Crystal and Molecular Structure of Bis(dithioformato)bis(triphenylphosphine)ruthenium(II)

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Crystals of the title compound are monoclinic, space group $P2_1/c$, $a = 11{\cdot}69(1)$, $b = 18{\cdot}38(2)$, $c = 17{\cdot}45(2)$ Å, $\beta = 114{\cdot}3(1)°$. The structure was determined by the heavy-atom method from diffractometer data, and refined by least-squares techniques to R 5·9% for 4012 independent reflections. The molecule has distorted octahedral co-ordination. The two thioformate groups have delocalized electrons, and are mutually *cis*. Hydrogen atom positions were established.

ALTHOUGH complexes containing dithio-anions such as dithiocarbamates and dithiocarbonates have been studied widely, those of carbodithioates have received less attention, possibly because of the poor stability of the free ligands. An alternative route to their preparation involves insertion of carbon disulphide into metal alkyl, aryl, or hydride bonds.[1-4] A recent example is $Ru(HCS_2)_2(PPh_3)_2$ [5] where two such insertions have taken place. We now report the details of an *X*-ray diffraction study of this complex.

EXPERIMENTAL

The dithioformato-complex was prepared, as described previously [5] from dichlorotris(triphenylphosphine)ruthenium.[6] Crystals were dissolved in chloroform and reprecipitated with methanol.

Crystal Data.—$C_{38}H_{32}P_2RuS_4$, $M = 780$, Monoclinic, $a = 11{\cdot}69(1)$, $b = 18{\cdot}38(2)$, $c = 17{\cdot}45(2)$ Å, $\beta = 114{\cdot}3(1)°$. $U = 3418(3)$ Å^3, $Z = 4$, $D_c = 1{\cdot}50(2)$, $F(000) = 398$. Space group $P2_1/c$ (C_{2h}^5). Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 7·88 cm^{-1}.

Crystallographic Measurements.—Intensity data in 2θ scan mode ($0 < 2\theta < 55°$) were collected from a crystal $0{\cdot}02 \times 0{\cdot}48 \times 0{\cdot}37$ mm on a Canberra-automated Picker diffractometer by use of zirconium-filtered Mo radiation. Cell dimensions were obtained from a least-squares fit of 18 diffractometer settings. Absorption corrections were applied,[7] A ranging from 0·77 to 0·98. $\sigma(I)$ Was taken as $[1{\cdot}02\ (\text{scan}) + 0{\cdot}98\ (\text{background})]^{1/2}$ and reflections having $I \leqslant 3\sigma(I)$ were not used, leaving 4012 in all. $\sigma(F_o)$ Was taken as $\{[\sigma(I)/(Lp.A)]^2 + 0{\cdot}02F_o{}^4\}^{1/2}/(2F_o)$ where Lp is the Lorentz-polarization factor. The first term relates to

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[1] E. Lindner, R. Grimmer, and H. Weber, *J. Organometallic Chem.*, 1970, **23**, 209.

[2] E. Lindner and R. Grimmer, *J. Organometallic Chem.*, 1970, **25**, 493.

[3] M. Freni, D. Guisto, and P. Pomiti, *J. Inorg. Nuclear Chem.*, 1971, **33**, 4093.

[4] F. W. Einstein, E. Enwall, N. Flitcroft, and J. M. Leach, *J. Inorg. Nuclear Chem.*, 1972, **34**, 885.

[5] R. O. Harris, N. K. Hota, L. Sadavoy, and J. M. C. Yuen, *J. Organometallic Chem.*, 1973, **54**, 259.

[6] T. A. Stephenson and G. Wilkinson, *Inorg. Chem.*, 1965, **4**, 778.

[7] P. Coppens, L. Leiserouitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

the variance in F_o in the absence of any errors in the absorption correction, extinction effects, *etc.*; the second term relates to the variance caused by these errors.

