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COORDINATED CSe. THE CRYSTAL AND MOLECULAR STRUCTURE OF DICHLOROCARBONYLSELENOCARBONYLBIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II), $RuCl_2(CO)(CSe)(PPh_3)_2$

GEORGE R. CLARK * and SUZANNE M. JAMES
Department of Chemistry, University of Auckland, Auckland (New Zealand)

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Summary

Single crystal X-ray analysis reveals that $RuCl_2(CO)(CSe)(PPh_3)_2$ is monoclinic, $a = 10.470(1)$, $b = 23.446(2)$, $c = 14.507(2)$ Å, $\beta = 94.75(1)°$, $Z = 4$, space group $P2_1/n$, $D_m = 1.508$ g cm^{-3}, $D_c = 1.525$ g cm^{-3}. The structure has been solved using conventional Patterson and Fourier syntheses and refined by least-squares methods to final residuals R and R_w of 0.074 and 0.091 respectively using 2208 observed reflections collected with an automated diffractometer. The benzene rings of the triphenylphosphine ligands have been constrained as rigid groups, all other non-hydrogen atoms have been assigned anisotropic thermal parameters. The complex is monomeric. The Ru coordination is octahedral with *cis*-CO and -CSe (linear), *cis*-chlorides, and *trans*-phosphines. The Ru—P distances are 2.425, 2.430(7), Ru—CO is 1.85(3), Ru—CSe is 1.83(3) Å. The *trans* influence of the —CSe ligand is very strong, as shown by the difference between the Ru—Cl distances (2.477, 2.428(6) Å).

Introduction

Since the preparation of *trans*-$RhX(CS)(PPh_3)_2$ (X = Cl, Br) by Baird and Wilkinson [1] in 1966, syntheses of transition metal—thiocarbonyl complexes have steadily increased, until a substantial number have now been formed with a variety of different transition metals [2—8]. Physical properties and chemical reactivity indicate that coordinated —CS ligands are excellent σ-donors, and are stronger π-acceptors than —CO [2,7—13]. Crystal structure analyses of *trans*-$RhCl(CS)(PPh_3)_2$ [14], $[Ir(CO)_2(CS)(PPh_3)_2]PF_6 \cdot Me_2CO$ [15], *trans*-$W(CO)_4(CNC_6H_{11})(CS)$ [16], $(\pi\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$ [17], and $(\pi\text{-}C_6H_5CO_2CH_3)Cr(CO)_2(CS)$ [18] show that thiocarbonyl complexes are characterised by linear metal—CS coordination, with short metal—C and long C—S bonds. The C—S distance has been correlated with ν_{cs} [16].

Attempts have been made to prepare analogous metal selenocarbonyl complexes, even though the CSe molecule itself has not been isolated [19]. Using an indirect synthetic route, Butler et al. have succeeded in stabilising the CSe by coordination to the metal atoms in the complexes (π-C_5H_5)Mn$(CO)_2$(CSe) and (π-$C_6H_5CO_2CH_3$)Cr$(CO)_2$(CSe) [20]. In the mass spectra, fragments due to loss of CSe with retention of CO are of low abundance, suggesting very strong metal—CSe bonding. Since metal—isoselenocarbonyl bonding could not be discounted, an X-ray study is reported to have been initiated [20], but no results have yet been published. Meanwhile, techniques developed for the chemical conversion of π-bonded —CS_2 to —CS [21,22] have been successfully applied to the CSe_2 system producing some ruthenium selenocarbonyl complexes. Their preparation, and a preliminary account of the crystal structure of $RuCl_2$(CO)(CSe)-$(PPh_3)_2$ have recently been reported [23]. Details of the refined crystal structure are now presented.

Experimental

Crystals were generously supplied by Dr. R.O. Harris, University of Toronto. Preliminary X-ray photography showed the crystals to belong to the monoclinic system with systematic absences ($h0l$ $h + l = 2n + 1$; $0k0$ $k = 2n + 1$) characteristic of the centrosymmetric space group $P2_1/n$. Accurate unit cell dimensions

