The Reactions of Di-μ-methylene-bis(pentamethylcyclopentadienyl)-dirhodium(IV) Complexes with Benzylmagnesium Chloride and with Alkynylmagnesium Chloride; *X*-Ray Structure of $[(\eta^5\text{-}C_5Me_5)Rh(CH_2Ph)(\mu\text{-}CH_2)_2Rh(\eta^4\text{-}C_5Me_5CH_2Ph)]$ †

Neil J. Meanwell, Arnold J. Smith, and Peter M. Maitlis *
Department of Chemistry, The University, Sheffield S3 7HF

Reaction of *trans*-$[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2Cl_2]$ (**1**) with RC≡CMgCl gave *trans*-$[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(RC_2)_2]$ (R = Ph or Bu^t). However attack on (**1**) by benzylmagnesium chloride occurred at one C_5Me_5 ring as well as at one rhodium to give $[(\eta^5\text{-}C_5Me_5)Rh(CH_2Ph)(\mu\text{-}CH_2)_2Rh(\eta^4\text{-}C_5Me_5CH_2Ph)]$ (**6**). The structure of (**6**) has been deduced by n.m.r. spectroscopy and confirmed by a single-crystal *X*-ray structure determination which showed the two rhodiums [2.559(3) Å apart] to be linked by two μ-methylene bridges. One rhodium (oxidation state formally +4) bears a σ-benzyl and an $\eta^5\text{-}C_5Me_5$ ring; the other rhodium (formally +2) is η^4-bound to $C_5Me_5CH_2Ph$ where the benzyl on the C_5 ring is *exo* to the metal. Reaction of $[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(MeCN)_2][PF_6]_2$ with R′C≡CH gave a complex $[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2CHCR'CHCR'CH)]PF_6$ (**7**) (R′ = *p*-chlorophenyl); on the basis of the n.m.r. spectra it is proposed that the two rhodiums are linked by a σ,σ,η^5-$CH_2CHCR'CHCR'CH$ bridge. The mode of formation of these complexes is discussed.

In our exploration of the chemistry of the dinuclear di-μ-methylene-bis(η^5-pentamethylcyclopentadienyl)dirhodium complexes, which formally have the metals in the +4 oxidation state, we have noted the extraordinary ability of the $(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2$ unit to survive transformations. Thus, the *trans*-dichloro-complex (**1**) is converted into (**2**; X = Br, I, or N_3) by metathesis (with Br^-, I^-, N_3^-, *etc.*),[1] into the *trans*-dicarbonyl dication (**2**; X = CO),[1] or into the dialkyls (**2**; X = Me, Et, Pr^n, or Bu^n), by reaction with the appropriate organo-aluminium or Grignard reagent.[2] Analogous and related chemistry involving the *cis* complexes is also observed. The integrity of the $(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2$ unit is preserved throughout these reactions, and also in the reaction with allyl Grignards to give (**3**).[3]

We now report reactions, of benzylmagnesium chloride with (**1**) and of $R'C_2H$ ($R' = C_6H_4Cl\text{-}p$) with (**4**), in which the integrity of the entire $(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2$ unit is no longer maintained, as well as the reaction of RC_2MgCl (R = Ph, Bu^t, or CH_2Ph) with (**1**), in which the integrity of the unit is maintained.

Results and Discussion

The Bis(alkynyl) Complexes trans-$[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(RC_2)_2]$ (**5**) (R = Ph *or* Bu^t).—The alkynyl Grignards RC_2MgCl (R = Ph or Bu^t) reacted with the dichloro complex (**1**) to give the *trans*-bis(alkynyl) complexes (**5a**; R = Ph) and (**5b**; R = Bu^t). The structures are clear from the n.m.r. spectra which show, for example, at δ 8.87 (**5b**) or 9.16 (**5a**) in the ^1H spectrum single triplet resonances due to the bridging methylenes, which indicate that the complexes have a *trans* geometry.[1,4] The presence of the ethynyl ligands is established by the double-doublets in the $^{13}C\text{-}\{^1H\}$ spectra at 107.4 (**5a**) and 84.6 (**5b**), due to RhC≡, with one large coupling (68.7 and 69.1 Hz respectively) to the nearer rhodium and a much smaller one (2.3 and 2.8 Hz) to the farther rhodium. By contrast, the farther ethynyl carbons, RhC≡*C*– [δ 99.6 (**5a**) and 106.0 (**5b**)], are triplets with very much smaller couplings to rhodium (6.8 and 6.5 Hz respectively). These data are very typical for rhodium σ-acetylide complexes.[5] The i.r. spectra also showed ν(C≡C) in the anticipated regions [2 205 (**5a**) and 2 105 (**5b**) cm^{-1}] indicating that the acetylides were indeed σ- and not π-bonded.

