Reactions of Co-ordinated Ligands. Part 35.[1] Evidence for Carbon–Carbon Double-bond Cleavage of Cyclopropenes in their Reaction with Dinuclear Cobalt, Rhodium, and Iridium Complexes; Crystal Structure† and Protolysis of [Rh$_2$(μ-CO)(μ-COCHCMe$_2$CH)(μ-C$_5$Me$_5$)$_2$]

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Reaction of 3,3-dimethylcyclopropene with [M^{1}M^2(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] (M^1 = M^2 = Rh or Co; M^1 = Rh, M^2 = Co; M^1 = Ir, M^2 = Co; M^1 = Rh, M^2 = Ir) affords 1 : 1 adducts, in which the carbon–carbon double bond has been broken. An *X*-ray crystallographic study on the dirhodium complex showed that the molecule consists of two Rh(η-C$_5$Me$_5$) fragments bridged by a carbonyl ligand and a complex ligand derived from CO and the cyclopropene. This ligand binds to the Rh$_2$ fragment *via* a μ-carbene functionality and a μ-ketene. The corresponding reaction of 1,3,3-trimethylcyclopropene with [CoRh(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] and [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] afforded one and two isomeric complexes respectively with related structures, thus providing insight into the reaction mechanism. Additional insight was provided by the observation that 3,3-dimethylcyclopropene reacts with [Co$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$], [CoRh(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$], [CoIr(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$], and [RhIr(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] to afford high yields of single isomeric adducts where 'carbonyl insertion' occurs into a carbon to cobalt or iridium bond. The mechanism of formation is discussed in terms of the interaction of cyclopropene with the two metal centres. The protolysis of the dirhodium species is also examined and leads to regioselective cleavage of the longest Rh–C σ bond *via* an S_E2 reaction pathway.

The reaction of mononuclear transition-metal species with cyclopropenium cations[2] and cyclopropenones[3,4] can lead to carbon–carbon bond cleavage and formation of metallacyclobutadienes and metallacyclobutenones. This type of reaction is thought to involve oxidative insertion into a carbon–carbon bond following prior co-ordination of the organic ligand.[5] There are also reactions of these small-ring molecules which lead to the formation of dinuclear nickel, palladium, or platinum complexes where a C$_3$R$_3$ or C$_2$R$_2$CO fragment formed by ring opening straddles perpendicularly the metal–metal vector.[6–9] However, it has not been established whether initial reaction of the three-membered ring occurs at a di- or mono-nuclear centre. With the intention of obtaining further understanding of these reactions we have treated cyclopropenes with the unsaturated dinuclear complexes [M^{1}M^2(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] (M^1 = M^2 = Rh;[10–12] M^1 = M^2 = Co;[13] M^1 = Rh, M^2 = Co;[14] M^1 = Ir, M^2 = Co;[15] M^1 = Rh, M^2 = Ir[16]). Such dinuclear species are known to react with diazoalkanes,[11,17–19] low-valent metal fragments,[11,17,20] and SO$_2$.[21] It has also been reported, following our preliminary communication,[22] that the Rh$_2$ species reacts with acetylene,[23] which is of special interest in view of a possible relationship[5] between cyclopropenes and alkynes in their reactions at dinuclear centres.

Results and Discussion

Addition of an excess of 3,3-dimethylcyclopropene to a hexane solution of [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] resulted in a change in colour from intense blue to orange. Partial removal of the solvent and cooling afforded a high yield of a red crystalline complex (**1**) (see Scheme 1), which was identified as a 1 : 1 adduct by elemental analysis. Examination of the i.r. spectrum revealed two absorptions at 1 809 and 1 683 cm^{-1} attributable, respectively, to a bridging carbonyl and an 'inserted' ketone carbonyl. The ^{1}H n.m.r. spectrum displayed, in addition to resonances due to two methyl and two pentamethylcyclopentadienyl groups, a one-proton multiplet at 9.46 p.p.m. [^2J(RhH) 2, ^4J(HH) 2.8 Hz], in a region diagnostic of a bridging alkylidene species. The other methine proton, which had its origin in the 3,3-dimethylcyclopropene, resonated at 2.55 p.p.m. [^2J(RhH) 2.5, ^4J(HH) 2.8 Hz]. The ^{13}C-{^{1}H} and proton-coupled ^{13}C spectra showed the presence of a μ-CO carbon resonance at 230.2 p.p.m. [^1J(RhC) 42.3 Hz] with a coupling constant characteristic of a carbonyl ligand bridging a Rh$_2$ fragment. The bridging alkylidene carbon resonated at 178.5 p.p.m. [^1J(RhC) 31.7 and 19.5; ^1J(CH) 149 Hz], again in a region characteristic of μ-alkylidenes. Although these observations showed that complex (**1**) is a 1 : 1 adduct, and that a carbonyl 'insertion' had occurred, the structure was not defined unequivocally, and therefore a single-crystal *X*-ray diffraction study was undertaken.

The molecular geometry of complex (**1**) in the solid state is illustrated in Figure 1; selected bond lengths and interbond angles are given in Table 1. The crystal structure consists of isolated molecules of (**1**) with no unusually short intermolecular contacts. The molecule consists of two Rh(η-C$_5$Me$_5$) units bridged by a carbonyl ligand and a complex ligand derived from CO and the cyclopropene. This ligand binds to the Rh$_2$ fragment *via* a μ-carbene functionality [C(7)] and a μ-ketene (or acyl and alkyl) group [C(2), C(3)]. The carbon atoms linked by a double bond in 3,3-dimethylcyclopropene are no longer directly bonded [C(3)$\cdots$C(7) 2.217(12) Å]. The ligand is, therefore, the product of at least formal insertion of CO into a Rh–C bond formed on cleavage of the C=C double bond in 3,3-dimethylcyclopropene. The Rh$_2$ fragment therefore forms part of a complex tricyclic dirhodiahexanone. The ring strains within the four-membered rings of this system are evident in the C–C–C and Rh–C–C angles, which are markedly lower than their idealised values [C(2)–C(3)–C(4) 104.8(7), C(3)–C(4)–C(7)

