Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 36.[1] Reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ † with Phenylacetylene to give the η^4-Cyclobutadiene Complex $[Rh(C_5Me_5)(C_4Ph_2HCPh{=}C_5Ph_2H_2)]$‡ and the η^4-Benzocyclobutadiene Complex $[Rh(C_5Me_5)(C_8Ph_4H_2)]$,§ Identified by *X*-Ray Structure Determinations

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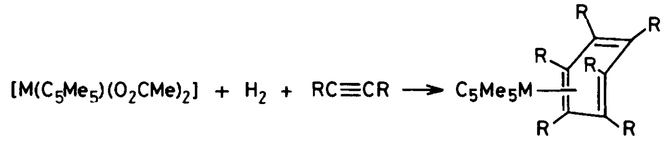
Reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ with PhC≡CH in acetonitrile in the presence of Na_2CO_3 gives two complexes (3) and (4) as well as some isomers of triphenylbenzene and acetophenone. Complexes (3) and (4) were characterised by ^{13}C n.m.r. spectroscopy and by single-crystal *X*-ray structure determinations. Complex (3) has the rhodium π-bonded η^5 to a C_5Me_5 ring and η^4 to the C_4 ring of a tetraphenylbenzocyclobutadiene. The benzocyclobutadiene is very close to planar and only a little distorted upon co-ordination; the structure of the ligand is best understood in terms of a '1,2-divinylcyclobutadiene' type of bonding. Complex (4) has the rhodium π-bonded η^5 to a C_5Me_5 ring and η^4 to a cyclobutadiene; this cyclobutadiene carries two phenyl substituents (1,3-) and an (unco-ordinated) 6-(1,3,6-triphenylfulvenyl) substituent. Possible routes by which (3) and (4) could be formed are discussed.

A NUMBER of authors, in particular Dickson and coworkers,[2] have examined the reactions of the cyclopentadienylrhodium(I) dicarbonyls $[Rh(C_5R_5)(CO)_2]$ (R = H or Me)[3] with various acetylenes. However, few reports have yet appeared concerning the reactions of pentamethylcyclopentadienylrhodium(III) complexes[3] with acetylenes although some years ago one of us reported the formation and the fluxional behaviour of the η^4-benzene complexes (1) by reaction of dimethyl acetylenedicarboxylate and hydrogen with $[M(C_5Me_5)(O_2CMe)_2]$ (M = Rh or Ir).[4]



(1; R = CO_2Me)

In general, the products from such reactions are complexes involving one, two, or [as in (1)] three acetylene units, in some cases with incorporation of CO from $[Rh(C_5R_5)(CO)_2]$. Both mono- and bi-nuclear complexes have been isolated and characterised.

Most of the reactions have been carried out using disubstituted acetylenes; few involving monosubstituted acetylenes have yet been investigated. We here report the reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ (2) with phenylacetylene which yields the two entirely novel types of complex (3) and (4).

RESULTS AND DISCUSSION

There is no reaction between phenylacetylene and (2) except in the presence of base. Under these conditions, in acetonitrile solvent, the reaction of (2) with excess of phenylacetylene goes very readily in the cold to give a dark coloured mixture which could be separated by column chromatography into two metal complexes (3) and (4). In addition, some acetophenone and isomers of triphenylbenzene are formed.

$[Rh(C_5Me_5)(C_8Ph_4H_2)]$, (3).—The complex (3) crystallised in red-brown needles and was shown by mass spectrometry to contain a tetramer of phenylacetylene less two hydrogens, as well as the $Rh(C_5Me_5)$ unit. The ^1H n.m.r. spectrum was uninformative as it consisted merely of a singlet (δ 1.5, 15 H, C_5Me_5) and a multiplet in the aromatic region (δ 7.3, 22 H). However, the ^{13}C n.m.r. showed, in addition to C_5Me_5 resonances [δ 9.0, s, $C_5\mathit{Me}_5$, and 92.0, d, C_5Me_5, J(Rh–C) = 6.1 Hz] and an unanalysable mass of aromatic resonances (δ 117—143), four sharp signals in the region (δ 72—89). Each consisted of a doublet (J = 9—11 Hz) arising from coupling to ^{103}Rh (100%, $I = \frac{1}{2}$) and they were clearly due to four inequivalent sp^2 carbons, not bearing hydrogens and bonded to rhodium. These data indicated the presence of an extremely asymmetric organic ligand, probably of the form $C_8Ph_4H_2$, bonded to $Rh(C_5Me_5)$.

The i.r. spectra gave no further information and, in order to determine the structure, a single-crystal *X*-ray determination was carried out. This showed the complex to be composed of a $Rh(\eta^5\text{-}C_5Me_5)$ unit linked (η^4) to the four-membered ring of a tetraphenylbenzocyclobutadiene as shown (Figures 1 and 2). There were two independent molecules per equivalent position in the crystal lattice and these are denoted by A and B. The two molecules differ somewhat in the relative positions of the C_5Me_5Rh moiety with respect to the benzocyclobutadiene ligand but the bond lengths and angles (Table 1) are not significantly different. In each case the metal is rather asymmetrically bonded to the C_4 ring (mean Rh–C 2.150 Å) which is itself only slightly distorted from square-planar geometry (mean C–C 1.475 Å). The metal is closer to the C_5Me_5 ring [out-of-plane distance 1.861 Å

