

The Structure of the Orange Complex $[\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4]\text{PF}_6$: Dithioformato[tetrakis(dimethylphenylphosphine)]ruthenium(II) Hexafluorophosphate

BY MICHAEL LAING

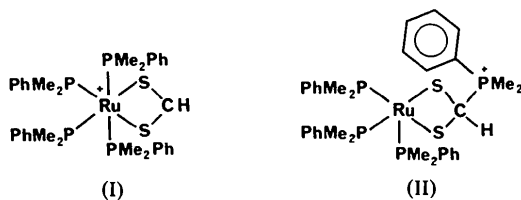
Chemistry Department, University of Natal, Durban 4001, South Africa

(Received 2 January 1978; accepted 4 February 1978)

$[\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ is orthorhombic, $Pbca$, $a = 13.550$ (10), $b = 19.480$ (15), $c = 28.880$ (25) Å, $Z = 8$. $R = 0.0816$ for 2649 counter data; Ru, two S and five P atoms anisotropic. The coordination about Ru is distorted octahedral. Bond lengths are: Ru–S 2.43, 2.44; Ru–P(ax) 2.42, 2.43; Ru–P(eq) 2.34, 2.36; S–C 1.65, 1.68 Å. Bond angles are: P(eq)–Ru–P(eq) 100; P(ax)–Ru–P(ax) 167; S–Ru–S 70; P(eq)–Ru–P(ax) 93, 92, 91, 99; S–Ru–P(ax) 87, 88, 83, 84; *trans* S–Ru–P(eq) 163, 167°. The distortions from regularity about the Ru atom are caused by close contacts between methyl and phenyl groups in each set of facial phosphine ligands, and between phenyl rings on the axial phosphines and one S atom. Because the x coordinate of the Ru atom is close to 0.25, one P–Ru–S vector is nearly collinear with b , and the P–Ru–P and second P–Ru–S vector lie in the xz plane at about 45° to the yz plane, the solution of the structure by the Patterson method is not straightforward. A brief discussion is given of the techniques used to obtain the coordinates of the heavy atoms of the cation.

Introduction

Reaction of $[\text{RuH}(\text{PMe}_2\text{Ph})_3]\text{PF}_6$ with CS_2 in cold deoxygenated methanol (Ashworth, 1977) yields the orange dithioformato complex $[\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ (I) which rearranges in boiling methanol to a purple isomer $[\text{Ru}\{\text{S}_2\text{C}(\text{H})\text{PMe}_2\text{Ph}\}(\text{PMe}_2\text{Ph})_3]\text{PF}_6$ (II) (Ashworth, Singleton & Laing, 1976a). This unusual rearrangement from a Ru^{II} complex of coordination number 6 and electron count 18 to one of coordination number 5 and electron count 16 (Sidgwick, 1927; Tolman, 1972) was evidently favoured by a reduction of the intramolecular interligand strains (Ashworth, Nolte, Singleton & Laing, 1977). The structure of the orange dithioformato complex has been determined to obtain detailed information about the non-bonded contacts between the dimethylphenylphosphine ligands.



Experimental

Crystals were supplied by Drs T. V. Ashworth and E. Singleton. Cell dimensions (Table 1) were obtained by least squares from 2θ , χ and ϕ angles for 25 reflexions measured on a Philips four-circle diffractometer. Intensities were measured for a crystal 0.2×0.2

$\times 0.2$ mm with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) for θ between 3 and 20°. The ω – 2θ scan technique was used; the scan width was 0.7°, the scan time was 23.3 s, and the background was counted for 23.3 s for each reflexion. Three reflexions were used as standards and remeasured after every 60 reflexions; no decomposition was observed. Of the 3984 reflexions measured (including space-group extinctions) 2649 were classed as observed, $I > 1.65\sigma(I)$. Only Lorentz–polarization corrections were applied; $\mu(\text{Mo } K\alpha) = 7.7 \text{ cm}^{-1}$.