TABLE 1

SUMMARY OF CRYSTAL DATA AND INTENSITY DATA COLLECTION

Compound: Dichlorocarbonylselenocarbonylbis(triphenylphosphine)ruthenium(II), $RuCl_2(CO)(CSe)$-$(PPh_3)_2$
Formula: $C_{38}H_{30}Cl_2OP_2RuSe$
Molecular weight: 815.54
Crystal habit: Needles with approximately hexagonal cross-section
$a = 10.470 \pm 0.001$ Å
$b = 23.446 \pm 0.002$ Å
$c = 14.507 \pm 0.002$ Å
$\beta = 93.75 \pm 0.01°$
$V = 3619$ Å^3
$Z = 4$
$\rho_c = 1.525$ g cm^{-3}
$\rho_o = 1.51$ g cm^{-3} (by flotation in $CHCl_3/CCl_4$)
Space group: $P2_1/n$ (No. 14, alternative setting)
Crystal dimensions: 0.14 × 0.12 × 0.10 mm
Crystal faces: (2 0 1, —2 0 1, 0 1 0, 0 1 1, 0 —1 1, 0 —1 0, 0 —1 —1, 0 1 —1)
Mosaic spread: 0.30°
Temperature: 291 K
X-radiation: CuK_α, $\lambda = 1.5418$ Å
$\mu = 74.14$ cm^{-1}
Primary collimator: 0.7 mm
Secondary collimator: 5.0 mm
Take-off angle: 4°
Scan speed: 2° in 2θ per second, using $2\theta/\omega$ scan.
Scan range: Symmetric scan of 1.20° in 2θ.
Background: 10 s stationary count at each end of scan range.
θ limits: 0—57°.
Standard reflections: 3 standards remeasured after every 200 reflections. Maximum variation 3.8%.
Observed data criterion: 2208 unique reflections with $I > 3\sigma(I)$.
Number of refined variables: 160.

were derived by a least squares fit to the diffractometer setting angles [24] of 12 reflections (representative of all regions of reciprocal space and in the theta range $15.4° < \theta < 32.8°$). Unit cell parameters and details of intensity data collection on a Hilger and Watts Y290 computer controlled diffractometer are given in Table 1. Although the crystal mosacity was greater than that generally considered acceptable for the $2\theta/\omega$ scan technique the importance of the compound justified the acceptance of this particular crystal. (All other crystals tested were found to have an even greater mosaic spread.) The generally satisfactory refinement and physically meaningful thermal parameters and standard deviations indicate that the effects of the large mosaic spread did not adversely affect the structure refinement.

The intensities of 5158 unique reflections were measured. Of these, 2208 were considered observed, $[I > 3\sigma(I)]$, and were used in subsequent calculations $(\sigma(I) = (T + [t/(t_1 + t_2)]^2(B_1 + B_2) + (pI)^2)^{1/2}$, where T is the total counts in time t, B_1 and B_2 are background counts in times t_1 and t_2. The value assigned to p was 0.04, but this was later increased to 0.06 as a result of a weighting scheme agreement analysis [25]. The data were corrected for Lorentz and polarisation effects, and for absorption (maximum and minimum transmission coefficients were 0.5658 and 0.4231 respectively [26]. Seven reflections whose count rates exceeded 8000 c s^{-1} were remeasured after insertion of an aluminium foil attenuator.

Structure determination and refinement

The position of the ruthenium atom was deduced from a threedimensional Patterson synthesis and all other non-hydrogen atoms were located from subsequent electron density maps. The structure was then refined using full matrix least squares techniques [27]. The atomic scattering factors used were tabulated values, corrected for the real component of dispersion [28]. The six phenyl groups were refined as rigid planar bodies with constant C—C distances of 1.392 Å and isotropic thermal parameters. The function minimised was $\Sigma w(|F_o|-|F_c|)^2$, with weights being $4F_o{}^2/\sigma^2(F^2)$. The residuals quoted below are $R = \Sigma(|F_o - F_c|)/\Sigma F_o$, $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2}$. After two least squares cycles employing isotropic temperature factors, first the ruthenium and selenium atoms ($R = 0.080$, $Rw = 0.090$), and then all remaining non-group atoms ($R = 0.077$, $Rw = 0.088$) were allowed to assume anisotropic thermal parameters. This model appeared satisfactorily, but on examination of a weighting scheme agreement analysis it was obvious that the more intense reflections were generally being overweighted in the least squares equations. Accordingly, the parameter 'p' in the σ calculation was increased to 0.06, and the structure was refined through two further cycles employing the new weights ($R = 0.074$, $Rw = 0.091$). A weighting analysis then showed that the contributions to the least squares equations of reflections in all F_o regions were approximately equal and refinement was terminated. The differences between F_o and F_c for the most intense reflections were random, indicating no extinction effects. A final "difference" electron density synthesis was then computed, and the absence of any large paeks indicated that there were no solvent molecules present.

