

THE ADDITION OF SMALL MOLECULES TO $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$

IV *. THE SUNLIGHT ASSISTED MAKING AND BREAKING OF ALKENE C–H BONDS ON THE DIRHODIUM CENTRE; THE CRYSTAL AND MOLECULAR STRUCTURES OF $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{CF}_3\}\text{H} \cdot \text{H}_2\text{O}$ AND $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CF}_2)\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$

RON S. DICKSON, GARY D. FALLON, SUSAN M. JENKINS,

Department of Chemistry, Monash University, Clayton, Victoria, 3168 (Australia)

BRIAN W. SKELTON and ALLAN H. WHITE

Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, W.A., 6009 (Australia)

(Received May 9th, 1986)

Summary

Bis-alkenyl complexes of the type $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{alkene} - \text{H})(\text{alkyne} + \text{H})$ are obtained when the alkyne complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ is treated with the following alkenes: $\text{H}_2\text{C}=\text{CH}_2$, $\text{H}_2\text{C}=\text{CHR}$ ($\text{R} = \text{Me}$, Bu^t , Ph , CN), $\text{H}_2\text{C}=\text{CF}_2$, $\text{RHC}=\text{CHR}'$ ($\text{R} = \text{R}' = \text{Me}$, Ph , Cl ; $\text{R} = \text{Me}$, $\text{R}' = \text{Et}$), cyclooctene and norbornene. An approximately equimolar amount of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$ is also formed. The reactions are greatly accelerated when the reaction mixtures are exposed to sunlight. There is some regioselectivity in the reactions with $\text{H}_2\text{C}=\text{CHR}$ and $\text{MeHC}=\text{CHEt}$, with a preference for C–H bond cleavage at the least crowded alkene-carbon. When the reaction with acrylonitrile is performed in the absence of sunlight, the complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})\{(\text{H}_2\text{C}=\text{CHCN})(\text{CF}_3\text{C}_2\text{CF}_3)\}$ can be isolated; upon exposure to sunlight, there is loss of CO and H-transfer to form two isomers of the appropriate bis-alkenyl complex.

The molecular geometries of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ and $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CF}_2)\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ have been ascertained by X-ray structure determination. Each molecule has two bridging alkenyl units spanning a Rh–Rh single bond; the dihedral angle between the two Rh–Rh–C=C planes is just above 90° . There is a cyclopentadienyl ring η^5 -attached to each metal. Crystal data: $\text{C}_{17}\text{H}_{13}\text{F}_6\text{NRh}_2 \cdot \text{H}_2\text{O}$, M 569.1, monoclinic, $P2_1/n$, a 15.014(7), b 14.882(7), c 8.590(5) Å, β 94.57(9)°, $Z = 4$, final R 0.056 for 2493 observed reflections;

* For Part III see ref. 7.

$C_{16}H_{12}F_8Rh_2$, M 562.1, monoclinic, $P2_1/c$, a 13.037(6), b 8.765(2), c 14.873(3) Å, β 103.16(3)°, $Z = 4$, final R 0.062 for 1820 observed reflections.

Introduction

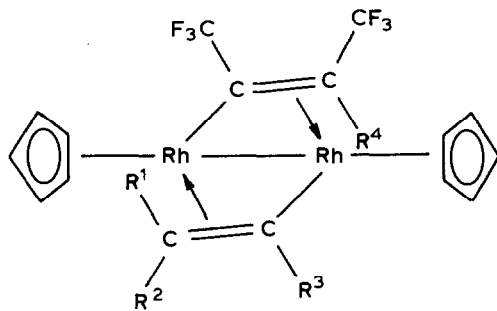
The making and breaking of C–H bonds is important in numerous catalytic cycles, including those based on alkenes [1,2]. In these systems, activation of the alkene is achieved through prior coordination to the transition metal catalyst. Although pathways have been established [3,4] for a range of reactions in which the intermediates are mononuclear metal derivatives, much less is known about related reactions occurring on polynuclear metal centres.

Previously, we have described the ability of the dinuclear complex $(\eta-C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ to coordinatively add nucleophilic substrates such as PR_3 , CNR [5], CR_2 [6] and NR [7]. In some of these reactions, the initial substrate addition is followed by an intramolecular reaction that leads to the formation of new C–X bonds. In this paper, we show that the complex $(\eta-C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ also reacts with a range of alkenes under mild conditions. These reactions are accomplished with an excess of the alkene in solution at room temperature, and are greatly accelerated by exposure to sunlight.

Results and discussion

The reaction with ethylene

The reaction between $(\eta-C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and an excess of ethylene occurs slowly in hexane at room temperature. With about ten equivalents of ethylene at ≤ 1 atm pressure, the reaction is still incomplete after three weeks. Exposure of a fresh reaction solution to pyrex filtered sunlight results in a dramatic acceleration of the reaction; no starting material was detected after 30 min. Work-up of the reaction mixture yielded the known [5] dicarbonyl complex $(\eta-C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (ca. 50% yield), a small amount (2%) of the trimeric complex $(\eta-C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$, and an orange-red crystalline product of formula $(\eta-C_5H_5)_2Rh_2(C_4F_6)(C_2H_4)$ (ca. 40% yield). The spectroscopic properties of this complex are consistent with the structure **1** ($R^1 = R^2 = R^3 = R^4 = H$). Thus,



(1)

the infrared spectrum shows no carbonyl absorptions, the 1H NMR spectrum reveals two C_5H_5 environments plus four signals for the protons derived from

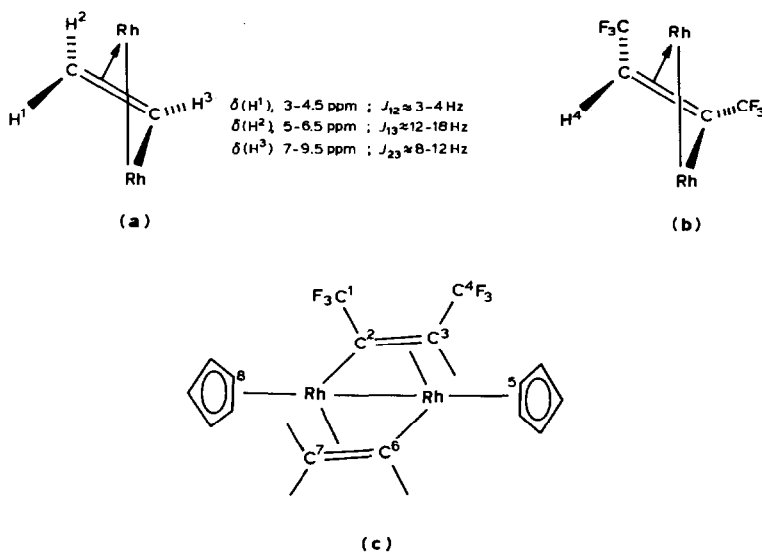


Fig. 1. Configuration of components of complex 1 assigned from NMR results.

ethylene, and in the ^{19}F NMR spectrum there are two CF_3 multiplets with one including *gem*-coupling to a proton. X-ray structure determinations reported below for the analogous complexes obtained from $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ and acrylonitrile or 1,1-difluoroethylene, confirm the structural features shown in 1.

Some aspects of the NMR spectra of 1 ($\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$) are interesting and deserve further comment. Data is available for a number of complexes that incorporate the ethenyl unit shown in Fig. 1a, and the chemical shift and coupling constant ranges are as shown [8]. Each proton shows first order coupling to all other protons. The ^1H NMR spectrum of 1 ($\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$) (see Fig. 2) is consistent with this data, but has the additional feature of Rh-H coupling. The low-field signal for H^3 is most impressive and is best analyzed [9] as an ABCXY system with $^3J(\text{H}^1\text{H}^3)$ 11.7, $^3J(\text{H}^2\text{H}^3)$ 7.5, $^2J(\text{RhH}^3)$ 3.2, and $^3J(\text{RhH}^3)$ 1.5 Hz. The

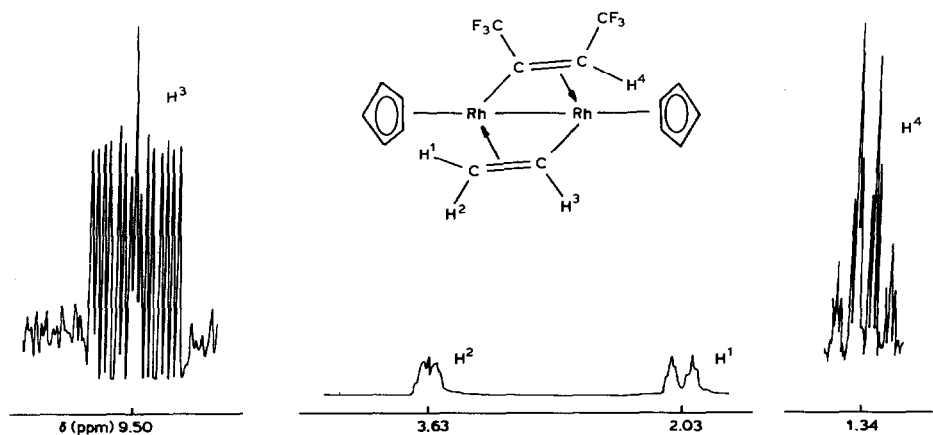


Fig. 2. ^1H NMR spectrum of complex 1; the resonances for H^3 and H^4 are magnified for clarity.

