Preparation of 6,6-Diarylfulvene Complexes of Rhodium(I) and their Reaction with Dioxygen

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Complexes $[RhL_2]^+$ [L = $P(OPh)_3$ or L_2 = cyclo-octa-1,5-diene] react with 6,6-diarylfulvenes $C_5H_4C(C_6H_4X\text{-}4)_2$ to yield products $[Rh\{C_5H_4C(C_6H_4X\text{-}4)_2\}L_2]^+$ in which the fulvene is bound to the metal through the five-membered ring. Corresponding reactions with $[Rh(CO)_2]^+$ yield complexes $[Rh\{C_5H_4C(C_6H_4X\text{-}4)_2\}_2]^+$ containing two fulvene ligands. Atmospheric oxidation of these complexes results in the linking of the exocyclic carbon atoms in the two fulvene ligands by a peroxide bridge. If the initial attack by O_2 is on the metal, the subsequent rearrangement may be viewed either as a transfer of singlet oxygen from metal to ligands or as a nucleophilic attack by peroxide on the (probably somewhat positively charged) exocyclic carbon atoms of the fulvene ligands.

There have been several reports of reactions between transition-metal complexes and 6,6-disubstituted derivatives of fulvene (5-methylenecyclopenta-1,3-diene). Under forcing conditions these reactions tend to yield η^5-cyclopentadienyl complexes: thus $[Mo(CO)_6]$ reacts with dialkyl- and diarylfulvenes $C_5H_4CR_2$ at high temperatures to yield $[Mo_2(CO)_6(\eta^5\text{-}C_5H_4CHR_2)_2]$,[1] $[Fe(CO)_5]$ combines with diphenylfulvene under similar conditions to form $[Fe_2(CO)_4(\eta^5\text{-}C_5H_4CHPh_2)_2]$,[2] and fulvenes of the type $C_5H_4C(CH_2R)_2$ have been shown [3] to react with $[Co_2(CO)_8]$ to give mixtures of $[Co(CO)_2\{\eta^5\text{-}C_5H_4CH(CH_2R)_2\}]$ and $[Co(CO)_2\{\eta^5\text{-}C_5H_4C(=CHR)CH_2R\}]$. Under milder conditions, however, complexes of the actual fulvenes have been isolated. Among the products of the reaction of $[Fe_2(CO)_9]$ with diphenylfulvene are $[Fe(CO)_3(C_5H_4CPh_2)]$, formulated as an η^4-diene complex, and $[Fe_2(CO)_8(C_5H_4CPh_2)]$, in which the two double bonds in the five-membered ring are believed to be co-ordinated to different metal atoms.[2] In each of these instances, the exocyclic double bond is believed not to be involved in complex formation, whereas in the complex $[Co_2(CO)_6(C_5H_4CPh_2)_2]$ each fulvene ligand is assumed to be attached to a cobalt atom through the exocyclic double bond only.[3] In $[Cr(CO)_3(C_5H_4CPh_2)]$,[4] Andrianov *et al.*[5] showed that the fulvene acts as a six-electron donor, and this has more recently been shown to be the case for the complexes $[Fe(\eta^5\text{-}C_5H_5)(C_5H_4CPh_2)]^+$ [6] and $[Mo(\eta^6\text{-}C_6H_6)(C_5H_4CPh_2)]$.[7]

We wished to investigate the chemistry of fulvene ligands co-ordinated to transition-metal ions in order to discover how the properties of the fulvene were modified by complex formation. Co-ordinatively unsaturated species of the type $[RhL_2]^+$, obtainable by the method described by Schrock and Osborn,[8] seemed ideal starting materials for the preparation of fulvene complexes under very mild conditions. In this paper we describe some fulvene complexes obtained by this route, and an intriguing example of the reactivity of complexed 6,6-diarylfulvenes.

Results and Discussion

Preparation of Fulvene Complexes.—The 6,6-diarylfulvenes used, of general formula $C_5H_4C(C_6H_4X\text{-}4)_2$ [X =H, (1a); Cl, (1b); OMe, (1c); or Me, (1d)], were obtained by reaction of the appropriate ketones $(4\text{-}XC_6H_4)_2CO$ with cyclopentadiene in the presence of base.

