Stereochemical Consequences of the Two-electron Oxidation of a Dirhodium Fulvalene Complex: The X-Ray Crystal Structures of trans-[Rh₂(CO)₂(PPh₃)₂-(η⁵:η′⁵-C₁₀H₈)] and cis-[Rh₂(CO)₂(PPh₃)₂(η⁵:η′⁵-C₁₀H₈)][PF₆]₂*

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Single-crystal X-ray diffraction studies on the dirhodium fulvalene complexes cis-[Rh₂(CO)₂(PPh₃)₂-(η⁵:η′⁵-C₁₀H₈)][PF₆]₂ (1) and trans-[Rh₂(CO)₂(PPh₃)₂(η⁵:η′⁵-C₁₀H₈)] (2), both as their n-hexane solvates, show the structures to be dramatically different. In the dication of (1) the rhodium atoms lie on the same side of the fulvalene ligand and are bonded to one another with Rh–Rh 2.930(2) Å; in (2) the metal atoms are on opposite sides of the hydrocarbon ligand at a separation of 5.662(1) Å. A detailed comparison of the two structures shows that the oxidation of complex (2) to (1) also results in changes in the geometry of the metal–ligand binding: the Rh–P distances increase by 0.067(4) Å; the ring centroid–Rh–P(CO) unit is planar in (2) but pyramidal in (1). The electronic factors behind the structural changes are examined by the extended-Hückel molecular-orbital method; the fulvalene ligands in complexes (1) and (2) have characteristics (C–C bond orders, ability to rotate about the central C–C bond) more similar to those of the fulvalene dianion than to free fulvalene. These conclusions are in accord with the structural observations, and with the assignment of formal oxidation states II and I to the rhodium atoms of (1) and (2) respectively. In the light of these results, brief comments are made on the apparently anomalous electrochemical behaviour of the complexes.

The one-electron oxidation of [Rh(CO)(PPh₃)(η-C₅H₅)] by [Fe(η-C₅H₅)₂][PF₆] or arenediazonium hexafluorophosphates results in the formation of the dicationic fulvalene complex [Rh₂(CO)₂(PPh₃)₂(η⁵:η′⁵-C₁₀H₈)][PF₆]₂ (1) (Scheme) which, in turn, undergoes two-electron reduction to neutral [Rh₂(CO)₂(PPh₃)₂(η⁵:η′⁵-C₁₀H₈)] (2).[1]

The results of cyclic voltammetric studies[1] on complexes (1) and (2) imply that the two species are related by a reversible two-electron process and, therefore, that they have very similar structures. However, the observed diamagnetism of (1) requires the presence of a direct rhodium–rhodium bond, and therefore a cis geometry in relation to the C₁₀H₈ ligand, and a trans structure is more likely for (2), by analogy with trans-[Co₂(CO)₄(η⁵:η′⁵-C₁₀H₈)].[2] In order to resolve this apparent contradiction the X-ray crystal structures of complexes (1) and (2) have been determined.

This study has also allowed us to evaluate the structural consequences of the two-electron oxidation of a binuclear complex; we have previously reported the effects of reversible one-electron oxidation in both mono- and bi-nuclear systems, namely [Mn(CO)(Ph₂PCH₂CH₂PPh₂)(η⁵-C₆H₆Ph)]ᶻ (Z = 0 or +1)[3] and [{Rh(CO)(PPh₃)(μ-RNNNR)}₂]ᶻ (Z = 0 or +1, R = p-tolyl).[4]

Results and Discussion

Single-crystal X-ray diffraction studies were carried out on [Rh₂(CO)₂(PPh₃)₂(η⁵:η′⁵-C₁₀H₈)][PF₆]₂ (1) and [Rh₂-(CO)₂(PPh₃)₂(η⁵:η′⁵-C₁₀H₈)] (2) in each case as their hexane
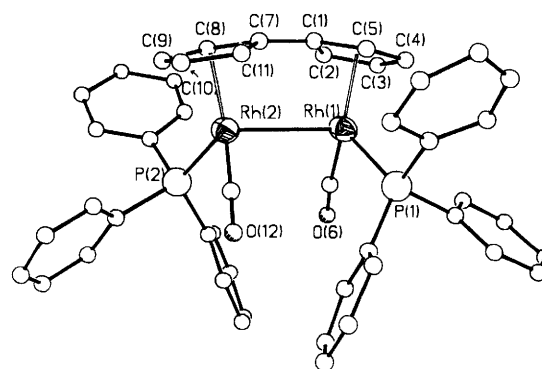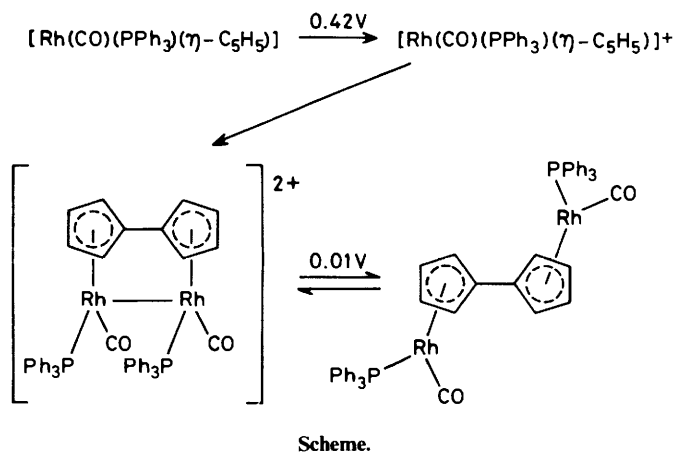

[Rh(CO)(PPh₃)(η–C₅H₅)] $\xrightarrow{0.42V}$ [Rh(CO)(PPh₃)(η–C₅H₅)]⁺

Scheme.