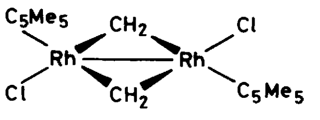
The Benzyl Complex $[(\eta^5\text{-}C_5Me_5)Rh(CH_2Ph)(\mu\text{-}CH_2)_2Rh(\eta^4\text{-}C_5Me_5CH_2Ph)]$ (**6**).—The complexes (**5a**) and (**5b**) are therefore exactly analogous to the 'normal' *trans*-dialkyl complexes (**2**; X = Me, Et, Pr^n, or Bu^n) formed from Grignards and complex (**1**); again, the $(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2$ unit has remained intact. However, when the *trans*-dichloro complex (**1**) was reacted with benzylmagnesium chloride a neutral organometallic complex (**6**) was obtained in moderate yield which no longer had the skeleton intact. This was not the expected dibenzyl complex (**2**; X = CH_2Ph), but an isomer thereof. This was shown most obviously by the presence in the ^1H n.m.r. spectrum of four resonances in the C_5Me_5 region, at δ 0.91, 1.12, 1.27, and 1.65 in the intensity ratio 2:1:2:5. This indicated that while one C_5Me_5 ring was still η^5, the other was probably η^4-bonded. This was confirmed by the ^{13}C resonances which showed one $\eta^5\text{-}C_5Me_5$ ring [δ 9.4 and 98.7 (d, *J*Rh 3.1 Hz)] and one $\eta^4\text{-}C_5Me_5$– [δ 11.1, 12.8, and 21.5; 91.0 (d, *J*Rh 7.6), 99.9 (d, *J*Rh 6.9), and 62.0 (d, *J*Rh 3.8 Hz)]. One benzyl group was σ-bonded to a rhodium [CH_2– carbon at δ 16.3 (d, *J*Rh 29.8 Hz), hydrogens at δ 1.58 (*J*Rh 4 Hz)] but the other was bonded to the $\eta^4\text{-}C_5Me_5$ ring.

The conclusions drawn from the n.m.r. spectra were fully confirmed by a single-crystal *X*-ray structure determination which showed (Figure) a dinuclear molecule with one rhodium [Rh(1)] η^5-bonded to a C_5Me_5 ring (mean Rh–C 2.241; distance to centroid, 1.898 Å) and σ-bonded to two bridging methylenes [Rh–CH_2 2.025(15) and 2.036(15) Å] and one terminal benzyl [Rh–CH_2Ph 2.105(20) Å]. The $Rh_2(\mu\text{-}CH_2)_2$ ring, although very asymmetric, is planar. The other rhodium [Rh(2)] is rather asymmetrically bound to an $\eta^4\text{-}C_5Me_5CH_2Ph$ ring [distances to C(21), 2.248(14), C(22), 2.165(15), C(23), 2.115(17), and C(24), 2.215(17); distance to centroid, 1.858 Å] and to the bridging methylenes [1.973(14) and 1.955(17) Å]. The rhodiums are also very close to each other, 2.559(3) Å, a clear indication of the presence of a metal–metal bond. In fact as Rh(1) is formally

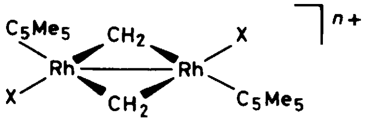
---

† 1-Benzyl-2-(1′—4′-η-5′-benzylpentamethylcyclopenta-1,3-diene)-di-μ-methylene-1-(η-pentamethylcyclopentadienyl)dirhodium(IV, II) (*Rh–Rh*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

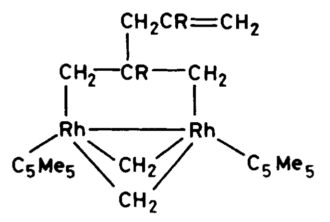


(1)



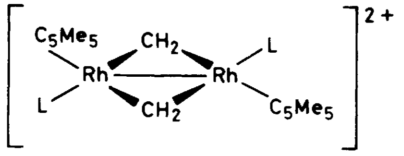
(2)

X = Br, I, N_3 (n = 0)
X = Me, Et, Pr^n, Bu^n (n = 0)
X = CO (n = 2)

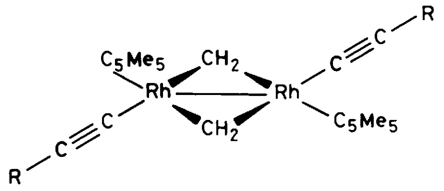


(3)

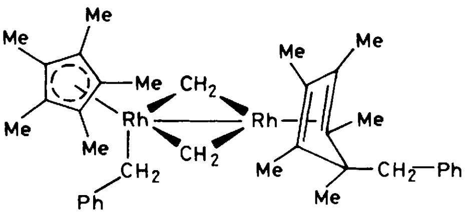
R = H,Me



(4a) L = MeCN
(4b) L = CO



(5a) R = Ph
(5b) R = Bu^t



(6)