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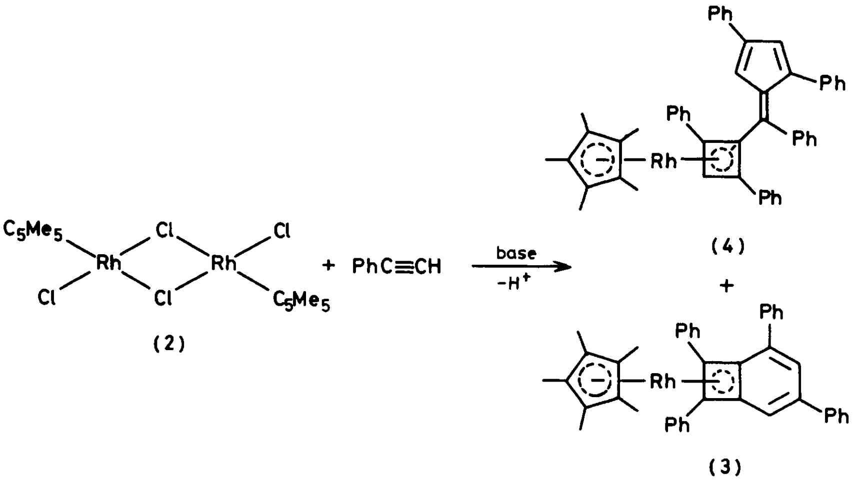
† *trans*-Di-μ-chloro-bis[chloro(1—5-η-pentamethylcyclopentadienyl)rhodium].

‡ [1—4-η-1,3-Diphenyl-2-(1′,3′,6′-triphenylfulven-6′-yl)cyclobutadiene](1—5-η-pentamethylcyclopentadienyl)rhodium.

§ 1—5-η-Pentamethylcyclopentadienyl(1,2,2a,6a-η-1,2,3,5-tetraphenylcyclobutabenzene)rhodium.



(molecule A) and 1.856 Å (molecule B)] than to the C_4 ring (out-of-plane distance 1.877, 1.878 Å). This may well be due to non-bonded interactions between the metal and the phenyls on the benzocyclobutadiene.

One rather surprising feature is that the four- and six-membered rings of the $C_8Ph_4H_2$ ligand are virtually co-planar; the dihedral angle between the two planes is 1.4° (molecule A) and 2.5° (molecule B). The phenyls on the C_4 ligand are bent away from the rhodium by small amounts [9.8, 8.6° for C(32) attached to C(8) and 7.9, 4.6° for C(26) attached to C(7)]. The ligand is therefore perturbed on co-ordination but only to a rather small extent.

TABLE 1

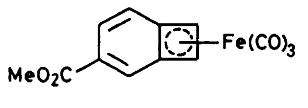
Selected bond lengths (Å) [a] and angles (°) [b] in [Rh(C_5Me_5)(η^4-$C_8Ph_4H_2$)] (3)

	Molecule A	Molecule B
Rh–C(1)	2.198(13)	2.182(12)
Rh–C(2)	2.159(12)	2.161(13)
Rh–C(7)	2.110(12)	2.146(13)
Rh–C(8)	2.122(12)	2.118(12)
Rh–C(38)	2.223(10)	2.268(9)
Rh–C(39)	2.223(11)	2.229(9)
Rh–C(40)	2.237(10)	2.191(10)
Rh–C(41)	2.245(10)	2.206(9)
Rh–C(42)	2.237(11)	2.254(9)
C(1)–C(2)	1.447(18)	1.436(18)
C(1)–C(7)	1.462(18)	1.509(17)
C(2)–C(8)	1.480(17)	1.462(17)
C(7)–C(8)	1.488(17)	1.518(17)
C(2)–C(3)	1.437(18)	1.439(18)
C(3)–C(4)	1.391(19)	1.382(18)
C(4)–C(5)	1.459(19)	1.426(18)
C(5)–C(6)	1.397(19)	1.390(19)
C(6)–C(1)	1.397(19)	1.425(18)

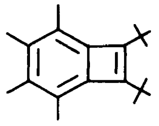
	Molecule A	Molecule B
C(2)–C(8)–C(7)	87	90.5
C(8)–C(7)–C(1)	91	86
C(7)–C(1)–C(2)	90	92
C(1)–C(2)–C(8)	92	91
C(1)–C(7)–C(26)	132	134
C(8)–C(7)–C(26)	136	139
C(2)–C(8)–C(32)	135	135
C(7)–C(8)–C(32)	136	133
C(2)–C(1)–C(6)	124	123
C(6)–C(1)–C(7)	146	145
C(1)–C(2)–C(3)	120	121
C(3)–C(2)–C(8)	148	148
C(2)–C(3)–C(4)	115	115
C(3)–C(4)–C(5)	123	124
C(4)–C(5)–C(6)	122	122
C(5)–C(6)–C(1)	115	115

[a] Estimated standard deviations (e.s.d.s) are given in parentheses. [b] E.s.d.s all 1°.

Although a number of benzocyclobutadiene complexes have been synthesised,[5] only the briefest account of an *X*-ray structure determination of one of them, (5), has appeared.[6,*] The high *R* factor and the lack of reported estimated standard deviations (e.s.d.s) for this structure make it difficult to evaluate the significance of the data. However, the conclusion which these authors drew, namely that the bonding is best understood in terms of a ' 1,2-divinylcyclobutadiene ' structure (as shown), also appears to fit complex (3).



(5)


(6)

In contrast, the *X*-ray structure of the tetramethyl-di-t-butylbenzocyclobutadiene (6) shows it to be closer to a ' 1,2-dimethylenecyclobutene ' structure, as shown.[7] The delocalisation of the electrons (associated with the C_4 ring carbons) upon complexation to the metals in (3) and (5) probably to some extent destroys the aromaticity of the benzene ring, but the effect is quite small and rather subtle.

[Rh(C_5Me_5)(C_4Ph_2HCPh=$C_5Ph_2H_2$)], (4).—The second complex (4) crystallised as black needles which give purple solutions. The mass spectroscopic molecular-weight determination indicated that it was composed of five phenylacetylene units less two hydrogens, as well as the Rh(C_5Me_5) group. The ^{13}C n.m.r. spectrum of (4) again showed a complex mass of aromatic carbon signals

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[*] The structure of a diphenyl-η^4-cyclobuta[*l*]phenanthrene-rhodium complex which is not dissimilar to (4) has been determined (M. D. Rausch, S. A. Gardner, E. F. Tokas, I. Bernal, G. M. Reisner, and A. Clearfield, *J. Chem. Soc., Chem. Commun.*, 1978, 187).