Figure 1. Molecular geometry of the dication of (1) showing the atomic labelling scheme used. Hydrogen atoms have been omitted for clarity

solvates. Selected derived bond lengths and inter-bond angles for (1) and (2) are in Tables 1 and 2 respectively, and the molecular geometries of the dication of (1) and of (2) are illustrated in Figures 1 and 2 respectively. Full details of the
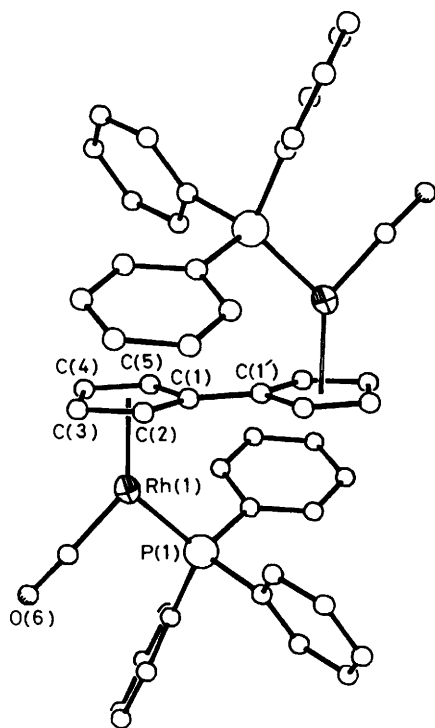
Figure 2. Molecular geometry of complex (2) showing the atomic labelling scheme used. Hydrogen atoms have been omitted for clarity

structure determinations are given in the Experimental section. Table 3 lists average molecular dimensions, including torsion angles, to allow direct comparison of (1) with (2).

The crystal structure of complex (1) as its hexane solvate shows no unusually short ion–ion or ion–solvent contacts. The solvent molecules are disordered along channels around a 2_1 axis parallel to b. The handedness of the individual crystal of (1)·0.5C$_6$H$_{14}$ used was determined by the η refinement method.[5] The value of η (which multiplies $\Delta f''$) refined to 1.09(18), indicating the correctness of the enantiomer of the dication of (1) depicted in Figure 1. The crystal structure of (2) as its hexane solvate also showed no unusually short intermolecular contacts.

Molecules of (2) lie about crystallographic inversion centres, which bisect the central C–C bond of the fulvalene moiety, and therefore have exact C_i symmetry. The solvent molecules are disordered about other inversion centres in the structure.

The dication of (1) shows approximate C_2 symmetry with the rhodium atoms on the same side of the fulvalene ligand, i.e. a cis configuration. Each rhodium atom is η^5-bonded to the fulvalene, terminally ligated by triphenylphosphine and CO ligands, and bonded to the other rhodium [Rh(1)–Rh(2) 2.930(2) Å]. In contrast, the Rh ••• Rh separation in complex (2) is very much larger [5.662(1) Å] as a consequence of the trans disposition of the rhodium atoms, i.e. on opposite sides of the fulvalene unit. In complex (2), as in (1), the rhodium atoms are η^5-bonded to the fulvalene ligand, and are further bonded to terminal triphenylphosphine and carbonyl ligands. Thus the ground-state structures of (1) and (2), in as much as they are reflected in their solid-state geometries, show a major

Table 1. Bond lengths (Å) and angles (°) for complex (1)

Rh(1)–Rh(2)	2.930(2)	Rh(1)–P(1)	2.312(4)	P(2)–C(211)	1.776(16)	P(2)–C(221)	1.839(16)
Rh(1)–C(3)	2.218(18)	Rh(1)–C(4)	2.242(16)	P(2)–C(231)	1.818(16)	C(3)–C(4)	1.408(23)
Rh(1)–C(5)	2.176(14)	Rh(1)–C(1)	2.244(15)	C(3)–C(2)	1.371(24)	C(4)–C(5)	1.373(23)
Rh(1)–C(2)	2.248(15)	Rh(1)–C(6)	1.860(17)	C(5)–C(1)	1.444(22)	C(1)–C(2)	1.426(21)
Rh(2)–P(2)	2.332(4)	Rh(2)–C(7)	2.254(15)	C(1)–C(7)	1.428(22)	C(6)–O(6)	1.123(20)
Rh(2)–C(8)	2.178(14)	Rh(2)–C(9)	2.199(17)	C(7)–C(8)	1.437(22)	C(7)–C(11)	1.501(25)
Rh(2)–C(10)	2.268(15)	Rh(2)–C(11)	2.223(13)	C(8)–C(9)	1.414(25)	C(9)–C(10)	1.337(23)
Rh(2)–C(12)	1.782(18)	P(1)–C(111)	1.811(17)	C(10)–C(11)	1.371(23)	C(12)–O(12)	1.199(21)
P(1)–C(121)	1.827(15)	P(1)–C(131)	1.807(18)				