Tetrahydrofuran solutions of $[Rh_2Cl_2\{P(OPh)_3\}_4]$ [9] and $AgClO_4$ were mixed, and (after removing the precipitate of AgCl) the yellow solution of $[Rh\{P(OPh)_3\}_2]^+$ was treated with an equimolar quantity of the fulvene (1a). Deep purple crystals obtained from the solution were shown by elemental analysis to be $[Rh(C_5H_4CPh_2)\{P(OPh)_3\}_2]ClO_4$, (2a). Use of the fulvene (1b) yielded the similarly coloured $[Rh\{C_5H_4C(C_6H_4Cl\text{-}4)_2\}\{P(OPh)_3\}_2]ClO_4$, (2b). In the same way, the cyclo-octa-1,5-diene (cod) complex $[Rh_2(cod)_2Cl_2]$ [10] was converted into the red products $[Rh(C_5H_4CPh_2)(cod)]ClO_4$ and $[Rh\{C_5H_4C(C_6H_4Cl\text{-}4)_2\}(cod)]ClO_4$, (3a) and (3b) respectively.

When a tetrahydrofuran solution of $[Rh(CO)_2]^+$ {obtained from $[Rh_2(CO)_4Cl_2]$ [11]} was treated with an equimolar quantity of compound (1a), the product obtained was a sparingly soluble deep blue complex (4a) whose i.r. spectrum contained no bands in the C–O stretching region. Elemental analysis showed it to be $[Rh(C_5H_4CPh_2)_2]ClO_4$, and it was subsequently obtained in better yield by doubling the quantity of fulvene added to the solution of $[Rh(CO)_2]^+$. In the same manner, the deeply coloured complexes $[Rh\{C_5H_4C(C_6H_4Cl\text{-}4)_2\}_2]ClO_4$, $[Rh\{C_5H_4C(C_6H_4OMe\text{-}4)_2\}_2]ClO_4$, and $[Rh\{C_5H_4C(C_6H_4Me\text{-}4)_2\}_2]PF_6$ (4b), (4c), and (4d), were obtained using fulvenes (1b), (1c), and (1d).

One further complex was prepared for comparison purposes. This was the blue complex $[Rh(CO)_2(C_5H_4CPh_2)Cl]$, (5a), obtained (as originally described by Altman and Wilkinson [3]) by treating $[Rh_2(CO)_4Cl_2]$ with compound (1a) in light petroleum.

N.M.R. Spectra and Structure of Fulvene Complexes.—Details of the ^1H and ^{13}C n.m.r. spectra are given in Tables 1 and 2 respectively. Weak noise decoupling was used to assist in assigning ^{13}C resonances.

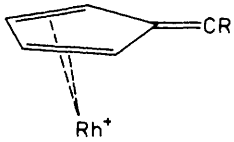
The spectra of compounds (2a) and (2b) each contained two complex resonances for the hydrogens attached to the five-membered ring, and two for the corresponding carbon atoms. The chemical shifts were markedly different from those for the same atoms in the free fulvenes (1a) and (1b). In the ^1H spectrum of (2b), irradiation at δ 5.33 simplified the resonance at δ 5.52 to a doublet of triplets [$|J(\text{Rh–H})| = 1$, $|J(\text{P–H}) + J(\text{P}'\text{–H})| = 4$ Hz], while irradiation at δ 5.52 reduced the resonance at δ 5.33 to a triplet [$|J(\text{P–H}) + J(\text{P}'\text{–H})| = 4$ Hz] with no detectable rhodium splitting. Both carbon resonances for complex (2b) exhibited rhodium splittings (*ca.* 4 Hz), but that at δ 87.8 also showed a sizeable phosphorus splitting [$|J(\text{P–C}) + J(\text{P}'\text{–C})| = 16$ Hz] whereas the splitting of the resonance at δ 102.8 was barely detectable. The coupling constants for (2a) were of similar magnitude. The resonances for the exocyclic carbon atom in the fulvene ligands in (2a) and (2b) exhibited triplet splittings [$|J(\text{P–C})| = 3$ Hz], and a slight phosphorus splitting was also observed for C^1 in the aryl substituents. Resonances for the remaining carbon atom in the five-membered ring were too weak for definite identification.