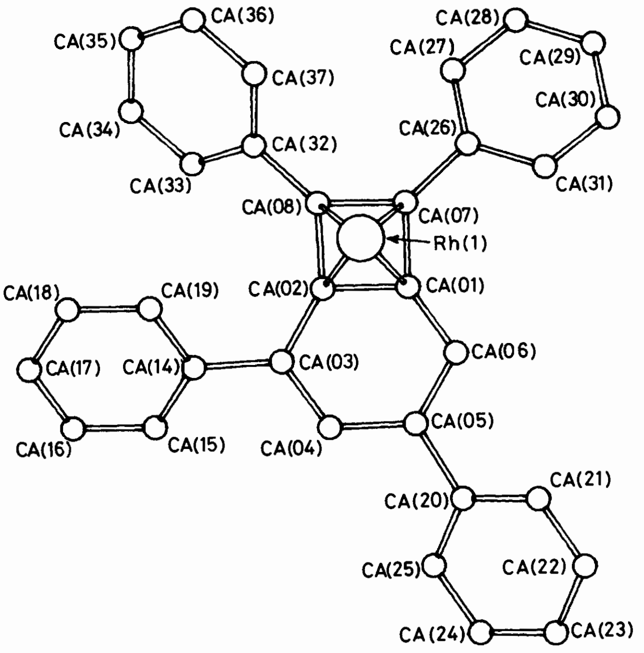


FIGURE 1 View of complex (3), $[Rh(C_5Me_5)(\eta^4\text{-}C_8Ph_4H_2)]$, onto the plane of the benzocyclobutadiene ligand (hydrogens and C_5Me_5 ring omitted for clarity)

from δ 120 to 153 p.p.m., resonances due to one type of C_5Me_5 [δ 9.5, s, $C_5\mathit{Me}_5$ and 95.2, d, C_5Me_5, J(Rh–C) = 6.1 Hz], and four doublets in the region δ 65—83 p.p.m. These last signals were clearly due to four carbons π-bonded to rhodium and suggested the presence of another asymmetric cyclobutadiene complex.

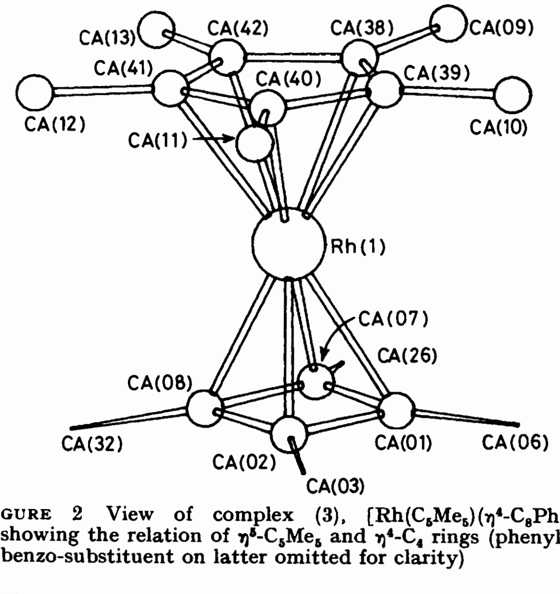


FIGURE 2 View of complex (3), $[Rh(C_5Me_5)(\eta^4\text{-}C_8Ph_4H_2)]$, showing the relation of $\eta^5\text{-}C_5Me_5$ and $\eta^4\text{-}C_4$ rings (phenyls and benzo-substituent on latter omitted for clarity)

The ^1H n.m.r. spectrum of (4) was again of little help in deducing the structure. In $CDCl_3$ its features consisted of a broad multiplet in the aromatic region (δ 6.8—7.5), some weak olefinic resonances (δ 4.9), and *two* singlets in the C_5Me_5 region (δ 1.5 and 1.6). The spectra did not show any significant variation with temperature, but the relative intensities of the C_5Me_5 resonances varied substantially with solvent. Further, the higher-field resonance of a freshly made-up chloroform solution was substantially weaker than that of an 'aged' solution.

Again, since the spectroscopic data were insufficient to define the structure of (4), a single-crystal *X*-ray determination was carried out. This showed the structure illustrated in Figure 3. The rhodium, η^5-bonded on the one side to the C_5Me_5 ligand, is η^4-bonded on the other to a trisubstituted cyclobutadiene. Two of the (opposing) substituents are phenyls, the third is an uncomplexed 6-(1,3,6-triphenylfulvenyl) group. The complexed C_4 ring is close to square planar (mean C–C 1.479 Å). Two of the ring carbons, C(1) and C(2), are a little closer (2.105, 2.102 Å) to the metal than the other two (2.125, 2.167 Å). This may well be because the carbon, C(4), furthest from the rhodium bears the largest substituent ($-CPh{=}C_5Ph_2H_2$). The alternation in bond length in the fulvenyl moiety is clearly shown; the double bonds range from 1.370 to 1.387 Å while the single bonds are significantly longer, between 1.442 and 1.473 Å.