Rh(2)–Rh(1)–P(1)	107.5(1)	Rh(2)–Rh(1)–C(3)	124.2(5)	C(10)–Rh(2)–C(12)	101.5(7)	C(11)–Rh(2)–C(12)	103.8(7)
P(1)–Rh(1)–C(3)	124.1(4)	Rh(2)–Rh(1)–C(4)	129.9(4)	Rh(1)–P(1)–C(111)	123.4(6)	Rh(1)–P(1)–C(121)	107.5(5)
P(1)–Rh(1)–C(4)	94.5(4)	C(3)–Rh(1)–C(4)	36.8(6)	C(111)–P(1)–C(121)	106.3(7)	Rh(1)–P(1)–C(131)	113.0(7)
Rh(2)–Rh(1)–C(5)	95.8(4)	P(1)–Rh(1)–C(5)	96.2(4)	C(111)–P(1)–C(131)	98.9(8)	C(121)–P(1)–C(131)	106.5(7)
C(3)–Rh(1)–C(5)	61.6(6)	C(4)–Rh(1)–C(5)	36.2(6)	Rh(2)–P(2)–C(211)	109.5(5)	Rh(2)–P(2)–C(221)	110.6(5)
Rh(2)–Rh(1)–C(1)	71.6(4)	P(1)–Rh(1)–C(1)	131.0(4)	C(211)–P(2)–C(221)	105.4(8)	Rh(2)–P(2)–C(231)	122.3(5)
C(3)–Rh(1)–C(1)	59.6(6)	C(4)–Rh(1)–C(1)	60.3(6)	C(211)–P(2)–C(231)	106.1(8)	C(221)–P(2)–C(231)	101.5(7)
C(5)–Rh(1)–C(1)	38.1(6)	Rh(2)–Rh(1)–C(2)	88.6(4)	Rh(1)–C(3)–C(4)	72.5(10)	Rh(1)–C(3)–C(2)	73.3(10)
P(1)–Rh(1)–C(2)	155.9(4)	C(3)–Rh(1)–C(2)	35.8(6)	C(4)–C(3)–C(2)	111.3(16)	Rh(1)–C(4)–C(3)	70.7(10)
C(4)–Rh(1)–C(2)	61.5(6)	C(5)–Rh(1)–C(2)	63.7(6)	Rh(1)–C(4)–C(5)	69.3(9)	C(3)–C(4)–C(5)	108.1(15)
C(1)–Rh(1)–C(2)	37.0(6)	Rh(2)–Rh(1)–C(6)	92.4(4)	Rh(1)–C(5)–C(4)	74.5(9)	Rh(1)–C(5)–C(1)	73.5(8)
P(1)–Rh(1)–C(6)	92.2(6)	C(3)–Rh(1)–C(6)	104.3(6)	C(4)–C(5)–C(1)	106.2(13)	Rh(1)–C(1)–C(5)	68.4(8)
C(4)–Rh(1)–C(6)	132.0(6)	C(5)–Rh(1)–C(6)	165.9(6)	Rh(1)–C(1)–C(2)	71.7(9)	C(5)–C(1)–C(2)	108.9(13)
C(1)–Rh(1)–C(6)	136.4(7)	C(2)–Rh(1)–C(6)	105.2(7)	Rh(1)–C(1)–C(7)	107.2(10)	C(5)–C(1)–C(7)	123.7(15)
Rh(1)–Rh(2)–P(2)	109.2(1)	Rh(1)–Rh(2)–C(7)	69.2(4)	C(2)–C(1)–C(7)	123.1(14)	Rh(1)–C(2)–C(3)	70.9(9)
P(2)–Rh(2)–C(7)	132.5(5)	Rh(1)–Rh(2)–C(8)	95.1(5)	Rh(1)–C(2)–C(1)	71.3(9)	C(3)–C(2)–C(1)	104.9(14)
P(2)–Rh(2)–C(8)	98.8(4)	C(7)–Rh(2)–C(8)	37.8(6)	Rh(1)–C(6)–O(6)	173.2(13)	Rh(2)–C(7)–C(1)	111.4(11)
Rh(1)–Rh(2)–C(9)	130.3(4)	P(2)–Rh(2)–C(9)	96.0(5)	Rh(2)–C(7)–C(8)	68.2(8)	C(1)–C(7)–C(8)	127.7(15)
C(7)–Rh(2)–C(9)	62.4(6)	C(8)–Rh(2)–C(9)	37.7(7)	Rh(2)–C(7)–C(11)	69.3(8)	C(1)–C(7)–C(11)	127.2(16)
Rh(1)–Rh(2)–C(10)	124.6(4)	P(2)–Rh(2)–C(10)	122.9(4)	C(8)–C(7)–C(11)	102.4(14)	Rh(2)–C(8)–C(7)	74.0(9)
C(7)–Rh(2)–C(10)	62.5(6)	C(8)–Rh(2)–C(10)	61.4(6)	Rh(2)–C(8)–C(9)	71.9(9)	C(7)–C(8)–C(9)	108.0(14)
C(9)–Rh(2)–C(10)	34.8(6)	Rh(1)–Rh(2)–C(11)	89.2(4)	Rh(2)–C(9)–C(8)	70.4(9)	Rh(2)–C(9)–C(10)	75.4(10)
P(2)–Rh(2)–C(11)	155.6(5)	C(7)–Rh(2)–C(11)	39.2(6)	C(8)–C(9)–C(10)	111.3(15)	Rh(2)–C(10)–C(9)	69.8(10)
C(8)–Rh(2)–C(11)	62.7(6)	C(9)–Rh(2)–C(11)	59.7(7)	Rh(2)–C(10)–C(11)	70.5(9)	C(9)–C(10)–C(11)	108.7(15)
C(10)–Rh(2)–C(11)	35.5(6)	Rh(1)–Rh(2)–C(12)	95.3(5)	Rh(2)–C(11)–C(7)	71.5(8)	Rh(2)–C(11)–C(10)	74.0(8)
P(2)–Rh(2)–C(12)	90.6(5)	C(7)–Rh(2)–C(12)	136.7(7)	C(7)–C(11)–C(10)	109.5(15)	Rh(2)–C(12)–O(12)	176.7(14)
C(8)–Rh(2)–C(12)	162.9(7)	C(9)–Rh(2)–C(12)	127.4(7)				

Table 2. Bond lengths (Å) and angles (°) for complex (2)

Rh(1)–P(1)	2.255(1)	Rh(1)–C(1)	2.324(5)
Rh(1)–C(2)	2.335(6)	Rh(1)–C(3)	2.236(5)
Rh(1)–C(4)	2.268(5)	Rh(1)–C(5)	2.293(5)
Rh(1)–C(6)	1.808(7)	P(1)–C(111)	1.846(5)
P(1)–C(121)	1.842(5)	P(1)–C(131)	1.843(5)
C(1)–C(2)	1.419(8)	C(1)–C(5)	1.444(7)
C(1)–C(1')	1.475(9)	C(2)–C(3)	1.416(7)
C(3)–C(4)	1.428(9)	C(4)–C(5)	1.390(7)
C(6)–O(6)	1.152(9)		