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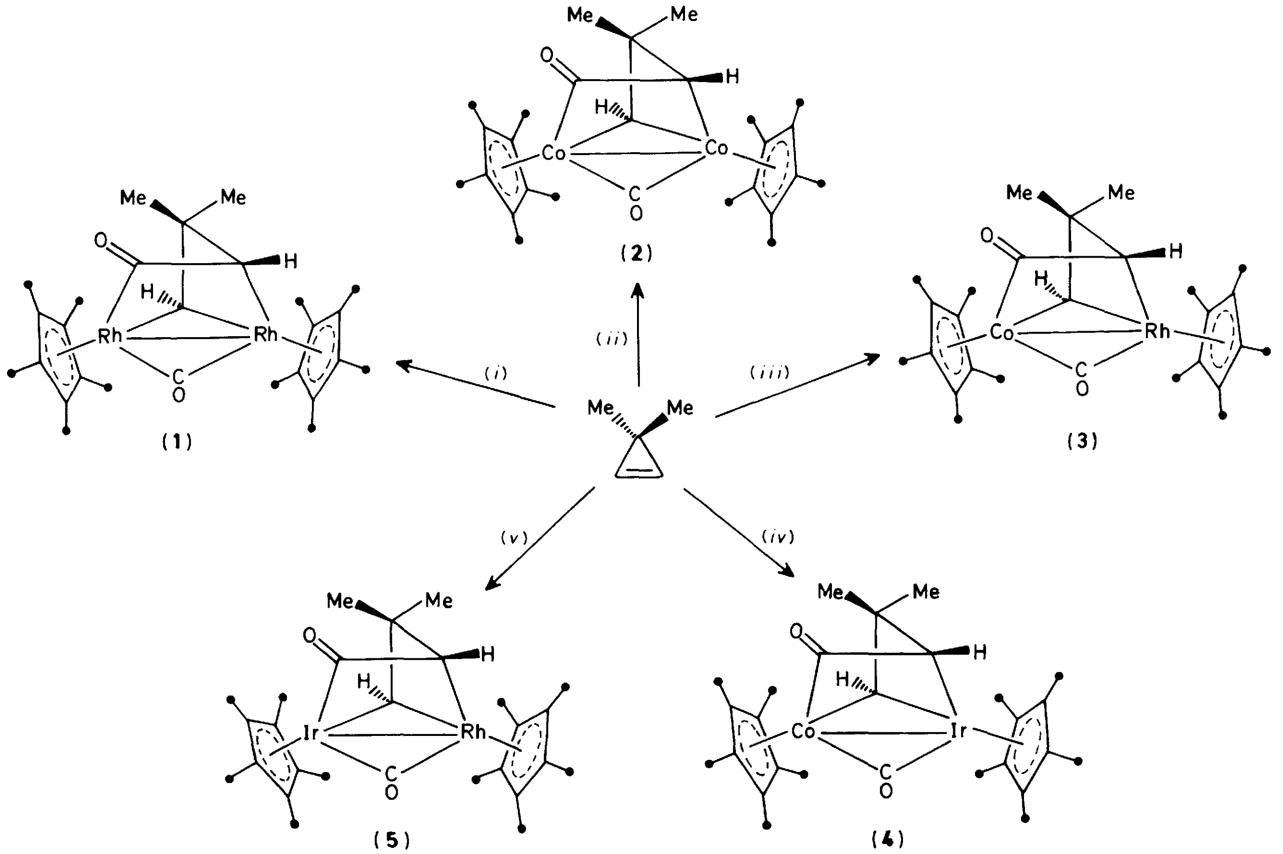
† μ-Carbonyl-μ-[3,3-dimethyl-1-oxobutane-1,2-diyl-4-ylidene-$C^{1,4}$(Rh^1)$C^{2,4}$(Rh^2)]-bis[(η-pentamethylcyclopentadienyl)rhodium] (*Rh–Rh*).

Supplementary data available (No. SUP 56339, 8 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



Scheme 1. (*i*), + $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$; (*ii*), + $[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$; (*iii*), + $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$; (*iv*), + $[CoIr(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$; (*v*), + $[RhIr(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$

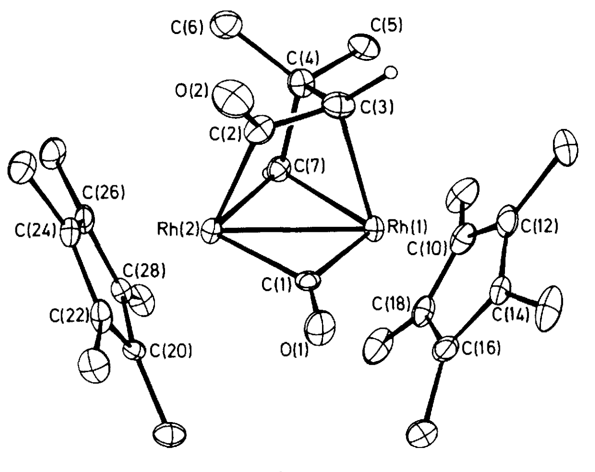


Figure 1. Molecular geometry of complex (**1**) showing the labelling scheme adopted. Methyl-group hydrogen atoms have been omitted for clarity. Non-hydrogen vibrational ellipsoids are drawn to enclose 30% probability density, hydrogen atoms as spheres of arbitrary radius

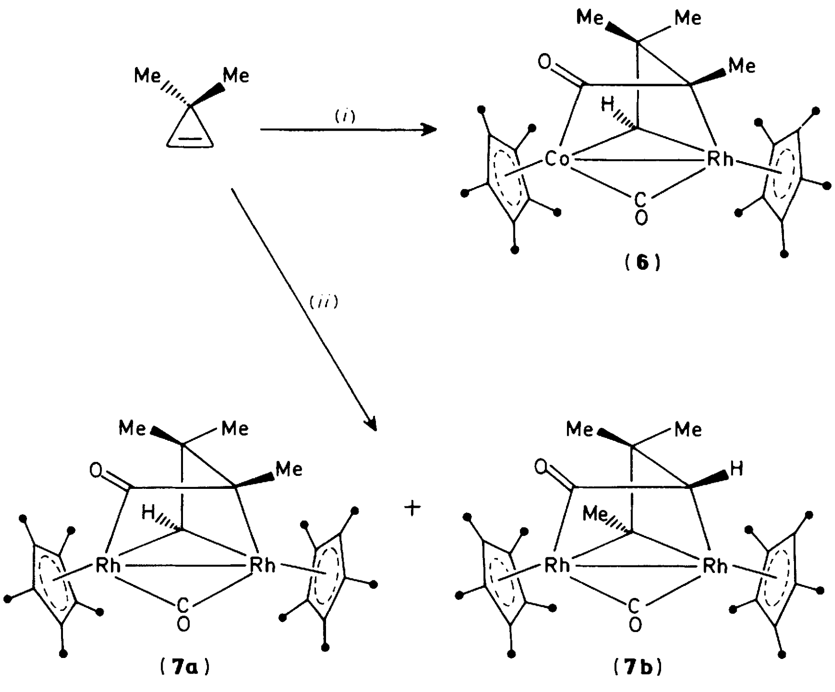
92.1(6), Rh(2)–C(2)–C(3) 104.2(5), Rh(1)–C(3)–C(2) 98.3(5), Rh(1)–C(3)–C(4) 92.3(5), and Rh(1)–C(7)–C(4) 99.2(5)°]. Assuming the complex ligand to act as a (neutral) four-electron donor the total valence-electron count at the Rh_2 centre is 34, giving a formal Rh–Rh bond order of unity. The Rh(1)–Rh(2) length [2.624(2)Å] is close to those in related Rh_2 species with bridging ligands (*e.g.* Rh–Rh 2.665(1) Å in $[Rh_2(CO)_2(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$,[24] 2.612(3) Å in $[Rh_2(\mu\text{-}CO)_2(\mu\text{-}C_5Br_4)(\eta\text{-}C_5Me_5)_2]$, and 2.663(1) Å in $[Rh_2(CO)_2\{\mu\text{-}C(CO_2Me)_2\}(\eta\text{-}C_5Me_5)_2]$[23]). The Rh(1)–Rh(2)–C(2)–C(3) unit can be viewed as a dirhodiacyclobutanone moiety and shows non-planarity [dihedral angle Rh(2)–C(2)–C(3)–Rh(1) 34.6(5)°] as do other recently characterised dimetallacyclobutane derivatives[25] (*e.g.* dihedral twist along the Os–Os bond in $[Os_2(\mu\text{-}CH_2CHCO_2Me)(CO)_8]$ is 21°).[25] The Rh(1)C(3)C(4)C(7) rhodiacyclobutane ring is also puckered [dihedral angle Rh(1)–C(3)–C(4)–C(7) 29.5(5)°]. The Rh(2)–C(2) acyl bond at 2.065(8) and Rh(1)–C(3) bond at 2.191(9) Å are somewhat longer (by *ca.* 0.06 and 0.10 Å respectively) than corresponding unstrained bonds (*e.g.* Rh–Me in *trans*-{difluoro[3,3′-trimethylenedinitrilobis(2-pentanone oximato)]borato}iodo(methyl)rhodium,[26] 2.090(4) Å, mean Rh–C(O)Me in $[\{Rh_2[C(O)Me](PMe_2Ph)_2\}_2(\mu\text{-}Cl)_3][PF_6]$[27] 2.003(5) Å). The μ-carbene function [C(7)] has equal Rh–C distances [Rh(1)–C(7) 2.059(7) and Rh(2)–C(7) 2.050(8) Å] despite some asymmetry in Rh–C(7)–C(4) angles [99.2(5) and 113.8(5)°]. These bond lengths are marginally longer than for the simple μ-methylene complex $[Rh_2(CO)_2(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$[24] [mean Rh–C 2.037(4) Å]. Other molecular parameters are unremarkable.