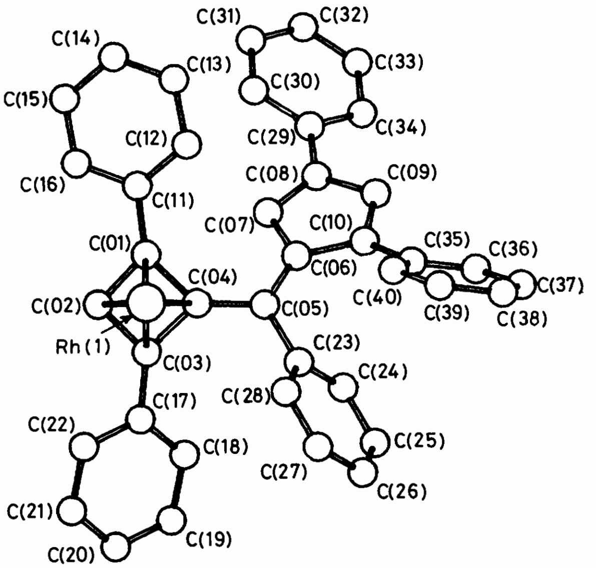
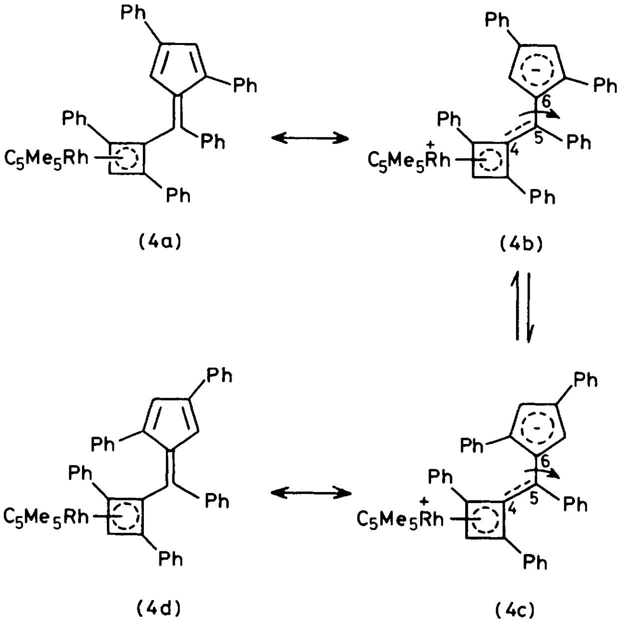


FIGURE 3 View of complex (4) $[Rh(C_5Me_5)(\eta^4\text{-}C_4Ph_2HCPh{=}C_5Ph_3H_2)]$ (hydrogens and C_5Me_5 ring omitted for clarity)

Owing to the steric interference between the phenyls the planar fulvenyl moiety is twisted away from co-planarity with the co-ordinated cyclobutadiene by 42°. Another consequence is that the phenyls attached to C(3), C(5), and C(10) are bent away by quite considerable amounts; the angles of the bonds to these phenyls from their planes are 7.8, 26.2, and 12.0° respectively. The phenyls attached to C(1) and C(8) are bent away very little (0.7 and 2.6° respectively). In view of this structure we suggest that the anomaly of two C_5Me_5 signals observed in the ^1H n.m.r. spectrum may be due to an isomerism caused by rotation about the C(5)–C(6) bond. [The alternative rotation about C(4)–C(5) leads to the optical enantiomers which would not be detected by this type of n.m.r. experiment.]

The isomer formed in the crystal, (4a), could isomerise to (4d) *via* dipolar forms, (4b) and (4c), in which the C(5)–C(6) bond order is very substantially reduced. The dipolar forms can be stabilised by a small movement of the metal and a twist about C(4)–C(5) to involve C(5) in π bonding (' stabilised α-carbonium ion ')[8] and also to create a 6π-electron cyclopentadienide anion in the C(6)—C(10) ring.



SCHEME 1

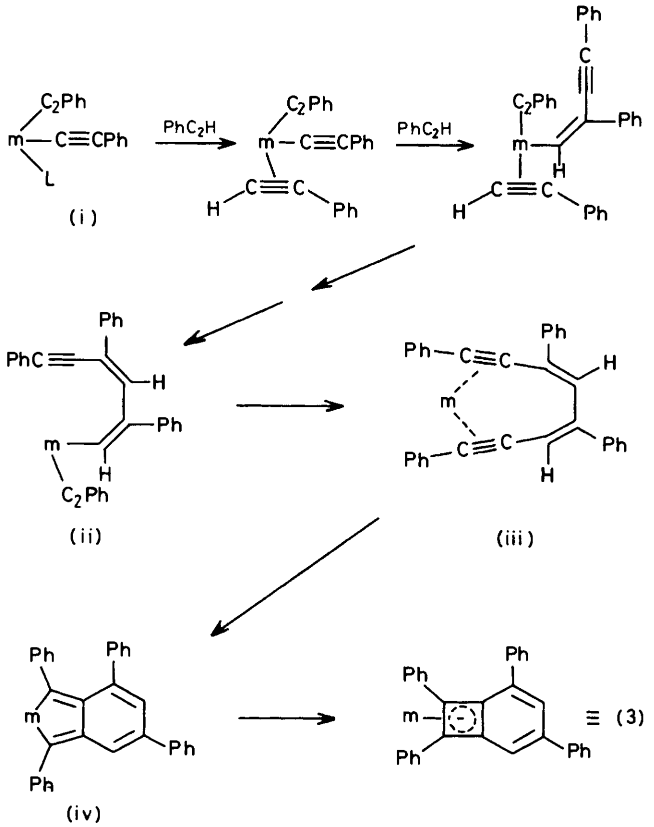
This explanation could also account for the observation of the isomers only in the ^1H n.m.r. spectrum of the C_5Me_5 hydrogens. The aromatic hydrogen pattern is too complex and the C_5Me_5 carbons are probably too well shielded from what is in effect quite a small perturbation for it to be observed.

Mechanism of the Formation of Complexes (3) *and* (4).—Any mechanistic discussion based on the limited evidence available from the *X*-ray structures must be very tentative. Nevertheless, the structures of complex (3) and especially of (4) are most unusual even by the rather exotic standards of the field of metal-catalysed acetylene oligomerisation reactions,[9] and warrant some preliminary speculation.