P(1)–Rh(1)–C(1)	103.8(1)	P(1)–Rh(1)–C(2)	128.4(1)
C(1)–Rh(1)–C(2)	35.5(2)	P(1)–Rh(1)–C(3)	163.4(1)
C(1)–Rh(1)–C(3)	60.0(2)	C(2)–Rh(1)–C(3)	36.0(2)
P(1)–Rh(1)–C(4)	140.5(2)	C(1)–Rh(1)–C(4)	59.7(2)
C(2)–Rh(1)–C(4)	60.1(2)	C(3)–Rh(1)–C(4)	36.9(2)
P(1)–Rh(1)–C(5)	109.3(1)	C(1)–Rh(1)–C(5)	36.4(2)
C(2)–Rh(1)–C(5)	60.1(2)	C(3)–Rh(1)–C(5)	60.7(2)
C(4)–Rh(1)–C(5)	35.5(2)	P(1)–Rh(1)–C(6)	90.6(2)
C(1)–Rh(1)–C(6)	162.0(3)	C(2)–Rh(1)–C(6)	126.6(3)
C(3)–Rh(1)–C(6)	104.6(3)	C(4)–Rh(1)–C(6)	114.7(2)
C(5)–Rh(1)–C(6)	147.0(2)	Rh(1)–P(1)–C(111)	117.4(2)
Rh(1)–P(1)–C(121)	116.8(2)	C(111)–P(1)–C(121)	100.6(2)
Rh(1)–P(1)–C(131)	113.1(2)	C(111)–P(1)–C(131)	103.9(2)
C(121)–P(1)–C(131)	103.2(2)	Rh(1)–C(1)–C(2)	72.7(3)
Rh(1)–C(1)–C(5)	70.6(3)	C(2)–C(1)–C(5)	108.1(4)
Rh(1)–C(1)–C(1')	127.1(4)	C(2)–C(1)–C(1')	126.3(6)
C(5)–C(1)–C(1')	125.3(6)	Rh(1)–C(2)–C(1)	71.9(3)
Rh(1)–C(2)–C(3)	68.2(3)	C(1)–C(2)–C(3)	107.2(5)
Rh(1)–C(3)–C(2)	75.8(3)	Rh(1)–C(3)–C(4)	72.8(3)
C(2)–C(3)–C(4)	108.3(5)	Rh(1)–C(4)–C(3)	70.3(3)
Rh(1)–C(4)–C(5)	73.2(3)	C(3)–C(4)–C(5)	108.6(4)
Rh(1)–C(5)–C(1)	73.0(3)	Rh(1)–C(5)–C(4)	71.3(3)
C(1)–C(5)–C(4)	107.6(5)	Rh(1)–C(6)–O(6)	177.7(6)

Table 3. Molecular dimensions of complexes (1) and (2)[a]

Parameter	(1)	(2)
Distances (Å)		
Rh–Rh	2.930(2)[b]	5.662(1)
Rh–P	2.332(4)	2.255(1)
Rh–C(O)	1.821(18)	1.808(7)
Rh–C(fulvalene)	2.225(10)	2.291(15)
P–C	1.813(8)	1.844(5)
C–C(central, $C_{10}H_8$)	1.428(22)	1.475(9)
C–C(intra-ring, $C_{10}H_8$)	1.408(15)	1.419(9)
C–O	1.161(21)	1.152(9)
Rh–η^5-C_5 plane	1.875	1.946
Angles (°)[c]		
Ct–Rh–P	124.2	133.2
Ct–Rh–C(O)	131.5	136.1
C(O)–Rh–P	91.4	90.6
Sum	347.1	359.9
Torsion angles (°)		
cis[d]	6.1(25)	6.8(6)
trans[d]	156.1(14)	180.0
(O)C–Rh–Rh–P	78.9(8)	
P–Rh–Rh–P	–106.7(2)	
OC–Rh–Rh–P	–14.2(5), –13.6(6)	

[a] Values quoted are averaged, where appropriate over chemically equivalent observations [assuming C_2 symmetry of the dication of (1)]. [b] Estimated standard deviations, s, are from least-squares variances for single observations and for averages over <5 observations, x, and $s = [\sum_n (x - <x>)^2/n(n - 1)]^{\frac{1}{2}}$ for $n > 5$. [c] Ct = η^5-C_5 ring centroid. [d] About central C–C bond of fulvalene; absolute values are given.

conformational change, *viz. cis–trans* isomerisation. The details of this change are revealed by inspection of Table 3. There has been what amounts to *ca.* 180° rotation about the C(1)–C(1') bond of complex (2) on oxidation to (1). Computer modelling shows that 180° rotation of one $C_5H_4Rh(CO)PPh_3$ moiety about this bond in (2) leads to a Rh ... Rh distance of 4.278 Å. The observed distance [2.930(2) Å] in (1) comes about by a distortion of the fulvalene ligand such that it becomes markedly non-planar, showing both an out-of-plane bend at atoms C(1) and C(7) (average 12°, towards the attached rhodium) and a twist [of 6.1° about C(1)–C(7)]. The resulting dihedral angle between the five-membered rings of the fulvalene ligand in complex (1) is 26.6°, as compared with 0° for (2) which shows an out-of-plane bend of 6.8° at C(1), *away* from its bonded rhodium atom. The flexibility of the fulvalene ligand towards distortions involving inter-ring dihedral angles of up to 32° has been noted.[6–10] One of the largest of these dihedral angles is in $[Ru_2(CO)_4(\eta^5:\eta'^5-C_{10}H_8)]$,[6] a compound valence-isoelectronic with the dication of (1). The diamagnetism and *cis* geometry of complex (1) is consistent with the presence of a Rh–Rh single bond, although it is rather long. Rhodium(II)–rhodium(II) bonds are known to be as short as 2.359(1) Å,[11] although at least one distance longer than that in (1) is known {in $[Rh_2(dmg)_4(PPh_3)_2]$,[12] Rh ··· Rh 2.936(2) Å; dmg = dimethylglyoximate}. The extremely long Rh(1)–Rh(2) bond in (1) may be partly attributed to the unwillingness of the fulvalene to distort further (as would be required to maintain rhodium ··· fulvalene bonding and reduce the Rh ··· Rh distance) and to steric factors. The importance of the first factor is emphasised by the rather long Ru–Ru and W–W distances observed in $[Ru_2(CO)_4(\eta^5:\eta'^5\text{-fulvalene})]$[6] and $[W_2(CO)_6(\eta^5:\eta'^5\text{-fulvalene})]$[7] [2.821(1) and 3.347(1) Å, respectively] {*cf.* Ru–Ru 2.735(2) and W–W 3.222(1) Å in $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$[13] and

$[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$[14]} which have inter-ring angles of 28.5 and 16.1°, respectively.

The importance of steric factors is reflected in the twisting of the P(1)–Rh(1)–Rh(2)–P(2) unit [torsion angle −106.7(2)°] and the disposition of the terminal ligands which serves to place the bulky phosphines as far apart as possible. The communication of this twisting to the fulvalene ligand may be seen in the *trans*-C–C–C–C torsion angles about C(1)–C(7) (see Table 3). In $[Ru_2(CO)_4(\eta^5:\eta'^5\text{-fulvalene})]$[6] which has less bulky ligands the twisting about the central C–C bond is smaller (2.3°) and the $(OC)_2Ru–Ru(CO)_2$ system is more nearly eclipsed (C–Ru–Ru–C torsion angles are 3.4, 2.3, 94.1, and −88.4°, *cf.* Table 3). The co-ordination geometry at rhodium in complex (1) reflects the desire to maximise Rh–Rh bonding. Whereas in (2) the C_5 ring centroid (Ct), Ru, P, and CO lie in a plane (hence Σ angles at Rh is 359.9°), in (1) these form a shallow pyramid pointing towards the second Rh atom (Σ angles at Rh averages 347.1°). Similar, although less marked, pyramidalisation at Ru is seen in $[Ru_2(CO)_4(\eta^5:\eta'^5\text{-fulvalene})]$[6] ($\Sigma$ angles averages 353.1°).