A Patterson map had a pattern of large peaks close to the origin which showed that the cation was octahedral with one L –Ru– L vector lying nearly parallel to b , and that the other two L –Ru– L vectors lay in the xz plane, each making an angle close to 45° with the yz plane. The pattern of peaks on the Harker sections and lines confirmed these deductions and gave the coordinates of the Ru atom. There was no way of differentiating the P from the S atoms. As a check, the structure was solved independently by direct methods. The intensity statistics were: $\langle |E| \rangle 0.72$, $\langle |E^2 - 1| \rangle 1.07$, $\langle |E^2| \rangle 0.94$; E 's > 3.0 0.63%, > 2.0 4.57%, > 1.0 20.9%; a distribution typical of slight hypersymmetry. The 305 largest E 's were used in the

Table 1. Crystal data

$\text{Ru}_2\text{P}_5\text{F}_6\text{C}_{33}\text{H}_{45}$	Orthorhombic, $Pbca$
$a = 13.550$ (10) Å	$D_m = 1.50$ (1) g cm^{-3}
$b = 19.480$ (15)	$D_c = 1.52$
$c = 28.880$ (25)	$M_r = 876$
$V = 7623$ Å ³	$Z = 8$

program *SAYRE* (Long, 1965) with $NBACK = 1$. The origin-fixing reflexions were chosen by hand, but the program was allowed to choose four variables (Table 2). The correct solution had the highest consistency index (0.9898) and was reached in the smallest number of cycles (5). 150 signs were positive, 155 were negative, and the E map clearly showed both the RuP_4S_2 group and the P of the PF_6^- ion. It was still impossible to differentiate between the P and S atoms in the cation.

A Fourier map, phased on Ru and seven P atoms, yielded coordinates for most of the C atoms, and the connectivity of the peaks allowed the S atoms to be identified. When all the atoms had been correctly placed, the structure was refined by block-diagonal least squares, first isotropically, then with the Ru, five P and two S atoms anisotropic. The final R was 0.0816

for 2649 observed data.* [This value of R is slightly higher than is usual for diffractometer data and is caused by a small systematic error that cannot be corrected for. This error arises from the combination of the long cell edges ($b = 19.48$, $c = 28.88$ Å), the short wavelength of the radiation (0.7107 Å) and the configuration of the diffractometer, which causes a small but unavoidable overlap of reflexions resulting in incorrect values for the background measurements in the vicinity of strong reflexions. The errors in the intensities probably cause the β_{ij} 's of the heavy atoms to be incorrect and their standard deviations should best be doubled.] Weighting was proportional to $1/\sigma(F)$; scattering factors for neutral atoms were used; that of Ru was corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1962). Final positional and isotropic thermal parameters are given in Table 3, bond lengths in Table 4, bond angles in Table 5 and non-bonded contacts in Table 6.

Table 2. Reflexions used as the starting set in the program *SAYRE*

h	k	l	E	Correct solution	
1	8	3	3.80	+	Origin definers
1	2	16	3.69	+	
9	1	15	3.37	+	
4	8	9	4.23	+	Variables
4	8	5	3.76	-	
2	8	9	3.75	-	
3	8	7	4.12	+	

Discussion

The coordination about the Ru atom in the cation is distorted octahedral. The four phosphine ligands are arranged as two pairs, one *trans* and one *cis*, with the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33434 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional atomic coordinates ($\times 10^5$ for Ru, $\times 10^4$ for all others) and B values