In order to gain additional insight into the mechanism of this reaction, 3,3-dimethylcyclopropene was also treated with $[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$, $[CoRh(\mu\text{-}C_5Me_5)_2]$, $[CoIr(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$, and $[RhIr(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ affording high yields of the red crystalline complexes (**2**), (**3**), (**4**), and (**5**) respectively (Scheme 1). Elemental analysis, i.r. and n.m.r. spectroscopy showed these compounds to be structural analogues of (**1**). Examination of the crude reaction mixture obtained from the heterodinuclear systems showed signals corresponding to only one isolated isomer. The complexes

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

Rh(1)–Rh(2)	2.624(2)	Rh(1)–C(1)	1.988(8)	C(4)–C(7)	1.513(11)	C(7)–H(7)	0.890(77)
Rh(1)–C(3)	2.191(9)	Rh(1)–C(7)	2.059(7)	C(10)–C(11)	1.510(11)	C(10)–C(12)	1.419(11)
Rh(1)–C(10)	2.286(9)	Rh(1)–C(12)	2.231(9)	C(10)–C(18)	1.425(13)	C(12)–C(13)	1.529(14)
Rh(1)–C(14)	2.253(8)	Rh(1)–C(16)	2.303(8)	C(12)–C(14)	1.415(11)	C(14)–C(15)	1.524(11)
Rh(1)–C(18)	2.292(9)	Rh(2)–C(1)	2.010(7)	C(14)–C(16)	1.442(11)	C(15)–C(17)	1.474(12)
Rh(2)–C(2)	2.065(8)	Rh(2)–C(7)	2.050(8)	C(16)–C(18)	1.444(10)	C(16)–C(19)	1.484(13)
Rh(2)–C(20)	2.312(7)	Rh(2)–C(22)	2.283(8)	C(20)–C(21)	1.505(11)	C(20)–C(22)	1.447(10)
Rh(2)–C(24)	2.231(8)	Rh(2)–C(26)	2.231(8)	C(20)–C(28)	1.425(9)	C(22)–C(23)	1.512(9)
Rh(2)–C(28)	2.303(7)	O(1)–C(1)	1.189(8)	C(22)–C(24)	1.425(11)	C(24)–C(25)	1.496(12)
O(2)–C(2)	1.215(10)	C(2)–C(3)	1.485(12)	C(24)–C(26)	1.452(10)	C(26)–C(27)	1.488(11)
C(3)–C(4)	1.566(10)	C(3)–H(3)	1.080(75)	C(26)–C(28)	1.466(12)	C(28)–C(29)	1.510(10)
C(4)–C(5)	1.535(12)	C(4)–C(6)	1.552(13)				
Rh(2)–Rh(1)–C(1)	49.4(2)	Rh(2)–Rh(1)–C(3)	71.1(2)	Rh(1)–C(3)–C(2)	98.3(5)	Rh(1)–C(3)–C(4)	92.3(5)
C(1)–Rh(1)–C(3)	86.3(3)	Rh(2)–Rh(1)–C(7)	50.2(2)	C(2)–C(3)–C(4)	104.8(7)	Rh(1)–C(3)–H(3)	113.6(46)
C(1)–Rh(1)–C(7)	99.1(3)	C(3)–Rh(2)–C(7)	62.8(3)	C(2)–C(3)–H(3)	112.8(45)	C(4)–C(3)–H(3)	129.2(41)
Rh(1)–Rh(2)–C(1)	48.6(2)	Rh(1)–Rh(2)–C(2)	72.8(2)	C(3)–C(4)–C(5)	112.5(7)	C(3)–C(4)–C(6)	116.1(7)
C(1)–Rh(2)–C(2)	72.6(3)	Rh(1)–Rh(2)–C(7)	50.5(2)	C(3)–C(4)–C(7)	92.1(6)	C(4)–C(4)–C(7)	115.7(7)
C(1)–Rh(2)–C(7)	98.8(3)	C(2)–Rh(2)–C(7)	79.0(3)	C(6)–C(4)–C(7)	114.3(7)	Rh(1)–C(7)–Rh(2)	79.4(2)
Rh(1)–C(1)–Rh(2)	82.0(3)	Rh(1)–C(1)–O(1)	139.6(6)	Rh(1)–C(7)–C(4)	99.2(5)	Rh(2)–C(7)–C(4)	113.8(5)
Rh(2)–C(1)–O(1)	138.3(6)	Rh(2)–C(2)–O(2)	127.5(6)	Rh(1)–C(7)–H(7)	128.3(53)	Rh(2)–C(7)–H(7)	120.4(53)
Rh(2)–C(2)–C(3)	104.2(5)	O(2)–C(2)–C(3)	128.1(8)	C(4)–C(7)–H(7)	111.5(50)		

* Estimated standard deviations in the least significant digit are given in parentheses here and throughout this paper.

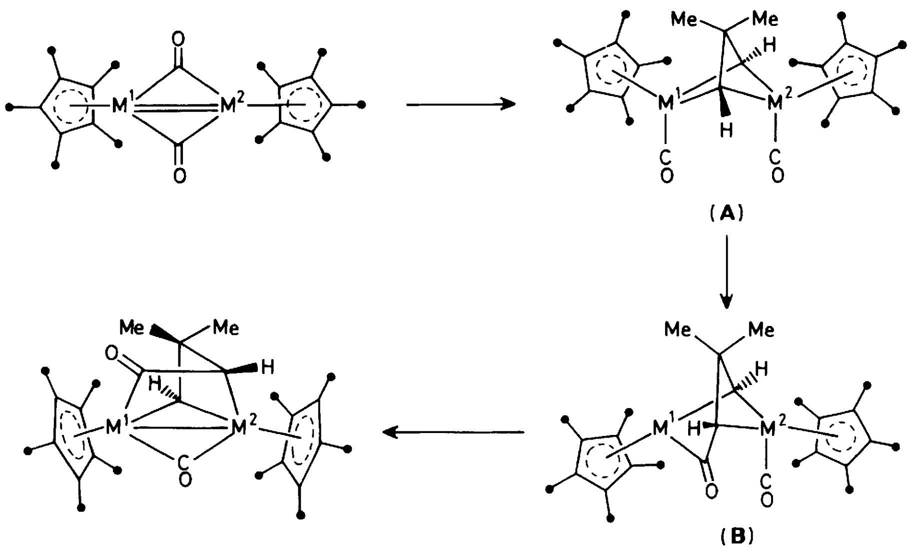


Scheme 2. (*i*), +[$CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$]; (*ii*), +[$Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$]

[$M^1M^2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$] exhibited different reactivities towards 3,3-dimethylcyclopropene, and comparative experiments established the reactivity sequence CoRh > RhRh > RhIr > CoIr > CoCo.

The corresponding reactions of 1,3,3-trimethylcyclopropene were also examined, however only the more reactive CoRh and RhRh systems afforded analogous products. The heterodinuclear complex [$CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$] reacted to give only one product (**6**), which was identified by elemental analysis, i.r. spectroscopy, and comparison of n.m.r. data, see Scheme 2, where the apparent carbonyl-insertion reaction has occurred regioselectively into a bond carrying a methyl-substituted carbon. In the case of the Rh_2 complex two adducts (**7a**) and (**7b**) (Scheme 2) were formed, the former predominating (9:1).