Analysis of the structures of the tetraphenylbenzocyclobutadiene and of the $C_4Ph_2HCPh{=}C_5Ph_2H_2$ ligands indicates that a mechanism must contain both oligomerisation and cyclisation steps for each and their occurrence in comparable amounts suggests some common steps in their formation. The loss of two acetylenic hydrogens (as H^+) probably occurs early since this can then be associated with the creation of vacant sites at the metal which then lead to σ-acetylide intermediates such as (i) at which the acetylene oligomerisation can then proceed.

$$[Rh_2(C_5Me_5)_2Cl_4] + PhC_2H + \text{base} + MeCN \longrightarrow 2[Rh(C_5Me_5)(MeCN)_3]^{2+}\cdot 2PhC_2^- \longrightarrow \underset{\text{(i)}}{[Rh(C_5Me_5)(PhC_2)_2(MeCN)]}$$

If (i) then inserts two further acetylenes into the rhodium–acetylide bond in a series of stepwise *cis* insertions * to give (ii) (Scheme 2), this brings together the required number of acetylene and acetylide units to form (3). Further reactions all involve simple steps with well known analogies such as the reductive coupling of (ii) to give a substituted complexed octa-3,5-diene-1,7-diyne (iii). There are numerous examples[5,11] of the transformation of α,ω-diynes into metallacyclopentadienes, (iii) $\longrightarrow$ (iv), which can then again reductively eliminate to give the cyclobutadiene, in this case (3). It will also be noted that the stereochemistry observed for (3) arises from a head-to-tail dimerisation of the acetylenes, which is analogous to that postulated in the $PdCl_2$-induced cyclotetramerisation of phenylacetylene to tetraphenyldihydropentalene.[10]



SCHEME 2 m = C_5Me_5Rh

The presence of a triphenylfulvene unit in the ligand of complex (4) suggests another analogy to the $PdCl_2$-induced reactions where such skeletons are frequently

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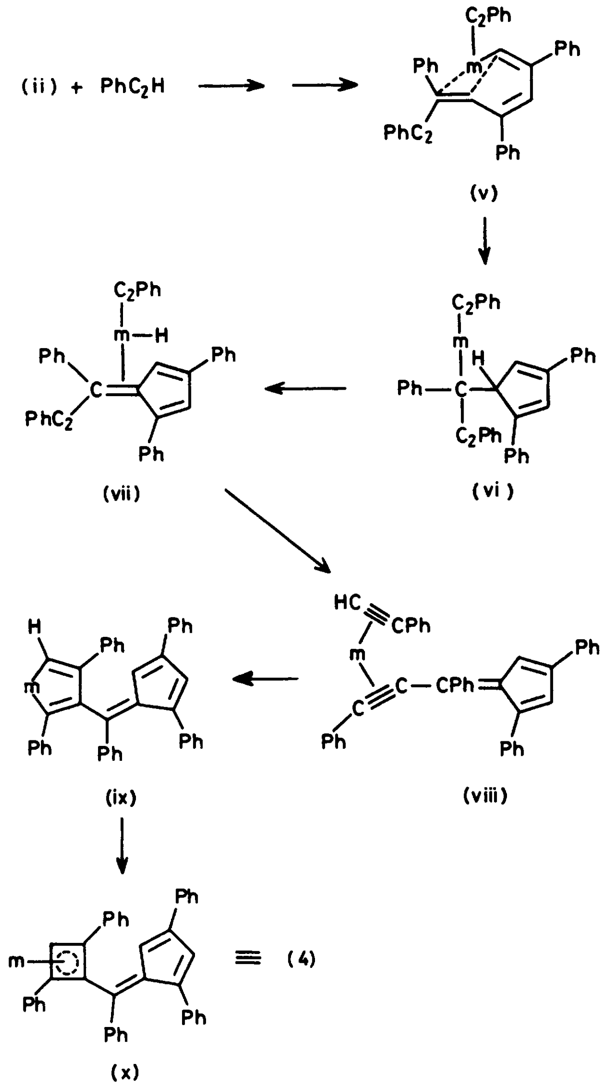
* Related processes have been shown to occur in the $PdCl_2$-induced oligomerisations of acetylenes.[9,10]

formed in cyclotrimerisation reactions. If this is so, then Scheme 3 shows a possible route to (4) from the intermediate (ii), presuming that a further insertion (ii) ⟶ (v) competes very effectively with the rearrangement (ii) ⟶ (iii) which eventually gives (3). While there are good precedents for stages (ii) ⟶ (v) ⟶ (vi) in palladium chemistry, the hydride transfer from a C_5 carbon in (vi) *via* the metal (vii) to give a π acetylene complex (viii) again is much more speculative. From there, however, the route *via* the metallacyclopentadiene (ix) to (x) (≡4) has parallels in Scheme 2.



SCHEME 3 m = C_5Me_5Rh

EXPERIMENTAL

All reactions were carried out under nitrogen. Microanalyses were carried out by the Department of Chemistry Microanalytical Service; n.m.r. spectra were run on Perkin-Elmer R-12B (^1H, 60 MHz) and JEOL PFT-100 (^{13}C) spectrometers.

Reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ *with Phenylacetylene*.—The complex $[Rh_2(C_5Me_5)_2Cl_4]$ (0.31 g, 0.5 mmol) and sodium carbonate (4.0 g) in acetonitrile (50 cm³) were stirred (20 °C, 0.5 h). The solution was cooled to −40 °C and phenylacetylene (1.85 g, 18.5 mmol) was added. The temperature was kept at −40 °C for 10 min and then the reaction mixture was allowed to warm up slowly, with stirring. After 18 h the solution was filtered, the solvent removed *in vacuo*, and the residue was dissolved in hexane and chromatographed on alumina (Brockman, II) in hexane. Triphenylbenzene (50 mg, mixture of isomers) was eluted first, followed by a red band which contained (3), in turn followed by a purple band containing (4) contaminated with acetophenone (identified by i.r.). The purple fraction requires further chromatography to remove the acetophenone. The yields of complexes (3) and (4) were 0.195 g (30%) and 0.146 g (20%) respectively, based on starting complex. Samples for microanalysis and *X*-ray structure determination were recrystallised from diethyl ether–ethanol.

