The authors wish to thank C. Carpentier and M. Muller for growing the crystals and G. Odou for technical assistance during the experiments.

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Structures of Two 6,6-Diarylfulvene Complexes of Rhodium: (1,5-Cyclooctadiene)-(6,6-diphenylfulvene)rhodium(I) Perchlorate, $[Rh(C_8H_{12})(C_{18}H_{14})]ClO_4$, (I), and [6,6-Bis(4-chlorophenyl)fulvene]bis(triphenyl phosphite)rhodium(I) Perchlorate, $[Rh(C_{18}H_{12}Cl_2)(C_{18}H_{15}O_3P)_2]ClO_4$, (II)

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(*Received* 10 *October* 1984; *accepted* 4 *February* 1985)

Abstract. Complex (I): $M_r = 540{\cdot}85$, monoclinic, $P2_1/n$, $a = 14{\cdot}435$ (5), $b = 10{\cdot}882$ (3), $c = 15{\cdot}141$ (4) Å, $\beta = 104{\cdot}62$ (3)°, $V = 2301{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}561$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 7·47 mm^{-1}, $F(000) = 1104$, $T = 290$ (1) K, $R = 0{\cdot}070$ for 1826 observed reflections. The Rh is coordinated to all five C atoms in the fulvene ring, with Rh—C distances varying between 2·180 (11) and 2·295 (12) Å, and to the four olefinic C atoms in the 1,5-cyclooctadiene, with Rh—C distances in the range 2·145 (14)–2·183 (14) Å. Complex (II): $M_r = 1122{\cdot}19$, triclinic, $P\bar{1}$, $a = 11{\cdot}537$ (2), $b = 12{\cdot}276$ (2), $c = 20{\cdot}135$ (2) Å, $\alpha = 75{\cdot}83$ (1), $\beta = 76{\cdot}72$ (1), $\gamma = 65{\cdot}44$ (1)°, $V = 2488{\cdot}15$ Å^3, $Z = 2$, $D_x = 1{\cdot}498$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·620 mm^{-1}, $F(000) = 1144$, $T = 290$ (1) K, $R = 0{\cdot}031$ for 9098 observed reflections. Again the Rh is coordinated to all five fulvene-ring C atoms, with Rh—C distances between 2·224 (2) and 2·412 (2) Å. The Rh—P distances are 2·226 (1) and 2·203 (1) Å. In each complex the exocyclic C atom in the fulvene ligand is bent away from the metal [by 4·4 and 8·8° in (I) and (II) respectively].

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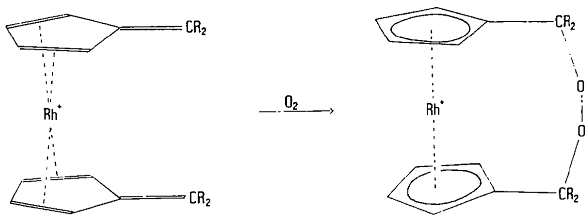
0108-2701/85/060850-06$01.50

Introduction. Recently we have described an unusual reaction of 6,6-diarylfulvene complexes of rhodium(I), $[Rh\{C_5H_4C(C_6H_4X-4)_2\}_2]^+$ (X = H, Cl, OMe or Me), with molecular oxygen (Jeffery, Probitts & Mawby, 1984).



In the course of the reaction (where $R = C_6H_4X-4$), the O_2 molecule becomes attached to the exocyclic C atoms in the two fulvene ligands, so that it forms a peroxide bridge linking the two substituted cyclopentadienyl rings (Jeffery, Mawby, Hursthouse & Walker, 1982).

We suggested that the attack by O_2 on the fulvene ligands occurred by way of an initial interaction with the *metal*, to give species $[Rh\{C_5H_4C(C_6H_4X-4)_2\}_2(O_2)]^+$. This seemed a reasonable hypothesis since Rh^I is known to form complexes with O_2 (McGinnety, Payne & Ibers, 1969; Bennett & Donaldson, 1971; Laing, Nolte & Singleton, 1975). If these species were regarded as being complexes of Rh^I with a singlet O_2 molecule (Bennett & Donaldson, 1971; Mason, 1968), the subsequent transfer could be regarded as being somewhat analogous to the reaction of singlet dioxygen with anthracene, in which the O_2 forms a peroxide bridge across the 9 and 10 positions in the centre ring (Dufraisse & Gerard, 1937). An alternative approach would be to consider the intermediates to be peroxide complexes of Rh^{III}, and to treat the subsequent step as a nucleophilic attack by peroxide ion on the exocyclic fulvene C atoms.