Table 1. Proton n.m.r. spectra [a]

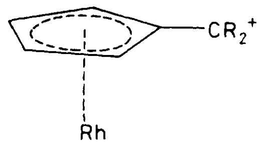
Compound	Fulvene ring	Arene rings	Arene substituents	Other ligands	
				Chemical shift	Assignment
(1a)	6.16 (c, 2),	7.27 (c, 10)			
	6.47 (c, 2)				
(1b)	6.11 (c, 2),	7.29 (8) [b]			
	6.51 (c, 2)				
(1c)	6.10 (c, 2),	7.00 (8) [b]	3.79 (s, 6)		
	6.41 (c, 2)				
(1d)	6.10 (c, 2),	7.11 (s, 8)	2.32 (s, 6)		
	6.44 (c, 2)				
(2a)	5.30 (c, 2),	*c*		*c*	$P(OPh)_3$
	5.52 (c, 2)				
(2b)	5.33 (c, 2),	*c*		*c*	$P(OPh)_3$
	5.52 (c, 2)				
(3a) [d]	5.80 (c, 2),	7.62 (c, 10)		2.35 (c, 4)	cod, CH_2
	6.96 (c, 2)			2.54 (c, 4)	cod, CH_2
				5.36 (c, 2)	cod, CH
				ca. 5.85	cod, CH [e]
(3b) [f]	5.91 (c, 2),	7.67 (8) [b]		2.36 (c, 4)	cod, CH_2
	7.01 (c, 2)			2.55 (c, 4)	cod, CH_2
				5.50 (c, 2)	cod, CH
				ca. 5.90	cod, CH [e]
(5a)	6.18 (c, 2),	7.17 (c, 10)			
	6.40 (c, 2)				
(6a)	5.70 (c, 2),	7.2—7.9 (c, 20)			
	6.10 (c, 2),				
	6.33 (c, 2),				
	6.66 (c, 2)				
(6b)	5.75 (c, 2),	7.22 (8), [b]			
	6.08 (c, 2),	7.62 (8) [b]			
	6.28 (c, 2),				
	6.65 (c, 2)				
(6c)	5.72 (c, 2),	6.95 (8), [b]	3.75 (s, 6),		
	6.07 (c, 2),	7.35 (8) [b]	3.88 (s, 6)		
	6.31 (c, 2),				
	6.58 (c, 2)				
(6d)	5.68 (c, 2),	7.07 (8), [b]	2.25 (s, 6),		
	6.08 (c, 2),	7.48 (8) [b]	2.39 (s, 6)		
	6.30 (c, 2),				
	6.55 (c, 2)				

[a] The solvent used was CD_3COCD_3 [$CDCl_3$ for (5a)]. Unless otherwise stated, spectra were recorded at ambient temperature. Multiplicities and relative areas are given in parentheses after the chemical shift values, which are given on the δ scale. [b] Centre of an A_2B_2 pattern. [c] Resonances due to arene-ring protons could not be assigned. [d] Spectrum recorded at 233 K. [e] Resonance partly obscured. [f] Spectrum recorded at 223 K.

Spectra for complex (3a) were recorded at low temperatures (see below). Again one five-membered-ring proton resonance (that at δ 6.96) was significantly split by rhodium [$|J(\text{Rh-H})|$ = 1 Hz] while the other was not, and both resonances for the corresponding carbon atoms showed rhodium splittings of *ca.* 5 Hz. Since the resonance for the remaining ring-carbon atom *also* showed a rhodium splitting (4 Hz), the metal–fulvene bonding may not be the simple η^4 interaction envisaged in structure (A); resonance structure (B) (containing an η^5-bonded carbonium ion) may also make an appreciable contribution.



(A)



(B)

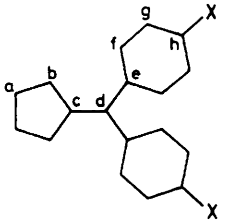
It was, however, clear from the pattern of resonances for the cyclo-octa-1,5-diene ligand in the spectra of complex (3a) that the fulvene ligand could not be regarded simply as a freely rotating η^5-cyclopentadienyl system. At 223 K the ^{13}C n.m.r. spectrum contained *two* doublet resonances, at δ 90.5 and 93.1 [$|J(\text{Rh-C})|$ = 10 and 11 Hz respectively], for the alkene carbon atoms in the cyclo-octadiene ligand. These resonances broadened as the temperature was raised, merging into a single hump at 323 K. Similarly, two resonances (at δ 5.36 and 5.85) were observed for the alkene protons in the diene ligand at 233 K, and these also broadened and eventually merged as the temperature was raised. Over the same temperature range there were no significant changes in the resonances for the fulvene ligand. At low temperatures, therefore, rotation of the fulvene and diene ligands must be slow on the n.m.r. time-scale, and the changes with rising temperature may be attributable to the increasing rate of rotation of either ligand about the metal–ligand axis.