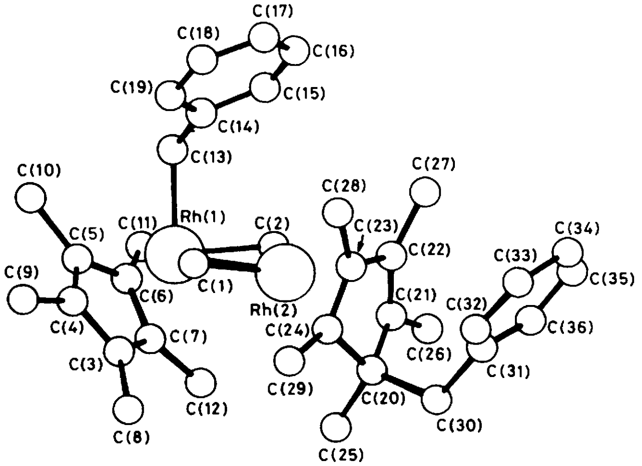
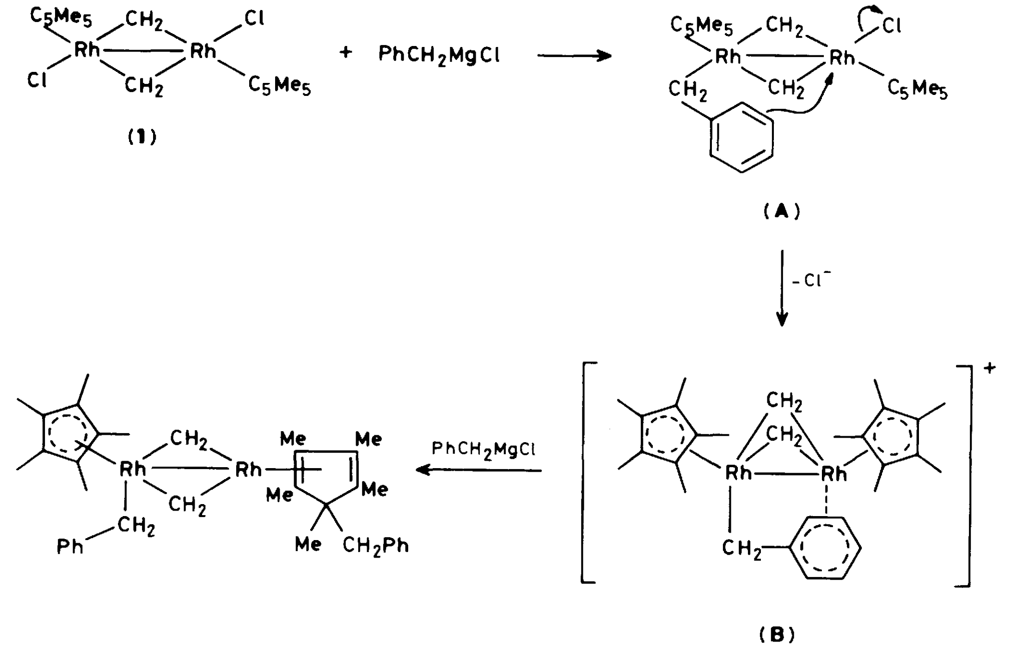


Figure. View of complex (**6**), hydrogen atoms omitted

in the +4 (d^5) and Rh(2) is formally in the +2 (d^7) oxidation state, a metal–metal bond is needed to pair up the odd electrons on each. These bond lengths may be compared to those in the related but more symmetrical complexes *cis*-$[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2Me_2]$ [Rh–Rh 2.620, Rh–CH_2 (bridging) av. 2.032, Rh–Me av. 2.118, and Rh–C_5 (ring) av. 2.277 Å][4] and *trans*-$[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(CO)_2]^{2+}$ [Rh–Rh 2.659, Rh–CH_2 2.060, Rh–C_5 (ring) mean 2.234 Å].[1] The similarities between the three structures are very marked indeed, despite the fact that the two previously determined ones have both rhodiums formally in the +4 oxidation state. This again shows that formal oxidation states are not good guides to structures, but should only be used for electron book-keeping, the purpose for which they were devised. The similarities between the three structures also extends to bond angles. For example, the angles Rh–CH_2–Rh in the four-membered rings are within 0.5° of 80° in all three compounds, while the angles CH_2–Rh–CH_2 are 97 and 102° in (**6**), 96° in the *cis*-dimethyl complex, and 100° in the dicarbonyl dication.

The *X*-ray determination also showed that the benzyl attached to the C_5Me_5 ring was *exo* to the metal. As a consequence of the η^4-bonding, the $C_5Me_5CH_2Ph$ ligand shows a dihedral angle [between the planes defined by C(21), C(22), C(23) and C(24), and C(21), C(20), and C(24)] of 29°, with the sp^3 carbon, C(20), pointing away from the rhodium as is normal. As might be anticipated from the fact that the stereochemistry about each metal is determined by steric factors, Rh(1) is more crowded than is Rh(2), since it has also to accommodate the σ-benzyl in its co-ordination sphere. This can be seen from the distances to the η^5- and to the η^4-C_5 bonded rings respectively [Rh(2) being closer to its ring than is Rh(1)], and also from the 'bend-back' of the methyls attached to the C_5Me_5 ring which is larger (av. 0.11 Å) than that of the methyls on the η^4-bonded atoms of the $C_5Me_5CH_2Ph$ ligand (av. 0.03 Å). The steric crowding at Rh(1) is also apparent from



Scheme 1.

the angles made by the two rings to the $Rh_2(\mu-CH_2)_2$ plane, 51° for C(3)—C(7) and 82° for C(21)—C(24).