There has been recent interest in the nature of the bonding between fulvene ligands and metal atoms or ions, focusing on the geometry of the fulvene ligand and the metal-fulvene bonding and on the charge distribution within the ligand (Hoffmann & Hofmann, 1976; Watts, 1981). We hoped that a study of the bonding between diarylfulvene ligands and Rh^I might help to explain the susceptibility of the exocyclic C atoms in such ligands to attack by O_2. Ideally we would have liked to investigate the structures of the cations $[Rh\{C_5H_4C(C_6H_4X-4)_2\}_2]^+$ themselves, but we were unable to grow crystals suitable for X-ray work. Instead we have studied the two 'model' complexes $[Rh(C_8H_{12})(C_5H_4CPh_2)]ClO_4$ [complex (I), where C_8H_{12} represents 1,5-cyclooctadiene] and $[Rh\{C_5H_4C(C_6H_4Cl-4)_2\}_2\{P(OPh)_3\}_2]ClO_4$ [complex (II)].

Experimental. Complexes (I) and (II) were prepared as described previously (Jeffery *et al.*, 1984). Crystals suitable for X-ray analysis were obtained by slow evaporation under nitrogen of solutions of the complexes in propanone–ethanol mixtures. Preliminary unit-cell parameters and space-group data were obtained by X-ray precession and Weissenberg photography, and accurate cell dimensions by least-squares fitting of 20 [for (I)] and 25 [for (II)] reflections with high 2θ values. The *SHELX*76 (Sheldrick, 1976) system of computer programs was used. Atomic scattering factors and f' and f'' were taken from *International Tables for X-ray Crystallography* (1974).

Determination of the structure of complex (I). Intensity data collected on a burgundy-coloured plate of approximate size 0·70 × 0·20 × 0·05 mm. Hilger & Watts Y290 four-circle diffractometer controlled by an LSI-11 microcomputer. ω-scanning technique used, with a count time per step of 1 s and 30 steps of 0·02°. Reflections collected to $\theta_{max} = 51°$. $R_{int} = 0·033$ for 2390 reflections, of which 556 with $I < 2\sigma(I)$ were classified as unobserved. Three standard reflections monitored periodically showed no significant change in intensities. Lorentz and polarization corrections and a semi-empirical absorption correction (North, Phillips & Matthews, 1968) applied. Systematic absences $h0l$ ($h + l$ odd) and $0k0$ (k odd) confirmed that the space group was $P2_1/n$. The structure was determined by the heavy-atom method, the Rh coordinates being obtained from a Patterson map and the remaining non-hydrogen atoms from a subsequent difference Fourier map. Full-matrix least-squares refinement on F (*SHELX*76; Sheldrick, 1976). The refinement proceeded with conversion to anisotropic thermal parameters and the insertion of H atoms as 'riders' in calculated positions (d_{C-H} = 1·08 Å). The refinement converged at $R = 0·070$, $wR = 0·071$ for 1826 observed reflections; $w = 4·9787/|\sigma^2(F_o) + 0·0002|F_o|^2|$. Eight reflections with large Δ/σ were omitted from the refinement. The perchlorate ion is disordered. A difference map calculated before the final refinement cycles revealed four major O sites around the central Cl. After refinement of these positions, a further difference map indicated some minor O sites, but attempts to refine a model with eight O sites and two sets of occupancies failed. In the final refinement cycles a model based on the four major O sites but with fixed Cl—O distances of 1·27 Å and O—Cl—O angles of 109·5° was used. Max. height in final difference Fourier synthesis 0·78 e Å^{-3}, in the region of the disordered perchlorate ion. Excluding the disordered atoms, in the last cycle of refinement $(\Delta/\sigma)_{max} \leq 0·2$.

Determination of the structure of complex (II). Preliminary precession photographs showed the crystal structure to be triclinic. Dark-red crystal 0·40 × 0·25 × 0·25 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation.