Final positions and thermal parameters for individual atoms together with

TABLE 2

FINAL ATOMIC AND RIGID GROUP PARAMETERS FOR $RuCl_2(CO)(CSe)(PPh_3)_2$ [a]

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.1526(2)	0.0459(1)	0.2426(1)	72(2)	14(0)	37(1)	−1(1)	8(1)	0(1)
Se	−0.1521(4)	−0.0130(2)	0.2567(3)	155(5)	34(1)	148(2)	−10(2)	45(4)	−4(1)
Cl(1)	0.1608(5)	0.0396(3)	0.0760(4)	100(7)	20(2)	53(4)	4(3)	14(4)	1(2)
Cl(2)	0.3667(5)	0.0903(3)	0.2681(5)	79(7)	26(2)	74(5)	−5(3)	−6(5)	4(2)
P(1)	0.0654(6)	0.1414(3)	0.2256(4)	90(7)	17(1)	45(4)	−1(3)	14(4)	2(2)
P(2)	0.2470(6)	−0.0487(3)	0.2544(4)	103(7)	18(1)	44(3)	1(3)	5(4)	3(2)
C(1)	−0.0079(23)	0.0156(10)	0.2460(19)	89(25)	14(6)	53(20)	4(10)	16(18)	6(9)
C(2)	0.1568(22)	0.0534(12)	0.3700(25)	190(48)	27(9)	79(23)	6(16)	61(29)	0(14)
O	0.1590(23)	0.0572(9)	0.4523(17)	283(39)	21(6)	78(16)	27(11)	3(21)	−5(9)

Group	x_c	y_c	z_c	δ	ϵ	η
11	0.127	0.208	0.418	117.946	−122.584	72.333
12	−0.235	0.136	0.163	94.687	166.636	57.708
13	0.168	0.229	0.076	−23.525	138.012	169.021
21	0.345	−0.069	0.466	−106.105	−108.450	−107.555
22	0.492	−0.083	0.142	−108.986	147.792	−159.393
23	0.048	−0.149	0.196	138.492	165.750	124.204

[a] Standard deviations are given in parentheses. The anisotropic temperature factor is of the form $\exp -2\pi i(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$ and is given × 10^4. Rigid group parameters are as defined in ref. 36.

TABLE 3

DERIVED POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR PHENYL RING CARBON ATOMS

Atom	*x/a*	*y/b*	*z/c*	*B*
C(11)	0.1904	0.2230	0.3401	5.2
C(12)	0.2241	0.2486	0.4248	7.3
C(13)	0.1608	0.2337	0.5027	6.1
C(14)	0.0636	0.1930	0.4959	5.4
C(15)	0.0299	0.1674	0.4112	5.3
C(16)	0.0932	0.1823	0.3333	3.7
C(21)	−0.1058	0.1407	0.1913	3.4
C(22)	−0.1979	0.1649	0.2442	4.4
C(23)	−0.3271	0.1602	0.2159	5.9
C(24)	−0.3642	0.1313	0.1347	4.9
C(25)	−0.2721	0.1071	0.0818	5.5
C(26)	−0.1429	0.1118	0.1101	4.2
C(31)	0.1285	0.1885	0.1383	5.2
C(32)	0.0502	0.2349	0.1143	6.7
C(33)	0.0897	0.2754	0.0520	8.9
C(34)	0.2075	0.2695	0.0137	6.9
C(35)	0.2858	0.2231	0.0377	6.1
C(36)	0.2463	0.1826	0.1000	6.0
C(41)	0.3045	−0.0638	0.3731	4.2
C(42)	0.4347	−0.0644	0.3996	5.0
C(43)	0.4752	−0.0696	0.4926	6.5
C(44)	0.3855	−0.0742	0.5589	7.5
C(45)	0.2553	−0.0736	0.5324	5.2
C(46)	0.2148	−0.0684	0.4394	5.1
C(51)	0.3854	−0.0667	0.1881	4.1
C(52)	0.4534	−0.0262	0.1410	4.8
C(53)	0.5600	−0.0425	0.0949	5.1
C(54)	0.5986	−0.0993	0.0959	4.5
C(55)	0.5306	−0.1398	0.1430	6.4
C(56)	0.4240	−0.1235	0.1891	5.8
C(61)	0.1336	−0.1059	0.2237	3.1
C(62)	0.1238	−0.1545	0.2780	3.5
C(63)	0.0382	−0.1976	0.2504	4.5
C(64)	−0.0376	−0.1921	0.1683	5.0
C(65)	−0.0278	−0.1435	0.1140	4.0
C(66)	0.0578	−0.1004	0.1416	3.6

rigid group parameters are given in Table 2. Derived parameters for phenyl ring carbon atoms are listed in Table 3. Tables of observed and calculated structure factors are available on request from the authors.