The effects of oxidation on metal–ligand bonding are not as dramatic as that on metal–metal bonding, although they are not insignificant. Thus, the Rh–P distances increase on oxidation [by *ca.* 0.067(4) Å], the Rh–C(O) distances are marginally (not statistically significantly) longer, and the Ru–C(fulvalene) distances are shorter in the dication of (1) as compared with (2). These changes may be attributed to reductions in the covalent radius and π-basicity of Rh on going from oxidation state I to II. The increase in the Rh–P distance is accompanied by a *decrease* in the P–C distances in the PPh_3 groups (see Table 3). This is consistent with lower π-donation from Rh to P in complex (1) than in (2) resulting in lower occupancy of the P–C σ* orbitals which play a part in the π-acceptor function of phosphines.[15]

Although the rather high standard deviations in C–C distances in complex (1) preclude any detailed discussion of the
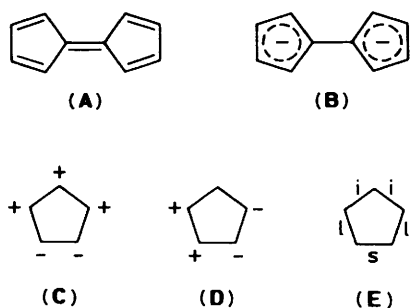
bonding within the fulvalene ligand, for (2) the situation is better. The inter-ring distance C(1)–C(1') [1.475(9) Å] is appropriate for an sp^2–sp^2 C–C single bond and is markedly longer than that in the substituted fulvalene $C_{10}H_4Bu^t_4$[16] [1.42(2) Å]. This is in accord with the implication above that in (2) [and (1)] the fulvalene ligand is best viewed as a dianion, i.e. as in (B) rather than (A), leading to a rhodium oxidation state of I in (2) and II in (1). The effect of the d^8-ML_2 fragment on the pattern of C–C distances in cyclopentadienyl complexes has been noted by Byers and Dahl[17] for $[Co(CO)_2(\eta\text{-}C_5Me_5)]$ and by Harlow et al.[18] in $[Co(PEt_3)_2(\eta\text{-}C_5H_5)]$. The effect of aligning the ML_2 plane with a C–C bond of the five-membered ring is to induce variation in the C–C distances due to preferential depopulation of one of the e_1 set of cyclo-pentadienide anion π orbitals [i.e. the interaction of the metal with (D) is larger than with (C)]. Hence the C–C bond lengths follow the pattern in (E) (s = short, i = intermediate, and l = long). Such a pattern is observed in complex (2), where the $Rh(CO)(PPh_3)$ plane lies approximately parallel to C(4)–C(5), the shortest of the fulvalene C–C bonds (see Figure 3). No such variation is seen in (1), partly because of the increased standard deviations, and presumably partly because oxidation at Rh would lessen this effect {cf. $[Co(PEt_3)_2(\eta\text{-}C_5H_5)]^{+}$[18] which also shows no such effect}. Pyramidalisation at Rh likewise would reduce the asymmetry of the frontier orbitals of the rhodium-based fragment {cf. $[Ru_2(CO)_4(\eta^5:\eta'^5\text{-fulvalene})]$[7] which also shows a pattern of C–C lengths unlike that in (E)}. Other features of the ligand geometry in complexes (1) and (2) are unremarkable.

To assess some of the qualitative conclusions concerning the electronic structure of the dication (1) and of (2) mentioned above, extended-Hückel molecular-orbital (e.H.m.o.)[19] calculations were performed on the model complex $[Rh_2(CO)_4$-$(\eta^5:\eta'^5\text{-fulvalene})]$ (3), and for fulvalene (4) and the fulvalene dianion (5). Idealised geometries were used with all C–C 1.42 Å, C_5 rings regular pentagons, all C–H 1.09 Å, Rh–C(O) 1.81 Å, C–O 1.15 Å, Rh–C–O 180°, (O)C–Rh–C(O) 90°, and Rh–C(fulvalene) 2.294 Å. Calculations were performed on the cis and trans geometries of (3) with exact C_{2v} and C_{2h} symmetries, and with an intermediate geometry (i.e. with C–C–C–C torsion angles about the central C–C bond of ±90° rather than 0 or 180°). The calculations therefore allowed crude computation of the barriers to rotation about the central C–C bond for (3), (4), and (5). These were 5.6, 27.8, and 5.4 kcal mol⁻¹ respectively. The bond orders of the central C–C bond in trans-(3), (4), and (5) as reflected in the total atomic overlap population were 0.933, 1.06, and 0.923 (cf. other overlap populations as below). Taken together these results show that both in terms of the ground-state bond orders (as indicated by net atomic overlap populations) and in the barriers to rotation the complexed fulvalene is closely similar to the fulvalene dianion (5) [rather than free fulvalene (4)]. The frontier-orbital energies for the $[Rh(CO)_2]_2$ and $C_{10}H_8$ moieties are likewise consistent with this view, i.e. that in complex (3) [and therefore in (2)] the rhodium atoms are best viewed as rhodium(I), d^8 centres. The
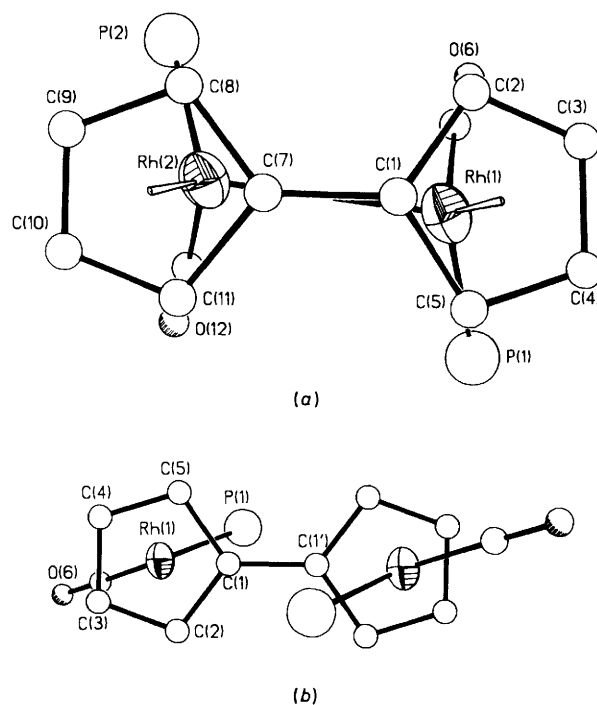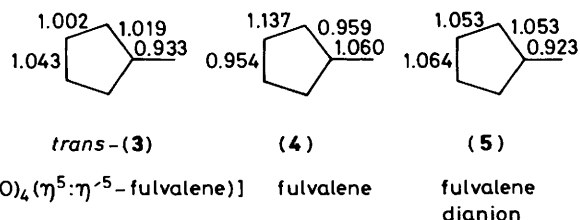
Figure 3. Fulvalene–rhodium carbonyl triphenylphosphine bonding in complexes (1) and (2) [(a) and (b) respectively]. All oxygen and hydrogen atoms and phenyl groups are omitted for clarity