ω–2θ mode, with a scan width of $(0.6 + 0.35\tan\theta)°$ in the range $1° \leq \theta \leq 27.5°$ and scan rate between 1·0 and 4·0° min^{-1} according to the detected intensity. Checks on three reference reflections showed no significant change in intensities over the period of data collection. Intensities corrected for Lorentz and polarization effects and for variable measuring time; no absorption correction. $R_{int} = 0.016$ for 11340 reflections, of which 2242 with $I \leq 2\sigma(I)$ were classified as unobserved. Limits on h, k and l: $h = -14$ to 14, $k = -15$ to 15, $l = 0$ to 26. The Rh and P positions were determined by direct methods using *MULTAN*80 (Main *et al.*, 1980), and those of all remaining non-hydrogen atoms by successive difference Fourier maps. Structure refinement by blocked full-matrix least-squares method, using a modified version of *SHELX*76 (Sheldrick, 1976). Anisotropic thermal parameters for non-hydrogen atoms were included in the final cycles. The H atoms were located from a difference map, and refined with isotropic thermal parameters. Refinement converged at $R = 0.031$, $wR = 0.036$ for 9098 observed reflections; $w = 0.5566/|\sigma^2(F_o) + 0.001|F_o|^2|$. In the final cycle of refinement the average $\Delta/\sigma \leq 0.2$, and final difference map gave $-0.42 \leq \Delta\rho \leq 0.58$ e Å^{-3}.

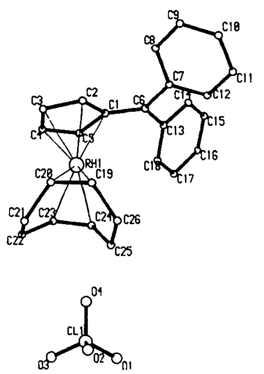


Fig. 1. The molecular structure of complex (I), showing the atomic numbering scheme.

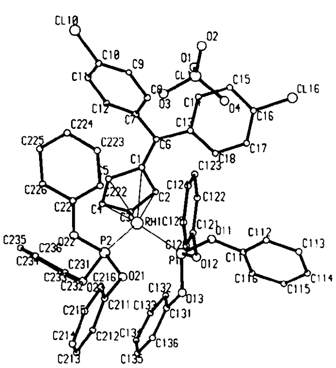


Fig. 2. The molecular structure of complex (II), showing the atomic numbering scheme.

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (×10⁴) *for* (I), *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma)$.

	x	y	z	U_{eq}(Å²)
C(1)	2174 (10)	2341 (12)	−982 (7)	878
C(2)	1761 (9)	3448 (11)	−698 (7)	889
C(3)	822 (9)	3155 (12)	−672 (7)	980
C(4)	664 (10)	1901 (12)	−841 (8)	982
C(5)	1499 (10)	1375 (12)	−979 (7)	897
C(6)	3092 (9)	2223 (12)	−1153 (7)	924
C(7)	3696 (10)	3308 (11)	−1199 (8)	854
C(8)	3293 (9)	4373 (14)	−1631 (8)	963
C(9)	3860 (11)	5399 (12)	−1697 (8)	1021
C(10)	4828 (12)	5332 (13)	−1339 (9)	1060
C(11)	5244 (9)	4245 (16)	−904 (8)	1070
C(12)	4675 (10)	3239 (12)	−850 (8)	941
C(13)	3486 (8)	1039 (12)	−1323 (8)	868
C(14)	3939 (8)	983 (12)	−2037 (8)	927
C(15)	4299 (9)	−93 (16)	−2255 (9)	1073
C(16)	4240 (9)	−1156 (14)	−1769 (12)	1184
C(17)	3786 (11)	−1139 (13)	−1051 (11)	1199
C(18)	3435 (9)	−24 (13)	−833 (9)	1037
C(19)	2565 (11)	3269 (12)	1566 (8)	1040
C(20)	1620 (11)	3280 (12)	1509 (8)	1079
C(21)	1160 (12)	2544 (17)	2167 (10)	1457
C(22)	919 (13)	1276 (17)	1885 (12)	1524
C(23)	1437 (13)	728 (13)	1246 (10)	1167
C(24)	2396 (15)	686 (12)	1394 (10)	1167
C(25)	3093 (12)	1165 (17)	2214 (12)	1487
C(26)	3293 (11)	2490 (16)	2224 (10)	1416
Cl	3320 (3)	2069 (4)	5132 (3)	1231
O(1)	3994 (3)	1301 (4)	5171 (3)	3675
O(2)	3660 (3)	3153 (4)	5214 (3)	3346
O(3)	2920 (3)	1855 (4)	5775 (3)	3544
O(4)	2707 (3)	1965 (4)	4368 (3)	5337
Rh	1853 (1)	2157 (1)	421 (1)	851