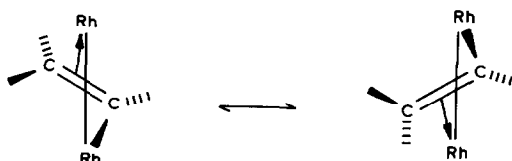


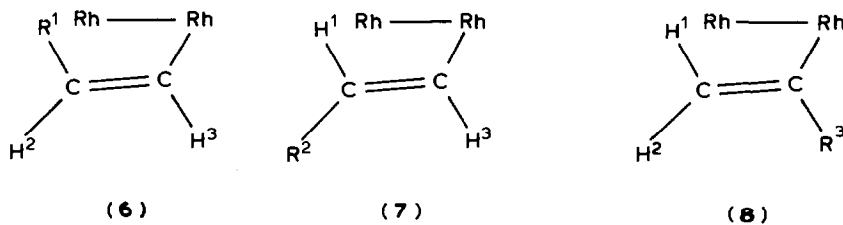
Fig. 3. Proposed fluxional behaviour for a μ_2 -ethenyl-dirhodium system.

observation of two different Rh–H³ coupling constants is significant in that it eliminates the possibility of fluxional behaviour involving interchange of the σ - and π -bonds within the ethenyl-Rh₂ unit. This type of movement is shown in Fig. 3 and has been detected [10] for some other systems containing a single, μ - η^2 ethenyl group. The stereochemistry of the unit shown in Fig. 1b can be established unambiguously from the ¹⁹F NMR data. The arrangement shown is indicated by the magnitude of the F–H and F–F coupling constants which fall within the normal ranges of 8–11 Hz (*gem*-C(H)CF₃) and 11–15 Hz (*vic*, *cis*-C(CF₃)C(CF₃)), respectively [11,12]. For the alternative geometry with *trans* CF₃ groups, a smaller ⁵J(FF) of 2–2.5 Hz would be expected. Chemical shifts for all carbon atoms except C² (Fig. 1c) are readily detected in the ¹³C{¹H} NMR spectrum. Resonances for the atoms C³ and C⁷ are observed at δ 56.7 (qdd; ²J(CF) 38, J(CRh) 16 and 4 Hz) and 53.8 ppm (d; J(CRh) 12 Hz), respectively. As expected [13–15], the σ -bonded carbon C⁶ is at lower field (δ 153.1 ppm (dd), J(CRh) 33 and 13 Hz). A weak multiplet at δ 144.3 ppm is probably due to C². The observation of two different Rh–C coupling constants for C⁶ provides confirmation that the alkenyl groups are not fluxional.

In the formation of **1** (R¹ = R² = R³ = R⁴ = H), there is facile cleavage of one of the vinylic C–H bonds. Similar reactions have been reported for some other systems, and representative examples (**2**–**5**) are shown in Fig. 4. In each of these systems, there is formation of a μ -hydrido- μ -alkenyl complex. It is possible that similar behaviour occurs initially with our system, and that there is subsequent migration of the hydride ligand to an unsaturated carbon of the CF₃C₂CF₃ group. We have no evidence to support this, however. Some further discussion of a possible mechanism for our reaction will be presented in a subsequent paper.

Reactions with 1-alkenes

The reactions between (η -C₅H₅)₂Rh₂(CO)(CF₃C₂CF₃) and some 1-alkenes, H₂C=CHR (R = Me, Ph, Bu^t) occur in a similar manner. With these systems, three regioisomers are theoretically possible since the R group can occupy any of the positions R¹, R² or R³ in **1**. The different arrangements of the vinylic hydrogens in these three isomers are shown more clearly in **6**, **7** and **8**. With 1-propene, two

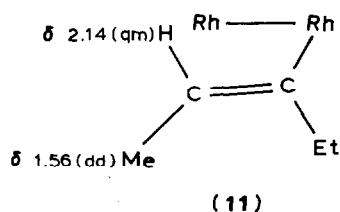
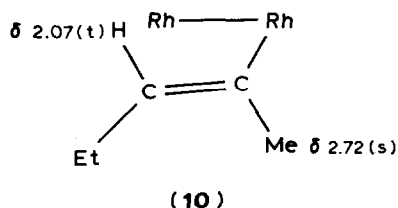
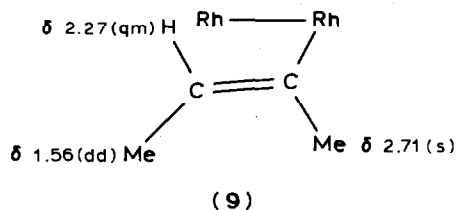


1-alkenes. The reactions involving $\text{H}_4\text{Os}_4(\text{CO})_{12}$ and $\text{H}_2\text{C}=\text{CHR}$ ($\text{R} = \text{Ph}$ or Bu^t) give $\text{H}_3\text{Os}_4(\mu\text{-CH}=\text{CHR})(\text{CO})_{11}$ only [17]; in this complex, the vinylic hydrogens are *trans* (see 7). In contrast, at least two isomers are identified in each of the other systems. Isomers incorporating the arrangements 6 and 8, but not 7, are obtained in reactions with $[(\text{Pr}_2^i\text{PCH}_2\text{CH}_2\text{PPr}_2^i)\text{Rh}]_2(\mu\text{-H})_2$; approximately equal amounts of the two isomers are isolated [15]. All three isomers are formed in the reaction of $\text{Re}_2(\text{CO})_{10}$ with $\text{H}_2\text{C}=\text{CHEt}$, but the isomer with the geometry 7 predominates [18]. Each of the other isomers is thermally unstable with respect to isomerization. In solution $6 \rightarrow 7$ with $t_{1/2} \sim 10$ min (CH_2Cl_2 , 25°C), and $8 \rightarrow 7$ with $t_{1/2} \sim 10$ h (toluene, no light, 25°C). On reaction of $\text{Re}_2(\text{CO})_{10}$ with other 1-alkenes, $\text{H}_2\text{C}=\text{CHR}$, 6 and 7 are isolated when $\text{R} = \text{Me}$, 7 only when $\text{R} = \text{Bu}^t$, and 7 is the major [19] or sole [18] product when $\text{R} = \text{Ph}$. The cumulative results, including our own, indicate that the preferred ethenyl arrangement is 7 unless its formation is inhibited by bulky substituents on ancillary ligands in the complex.

Reactions with internal alkenes

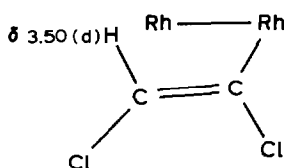
There are relatively few examples of the activation of internal alkenes, $\text{RHC}=\text{CHR}'$, by binuclear complexes. The rhenium complex $\text{Re}_2(\text{CO})_8(\mu\text{-CMe}=\text{CHMe})$ has been obtained in fairly low yield by photolysis of a mixture of $\text{Re}_2(\text{CO})_{10}$ and 2-butene [18]. In reactions of $[(\text{Pr}_2^i\text{PCH}_2\text{CH}_2\text{PPr}_2^i)\text{Rh}]_2(\mu\text{-H})_2$ with *trans*-2-butene and *cis*-2-pentene, there is isomerization of the alkenes to 1-butene and 1-pentene respectively, and these terminal alkenes then give the appropriate μ -alkenyl product 4 [15].

With our system, we find that the alkenes 2-butene, 2-pentene, stilbene and 1,2-dichloroethylene react readily to give products derived from the *cis*-disubstituted alkene. Treatment of $(\eta\text{-C}_3\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ with a mixture of *cis*- and *trans*-2-butene gave $(\eta\text{-C}_3\text{H}_5)_2\text{Rh}_2(\text{CMe}=\text{CHMe})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$. NMR results (see 9) indicate that the product is formed from the *cis*-alkene only. The analogous

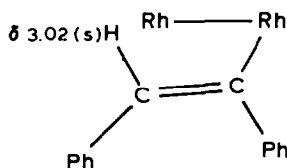


reaction with *cis*-2-pentene gives two regioisomers. NMR results show that 10 is incorporated in the major and 11 in the minor isomer; the proportion is 3/2. Identification of the isomers containing 9-11 is based largely on the appearance of the methyl resonances; the expected multiplicities are dd and s for Me^2 and Me^3

respectively. Reactions with *cis*- and *trans*-1,2-dichloroethylene both give the same product which is derived from the *cis*-isomer (see 12). It has not been possible to



(12)



(13)

establish whether the isomerization of *trans*-ClH=CClH occurs before or after C-H bond cleavage. Similar reactions have been done with both *cis*- and *trans*-stilbene. The *cis*-alkene gives a product with the alkenyl arrangement (13), but the reaction with *trans*-PhHC=CHPh is more complicated. This gives three products, one being the same as that obtained from *cis*-PhHC=CHPh. The other two convert in solution to this same product, but they have not yet been fully identified. Further investigation of this system will be included in a later paper.

Attempted addition reactions with highly substituted alkenes such as 2,3-dimethyl-2-butene, $\text{Me}_2\text{C}=\text{CMe}_2$, have not been successful. Little or no reaction is observed at room temperature, even in sunlight.

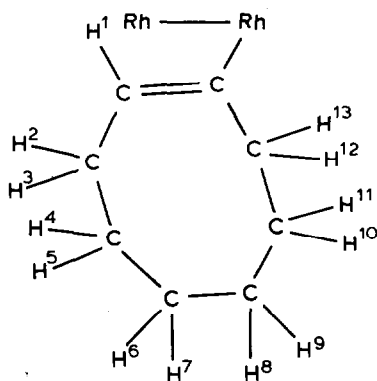
Reactions with cyclic alkenes

In previous work, it has often proved difficult to cleave C-H bonds in cyclic alkenes by reaction with di- and poly-nuclear complexes. For example, the reaction of cyclooctadiene with $\text{Ru}_3(\text{CO})_{12}$ or $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ occurs only under forcing conditions, and the yield of $\text{HRu}_3(\text{CO})_9(\text{C}_8\text{H}_{11})$ is only 4% [20]. Similarly, the complexes $\text{H}_3\text{Os}_4(\text{CO})_{11}(\text{alkene}-\text{H})$ are obtained in yields of $\leq 10\%$ from reaction of $\text{H}_4\text{Os}_4(\text{CO})_{12}$ with the cyclic alkenes cyclooctatetraene, 1,5-cyclooctadiene, cyclohexene and norbornene [21]. The complex $[(\text{Pr}_2\text{PCH}_2\text{CH}_2\text{PPr}_2)_2\text{Rh}_2](\mu\text{-H})_2$ shows little or no tendency to react with cyclic alkenes [15]. The few successful reactions that have been accomplished involve C_5 or C_6 ring systems. Examples include the reaction between $\text{Os}_3(\text{CO})_{12}$ and cyclopentene in which there is 1,2-elimination of H_2 to give the cyclopenta-1,2-diylydene complex $\text{H}_2\text{Os}_3(\text{C}_5\text{H}_6)(\text{CO})_9$ [22] and the formation of $\text{Re}_2(\text{CO})_8(\mu\text{-H})(\mu\text{-C}_6\text{H}_{11})$ by photolysis of a mixture of $\text{Re}_2(\text{CO})_{10}$ and cyclohexene [19]. Continuing interest [23] in the activation of C-H bonds in cyclic alkenes prompted us to examine the reactions of these systems with $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$. We find that the reactions occur readily with a range of cyclic alkenes including cyclooctene and norbornene*.