trans-(3)   (4)   (5)
[Rh₂(CO)₄(η⁵:η'⁵-fulvalene)]   fulvalene   fulvalene dianion

variation in intra-ring C–C bond order induced by the $Rh(CO)_2$ moiety is clearly seen in trans-(3).

The Rh ⋯ Rh overlap population for cis-(3) (where Rh ⋯ Rh is 3.86 Å under the idealised C_{2v} symmetry used) is −0.014. This may be traced in part to the highest occupied molecular orbital (h.o.m.o.) of cis-(3) which has Rh ⋯ Rh σ^* and π^* components as depicted below. Harlow et al.[18] reported a h.o.m.o. analogous to that of complex (3) for the mono-nuclear species $[Co(PEt_3)_2(\eta\text{-}C_5H_5)]$, of course with no metal ⋯ metal interaction. Clearly if cis-(3) were oxidised the Rh ⋯ Rh bond order would rise. Pyramidalisation at Rh in the manner observed in (1) would cause enhanced hybridisation of the orbitals involved in the Rh ⋯ Rh interaction depicted, making them more nearly σ in character [cf. the frontier orbitals of the pyramidal $ML_2(C_5H_5)$ fragment[20], thereby increasing the magnitude of the Rh ⋯ Rh interaction. As might be expected the small energy preference for trans-(3) compared with cis-(3) (ca. 3 kcal mol⁻¹ as calculated from the sum of one-electron orbital energies) can be traced to unfavourable four-electron Rh ⋯ Rh interactions (e.g. that in the h.o.m.o. and its lower-energy Rh ⋯ Rh bonding partner).

Of the many fulvalene complexes now known,[6] electron-transfer reactions are largely confined to $[M_2(\eta^5:\eta'^5\text{-}C_{10}H_8)_2]^Z$; for M = V,[21] Fe[22] Co,[23] and Ni[24] neutral, monocationic, and dicationic species are all isolable.

The bonding[22,24–27] in $[M_2(\eta^5:\eta'^5\text{-}C_{10}H_8)_2]^Z$ has attracted attention due to the observed diamagnetism of the dications and
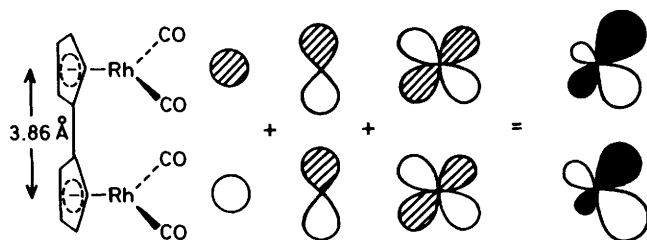
because of the possibility of either trapped valence states or delocalisation in the monocations. Surprisingly, however, only one structural comparison of a redox-related pair of complexes (M = Fe, $Z = 0$ or $+1$)[8] has been made; the reduction in metal–metal bond distance [Fe $\cdots$ Fe shortens by 0.34(2) Å] and only small changes in the geometry of the $C_{10}H_8$ ligands has been taken to imply a degree of direct iron–iron interaction.[8]

Other redox-related series include $[V_2L_2(\eta^5:\eta'^5\text{-}C_{10}H_8)]^Z$ ($Z = 0, +1,$ or $+2$; $L = CO$ or $MeCN^{21}$), $[Mo_2(CO)_6(\eta^5:\eta'^5\text{-}C_{10}H_8)]^Z$ ($Z = 0$ or -2),[28] and $[Nb_2(\mu\text{-}NR)_2(\eta^5:\eta'^5\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2]^Z$ ($Z = 0$ or $+1$, $R = C_6H_4OMe\text{-}p$).[9] The niobium complexes have been structurally characterised but there is relatively little change in the geometry. Thus, the Nb–Nb distance varies from 2.834(1) ($Z = 0$) to 2.921(1) Å ($Z = +1$), and the C_5H_4–C_5H_4 bond distance decreases from 1.53(3) ($Z = 0$) to 1.46(1) Å ($Z = +1$).

Comments on the Cyclic Voltammetry of Complexes (1) and (2).—The discovery of a large structural change when complex (1) is reduced to (2) poses a major problem with regard to the cyclic voltammetry of the two species.[1] The cyclic voltammogram of the neutral compound (2) shows[1] an oxidation wave of two-electron height with a peak separation of *ca.* 35 mV, entirely consistent with the one-electron oxidation of each of two essentially non-interacting metal centres. However, dication (1), which we have now shown to contain a direct metal–metal bond, would be expected to show two well separated one-electron reduction waves {*cf.* the bis(fulvalene) complex $[Fe_2(C_{10}H_8)_2]$ is oxidised[27] to mono- and di-cations with the corresponding cyclic voltammetric waves separated by *ca.* 0.6 V}. Surprisingly, therefore, the cyclic voltammograms of (1) and (2) are identical.