Discussion. The final atomic coordinates for complexes (I) and (II) are listed in Tables 1 and 2 respectively.* Selected bond distances and angles are given in Tables 3 and 4. Included in these tables are indications of the range of C—C bond lengths within individual phenyl rings, but information on the corresponding angles has been omitted because the departures from regular geometry were insignificant. The molecular structures of (I) and (II) are shown in Figs. 1 and 2 respectively (Motherwell, 1972), with the arbitrary atom-numbering schemes used in the structure analysis.

In each complex, the Rh is coordinated to the essentially planar five-membered ring of the fulvene ligand, with the metal lying 1·876 and 1·921 Å out of the mean plane of the ring in (I) and (II) respectively. If one were to regard the fulvene ligand in these complexes as a conventional η^4-diene ligand bonded to the metal through the two double bonds within the five-membered ring [as shown in structure (*A*)], then each cation could be viewed as an approximately planar four-coordinate complex of Rh^I, with the double bonds of the fulvene and [in complex (I)] of the 1,5-cyclooctadiene roughly at right-angles to the plane. Inspection of the distances

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42043 (68 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

between the metal and the five ring C atoms in the fulvene reveals, however, that this is an oversimplified view of the bonding. In each complex the Rh—C(1) distance is greater than those to the other four ring C atoms, but the difference [particularly in the case of complex (I)] is not great, and C(1) is clearly involved in the bonding to the metal. Within the fulvene ligand, the variations in C—C bond lengths are much less marked than they are for a free fulvene such as dimethylfulvene, where the bonds C(2)—C(3) and C(4)—C(5) [1·346 (10) Å] and C(1)—C(6) [1·343 (1) Å] are

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^4$) *for* (II), *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma).$$