With regard to the mechanism of these reactions, the absence of cross-over products in the reaction with the heterodinuclear systems allows the exclusion of pathways for the cleavage of the carbon–carbon double bond in the cyclopropenes upon reaction with [$M^1M^2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$], which involve break-up of the dinuclear system and then reaction at one metal centre. A second alternative pathway involves an initial interaction between the cyclopropene and only one of the metal centres present in the dinuclear complex. Such a reaction has a parallel in the reported[28,29] formation of a 1:1 adduct on reaction of the



Scheme 3.

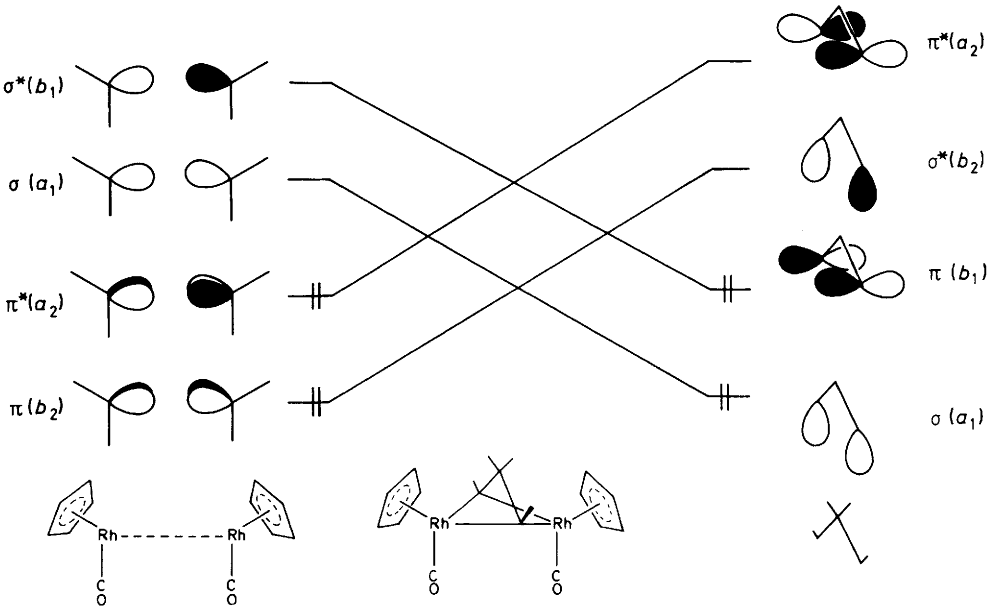
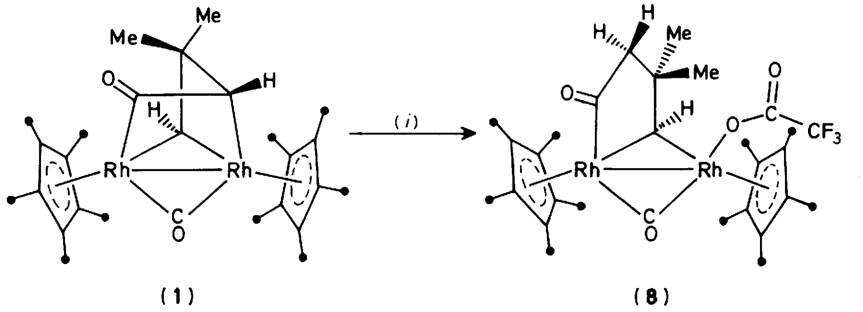


Figure 2. Qualitative orbital-interaction diagram for approach of $RCCR_2CR$ and $\{Rh(CO)(\eta\text{-}C_5R_5)\}_2$ fragments, as discussed in the text. Symmetry labels are appropriate for C_{2v} symmetry

32-electron $[M^1M^2(\mu\text{-}CO)_2(\eta\text{-}C_5R_5)_2]$ (R = H or Me) species with a donor phosphorus ligand, where the major bonding interaction between the two metal fragments in the adduct is the donation of electron density from the phosphorus-substituted metal centre to the carbonyl π^* orbitals of the $M(CO)_2(\eta\text{-}C_5R_5)$ fragment. Clearly a related interaction between one of the metal centres and the cyclopropene could be envisaged, however, there is then no precedent for a reaction which results in cleavage of the carbon–carbon double bond, and it is more likely that this important step involves both metal centres.

Examination of the structure of (**1**) suggests that a plausible precursor is the bis-μ-carbene complex (**A**) (Scheme 3). Such a species could arise *via* interaction of the cyclopropene with a dinuclear centre, and an insight into this reaction pathway was provided by a published[5] fragment-orbital analysis of the dinuclear species $[Ni_2(CO)_3(\eta\text{-}C_3H_3)]^+$ where an open C_3H_3 unit straddles the Ni–Ni vector. Since the fragments $Ni(CO)_2$ and $Rh(CO)(\eta\text{-}C_5Me_5)$ are isolobal it is relatively easy to extend the arguments developed for the Ni_2 system. Figure 2 shows a qualitative scheme for the important orbital interactions between an opened C_3H_4 and $[Rh_2(CO)_2(\eta\text{-}C_5Me_5)_2]$ [*cf.* a similar diagram in ref. 5 for $Ni_2(CO)_4$ interacting with $C_3R_3{}^+$]. The $Rh(CO)(\eta\text{-}C_5Me_5)$ fragment has frontier orbitals of σ and π pseudo-symmetry, containing the electrons which combine to give dimer fragment orbitals of a_1, b_1, b_2, and a_2 symmetry for the idealised C_{2v} symmetry shown. The energy ordering illustrated is likely to be appropriate for the fairly long (non-bonding) Rh ··· Rh distance postulated in the intermediate (**A**) (Scheme 3) [*cf.* the ordering shown for $Rh_2(CO)_2(\eta\text{-}C_5H_5)_2$ in ref. 12 and which, for the shorter Rh ··· Rh distance chosen, implies a Rh–Rh bond order of two]. Clearly the interactions depicted in Figure 2 allow population of cyclopropene σ* and π* orbitals as well as depopulation of σ and π each of which finds a symmetry match in the Rh_2 fragment. As



Scheme 4. (*i*), $+CF_3CO_2H$

argued by Jemmis and Hoffmann,[5] the opening of the ring allows the σ and σ* orbitals of the cyclopropene to interact more effectively with the dimetal unit. The increased bonding between cyclopropene and Rh_2 fragments that results drives the cleavage of the carbon–carbon double bond to completion. As the C=C bond is broken, so is the Rh=Rh bond, of order two in $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$.

