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DITHIOMETHYLESTER COMPLEXES OF RUTHENIUM: CRYSTAL STRUCTURES OF η^2-DITHIOMETHYLESTERCARBONYLTOLYLISOCYANIDEBIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II) PERCHLORATE, $[Ru(\eta^2-CS_2Me)(CO)\{CN(p\text{-tolyl})\}(PPh_3)_2]ClO_4.\frac{1}{2}CHCl_3.\frac{1}{2}H_2O$, AND η^2-DITHIOMETHYLESTERDICARBONYLBIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) PERCHLORATE, $[Ru(\eta^2-CS_2Me)(CO)_2(PPh_3)_2]ClO_4.C_6H_{12}$

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Summary

Three-dimensional structures of the title compounds have been investigated by conventional X-ray methods using data collected on an automatic diffractometer. Crystals of $[Ru(\eta^2-CS_2Me)(CO)\{CN(p\text{-tolyl})\}(PPh_3)_2]ClO_4.\frac{1}{2}CHCl_3.\frac{1}{2}H_2O$ are orthorhombic, a = 20.690(4), b = 16.118(3), c = 15.087(2) Å Z = 4, space group $Pna2_1$ or $Pnma$. The two triphenylphosphine ligands are approximately mirror related, while all the remaining atoms of the cation lie close to, or on, the equatorial plane. It has not proved possible to differentiate between real and false mirror planes and thus to distinguish between the two possible space groups. The perchlorate ion and the chloroform and water molecules are disordered. The analysis has established that the dithioester ligand is coordinated through the carbon and unmethylated sulphur atoms.

Crystals of $[Ru(\eta^2-CS_2Me)(CO)_2(PPh_3)_2]ClO_4.C_6H_{12}$ are monoclinic, a = 12.2982(8), b = 23.171(2), c = 14.781(2) Å, β = 100.970(6)°, Z = 4, ρ_c =

1.536 g cm^{-3}, ρ_o = 1.53 g cm^{-3}, space group $P2_1/n$. Least-squares refinement converged with R = 0.072 and R_w = 0.080 for 3049 observed reflections. The cation is monomeric. Coordination about the ruthenium atom is that of a distorted octahedron, in which the triphenylphosphine ligands are mutually *trans*. The dithiomethylester ligand is coordinated through the carbon and the unmethylated sulphur atoms, such that Ru-C is 2.04(1) Å and Ru-S is 2.459(4) Å. The C-S bond distances of 1.67 and 1.64(1) Å are equivalent. The Ru-P bond distances are 2.415 and 2.423(3) Å.

Introduction

A recently-developed synthetic route to thiocarbonyl complexes begins with the reaction of CS_2 on suitable metal species to form π-CS_2 complexes, which can be methylated with MeX[X = I,CF_3SO_3] to form methyl dithioester complexes [1]. Subsequent reaction with aqueous acids liberates methylthiol and forms the coordinated thiocarbonyl ligand [2].

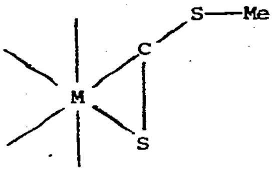
The dithioester ligand, $-CS_2Me$, is believed to be bound through C and S, rather than through two S atoms because:

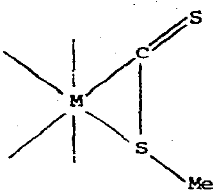
(i) The i.r. spectrum is unlike that reported for the dithioacetate complex $Re(S_2CMe)(CO)_4$ [i.e. ligand bound through two S atoms] [3].

(ii) $Os(CS_2)(CO)_2(PPh_3)_2$, when treated with excess methyl iodide, produced a dithiocarbene complex in which both S atoms of the coordinated $-CS_2$ were methylated, implying that the initial methylation resulting in the methylester group occurred at S rather than C.

(iii) Reaction with acid to produce a thiocarbonyl and liberate methylthiol is likely only for the dithioester mode of coordination.

However, even if this formulation is accepted, there are still two possible isomeric structures for a chelate dithioester:





In order to resolve this ambiguity and to provide structural data for the dithioester ligand we have undertaken the single crystal X-ray structure determinations of two complexes containing this ligand. A preliminary account of the structure of one of the complexes has been communicated previously [4]. We now describe details of the structure determinations of both complexes.

X-ray experimental

The procedures adopted for photography and intensity data collection were similar for both complexes. Preliminary Weissenberg or precession photographs were recorded to establish approximate unit cell sizes and space group symmetries, with accurate cell dimensions being determined from a least-squares refinement to the setting angles of twelve high-theta reflections using a Hilger and Watts four-circle automatic diffractometer [5]. Intensity data were collected using symmetric $2\theta-\omega$ scans with stationary background measurements at each end of the scan range. Three standard reflections were remeasured after every 200 measurements to monitor crystal alignment and stability and to provide scale factors where necessary. The data were corrected for Lorentz and polarisation factors and for absorption [6]. The observed data criterion was $I > 3\sigma(I)$ $\{\sigma(I) = [T + t^2B + (pI)^2]^{\frac{1}{2}}$, T = integrated peak count, B = average background count, t = ratio of scan to background times, p was initially assigned as 0.04 and did not require subsequent modification during the refinement of either complex$\}$[7].

TABLE 1

POSITIONAL PARAMETERS FOR $[\mathrm{Ru}(\eta^2\text{-}\mathrm{CS_2Me})(\mathrm{CO})\{\mathrm{CN}(p\text{-tolyl})\}(\mathrm{PPh_3})_2]$-$\mathrm{ClO_4}\cdot\frac{1}{2}\mathrm{CHCl_2}\cdot\frac{1}{2}\mathrm{H_2O}$ IN SPACE GROUP $Pna2_1$