	x	y	z	U_{eq}(Å^2)
Rh	2252 (1)	3026 (1)	7541 (1)	288
P(1)	1488 (1)	4662 (1)	6750 (1)	291
O(11)	327 (2)	5694 (1)	7121 (1)	375
C(111)	−352 (2)	6861 (2)	6776 (1)	418
C(112)	129 (3)	7749 (3)	6697 (2)	640
C(113)	−581 (4)	8920 (3)	6392 (2)	857
C(114)	−1710 (4)	9177 (3)	6187 (2)	792
C(115)	−2163 (3)	8272 (4)	6266 (2)	829
C(116)	−1481 (3)	7094 (3)	6572 (2)	603
O(12)	2396 (2)	5343 (1)	6299 (1)	372
C(121)	3472 (2)	5338 (2)	6504 (1)	342
C(122)	3475 (2)	5504 (2)	7151 (1)	419
C(123)	4575 (3)	5542 (2)	7294 (2)	503
C(124)	5630 (3)	5426 (3)	6794 (2)	564
C(125)	5614 (3)	5263 (3)	6152 (2)	560
C(126)	4525 (2)	5221 (2)	5999 (1)	420
O(13)	975 (2)	4621 (2)	6089 (1)	413
C(131)	323 (2)	3899 (2)	6073 (1)	386
C(132)	−619 (3)	3732 (3)	6595 (2)	510
C(133)	−1234 (3)	3019 (3)	6512 (2)	677
C(134)	−906 (4)	2489 (3)	5948 (2)	742
C(135)	0 (4)	2694 (4)	5428 (2)	802
C(136)	655 (3)	3399 (3)	5477 (2)	566
P(2)	3728 (1)	2004 (1)	6768 (1)	293
O(21)	4058 (2)	2771 (1)	6043 (1)	360
C(211)	4993 (2)	2274 (2)	5500 (1)	350
C(212)	4687 (3)	1767 (3)	5055 (1)	526
C(213)	5593 (4)	1347 (3)	4506 (2)	647
C(214)	6774 (3)	1444 (3)	4392 (2)	571
C(215)	7056 (3)	1952 (3)	4838 (1)	493
C(216)	6161 (2)	2358 (2)	5404 (1)	400
O(22)	5099 (2)	1060 (1)	6967 (1)	401
C(221)	5731 (2)	1142 (2)	7462 (1)	363
C(222)	5803 (3)	2211 (2)	7494 (1)	455
C(223)	6464 (3)	2217 (3)	7985 (2)	569
C(224)	7052 (3)	1166 (4)	8417 (2)	618
C(225)	6974 (3)	102 (3)	8373 (2)	678
C(226)	6294 (3)	70 (2)	7890 (2)	517
O(23)	3363 (2)	1082 (1)	6483 (1)	380
C(231)	2915 (2)	241 (2)	6952 (1)	382
C(232)	1618 (3)	494 (3)	7043 (2)	523
C(233)	1167 (3)	−340 (4)	7517 (2)	724
C(234)	2004 (5)	−1348 (4)	7869 (2)	752
C(235)	3268 (4)	−1580 (3)	7765 (2)	631
C(236)	3752 (3)	−787 (2)	7298 (1)	454
C(1)	1986 (2)	3156 (2)	8746 (1)	296
C(2)	776 (2)	3518 (2)	8484 (1)	322
C(3)	744 (2)	2504 (2)	8299 (1)	379
C(4)	1948 (3)	1538 (2)	8355 (1)	378
C(5)	2735 (2)	1937 (2)	8579 (1)	337
C(6)	2380 (2)	3787 (2)	9071 (1)	294
C(7)	3575 (2)	3173 (2)	9383 (1)	310
C(8)	4432 (2)	3748 (2)	9301 (1)	372
C(9)	5525 (2)	3212 (2)	9619 (1)	425
C(10)	5762 (2)	2082 (2)	10026 (1)	421
C(11)	4949 (3)	1498 (2)	10131 (1)	445
C(12)	3846 (2)	2029 (2)	9809 (1)	383
Cl(10)	7147 (1)	1404 (1)	10421 (1)	667
C(13)	1595 (2)	5038 (2)	9191 (1)	309
C(14)	1693 (2)	5367 (2)	9790 (1)	368
C(15)	982 (2)	6527 (2)	9938 (1)	397
C(16)	149 (2)	7358 (2)	9492 (1)	370
C(17)	25 (2)	7064 (2)	8903 (1)	384
C(18)	754 (2)	5908 (2)	8751 (1)	337
Cl(16)	−726 (1)	8814 (1)	9681 (1)	576
Cl(1)	6992 (1)	5866 (1)	8367 (1)	531
O(1)	6054 (3)	5715 (3)	8903 (2)	1158
O(2)	7871 (3)	6190 (3)	8573 (2)	1059
O(3)	7667 (3)	4824 (4)	8065 (2)	1283
O(4)	6374 (3)	6805 (4)	7846 (2)	1135

Table 3. *Selected bond distances* (Å) *and angles* (°) *for complex* (I)

Rh—C(1)	2·295 (12)	C(3)—C(4)	1·396 (18)
Rh—C(2)	2·180 (11)	C(4)—C(5)	1·397 (21)
Rh—C(3)	2·212 (11)	C(6)—C(7)	1·481 (19)
Rh—C(4)	2·241 (11)	C(6)—C(13)	1·457 (19)
Rh—C(5)	2·222 (10)	C(19)—C(20)	1·345 (23)
Rh—C(19)	2·151 (12)	C(19)—C(26)	1·512 (19)
Rh—C(20)	2·145 (14)	C(20)—C(21)	1·552 (24)
Rh—C(23)	2·173 (16)	C(21)—C(22)	1·461 (26)
Rh—C(24)	2·183 (14)	C(22)—C(23)	1·489 (26)
C(1)—C(2)	1·457 (18)	C(23)—C(24)	1·346 (28)
C(1)—C(5)	1·434 (19)	C(24)—C(25)	1·482 (22)
C(1)—C(6)	1·419 (20)	C(25)—C(26)	1·469 (25)
C(2)—C(3)	1·403 (19)		