The fact that the benzyl on the C_5 ring is *exo* to the metal indicates that it was probably formed by a direct nucleophilic attack at the ring, not at the metal. In contrast, the presence of the rhodium-bound benzyl shows that attack also occurs at the metal.* We rationalise this in terms of Scheme 1, where the first step is displacement of one chloride by benzyl to give a σ-benzyl-chloro intermediate (**A**) which then spontaneously ionises off the remaining chloride assisted by the benzyl, σ-bonded to one rhodium and becoming η^2-bonded to the other in a cationic intermediate (**B**). In the presence of more benzyl Grignard this then reacts by attacking the C_5Me_5 ring to give (**6**). Attack by nucleophiles on C_5Me_5 rings attached to rhodium is rather rare; however we may note that $[(C_5Me_5)Rh(C_5H_5)]Cl$ gives $[(C_5Me_5H)Rh(C_5H_5)]$ on reaction with BH_4^-, where the entering hydride is *exo* to the metal on the η^4-pentamethylcyclopentadiene ring.[6]

This reaction should also be compared and contrasted with that of allyl Grignards on the dichloro complex (**1**) where the product (**3**) still has the $(C_5Me_5)_2Rh_2(\mu-CH_2)_2$ unit intact and where the rhodiums are now *cis* bridged by a $-CH_2CR(CH_2CR=CH_2)CH_2-$ ligand arising from the coupling of two allyls.[3] Such a coupling would be much more difficult with two benzyls, which may explain why the reaction takes the course shown.

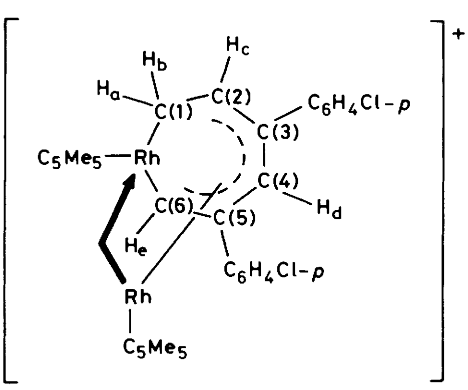
The Formation of Complex $[(C_5Me_5)_2Rh_2\{\mu-CH_2CHC(C_6H_4Cl-p)CHC(C_6H_4Cl-p)CH\}]PF_6$ (**7**).—By contrast to the formation of the bis(alkynyl) complexes (**5**) from (**1**) and the acetylenic Grignard, a quite different reaction occurred when monosubstituted acetylenes were reacted with the dicationic bis(acetonitrile) complex (**4a**) under conditions such that deprotonation could occur. The n.m.r. spectra of the products (usually obtained impure as red oils) showed that considerable changes had occurred in the molecules. Only the complex (**7**) from *p*-chlorophenylacetylene could be obtained as a homogeneous solid, but even that was not crystalline and characterisation was based on extensive n.m.r. investigations. The main features of the spectra from the products of reactions with other acetylenes suggested that they reacted similarly.

Although problems with the microanalyses resulted in larger than normal deviations from expected values, (**7**) was a single complex and the analytical data clearly showed it to be a dinuclear monocation and to contain two *p*-chlorophenyl acetylenes. The i.r. spectra showed no evidence for the presence of σ-acetylides. The ^1H and the $^{13}C-\{^1H\}$ n.m.r. spectra showed the presence of two different $\eta^5-C_5Me_5$ rings, two different *p*-chlorophenyls, and no resonances in the regions associated with μ-methylene bridges. The spectra were analysed and assigned using H–H decoupling (and the derived H–H coupling constants) and the J. Mod. technique[7] to determine the number of hydrogens on each carbon. This analysis indicated that the five remaining single hydrogens were attached to four different carbons. One of these carbons [C(1), δ 44.3, sp^3] was shown to have two different hydrogens and to be directly bound to a rhodium (d, J 15.6 Hz). The other three carbons [C(2), C(4), and C(6); δ 55.2, 76.8, and 154.3] had one hydrogen each and were at lower field indicating that they were unsaturated. The first two were also coupled to one rhodium (doublets, J 8.1 and 5.2 Hz), but the one at lowest field [C(6)] appeared as a double-doublet (δ 154.3, J 16.3 and 36 Hz) in the ^1H-decoupled spectrum, indicating that it was strongly bound to both metals. In addition, there were two further carbons present [C(3) and C(5) at δ 107.8 and 81.7] that did not bear hydrogens and which were also bonded to rhodium (J 4.6 and 7.8 Hz), which we assign to carbons bearing the two different *p*-chlorophenyls. The relationships of the CH's can be deduced from their H–H couplings; thus for example, both of the hydrogens on C(1) (H_a and H_b) are coupled (11 and 8 Hz) to one further hydrogen (H_c) which must therefore be on an adjacent carbon, C(2). However, H_c is only weakly coupled to H_d (1.5 Hz) which implies that a carbon bearing no hydrogens separates C(2) and C(4); a similar argument applies to the relation between H_d and H_e.