Physical characterisation of complex (3): red-brown needles, m.p. 198—199 °C [Found: C, 78.5; H, 5.3%; *M* (mass spectroscopic) 644. $C_{42}H_{37}Rh$ requires C, 78.8; H, 5.4%; *M* 644]; ^1H n.m.r. ($CDCl_3$) δ 1.5 (15 H, C_5Me_5) and 7.3 (22 H, aromatic); ^{13}C-{^1H} n.m.r. (CD_2Cl_2) δ 9.0 (s, $C_5\mathit{Me}_5$), 92.0 [d, C_5Me_5, J(Rh–C) = 6.1], 72.6 [d, J(Rh–C) = 10.7], 75.8 (d, J = 12.2), 84.0 (d, J = 9.1), 88.9 (d, J = 9.1 Hz), and 117.8—143.1 (⩾18 lines, aromatic).

Physical characterisation of complex (4): black needles, m.p. 213—214 °C [Found: C, 79.9; H, 6.0%; *M* (mass spectroscopic) 746. $C_{50}H_{43}Rh$ requires C, 80.4; 5.8%; *M* 746]; ^1H n.m.r. ($CDCl_3$) δ 1.48, 1.58 (C_5Me_5, variable ratio), 4.9 and 6.8—7.5 (aromatic); ^{13}C-{^1H} (CD_2Cl_2) δ 9.5 ($C_5\mathit{Me}_5$), 65.0 [d, J(Rh–C) = 12.2], 66.4 (d, J = 10.7), 76.5 (d, J = 12.2), 82.8 (d, J = 10.7), 95.2 (d, C_5Me_5, J = 6.1 Hz), and 120.9—152.9 (⩾27 lines, aromatic).

TABLE 2

Selected bond lengths (Å) and angles (°) in $[Rh(C_5Me_5)(\eta^4\text{-}C_4Ph_2HCPh{=}C_5Ph_2H_2)]$ (4) with estimated standard deviations in parentheses

Rh–C(1)	2.105(7)	Rh–C(41)	2.191(8)
Rh–C(2)	2.102(7)	Rh–C(42)	2.245(8)
Rh–C(3)	2.125(7)	Rh–C(43)	2.240(10)
Rh–C(4)	2.167(6)	Rh–C(44)	2.209(9)
		Rh–C(45)	2.171(9)
C(1)–C(2)	1.468(9)	C(5)–C(6)	1.381(9)
C(2)–C(3)	1.457(10)	C(6)–C(7)	1.456(9)
C(3)–C(4)	1.493(9)	C(7)–C(8)	1.387(10)
C(4)–C(1)	1.495(9)	C(8)–C(9)	1.454(10)
C(1)–C(11)	1.476(10)	C(9)–C(10)	1.370(10)
C(3)–C(17)	1.463(10)	C(10)–C(6)	1.473(10)
C(4)–C(5)	1.442(9)	C(3)–C(17)	1.463(10)
		C(5)–C(23)	1.491(9)
		C(8)–C(29)	1.476(10)
		C(10)–C(35)	1.477(10)
C(1)–C(2)–C(3)	90.9(5)	C(4)–C(5)–C(6)	121.2(6)
C(2)–C(3)–C(4)	90.5(5)	C(4)–C(5)–C(23)	117.8(6)
C(3)–C(4)–C(1)	88.5(5)	C(6)–C(5)–C(23)	120.8(6)
C(4)–C(1)–C(2)	90.0(5)	C(5)–C(6)–C(7)	124.9(6)
C(2)–C(3)–C(17)	128.8(6)	C(5)–C(6)–C(10)	128.2(6)
C(4)–C(3)–C(17)	139.2(6)	C(7)–C(6)–C(10)	106.6(6)
C(2)–C(1)–C(11)	129.4(6)	C(6)–C(7)–C(8)	107.4(6)
C(4)–C(1)–C(11)	140.5(6)	C(7)–C(8)–C(9)	109.3(6)
C(1)–C(4)–C(5)	137.3(6)	C(8)–C(9)–C(10)	108.5(6)
C(3)–C(4)–C(5)	133.7(6)	C(9)–C(10)–C(6)	108.2(6)

X-Ray Structure Determinations of $[Rh(C_5Me_5)(C_8Ph_4H_2)]$ (3) *and* $[Rh(C_5Me_5)(C_4Ph_2HCPh{=}C_5Ph_2H_2)]$ (4).—*Crystal data* (3). $C_{42}H_{37}Rh$, M = 644.66, Triclinic, a = 24.49(6), b = 18.91(5), c = 7.98(2) Å, α = 99.1(1), β = 78.5(1), γ = 117.3-

TABLE 3

Atomic co-ordinates ($\times 10^5$ for Rh; $\times 10^4$ for others) for complex [$Rh(C_5Me_5)(\eta^4\text{-}C_8Ph_4H_2)$] (3), molecules A and B, e.s.d.s in parentheses