	x	y	z	B (Å ²)		x	y	z	B (Å ²)
Ru	23491 (8)	03926 (6)	13859 (4)	-	C(2.8)	-0213 (13)	0759 (9)	1861 (6)	5.2 (4)
S(1)	2312 (3)	-0856 (2)	1398 (1)	-	C(3.1)	1675 (10)	0383 (8)	0168 (5)	3.1 (3)
S(2)	3371 (3)	-0036 (2)	2021 (1)	-	C(3.2)	1880 (12)	-0271 (8)	-0005 (5)	4.2 (4)
P(1)	3880 (3)	0300 (2)	0960 (1)	-	C(3.3)	2209 (12)	-0335 (8)	-0483 (5)	5.0 (4)
P(2)	1037 (3)	0372 (2)	1959 (1)	-	C(3.4)	2364 (13)	0224 (9)	-0758 (6)	5.6 (4)
P(3)	1245 (3)	0451 (2)	0765 (1)	-	C(3.5)	2158 (13)	0874 (9)	-0600 (6)	5.5 (4)
P(4)	2631 (3)	1571 (2)	1511 (1)	-	C(3.6)	1786 (13)	0983 (8)	-0127 (6)	4.6 (4)
P(5)	2397 (4)	1996 (2)	3580 (2)	-	C(3.7)	0352 (11)	1188 (8)	0704 (6)	4.1 (4)
C(1)	3071 (12)	-0831 (8)	1846 (5)	4.1 (4)	C(3.8)	0384 (11)	-0268 (8)	0784 (5)	3.6 (4)
C(1.1)	4353 (11)	-0556 (7)	0862 (5)	3.0 (3)	C(4.1)	3232 (12)	2102 (8)	1063 (5)	3.8 (4)
C(1.2)	5028 (12)	-0872 (8)	1176 (6)	4.8 (4)	C(4.2)	2727 (13)	2239 (8)	0649 (5)	4.7 (4)
C(1.3)	5395 (13)	-1545 (9)	1078 (6)	5.0 (4)	C(4.3)	3185 (14)	2658 (9)	0293 (6)	5.5 (5)
C(1.4)	5092 (13)	-1877 (9)	0689 (6)	5.0 (4)	C(4.4)	4130 (14)	2904 (9)	0366 (6)	5.8 (5)
C(1.5)	4413 (13)	-1603 (9)	0375 (6)	4.9 (4)	C(4.5)	4626 (14)	2792 (9)	0788 (7)	6.1 (5)
C(1.6)	4033 (12)	-0929 (8)	0467 (5)	4.2 (4)	C(4.6)	4208 (13)	2374 (9)	1149 (6)	5.1 (4)
C(1.7)	4965 (12)	0686 (8)	1247 (6)	4.6 (4)	C(4.7)	3404 (13)	1726 (8)	2020 (6)	4.8 (4)
C(1.8)	4046 (12)	0680 (8)	0385 (5)	3.9 (4)	C(4.8)	1580 (13)	2146 (9)	1637 (6)	5.2 (4)
C(2.1)	0647 (12)	-0483 (8)	2164 (5)	3.9 (4)	F(1)	1396 (9)	2005 (6)	3320 (4)	9.0 (3)
C(2.2)	-0134 (14)	-0809 (9)	1968 (6)	5.8 (5)	F(2)	1781 (11)	1886 (7)	4036 (5)	11.0 (4)
C(2.3)	-0445 (15)	-1515 (10)	2114 (7)	7.2 (6)	F(3)	2438 (8)	1194 (5)	3515 (3)	6.2 (2)
C(2.4)	0173 (16)	-1757 (10)	2466 (8)	7.3 (5)	F(4)	2347 (8)	2808 (5)	3640 (4)	7.6 (3)
C(2.5)	0923 (15)	-1498 (10)	2671 (7)	6.9 (5)	F(5)	2978 (10)	2070 (7)	3126 (5)	10.2 (4)
C(2.6)	1213 (14)	-0784 (9)	2514 (7)	6.1 (5)	F(6)	3334 (10)	1952 (7)	3895 (4)	9.9 (4)
C(2.7)	1333 (13)	0786 (8)	2510 (6)	5.5 (4)					

Table 4. Bond lengths (Å)

Ru—S(1)	2.43 (1)	P(2)—C(2.1)	1.85 (2)
Ru—S(2)	2.44	P(2)—C(2.7)	1.83
Ru—P(1)	2.42	P(2)—C(2.8)	1.88
Ru—P(2)	2.43	P(3)—C(3.1)	1.82
Ru—P(3)	2.34	P(3)—C(3.7)	1.89
Ru—P(4)	2.36	P(3)—C(3.8)	1.82
S(1)—C(1)	1.65 (2)	P(4)—C(4.1)	1.85
S(2)—C(1)	1.68	P(4)—C(4.7)	1.83
P(1)—C(1.1)	1.81	P(4)—C(4.8)	1.85
P(1)—C(1.7)	1.85	P—F range	1.54–1.59
P(1)—C(1.8)	1.83	mean	1.56

Table 5. Bond angles (°)