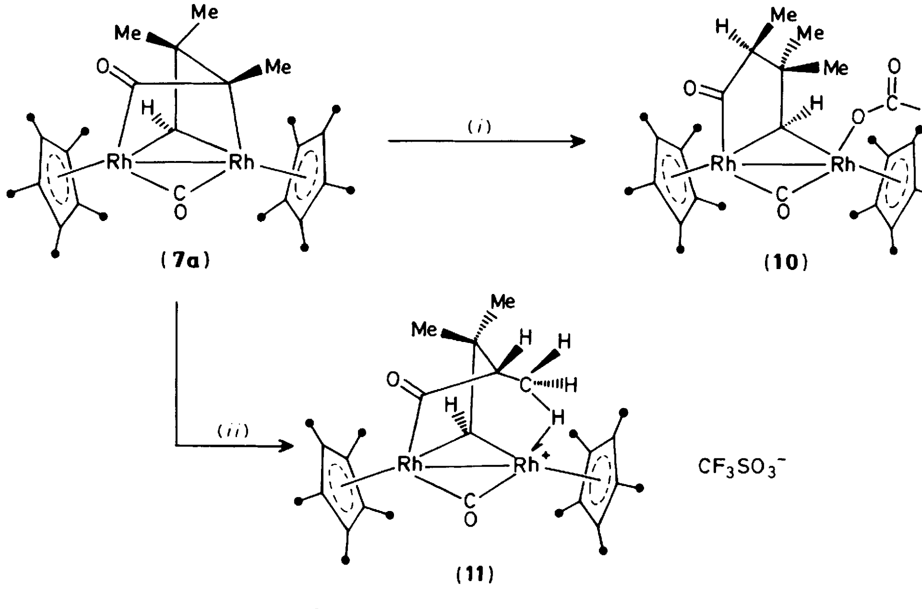
With the formation of a bis-μ-carbene intermediate (**A**), an alkyl migration can then occur onto a co-ordinated carbon monoxide, the resulting intermediate (**B**) collapsing *via* metal–metal bond formation and establishment of a bridging carbonyl to form the isolated products. In the context of the 'carbonyl insertion' step it is interesting that the molecule $[Ru_2(\mu\text{-}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$, which also contains a μ-methylene group not supported by a metal–metal bond, readily forms a bridging acyl complex on treatment with carbon monoxide.[30] The results with 1,3,3-trimethylcyclopropene are consistent with such a mechanism since the more substituted μ-carbene carbon would be expected to migrate preferentially onto CO co-ordinated to a d^6-metal centre. Moreover, in the case of the heterodinuclear systems, alkyl migration to a carbonyl ligand bound to the lighter metal centre would be anticipated.[31] Thus, formation of complexes (**3**), (**4**), and (**6**) is expected, whereas formation of (**5**) seems anomalous. In the theoretical analysis[31] of the alkyl migration from a transition metal to a co-ordinated CO it has been suggested that the migration reaction should become slightly more difficult as one descends a triad because of the change in the electronegativity and the overlap ability of the metal orbitals. However, because of the lanthanide contraction, the nominal electronegativity values may lie in the order Co > Ir > Rh, thus perhaps explaining the formation of complex (**5**).

It has previously been shown that the complexes $[M_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ (M = Co or Rh) react with electrophiles. Sulphur dioxide[32] affords an insertion product, and the proton acids HX (X = BF_4, CF_3CO_2, or CF_3SO_3)[33] react initially by protonating the rhodium–rhodium bond, this being followed by a disproportionation reaction, and the formation of a trinuclear triply bridged methylidyne cation. In the case of the corresponding reaction with HX (X = Cl or Br)[33] the dinuclear complexes $[Rh_2X(Me)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ are formed. It was, therefore, of interest to examine the reaction of complex (**1**) with protons, since this unusual molecule contains a metal–metal bond, and four different Rh–C σ bonds contained within a tricyclic system. Reaction of (**1**) with CF_3CO_2H in diethyl ether afforded reddish purple crystals of (**8**) (Scheme 4), which analysed as a 1 : 1 adduct. A solution of the adduct in acetone did not conduct electricity suggesting that the trifluoroacetate group was σ-bonded to a rhodium centre. The presence of the CF_3CO_2 group was confirmed by the appearance in the ^{19}F n.m.r. spectrum of a singlet resonance with an appropriate chemical shift.

Examination of the ^1H and ^{13}C n.m.r. spectra of complex (**8**) showed that reaction of (**1**) with CF_3CO_2H had led to selective cleavage of one Rh–C σ bond (Scheme 4). The ^1H signal in the spectrum of (**1**) assigned to COC*H*Rh was replaced in the corresponding spectrum of (**8**) by an AB system attributable to a CH_2 group. This was confirmed by the appearance in the proton-coupled ^{13}C spectrum of complex (**8**) of a triplet [^1J(CH) 125 Hz] centred at 69.6 p.p.m. Aside from these changes, the spectra of (**1**) and (**8**) were similar, which is consistent with protolytic cleavage of the longest and most strained Rh–C σ bond present in (**1**) and the formation of (**8**) with the illustrated structure, where ring opening removes the strain associated with the two four-membered (Rh_2C_2 and RhC_3) rings and allows the five-membered ring containing the acyl group to flip and adopt a more open structure.

An attempt to provide an answer to the question as to the stereochemistry of the electrophilic cleavage of the Rh–C σ bond by treating complex (**1**) with CF_3CO_2D was frustrated by keto–enol tautomerism. The ^1H n.m.r. spectrum of the product (**9**) was essentially identical to that of (**8**) except that superimposed on an AB quartet at 2.72 p.p.m. [^2J(HH) 17.9 Hz] and 2.40 p.p.m. [^2J(HH) 17.9 Hz] there were two slightly broadened singlets of approximately equal intensity at chemical shifts attributable to both methylene sites. Integration of the μ-alkylidene proton *versus* these signals indicated there was no significant CD_2-containing species. If deuteriation were regiospecific with the deuterium occupying only one methylene site, either a singlet or a doublet would be observed for the CHD groups, perhaps with small HD coupling. The doublet would be obtained only if the proton occupied the site in the 'W' arrangement from the bridging CH group thus giving rise to a small ^4J(HH) coupling. These observations suggest that H/D exchange has occurred to afford some CH_2-containing complex, as well as species in which D occupies both methylene sites equally.

Greater insight into the stereochemistry was provided by a study of the corresponding protolysis of the trimethyl-substituted system (**7a**). Whereas, CF_3CO_2H reacted in diethyl ether to give an analogous complex (**10**), reaction with CF_3SO_3H in toluene afforded a dark green powder (**11**) (Scheme 5). Examination of the ^1H n.m.r. spectrum of complex (**11**) showed resonances due to two different methyl groups, η-C_5Me_5 methyl groups, and a low-field multiplet at 10.72 p.p.m. due to a μ-C*H* group. In addition there was a three-proton resonance at −2.1 p.p.m., the chemical shift of which was temperature invariant between 22 and −80 °C. In the low-temperature (−75 °C) proton-coupled ^{13}C spectrum the *C*HMe carbon resonates at 68.4 p.p.m. [^2J(RhC) 3.7, ^1J(CH) 136 Hz], whilst the three methyl groups occur at 32.5, 23.7, and 17.1 p.p.m., all with ^1J(CH) 125 Hz. This suggests that, as illustrated in Scheme 5, the C–H bond of a methyl group interacts with the electron-deficient rhodium centre. Attempts



Scheme 5. (*i*), CF_3CO_2H; (*ii*), CF_3SO_3H

to observe the static structure where a reduced ^1J(CH) coupling would be expected were frustrated by precipitation at low temperatures.

Thus, it would appear that a methyl group rather than the proton of the CHMe group formed on ring opening interacts in a transannular manner with the electron-deficient metal centre, leading to the tentative suggestion that protonation occurs stereospecifically from the rear of the Rh–C σ bond, *i.e.* an S_E2 (inversion) reaction.[34]

Experimental

All experiments were performed in an atmosphere of dry oxygen-free nitrogen using standard Schlenk-tube techniques. Solvents were freshly distilled in a nitrogen atmosphere. Unless otherwise stated all chemicals were reagent grade used as received. Other materials were prepared as in the given literature reference: $[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[13] $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[10,11] $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[14] $[CoIr(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[15] $[RhIr(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[16] 3,3-dimethylcyclopropene,[35,36] and 1,3,3-trimethylcyclopropene.[37,38]

I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer, ^{1}H, ^{2}D, ^{19}F, and ^{13}C n.m.r. spectra on JEOL FX 90 Q and FX 200 spectrometers; chemical shifts were referenced to $SiMe_4$ (internal) and $CFCl_3$ (external), and coupling constants are in Hz.