The ^1H n.m.r. spectrum of complex (3b) was similar to that of (3a), but even at low temperatures the complex was too short-lived in solution for a satisfactory ^{13}C spectrum to be

Table 2. Carbon-13 n.m.r. spectra [*]

	Fulvene ligands							
Compound	a,b	c	d	e	f,g	h	X	Other ligands
(1a)	124.7 (s), 133.0 (s)	144.6 (s)	152.1 (s)	141.8 (s)	128.5 (s), 132.4 (s)	129.4 (s)		
(1b)	124.5 (s), 133.9 (s)	145.4 (s)	149.1 (s)	140.2 (s)	128.9 (s), 134.1 (s)	135.5 (s)		
(1c)	124.7 (s), 131.8 (s)	143.0 (s)	152.5 (s)	134.5 (s)	114.1 (s), 134.5 (s)	161.5 (s)	55.6 (s)	
(1d)	124.8 (s), 132.5 (s)	144.0 (s)	152.7 (s)	139.7 (s)	129.3 (s), 132.7 (s)	139.3 (s)	21.2 (s)	
(2a)	88.4 (dt), 102.8 (dt)	†	156.0 (t)	141.0 (t)	129.9 (s), 132.7 (s)	132.5 (s)		121.6 (t) $P(OPh)_3$, C^2 126.7 (s) $P(OPh)_3$, C^4 131.1 (s) $P(OPh)_3$, C^3 151.5 (t) $P(OPh)_3$, C^1
(2b)	87.8 (dt), 102.8 (dt)	†	150.8 (t)	139.5 (t)	130.2 (s), 133.9 (s)	138.1 (s)		121.6 (t) $P(OPh)_3$, C^2 126.8 (s) $P(OPh)_3$, C^4 131.2 (s) $P(OPh)_3$, C^3 151.6 (t) $P(OPh)_3$, C^1
(3a)	86.9 (d), 106.7 (d)	119.4 (d)	156.3 (s)	141.1 (s)	129.9 (s), 131.9 (s)	132.1 (s)		90.5 (d) cod, CH 93.1 (d) cod, CH
(5a)	85.6 (d), 92.6 (d)	121.1 (d)	140.6 (s)	139.5 (s)	128.7 (s), 133.8 (s)	129.5 (s)		181.4 (d) CO
(6a)	88.2 (d), 90.1 (d), 92.4 (d), 93.4 (d)	114.1 (d)	88.1 (s)	140.3 (s), 141.7 (s)	‡	‡		
(6b)	88.7 (d), 90.7 (d), 92.6 (d), 93.2 (d)	112.8 (d)	87.9 (s)	138.7 (s), 139.9 (s)	128.6 (s), 129.7 (s), § 130.8 (s)	135.1 (s), 135.2 (s)		
(6c)	88.0 (d), 90.0 (d), 92.5 (d), 93.6 (d)	114.8 (d)	87.9 (s)	132.5 (s), 134.1 (s)	114.6 (s), 114.7 (s), 128.4 (s), 130.4 (s)	160.7 (s) §	55.7 (s), 55.8 (s)	
(6d)	88.1 (d), 90.0 (d), 92.4 (d), 93.4 (d)	114.4 (d)	88.0 (s)	137.6 (s), 139.2 (s)	126.8 (s), 129.0 (s), 129.8 (s), 129.9 (s)	138.9 (s), 139.0 (s)	20.9 (s), 21.1 (s)	

[*] The solvent used was CD_3COCD_3 [$CDCl_3$ for (5a)]. Spectra were recorded at ambient temperature [223 K for (3a)]. Multiplicities are given in parentheses after the chemical shift values, which are given on the δ scale. The lettering system for the fulvene resonances is as follows:



† Resonance too weak to be identified. ‡ Assignment difficult due to overlapping resonances. § Accidental equivalence of resonances.

obtained. The complexes (4a)—(4d) were insufficiently soluble in solvents suitable for n.m.r. spectroscopy to allow spectra to be recorded. Presumably the metal ion is bonded to the five-membered ring in each fulvene ligand, so that it is effectively sandwiched between the two rings.