S(1)—Ru—S(2)	70 (1)	Ru—P(1)—C(1.1)	117 (1)
P(1)—Ru—P(2)	167	Ru—P(1)—C(1.7)	115
P(1)—Ru—P(3)	99	Ru—P(1)—C(1.8)	122
P(1)—Ru—P(4)	91	Ru—P(2)—C(2.1)	116
P(2)—Ru—P(3)	93	Ru—P(2)—C(2.7)	115
P(2)—Ru—P(4)	92	Ru—P(2)—C(2.8)	124
P(3)—Ru—P(4)	100	Ru—P(3)—C(3.1)	121
P(1)—Ru—S(1)	87	Ru—P(3)—C(3.7)	121
P(1)—Ru—S(2)	83	Ru—P(3)—C(3.8)	110
P(2)—Ru—S(1)	88	Ru—P(4)—C(4.1)	121
P(2)—Ru—S(2)	84	Ru—P(4)—C(4.7)	112
P(3)—Ru—S(1)	93	Ru—P(4)—C(4.8)	120
P(3)—Ru—S(2)	163	Ru—S(1)—C(1)	88
P(4)—Ru—S(1)	167	Ru—S(2)—C(1)	87
P(4)—Ru—S(2)	97	S(1)—C(1)—S(2)	114
C(1.1)—P(1)—C(1.7)	99 (2)	C(3.1)—P(3)—C(3.7)	100 (2)
C(1.1)—P(1)—C(1.8)	101	C(3.1)—P(3)—C(3.8)	100
C(1.7)—P(1)—C(1.8)	98	C(3.7)—P(3)—C(3.8)	100
C(2.1)—P(2)—C(2.7)	100	C(4.1)—P(4)—C(4.7)	103
C(2.1)—P(2)—C(2.8)	99	C(4.1)—P(4)—C(4.8)	98
C(2.7)—P(2)—C(2.8)	99	C(4.7)—P(4)—C(4.8)	100

Table 6. Intramolecular non-bonded contacts (Å)

S(1)⋯C(1.1)	3.22	P(1)⋯C(1)	3.55
S(1)⋯C(2.1)	3.24	P(2)⋯C(1)	3.64
C(2.8)⋯C(4.8)	3.69	C(1.8)⋯C(3.1)	3.32
C(2.8)⋯C(3.7)	3.53	C(1.8)⋯C(4.1)	3.57
C(3.7)⋯C(4.8)	3.67	C(4.2)⋯C(3.6)	3.56

bidentate dithioformate group completing the octahedron (Fig. 1).

The pattern of Ru—P lengths is as expected: the *trans* diaxial pair (2.42, 2.43 Å) are significantly longer than the *cis* equatorial pair (2.34, 2.36 Å), with the shorter Ru—P(eq) *trans* to the longer Ru—S. The P—Ru—P angles in each facial set (91 to 100°, Table 5) are similar to those found in $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^+$ (Laing & Pope, 1976) and $[\text{Ru}(\text{O}_2\text{CMe})(\text{PMe}_2\text{Ph})_4]^+$ (Ashworth, Nolte & Singleton, 1976). The pair of axial phosphines bend toward the (S₂CH) group, P(1)—Ru—P(2) 167°, to relieve the compression strains between them and the equatorial pair of phosphines. There are also significant differences between the four S—Ru—P(ax)

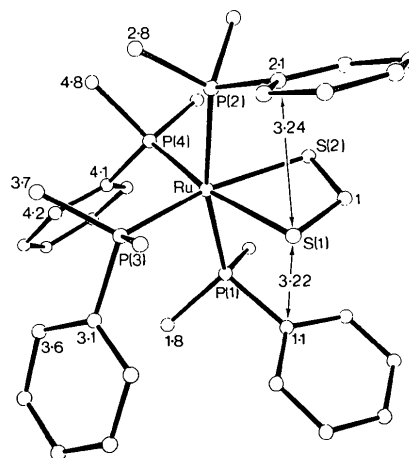


Fig. 1. A projection of the cation (I) showing the numbering system and the close contacts between S(1) and the two phenyl rings of the axial PMe_2Ph groups. C atoms are indicated only by their identity numbers.

angles. The two large angles are associated with S(1) because it is in close contact with the phenyl ring on each of the axial P(1) and P(2) (Tables 5 and 6; Fig. 1).