Atom	*x/a*	*y/b*	*z/c*
Ru	0.3056(2)	-0.0077(3)	0.0052(8)
S(1)	0.4316(8)	-0.0283(9)	-0.0065(22)
S(2)	0.4051(12)	0.1562(11)	0.0160(22)
P(1)	0.3024(9)	-0.0145(15)	-0.1537(17)
P(2)	0.2979(9)	-0.0063(14)	0.1633(13)
Cl(1)	0.4828(6)	-0.3322(7)	0.0143(18)
C(1)	0.261(4)	0.050(6)	0.009(12)
C(2)	0.384(2)	0.061(3)	0.031(4)
C(3)	0.339(4)	0.195(4)	-0.020(7)
C(4)	0.262(2)	-0.123(2)	0.017(5)
O(1)	0.210(2)	0.111(2)	0.001(5)
N	0.244(1)	-0.188(2)	0.015(4)
C(t1)	0.222(2)	-0.265(3)	-0.008(5)
C(t2)	0.153(2)	-0.279(3)	0.012(8)
C(t3)	0.129(2)	-0.360(3)	0.004(8)
C(t4)	0.177(3)	-0.428(4)	0.013(11)
C(t5)	0.236(2)	-0.416(2)	-0.008(6)
C(t6)	0.263(2)	-0.337(3)	-0.001(6)
C(t7)	0.129(3)	-0.516(4)	0.019(6)
Cl(2)	0.477(3)	0.362(4)	0.094(4)
Cl(3)	0.366(2)	0.387(2)	0.006(6)
Cl(4)	0.468(2)	0.347(4)	-0.114(3)
C(5)	0.445(7)	0.401(8)	-0.024(10)
O(2)	0.525(2)	0.402(2)	-0.000(7)
O(3)	0.434(3)	-0.388(3)	0.013(6)
O(4)	0.468(4)	-0.240(6)	-0.028(6)
O(5)	0.516(4)	-0.355(6)	-0.086(6)
O(6)	0.509(5)	-0.361(7)	0.097(9)
Phenyl groups			
Ph1			
C(11)	0.220(1)	0.004(2)	0.808(2)
C(12)	0.172(2)	-0.030(2)	0.846(2)
C(13)	0.108(3)	-0.017(4)	0.796(5)
C(14)	0.099(4)	0.029(4)	0.703(5)

TABLE 1 continued..

C(15)	0.143(4)	0.073(4)	0.703(5)
C(16)	0.215(2)	0.051(2)	0.728(3)
Ph2			
C(21)	0.323(2)	-0.104(2)	0.783(3)
C(22)	0.363(2)	-0.161(3)	0.822(3)
C(23)	0.394(2)	-0.241(3)	0.793(4)
C(24)	0.362(3)	-0.264(4)	0.714(5)
C(25)	0.323(3)	-0.205(4)	0.647(5)
C(26)	0.295(2)	-0.116(2)	0.709(3)
Ph3			
C(31)	0.346(3)	0.078(3)	0.803(4)
C(32)	0.328(3)	0.155(3)	0.811(4)
C(33)	0.358(2)	0.220(3)	0.751(3)
C(34)	0.431(3)	0.188(4)	0.704(4)
C(35)	0.446(3)	0.111(4)	0.709(4)
C(36)	0.405(4)	0.042(4)	0.744(5)
Ph4			
C(41)	0.213(3)	0.008(5)	0.224(5)
C(42)	0.168(4)	-0.060(5)	0.157(6)
C(43)	0.106(2)	-0.032(3)	0.191(3)
C(44)	0.093(2)	-0.011(3)	0.273(3)
C(45)	0.147(2)	0.047(2)	0.328(3)
C(46)	0.202(3)	0.055(4)	0.273(5)
Ph5			
C(51)	0.330(4)	-0.104(4)	0.209(5)
C(52)	0.371(3)	-0.155(4)	0.162(4)
C(53)	0.382(2)	-0.224(3)	0.232(4)
C(54)	0.372(3)	-0.239(3)	0.312(4)
C(55)	0.320(4)	-0.195(5)	0.332(5)
C(56)	0.314(4)	-0.130(5)	0.302(5)
Ph6			
C(61)	0.352(2)	0.070(3)	0.222(3)
C(62)	0.324(2)	0.148(3)	0.226(3)
C(63)	0.373(6)	0.213(7)	0.246(9)
C(64)	0.414(3)	0.208(4)	0.276(4)
C(65)	0.456(5)	0.131(6)	0.264(7)
C(66)	0.412(3)	0.057(3)	0.252(3)

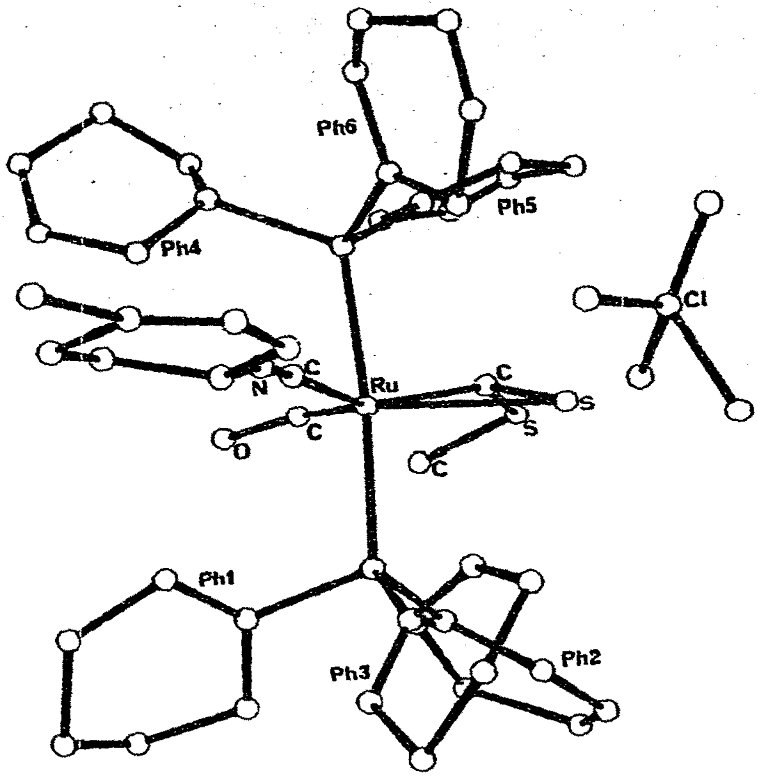


Fig. 1. A general view of $[Ru(\eta^2\text{-}CS_2Me)(CO)\{CN(p\text{-tolyl})\}(PPh_3)_2]ClO_4$. The unreliability of individual atom positions is obvious from the apparent distortions of the phenyl rings.

(a) $[Ru(\eta^2\text{-}CS_2Me)(CO)\{CN(p\text{-tolyl})\}(PPh_3)_2]ClO_4\cdot\frac{1}{2}CHCl_3\cdot\frac{1}{2}H_2O$

Crystal Data

$C_{47}H_{40}NOP_2RuS_2\cdot ClO_4\cdot\frac{1}{2}CHCl_3\cdot\frac{1}{2}H_2O$, M = 1029.09, Orthorhombic needles, a = 20.690(4), b = 16.118(3), c = 15.087(2) Å, V = 5031.23 Å^3, T = 291 K, space groups $Pna2_1$ or $Pnma$ (b and c interchanged), Z = 4, d_c = 1.358, Cu-K_α radiation of λ = 1.5418 Å, Ni filter, μ(Cu-K_α) = 55.28 cm^{-1}, crystal size 0.12 x 0.12 x 0.23 mm, mosaic spread 0.15°, scan range 1.20° in 2θ, scan speed 0.005° s^{-1}, background count times 10 s, theta limit 57°, observed reflections 1165.

