimated standard deviations are given with each parameter).

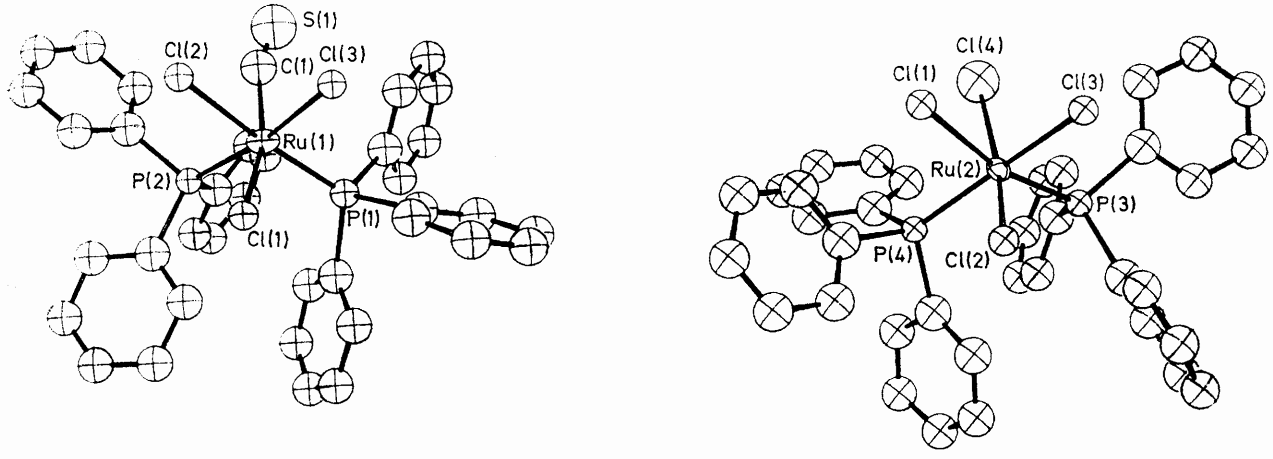

FIGURE 2 Projection of two halves of the complete molecule, viewed from the plane of the bridging chlorine atoms toward each ruthenium in turn

in Table 4. Structure factor tables are deposited as Supplementary Publication No. 20968 (4 pp.).*

DISCUSSION

This structure is formally very similar to that reported by Alcock and Raspin, $(PPhEt_2)_3RuCl_3Ru(PPhEt_2)_2Cl$.[2] In that similarly bridged dimer, comparable distances are: Ru—Ru, 3·367 Å, Ru—Cl (bridged), 2·50 Å, and Ru—P, 2·30 Å. This type of inter-ruthenium distance has been interpreted by Crozat and Watkins [3] as indicating a zero bond-order between the ruthenium atoms. In the present structure, there is a marginally significant difference between the Ru–Cl (bridged) distances *trans* to phosphine (2·46 Å) and those *trans* to Cl or CS (2·57 Å).

TABLE 3

Fractional co-ordinates (× 10³) for atoms in phenyl rings. Atoms in the same ring are listed vertically. For all atoms, U = 0·062 Å²

x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Substituents of P(1)								
−48	395	114	84	413	21	5	308	−18
−102	362	91	59	468	−2	−8	249	−1
−161	385	126	103	503	−50	−36	218	−79
−162	436	169	159	488	−75	−44	244	−163
−112	471	187	183	434	−61	−28	300	−184
−52	448	158	142	395	−9	−2	333	−106
Substituents of P(2)								
60	458	301	120	377	423	−13	374	395
109	480	242	115	336	498	−12	385	493
106	541	222	162	341	572	−72	385	540
63	574	265	209	378	562	−123	370	491
17	555	326	219	415	488	−126	355	397
17	494	344	170	414	415	−66	358	347
Substituents of P(3)								
187	126	34	300	99	234	162	44	178
145	132	−43	253	141	219	183	16	261
172	129	−137	272	201	235	169	−45	267
233	117	−147	330	212	268	141	−71	184
274	106	−75	375	172	289	124	−47	110
249	112	20	358	113	270	135	15	103
Substituents of P(4)								
20	168	445	128	95	430	11	62	354
55	188	523	186	123	448	−35	57	427
21	223	592	227	93	514	−82	12	412
−39	237	574	207	45	558	−77	−23	338
−73	223	495	150	20	549	−31	−22	270
−41	185	428	109	47	479	−15	24	279