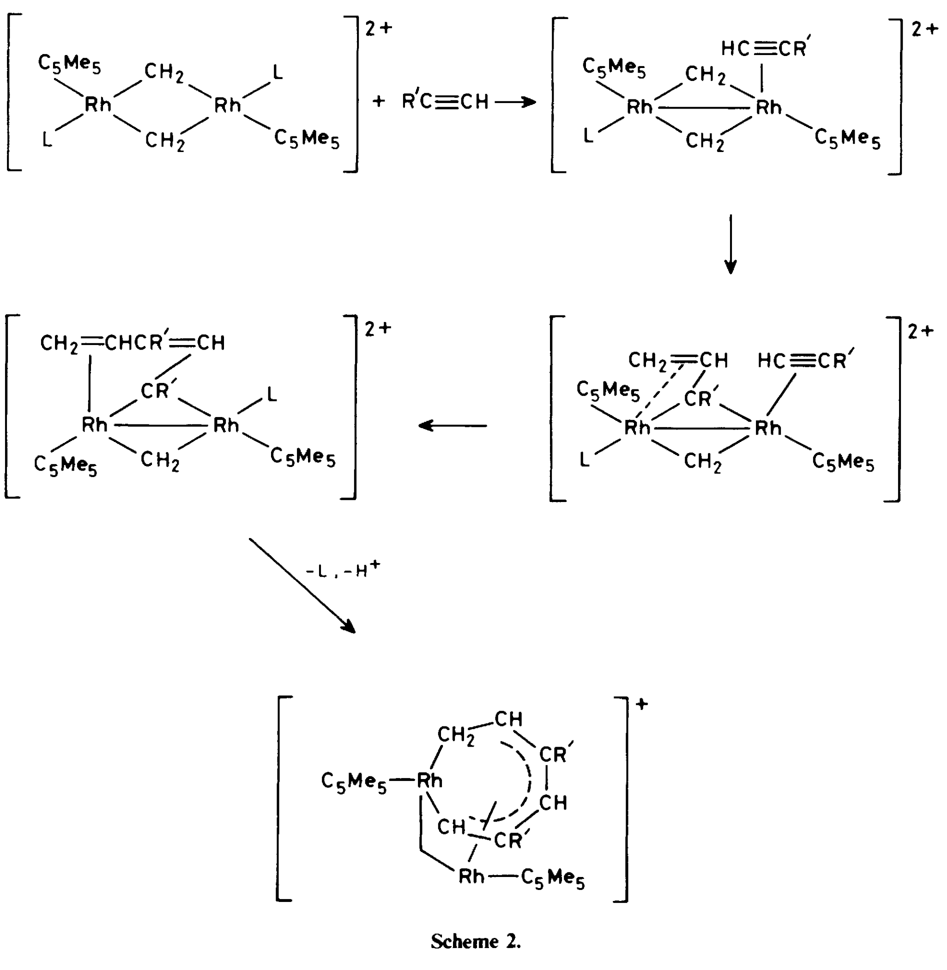
We propose the structure shown for (**7**) on the basis of the

---

* An alternative would be the initial formation of a dibenzyl complex (**2**; X = CH_2Ph) which then rearranges to (**6**) *via* an ionic, bimolecular reaction. We have no evidence for this.



(7)



Scheme 2.

n.m.r. spectra. It formally arises from the insertion of two acetylenes (head to tail) into a Rh–CH_2 bond, followed by loss of a proton and coupling with the other CH_2. There has been considerable interest in the reactions of acetylenes with bridging methylenes in dinuclear complexes [8,9] and the route proposed in Scheme 2 derives in part from those studies.

Experimental

All reactions were carried out under dry nitrogen using carefully dried and purified solvents. N.m.r. spectra were recorded on Bruker AM-250 and WH-400 spectrometers; microanalytical data were obtained by the University of Sheffield Microanalytical Service.