That complexes (1) and (2) are both fully structurally characterised will provide an invaluable basis for the interpretation of the more detailed electrochemical studies clearly required. One possible explanation for the cyclic voltammetric data so far obtained, derived from the theoretical analysis given above, is that *cis-* and *trans-*(2) are in rapid equilibrium in solution. The e.H.m.o. study also implies that *cis-*(2) would be marginally more readily oxidised than *trans-*(2) [the h.o.m.o. of *cis-*(3) lies 0.09 eV higher in energy than that of *trans-*(3)]. Finally, we note that we cannot *assume* that we are observing the ground-state isomers of complexes (1) and (2) in their solid-state structures, although it seems likely that the solution-state molecular geometries would be closely related to those in the crystal [particularly for the dication of (1)].

Experimental

The structure analyses were carried out by conventional single-crystal *X*-ray diffraction techniques at room temperature on single crystals mounted under N_2 in thin-walled glass capillaries and using graphite-monochromated Mo-K_α *X*-radiation on a Nicolet *P*3*m* diffractometer. Integrated intensities were measured for a unique volume of reciprocal space in the range $4 < 2\theta < 50°$ using variable scan speeds based on a 2-s prescan. Check reflections were remeasured after every 50 data to

Table 4. Structure analyses

Data collection	(1)	(2)
Crystal colour and habit	Orange needles	Orange-red prisms
Method of crystal growth	Crystallised from CH_2Cl_2–hexane solution	Crystallised from CH_2Cl_2–hexane solution
Approximate crystal size (mm)	$0.1 \times 0.12 \times 0.4$	$0.3 \times 0.3 \times 0.1$
Method of data collection	ω(wyckoff)	θ—2θ
Scan speeds (° min^{-1})		
minimum	0.5	2.0
maximum	29.3	29.3
Scan width (°)	0.6	$2.0 + \Delta_{\alpha_1\alpha_2}$
Check reflections	(7,2,1), (0,5,9), (0,2,12)	$(-8,1,3), (-3,4,-3), (3,1,-9)$
Number of data collected		
Total	5 072	4 176
unique	5 042	3 821
observed, N_0	2 510	3 109
Criterion for observed, n in $I > n\sigma(I)$	2.5	1.5
Transmission coefficient range	0.916—0.890	0.922—0.790
Refinement		
Solution method	Patterson	Patterson
Anisotropic atoms	All non-H, except solvent C	All non-H
Isotropic atoms	Solvent, all H	All H
No. of parameters refined, N_v	638	281
Final R[*]	0.0554	0.0457
R'	0.0477	0.0427
g	0.0001	0.0006
S	1.298	1.135
Largest final difference electron-density features (e Å^{-3})	0.54	0.47
Shift/e.s.d. in last cycles of refinement		
maximum	0.131	0.024
average	0.032	0.006

[*] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$, and $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$.

monitor experimental stability which was good. Absorption corrections were applied by Gaussian quadrature based on the indexed crystal faces. Full numerical details of the data collection and structure refinement are given in Table 4. The structures were solved by standard heavy-atom methods and refined by blocked-cascade full-matrix least squares. Hydrogen atoms were incorporated in idealised geometries with C–H 0.96 Å and isotropic vibrational parameters fixed at *ca.* 1.2 times that of their attached carbon atoms. The solvent molecules were not well defined in either structure but were modelled by partial occupancy carbon atoms around screw axes for complex (1) and inversion centres in (2), leading to the approximate stoicheiometries quoted. Intensity data were assigned individual weights $w = (\sigma_c^2 + gF_o^2)^{-1}$ where σ_c is the variance due to counting statistics alone and g was chosen to minimise the variation in $\Sigma w(|F_o| - |F_c|)^2$ with $|F_o|$. Refinements converged smoothly to give the final residuals listed in Table 4.

Final non-hydrogen atomic parameters for (1) and (2) as their hexane solvates are given in Tables 5 and 6, respectively. All calculations were carried out with the SHELXTL[29] program package on a Data General Eclipse (R) minicomputer. Complex neutral-atom scattering factors were used, taken from ref. 30.

Table 5. Atomic co-ordinates (× 10⁴) for complex (1)

Atom	x	y	z	Atom	x	y	z
Rh(1)	1 319(1)	2 391(1)	1 559(1)	C(212)	−882(10)	1 150(17)	590(6)
Rh(2)	839(1)	−65(1)	1 308(1)	C(213)	−1 590(11)	1 476(23)	617(8)
P(1)	2 595(2)	2 383(4)	1 593(2)	C(214)	−2 077(11)	512(21)	486(7)
P(2)	424(2)	−121(4)	445(2)	C(215)	−1 774(14)	−703(22)	345(9)
C(3)	614(9)	3 755(18)	1 949(6)	C(216)	−1 038(11)	−884(20)	301(7)
C(4)	1 185(9)	3 453(15)	2 298(6)	C(221)	615(8)	−1 601(14)	150(6)
C(5)	1 143(8)	2 238(15)	2 398(5)	C(222)	808(9)	−2 559(14)	438(7)
C(1)	473(9)	1 823(13)	2 150(5)	C(223)	957(13)	−3 626(18)	218(9)
C(2)	171(8)	2 781(13)	1 846(6)	C(224)	874(14)	−3 734(21)	−323(12)
C(6)	1 318(10)	2 847(12)	859(7)	C(225)	653(14)	−2 846(20)	−621(8)
O(6)	1 323(8)	3 236(10)	454(5)	C(226)	508(10)	−1 782(17)	−388(7)
C(7)	312(10)	582(15)	2 055(5)	C(231)	776(9)	897(15)	−54(6)
C(8)	−225(7)	90(18)	1 700(5)	C(232)	364(11)	1 673(17)	−315(8)
C(9)	−68(9)	−1 149(14)	1 634(7)	C(233)	641(14)	2 321(21)	−733(8)
C(10)	527(8)	−1 477(14)	1 909(6)	C(234)	1 358(11)	2 196(16)	−899(6)
C(11)	805(11)	−480(15)	2 157(5)	C(235)	1 777(9)	1 446(15)	−635(7)
C(12)	1 727(10)	−579(15)	1 108(6)	C(236)	1 487(9)	794(13)	−224(6)
O(12)	2 319(6)	−977(11)	987(5)	P(3)	9 061(4)	5 596(5)	1 128(2)
C(111)	3 165(10)	1 429(15)	1 184(5)	P(4)	7 841(3)	1 812(5)	2 288(2)
C(112)	3 063(11)	1 539(14)	651(6)	F(1)	8 335(7)	5 125(13)	935(4)
C(113)	3 534(9)	859(21)	335(7)	F(2)	8 958(7)	4 946(12)	1 670(4)
C(114)	4 026(10)	104(24)	488(7)	F(3)	9 833(6)	6 078(10)	1 341(5)
C(115)	4 114(12)	2(22)	1 003(9)	F(4)	9 203(7)	6 253(10)	609(4)
C(116)	3 685(11)	687(18)	1 376(7)	F(5)	8 680(7)	6 776(9)	1 350(4)
C(121)	2 862(8)	2 058(13)	2 267(5)	F(6)	9 482(8)	4 405(9)	906(5)
C(122)	2 785(9)	876(16)	2 448(7)	F(7)	8 378(9)	1 230(11)	2 708(7)
C(123)	2 963(10)	734(19)	2 970(8)	F(8)	8 559(7)	2 387(15)	2 065(5)
C(124)	3 081(14)	1 652(26)	3 316(7)	F(9)	7 371(8)	2 326(14)	1 876(5)
C(125)	3 172(13)	2 717(22)	3 101(9)	F(10)	7 243(8)	1 138(15)	2 543(5)
C(126)	3 062(10)	2 954(18)	2 602(6)	F(11)	7 741(7)	2 870(11)	2 668(5)
C(131)	2 998(11)	3 826(15)	1 431(5)	F(12)	7 986(9)	640(11)	1 933(5)
C(132)	2 549(11)	4 810(13)	1 321(6)	C(13)*	5 103(24)	2 130(41)	2 649(17)
C(133)	2 850(20)	5 944(22)	1 190(9)	C(14)*	5 527(24)	2 822(41)	2 343(17)
C(134)	3 636(19)	6 141(24)	1 190(12)	C(15)*	4 940(39)	1 676(62)	2 314(34)
C(135)	4 034(15)	5 164(24)	1 295(10)	C(16)*	5 097(39)	3 088(77)	2 834(27)
C(136)	3 762(12)	3 959(20)	1 434(9)	C(17)*	5 205(23)	4 056(41)	2 489(16)
C(211)	−553(9)	33(17)	433(5)	C(18)*	5 378(26)	1 343(37)	2 064(16)