Because of the disorder in the structure, it is unfortunately impossible to delimit the thiocarbonyl ligand satisfactorily. Very few compounds containing this ligand have been reported. In the most nearly comparable of these, $RhClCS(PPh_3)_2$,[4] the Rh–C–S moiety is almost linear, with Rh–C = 1·79 Å and C–S = 1·54 Å. By comparison, the thiocarbonyl group is much compressed and the metal–sulphur distance *ca.* 0·35 Å too short in the present structure. This compression is almost exactly balanced, however, by the lengthening of the Ru–Cl (terminal) bond compared with that of Alcock and Raspin [2] (2·40 Å). The most probable interpretation then is that the bond lengths and positions given here are only a rough indication of the almost continuous tube of electron density along the mixed Ru–Cl and Ru–C–S directions.

TABLE 4

Intramolecular distances (Å) and angles (°) for structure as in Figure 1(a). Standard deviations refer to last digit given

Ru(1)–Ru(2)	3·35 (2)	Ru(1)–Cl(1)	2·46 (2)
Ru(1)–Cl(2)	2·58 (2)	Ru(1)–Cl(3)	2·48 (2)
Ru(1)–P(1)	2·27 (2)	Ru(1)–P(2)	2·36 (2)
Ru(1)–C(1)	1·98 (10)	Ru(1) · · · S(1)	3·08 (3)
Ru(2)–Cl(1)	2·54 (2)	Ru(2)–Cl(2)	2·47 (2)
Ru(2)–Cl(3)	2·45 (2)	Ru(2)–Cl(4)	2·70 (3)
Ru(2)–P(3)	2·26 (2)	Ru(2)–P(4)	2·33 (2)
C(1)–S(1)	1·14 (10)		
Cl(1)–Ru(1)–Cl(2)	78·5 (7)	Cl(1)–Ru(2)–Cl(2)	79·1 (7)
Cl(1)–Ru(1)–Cl(3)	82·5 (7)	Cl(1)–Ru(2)–Cl(3)	81·3 (7)
Cl(2)–Ru(1)–Cl(3)	77·1 (7)	Cl(2)–Ru(2)–Cl(3)	79·8 (7)
Cl(1)–Ru(1)–P(1)	93·7 (7)	Cl(2)–Ru(2)–P(3)	104·0 (8)
Cl(1)–Ru(1)–P(2)	97·5 (7)	Cl(2)–Ru(2)–P(4)	88·5 (7)
Cl(2)–Ru(1)–P(2)	93·7 (7)	Cl(1)–Ru(2)–P(4)	90·9 (7)
Cl(3)–Ru(1)–P(1)	90·4 (7)	Cl(3)–Ru(2)–P(3)	85·2 (8)
P(1)–Ru(1)–P(2)	98·9 (9)	P(3)–Ru(2)–P(4)	103·4 (9)
Cl(2)–Ru(1)–C(1)	81 (3)	Cl(1)–Ru(2)–Cl(4)	87·6 (7)
Cl(3)–Ru(1)–C(1)	91 (3)	Cl(3)–Ru(2)–Cl(4)	97·1 (7)
P(1)–Ru(1)–C(1)	106 (3)	P(3)–Ru(2)–Cl(4)	88·6 (9)
P(2)–Ru(1)–C(1)	86 (3)	P(4)–Ru(2)–Cl(4)	93·0 (8)
Ru(1)–Cl(1)–Ru(2)	84·3 (5)	Ru(1)–Cl(2)–Ru(2)	83·3 (6)
Ru(1)–Cl(3)–Ru(2)	85·8(6)		

The overall packing in the crystal is evidently governed by the triphenylphosphine groups. Their conformations are, in turn, much restricted by the requirement that they be in two *cis*-bonded pairs, with one ligand eclipsing another across the bridge. The disorder in the crystal is doubtless due to the fact that the two orientations would be virtually indistinguishable for packing considerations. A recently reported compound containing molecular nitrogen,[5] $(PPh_3)_2ClRuCl_3Ru(N_2)(PPh_3)_2$, would be almost identical to the present compound for packing, and might be predicted to have similar disorder.

The calculations were carried out using the facilities of the Edinburgh Regional Computing Centre. For most purposes, the programmes known as XRAY70 [6] were used, but the constrained refinement of phenyl rings used a programme kindly supplied by Dr. G. S. Pawley. We also thank Drs. T. A. Stephenson, J. D. Owen, and C. A. Beevers for discussion and material, and the S.R.C. for a studentship (to A. J. F. F.).

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* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).

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