It was first found in $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^+$ (Laing & Pope, 1976) that for three facially arranged PMe_2Ph ligands, one Ru—P—C(Me) angle in each ligand systematically exceeds 120°, that the P—C bonds to these methyl groups are approximately parallel to each other and perpendicular to the plane of the three P atoms, and that the Me⋯Me separations are between 3.5 and 3.8 Å. The same result was observed in the purple isomer (II) (Ashworth, Singleton & Laing, 1976a) and $[\text{RuH}(\text{C}_4\text{H}_9)(\text{PMe}_2\text{Ph})_3]^+$ (Ashworth, Singleton & Laing, 1976b), and has been used to explain the reactivity of the parent compound $[\text{RuH}(\text{PMe}_2\text{Ph})_3]^+$ (Ashworth, Nolte, Singleton & Laing, 1977).

The two facial arrangements in (I) are shown in Fig. 2. Set A has the same arrangement of methyl groups as in the three-ligand cases $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^+$ and $[\text{RuH}(\text{C}_4\text{H}_9)(\text{PMe}_2\text{Ph})_3]^+$. Set B is different. It is now the phenyl rings of P(3) and P(4) which stand perpendicular to the plane of the P atoms, and the short separations are between these phenyl rings and the methyl group C(1.8) of the axial phosphine P(1). Once again the Ru—P—C angles are large (~120°) for the groups involved in these non-bonded contacts.

There are two possible arrangements for the phenyl rings of the phosphine groups in the idealized facial $(\text{PMe}_2\text{Ph})_3$ geometry. In one, the phenyl rings are related by a threefold axis; in the other, two of the phenyl rings face each other. The difference is shown schematically in Fig. 3. Arrangement M is found in (I), but in the purple isomer (II) and in $[\text{Ru}(\text{O}_2\text{CMe})(\text{PMe}_2\text{Ph})_4]^+$ it is arrangement 3 which is found. In other words, two internal rotation isomers exist for a

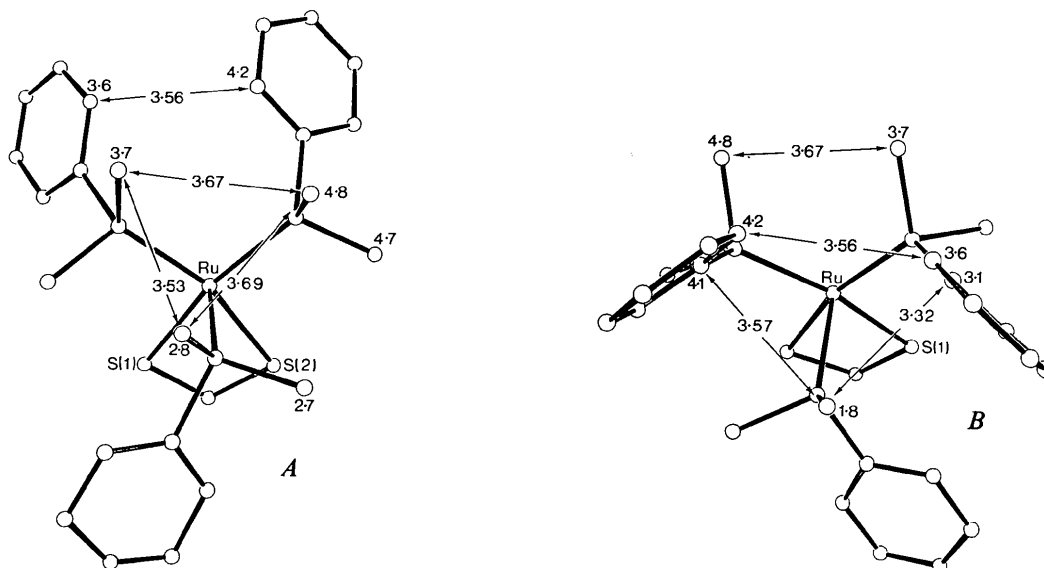


Fig. 2. Projections of the two sets of facially arranged PMe_2Ph ligands. Arrangement *A* has three P—Me bonds approximately parallel to each other and perpendicular to the plane of P(2), P(3) and P(4). In set *B*, the phenyl rings from P(3) and P(4) are approximately perpendicular to the plane of the P atoms and are in close contact with one methyl group on P(1).