Reactions of 3,3-*Dimethylcyclopropene*.—(*a*) *With* $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. A suspension of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.5 g, 0.94 mmol) in hexane (100 cm^3) contained in a Young's tube was degassed by a freeze-pump–thaw cycle and cooled to −196 °C. 3,3-Dimethylcyclopropene (0.4 cm^3) was then added *via* a syringe and the tube and contents sealed under nitrogen. On warming to room temperature the colour of the reaction mixture changed from mauve-purple to orange-red. The volatile material was removed *in vacuo*, the residue dissoved in hexane (10 cm^3) and filtered through a Celite pad (4 × 3 cm) to yield a clear orange-red solution. Reduction of the volume of the solvent to *ca.* 3 cm^3 and cooling (−78 °C) afforded red *crystals* of complex (**1**) (0.45 g, 80%) (Found: C, 53.7; H, 6.6. $C_{27}H_{38}O_2Rh_2$ requires C, 54.0; H, 6.3%), $\nu_{max.}$(CO) 1 809s and 1 683m cm^{-1} (pentane). N.m.r. (C_6D_6): ^{1}H, δ 9.46 [dt, 1 H, CH, ^2J(Rh^{1}H) 2, ^2J(Rh^{2}H) 2, ^4J(HH) 2.8], 2.55 [dd, 1 H, CH, ^2J(Rh^{1}H) 2.5, ^4J(HH) 2.8], 1.79 [d, 15 H, C_5Me_5, ^3J(RhH) 0.48], 1.62 [d, 15 H, C_5Me_5, ^3J(RhH) 0.48], 1.55 (s, 3 H, Me), and 1.12 p.p.m. (s, 3 H, Me); ^{13}C-{^{1}H}, δ 230.2 [t, μ-CO, ^1J(RhC) 42.3], 216.3 [d, ketonic CO, ^1J(Rh^{2}C) 23], 178.5 [dd, CH, ^1J(RhC) 31.7, 19.5, ^1J(CH) 149], 101.4 [d, C_5Me_5, ^1J(RhC) 3.9], 101.2 [d, C_5Me_5, ^1J(RhC) 3.9], 55.8 [d, CMe_2, ^2J(RhC) 4.9], 53.5 [d, CH, ^1J(Rh^{1}C) 17.1, ^1J(CH) 145], 35.75 (s, Me), 29.0 (s, Me), 10.0 (s, C_5Me_5), and 9.39 p.p.m. (s, C_5Me_5).

(*b*) With $[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. A similar reaction (3 d) afforded red *crystals* of complex (**2**) (60%) (Found: C, 63.3, H, 7.4. $C_{27}H_{38}Co_2O_2$ requires C, 63.3; H, 7.4%), $\nu_{max.}$(CO) 1 781s and 1 629m cm^{-1} (hexane). N.m.r. (C_6D_6): ^{1}H, δ 10.83 [d, 1 H, CH, ^4J(HH) 2.6], 3.56 [d, 1 H, CH, ^4J(HH) 2.6], 1.73 (s, 3 H, Me), 1.66 (s, 15 H, C_5Me_5), 1.46 (s, 15 H, C_5Me_5), and 1.15 p.p.m. (s, 3 H, Me); ^{13}C-{^{1}H}, δ 230.9 (μ-CO), 224.1 (ketonic, CO), 205.2 (CH), 98.1 (C_5Me_5), 97.8 (C_5Me_5), 55.8 (CMe_2), 52.0 (CH), 38.0 (Me), 29.2 (Me), 10.3 (C_5Me_5), and 9.2 p.p.m. (C_5Me_5).

(*c*) *With* $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. Similarly, reaction (1.5 h) gave red *crystals* of complex (**3**) (80%) (Found: C, 57.8; H, 7.3. $C_{27}H_{38}CoO_2Rh$ requires C, 58.3; H, 6.8%), $\nu_{max.}$(CO) 1 805s and 1 679m cm^{-1} (hexane). N.m.r. (C_6D_6): ^{1}H, δ 9.95 [dd, 1 H, CH, ^4J(HH) 2.93, ^2J(RhH) 1.5], 2.02 [t, 1 H, CH, ^4J(HH) 2.93, ^2J(RhH) 2.9], 1.67 (s, 15 H, C_5Me_5), 1.65 (s, 15 H, C_5Me_5), 1.57 (s, 3 H, Me), and 1.19 p.p.m. (s, 3 H, Me); ^{13}C-{^{1}H}, δ 225.1 [d, ketonic, CO, ^2J(RhC) 3.9], 189.7 [d, CH, ^1J(RhC) 19.5], 100.4 [d, Rh(C_5Me_5), ^1J(RhC) 3.6], 96.4 [s, Co(C_5Me_5)], 54.7 [d, CMe_2, ^2J(RhC) 3.9], 49.7 [d, CH, ^1J(RhC) 19.5], 35.1 (s, Me), 28.1 (s, Me), 9.0 (s, C_5Me_5), and 7.6 p.p.m. (s, C_5Me_5).

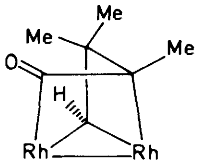
(*d*) *With* $[CoIr(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. Reaction (36 h) afforded red *crystals* of complex (**4**) (80%) (Found: C, 49.7; H, 6.2. $C_{27}H_{38}CoIrO_2$ requires C, 50.2; H, 5.9%), $\nu_{max.}$(CO) 1 777s and 1 681m cm^{-1} (hexane). N.m.r. (C_6D_6): ^{1}H, δ 9.46 (br, 1 H, CH), 2.32 (br, 1 H, CH), 1.74 (s, 15 H, C_5Me_5), 1.66 (s, 15 H, C_5Me_5), 1.51 (s, 3 H, Me), and 1.20 p.p.m. (s, 3 H, Me); ^{13}C-{^{1}H}, δ 235.6 (CO), 230.7 (CO), 154.6 [CH, ^1J(CH) 147], 97.9 (C_5Me_5), 96.8 (C_5Me_5), 56.6 (CMe_2), 40.1 [CH, ^1J(CH) 141], 37.7 (Me), 30.2 (Me), 9.9 (C_5Me_5), and 8.9 p.p.m. (C_5Me_5).

(*e*) *With* $[RhIr(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. A similar reaction (16 h) gave red *crystals* of complex (**5**) (80%) (Found: C, 46.6; H, 5.8. $C_{27}H_{38}IrO_2Rh$ requires C, 47.0; H, 5.5%), $\nu_{max.}$(CO) 1 787s and

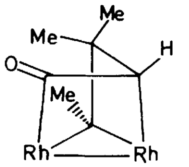
1 669m cm^{-1} (hexane). N.m.r. (C_6D_6): ^{1}H, δ 9.11 [t, 1 H, CH, ^4J(HH) 2.2, ^2J(RhH) 2.1], 2.33 [t, 1 H, CH, ^4J(HH) 2.2, ^2J(RhH) 2.2], 1.78 (s, 15 H, C_5Me_5), 1.73 (s, 3 H, Me), 1.68 (s, 15 H, C_5Me_5), and 1.10 p.p.m. (s, 3 H, Me); ^{13}C-{^{1}H}, δ 217.9 [d, μ-CO, ^1J(RhC) 38.6], 200.4 (s, ketonic, CO), 147.5 [d, CH, ^1J(RhC) 14.7], 101.6 [d, Rh(*C*$_5$Me$_5$), ^1J(RhC) 3.68], 98.7 [s, Ir(*C*$_5$Me$_5$)], 62.3 [d, CH, ^1J(RhC) 18.4], 55.6 (s, *C*Me$_2$), 36.9 (s, Me), 29.3 (s, Me), 10.8 (s, C$_5$*Me*$_5$), and 9.7 p.p.m. (s, C$_5$*Me*$_5$).