Structure Analysis.—Initial phasing was by the heavy-atom method. Least-squares full-matrix refinement with non-hydrogen scattering factors from ref. 8 was uneventful. The last Fourier difference map showed all the hydrogen atoms positions although some of these (associated with phenyl rings) had peaks of low density comparable to those of a number of spurious peaks. All hydrogen positions were included in F_c, with the scattering factor of ref. 9 and the same anisotropic thermal factors as their associated carbon atoms. The final R was 5·9%.* Final atomic parameters (non-hydrogen) are given in Table 1, and calculated hydrogen positions in Table 2.

TABLE 1

Fractional positional co-ordinates (× 10⁴) and anisotropic temperature factors (× 10⁴) *

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	−733(1)	407(0)	1896(0)	49(1)	18(0)	20(0)	−1(0)	13(0)	−2(0)
S(1)	−993(3)	−769(2)	2382(2)	85(3)	23(1)	39(1)	−6(1)	21(1)	1(1)
S(2)	−2233(3)	−288(2)	716(2)	87(3)	30(1)	29(1)	−7(1)	11(1)	−6(1)
S(3)	−467(3)	1344(2)	1039(2)	87(3)	27(1)	29(1)	−2(1)	22(1)	5(1)
S(4)	824(3)	12(2)	1382(2)	77(3)	33(1)	38(1)	1(1)	27(1)	−8(1)
C(011)	−1985(10)	−9871(6)	1382(7)	87(11)	34(4)	36(5)	−4(6)	14(6)	−4(4)
C(021)	536(11)	794(7)	848(7)	89(11)	35(4)	42(5)	−9(6)	30(6)	−6(4)
P(1)	961(2)	776(1)	3141(1)	50(2)	18(1)	22(1)	1(1)	11(1)	0(1)
P(2)	−2466(2)	939(1)	2016(1)	49(2)	22(1)	22(1)	0(1)	13(1)	0(1)
C(111)	2067(8)	1362(5)	2942(6)	48(8)	16(3)	33(4)	−1(4)	11(5)	−5(3)
C(112)	3170(10)	1087(6)	2949(7)	78(10)	24(4)	42(5)	1(5)	25(6)	−3(3)
C(113)	3985(10)	1537(7)	2732(8)	80(11)	36(5)	63(6)	−10(6)	46(7)	−6(4)
C(114)	3660(10)	2257(6)	2486(6)	98(11)	27(4)	36(4)	−20(5)	34(6)	−5(3)
C(115)	2564(10)	2534(6)	2484(6)	85(10)	24(3)	28(4)	−9(5)	13(5)	5(3)
C(116)	1762(9)	2090(6)	2686(6)	63(9)	24(3)	27(4)	4(4)	10(5)	1(3)
C(121)	746(8)	1219(5)	4023(5)	47(8)	25(3)	22(3)	9(4)	3(4)	−2(3)
C(122)	49(9)	828(6)	4368(6)	60(8)	40(4)	32(4)	1(5)	17(5)	−4(3)
C(123)	−81(12)	1096(8)	5086(7)	109(14)	60(7)	35(5)	7(8)	35(7)	−4(5)
C(124)	504(13)	1721(7)	5455(7)	143(15)	39(5)	33(5)	12(7)	32(7)	−9(4)
C(125)	1194(12)	2114(7)	5124(7)	140(14)	44(5)	26(4)	12(7)	27(7)	−7(4)
C(126)	1353(11)	1870(6)	4406(6)	102(12)	32(4)	27(4)	11(6)	6(6)	−10(3)
C(131)	2048(8)	48(5)	3766(5)	50(8)	17(3)	29(4)	10(4)	7(4)	9(3)
C(132)	2079(10)	−626(6)	3418(7)	77(10)	25(4)	39(5)	10(5)	7(6)	5(3)
C(133)	2904(12)	−1161(7)	3908(8)	97(13)	32(4)	53(6)	7(6)	10(7)	−3(4)
C(134)	3700(11)	−1039(7)	4749(7)	97(12)	30(4)	50(6)	12(6)	27(7)	5(4)
C(135)	3681(12)	−378(7)	5090(7)	122(13)	45(5)	31(4)	35(7)	22(6)	11(4)
C(136)	2846(11)	194(6)	4600(6)	101(12)	32(4)	26(4)	12(6)	6(6)	7(3)
C(211)	−2199(8)	1671(5)	2780(5)	54(8)	18(3)	30(4)	0(4)	13(4)	2(3)
C(212)	−1576(9)	2290(6)	2675(6)	48(8)	27(4)	41(5)	1(4)	6(5)	3(3)
C(213)	−1360(11)	2914(6)	3183(7)	111(12)	17(3)	43(5)	−13(5)	14(6)	−8(3)
C(214)	−1854(12)	2916(7)	3793(7)	139(15)	33(5)	37(5)	14(7)	19(7)	−1(4)
C(215)	−2440(13)	2298(7)	3938(7)	137(15)	37(5)	36(5)	13(7)	26(7)	−8(4)
C(216)	−2632(10)	1670(6)	3422(6)	107(11)	34(4)	25(4)	16(5)	21(6)	−8(3)
C(221)	−3557(8)	311(5)	2198(5)	58(8)	24(3)	31(3)	−5(4)	24(4)	−3(3)
C(222)	−4782(10)	2208(6)	1612(7)	67(10)	26(4)	48(5)	−11(5)	29(6)	−6(3)
C(223)	−5587(11)	−277(7)	1744(8)	96(12)	35(5)	51(6)	−8(6)	37(7)	−8(4)
C(224)	−5154(13)	−693(7)	2493(9)	121(14)	36(5)	77(8)	−27(7)	70(9)	−23(5)
C(225)	−3932(13)	−610(7)	3084(7)	144(16)	36(5)	47(5)	−18(7)	61(8)	−8(4)
C(226)	−3119(11)	−116(6)	2930(7)	116(12)	28(4)	40(5)	−14(5)	42(7)	−5(3)
C(231)	−3585(8)	1450(5)	1074(6)	53(7)	22(3)	31(4)	8(4)	10(4)	0(3)
C(232)	−4412(9)	1940(6)	1212(6)	57(9)	31(4)	37(4)	−4(5)	12(5)	−2(3)
C(233)	−5311(10)	2319(6)	532(7)	71(10)	27(4)	40(5)	10(5)	12(6)	11(3)
C(234)	−5396(10)	2215(6)	−289(6)	82(10)	29(4)	33(4)	−4(5)	9(5)	−1(3)
C(235)	−4565(10)	1732(6)	−403(6)	95(11)	32(4)	27(4)	−8(5)	8(6)	0(3)
C(236)	−3665(10)	1346(6)	255(6)	74(10)	36(4)	27(4)	−12(5)	13(5)	9(3)