The patterson map did not allow differentiation between the two possible space groups. Since the molecule was not expected to possess

TABLE 2

INTERATOMIC DISTANCES (Å) FOR $[Ru(\eta^2\text{-}CS_2Me)(CO)\{CN(p\text{-tolyl})\}(PPh_3)_2]\text{-}ClO_4.\frac{1}{2}CHCl_3.\frac{1}{2}H_2O$ IN SPACE GROUP (i) *Pna*2_1, AND (ii) *Pnma*

	(i)	(ii)
Ru - P(1)	2.40(2)	2.400(8)
Ru - P(2)	2.39(2)	
Ru - S(1)	2.63(2)	2.59(1)
Ru - C(2)	2.02(6)	1.99(2)
Ru - C(1)	1.31(7)	1.10(6)
Ru - C(4)	2.08(6)	2.06(6)
C(1) - O(1)	1.44(9)	1.65(6)
C(2) - S(1)	1.84(6)	1.79(3)
C(2) - S(2)	1.60(6)	1.56(3)
S(2) - C(3)	1.61(9)	1.57(4)
C(4) - N	1.11(7)	1.09(7)
N - C(t1)	1.37(7)	1.37(4)
C(t1) - C(t2)	1.47(9)	1.44(5)
C(t2) - C(t3)	1.41(11)	1.48(6)
C(t3) - C(t4)	1.49(13)	1.52(7)
C(t4) - C(t5)	1.24(12)	1.30(6)
C(t5) - C(t6)	1.39(9)	1.42(5)
C(t6) - C(t1)	1.45(8)	1.39(4)
C(t4) - C(t7)	1.72(13)	1.76(7)
Cl(1) - O(3)	1.35(7)	1.41(4)
Cl(1) - O(4)	1.65(9)	1.51(5)
Cl(1) - O(5)	1.70(9)	1.35(4)
Cl(1) - O(6)	1.44(12)	
C(5) - Cl(2)	1.99(15)	1.80(9)
C(5) - Cl(3)	1.70(15)	1.91(9)
C(5) - Cl(4)	1.67(15)	

Triphenylphosphine ligands only in (i)

P(1) - C(11)	1.82(4)	P(2) - C(41)	1.99(8)
P(1) - C(21)	1.77(4)	P(2) - C(51)	1.84(8)
P(1) - C(31)	1.86(6)	P(2) - C(61)	1.88(5)
Ph1		Ph4	
C(11) - C(12)	1.28(5)	C(41) - C(42)	1.76(12)
C(12) - C(13)	1.53(7)	C(42) - C(43)	1.47(10)
C(13) - C(14)	1.60(9)	C(43) - C(44)	1.43(6)
C(14) - C(15)	1.16(10)	C(44) - C(45)	1.51(6)
C(15) - C(16)	1.58(8)	C(45) - C(46)	1.42(8)
C(16) - C(11)	1.42(5)	C(46) - C(41)	1.08(11)

TABLE 2 continued..

Ph2		Ph5	
C(21) - C(22)	1.37(6)	C(51) - C(52)	1.37(10)
C(22) - C(23)	1.51(7)	C(52) - C(53)	1.56(8)
C(23) - C(24)	1.42(9)	C(53) - C(54)	1.26(8)
C(24) - C(25)	1.60(10)	C(54) - C(55)	1.33(10)
C(25) - C(26)	1.82(8)	C(55) - C(56)	1.16(12)
C(26) - C(21)	1.28(5)	C(56) - C(51)	1.50(11)
Ph3		Ph6	
C(31) - C(32)	1.30(8)	C(61) - C(62)	1.39(7)
C(32) - C(33)	1.52(7)	C(62) - C(63)	1.49(13)
C(33) - C(34)	1.75(7)	C(63) - C(64)	0.97(14)
C(34) - C(35)	1.28(8)	C(64) - C(65)	1.52(11)
C(35) - C(36)	1.50(9)	C(65) - C(66)	1.51(11)
C(36) - C(31)	1.62(9)	C(66) - C(61)	1.34(7)

mirror symmetry, the non-centrosymmetric space group $Pna2_1$ was initially chosen for the structure determination. A structure factor calculation based on the ruthenium atom position gave non-zero amplitudes only when $h + k = 2n$ and the subsequent electron density map contained two false mirror planes. From the map it was possible to deduce the positions of five more atoms, three of which had z coordinates of 0.0 with the other two being symmetrically disposed with respect to the $z = 0$ plane. These peaks were assigned as the two sulphur atoms, the chlorine of the perchlorate, and the phosphorus atoms of the coordinated triphenylphosphines. There was no indication from the shape of the peaks that the two phosphorus atoms were not truly mirror related, and when the phenyl rings were located from subsequent maps they too closely obeyed the mirror symmetry. The perchlorate and chloroform molecules were also symmetric about $z = 0$. Refinement was attempted [8] in both space groups and, with all the heavier atoms (Ru, P, S, Cl) assigned anisotropic thermal motion, returned reliability factors R of 0.207 for space group $Pna2_1$ and 0.195 for space group $Pnma$. The function minimised was $\Sigma w(|Fo|-|Fc|)^2$, with weights $w = 4|Fo|^2/(\sigma^2(Fo)^2)$. Residuals quoted are $R = \Sigma(|Fo|-|Fc|)^2/\Sigma|Fo|^2$ and $R_w = \{\Sigma w(|Fo|-|Fc|)^2/\Sigma w|Fo|^2\}^{\frac{1}{2}}$.