trans-$[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(C_2R)_2]$ [R = Ph (**5a**) *or* Bu^t (**5b**)].—A solution of phenylethynylmagnesium chloride in diethyl ether–tetrahydrofuran (1 : 1 v/v, 4 cm^3, 2.00 mmol; made from isopropylmagnesium chloride in diethyl ether and freshly distilled phenylacetylene in tetrahydrofuran) was added dropwise to a stirred solution of complex (**1**) (200 mg, 0.35 mmol) in toluene (20 cm^3). The colour changed from deep red to light orange; the solution was stirred (15 min at 20 °C) and aqueous acetone (2 cm^3, 1 : 1 v/v) then added. Conventional work-up [see below for (**6**)] gave complex (**5a**) (165 mg, 67%) as bright orange crystals. A similar reaction but using complex (**1**) in pentane gave complex (**5b**) (145 mg, 47%) [Found for (**5a**): C, 66.1; H, 6.4. $C_{38}H_{44}Rh_2$ requires C, 64.6; H, 6.2%. Found for (**5b**): C, 62.9; H, 8.1. $C_{34}H_{52}Rh_2$ requires C, 61.3; H, 7.9%]. I.r. ν(C≡C): 2 205w (**5a**) and 2 105s (**5b**) cm^{-1}. ^1H N.m.r. in $CDCl_3$: (**5a**), δ 1.85 (s, C_5Me_5), 7.1 (m, phenyl), 9.16 [t, J_{Rh} 1 Hz, $Rh_2(\mu\text{-}CH_2)_2$]; (**5b**), δ 0.96 (s, Bu^t), 1.62 (s, C_5Me_5), 8.87 [t, J_{Rh} 0.6 Hz, $Rh_2(\mu\text{-}CH_2)_2$]. ^{13}C N.m.r. in $CDCl_3$: (**5a**), δ 10.1 ($C_5\mathit{Me}_5$), 103.1 (t, J_{Rh} 2, C_5Me_5), 164.4 [t, J_{Rh} 24, $Rh_2(CH_2)_2$], 107.4 (dd, J_{Rh} 68.7, 2.3, Rh–C≡), 99.6 (t, J_{Rh} 6.8, ≡*C*Ph), 124.2, 127.2, 128.2, 129.0 (4 × s, phenyl); (**5b**), δ 10.1 and 102.3 (C_5Me_5), 164.4 [t, J_{Rh} 24.6, $Rh_2(CH_2)_2$], 84.6 (dd, J_{Rh} 69.1, 2.8, Rh–C≡), 106.0 (t, J_{Rh} 6.5, ≡*C*–Bu^t), 28.7 and 33.1 (2 × s, Bu^t).

$[(\eta^5\text{-}C_5Me_5)Rh(CH_2Ph)(\mu\text{-}CH_2)_2Rh(\eta^4\text{-}C_5Me_5CH_2Ph)]$ (**6**).—A solution of benzylmagnesium chloride (4 mmol) in diethyl ether (16 cm^3) was added to a solution of $[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2Cl_2]$ (**1**) (200 mg, 0.35 mmol) in toluene (40 cm^3) over 5 min (20 °C). The colour lightened from red to yellow; the solution was stirred a further 5 min and then aqueous acetone (1:1, 3 cm^3) was added. The resultant white precipitate was filtered off, the solvents removed from the filtrate, and the residue extracted into pentane (3 × 15 cm^3); after filtration and removal of the pentane, crystallisation of the residue from cold methanol (3 cm^3) gave light yellow needles of complex (**6**) (0.11 g, 46%). A sample was recrystallised by slow diffusion of acetonitrile into a concentrated solution of (**6**) in toluene; one of the crystals so formed was chosen for the *X*-ray analysis [Found: C, 62.3; H, 7.3. $C_{36}H_{48}Rh_2$ requires C, 63.0; H, 7.0%]. ^{1}H N.m.r. ($CDCl_3$): δ 0.91 (s, 6 H, 2 × Me), 1.12 (s, 3 H, Me), 1.27 (s, 6 H, 2 × Me), 1.58 [d, 2 H, *J*Rh 4 Hz, $RhCH_2Ph$], 1.65 (s, 15 H, C_5Me_5), 2.28 (s, 2 H, $C_5Me_5CH_2Ph$), 6.6—7.1 (m, 10 H, Ph), 6.84 (s, 2 H, $RhCH_2Rh$, axial), and 7.6 [d, 2 H, *J*Rh 2 Hz, $RhCH_2Rh$, equatorial]. ^{13}C N.m.r. ($CDCl_3$): δ 9.4 (s, C_5Me_5), 11.1 and 12.8 (s, C_5Me_4–), 16.3 (d, $RhCH_2Ph$, *J*Rh 29.8 Hz), 21.5 (s, C_5–*Me*), 42.3 (s, C_5–CH_2Ph), 62.0 [d, *C*$MeCH_2Ph$, *J*Rh 3.8], 91.0 and 99.9 [2 × d, *J*Rh 7.6 and 6.9, C_4Me_4], 98.7 (d, *J*Rh 3.1, C_5Me_5), 121.2, 125.6, 126.8, 127.2, 128.3, 129.6, 139.5, and 152.7 (all s, aromatic carbons, *p*-, *p*-, *m*-, *m*-, *o*-, *o*-, *i*-, and *i*-respectively), and 164.0 [dd, *J*Rh 32.0 and 43.3, $Rh_2(\mu\text{-}CH_2)_2$].

Table 1. Selected bond lengths (Å) and angles (°) for (**6**) with (e.s.d.s in parentheses)