The reaction with cyclooctene is typical of these systems. When a solution containing $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ and cyclooctene, C_8H_{14} , is exposed to sunlight for 1 h, the major products obtained are $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$

* The reactions with cyclic polyenes (e.g. cyclooctadiene, norbornadiene, cyclooctatetraene) and arenes (e.g. benzene, toluene) occur readily but are more complicated than the reactions described here. They will be discussed in a subsequent paper.

(50% yield) and $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{C}_8\text{H}_{13})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ (34% yield). NMR data for the latter complex (see Experimental) is consistent with the structure 14.

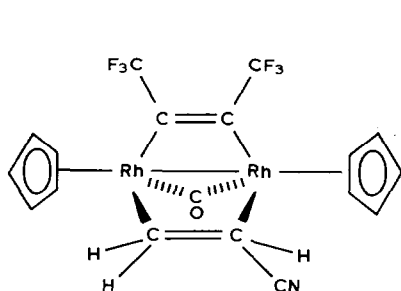


(14)

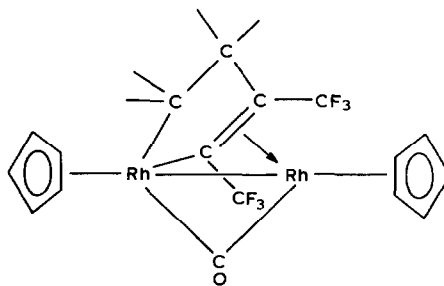
Reactions with activated alkenes

Some reactions with cyanoalkenes have been attempted, and the reaction with acrylonitrile, $\text{H}_2\text{C}=\text{CHCN}$, is especially interesting. When this reaction is done in the absence of sunlight, a product of formula $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{C}_2\text{H}_3\text{CN})(\text{C}_4\text{F}_6)$ is obtained. A bridging carbonyl absorption is observed at 1855 cm^{-1} in the infrared spectrum, and a band at 2220 cm^{-1} is assigned to $\nu(\text{C}\equiv\text{N})$. In the bis(alkenyl) complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$, which is discussed below, $\nu(\text{C}\equiv\text{N})$ is observed at 2217 cm^{-1} ; the molecular structure of this complex has been determined (vide infra) and it shows no interaction of the nitrile group with the metal atoms. Thus, it seems reasonable to conclude that the nitrile substituent is also 'free' in the present complex. In the NMR spectra, all resonances for the hydrogens of the coordinated acrylonitrile are found as multiplets in the region $\delta\ 1.85\text{--}2.23$. Each of the two CF_3 resonances is a quartet with $J(\text{F}\text{--}\text{F})\ 12\text{ Hz}$, but expansion of the spectrum shows that one of these quartets is actually a quartet of doublets with $J(\text{F}\text{--}\text{H})\ 2.3\text{ Hz}$. This is a small coupling constant compared to the values of ca. 9 Hz found for other complexes discussed in this paper which have a *gem*- $\text{C}(\text{CF}_3)\text{H}$ group. Thus, the ^{19}F spectrum indicates that there has not been H-transfer from $\text{H}_2\text{C}=\text{CHCN}$ to $\text{CF}_3\text{C}\equiv\text{CCF}_3$ in this complex.

The structures 15 and 16 are reasonably, but not entirely, consistent with these



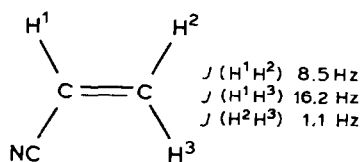
(15)



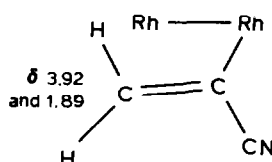
(16)

data. The proposed structure **15** is interesting because complexes in which an intact alkene bridges a M–M bond are rare *, and it is also unusual to have both monoalkene and monoalkyne ligands present within the same complex [26]. The metallacyclopentene structure **16** is related to a range of binuclear metallacyclopentadiene complexes ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(C₄R₄) [27,28]. A carbonyl needs to be retained in the present structure because there is only one 'ene' function in the metallacyclic ring.

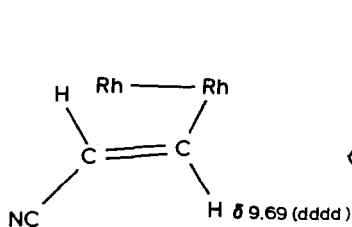
The observed multiplicities for the three acrylonitrile protons are ddd (J 8.5, 4.0 and 1.1), dq (J 16.2 and 2.3), and ddd (J 16.2, 8.5 and 1.0 Hz). As shown in **17** these multiplets can be assigned to the protons H², H³ and H¹ respectively. H² also couples to both rhodium atoms ($J(\text{H-Rh})$ 4 and 1 Hz), H³ couples to a CF₃ group ($J(\text{H-CF}_3)$ 2.3 Hz), and H¹ couples to one rhodium ($J(\text{H-Rh})$ 1.0 Hz). The observed coupling between H³ and CF₃ is difficult to rationalize in terms of the two proposed structures. If H–CF₃ coupling occurred in **15**, it should not be restricted to just one of the hydrogens. Coupling across the H–C–C–CF₃ system present in **16** has not been observed in any of the several rhodacyclopentadiene complexes ($\eta\text{-C}_5\text{H}_5$)₂Rh₂{C₄HR(CF₃)₂} we have prepared [29]. Nor is it detected in mononuclear complexes of the type (tmhd)Rh{CH₂CH₂C(CF₃)=C(CF₃)}L₂ which contain a rhodacyclopentene ring [30]. Thus, we are left in some doubt about the arrangement of these groups. Unfortunately, attempts to grow crystals of the compound suitable for X-ray diffraction have not been successful.



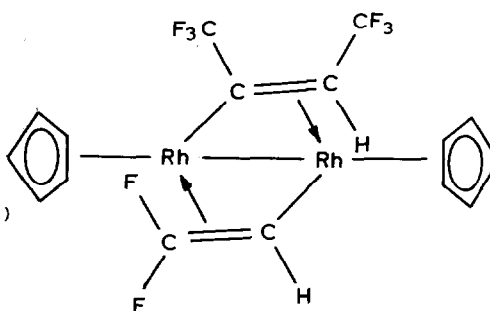
(17)



(18)



(19)



(20)

* A brief search of the recent literature has not revealed any complexes with the μ -alkene-M₂ arrangement. In the tetrafluoroethylene complex Fe₂(CO)₆(μ -SCMe)₂(μ -C₂F₄), the alkene bridges two metals but there is no metal–metal bond [24]. The acrylonitrile ligands in Re₂(CO)₈(H₂C=CHCN) are thought to be *N*-bonded [18]. The alkene ligands in cluster complexes such as Os₃(CO)₁₁(alkene) are η^2 -bonded to just one metal [25].

Exposure of a solution of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{C}_2\text{H}_3\text{CN})(\text{C}_4\text{F}_6)$ to sunlight results in rapid C–H bond cleavage with the formation of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ and $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\text{C}(\text{CN})=\text{CH}_2\}\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ in the ratio 2/1. The total conversion is 60% after 45 min. When these products are formed directly, by sunlight irradiation of a solution containing $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ and acrylonitrile, the proportion of the two regioisomers is again 2/1. The two isomers are readily identified from the NMR data given in **18** and **19**. The crystal structure of **19** is described below. The formation of two isomers in these reactions is probably more consistent with an intermediate like **15** rather than **16**.

In similar reactions with fumaronitrile and tetracyanoethylene, infrared data again indicates the formation of bridging carbonyl species of the type $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\text{alkene})(\text{CF}_3\text{C}_2\text{CF}_3)$. However, these complexes decompose in solution, and they have not been fully characterized.

The product obtained from sunlight irradiation of a mixture of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ and 1,1-difluoroethylene, $\text{H}_2\text{C}=\text{CF}_2$, has the formula $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{C}_2\text{H}_2\text{F}_2 \cdot \text{C}_4\text{F}_6)$, but it is not easy to characterize from NMR data. In the ^1H spectrum, two C_5H_5 resonances are observed plus multiplets at δ 8.02 and 3.63 for the two hydrogens from the alkene. The ^{19}F spectrum shows two CF_3 resonances plus doublet of multiplet signals for the two fluorines from the alkene.

TABLE 1

SUMMARY OF CRYSTAL STRUCTURE DATA FOR $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\} \cdot \text{H}_2\text{O}$ AND $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CF}_2)\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$

Mol. formula	$\text{C}_{17}\text{H}_{15}\text{F}_6\text{NORh}_2$	$\text{C}_{16}\text{H}_{12}\text{F}_8\text{Rh}_2$
Mol. wt.	569.1	562.1
<i>(a) Crystal data</i>		
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
Cell dimensions		
<i>a</i> (Å)	15.014(7)	13.037(6)
<i>b</i> (Å)	14.882(7)	8.765(2)
<i>c</i> (Å)	8.590(5)	14.873(3)
β (°)	94.57(9)	103.16(3)
<i>U</i> (Å ³)	1913(2)	1655(1)
Density, calcd.	1.98 (<i>Z</i> = 4)	2.26 (<i>Z</i> = 4)
measd. (g cm ⁻³)	2.01(3)	2.26(1)
<i>F</i> (000)	1096	1080
μ (Mo- <i>K</i> _α) (cm ⁻¹)	17.3	19.4
<i>(b) Data collection</i>		
Instrument	Philips PW1100	Syntex $P\bar{1}$
Radiation	Mo- <i>K</i> _α	Mo- <i>K</i> _α
<i>T</i> (K)	295	295
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{\text{max}}$ (°)	60	50
Scan rate (° s ⁻¹)	0.04	0.04
Total data	5560	2932
Data <i>I</i> > 3σ(<i>I</i>)	2493	1820
Final <i>R</i> and <i>R</i> _w	0.056, 0.056	0.062, 0.064

The latter are observed at δ 38.2 and 106.4, and this widely disparate nature of the CF_2 chemical shifts is not expected for a structure of the type **20**. This structure is, however, established from X-ray results which are detailed below. We have no explanation for this unusual feature of the ^{19}F NMR spectrum.