* In the form: $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

DISCUSSION

The crystal structure consists of discrete molecules having the dimensions shown in Table 3 and conformation shown in the Figure. The ruthenium environment is distorted octahedral with the dithioformate groups *cis*. Although the structure is distorted from octahedral the central part (omitting the phenyl groups) has an almost exact two-fold axis through ruthenium. A best-molecular-fit routine[10] shows the maximum relative displacement, only 0·047 Å, to be that of P(1) and its diad-relative P(2). The 'bite' angle of the dithioformate group is 71°, the angular difference from 360° being more or less equally shared between the other two ligands in the same plane as the dithioformate

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* Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20839 (5 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[9] R. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[10] S. C. Nyburg, unpublished computer programme.

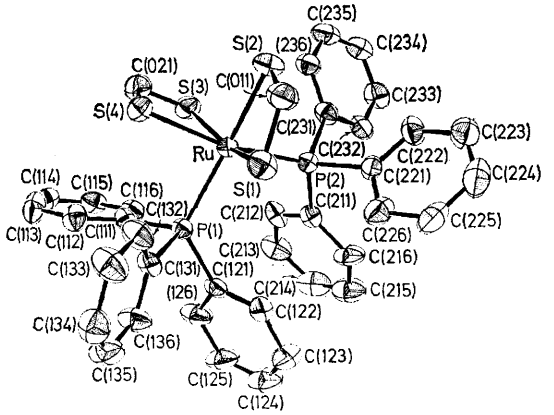
group. The Ru–S distances are of two kinds, phosphorus *trans* to sulphur 2·45, mutually *trans* sulphur atoms, 2·39 Å.