Phenyl rings

C(7)–C(12)	1·367–1·413,	average 1·389 (20)
C(13)–C(18)	1·355–1·404,	average 1·386 (21)

C(5)—C(1)—C(2)	106·0 (12)	C(6)—C(7)—C(12)	119·8 (11)
C(6)—C(1)—C(2)	126·8 (12)	C(6)—C(13)—C(14)	117·0 (11)
C(6)—C(1)—C(5)	126·9 (12)	C(6)—C(13)—C(18)	124·6 (12)
C(1)—C(2)—C(3)	106·9 (11)	C(20)—C(19)—C(26)	124·9 (13)
C(2)—C(3)—C(4)	109·4 (12)	C(19)—C(20)—C(21)	123·1 (12)
C(3)—C(4)—C(5)	108·7 (12)	C(20)—C(21)—C(22)	114·2 (14)
C(1)—C(5)—C(4)	108·2 (11)	C(21)—C(22)—C(23)	116·5 (16)
C(1)—C(6)—C(7)	121·7 (12)	C(22)—C(23)—C(24)	124·8 (13)
C(1)—C(6)—C(13)	122·4 (12)	C(23)—C(24)—C(25)	125·4 (16)
C(7)—C(6)—C(13)	115·8 (12)	C(24)—C(25)—C(26)	116·3 (13)
C(6)—C(7)—C(8)	120·5 (12)	C(19)—C(26)—C(25)	116·2 (12)

Table 4. *Selected bond distances* (Å) *and angles* (°) *for complex* (II)

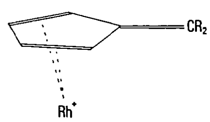
Rh—P(1)	2·226 (1)	C(3)—C(4)	1·409 (3)
Rh—P(2)	2·203 (1)	C(4)—C(5)	1·391 (4)
Rh—C(1)	2·412 (2)	C(6)—C(7)	1·473 (3)
Rh—C(2)	2·258 (2)	C(6)—C(13)	1·470 (3)
Rh—C(3)	2·236 (3)	C(10)—Cl(10)	1·741 (3)
Rh—C(4)	2·224 (2)	C(16)—Cl(16)	1·736 (2)
Rh—C(5)	2·240 (2)	Cl(1)—O(1)	1·378 (4)
C(1)—C(2)	1·461 (3)	Cl(1)—O(2)	1·402 (5)
C(1)—C(5)	1·463 (3)	Cl(1)—O(3)	1·396 (4)
C(1)—C(6)	1·382 (4)	Cl(1)—O(4)	1·417 (3)
C(2)—C(3)	1·402 (4)		

Phenyl rings

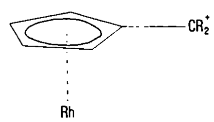
C(7)–C(12)	1·353–1·405,	average 1·385 (4)
C(13)–C(18)	1·374–1·405,	average 1·386 (3)
C(111)–C(116)	1·344–1·391,	average 1·372 (6)
C(121)–C(126)	1·362–1·385,	average 1·374 (4)
C(131)–C(136)	1·348–1·398,	average 1·375 (6)
C(211)–C(216)	1·360–1·387,	average 1·376 (5)
C(221)–C(226)	1·366–1·397,	average 1·377 (5)
C(231)–C(236)	1·340–1·403,	average 1·372 (5)
P—O bonds:	1·592–1·616,	average 1·598 (2)
O—C(phenyl) bonds:	1·390–1·407,	average 1·400 (3)

P(1)—Rh—P(2)	92·9 (1)	C(6)—C(1)—C(5)	126·4 (2)
P(1)—Rh—C(1)	121·9 (1)	C(1)—C(2)—C(3)	108·7 (2)
P(2)—Rh—C(1)	138·4 (1)	C(2)—C(3)—C(4)	108·7 (3)
P(1)—Rh—C(2)	101·7 (1)	C(3)—C(4)—C(5)	108·5 (2)
P(2)—Rh—C(2)	163·1 (1)	C(1)—C(5)—C(4)	109·3 (2)
P(1)—Rh—C(3)	114·6 (1)	C(1)—C(6)—C(7)	120·3 (2)
P(2)—Rh—C(3)	128·8 (1)	C(1)—C(6)—C(13)	123·3 (2)
P(1)—Rh—C(4)	149·8 (1)	C(7)—C(6)—C(13)	116·1 (2)
P(2)—Rh—C(4)	101·9 (1)	C(6)—C(7)—C(8)	120·8 (2)
P(1)—Rh—C(5)	158·2 (1)	C(6)—C(7)—C(12)	121·0 (2)
P(2)—Rh—C(5)	106·2 (1)	C(6)—C(13)—C(14)	117·8 (2)
C(5)—C(1)—C(2)	103·7 (2)	C(6)—C(13)—C(18)	124·0 (2)
C(6)—C(1)—C(2)	129·9 (2)		