Altman and Wilkinson [3] suggested that (5a) was a planar four-co-ordinate complex of rhodium(I) in which the fulvene was linked to the metal through the exocyclic double bond and the two carbonyl ligands were mutually *cis* (since there are two C–O stretching bands of similar intensity in the i.r. spectrum of the complex). We found, however, that certain features of the ^{13}C n.m.r. spectrum of (5a) in $CDCl_3$ were at odds with such a structure. The spectrum contained only *one* resonance (at δ 181.4) for the carbonyl ligands: this was a doublet with $|J(Rh-C)| = 72$ Hz {as compared with a value of 75 Hz for $[Rh(CO)Cl(PMe_2Ph)_2]$ [12]}. This does not fit the structure proposed by Altman and Wilkinson, in which the carbonyl ligands are necessarily inequivalent. In addition, the resonances for the hydrogen-bearing carbon atoms in the five-membered ring were all doublets with $|J(Rh-C)|$ *ca.* 7 Hz, and the resonance for the remaining carbon atom in the ring exhibited a smaller splitting [$|J(Rh-C)| = 4$ Hz], whereas that for the exocyclic carbon atom was not split. A structure compatible with all the data would be a square-based pyramid, with chloride in the apical position, carbonyl ligands in mutually *cis* positions in the base, and the two double bonds in the fulvene five-membered ring completing the co-ordination of the metal ion.

Table 3. Analytical data

Compound	Found (%)		Calculated (%)	
	C	H	C	H
(1a)	93.75	6.00	93.85	6.15
(1b)	72.25	4.15	72.25	4.05
(1c)	82.95	6.30	82.75	6.25
(1d)	92.80	7.10	93.00	7.00
(2a)	61.60	4.30	61.60	4.20
(2b)	57.85	3.65	57.80	3.75
(3a)	57.75	4.70	57.75	4.85
(3b)	50.60	3.85	51.20	3.95
(4a)	65.35	4.30	65.20	4.25
(4b)	53.65	3.10	54.00	3.00
(4c)	61.30	4.80	61.35	4.65
(4d)	62.65	4.80	62.85	4.75
(5a)	56.70	3.15	56.55	3.30
(6a)	62.15	4.10	62.20	4.05
(6b)	51.95	2.90	51.90	2.90
(6c)	58.85	4.55	58.95	4.45
(6d)	60.15	4.45	60.30	4.55

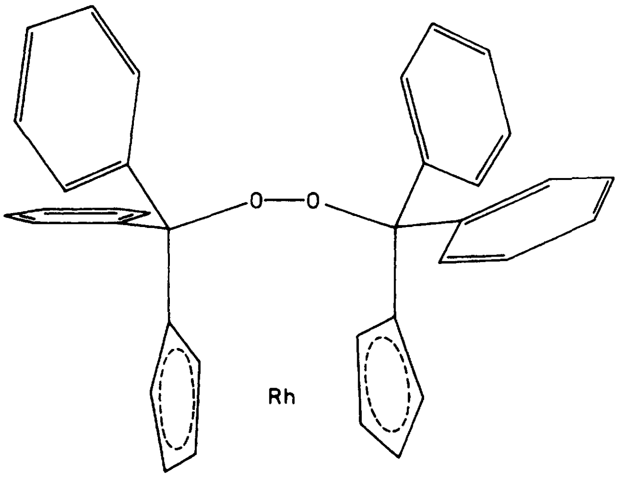


Figure. Structure of the cation of complex (6a)

Reaction of Complexes (4a)—(4d) *with Dioxygen.*—Propanone suspensions of complexes (4a)—(4d) were rapidly decolourized on exposure to air or dioxygen, and white crystals of complexes (6a)—(6d) were obtained after recrystallization. Analytical data were as expected for the addition of one molecule of dioxygen to (4a)—(4d).