TABLE 3

INTERATOMIC ANGLES (°) FOR $[Ru(\eta^2\text{-}CS_2Me)(CO)\{CN(p\text{-tolyl})\}(PPh_3)_2]\text{-}ClO_4.\frac{1}{2}CHCl_3.\frac{1}{2}H_2O$ IN SPACE GROUP (i) *Pna*2_1 AND (ii) *Pnma*

	(i)	(ii)
P(1) - Ru - P(2)	174(1)	173.4(3)
C(1) - Ru - C(4)	109(5)	114(4)
C(1) - Ru - C(2)	100(4)	93(3)
S(1) - Ru - C(4)	109(2)	109(2)
S(1) - Ru - C(2)	44(2)	43.7(7)
C(1) - Ru - P(1)	85(3)	89(3)
C(2) - Ru - P(1)	82(2)	93.1(8)
C(4) - Ru - P(1)	84(2)	88(2)
S(1) - Ru - P(1)	98(1)	93.0(7)
Ru - C(2) - S(1)	86(1)	86.4(4)
Ru - C(2) - S(2)	136(1)	143.7(6)
S(1) - C(2) - S(2)	124(2)	129.9(9)
C(2) - S(2) - C(3)	101(4)	96(2)
Ru - C(1) - O(1)	173(2)	169(1)
Ru - C(4) - N	170(2)	172(2)
C(4) - N - C(t1)	167(4)	179(4)
N - C(t1) - C(t2)	115(4)	116(2)
N - C(t1) - C(t6)	121(3)	124(2)
C(t1) - C(t2) - C(t3)	119(4)	122(2)
C(t2) - C(t3) - C(t4)	115(5)	106(3)
C(t3) - C(t4) - C(t5)	122(5)	135(3)
C(t4) - C(t5) - C(t6)	124(6)	113(3)
C(t5) - C(t6) - C(t1)	121(4)	123(2)
C(t6) - C(t1) - C(t2)	115(4)	121(2)
C(t3) - C(t4) - C(t7)	103(4)	101(2)
O(3) - Cl(1) - O(4)	117(4)	123(2)
O(3) - Cl(1) - O(5)	98(4)	106(2)
O(3) - Cl(1) - O(6)	95(6)	106(2)
O(4) - Cl(1) - O(5)	86(4)	102(2)
O(4) - Cl(1) - O(6)	134(6)	102(2)
O(5) - Cl(1) - O(6)	123(6)	120
Cl(2) - C(5) - Cl(3)	92(3)	93(1)
Cl(2) - C(5) - Cl(4)	118(3)	124.8
Cl(3) - C(5) - Cl(4)	115(3)	93(1)

TABLE 3 continued..

Triphenylphosphine Ligands only in (i)

Ru - P(1) - C(11)	110(1)	Ru - P(2) - C(41)	121(2)
Ru - P(1) - C(21)	124(1)	Ru - P(2) - C(51)	110(2)
Ru - P(1) - C(31)	108(1)	Ru - P(2) - C(61)	117(2)
Ph1		Ph4	
C(11) - C(12) - C(13)	112(3)	C(41) - C(42) - C(43)	94(3)
C(12) - C(13) - C(14)	128(3)	C(42) - C(43) - C(44)	128(4)
C(13) - C(14) - C(15)	100(4)	C(43) - C(44) - C(45)	122(3)
C(14) - C(15) - C(16)	128(4)	C(44) - C(45) - C(46)	107(4)
C(15) - C(16) - C(11)	113(3)	C(45) - C(46) - C(41)	121(5)
C(16) - C(11) - C(12)	124(3)	C(46) - C(41) - C(42)	135(5)
Ph2		Ph5	
C(21) - C(22) - C(23)	135(3)	C(51) - C(52) - C(53)	101(4)
C(22) - C(23) - C(24)	106(4)	C(52) - C(53) - C(54)	139(4)
C(23) - C(24) - C(25)	128(4)	C(53) - C(54) - C(55)	105(4)
C(24) - C(25) - C(26)	108(3)	C(54) - C(55) - C(56)	119(5)
C(25) - C(26) - C(21)	115(3)	C(55) - C(56) - C(51)	127(5)
C(26) - C(21) - C(22)	123(3)	C(56) - C(51) - C(52)	117(4)
Ph3		Ph6	
C(31) - C(32) - C(33)	119(4)	C(61) - C(62) - C(63)	112(5)
C(32) - C(33) - C(34)	113(3)	C(62) - C(63) - C(64)	129(4)
C(33) - C(34) - C(35)	119(3)	C(63) - C(64) - C(65)	122(8)
C(34) - C(35) - C(36)	127(4)	C(64) - C(65) - C(66)	108(3)
C(35) - C(36) - C(31)	111(3)	C(65) - C(66) - C(61)	119(5)
C(36) - C(31) - C(32)	128(5)	C(66) - C(61) - C(62)	121(3)

Atomic scattering factors used were from standard listings with those for the heavier atoms corrected for dispersion effects [9].

A Fourier map, computed in space group *Pnma* and using input phased on the ruthenium atom alone, contained no false mirror symmetry. In an attempt to relocate the atoms from this map it was found that one of the sulphur atoms should have been transposed to the opposite side of the second mirror plane in the first $Pna2_1$ map. It was also concluded that the chloroform molecule should be half-weighted and that an extra peak which was present corresponded to a half-weighted water molecule. With these corrections, least-

TABLE 4

POSITIONAL PARAMETERS FOR $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4\cdot C_6H_{12}$

Atom	*x/a*	*y/b*	*z/c*
Ru	0.2025(1)	0.0727(0)	0.3522(1)
P(1)	0.2009(5)	0.1622(1)	0.4358(2)
P(2)	0.2878(4)	0.4800(1)	0.2217(2)
S(1)	0.3696(4)	0.0469(1)	0.4647(2)
S(2)	0.4653(4)	0.1038(1)	0.3102(3)
Cl	−0.2576(5)	0.1139(2)	0.1534(3)
C(1)	0.1484(14)	0.1102(5)	0.2382(10)
C(2)	0.0562(19)	0.0524(5)	0.3813(9)
C(3)	0.3704(13)	0.0796(5)	0.3643(9)
C(4)	0.5955(15)	0.0928(7)	0.3891(11)
O(1)	0.1206(11)	0.1331(4)	0.1720(6)
O(2)	−0.0207(11)	0.0376(5)	0.4008(8)
O(3)	−0.1922(28)	0.0886(14)	0.2107(23)
O(4)	−0.3141(17)	0.0761(8)	0.0866(13)
O(5)	−0.3313(18)	0.1468(9)	0.1927(14)
O(6)	−0.2093(20)	0.1573(9)	0.1029(15)
C(5)	0.3524(16)	0.0972(7)	−0.0328(11)
C(6)	0.4366(27)	0.1406(12)	0.0543(20)
C(7)	0.4485(22)	0.1943(9)	0.1065(13)
C(8)	0.3790(33)	0.1807(12)	0.1213(18)
C(9)	0.3081(29)	0.1652(11)	0.0978(18)
C(10)	0.3276(28)	0.1207(12)	−0.0194(24)
Phenyl groups			
Ph1			
C(11)	0.3334(13)	0.2001(5)	0.4547(9)
C(12)	0.4017(17)	0.2018(7)	0.5424(11)
C(13)	0.5051(21)	0.2317(9)	0.5534(15)
C(14)	0.5345(21)	0.2573(10)	0.4733(17)
C(15)	0.4666(18)	0.2583(7)	0.3913(12)
C(16)	0.3618(16)	0.2268(6)	0.3786(11)
Ph2			
C(21)	0.1709(12)	0.1537(5)	0.5517(8)
C(22)	0.1549(14)	0.2034(6)	0.5999(10)
C(23)	0.1338(15)	0.1978(6)	0.6890(10)
C(24)	0.1283(15)	0.1428(6)	0.7304(10)
C(25)	0.1461(13)	0.0947(6)	0.6808(9)
C(26)	0.1646(13)	0.0996(6)	0.5898(9)