appreciably shorter than C(1)—C(2) and C(1)—C(5) [1·439 (8) Å] and C(3)—C(4) [1·435 (16) Å] (Norman & Post, 1961). In both (I) and (II), the lengths of the three bonds C(2)—C(3), C(3)—C(4) and C(4)—C(5) differ very little from one another. The other two bonds within the ring, C(1)—C(2) and C(1)—C(5), are *somewhat* longer, the difference in length between these and the rest certainly being significant in the case of complex (II). The bond C(1)—C(6) is appreciably longer in the complexes than it is in free dimethylfulvene. Interestingly, a preliminary account of the structure of the related complex $[Rh\{2,4\text{-}(Me_3C)_2\text{-}C_5H_2CH(CMe_3)\}(C_8H_{12})]ClO_4$ shows the C(1)—C(6) bond to be even *shorter* [1·29 (2) Å] than the corresponding bond in free dimethylfulvene. Unfortunately the pattern of C—C bond lengths within the five-membered ring in this compound is rather irregular, no doubt due to the presence of the bulky substituents on C(2) and C(4) (Moran, Green & Orpen, 1983).

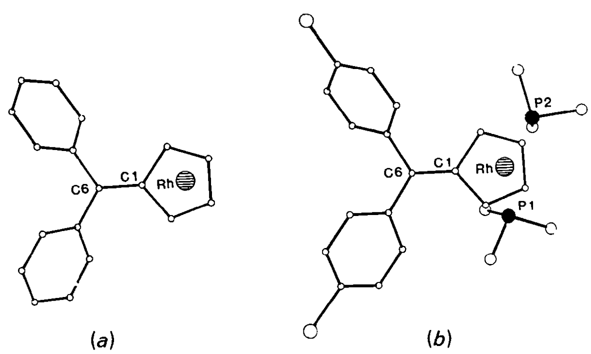


(*A*)



(*B*)

While structure (*A*) is evidently not in itself a satisfactory description of the metal—fulvene bonding in complexes (I) and (II), the same also applies to structure (*B*): Figs. 3(*a*) and 3(*b*), where the complex cations are viewed at right-angles to the plane of the five-membered ring, emphasize the non-central position of the Rh. Evidently the bonding is best described as a resonance hybrid of both structures. To the extent that structure (*B*) contributes to the bonding, there *will* be a positive charge on the exocyclic C atom C(6), making it susceptible to nucleophilic attack. It should be noted that there is no evidence of a direct interaction between C(6) and the metal, the Rh—C(6) distance being 3·32 (2) and 3·48 (1) Å in complexes (I) and (II) respectively. In each complex the C(1)—C(6) bond is bent *away* from the metal, the angle between this bond and the plane of the ring being 4·4° for complex (I) and 8·8° for (II).



(*a*) (*b*)

Fig. 3. (*a*) Complex (I) and (*b*) complex (II) viewed at right-angles to the plane of the five-membered ring of the fulvene ligand. The perchlorate anions and [in (I)] the cyclooctadiene ligand have been omitted.