Crystal and molecular structures of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{-H}\} \cdot \text{H}_2\text{O}$ and $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CF}_2)\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$

Spectroscopic data on the large number of related complexes obtained in this work is consistent with the general formula $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{alkene} - \text{H})(\text{alkyne} + \text{H})$. It was important to confirm that our proposed structure was correct. We chose the

TABLE 2

FINAL POSITIONAL PARAMETERS FOR $\text{C}_{17}\text{H}_{15}\text{F}_6\text{NORh}_2$ (e.s.d. values in parentheses)

Atom	x	y	z
Rh(1)	0.37595(5)	0.37458(7)	0.44590(9)
Rh(2)	0.20521(5)	0.37237(7)	0.49270(9)
C(5)	0.3068(7)	0.4652(7)	0.5583(13)
C(6)	0.2315(8)	0.5173(8)	0.4918(14)
C(7)	0.1829(9)	0.5698(9)	0.5979(17)
C(1)	0.3682(11)	0.4384(11)	0.0925(15)
C(2)	0.3176(8)	0.4326(9)	0.2328(12)
C(3)	0.2640(7)	0.3614(8)	0.2869(13)
C(4)	0.2445(10)	0.2806(10)	0.1875(16)
F(11)	0.4299(6)	0.3768(7)	0.0714(10)
F(12)	0.4130(8)	0.5172(7)	0.0903(12)
F(13)	0.3118(7)	0.4359(9)	-0.0413(10)
F(41)	0.2478(7)	0.2036(6)	0.2672(11)
F(42)	0.3008(8)	0.2651(8)	0.0812(12)
F(43)	0.1676(7)	0.2829(7)	0.1159(12)
N	0.1474(10)	0.6097(11)	0.6830(17)
C(11)	0.4697(9)	0.2663(10)	0.3956(17)
C(12)	0.5175(10)	0.3488(10)	0.4195(19)
C(13)	0.5137(9)	0.3818(11)	0.5656(18)
C(14)	0.4599(10)	0.3169(10)	0.6412(17)
C(15)	0.4349(9)	0.2478(10)	0.5393(17)
C(21)	0.1446(21)	0.2445(18)	0.5476(32)
C(22)	0.1837(13)	0.2767(15)	0.6902(29)
C(23)	0.1346(14)	0.3551(13)	0.7105(21)
C(24)	0.0704(13)	0.3782(15)	0.5818(27)
C(25)	0.0742(19)	0.3028(18)	0.4812(27)
C(31)	0.1752(21)	0.2378(23)	0.6032(39)
C(32)	0.1650(29)	0.3079(29)	0.7176(38)
C(33)	0.1002(29)	0.3671(27)	0.6508(54)
C(34)	0.0592(29)	0.3376(29)	0.5080(55)
C(35)	0.1105(21)	0.2578(22)	0.4785(31)
O	0.4290(8)	0.0077(8)	0.3950(15)
C(10) ^a	0.479(-)	0.312(-)	0.512(-)
C(20) ^a	0.121(-)	0.311(-)	0.602(-)
C(30) ^a	0.122(-)	0.302(-)	0.592(-)

^a C(10), C(20) and C(30) are centroids of rings $n = 1, 2, 3$. Site occupancies for rings 2 and 3 respectively are 0.64(4), 0.36(4).

complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ for crystal structure determination because it was hoped that we could also structurally characterize the intermediate $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{C}_2\text{H}_3\text{CN})(\text{C}_4\text{F}_6)$. Unfortunately, the crystals of the latter were not suitable for X-ray study. Some aspects of the spectroscopic data for the complex obtained from $\text{CH}_2=\text{CF}_2$ were confusing; in particular, there were indications that the two alkene fluorines were in very different chemical environments. Uncertainty about the nature of this complex led us to determine its crystal and molecular structure. It turns out to be analogous to that of the acrylonitrile complex and consequently the structures of the two complexes are considered together.

Crystallography

Well-formed single crystals of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\} \cdot \text{H}_2\text{O}$ were grown from hexane/dichloromethane; a crystal of dimensions $0.12 \times 0.15 \times 0.18$ mm was selected. Crystal structure data are summarized in Table 1. Intensity data were processed as described previously [31]. A numerical absorption correction was applied, and atomic scattering factors for neutral atoms were taken from ref. 32. All calculations were performed on a DEC/VAX 11/780 computer. The program used for least-squares refinement was that due to Sheldrick [33]. The

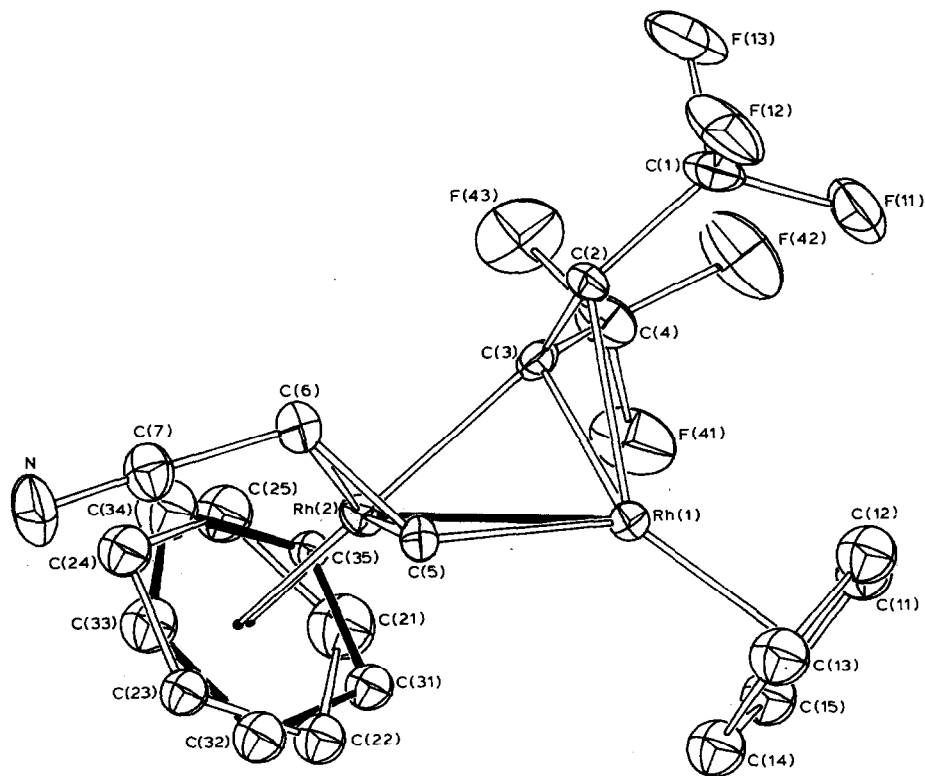


Fig. 5. Molecular structure of the complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$; 20% thermal ellipsoids are shown for the non-hydrogen atoms, together with the atom labelling scheme.

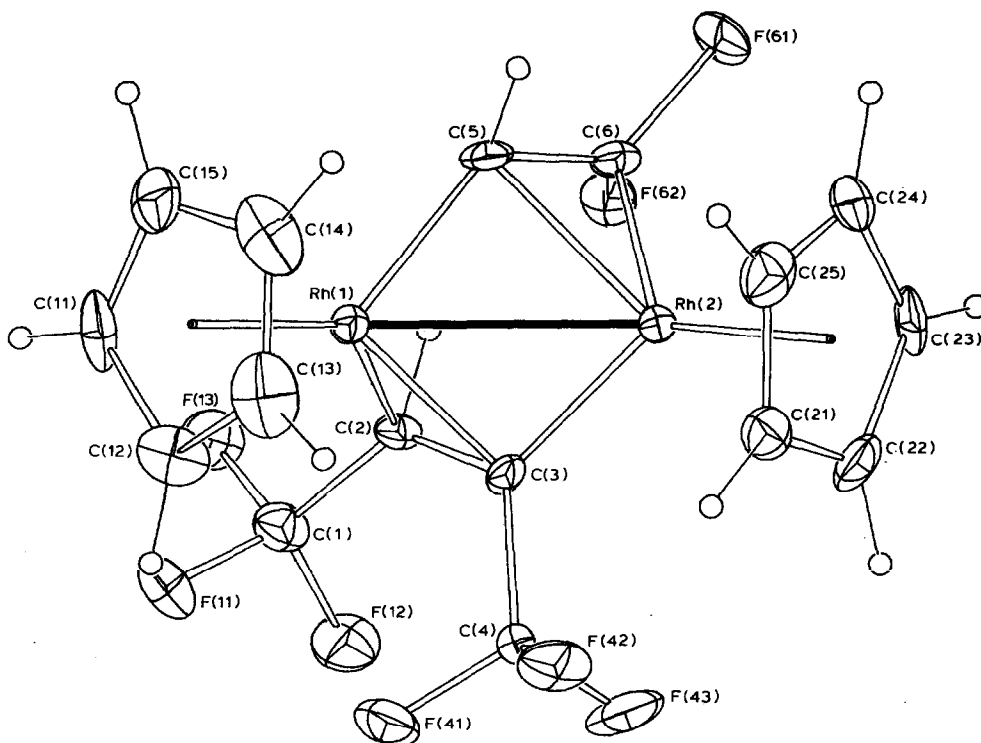


Fig. 6. Molecular structure of the complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CF}_2)\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$, showing 20% thermal ellipsoids for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1. The skeletal atom numbering scheme is shown.

structure was solved by conventional heavy-atom methods. Refinement of positional and isotropic temperature factors for Rh reduced R to 0.192. A difference Fourier synthesis at this stage yielded positions for the rest of the atoms except * those of the cyclopentadienyl ring associated with Rh(2) which appeared to be disordered. Several cycles of full-matrix least-squares refinement of all positional and anisotropic temperature factors (those of the cyclopentadienyl ring associated with Rh(1) and the water of crystallization were refined isotropically), reduced R to 0.083. At this stage, the disordered cyclopentadienyl ring could not be resolved into its component parts. Two sets of idealized coordinates for a cyclopentadienyl ring of typical dimensions were introduced into the calculation and with refinement of their occupancy R and R_w ($w = 1/\sigma^2(F)$) at convergence were 0.056, 0.056. A refinement was carried out with the constraints on the disordered cyclopentadienyl ring removed, but this resulted in atoms refining to chemically unacceptable positions. Hydrogen atoms were not included in the calculation. Atomic coordinates are given in Table 2, and Fig. 5 shows the atom labelling scheme.