TABLE 4 continued..

Ph3			
C(31)	0.1019(13)	0.2168(5)	0.3830(8)
C(32)	0.0017(15)	0.1992(6)	0.3335(10)
C(33)	-0.0826(15)	0.2400(6)	0.2955(10)
C(34)	-0.0527(18)	0.2986(7)	0.3086(12)
C(35)	0.0497(17)	0.3162(7)	0.3551(12)
C(36)	0.1312(14)	0.2761(6)	0.3951(9)
Ph4			
C(41)	0.1065(12)	-0.0339(5)	0.1777(8)
C(42)	0.1277(12)	-0.0768(6)	0.1115(9)
C(43)	0.0399(14)	-0.0907(5)	0.0362(9)
C(44)	-0.0652(14)	-0.0665(6)	0.0310(9)
C(45)	-0.0852(13)	-0.0254(5)	0.0942(9)
C(46)	0.0024(13)	-0.0098(5)	0.1678(9)
Ph5			
C(51)	0.3466(12)	-0.0314(5)	0.2451(8)
C(52)	0.4304(14)	-0.0537(5)	0.3046(9)
C(53)	0.5401(15)	-0.0539(6)	0.2842(10)
C(54)	0.5587(16)	-0.0326(7)	0.2026(12)
C(55)	0.4661(17)	-0.0121(7)	0.1379(12)
C(56)	0.3565(15)	-0.0092(6)	0.1572(10)
Ph6			
C(61)	0.1952(13)	-0.0830(5)	0.3508(9)
C(62)	0.1704(12)	-0.0756(6)	0.4371(9)
C(63)	0.1557(14)	-0.1259(6)	0.4897(10)
C(64)	0.1691(15)	-0.1802(7)	0.4536(11)
C(65)	0.1990(16)	-0.1867(7)	0.3710(11)
C(66)	0.2159(13)	-0.1373(6)	0.3164(9)

squares refinement initially with phenyl rings described as rigid groups - and later with individual isotropic carbon atoms, reduced the residuals R and R_w to 0.116 and 0.117 for *Pnma* and 0.110 and 0.109 for $Pna2_1$. Since this difference was not significant it appeared that the data would not allow a distinction to be made between a slightly disordered molecule in space group *Pnma* and true differences between the two halves of the molecule in space group $Pna2_1$. Refinement was therefore terminated with the distinction unresolved. Atom positions resulting from the refinement in space group $Pna2_1$ are given in Table 1. The atomic numbering scheme is shown in Fig. 1.

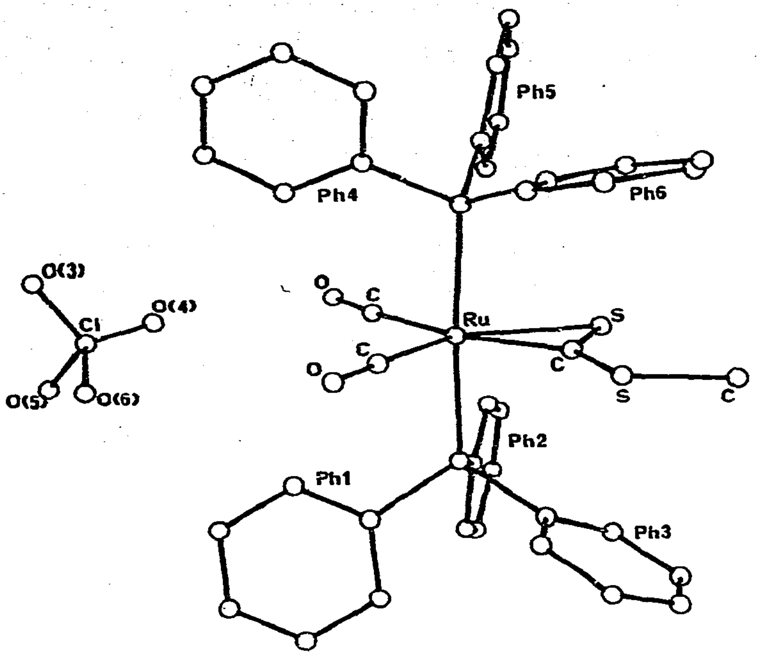


Fig. 2. A general view of $[Ru(\eta^2-CS_2Me)(CO)_2(PPh_3)_2]ClO_4$.

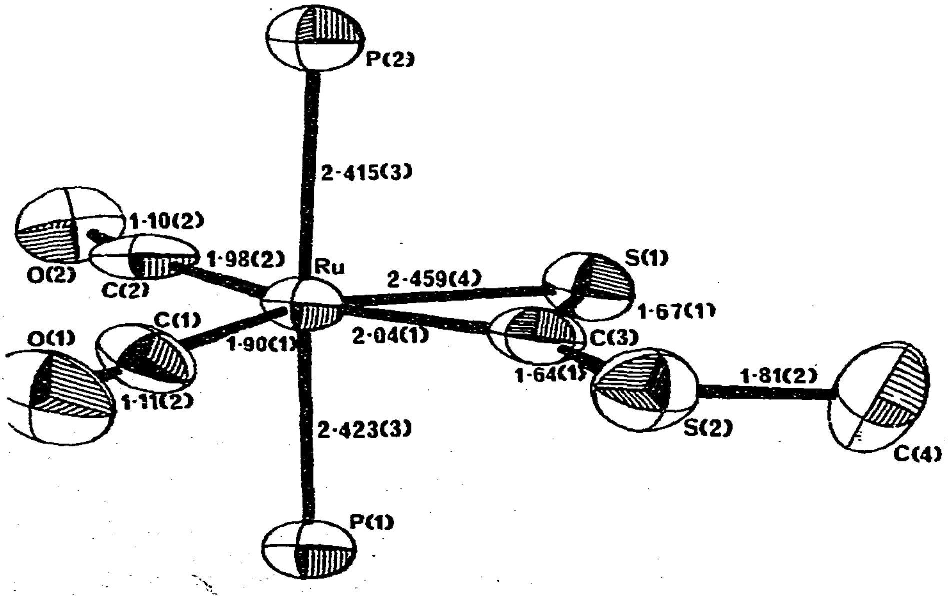


Fig. 3. Coordination geometry in $[Ru(\eta^2-CS_2Me)(CO)_2(PPh_3)_2]ClO_4$.
The anisotropic thermal ellipsoids represent 50% probability boundaries.