Rh(1)–Rh(2)	2.559(3)	Rh(1)–C(3)	2.262(19)
Rh(1)–C(1)	2.025(15)	Rh(1)–C(4)	2.241(17)
Rh(1)–C(2)	2.036(15)	Rh(1)–C(5)	2.193(16)
Rh(2)–C(1)	1.973(14)	Rh(1)–C(6)	2.241(16)
Rh(2)–C(2)	1.955(17)	Rh(1)–C(7)	2.266(15)
Rh(1)–C(13)	2.105(20)	mean	2.241
C(13)–C(14)	1.42(3)	Rh(2)–C(21)	2.248(14)
C(20)–C(30)	1.57(2)	Rh(2)–C(22)	2.165(15)
C(30)–C(31)	1.52(3)	Rh(2)–C(23)	2.115(17)
		Rh(2)–C(24)	2.215(17)
C(1)–Rh(1)–C(2)	97.0(6)	C(21)–C(20)–C(24)	98(1)
C(1)–Rh(2)–C(2)	101.5(6)	C(21)–C(20)–C(25)	114(1)
Rh(1)–C(1)–Rh(2)	79.6(6)	C(25)–C(20)–C(30)	107(1)
Rh(1)–C(2)–Rh(2)	79.7(6)	C(24)–C(20)–C(30)	113(1)
Rh(1)–C(13)–C(14)	122(1)	C(20)–C(30)–C(31)	115(1)

Crystal Structure Determination of (**6**).—*Crystal data.* $C_{36}H_{48}Rh_2$, *M* 687, triclinic, *a* = 10.719(7), *b* = 10.789(14), *c* = 14.484(16) Å, α = 103.74(9), β = 97.67(7), γ = 90.28(8)°, *U* = 1 611.4 Å^3, *Z* = 2, D_c = 1.42 g cm^{-3}, *F*(000) = 707.93, space group $P\bar{1}$ (indicated by statistics and used successfully in refinement), Mo-K_α radiation (graphite monochromator), λ = 0.710 69 Å, μ = 10.29 cm^{-1}.

Unit-cell parameters were obtained from a least-squares fit of the setting angles of 25 well centred reflections. *X*-Ray reflection data in the range 3.5 $\leqslant 2\theta \leqslant$ 45° were collected on a Nicolet *R3M* four-circle automatic diffractometer from a lath-shaped crystal measuring approximately 0.07 × 0.16 × 0.5 mm. 1979 Independent reflections with $I \geqslant 3.5\sigma(I)$ were obtained and corrected for Lorentz and polarisation effects. An empirical absorption correction based on ψ-scans of 6 reflections was also applied. The maximum and minimum transmission factors obtained were 0.842 and 0.744.

The structure was solved by Patterson and difference-Fourier methods and refined by cascade blocked-diagonal matrix least squares with weights $w_i = 1/[\sigma^2(F_i) + 0.0006\,F_i^2]$ to a final *R* value of 0.0649 (*R*′ = 0.0551). All the non-hydrogen atoms were refined with independent positional and anisotropic thermal vibration parameters. Sufficient hydrogen atoms were located from a low-angle difference Fourier synthesis to define approximate torsion angles for all the methyl groups. All hydrogen atoms were constrained to ride on the adjacent heavy atom with calculated bond lengths and angles; the hydrogen (isotropic) vibration parameters were fixed at 1.2 times the U_{eq} values for their respective neighbours.

The parameter shifts obtained on the final cycle of refinement were, in all cases, less than 0.2 of the corresponding e.s.d.s. A final difference Fourier synthesis showed no peak higher than 0.8 e Å^{-3} and none which could be interpreted as an atom. The final analysis of variance against sinθ and against $|F|$ showed no unusual features; neither did the normal probability plot. The SHELXTL suite of crystallographic programs (G. M. Sheldrick) was used throughout.

Selected bond lengths are given in Table 1 and atomic co-ordinates in Table 2.

$[(C_5Me_5)\overline{Rh\{\eta^5\text{-}CH_2CHC(C_6H_4Cl\text{-}p)CHC(C_6H_4Cl\text{-}p)C}H\}\text{-}Rh(C_5Me_5)]PF_6$ (**7**).—A solution of *p*-chlorophenylacetylene

Table 2. Atom co-ordinates (× 10^4) for complex (**6**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	2 202(1)	1 701(1)	2 731(1)	C(18)	6 678(23)	3 570(25)	4 250(20)
Rh(2)	3 753(1)	−90(1)	2 379(1)	C(19)	5 394(18)	3 600(16)	4 025(12)
C(1)	3 444(14)	980(13)	3 630(11)	C(20)	3 876(16)	−2 664(14)	2 011(11)
C(2)	2 846(14)	813(15)	1 490(11)	C(21)	4 112(15)	−1 890(15)	1 310(10)
C(3)	442(16)	971(15)	3 166(13)	C(22)	5 191(14)	−1 145(13)	1 644(10)
C(4)	764(15)	2 192(16)	3 737(12)	C(23)	5 409(15)	−1 073(15)	2 663(12)
C(5)	668(15)	2 975(15)	3 117(12)	C(24)	4 492(18)	−1 741(15)	2 914(11)
C(6)	324(15)	2 314(16)	2 150(11)	C(25)	2 509(17)	−2 965(15)	2 010(12)
C(7)	165(14)	1 033(15)	2 225(12)	C(26)	3 525(16)	−2 240(15)	278(10)
C(8)	372(16)	−174(17)	3 563(16)	C(27)	6 006(16)	−523(15)	1 121(11)
C(9)	1 008(19)	2 568(20)	4 829(13)	C(28)	6 538(14)	−351(14)	3 332(12)
C(10)	799(18)	4 447(16)	3 426(15)	C(29)	4 419(19)	−1 975(16)	3 868(13)
C(11)	49(16)	2 871(19)	1 298(13)	C(30)	4 547(15)	−3 974(14)	1 784(12)
C(12)	−314(18)	−43(20)	1 375(14)	C(31)	5 941(19)	−3 866(14)	1 717(12)
C(13)	3 422(20)	3 253(16)	2 771(16)	C(32)	6 852(18)	−3 783(16)	2 448(12)
C(14)	4 737(23)	3 238(16)	3 076(16)	C(33)	8 097(17)	−3 687(16)	2 347(16)
C(15)	5 549(22)	2 913(16)	2 398(16)	C(34)	8 447(22)	−3 649(17)	1 454(18)
C(16)	6 769(20)	2 924(17)	2 626(15)	C(35)	7 507(25)	−3 728(18)	735(17)
C(17)	7 385(21)	3 227(22)	3 551(20)	C(36)	6 254(20)	−3 868(16)	851(15)