TABLE 2

Calculated hydrogen positions

Atom	*x*	*y*	*z*
H(011)	−241	−151	119
H(021)	96	93	42
H(112)	339	53	312
H(113)	486	133	276
H(114)	425	260	230
H(115)	234	310	233
H(116)	89	231	264
H(122)	−38	32	408
H(123)	−63	82	536
H(124)	42	190	601
H(125)	161	261	543
H(126)	191	217	416
H(132)	147	−73	277
H(133)	293	−168	363
H(134)	432	−145	513
H(135)	432	−31	574
H(136)	282	72	485
H(212)	−125	228	218
H(213)	−84	337	311
H(214)	−178	340	416
H(215)	−274	231	444
H(216)	−310	120	352
H(222)	−512	51	104
H(223)	−653	−33	127
H(224)	−576	−107	262
H(225)	−362	−92	365
H(226)	−216	−7	338
H(232)	−436	202	183
H(233)	−594	269	64
H(234)	−608	250	−82
H(235)	−462	165	−103
H(236)	−305	98	13

The C–S distances are all close to 1·68 Å implying electron delocalization in the HCS_2 ligand, a view which is further supported by the ^1H n.m.r. spectrum which shows the carbon protons to be very strongly deshielded.[5] Similar delocalization is found in the rhenium complex [11] $Re(CO)_2(HCS_2)(PPh_3)_2$ and in $(PhCS_2)_2Pd$ and its nickel analogue.[12]



ORTEP plot of molecule showing 50% probability ellipsoids and the atom numbering system used in the analysis

Although the dithioformate hydrogen atoms were not revealed in the reported analyses of the rhenium complex [11] they were revealed on our final difference maps in positions close to those expected.

TABLE 3

Molecular geometry about ruthenium

(*a*) Bond lengths (Å)

Ru–P(1)	2·357(2)	C(011)–S(1)	1·70(1)
Ru–P(2)	2·335(3)	C(011)–S(2)	1·68(1)
Ru–S(1)	2·386(3)	C(021)–S(3)	1·68(1)
Ru–S(2)	2·445(3)	C(021)–S(4)	1·67(1)
Ru–S(3)	2·386(3)		
Ru–S(4)	2·448(3)		

(*b*) Bond angles (deg.)

S(1)–Ru–P(2)	96·0	P(1)–Ru–S(1)	96·6
P(2)–Ru–S(3)	95·5	S(1)–Ru–S(2)	71·0
S(3)–Ru–S(4)	71·0	S(2)–Ru–S(4)	85·4
S(4)–Ru–S(1)	94·9	S(4)–Ru–P(1)	87·4
		P(1)–Ru–P(2)	101·3
		P(2)–Ru–S(2)	87·0
		S(2)–Ru–S(3)	94·8
		S(3)–Ru–P(1)	95·3

A *trans*- rather than *cis*-configuration of dithioformate groups might have been expected, to minimize interaction between the two bulky triphenylphosphine groups. The *cis*-configuration could result either from the stereochemistry of the precursor, $RuH_4(PPh_3)_3$ or from the electronic requirements of the dithio-ligands. If π-donation from the metal were important, a *cis*-configuration would be expected. The structure [11] of $Re(HCS_2)(CO)_2(PPh_3)_2$ does not support the electronic argument. In this the dithioformate ligand is *trans* to the two carbonyl groups and, although the carbonyl stretching frequencies are slightly higher than in other comparable rhenium complexes, they are not significantly so. The phenyl rings show no unexpected features and there appear to be no short intermolecular contacts.

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[11] V. G. Albano, P. L. Bellon, and G. Ciani, *J. Organometallic Chem.*, 1971, **31**, 75.

[12] C. Furlani and M. L. Luciani, *Inorg. Chem.*, 1968, **7**, 1587.