Tables of thermal parameters and observed and calculated structure factors are available on request from the authors (G.R.C.).

(b) $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4.C_6H_{12}$

Crystal Data

$C_{40}H_{33}O_2P_2RuS_2.ClO_4.C_6H_{12}$, M = 956.40, Monoclinic needles, a = 12.2982(8), b = 23.171(2), c = 14.781(2) Å, β = 100.970(6)°, V = 4135.05 Å^3, T = 291 K, space group $P2_1/n$ (No. 14 alternative setting), Z = 4, d_o = 1.53, d_c = 1.536, Cu-K_α radiation of λ = 1.5418 Å, Ni filter, μ(Cu-K_α) = 58.09 cm^{-1}, crystal size 0.28 x 0.07 x 0.18 mm, mosaic spread 0.15°, scan range 1.60° in 2θ, scan speed 0.005° s^{-1}, background count times 30 s, theta limit 55°, observed reflections 3049.

The structure was solved by conventional Patterson and Fourier synthesis and refined using the full-matrix least-squares equations. The carbon atoms of the cyclohexane molecule (disordered) and phenyl groups, and the oxygen atoms of the perchlorate anion, were restricted to isotropic temperature factors, all other non-hydrogen atoms were assigned anisotropic thermal parameters. Final residuals were R = 0.072 and R_w = 0.080. Final atomic positions are listed in Table 4. The atomic numbering scheme is outlined in Figs. 2 and 3. Tables of thermal parameters and observed and calculated structure factors are available on request from the authors (G.R.C.).

Description of the crystal structures

(a) The structure of $[Ru(\eta^2\text{-}CS_2Me)(CO)\{CN(p\text{-tolyl})\}(PPh_3)_2]ClO_4$.

A detailed description of the first structure attempted will not be made because of the high standard deviations in the atom parameters, the large values of R and R_w when work was terminated and the incomplete refinement of the model. However, a few general observations can be made. There is no doubt that the basic structure is correct and that the complex exists as monomeric ions as depicted in Fig. 1. The mode of coordination of the dithiomethylester ligand is with the methyl group bonded to the uncoordinated sulphur atom. However, the lack of accuracy in the atom positions means that little significance can be attached to specific bond lengths and angles. Disorder is evident in both the -CO and -CNR ligands and, although the Ru-P distances are within the expected range, there is considerable variation in the angles about the phosphorus atom and in the P-C distances. The phenyl rings were initially refined as rigid bodies but, on the final cycles when the carbon atoms were allowed to refine individually, considerable distortion from regular planar rings resulted.

The diagram (Fig. 1) and atom parameters (Table 1) have been given for the noncentrosymmetric space group $Pna2_1$ while bond distances and angles for both space groups are listed in Tables 2 and 3.

(b) The structure of $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)]ClO_4.C_6H_{12}$.

Fig. 2 shows a general view of this molecule, fig. 3 shows the inner coordination sphere with thermal ellipsoids representing 50% probability boundaries, and fig. 4 shows the molecular packing.

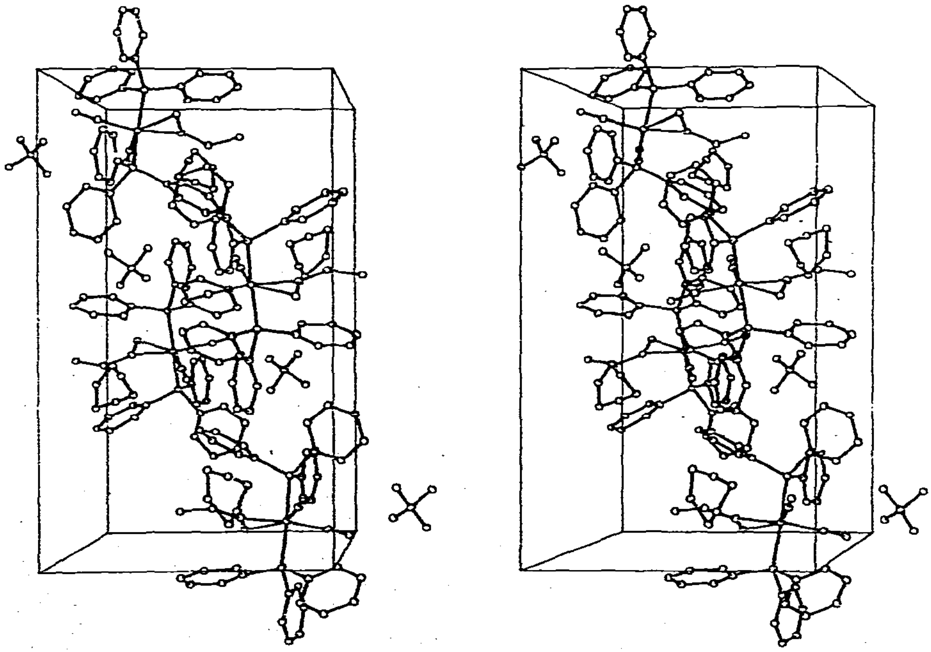
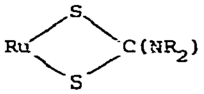


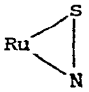
Fig. 4. A stereoscopic view of the molecular packing of $[Ru(\eta^2\text{-}CS_2Me)(CO)_2\text{-}(PPh_3)_2]ClO_4.C_6H_{12}$.

The crystal structure consists of monomeric ions. Coordination about the ruthenium atom is that of a distorted octahedron with the triphenylphosphine ligands mutually *trans* and the carbonyl and dithiomethylester ligands lying in the equatorial plane.