The crystals of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CF}_2)\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ were grown from hexane/dichloromethane; a very small crystal of dimensions $0.02 \times 0.35 \times 0.06$ mm

* An artefact in the difference map ($4.5 \text{ e } \text{\AA}^{-3}$) was interpreted as being the oxygen atom of a water of crystallization. It is included as such in the refinement.

TABLE 3

FINAL POSITIONAL PARAMETERS FOR $C_{16}H_{12}F_8Rh_2$ (e.s.d. values in parentheses)

Atom	x	y	z
Rh(1)	0.22091(9)	0.1083(2)	0.20454(8)
Rh(2)	0.18930(9)	0.0182(2)	0.36461(8)
C(11)	0.256(1)	0.141(2)	0.069(1)
C(12)	0.342(1)	0.051(2)	0.127(1)
C(13)	0.303(2)	-0.077(2)	0.146(1)
C(14)	0.194(2)	-0.084(2)	0.110(1)
C(15)	0.169(2)	0.057(3)	0.059(1)
C(21)	0.274(1)	-0.195(2)	0.421(1)
C(22)	0.271(1)	-0.102(2)	0.493(1)
C(23)	0.164(1)	-0.076(2)	0.494(1)
C(24)	0.102(1)	-0.162(2)	0.420(1)
C(25)	0.170(2)	-0.238(2)	0.377(1)
C(1)	0.332(1)	0.431(2)	0.261(1)
F(11)	0.3928(8)	0.394(1)	0.2052(7)
F(12)	0.3938(8)	0.499(1)	0.3348(7)
F(13)	0.2687(8)	0.545(1)	0.2186(7)
C(2)	0.265(1)	0.308(2)	0.287(1)
C(3)	0.295(1)	0.172(2)	0.337(1)
C(4)	0.413(1)	0.141(2)	0.378(1)
F(41)	0.4756(7)	0.208(1)	0.3335(8)
F(42)	0.4378(8)	0.196(1)	0.4636(7)
F(43)	0.4384(7)	-0.002(1)	0.3834(8)
C(5)	0.088(1)	0.109(2)	0.243(1)
C(6)	0.066(1)	0.168(2)	0.325(1)
F(61)	-0.0259(7)	0.126(1)	0.3503(7)
F(62)	0.0763(7)	0.318(1)	0.3525(6)
C(10) ^a	0.253(-)	0.018(-)	0.102(-)
C(20) ^a	0.196(-)	-0.155(-)	0.441(-)

^a C(10) and C(20) are centroids of rings $n = 1, 2$.

was used. Table 1 summarizes the crystal structure data. The 'observed' data were used in the 9×9 block-diagonal least squares refinement after Gaussian absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})H$ were not located and were included constrained at estimated values. Residuals on $|F|$ at convergence were $R = 0.062$; $R_w = 0.064$ ($w = 1/\sigma^2(F)$; $\sigma^2(I) = \sigma_{diff}^2(I) + 0.00042\sigma^4(I)$). Neutral complex scattering factors were used [32]; computation used the XTAL-83 program system [34] implemented by S.R. Hall on a Perkin-Elmer 3240 computer. Atomic coordinates are given in Table 3, and Fig. 6 shows the atom labelling scheme.

Discussion of the structure

The molecular structures of the two complexes, which are shown in Figs. 5 and 6, are similar. The two figures provide different views of the geometric features. Tables 4 to 6 present selected bond parameters.

A metal-metal single bond is indicated by the Rh-Rh distances of ca. 2.63 Å. There are two alkenyl units, and each is attached in η^1, η^2 manner to the Rh-Rh

TABLE 4. RHODIUM ATOM ENVIRONMENTS, $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})(\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H})$ (The first column in each matrix is the metal–ligand distance (Å). Other entries are the angles (°) subtended at the metal by the relevant atoms at the head of each row and column. C(*n*0) is the centroid of cyclopentadienyl *n*)

Rh(1)	<i>r</i> (Å)	C(2)	C(3)	C(5)	C(10)
Rh(2)	2.627(1)	78.4(3)	49.8(3)	51.9(3)	138.4(–)
C(11)	2.20(1)	110.5(5)	107.2(5)	162.3(5)	33.3(–)
C(12)	2.19(2)	108.4(5)	130.8(5)	135.6(5)	31.8(–)
C(13)	2.24(1)	132.2(5)	166.2(5)	104.0(5)	33.3(–)
C(14)	2.19(1)	168.8(5)	147.9(5)	100.6(5)	32.2(–)
C(15)	2.21(1)	141.1(5)	115.8(5)	127.6(5)	32.9(–)
C(2)	2.15(1)	–	39.5(5)	87.0(5)	137.4(–)
C(3)	2.09(1)	39.5(5)	–	87.5(4)	139.7(–)
C(5)	2.00(1)	87.0(5)	87.5(4)	–	130.0(–)
C(10)	1.86(–)	137.4(–)	139.7(–)	130.0(–)	–

Rh(2)	<i>r</i> (Å)	C(3)	C(5)	C(6)	C(20)	C(30)
Rh(1)	2.627(1)	51.3(3)	48.4(3)	79.0(3)	142.1(–)	139.9(–)
C(3)	2.04(1)	–	86.0(4)	89.2(5)	138.8(–)	133.8(–)
C(5)	2.10(1)	86.0(4)	–	39.4(4)	133.5(–)	137.6(–)
C(6)	2.19(1)	89.2(5)	39.4(4)	–	127.5(–)	132.6(–)
C(20) ^a	1.86(–)	138.8(–)	133.5(–)	127.5(–)	–	5.2(–)
C(30) ^a	1.89(–)	133.8(–)	137.6(–)	132.6(–)	5.2(–)	–

^a Individual carbon atoms for these rings not included because rings are disordered and were constrained during structure solution.

TABLE 5. RHODIUM ATOM ENVIRONMENTS, $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CF}_2)(\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H})$ (The first column in each matrix is the metal–ligand distance (Å). Other entries are the angles (°) subtended at the metal by the relevant atoms at the head of each row and column. C(*n*0) is the centroid of cyclopentadienyl *n*)

Rh(1)	<i>r</i> (Å)	C(2)	C(3)	C(5)	C(10)
Rh(2)	2.628(2)	78.6(4)	49.6(5)	53.4(4)	136.8(–)
C(11)	2.18(2)	109.7(7)	134.0(7)	131.1(7)	33.0(–)
C(12)	2.21(2)	110.8(6)	109.1(6)	160.4(7)	32.0(–)
C(13)	2.23(2)	137.1(7)	114.3(7)	131.0(8)	31.2(–)
C(14)	2.17(2)	171.5(8)	143.1(7)	99.7(8)	33.5(–)
C(15)	2.16(2)	136.5(8)	169.5(7)	101.4(7)	33.1(–)
C(2)	2.14(2)	–	39.2(6)	88.2(7)	138.0(–)
C(3)	2.07(1)	39.2(6)	–	88.5(6)	139.5(–)
C(5)	1.95(2)	88.2(7)	88.5(6)	–	128.7(–)
C(10)	1.85(–)	138.0(–)	139.5(–)	128.7(–)	–

Rh(2)	<i>r</i> (Å)	C(3)	C(5)	C(6)	C(20)
Rh(1)	2.628(2)	50.8(4)	46.8(4)	79.7(4)	142.3(–)
C(21)	2.24(2)	109.3(6)	141.7(7)	158.3(6)	31.8(–)
C(22)	2.23(2)	105.7(6)	169.9(7)	137.8(7)	32.3(–)
C(23)	2.18(2)	132.1(6)	134.1(6)	103.2(7)	33.2(–)
C(24)	2.21(2)	167.6(6)	108.0(6)	97.4(6)	32.8(–)
C(25)	2.28(2)	139.9(7)	112.3(6)	124.1(7)	31.3(–)
C(3)	2.03(2)	–	84.4(6)	92.3(6)	135.4(–)
C(5)	2.14(1)	84.4(6)	–	39.3(6)	138.2(–)
C(6)	2.06(1)	92.3(6)	39.3(6)	–	127.9(–)
C(20)	1.88(–)	135.4(–)	138.2(–)	127.9(–)	–

TABLE 6

OTHER LIGAND GEOMETRIES (DISTANCES (Å), ANGLES (°) FOR (a) $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ AND (b) $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CF}_2)\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$

	a	b
C(1)–C(2)	1.48(2)	1.49(2)
C(2)–C(3)	1.43(2)	1.41(2)
C(3)–C(4)	1.49(2)	1.54(2)
C(5)–C(6)	1.45(2)	1.41(2)
C(6)–C(7)	1.44(2)	–
C(7)–N	1.11(2)	–
C(6)–F(61)	–	1.38(2)
C(6)–F(62)	–	1.37(2)
Rh(1)–C(2)–C(1)	119.1(10)	122.6(11)
Rh(1)–C(2)–C(3)	68.1(8)	67.8(9)
C(1)–C(2)–C(3)	129(1)	129(1)
Rh(1)–C(3)–Rh(2)	79.1(5)	79.6(5)
Rh(1)–C(3)–C(2)	72.7(8)	73.0(8)
Rh(1)–C(3)–C(4)	123.6(10)	122.1(11)
Rh(2)–C(3)–C(2)	121.1(10)	122.9(10)
Rh(2)–C(3)–C(4)	119.5(11)	117.5(11)
C(2)–C(3)–C(4)	119.2(14)	119.5(14)
Rh(1)–C(5)–Rh(2)	80.0(5)	79.8(5)
Rh(1)–C(5)–C(6)	126.3(11)	128.4(10)
Rh(2)–C(5)–C(6)	74.1(8)	67.1(8)
Rh(2)–C(6)–C(5)	67.0(8)	73.6(9)
Rh(2)–C(6)–C(7)	115.5(11)	–
Rh(2)–C(6)–F(61)	–	114.7(10)
Rh(2)–C(6)–F(62)	–	120.4(9)
C(5)–C(6)–F(61)	–	119.6(13)
C(5)–C(6)–F(62)	–	125.7(15)
F(61)–C(6)–F(62)	–	101.9(12)
C(6)–C(7)–N	177.4(21)	–

bond. Good least-squares planes are defined by the sets of atoms [Rh(2), C(1), C(2), C(3), C(4)] and [Rh(1), C(5), C(6), C(7), F(61)], and the dihedral angles between these planes are 95.8 and 90.6° for the acrylonitrile and difluoroethylene complexes respectively. The $\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}$ group is common to both complexes, and the two sets of bond parameters for C(1), C(2), C(3) and C(4) are nearly identical. There are minor variations in the Rh–C and C=C parameters for the units $\text{CH}=\text{CHCN}$ and $\text{CH}=\text{CF}_2$, the most significant being in the Rh(2)–C(6) π -bonding distances; the appropriate distances are 2.19(1) and 2.06(1) Å for the cyano and difluoro systems, respectively. The shorter distance in the latter complex presumably reflects the strong electron-withdrawing influence of the two fluorine atoms attached to the terminal carbon; the inductive effect of the one cyano group in the former complex would be less.