The n.m.r. spectra of complexes (6a)—(6d) in CD_3COCD_3 solution were unexpectedly complicated. Thus the ^1H n.m.r. spectrum of (6d), of empirical formula $[Rh\{C_5H_4C(C_6H_4Me\text{-}4)_2\}_2O_2]PF_6$, contained four multiplet resonances for the fulvene-ring protons, two separate A_2B_2 patterns for the arene-ring protons, and two singlets for the methyl protons. Similarly the ^{13}C n.m.r. spectrum contained four doublet resonances [$|J(Rh-C)| = 7$ Hz] for the hydrogen-bearing carbon atoms in the fulvene ring, two complete sets of singlets for the arene-ring carbon atoms, and two singlets for the methyl-carbon atoms. Other key features of the ^{13}C spectra of complexes (6a)—(6d) were that the resonance for the remaining carbon atom in the fulvene ring was as strongly coupled to rhodium as the other four, and that the resonance for the exocyclic carbon atom in each fulvene ligand was at much higher field (*ca.* δ 88) than in the free fulvenes or the complexes described earlier in the paper.

The reason for these changes in spectra was revealed by the crystal structure * of complex (6a), which showed (see Figure) that the molecule of dioxygen had formed a peroxide bridge between the exocyclic carbon atoms in the two fulvene ligands.[13] Each fulvene ring was therefore converted into an η^5-cyclopentadienyl ring (hence the similar values for all the Rh-C coupling constants), and the exocyclic carbon atoms were now sp^3-hybridized (causing the large changes in chemical shift). Since each complex (6) exhibited only one resonance for both exocyclic carbon atoms and one for the cyclopentadienyl carbon atoms to which they were attached, the two 'halves' of the ligand, linked through the peroxide bridge, were evidently equivalent, and the complexity of the spectra resulted from the fact that within a given half of the ligand all the cyclopentadienyl-ring carbon atoms were inequivalent and the two aryl groups were inequivalent.

It seems likely that the reactions of complexes (4a)—(4d) with dioxygen proceed by way of intermediates in which the dioxygen is complexed to rhodium. The subsequent rearrangement can be viewed in two rather different ways. As Mason [14] and Vaska [15] have commented, transition-metal dioxygen complexes are commonly diamagnetic, and the intermediates in these reactions could be envisaged as being complexes of rhodium(I) with a singlet O_2 molecule. The result of the subsequent transfer of O_2 from metal to ligands is that the five-membered rings become aromatic, but at the expense of any delocalization between five- and six-membered rings that exists in (4a)—(4d). This is rather similar to the effect of the reaction of singlet O_2 with anthracene, in which the dioxygen adds across the 9 and 10 positions in the centre ring, leaving two fully aromatic outer rings but eliminating delocalization between them.[16] Alternatively, the intermediates might be viewed as peroxide complexes of rhodium(III). As mentioned earlier, the ^{13}C n.m.r. spectra of the fulvene complexes seem to indicate the importance of resonance structures where the fulvene ring is η^5-bonded to the metal and a positive charge resides on the exocyclic carbon atom. Thus the rearrangement could be viewed as a nucleophilic attack by peroxide on the exocyclic carbon atoms of the two fulvene ligands.

Experimental

Except where otherwise indicated, all operations were carried out under an atmosphere of nitrogen, using dry, oxygen-free solvents. Details of the instruments used to obtain most of the ^1H and ^{13}C n.m.r. spectra have been given elsewhere,[17] but the spectra of selected complexes were recorded on a Bruker WH400 spectrometer with operating frequencies for ^1H and ^{13}C of 400 and 100 MHz respectively.

Preparation of Compounds.—Analytical data for the fulvenes and fulvene complexes are given in Table 3. The complexes $[Rh_2Cl_2\{P(OPh)_3\}_4]$,[9] $[Rh_2(cod)_2Cl_2]$,[10] $[Rh_2(CO)_4Cl_2]$,[11] and (5a) [3] were prepared as described in the literature.

Compound (1a). To a solution of sodium (1.00 g) in ethanol

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* Details of the fully refined structure and availability of supplementary data can be found in ref. 13. There will be no further publication by us on this structure.