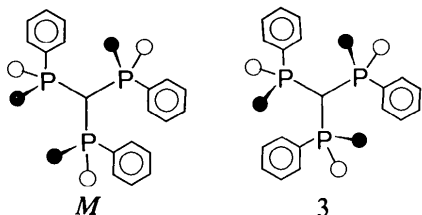


Fig. 3. The two possible arrangements of the phenyl rings in an idealized facial geometry for three PMe_2Ph groups: 3 and *M*. Both arrangements have been found in complexes containing $[\text{Ru}(\text{PMe}_2\text{Ph})_3]$ and $[\text{Ru}(\text{PMe}_2\text{Ph})_4]^+$ fragments – see text.

compound of the class $[\text{M}(\text{LL})(\text{PMe}_2\text{Ph})_4]^+$, with the implication that a second form of the orange compound (I) should be isolable. A similar phenomenon has been observed in $[\text{RhCl}(\text{PPh}_3)_3]$ (Bennett & Donaldson, 1977). There are two forms, orange and red, in which the principal differences are the P—Rh—P and P—Rh—Cl angles arising from differences in the arrangements of the phenyl rings on the PPh_3 groups.

The different arrangements of the methyl and phenyl groups in the two facial sets of $(\text{PMe}_2\text{Ph})_3$ ligands in the acetate result in the phenyl groups on the axial phosphines not being on the same side of the molecule as is found in (I). Thus, in the acetate both O atoms are shielded, but by only one phenyl ring: the phenyl ring on P(1) lies above O(1), while that on P(2) lies above O(2) – see Tables 3 and 4, and the figure in Ashworth, Nolte & Singleton (1976). As a result, two P—Ru—O angles are opened: P(1)—Ru—O(1) and P(2)—Ru—O(2) 87° , while P(1)—Ru—O(2) and P(2)—Ru—O(1)

are about 5° smaller. The same effect is found in (I), but the phenyl rings on the axial phosphines both lie over the same atom, S(1).

Is it possible to decide which of the two arrangements of the four PMe_2Ph ligands is more stable – that in $[\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4]^+$ or that in $[\text{Ru}(\text{O}_2\text{CMe})(\text{PMe}_2\text{Ph})_4]^+$? The angular strain in each PMe_2Ph ligand can be estimated if one assumes that a coordinated PMe_2Ph ligand suffering negligible angular distortion has a mean Ru—P—C angle of 115° (O'Flynn & McDonald, 1976). Table 7 compares the deviations from ideality for the Ru—P—C angles in (I) and the related acetate. The equatorial phosphines suffer greater distortion than do the axial phosphines, and the total strain in (I) is less than that found in the acetate. While this difference is probably real, no great reliance should be placed on it as a quantitative measure because the sum of the Ru—P—C angular distortions in the highly reactive parent compound $[\text{RuH}(\text{PMe}_2\text{Ph})_5]^+$ is less than that in the acetate (Ashworth, Nolte, Singleton & Laing, 1977). It is evident that the internal strain energy in this class of complexes is also taken up in distortions of P—Ru—P angles and even in stretching of Ru—P bonds when distortions of the Ru—P—C angles can no longer accommodate the excess energy. This effect is seen in $[\text{RuH}(\text{PMe}_2\text{Ph})_5]^+$ where P—Ru—P angles of 88 , 100 and 101° are found.

The bonding between the Ru atom and the S_2C moiety deserves comment. In both (I) and the purple isomer (II), the two Ru—S lengths are equal as are the

Table 7. Ru—P—C angles ($^\circ$) and deviations from $115^\circ (\pm 1^\circ)$

	[Ru(S ₂ CH)- (PMe ₂ Ph) ₄] ⁺ (This work)		[Ru(O ₂ CMe)- (PMe ₂ Ph) ₄] ⁺ (Ashworth, Nolte & Singleton, 1976)	
	Angle	Deviation	Angle	Deviation
Axial P(1)	117 (Ph)	2	113 (Ph)	2
	115	0	113	2
	122	7	126	11
	Sum	9	Sum	15
Axial P(2)	116 (Ph)	1	113 (Ph)	2
	115	0	113	2
	124	9	126	11
	Sum	10	Sum	15
Equatorial P(3)	121 (Ph)	6	108 (Ph)	7
	121	6	121	6
	110	5	121	6
	Sum	17	Sum	19
Equatorial P(4)	121 (Ph)	6	121 (Ph)	6
	112	3	107	8
	120	5	123	8
	Sum	14	Sum	22
Total deviation	50		71	