Molecule A

Atom	*x*	*y*	*z*
Rh(A)	−5 220(5)	20 402(6)	4 824(13)
CA(01)	−699(5)	2 104(7)	−2 071(15)
CA(02)	−79(5)	2 686(7)	−1 791(14)
CA(03)	92(5)	3 524(7)	−1 725(14)
CA(04)	−380(6)	3 713(8)	−1 898(15)
CA(05)	−998(6)	3 112(8)	−2 211(15)
CA(06)	−1 162(6)	2 296(8)	−2 332(15)
CA(07)	−529(5)	1 463(7)	−2 009(15)
CA(08)	115(5)	2 054(7)	−1 760(15)
CA(09)	−1 856(8)	661(13)	2 364(26)
CA(10)	−1 644(9)	2 495(14)	2 611(22)
CA(11)	−211(10)	3 658(11)	3 222(22)
CA(12)	422(7)	2 504(11)	3 450(19)
CA(13)	−577(10)	678(11)	2 777(22)
CA(14)	726(3)	4 154(5)	−1 471(12)
CA(15)	993(4)	4 875(5)	−2 243(11)
CA(16)	1 603(4)	5 433(4)	−2 057(11)
CA(17)	1 947(3)	5 270(5)	−1 099(12)
CA(18)	1 680(4)	4 549(5)	−327(11)
CA(19)	1 070(4)	3 991(4)	−513(11)
CA(20)	−1 474(4)	3 374(6)	−2 425(12)
CA(21)	−2 103(4)	2 873(5)	−1 969(12)
CA(22)	−2 555(3)	3 081(6)	−2 255(12)
CA(23)	−2 377(4)	3 791(6)	−2 998(12)
CA(24)	−1 747(4)	4 292(5)	−3 455(12)
CA(25)	−1 295(3)	4 084(6)	−3 168(12)
CA(26)	−850(4)	591(4)	−2 444(13)
CA(27)	−536(3)	123(5)	−3 068(14)
CA(28)	−867(4)	−680(5)	−3 621(13)
CA(29)	−1 511(4)	−1 015(4)	−3 150(13)
CA(30)	−1 825(3)	−548(5)	−2 927(14)
CA(31)	−1 495(4)	255(5)	−2 373(13)
CA(32)	720(3)	2 027(5)	−1 852(11)
CA(33)	1 257(4)	2 581(5)	−2 765(11)
CA(34)	1 829(3)	2 575(5)	−2 809(10)
CA(35)	1 864(3)	2 014(5)	−1 941(11)
CA(36)	1 327(4)	1 460(5)	−1 027(11)
CA(37)	755(3)	1 466(5)	−983(10)
CA(38)	−1 260(4)	1 422(6)	2 592(12)
CA(39)	−1 147(4)	2 250(7)	2 722(12)
CA(40)	−510(5)	2 744(5)	3 019(12)
CA(41)	−229(3)	2 221(7)	3 072(12)

Molecule B

Atom	*x*	*y*	*z*
Rh(B)	44 799(5)	20 065(7)	5 100(13)
CB(01)	4 071(5)	2 327(7)	3 022(14)
CB(02)	4 697(5)	2 923(7)	2 605(13)
CB(03)	4 822(5)	3 725(7)	2 369(14)
CB(04)	4 305(5)	3 867(8)	2 618(16)
CB(05)	3 683(5)	3 270(8)	2 998(15)
CB(06)	3 548(6)	2 494(7)	3 258(15)
CB(07)	4 287(5)	1 707(6)	3 116(15)
CB(08)	4 942(5)	2 358(7)	2 694(14)
CB(09)	4 911(8)	3 215(9)	−2 658(18)
CB(10)	5 712(6)	2 256(9)	−2 452(19)
CB(11)	4 732(7)	479(9)	−1 358(19)
CB(12)	3 364(7)	311(10)	−1 062(22)
CB(13)	3 478(7)	2 034(11)	−1 825(21)
CB(14)	5 462(3)	4 368(5)	1 917(13)
CB(15)	5 627(4)	5 156(6)	2 594(11)
CB(16)	6 224(4)	5 754(4)	2 113(12)
CB(17)	6 655(3)	5 565(5)	954(13)
CB(18)	6 491(4)	4 778(6)	277(11)
CB(19)	5 894(4)	4 179(4)	759(12)
CB(20)	3 159(3)	3 499(5)	3 164(12)
CB(21)	2 632(4)	2 991(4)	2 395(11)
CB(22)	2 136(3)	3 186(5)	2 569(12)
CB(23)	2 166(3)	3 889(5)	3 513(12)
CB(24)	2 693(4)	4 397(4)	4 282(11)
CB(25)	3 189(3)	4 202(5)	4 108(12)
CB(26)	3 979(4)	903(4)	3 622(12)
CB(27)	4 300(3)	549(5)	4 155(12)
CB(28)	3 997(4)	−258(5)	4 482(12)
CB(29)	3 372(4)	−711(4)	4 278(12)
CB(30)	3 051(3)	−358(5)	3 746(12)
CB(31)	3 354(4)	450(5)	3 418(12)
CB(32)	5 569(3)	2 425(5)	2 730(11)
CB(33)	6 023(4)	3 139(4)	3 373(11)
CB(34)	6 614(3)	3 209(4)	3 423(11)
CB(35)	6 751(3)	2 564(5)	2 830(11)
CB(36)	6 298(4)	1 850(4)	2 187(11)
CB(37)	5 706(3)	1 780(4)	2 137(11)
CB(38)	4 664(4)	2 370(4)	−2 198(11)
CB(39)	5 017(3)	1 945(5)	−2 070(12)
CB(40)	4 582(4)	1 151(5)	−1 574(12)
CB(41)	3 959(3)	1 085(5)	−1 395(11)
CB(42)	4 010(3)	1 838(5)	−1 781(12)