(20.0 cm^3) were added Ph_2CO (8.00 g) and cyclopentadiene (4.0 cm^3). The solution was refluxed for 0.5 h and then allowed to cool. The red crystals formed on cooling were filtered off and recrystallized from ethanol (yield 45%). Compound (1d) was prepared in the same way, using $(4\text{-}MeC_6H_4)_2CO$ in place of Ph_2CO.

Compound (1b). A solution of sodium (0.50 g) in ethanol (40.0 cm^3) was stirred with $(4\text{-}ClC_6H_4)_2CO$ (5.00 g) and cyclopentadiene (3.2 cm^3) at 308 K for 2.5 h. Ethanol (40.0 cm^3) was then added and the solution was allowed to cool. The orange precipitate was filtered off and washed with ethanol. Compound (1b) was extracted from this solid with light petroleum (b.p. 313—333 K) and then recrystallized from hexane (yield 35%).

Compound (1c). A solution of sodium (1.00 g) in ethanol (30.0 cm^3) was treated with $(4\text{-}MeOC_6H_4)_2CO$ (10.00 g) and cyclopentadiene (3.3 cm^3). The solution was heated under reflux until all the ketone had dissolved. On cooling, some unreacted ketone was precipitated. This was filtered off, and the filtrate was then evaporated to dryness under reduced pressure. Compound (1c) was extracted from the residual solid with light petroleum (b.p. 313—333 K): slow evaporation of the light petroleum under a stream of nitrogen yielded orange needles of (1c) (yield 10%).

Compound (2a). To a solution of $[Rh_2Cl_2\{P(OPh)_3\}_4]$ (0.38 g) in tetrahydrofuran (15.0 cm^3) was added, with stirring, a solution of $AgClO_4$ (0.11 g) in the same solvent (15.0 cm^3). After 0.3 h the precipitate of AgCl was filtered off, and a solution of compound (1a) (0.12 g) in tetrahydrofuran (10.0 cm^3) was added to the filtrate, which immediately changed colour from yellow to purple. The solution was slowly reduced in volume under a stream of nitrogen. The purple crystals which were formed were filtered off and washed with ethoxyethane (yield 64%). Compound (2b) was prepared in the same way, using fulvene (1b).

Compound (3a). Solutions of $[\{Rh(cod)Cl\}_2]$ (0.20 g) in tetrahydrofuran (10.0 cm^3) and $AgClO_4$ (0.17 g) in tetrahydrofuran (5.0 cm^3) were mixed with stirring. After 0.4 h the precipitate of AgCl was filtered off, and a solution of compound (1a) (0.18 g) in tetrahydrofuran (5.0 cm^3) was added to the filtrate, causing a colour change from yellow to maroon. Reduction in the volume of the solution under a stream of nitrogen resulted in precipitation of red crystals. These were filtered off and recrystallized from a mixture of propanone and ethanol (yield 55%). Compound (3b) was prepared in the same manner, using fulvene (1b).

Compound (4a). Solutions of $[Rh_2(CO)_4Cl_2]$ (0.19 g) in tetrahydrofuran (15.0 cm^3) and $AgClO_4$ (0.21 g) in tetrahydrofuran (15.0 cm^3) were mixed with stirring. After 0.3 h the precipitate of AgCl was filtered off, and a solution of compound (1a) (0.46 g) in tetrahydrofuran (10.0 cm^3) was added to the filtrate, which immediately became dark blue in colour. Slow reduction in the volume of the solution under a stream of nitrogen yielded deep blue crystals, which were filtered off and washed with ethoxyethane (yield 52%). Compounds (4b) and (4c) were obtained in similar yield using fulvenes (1b) and (1c). For the preparation of (4d), $AgPF_6$ (0.25 g) was used in place of $AgClO_4$, and the fulvene used was (1d).

Compound (6a). Oxygen was bubbled through a suspension of compound (4a) (0.10 g) in propanone (20.0 cm^3) until the blue colour of the complex had disappeared, leaving an almost colourless solution. Ethanol (10.0 cm^3) was added, and slow evaporation of the solvent under a stream of nitrogen left off-white crystals in virtually quantitative yield. Recrystallization from a mixture of propanone and ethanol yielded white crystals. Compounds (6b)—(6d) were obtained from (4b)—(4d) by the same method.

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