(70 mg, 0.53 mmol) in acetone (2 cm^3) was added to a solution of $[(C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(MeCN)_2][PF_6]_2$ (**4a**) (200 mg, 0.23 mmol) in acetone (2 cm^3). The mixture darkened and then formed a deep red solution (after 2 min), from which, after removal of solvent, a red oil was obtained. This was precipitated from acetone solution by addition of diethyl ether to give complex (**7**) as a bright red solid (0.19 g, 78%) [Found: C, 48.3, H, 4.6, Cl, 9.0. $C_{38}H_{43}Cl_2F_6PRh_2$ requires C, 49.5, H, 4.7, Cl, 7.7%]. I.r.: 835s cm^{-1} (PF_6). ^1H N.m.r. $[(CD_3)_2CO]$: δ 0.46 (dd, H_a, JRh 1.5, JH_c 11 Hz), 1.38 (s, C_5Me_5), 1.88 (dd, H_b, JRh 2.5, JH_c 8 Hz), 2.00 (s, C_5Me_5), 3.73 (m, H_c, JRh 1.5, JH_a 11, JH_b 8, JH_d 1.5 Hz), 5.41 (m, H_d), 7.42 (m, aromatic), 8.45 (dd, H_e, JRh 1.5, JH_d 3.5 Hz). $^{13}C\text{-}\{^1H\}$ N.m.r. $[CD_2Cl_2]$: δ 9.7, 10.5 (2 × C_5*Me*$_5$), 101.5 (d), 102.3 (d, 2 × *C*$_5$Me$_5$, JRh 6.3, 4.7 Hz), 44.3 [d, JRh 15.6, C(1)], 55.2 [d, JRh 8.1, C(2)], 107.8 [d, JRh 4.6, C(3)], 76.8 [d, JRh 5.2, C(4)], 81.7 [d, JRh 7.8, C(5)], 154.3 [dd, JRh 16.3 and 36 Hz, C(6)], 127.6, 128.5, 129.7, 129.8 (all s, aromatic >CH), 132.3, 133.3, 135.9, 138.6 (all s, aromatic >C–).

Acknowledgements

We thank the S.E.R.C. for support of this work, Johnson Matthey for the loan of rhodium chloride, Drs. B. E. Mann, B. F. Taylor, and C. M. Spencer for n.m.r. spectra, and Mr. H. Adams for assistance with the crystal structure determination.

References

1 K. Isobe, S. Okeya, N. J. Meanwell, A. J. Smith, H. Adams, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 1215; see also, N. J. Meanwell, A. J. Smith, H. Adams, and P. M. Maitlis, *Organometallics*, 1983, **2**, 1705.

2 S. Okeya, N. J. Meanwell, B. F. Taylor, K. Isobe, A. Vázquez de Miguel, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 1453.

3 B. E. Mann, N. J. Meanwell, C. M. Spencer, B. F. Taylor, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1985, 1555.

4 K. Isobe, A. Vázquez de Miguel, P. M. Bailey, S. Okeya, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1983, 1441.

5 B. E. Mann and B. F. Taylor, '^{13}C N.m.r. Data for Organometallic Compounds,' Academic Press, London, 1981, p. 103.

6 K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc. A*, 1970, 2875; see also, G. E. Herberich, C. Engelke, and W. Pahlman, *Chem. Ber.*, 1979, **112**, 607.

7 R. Benn and H. Gunther, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 355.

8 S. A. R. Knox, *Pure Appl. Chem.*, 1984, **56**, 81; see also, A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Chem. Commun.*, 1980, 803; P. Q. Adams, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, and P. Woodward, *ibid.*, 1983, 222; D. L. Davies, S. A. R. Knox, K. A. Mead, M. J. Morris, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 2293.

9 J. Levisalles, F. Rose-Munch, H. Rudler, J-C. Daran, Y. Dromzee, and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, 1981, 153; J. Levisalles, F. Rose-Munch, H. Rudler, J-C. Daran, Y. Dromzee, Y. Jeannin, D. Ades, and M. Fontanille, *ibid.*, 1981, 1055.

Received 16*th August* 1985; *Paper* 5/1428