Reactions of 1,3,3-*Trimethylcyclopropene*.—(*a*) *With* [CoRh(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$]. A similar reaction between [CoRh(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] (0.5 g, mmol) and 1,3,3-trimethylcyclopropene (0.4 cm^3) in hexane (100 cm^3) gave after 60 h red *crystals* of complex (**6**) (85%) (Found: C, 58.4; H, 7.4. $C_{28}H_{40}CoO_2Rh$ requires C, 58.9; H, 7.1%), $\nu_{max.}$(CO) 1 805s and 1 665m cm^{-1} (hexane). N.m.r. (C_6D_6): ^{1}H, δ 9.95 [d, 1 H, CH, ^2J(RhH) 1.46], 1.67 (s, 15 H, C_5Me_5), 1.62 (s, 15 H, C_5Me_5), 1.49 (s, 3 H, Me), 1.05 (s, 3 H, Me), and 0.73 p.p.m. [d, 3 H, Me, ^3J(RhH) 1.1]; ^{13}C-{^{1}H}, δ 247.7 [d, μ-CO, ^1J(RhH) 40.4], 229.2 [d, ketonic, CO, ^2J(RhC) 3.6], 193.3 [d, CH, ^1J(RhC) 20.2], 101.5 [d, Rh(*C*$_5$Me$_5$), ^1J(RhC) 3.7], 97.7 [s, Co(*C*$_5$Me$_5$)], 58.7 (s, Me), 12.2 (s, C*Me*), 10.1 (s, C$_5$*Me*$_5$), and 9.0 p.p.m. (s, C$_5$*Me*$_5$).

(*b*) *With* [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$]. A similar reaction (24 h) afforded red *crystals* of complexes (**7a**) and (**7b**) (85%) (Found: C, 54.3, H, 6.9. $C_{28}H_{40}O_2Rh_2$ requires C, 54.8; H, 6.4%), $\nu_{max.}$(CO) 1 813s and 1 681m cm^{-1} (hexane). N.m.r. CDCl$_3$: ^{1}H, [major isomer (**7a**)], δ 9.56 [t, 1 H, CH, ^2J(RhH) 1.83], 1.84 [d, 15 H, C_5Me_5, ^3J(RhH) 0.6], 1.76 [d, 15 H, C_5Me_5, ^3J(RhH) 0.6], 1.43 (s, 3 H, Me), 0.80 (s, 3 H, Me), and 0.56 p.p.m. [d, 3 H, CMe, ^3J(RhH) 1.22]; ^{13}C-{^{1}H}, δ 230.2 [t, μ-CO, ^1J(RhC) 44], 222.5 [d, ketonic, CO, ^1J(RhC) 25.7], 181.5 [dd, CH, ^1J(RhC) 18.4, 31.2], 101.3 [d, *C*$_5$Me$_5$, ^1J(RhC) 3.7], 101.2 [d, *C*$_5$Me$_5$, ^1J(RhC) 3.7], 60.6 [d, CMe, ^1J(RhC) 14.7], 57.9 [d, *C*Me$_2$, ^2J(RhC) 3.7], 31.5 (s, Me), 28.3 (s, Me), 11.2 (s, C*Me*), 9.8 (s, C$_5$*Me*$_5$), and 9.3 p.p.m. (s, C$_5$*Me*$_5$); ^{1}H [minor isomer (**7b**)], δ 2.74 (m, 3 H, Me), 1.78 [d, 15 H, C_5Me_5, ^3J(RhH) 0.6], and 1.74 p.p.m. [d, 15 H, C_5Me_5, ^3J(RhH) 0.6]; ^{13}C-{^{1}H}, δ 102.3 [d, *C*$_5$Me$_5$, ^1J(RhC) 3.7], 101.8 [d, *C*$_5$Me$_5$, ^1J(RhC) 3.7], 53.85 [d, CH, ^1J(RhC) 18.4], 53.4 (s, *C*Me$_2$), 32.0 (s, Me), 29.7 (s, Me), 25.3 (s, Me), 9.6 (s, C$_5$*Me*$_5$), and 8.7 p.p.m. (s, C$_5$*Me*$_5$). Other signals of the minor isomer were too weak for observations. Integration of C_5Me_5 ^{1}H resonances shows that the major:minor ratio is 9:1.



major



minor

Protonation of Complex (**1**).—(*a*) *With trifluoroacetic acid*. Trifluoroacetic acid (0.1 cm^3, 0.15 g, 1.3 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of complex (**1**) (0.3 g, 0.5 mmol) in diethyl ether (10 cm^3). Upon warming to room temperature a dark red solid was precipitated. This was collected and washed with diethyl ether (2 × 10 cm^3) affording reddish purple *crystals* of complex (**8**) (0.34 g, 95%) (Found: C, 48.4; H, 6.0. $C_{29}H_{39}F_3O_4Rh_2$ requires C, 48.7; H, 5.6%), $\nu_{max.}$ 1 853s and 1 681m cm^{-1} (CH$_2$Cl$_2$). N.m.r. (CDCl$_3$): ^{1}H, δ 10.93 [dt, 1 H, CH, ^4J(HH) 1.46, ^2J(RhH) 2.2], 2.73 [AB quartet, 1 H, CH$_3$, ^2J(HH) 18.5], 2.38 [AB quartet, 1 H, CH$_2$, ^2J(HH) 18.5, ^4J(HH) 1.46], 1.82 (s, 15 H, C_5Me_5), 1.55 (s, 3 H, Me), and 1.47 p.p.m. (s, 3 H, Me); ^{13}C-{^{1}H}, δ 237.3 [d, ketonic, CO, ^1J(RhC) 31.7], 222.1 [dd, μ-CO, ^1J(RhC) 36.6, 51.3], 215.5 [dd, CH, ^1J(RhCO) 31.2, ^1J(RhC) 27.3], 161.0 [q, CF$_3$*C*O$_2$, ^2J(CF) −31.7], 114.5 [q, CF$_3$*C*O$_2$, *J*(CF) −290.5], 104.9 [d, *C*$_5$Me$_5$, ^1J(RhC) 3.9], 102.1 [d, *C*$_5$Me$_5$, ^1J(RhC) 5.9], 69.6 [s, CH$_2$, ^1J(CH) 125], 49.7 (s, *C*Me$_2$), 36.0 (s, Me), 25.6 (s, Me), and 9.8 p.p.m. (s, C$_5$*Me*$_5$); ^{19}F, δ −75.03 p.p.m. (s, CF$_3$).

(*b*) *With deuteriotrifluoroacetic acid*. A similar reaction with CF$_3$CO$_2$D afforded complex (**9**), $\nu_{max.}$ 1 849s and 1 673s cm^{-1} (CH$_2$Cl$_2$). N.m.r.: ^{1}H (CDCl$_3$), δ 10.93 (m, 1 H, CH), 2.72 [AB quartet, 0.5 H, C*H*D, ^2J(HH) 17.9], 2.40 [AB quartet, 0.5 H, C*H*D, ^2J(HH) 17.9, ^4J(HH) 1.1], 1.82 (s, 15 H, C_5Me_5), 1.65 (s, 15 H, C_5Me_5), 1.55 (s, 3 H, Me), and 1.47 p.p.m. (s, 3 H, Me). Superimposed on the AB quartet were two singlets at 2.67 and 2.42 p.p.m.

Protonation of Complex (**7a**).—(*a*) *With trifluoroacetic acid*. A similar reaction between complex (**7a**) and CF$_3$CO$_2$H afforded a dark red solid (**10**) (95%), $\nu_{max.}$ (CO) 1 853s and 1 685m cm^{-1} (CH$_2$Cl$_2$). N.m.r. (CDCl$_3$): ^{1}H, δ 11.12 [t, 1 H, CH, ^2J(RhH) 2], 2.80 [q, 1 H, CH, ^3J(HH) 7.3], 1.82 (s, 15 H, C_5Me_5), 1.64 (s, 15 H, C_5Me_5), 1.39 (s, 3 H, Me), 1.33 (s, 3 H, Me), and 0.82 p.p.m. [d, 3 H, Me, ^3J(HH) 7.3]; ^{13}C-{^{1}H}, δ 239.8 [d, ketonic, CO, ^1J(RhC) 31.2], 222.0 [dd, μ-CO, ^1J(RhC) 49.6], 215.3 [t, CH, ^1J(RhC) 26], 160.9 [q, CF$_3$*C*O$_2$, ^2J(CF) −37], 115.3 [q, *C*F$_3$CO$_2$, *J*(CF) −292], 106.0 (s, *C*$_5$Me$_5$), 102.7 [d, *C*$_5$Me$_5$, ^1J(RhC) 5.5], 71.2 (s, *C*HMe), 58.6 (s, *C*Me$_2$), 29.3 (s, Me), 24.7 (s, Me), 13.1 (s, CH*Me*), 10.2 (s, C$_5$*Me*$_5$), and 9.6 p.p.m. (s, C$_5$*Me*$_5$).