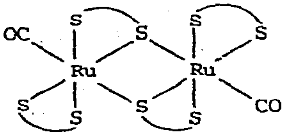
The dithiomethylester ligand is coordinated through the carbon and the *unmethylated* sulphur atom contrary to predictions based on i.r. stretching frequencies [4]. The Ru-C distance for this ligand, 2.04(1), is slightly longer than the sum of the covalent radii [10] and is within the range of Ru-C distances found in Ru-CO ligands [11]. The Ru-S distance of 2.459(4) is the longest Ru-S bond length reported for bonding of ruthenium to non-bridged sulphur atoms. For ruthenium dithiocarboxamido complexes where the ligands are bound through two sulphur atoms, i.e.



the average value of the Ru-S bond is 2.395(4) when R = CH_3CH_2 [12] and 2.400(7) when R = isopropyl [13] giving a range of values 2.386 - 2.414. When the pyridine-2-thiolato ligand is bound to ruthenium through both S and N, i.e.



Ru-S distances of 2.434(2) and 2.437(2) are found [14] which are significantly longer than for the thiocarboxamido ligands but considerably shorter than Ru-S for the dithioester ligand. Similarly, for the compound $Ru(HCS_2)_2(PPh_3)_2$, the Ru-S distances are 2.386, 2.386, 2.445, 2.448(3), with the longer distances being for bonds which are *trans* to the phosphine ligand and the shorter distances for bonds *trans* to the sulphur of the other thiocarboxamido ligand [15]. It is of interest, however, that in the compound



where the sulphurs are bridged by $CN(CH_3CH_2)_2$ [12], the Ru-S distances for the bridging sulphur atoms differ significantly with different ligands *trans* to the sulphur atom. If the bridging S is *trans* to the sulphur of another thiocarboxamido ligand then Ru-S distances are 2.397(4) and 2.400(4) but if S is *trans* to a -CO ligand then the Ru-S distances are 2.535(4) and 2.570(3). The carbonyl ligand thus appears to have a greater *trans* influence than the thiocarboxamido sulphur atoms. Since the Ru-S bond distances quoted above are all for complexes where the *trans* ligand is another thiocarboxamido or related group, the increase in the Ru-S bond distance in the dithioester complex can be explained by the *trans* influence of the carbonyl ligand which lies *trans* to the S atom of the bidentate ligand.

The C-S bond distances in the ligand, 1.67(1) and 1.64(1), are equivalent and are intermediate between C-S single bonds (which are generally found in the range 1.79 - 1.86) [16] and C=S double bonds (which are found to be 1.55 - 1.56) [17]. This implies that there is some degree of multiple bonding in the C-S bonds in the ligand and this compares favourably with C-S bonding in other carbenoid complexes where S is one of the heteroatoms [18-20]. It has been postulated [18] that this bonding is the result of delocalisation of the unhybridised p_z orbital of the carbon atom between the neighbouring heteroatoms, thus increasing the bond order to *ca* 1.5. The S-CH_3 distance of 1.81(2) is in the range for C-S single bonds mentioned earlier and is equivalent to the S-CH_3 bond distance in the monohaptodithioester complex [19]. The angle of the methylated sulphur, 105.3(7)°, is also equivalent to the angle in the monohaptoester but less than the tetrahedral angle because of the lone pair interaction on the sulphur atom.

The dithioester ligand is not planar as S(2) is 0.01 Å out of the plane of the ruthenium and the coordinating S and C atoms and the methyl carbon is displaced 0.14 Å in the same direction as the sulphur.

The Ru-CO distances, 1.98(2) and 1.90(1), although differing from one another, are typical of those previously reported for ruthenium carbonyls. The increase in the bond distance when -CO is *trans* to the carbon atom of the dithioester ligand reflects the π-acceptor ability of the carbenoid carbon atom. The -CO distances are equivalent (1.11(2), 1.10(2)) and

TABLE 5

INTERATOMIC DISTANCES (Å) FOR $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4 \cdot C_6H_{12}$

Coordination Sphere			
Ru - P(1)	2.415(3)	C(1) - O(1)	1.110(17)
Ru - P(2)	2.423(3)	C(2) - O(2)	1.095(19)
Ru - S(1)	2.459(4)	C(3) - S(1)	1.667(13)
Ru - C(1)	1.899(14)	C(3) - S(2)	1.635(13)
Ru - C(2)	1.984(16)	S(2) - C(4)	1.810(16)
Ru - C(3)	2.043(13)		
Triphenylphosphine ligands			
P(1) - C(11)	1.825(13)	P(2) - C(41)	1.808(12)
P(1) - C(21)	1.830(12)	P(2) - C(51)	1.831(12)
P(1) - C(31)	1.826(13)	P(2) - C(61)	1.845(19)
Ph1		Ph4	
C(11) - C(12)	1.41(2)	C(41) - C(42)	1.45(2)
C(12) - C(13)	1.43(3)	C(42) - C(43)	1.42(2)
C(13) - C(14)	1.43(3)	C(43) - C(44)	1.40(2)
C(14) - C(15)	1.34(2)	C(44) - C(45)	1.39(2)
C(15) - C(16)	1.46(2)	C(45) - C(46)	1.42(2)
C(16) - C(11)	1.39(2)	C(46) - C(41)	1.38(2)
Ph2		Ph5	
C(21) - C(22)	1.39(2)	C(51) - C(52)	1.33(2)
C(22) - C(23)	1.40(2)	C(52) - C(53)	1.44(2)
C(23) - C(24)	1.42(2)	C(53) - C(54)	1.36(2)
C(24) - C(25)	1.38(2)	C(54) - C(55)	1.42(2)
C(25) - C(26)	1.41(2)	C(55) - C(56)	1.43(2)
C(26) - C(21)	1.38(2)	C(56) - C(51)	1.43(2)
Ph3		Ph6	
C(31) - C(32)	1.37(2)	C(61) - C(62)	1.38(3)
C(32) - C(33)	1.44(2)	C(62) - C(63)	1.43(2)
C(33) - C(34)	1.41(2)	C(63) - C(64)	1.39(2)
C(34) - C(35)	1.38(2)	C(64) - C(65)	1.35(2)
C(35) - C(36)	1.41(2)	C(65) - C(66)	1.44(2)
C(36) - C(31)	1.42(2)	C(66) - C(61)	1.40(2)
Anion ClO_4^-			
Cl - O(3)	1.20(3)	Cl - O(5)	1.39(2)
Cl - O(4)	1.40(2)	Cl - O(6)	1.45(2)
Solvent C_6H_{12}			
C(5) - C(6)	1.80(3)	C(8) - C(9)	0.95(4)
C(6) - C(7)	1.46(4)	C(9) - C(10)	2.07(4)
C(7) - C(8)	0.98(4)	C(10) - C(5)	0.67(3)