Description of the structure

The atomic numbering scheme is given in the ORTEP diagram, Fig. 1, together with bond distances in the inner coordination sphere. The thermal ellipses represent 30% probability boundaries. The molecular packing is seen in the stereoscopic diagram of Fig. 2.

The crystal contains monomers of neutral complex, packed such that there is only one intermolecular approach which is shorter than 3.5 Å (C(43)—C(43)′ at 3.31 Å). The octahedral ruthenium coordination consists of *cis*-carbonyl and selenocarbonyl, *cis*-chlorides, and *trans*-phosphine ligands. The selenocarbonyl

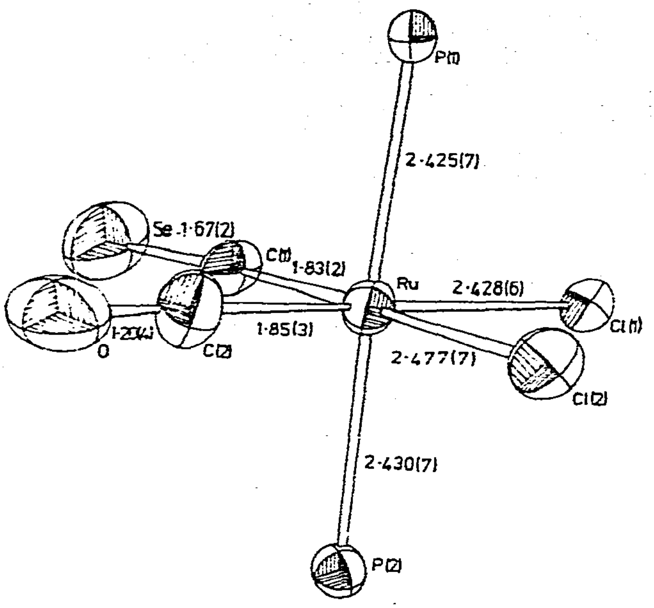

Fig. 1. The inner coordination geometry in $RuCl_2(CO)(CSe)(PPh_3)_2$.

rather than isoselenocarbonyl mode of coordination is confirmed. The two Ru—P distances are equivalent (2.425, 2.430(7) Å), and are typical of the Ru—P distances found in other octahedral ruthenium complexes where the two phosphine ligands are mutually *trans*, e.g. $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$ (2.429, 2.438(4)

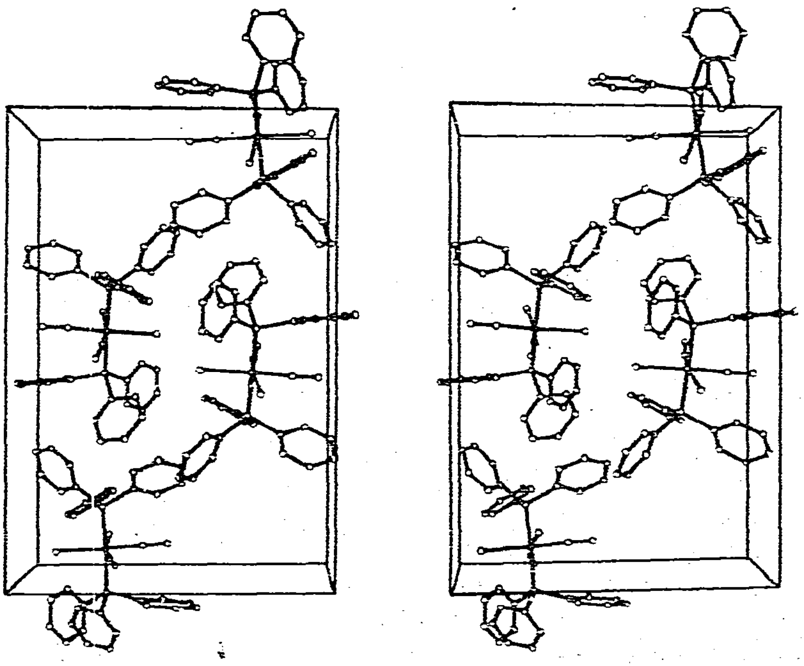

Fig. 2. A stereoscopic view of the molecular packing.