* Partial site occupancy [0.36(4)—0.58(4)].

Table 6. Atomic co-ordinates (× 10⁴) for complex (2)

Atom	x	y	z	Atom	x	y	z
Rh(1)	4 298(1)	−5 441(1)	−3 526(1)	C(122)	1 355(3)	−4 534(6)	−5 096(3)
P(1)	3 034(1)	−4 215(1)	−4 005(1)	C(123)	787(4)	−5 115(7)	−5 764(4)
C(1)	5 158(3)	−5 227(5)	−4 570(3)	C(124)	1 098(4)	−6 161(7)	−6 214(4)
C(2)	5 245(4)	−6 627(6)	−4 282(3)	C(125)	1 972(5)	−6 636(7)	−5 990(4)
C(3)	5 613(3)	−6 579(7)	−3 427(3)	C(126)	2 542(4)	−6 070(6)	−5 309(3)
C(4)	5 819(4)	−5 158(7)	−3 205(3)	C(131)	3 269(3)	−2 484(5)	−4 412(3)
C(5)	5 521(3)	−4 319(6)	−3 890(3)	C(132)	2 852(4)	−2 003(6)	−5 176(4)
C(6)	3 779(4)	−6 150(8)	−2 700(4)	C(133)	3 070(5)	−701(7)	−5 462(5)
O(6)	3 476(4)	−6 602(7)	−2 158(4)	C(134)	3 688(5)	127(7)	−4 981(5)
C(111)	2 264(3)	−3 833(6)	−3 269(3)	C(135)	4 120(5)	−326(7)	−4 225(4)
C(112)	1 734(4)	−4 897(7)	−3 032(3)	C(136)	3 918(4)	−1 644(6)	−3 943(4)
C(113)	1 176(4)	−4 658(9)	−2 455(4)	C(7)*	96(39)	5 989(51)	475(30)
C(114)	1 139(4)	−3 348(10)	−2 106(4)	C(8)	658(23)	4 619(21)	507(21)
C(115)	1 652(5)	−2 313(9)	−2 336(4)	C(9)	1 503(16)	3 816(21)	1 175(13)
C(116)	2 218(4)	−2 536(7)	−2 911(4)	C(10)*	460(28)	3 754(37)	274(21)
C(121)	2 238(3)	−4 999(5)	−4 864(3)				

* Partial site occupancy (0.5).

Crystal Data.—For (1)·0.5C₆H₁₄. C₄₈H₃₈F₁₂O₂P₄Rh₂· 0.5C₆H₁₄, $M = 1\,247.5$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 18.115(10)$, $b = 11.091(4)$, $c = 25.580(11)$ Å, $U = 5\,137(4)$ Å³, $Z = 4$, $D_c = 1.61$ g cm⁻³, $F(000) = 2\,400$, graphite-monochromated X-radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 8.33 cm⁻¹, $T = 293$ K. Crystal faces [distance from origin (mm)]: (1 0 0) [0.05], ($\bar{1}$ 0 0) [0.05], (0 1 0) [0.20], (0 $\bar{1}$ 0) [0.20], (0 0 1) [0.06], (0 0 $\bar{1}$) [0.06].

For (2)·0.66C₆H₁₄· C₄₈H₃₈O₂P₂Rh₂·0.66C₆H₁₄, $M = 914.2$, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.016(3)$, $b = 9.571(2)$, $c = 16.402(4)$ Å, $\beta = 99.96(2)°$, $U = 2\,321(1)$ Å³, $Z = 2$, $D_c = 1.31$ g cm⁻³, $F(000) = 924$, graphite-monochrom-

ated X-radiation, $\bar{\lambda} = 0.710\,69$ Å, $\mu(Mo\text{-}K_\alpha) = 8.00\,cm^{-1}$, $T = 293$ K. Crystal faces [distance from origin (mm)]: $(1\,0\,0)$ [0.05], $(\bar{1}\,0\,0)$ [0.05], $(0\,1\,\bar{1})$ [0.15], $(0\,\bar{1}\,1)$ [0.15], $(0\,1\,2)$ [0.15], $(0\,\bar{1}\,\bar{2})$ [0.15].

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