TABLE 4

Atomic co-ordinates ($\times 10^5$ for Rh; $\times 10^4$ for others) for complex (4) [$Rh(C_5Me_5)(\eta^4\text{-}C_4Ph_2HCPh{=}C_5Ph_2H_2)$] with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Rh	4 969(5)	14 887(3)	17 564(3)
C(01)	−245(5)	991(3)	734(3)
C(02)	1 084(6)	852(3)	960(3)
C(03)	1 374(5)	1 555(4)	810(3)
C(04)	31(5)	1 710(3)	556(3)
C(05)	−643(5)	2 291(3)	202(3)
C(06)	−1 761(6)	2 215(3)	−293(3)
C(07)	−2 159(6)	1 602(3)	−727(3)
C(08)	−3 254(6)	1 755(3)	−1 222(3)
C(09)	−3 601(6)	2 454(4)	−1 102(3)
C(10)	−2 714(6)	2 735(3)	−548(3)
C(11)	−1 303(6)	523(4)	699(3)
C(12)	−2 525(6)	762(4)	645(4)
C(13)	−3 485(8)	276(5)	638(5)
C(14)	−3 221(9)	−419(5)	699(5)
C(15)	−2 005(9)	−648(4)	759(5)
C(16)	−1 039(8)	−178(4)	758(4)
C(17)	2 574(6)	1 858(4)	779(4)
C(18)	2 733(7)	2 364(4)	268(4)
C(19)	3 968(8)	2 588(5)	243(5)
C(20)	4 977(8)	2 302(5)	706(6)
C(21)	4 814(8)	1 793(6)	1 210(6)
C(22)	3 613(6)	1 571(5)	1 254(5)
C(23)	−47(6)	2 973(3)	337(3)
C(24)	−50(6)	3 403(4)	−269(4)
C(25)	536(7)	4 038(4)	−170(5)
C(26)	1 122(7)	4 248(4)	551(5)
C(27)	1 133(7)	3 814(4)	1 156(4)
C(28)	553(6)	3 177(4)	1 057(4)
C(29)	−3 997(6)	1 292(4)	−1 776(4)
C(30)	−4 014(7)	585(4)	−1 645(4)
C(31)	−4 794(9)	159(5)	−2 171(5)
C(32)	−5 529(9)	444(5)	−2 809(5)
C(33)	−5 501(8)	1 132(5)	−2 946(5)
C(34)	−4 732(7)	1 574(5)	−2 433(4)
C(35)	−2 892(5)	3 390(3)	−182(4)
C(36)	−3 432(7)	3 949(4)	−622(5)
C(37)	−3 675(8)	4 558(5)	−258(6)
C(38)	−3 394(8)	4 604(5)	531(6)
C(39)	−2 861(7)	4 054(5)	964(5)
C(40)	−2 603(6)	3 443(4)	609(4)
C(41)	1 548(7)	1 388(4)	2 916(4)
C(42)	1 132(8)	2 070(4)	2 834(4)
C(43)	−204(9)	2 049(5)	2 668(4)
C(44)	−554(7)	1 335(5)	2 667(4)
C(45)	513(8)	938(4)	2 802(4)
C(46)	2 903(9)	1 171(6)	3 145(5)
C(47)	2 003(12)	2 685(5)	2 965(5)
C(48)	−1 046(14)	2 655(8)	2 601(6)
C(49)	−1 878(10)	1 071(9)	2 570(6)
C(50)	591(13)	150(5)	2 846(5)

(1)°, $U = 3\,208.6$ Å^3, $Z = 4$, $D_c = 1.33$ g cm^{-3}, $F(000) = 1\,336$, space group $P\bar{1}$ (C_i^1, no. 2), Mo-K_α radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 5.45 cm^{-1}.

Unit-cell parameters were obtained from a least-squares fit to the setting angles of 54 reflections centred manually. Approximate crystal size: 0.5 × 0.08 × 0.03 mm. (The Delaunay cell, $a = 24.197$, $b = 18.915$, $c = 7.979$ Å, $\alpha = 99.12$, $\beta = 97.37$, and $\gamma = 114.33°$, was not used.)

Crystal data (4). $C_{50}H_{43}Rh$, $M = 746.80$, Monoclinic, $a = 11.035(8)$, $b = 19.66(1)$, $c = 18.03(1)$ Å, $\beta = 101.37(1)°$, $U = 3\,835$ Å^3, $Z = 4$, $D_c = 1.29$ g cm^{-3}, $F(000) = 1\,552$, space group $P2_1/c$, Mo-K_α radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu = 4.69$ cm^{-1}.

Unit-cell parameters were obtained from a least-squares fit to the setting angles of 86 reflections centred manually.

Single-crystal *X*-ray data [complex (3)]* in the range $6.5 < 2\theta < 50°$ were collected on a Stoe STADI-2 diffractometer. 4 444 Independent reflections with intensity $I > 3\sigma(I)$ and background difference $\Delta < 4\sigma(B)$ were corrected for Lorentz and polarization but not for absorption. The structure was solved by Patterson and Fourier methods and block-diagonal matrix least-squares refinement reduced R to 0.054; the carbon atoms of the phenyl rings and of the cyclopentadienyl rings were treated as groups of fixed overall geometry, and all the thermal parameters as anisotropic. There are two independent molecules per equivalent position with the rhodium atoms separated by half a cell in the *a* direction.

Single-crystal *X*-ray data on complex (4) were collected and processed as for complex (3). 4 298 Independent reflections were used to solve the structure using Patterson and Fourier methods. Individual atom refinement using anisotropic thermal parameters for non-hydrogen atoms reduced R to 0.049.

The overall geometries of the molecules are shown in Figures 1—3. Atomic co-ordinates are in Tables 3 and 4, bond distances and angles in Tables 1 and 2. Tables of structure factors, the anisotropic thermal parameters, and equations of planes are listed in Supplementary Publication No. SUP 23278 (102 pp.).†

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* A preliminary data set comprising 2 602 reflections from the same crystal was collected on a PW1100 four-circle diffractometer at the Polytechnic of North London. We thank Drs. P. G. Owston and M. McPartlin for their co-operation in the use of this equipment and in the data collection and processing.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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