We have searched for possible structural explanations of the large chemical shift difference observed for F(61) and F(62) in the ^{19}F NMR spectrum of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CF}_2)\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$. Some relevant bond parameters for the complex, and those reported [35] for the gas phase structure of free $\text{CH}_2=\text{CF}_2$, are shown in Fig. 7. The angle F–C–F is somewhat sharper in the complex than in the

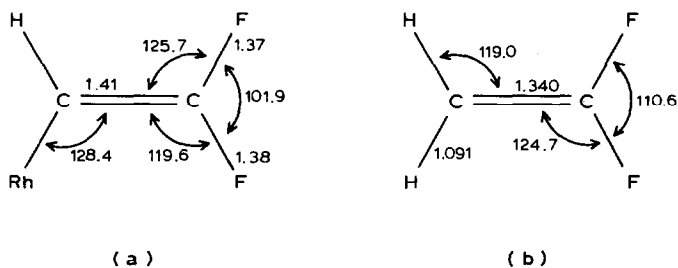


Fig. 7. Some bond parameters for (a) the coordinated alkenyl group $\text{CH}=\text{CF}_2$ and (b) the free alkene $\text{H}_2\text{C}=\text{CF}_2$.

free alkyne, and there are other minor changes upon coordination, but we see no geometric features that would account for the NMR results.

Other ligand geometries (Supplementary Table 3) are as expected for complexes of this type. An unexpected aspect of the molecular structure of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}=\text{CHCN})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ is the inclusion of an isolated oxygen atom which presumably belongs to a water of crystallization*. The closest contact for this atom is $\text{O} \cdots \text{O}'$ 2.69(2) Å; no other atoms are observed within 3.5 Å of the oxygen atom.

The structures of several other bi- and poly-nuclear alkenyl complexes have been reported. The most pertinent to this work are those of the 1-methylindenyl complex $(\text{C}_9\text{H}_6\text{CH}_3)_2\text{Rh}_2(\text{CH}=\text{CH}_2)(\text{CMe}=\text{CHMe})$ [36], the bisphosphine complex $(\text{Pr}^i\text{PCH}_2\text{CH}_2\text{PPr}^i)_2\text{Rh}_2(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)$ [15] and the phosphite complexes $\{\text{P}(\text{OPr}^i)_3\}_4\text{Rh}_2(\mu\text{-H})(\mu\text{-CR}=\text{CHR})$ ($\text{R} = \text{Me}$ or *p*-tolyl) [10]. The alkenyl C=C distances in these complexes span the range 1.36 to 1.43 Å; the C=C distances we observe are towards the upper end of this range. The spread of Rh-C σ -bonding distances in the reported structures is 2.05 to 2.11 Å, and our corresponding distances are at or beyond the lower end of this range. In all of the above complexes, plus some polynuclear osmium complexes of the types $\text{Os}_3(\text{CO})_{10}(\text{alkene}-\text{H})(\mu\text{-H})$ [37,38], $\text{Os}_4(\text{CO})_{11}(\text{alkene}-\text{H})(\mu\text{-H})$ [39] and $\text{Os}_4(\text{CO})_{11}(\text{alkene}-\text{H})(\mu\text{-H})_3$ [40], there is some difference in the two alkenyl C-M π -bonding distances. The shorter distance is always to the carbon which is σ -bonded to the other metal. The same effect is found for three of the four such interactions in our complexes. The opposite trend is observed for the $\text{Rh}_2(\mu\text{-CH}=\text{CF}_2)$ system and, as

* We are not certain that this is the correct interpretation of this artefact. There is no evidence from elemental analysis or from infrared results for water in crystals of the complex. A referee has suggested that the two peaks O and O', separated by 2.69 Å, could be the chlorine atoms from a molecule of dichloromethane solvent disordered across the inversion centre and present at an approximate total occupancy of 0.5. We have tried to check this possibility in two ways. First, we have refined the structure with $\frac{1}{2}\text{Cl}$ included in place of O, and then scrutinized the Fourier map. We note that the Cl has a high thermal parameter and that there is no significant electron density in positions where the carbon of CH_2Cl_2 could be located. This latter observation is not conclusive because only $\frac{1}{4}\text{C}$ is expected at each location. Second, we submitted some crystals of the complex for microprobe analysis. This provided no evidence for chlorine (calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_6\text{NRh}_2 \cdot 0.5 \text{CH}_2\text{Cl}_2$; Cl, 6.0%). Since this atom has no effect on the molecular structure of the complex, further effort to try to resolve the problem does not seem warranted.

discussed above, this probably reflects the very strong acceptor properties of the CF_2 carbon.

Summary and conclusions

The complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ is an excellent centre for the coordination of nucleophilic ligands. When solutions containing alkenes and $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ are exposed to sunlight, there is facile transfer of H from the alkene to one of the $=\text{C}(\text{CF}_3)$ carbons to give the bis-alkenyl complexes $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{alkene} - \text{H})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$. This is an interesting reaction because C-H bond activation generally requires electron-rich metal centres. It seems likely that the reactions proceed by initial nucleophilic attack of the intact alkene on the dirhodium compound to give intermediates of the type $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{alkene})(\text{CF}_3\text{C}_2\text{CF}_3)$. Indeed, such a complex can be isolated, but not fully characterized, when the alkene is acrylonitrile. Subsequent decarbonylation is accompanied by intramolecular H-transfer from the coordinated alkene to the alkyne ligand. Although the precise role of sunlight in activating these systems has not yet been elucidated, it seems to assist both steps.

The formation of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{alkene} - \text{H})\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ has been achieved with a range of acyclic and cyclic alkenes. With the substituted alkenes, $\text{H}_2\text{C}=\text{CHR}$ and $\text{RHC}=\text{CHR}'$, isomeric products are possible but the reactions generally proceed with some regioselectivity. Steric factors favor C-H bond cleavage at the least crowded alkene carbon.

An extension of this investigation will embrace acyclic and cyclic dienes and polyenes, and arenes. We have established that more than one C-H bond can be activated in many of these systems. The results will be discussed in a subsequent paper.

Experimental

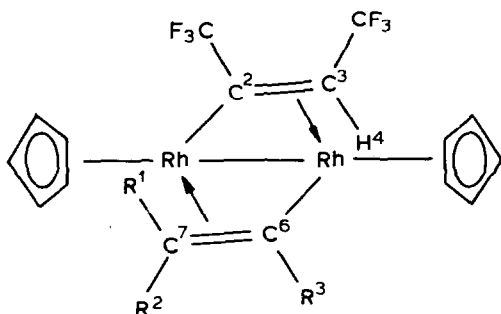
General

The general comments of parts I-III [5-7] are applicable. Generally, reactions were done in pyrex Carius tubes. These were placed in sunlight that had passed through a glass window pane.

Alkenes were obtained from the following sources; gases were used as received, liquids were distilled prior to use. Acrylonitrile (BDH Chemicals, Poole, England); 2-butene as a *cis/trans* mixture, ethylene and propene (Commonwealth Industrial Gases Ltd., Melbourne, Australia); *cis*-1,2-dichloroethylene (TCI, Tokyo, Japan); cyclooctene (Koch Light Laboratories, Bucks, England); 1,1-difluoroethylene (PCR Incorporated, Gainseville, USA); 3,3'-dimethyl-1-butene, norbornene, 2-pentene as a *cis/trans* mixture, *cis*-stilbene, *trans*-stilbene and styrene (EGA-Chemie, Steinheim, West Germany).

Reactions of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ with alkenes

The following diagram indicates the labelling of the hydrogens or substituents referred to in the NMR spectra. The reaction with ethylene is typical and is described in detail.