TABLE 4

INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $[RuCl_2(CO)(CSe)(PPh_3)_2]$ (Standard deviations are given in parentheses)

Ru—Cl(1)	2.428(6)	Cl(1)—Ru—C(2)	176.1(11)
Ru—Cl(2)	2.477(7)	Cl(2)—Ru—P(1)	87.6(3)
Ru—P(1)	2.425(7)	Cl(2)—Ru—P(2)	90.8(3)
Ru—P(2)	2.430(7)	Cl(2)—Ru—C(1)	169.6(9)
Ru—C(1)	1.828(25)	Cl(2)—Ru—C(2)	81.3(11)
Ru—C(2)	1.854(34)	P(1)—Ru—P(2)	177.4(4)
C(1)—Se	1.668(25)	P(1)—Ru—C(1)	91.2(8)
C(2)	1.196(40)	P(1)—Ru—C(2)	89.9(11)
		P(2)—Ru—C(1)	90.8(8)
Cl(1)—Ru—Cl(2)	94.8(3)	P(2)—Ru—C(2)	91.9(11)
Cl(1)—Ru—P(1)	89.6(3)	C(1)—Ru—C(2)	88.4(13)
Cl(1)—Ru—P(2)	88.5(3)	Ru—C(1)—Se	176.1(2)
Cl(1)—Ru—C(1)	95.5(8)	Ru—C(2)—O	178.8(11)

Å [29]); $[RuCl(CO)_2(HN_2C_6H_5)(PPh_3)_2]ClO_4 \cdot CH_2Cl_2$ (2.439, 2.415(2) Å [30]), $RuCl_3(NO)(PPh_2Me)_2$ (2.441, 2.429(2) Å) [31]; $Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$ (2.425, 2.426(2) Å [32]), and $RuCl(SO_4)(NO)(PPh_3)_2$ 2.454(3) Å [33]. The P(1)—Ru—P(2) angle is 177.4(4)°.

The equatorial plane is occupied by the —CO, —CSe, and two —Cl ligands. Since the —CO and —CSe ligands are each trans to —Cl, any difference in the Ru—C bond lengths reflects a difference in the ability of the donor atom to accept π electron density by back-donation from the metal centre. The observed bond lengths are Ru—CO, 1.85(3) and Ru—CSe, 1.83(3) Å. The Ru—CSe distance is the shorter, but the standard deviations are such that no significance can be placed on the difference. Both are within the wide range of distances found for Ru—CO, 1.77—2.05 Å [34]. The C—Se bond distance [1.67(3) Å] in a metal—selenocarbonyl complex has not been previously measured crystallographically, although a value of 1.7090 Å has been found for CSe in the compound OCSe using microwave spectroscopy [35].

The Ru—Cl distances [2.428(6) and 2.477(7) Å] are at the upper end of the range found in many octahedral complexes. Typical values are 2.393, 2.386, 2.385(3) Å in $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$ [29], 2.392, 2.398, 2.384(2) Å in $Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$ [32], and 2.357, 2.405, 2.391(2) Å in $RuCl_2(NO)(PMePh_2)_2$ [31].

The most obvious irregularity in the coordination geometry involves these two Ru—Cl bond lengths, with Ru—Cl(1) [Cl *trans* to CO] being 2.428(6) Å while Ru—Cl(2) [Cl *trans* to CSe] is 2.477(7) Å. The difference (7.5 σ) shows that the coordinated selenocarbonyl ligand exerts a very high *trans* effect, greater even than CO. In the few crystal structures of complexes containing coordinated thiocarbonyl, no mention has been made of a structural *trans* effect for —CS [16]. However, the comparatively long W—C(—CNC_6H_{11}) distance of 2.158(23) Å for the ligand CNC_6H_{11} *trans* to CS in *trans*-$W(CO)_4(CNC_6H_{11})(CS)$ may possibly be a manifestation of a strong *trans* effect for the —CS ligand [16].

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