TABLE 6

INTERATOMIC ANGLES (°) FOR $[Ru(n^2-CS_2Me)(CO)_2(PPh_3)_2]ClO_4 \cdot C_6H_{12}$

Coordination Sphere			
P(1) - Ru - P(2)	175.9(1)	S(1) - C(3) - S(2)	135.7(3)
S(1) - Ru - C(3)	42.2(4)	C(3) - S(2) - C(4)	105.3(7)
C(1) - Ru - C(2)	97.0(8)	Ru - C(1) - O(1)	177.3(5)
C(2) - Ru - S(1)	118.1(5)	Ru - C(2) - O(2)	174.6(6)
P(1) - Ru - C(2)	91.5(4)	P(1) - Ru - S(1)	87.1(1)
P(1) - Ru - C(1)	91.1(2)	P(1) - Ru - C(3)	89.7(4)
Triphenylphosphine Ligands			
Ru - P(1) - C(11)	113.4(4)	Ru - P(2) - C(41)	116.1(4)
Ru - P(1) - C(21)	114.2(4)	Ru - P(2) - C(51)	111.9(4)
Ru - P(1) - C(31)	116.5(4)	Ru - P(2) - C(61)	114.7(6)
Ph1		Ph4	
C(11) - C(12) - C(13)	118.8(10)	C(41) - C(42) - C(43)	118.2(7)
C(12) - C(13) - C(14)	117.8(12)	C(42) - C(43) - C(44)	120.3(8)
C(13) - C(14) - C(15)	123.2(12)	C(43) - C(44) - C(45)	121.2(8)
C(14) - C(15) - C(16)	119.4(12)	C(44) - C(45) - C(46)	118.9(8)
C(15) - C(16) - C(11)	118.1(9)	C(45) - C(46) - C(41)	122.1(8)
C(16) - C(11) - C(12)	122.5(10)	C(46) - C(41) - C(42)	119.2(8)
Ph2		Ph5	
C(21) - C(22) - C(23)	118.5(8)	C(51) - C(52) - C(53)	120.3(12)
C(22) - C(23) - C(24)	121.6(9)	C(52) - C(53) - C(54)	120.4(13)
C(23) - C(24) - C(25)	118.2(9)	C(53) - C(54) - C(55)	117.9(14)
C(24) - C(25) - C(26)	120.9(9)	C(54) - C(55) - C(56)	123.0(15)
C(25) - C(26) - C(21)	119.6(8)	C(55) - C(56) - C(51)	114.4(12)
C(26) - C(21) - C(22)	121.2(9)	C(56) - C(51) - C(52)	123.7(12)
Ph3		Ph6	
C(31) - C(32) - C(33)	121.5(8)	C(61) - C(62) - C(63)	118.3(13)
C(32) - C(33) - C(34)	115.5(10)	C(62) - C(63) - C(64)	119.6(14)
C(33) - C(34) - C(35)	122.9(10)	C(63) - C(64) - C(65)	121.4(14)
C(34) - C(35) - C(36)	121.6(10)	C(64) - C(65) - C(66)	120.9(15)
C(35) - C(36) - C(31)	116.1(9)	C(65) - C(66) - C(61)	117.2(14)
C(36) - C(31) - C(32)	122.3(14)	C(66) - C(61) - C(62)	122.4(14)
Anion ClO_4^-			
O(3) - Cl - O(4)	114.4(17)	O(4) - Cl - O(5)	111.2(11)
O(3) - Cl - O(5)	112.0(17)	O(4) - Cl - O(6)	105.6(11)
O(3) - Cl - O(6)	114.7(17)	O(5) - Cl - O(6)	101.5(11)
Solvent C_6H_{12}			
C(5) - C(6) - C(7)	147.5(13)	C(8) - C(9) - C(10)	104.5(23)
C(6) - C(7) - C(8)	80.7(23)	C(9) - C(10) - C(5)	141.4(20)
C(7) - C(8) - C(9)	145.8(27)	C(10) - C(5) - C(6)	64.4(29)

TABLE 7

INTERMOLECULAR APPROACHES <3.5 Å for $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4\cdot C_6H_{12}$

O(1) - C(43)^2	3.47	C(23) - C(6)^3	3.45
O(1) - C(44)^2	3.33	C(22) - C(6)^3	3.49
O(2) - O(2)^2	3.37	C(43) - C(45)^2	3.42
O(2) - C(62)^2	3.40	C(44) - C(9)^2	3.44
O(2) - C(63)^2	3.26	C(54) - C(5)^2	3.28
C(64) - C(6)^4	3.29	C(65) - C(7)^4	3.23
C(64) - C(7)^4	3.42	C(65) - C(8)^4	3.47
C(65) - C(6)^4	3.35		

Atom transformations				
	2	−x	−y	−z
	3	½+x	½−y	½+z
	4	½−x	½+y	½−z

within the expected range. However, the Ru-C-O angles (177.3(5) and 174.6(6)) do deviate from linearity, presumably as the result of the packing of the molecules into the unit cell. The compactness of the packing can be seen from Table 7 which shows O(1) to be <3.5 Å from a phenyl ring, while O(2) is closer than 3.5 Å to another phenyl ring and a symmetry related oxygen atom.

The angle made at the ruthenium atom by the two carbonyl ligands (97.0(8)) is larger than the angle of a regular octahedron but is a result of the distortion introduced by coordination of a bidentate ligand.

Packing of the triphenylphosphines places the phenyl rings in approximately mirror related positions but the angle at which the groups are oriented leads to distortion from mirror symmetry as can be seen in Fig. 4. There are several close intermolecular contacts (<3.5 Å) (Table 7) but of these only two are between phenyl rings.

The perchlorate anion is distorted from ideal tetrahedral symmetry as can be seen from the variation in bond lengths (1.20(3) - 1.45(2)) and bond angles about the chlorine atom (101(1) - 115(2)). This disorder is reflected in the large isotropic temperature parameters of the oxygen atoms and is probably the result of packing forces in the crystal as the anion is sandwiched between the carbonyl ligands and the solvent molecule.

Packing forces in the crystal could also account for the disorder in the solvent molecule since most of the atoms in the cyclohexane ring are less than 3.5 Å from the atoms of other molecules. It is also possible that each cyclohexane molecule takes up a slightly different orientation in the crystal and the distorted molecule we have found is merely the average of these.

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