In complexes (I) and (II), the fulvene is bonded to a metal ion with the electron configuration d^8, and the metal requires six electrons from the fulvene to achieve a share in eighteen electrons. It is interesting to note how the geometry of the fulvene ligand and the metal—fulvene bonding alter with changes either in the electron configuration of the metal or in the number of electrons the metal requires from the fulvene to reach a total of eighteen. In complexes such as $[Fe(\eta^5\text{-}C_5H_5)(C_5H_4CPh_2)]^+$ (Behrens, 1979), $[Cr(CO)_3(C_5H_4CR_2)]$ [R = H (Koch, Edelmann & Behrens, 1982) or Ph (Andrianov, Struchkov, Setkina, Zhdanovich, Zhakaeva & Kursanov, 1975)], $[Mo(\eta^6\text{-}C_6H_6)(C_5H_4CR_2)]$ and $[W(\eta^6\text{-}C_6H_5Me)(C_5H_4CR_2)]$ (R = Me or Ph) (Green, Izquierdo, Martin-Polo, Mtetwa & Prout, 1983), where the metal atom or ion has the d^6 configuration and requires six electrons from the fulvene, C(1) is clearly involved in the bonding to the metal (indeed in several instances it appears to be the closest C atom to the metal), and the exocyclic carbon atom C(6) is bent in towards the metal at angles varying from 20·7 to 41°. Watts (1981) has suggested that in these complexes the fulvene is attached to the metal in its dipolar form $^-C_5H_4C^+R_2$, with the five-membered ring acting as a six-electron donor, and that the bending-in of C(6) allows an interaction with the metal which reduces the positive charge on the C atom.

In $[Fe(CO)_3(C_5H_4CPh_2)]$, the metal has the configuration d^8, and requires only *four* electrons from the fulvene to achieve a total of eighteen. Here the bond C(1)—C(6) is appreciably shorter, and it appears that neither C(1) nor C(6) is directly bonded to the metal. The C(1)—C(6) bond is bent *away* from the metal at an angle of 18·5° to the plane of the five-membered ring (Edelmann, Lubke & Behrens, 1982). Finally, in $[Ni(C_5H_4CPh_2)(C_8H_{12})]$, the metal has the configuration d^{10} and again requires only four electrons from the fulvene for a total of eighteen. As in the case of the Fe^0 complex, the bond C(1)—C(6) is fairly short, and neither C(1) nor C(6) is involved in the bonding to the metal. The tilt of C(6) away from the metal is, however, rather less pronouned: in the two inequivalent molecules in the structure the angles are 6·0 and 10·2° (Edelmann *et al.*, 1982).

Thus it can be seen that the geometry of the metal—fulvene bonding in complexes (I) and (II) differs significantly both from that for complexes where the metal has a different configuration (d^6) but requires the same number of electrons (six) as does the Rh to achieve a total of eighteen, and from that for the complex $[Fe(CO)_3(C_5H_4CPh_2)]$, where the metal has the same configuration (d^8) as Rh^+ but requires a smaller number of electrons (four) to reach eighteen. In terms of the number of fulvene C atoms involved in the bonding to the metal, the complexes (I) and (II) are clearly intermediate between these two cases.

We thank the SERC for a maintenance grant to EJP, and Johnson Matthey Chemicals for a loan of rhodium(III) chloride.

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Structure of (Di-2-pyridylamine)salicylaldehydatocopper(II) Perchlorate, $[Cu(C_7H_5O_2)(C_{10}H_9N_3)]ClO_4$

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(*Received* 9 *July* 1984; *accepted* 24 *January* 1985)

Abstract. $M_r = 455\cdot31$, triclinic, $P\bar{1}$, $a = 9\cdot363\ (2)$, $b = 9\cdot964\ (3)$, $c = 10\cdot093\ (2)$ Å, $\alpha = 75\cdot39\ (2)$, $\beta = 73\cdot49\ (4)$, $\gamma = 83\cdot34\ (3)°$, $V = 872\cdot6\ (4)$ Å^3, $Z = 2$, $D_m = 1\cdot70\ (2)$, $D_x = 1\cdot733$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0\cdot71073$ Å, $\mu = 1\cdot448$ mm^{-1}, $F(000) = 462$, $T = 291$ K. Final $R = 0\cdot045$ for 2434 unique observed reflections. The structure consists of a dimeric unit involving two perchlorate anions with a positional disorder. The coordination sphere of copper can be described as an elongated octahedron due to the Jahn–Teller effect. The basal plane is formed by two nitrogen atoms of the two heterocycles of the dipyridylamine and two oxygen atoms of the salicylaldehyde group. Two large apical copper–oxygen distances are found: one toward the oxygen atom of the perchlorate anion and the other one, linking two monomeric units, toward the oxygen atom of the nearest salicylaldehyde molecule.

0108-2701/85/060855-04$01.50