S—C lengths. This is in contrast to the four-coordinate *trans*-[PtH(S₂CH){P(C₆H₁₁)₃]₂] (Albinati, Musco, Carturan & Strukul, 1976) and the five-coordinate [Ir(S₂CPPH₃)(CO)(PPh₃)₂]⁺ (Clark, Collins, James, Roper & Town, 1976). In the Pt compound, the S₂CH group is a monodentate ligand, with a single Pt—S bond of 2.37 Å, while in the Ir compound the S₂C moiety is asymmetrically bonded with Ir—S = 2.31 and 2.38 Å. The S₂CH group in the six-coordinate [Re(S₂CH)(CO)₂(PPh₃)₂] (Albano, Bellon & Ciani, 1971) acts as a symmetrical bidentate dithioformate anion, with Re—S = 2.50 and 2.53 Å. In [Ru(S₂CH)₂(PPh₃)₂] (Kalinin, Gusev & Struchkov, 1973) the dithioformate ligands are again bidentate but the Ru—S bonds differ in length: 2.45, 2.39; 2.45, 2.38 Å, with the longer Ru—S *trans* to Ru—P. Thus it is not the formal *d*-electron count, or the coordination number or geometry of the metal atom alone which determines the

nature of the bonding between the metal and the two S atoms. It seems that equivalent M—S bonds are associated with *d*²*sp*³ and *dsp*³ hybridization (where the *d* orbital is *d*_{*x*²-*y*²} and where the two M—S are in similar environments and form part of a square plane).

A comparison of the structures of (I) and the purple isomer (II) shows that all the Ru—L bonds in the 16-electron five-coordinate complex are shorter (and presumably stronger) than the analogous bonds in the 18-electron six-coordinate isomer.

I thank the South African Council for Scientific and Industrial Research for financial support; Drs T. V. Ashworth and E. Singleton (National Chemical Research Laboratory, CSIR) for suggesting the problem and supplying the crystals, and for their co-operation and stimulating discussions; Dr G. Gafner (National Physical Research Laboratory, CSIR) for collecting the intensities; and Mrs P. Sommerville (UND) for assistance in the laboratory.

References

- ALBANO, V. G., BELLON, P. L. & CIANI, G. (1971). *J. Organomet. Chem.* **31**, 75–87.
- ALBINATI, A., MUSCO, A., CARTURAN, G. & STRUKUL, G. (1976). *Inorg. Chim. Acta*, **18**, 219–223.
- ASHWORTH, T. V. (1977). PhD Thesis, Univ. of South Africa, Pretoria.
- ASHWORTH, T. V., NOLTE, M. J. & SINGLETON, E. (1976). *J. Chem. Soc. Dalton Trans.* pp. 2184–2186.
- ASHWORTH, T. V., NOLTE, M. J., SINGLETON, E. & LAING, M. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1816–1822.
- ASHWORTH, T. V., SINGLETON, E. & LAING, M. (1976a). *Chem. Commun.* pp. 875–876.
- ASHWORTH, T. V., SINGLETON, E. & LAING, M. (1976b). *J. Organomet. Chem.* **117**, C113–C115.
- BENNETT, M. J. & DONALDSON, P. B. (1977). *Inorg. Chem.* **16**, 655–660.
- CLARK, G. R., COLLINS, T. J., JAMES, S. M., ROPER, W. R. & TOWN, K. G. (1976). *Chem. Commun.* pp. 475–476.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202, 203, 211, 216. Birmingham: Kynoch Press.
- KALININ, A. E., GUSEV, A. I. & STRUCHKOV, YU. T. (1973). *J. Struct. Chem. (USSR)*, **14**, 804–811.
- LAING, M. & POPE, L. (1976). *Acta Cryst.* **B32**, 1547–1550.
- LONG, R. E. (1965). PhD Thesis, Univ. of California, Los Angeles. (*SA YRE* is a local modification.)
- O'FLYNN, K. H. P. & McDONALD, W. S. (1976). *Acta Cryst.* **B32**, 1596–1597.
- SIDGWICK, N. V. (1927). *The Electronic Theory of Valency*. Ch. 10. Oxford: Clarendon Press.
- TOLMAN, C. A. (1972). *Chem. Soc. Rev.* pp. 337–353.