Ethylene (0.055 g) was condensed into a Carius tube containing $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{(CO)(CF}_3\text{C}_2\text{CF}_3)$ (0.100 g, mole ratio ca. 10/1) and hexane (15 ml). When the tube was exposed to sunlight, there was a color change from green to orange within 30 min. Removal of solvent and TLC with a 9/1 mixture of X4/Et₂O as eluent separated $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{(CO)}_2\text{(CF}_3\text{C}_2\text{CF}_3)$ [5] (0.052 g, 49%) and $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3\text{(CO)(CF}_3\text{C}_2\text{CF}_3)$ [4] [0.003 g, 2%) from an orange-red band. The latter gave orange-red crystals of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{(CHCH}_2\text{)}\{\text{C(CF}_3\text{)C(CF}_3\text{)H}\}$ (0.040 g, 40%) m.p. 159–160°C (Found: C, 36.7; H, 2.5; F, 21.5. C₁₆H₁₄F₆Rh₂ calcd.: C, 36.5; H, 2.7; F, 21.7%). Infrared: no strong absorptions in the region 2100–1600 cm⁻¹. ¹H NMR spectrum (CDCl₃): δ 9.50 (dddd, $J(\text{H}^1\text{-H}^3)$ 11.7, $J(\text{H}^2\text{-H}^3)$ 7.5, $J(\text{Rh-H}^3)$ 3.2 and 1.5 Hz, 1H, H³), 5.49 (s, 5H, C₅H₅), 5.33 (s, 5H, C₅H₅), 3.63 (m, 1H, H²), 2.03 (dm, $J(\text{H}^3\text{-H}^1)$ 11.7 Hz, 1H, H¹), 1.34 (qdd, $J(\text{F-H}^4)$ 9.7, $J(\text{Rh-H}^4) \approx J(\text{Rh-H}^4) \approx 2$ Hz, 1H, H⁴). ¹⁹F NMR spectrum (CDCl₃): δ 49.2 (q, $J(\text{F-F})$ 12 Hz, 3F, CF₃), 53.9 (m(A₃B₃X system), $J(\text{F-F})$ 12, $J(\text{H}^4\text{-F})$ 10 Hz, 3F, =C(CF₃)H). ¹³C{¹H} NMR spectrum (CDCl₃): δ 153.1 (dd, $J(\text{Rh-C})$ 33 and 13 Hz, C⁶), 144.3 (weak multiplet, C²), 128.7 (q, $J(\text{F-C})$ 274 Hz, CF₃), 126.5 (q, $J(\text{F-C})$ 274 Hz, CF₃), 88.2 (d, $J(\text{Rh-C})$ 5 Hz, C₅H₅), 86.0 (d, $J(\text{Rh-C})$ 5 Hz, C₅H₅), 56.7 (qdd, $J(\text{F-C})$ 38, $J(\text{Rh-C})$ 16 and 4 Hz, C³), 53.8 (d, $J(\text{Rh-C})$ 12 Hz, C⁷). Mass spectrum: 526 (5%, M), 525 (6%, M - H), 524 (32%, M - 2H), 498 (7%, M - C₂H₄), 233 (100%, C₁₀H₁₀Rh⁺).

Results for the reactions with other alkenes are summarized below:

(i) $\text{H}_2\text{C=CHMe}$. (mole ratio 20/1; irradiation time 30 min) gave $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{(CO)}_2\text{(CF}_3\text{C}_2\text{CF}_3)$ (51%) and $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3\text{(CO)(CF}_3\text{C}_2\text{CF}_3)$ (1%) plus two isomers of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{(C}_2\text{H}_2\text{Me)}\{\text{C(CF}_3\text{)C(CF}_3\text{)H}\}$ which could not be separated by chromatography. The isomer mixture was isolated as orange crystals (42% total yield; ratio of isomers 3/2 as indicated by NMR) (Found: C, 38.1; H, 3.1; F, 21.3. C₁₇H₁₆F₆Rh₂ calcd.: C, 37.8; H, 3.0; F, 21.1%). Mass spectrum: 540 (3%, M), 539 (2%, M - H), 538 (12%, M - 2H), 521 (1%, M - F), 498 (1%, M - C₃H₆), 233 (100%, C₁₀H₁₀Rh⁺). NMR spectra (CDCl₃): *major isomer*, ¹H, δ 9.04 (dm, $J(\text{H}^1\text{-H}^3)$ 8.5 Hz, 1H, H³), 5.47 (s, 5H, C₅H₅), 5.26 (s, 5H, C₅H₅), 2.86 (m, 1H, H¹), 1.58 (dd, $J(\text{H}^3\text{-Me}^2)$ 5.9, $J(\text{H}^1\text{-Me}^2)$ 1.5 Hz, 3H, Me²), 1.37 (qdd, $J(\text{CF}_3\text{-H}^4)$ 9.7, $J(\text{Rh-H}^4) \approx J(\text{Rh-H}^4) \approx 2$ Hz, 1H, H⁴); ¹⁹F, δ 48.6 (q, $J(\text{F-F})$ 12.2 Hz, 3F, CF₃), 53.9 (m(A₃B₃X system), $J(\text{F-F})$ 12.2, $J(\text{H}^4\text{-F})$ 10.9 Hz, 3F, C=C(CF₃)H; *minor isomer*, ¹H, δ 5.47 (s, 5H, C₅H₅), 5.29 (s, 5H, C₅H₅), 3.19 (m, 1H, H¹ or H²) 2.70 (s, 3H, Me³), 1.56 (m, 1H, H¹ or H²), 1.32 (qdd, $J(\text{CF}_3\text{-H}^4)$ 11.0, $J(\text{Rh-H}^4) \approx J(\text{Rh-H}^4) \approx 2$ Hz, 1H, H⁴); ¹⁹F, δ 49.3 (q, $J(\text{F-F})$ 12.2 Hz, 3F,

CF_3), 53.7 (m($\text{A}_3\text{B}_3\text{X}$ system), $J(\text{F}-\text{F})$ 12.2, $J(\text{H}^4-\text{F})$ 11.0 Hz, 3F, $\text{C}=\text{C}(\text{CF}_3)\text{H}$).

(ii) $\text{H}_2\text{C}=\text{CHPh}$. (mole ratio 10/1; irradiation time 45 min) gave ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CO)₂(CF₃C₂CF₃) (53%), ($\eta\text{-C}_5\text{H}_5$)₃Rh₃(CO)(CF₃C₂CF₃) (2%) and ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CHCHPh){C(CF₃)C(CF₃)H} (38%) m.p. 111°C (Found: C, 43.9; H, 3.2; F, 19.2. C₂₂H₁₈F₆Rh₂ calcd.: C, 43.9; H, 3.0; F, 18.9%). ¹H NMR spectrum (CDCl₃): δ 9.98 (ddd, $J(\text{H}^1-\text{H}^3)$ 11.7, $J(\text{Rh}-\text{H}^3)$ 3.5 and 1.2 Hz, 1H, H³), 7.20 (m, 5H, Ph), 5.55 (d, $J(\text{Rh}-\text{H})$ 0.6 Hz, 5H, C₅H₅), 4.98 (s, 5H, C₅H₅), 3.70 (dd, $J(\text{H}^3-\text{H}^1)$ 11.7, $J(\text{Rh}-\text{H}^1)$ ca. 2 Hz, 1H, H¹), 1.62 (dd, $J(\text{CF}_3-\text{H}^4)$ 9.7, $J(\text{Rh}-\text{H}^4)$ $\approx J(\text{Rh}'-\text{H}^4)$ 2 Hz, 1H, H⁴). ¹⁹F spectrum (CDCl₃): δ 48.6 (q, $J(\text{F}-\text{F})$ 13.2 Hz, 3F, CF₃), 53.7 (m($\text{A}_3\text{B}_3\text{MX}$ system), $J(\text{F}-\text{F})$ 13.2, $J(\text{H}^4-\text{F})$ 9.7, $J(\text{Rh}-\text{F})$ 2.3 Hz, 3F, $\text{C}=\text{C}(\text{CF}_3)\text{H}$). Mass spectrum: 602 (2%, M), 601 (1%, M - H), 600 (4%, M - 2H), 498 (8%, M - C₂H₃Ph), 438 (3%, M - C₄H₂F₆), 233 (100%, C₁₀H₁₀Rh⁺).

(iii) $\text{H}_2\text{C}=\text{CHBu}^t$. (mole ratio 10/1; irradiation time 30 min) gave ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CO)₂(CF₃C₂CF₃) (48%), ($\eta\text{-C}_5\text{H}_5$)₃Rh₃(CO)(CF₃C₂CF₃) (3%) and ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CHCHBu^t){C(CF₃)C(CF₃)H} (37%) m.p. 160°C (Found: C, 41.1; H, 3.7; F, 19.4. C₂₀H₂₂F₆Rh₂ calcd.: C, 41.3; H, 3.8; F, 19.6%). ¹H NMR spectrum (CDCl₃): δ 9.13 (ddd, $J(\text{H}^1-\text{H}^3)$ 12.0, $J(\text{Rh}-\text{H}^3)$ 3.5 and 1.1 Hz, 1H, H³), 5.48 (s, 5H, C₅H₅), 5.35 (s, 5H, C₅H₅), 2.79 (dd, $J(\text{H}^3-\text{H}^1)$ 12.0, $J(\text{Rh}-\text{H}^1)$ 2.1 Hz, 1H, H¹), 1.25 (qdd, $J(\text{CF}_3-\text{H}^4)$ 9.6, $J(\text{Rh}-\text{H}^4) \approx J(\text{Rh}'-\text{H}_4)$ 2.0 Hz, 1H, H⁴), 0.97 (s, 9H, Bu^t). ¹⁹F NMR spectrum (CDCl₃): δ 47.5 (q, $J(\text{F}-\text{F})$ 13.7 Hz, 3F, CF₃), 53.7 (m, ($\text{A}_3\text{B}_3\text{MX}$ system), $J(\text{F}-\text{F})$ 13.7, $J(\text{H}^4-\text{F})$ 9.6, $J(\text{Rh}-\text{F})$ 2.7 Hz, 3F, $\text{C}=\text{C}(\text{CF}_3)\text{H}$). Mass spectrum: 582 (3%, M), 580 (40%, M - 2H), 498 (2%, M - C₆H₁₂), 418 (6%, M - C₄H₂F₆), 233 (100%, C₁₀H₁₀Rh⁺).

(iv) $\text{HMeC}=\text{CMeH}$. (mole ratio 10/1; irradiation time 60 min) gave ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CO)₂(CF₃C₂CF₃) (49%) and ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CMeCHMe){C(CF₃)C(CF₃)H} (40%) m.p. 169°C (Found: C, 39.2; H, 3.0; F, 20.6. C₁₈H₁₈F₆Rh₂ calcd.: C, 39.0; H, 3.3; F, 20.6%). ¹H NMR spectrum (CDCl₃): δ 5.45 (s, 5H, C₅H₅), 5.22 (s, 5H, C₅H₅), 2.71 (s, 3H, Me³), 2.27 (qm, $J(\text{Me}-\text{H})$ ca. 6 Hz, 1H, H¹), 1.56 (dd, $J(\text{H}^1-\text{Me})$ 6.1, $J(\text{Rh}-\text{Me})$ 1.6 Hz, 3H, Me²), 1.29 (dd, $J(\text{CF}_3-\text{H}^4)$ 9.7, $J(\text{Rh}-\text{H}) \approx J(\text{Rh}'-\text{H})$ 2.1 Hz, 1H, H⁴). ¹⁹F NMR spectrum (CDCl₃): δ 48.4 (q, $J(\text{F}-\text{F})$ 13.2 Hz, 3F, CF₃), 53.3 (m($\text{A}_3\text{B}_3\text{MX}$ system), $J(\text{F}-\text{F})$ 13.2, $J(\text{H}^4-\text{F})$ 9.7, $J(\text{Rh}-\text{F})$ 2.5 Hz, 3F, $\text{C}=\text{C}(\text{CF}_3)\text{H}$). Mass spectrum: 554 (1%, M), 553 (1%, M - H), 552 (5%, M - 2H), 498 (9%, M - C₄H₈), 233 (100%, C₁₀H₁₀Rh⁺).