(*b*) *With trifluoromethylsulphuric acid*. The acid CF$_3$SO$_3$H (0.05 cm^3, 0.085 g, 0.57 mmol) was added dropwise to a cooled (−78 °C) stirred solution of complex (**7a**) (0.135 g, 0.22 mmol) in toluene (10 cm^3). The reaction mixture was allowed to warm briefly to room temperature and the solvent removed *in vacuo*. The dark residue was washed (3 × 20 cm^3) with hexane, and the resultant green powder was recrystallised (−20 °C) from CH$_2$Cl$_2$–hexane to give complex (**11**) (0.14 g, 83%), $\nu_{max.}$ 1 857s, 1 827s, and 1 677m cm^{-1} (CH$_2$Cl$_2$). N.m.r. (CD$_2$Cl$_2$): ^{1}H, δ 10.72 (m, 1 H, CH), 1.83 (s, 15 H, C_5Me_5), 1.68 (s, 15 H, C_5Me_5), 1.58 (s, 3 H, Me), 1.21 [d, 3 H, Me, *J*(HH) 3.7], and −2.1 [*J*(RhH) 6.35, *J*(HH) 3]; ^{13}C-{^{1}H} (−75 °C), δ 242.7 [d, ketonic, CO, ^1J(RhC) 31.2], 223.5 [dd, μ-CO, ^1J(RhC) 40.5, ^1J(RhCO) 53.3], 220.0 [t, CH, ^1J(RhC) 29.4, ^1J(CH) 123], 119.7 [q, CF$_3$, ^1J(CF) −320], 106.9 (s, *C*$_5$Me$_5$), 106.7 (s, *C*$_5$Me$_5$), 68.4 [d, *CH*Me, ^2J(RhC) 3.7, ^1J(CH) 136], 58.0 (s, *C*Me$_2$), 32.5 [s, Me, ^{1}H-coupled spectrum, ^1J(CH) 125], 23.7 [s, Me, ^{1}H-coupled spectrum, ^1J(CH) 125], 17.1 [s, Me, ^{1}H-coupled spectrum, ^1J(CH) 125], 10.6 (s, C$_5$*Me*$_5$), and 9.5 p.p.m. (s, C$_5$*Me*$_5$).

X-*Ray Crystal Structure Analysis of Complex* (**1**).—A small single crystal of complex (**1**) (maximum linear dimension *ca.* 0.4 mm) was mounted under N$_2$ in a thin-walled glass capillary. Intensity data were collected by a Wyckoff ω-scan technique for a unique quadrant of reciprocal space in the range $3 > 2\theta > 50°$, with the crystal temperature maintained at 230 K by use of the Nicolet LT-1 crystal-cooling device. Scan speeds varied between 2.93 and 29.3° min^{-1} based on a 2-s prescan of the reflection; for $2\theta > 35°$ only reflections with prescan counts > 15 were recorded. Of the 4 002 reflection intensities measured, 3 439 remained after averaging of duplicate and symmetry-equivalent observations; of these 3 201 with $I > 2\sigma(I)$ were used for structure solution and refinement. Two check reflections [(−2 −2 −5) and (3 −3 6)] were remeasured after every 50 scans, but showed no significant variation in the course (46 h) of data collection. The structure was solved by heavy-atom methods (Patterson and Fourier difference). All non-hydrogen atoms were refined with anisotropic vibrational parameters and without positional constraints. Hydrogen atoms were constrained to idealised geometries [C–H 0.96 Å, H–C–H 109.5°],

Table 2. Atomic co-ordinates (× 10^4)

Atom	x	y	z	Atom	x	y	z
Rh(1)	3 260(1)	1 360(1)	1 154(1)	C(15)	5 604(6)	1 372(12)	1 767(5)
Rh(2)	1 909(1)	767(1)	1 821(1)	C(16)	4 352(5)	−359(9)	1 022(4)
O(1)	3 884(4)	370(7)	2 661(3)	C(17)	4 600(6)	−1 653(10)	1 467(5)
O(2)	2 402(5)	3 427(7)	2 672(3)	C(18)	3 655(5)	−257(10)	367(4)
C(1)	3 317(5)	701(8)	2 145(4)	C(19)	3 056(7)	−1 447(11)	6(6)
C(2)	2 359(3)	2 837(9)	2 102(4)	C(20)	1 568(5)	−1 590(8)	2 064(4)
C(3)	2 694(6)	3 384(9)	1 475(4)	C(21)	2 183(6)	−2 877(9)	2 019(4)
C(4)	1 811(5)	3 310(9)	848(4)	C(22)	1 602(5)	−714(9)	2 691(4)
C(5)	1 978(7)	4 050(9)	172(4)	C(23)	2 240(6)	−949(10)	3 412(4)
C(6)	890(6)	3 965(10)	995(5)	C(24)	897(5)	372(9)	2 523(4)
C(7)	1 830(5)	1 679(8)	841(4)	C(25)	664(6)	1 468(10)	3 030(5)
C(10)	3 701(6)	1 157(11)	88(4)	C(26)	411(5)	190(9)	1 788(4)
C(11)	3 181(7)	1 593(13)	−647(4)	C(27)	−472(6)	919(11)	1 427(5)
C(12)	4 381(6)	1 955(10)	576(4)	C(28)	831(5)	−1 065(8)	1 512(4)
C(13)	4 707(7)	3 492(11)	475(6)	C(29)	525(6)	−1 653(10)	768(4)
C(14)	4 792(5)	1 038(9)	1 145(4)				

with the exception of H(3) and H(7) which were refined freely, and assigned fixed isotropic vibrational parameters *ca.* 1.2 times that of the carbon to which they are bonded. Refinement, by blocked-cascade full-matrix least squares, converged to R = 0.051, R' = 0.063, and S = 1.60.* Reflections were assigned individual weights $w = [\sigma^2(F_o) + F_o^2]^{-1}$ where $\sigma^2(F_o)$ is the variance in F_o derived from counting statistics and g (= 0.0008) was chosen to minimise the variation of $\Sigma w(|F_o| - |F_o|)^2$ with $|F_o|$. The final electron-density difference synthesis showed no features of magnitude >2 e Å^{-3}, all of the larger peaks being within 1 Å of a rhodium atom.

Table 2 lists the atomic parameters for the non-hydrogen atoms. All calculations were carried out using the SHELTXL package[39] with complex neutral atom scattering factors from ref. 40.

Crystal data. $C_{27}H_{38}O_2Rh_2$, M = 600.1, monoclinic, a = 14.544(7), b = 9.280(5), c = 19.258(9) Å, β = 102.28(4)°, U = 2 540(2) Å^3, Z = 4, D_c = 1.57 g cm^{-3}, $F(000)$ = 1 224 e, space group $P2_1/c$ (no. 14), Mo-K_α X-radiation, $\bar{\lambda}$ = 0.710 69 Å, $\mu(\text{Mo-}K)_\alpha$ = 12.99 cm^{-1}, T = 230 K.

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* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, and $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$; N_o = 2 201, N_v = 324.

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