(v) *cis*- $\text{HMeC}=\text{CHEt}$. (mole ratio 10/1; irradiation time 30 min) gave ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CO)₂(CF₃C₂CF₃) (46%), ($\eta\text{-C}_5\text{H}_5$)₃Rh₃(CO)(CF₃C₂CF₃) (4%) and two isomers of ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(C₂HMeEt){C(CF₃)C(CF₃)H}. The major isomer was ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CMeCHEt){C(CF₃)C(CF₃)H} (24%) m.p. 157°C (Found: C, 40.6; H, 3.5; F, 20.1. C₁₉H₂₀F₆Rh₂ calcd.: C, 40.2; H, 3.6; F, 20.1%). ¹H NMR spectrum (CDCl₃): δ 5.45 (s, 5H, C₅H₅), 5.22 (s, 5H, C₅H₅), 2.72 (s, 3H, Me³), 2.07 (t, $J(\text{CH}_2-\text{H}^1)$ 4.4 Hz, 1H, H¹), 1.91 and 1.69 (m, 2H, CH₂), 1.29 (qdd, $J(\text{CF}_3-\text{H}^4)$ 9.8, $J(\text{Rh}-\text{H}^4) \approx J(\text{Rh}'-\text{H}^4) \approx 2$ Hz, 1H, H⁴), 1.01 (t, $J(\text{CH}_2-\text{CH}_3)$ 7.3 Hz, 3H, CH₂Me). ¹⁹F NMR spectrum (CDCl₃): δ 48.5 (q, $J(\text{F}-\text{F})$ 13.1 Hz, 3F, CF₃), 53.2 (m($\text{A}_3\text{B}_3\text{MX}$ system), $J(\text{F}-\text{F})$ 13.1, $J(\text{H}^4-\text{F})$ 9.8, $J(\text{Rh}-\text{F})$ 2.5 Hz, 3F, $\text{C}=\text{C}(\text{CF}_3)\text{H}$). Mass spectrum: 568 (2%, M), 567 (2%, M - H), 566 (9%, M - 2H), 498 (6%, M - C₅H₁₀), 233 (100%, C₁₀H₁₀Rh⁺).

The minor isomer was ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CEtCHMe){C(CF₃)C(CF₃)H} (16%) m.p. 170°C (Found: C, 40.3; H, 3.7; F, 20.1. C₁₉H₂₀F₆Rh₂ calcd.: C, 40.2; H, 3.6; F, 20.1%). ¹H NMR spectrum (CDCl₃): δ 5.45 (s, 5H, C₅H₅), 5.22 (s, 5H, C₅H₅), 2.79

(m, 2H, CH₂), 2.14 (qm, $J(\text{CH}_3\text{-H}^1)$ 6.1 Hz, 1H, H¹), 1.56 (dd, $J(\text{H-Me}^2)$ 6.1, $J(\text{Rh-Me}^2)$ 1.5 Hz, 3H, Me²), 1.29 (qdd, $J(\text{F-H}^4)$ 9.8, $J(\text{Rh-H}^4) \approx J(\text{Rh}^1\text{-H}^4) \approx 2$ Hz, 1H, H⁴), 1.12 (t, $J(\text{CH}_2\text{-CH}_3)$ 7.4 Hz, 3H, CH₂Me). ¹⁹F NMR spectrum (CDCl₃): δ 48.5 (q, $J(\text{F-F})$ 13.3 Hz, 3F, CF₃), 53.2 (m, (A₃B₃MX system), $J(\text{F-F})$ 13.3, $J(\text{H}^4\text{-F})$ 9.8, $J(\text{Rh-F})$ 2.5 Hz, 3F, C=C(CF₃)H). Mass spectrum: 568 (3%, M), 567 (2%, M-H), 566 (8%, M-2H), 498 (4%, M-C₅H₁₀), 233 (100%, C₁₀H₁₀Rh⁺).

(vi) *cis-CIHC=CHCl*. (mole ratio 10/1; irradiation time 30 min) gave ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CO)₂(CF₃C₂CF₃) (50%) and ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CClCHCl){C(CF₃)C(CF₃)H} (50%) m.p. 172°C dec. (Found: C, 32.6; H, 2.2; Cl, 11.9; F, 19.0. C₁₆H₁₂Cl₂F₆Rh₂ calcd.: C, 32.3; H, 2.0; Cl, 11.9; F, 19.2%). ¹H NMR spectrum (CDCl₃): δ 5.56 (s, 5H, C₅H₅), 5.43 (s, 5H, C₅H₅), 3.50 (d, $J(\text{Rh-H})$ 2.9 Hz, 1H, H¹), 1.47 (qdd, $J(\text{CF}_3\text{-H}^4)$ 9.1, $J(\text{Rh-H}^4) \approx J(\text{Rh}^1\text{-H}^4) \approx 2$ Hz, 1H, H⁴). ¹⁹F NMR spectrum (CDCl₃): δ 49.3 (q, $J(\text{F-F})$ 13.3 Hz, 3F, CF₃), 53.9 (m, 3F, CF₃). Mass spectrum (peaks for ³⁵Cl only are listed): 594 (6%, M), 558 (17%, M-Cl), 524 (85%, M-2Cl), 459 (22%, M-2Cl-C₅H₅), 406 (75%, n.a.), 233 (100%, C₁₀H₁₀Rh⁺).

(vii) *PhHC=CHPh*. (mole ratio 10/1; irradiation time 45 min) gave ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CO)₂(CF₃C₂CF₃) (52%), ($\eta\text{-C}_5\text{H}_5$)₃Rh₃(CO)(CF₃C₂CF₃) (2%) and ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CPhCHPh){C(CF₃)C(CF₃)H} (41%) m.p. 209°C. (Found: C, 49.4; H, 3.1; F, 16.8. C₂₈H₂₂F₆Rh₂ calcd.: C, 49.6; H, 3.3; F, 16.8%). ¹H NMR spectrum (CDCl₃): 7.38-6.63 (five multiplets, 10H, 2 × Ph), 5.19 (s, 5H, C₅H₅), 5.11 (s, 5H, C₅H₅), 3.02 (s, 1H, H¹), 1.80 (qm, $J(\text{CF}_3\text{-H}^4)$ 9.6 Hz, 1H, H⁴). ¹⁹F NMR spectrum (CDCl₃): 47.9 (q, $J(\text{F-F})$ 13.4 Hz, 3F, CF₃), 53.2 (m, (A₃B₃X system) $J(\text{F-F})$ 13.4, $J(\text{H}^4\text{-F})$ 9.6 Hz, 3F, C=C(CF₃)H). Mass spectrum: 682 (2%, n.a.), 678 (3%, M), 677 (3%, M-H), 676 (10%, M-2H), 512 (20%, M-CPh₂), 233 (100%, C₁₀H₁₀Rh⁺).

(viii) *H₃C=CHCN*. (mole ratio 5/1; irradiation time 30 min) gave ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CO)₂(CF₃C₂CF₃) (43%), ($\eta\text{-C}_5\text{H}_5$)₃Rh₃(CO)(CF₃C₂CF₃) (2%) and two isomers of ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(C₂H₂CN){C(CF₃)C(CF₃)H}. The minor isomer was ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(CH=CHCN){C(CF₃)C(CF₃)H} (29%) m.p. 155-156°C. (Found: C, 36.8; H, 2.2; N, 2.4. C₁₇H₁₃F₆NRh₂ calcd.: C, 37.0; H, 2.4; N, 2.5%). Infrared spectrum (CH₂Cl₂): $\nu(\text{C}\equiv\text{N})$ at 2217 cm⁻¹. ¹H NMR spectrum (CDCl₃): δ 9.69 (ddd, $J(\text{H}^1\text{-H}^3)$ 11.2, $J(\text{Rh-H}^3)$ 2.7, $J(\text{Rh}^1\text{-H}^3)$ 1.3 Hz, 1H, H³), 5.55 (s, 5H, C₅H₅), 5.45 (s, 5H, C₅H₅), 2.16 (dm, $J(\text{H}^3\text{-H}^1)$ 11.2 Hz, 1H, H¹), 1.32 (qdd, $J(\text{CF}_3\text{-H}^4)$ 9.4, $J(\text{Rh-H}^4) \approx J(\text{Rh}^1\text{-H}^4) \approx 2$ Hz, 1H, H⁴). ¹⁹F NMR spectrum (CDCl₃): δ 49.4 (q, $J(\text{F-F})$ 12.2 Hz, 3F, CF₃), 54.3 (m(A₃B₃X system), $J(\text{F-F})$ 12.2, $J(\text{H}^4\text{-F})$ 9.4 Hz, 3F, C=C(CF₃)H). Mass spectrum: 551 (5%, M), 550 (2%, M-H), 549 (12%, M-2H), 336 (5%, C₁₀H₁₀Rh₂⁺), 233 (100%, C₁₀H₁₀Rh⁺).

The major isomer was ($\eta\text{-C}_5\text{H}_5$)₂Rh₂(C(CN)=CH₂){C(CF₃)C(CF₃)H} (20%) m.p. 172-174°C. (Found: C, 37.4; H, 2.1; F, 20.4; N, 2.5. C₁₇H₁₃F₆NRh₂ calcd.: C, 37.1; H, 2.4; F, 20.7; N, 2.5%). Infrared spectrum (CH₂Cl₂): $\nu(\text{C}\equiv\text{N})$ at 2210 cm⁻¹. ¹H NMR spectrum (CDCl₃): δ 5.56 (s, 5H, C₅H₅), 5.49 (s, 5H, C₅H₅), 3.92 (dd, $J(\text{H}^1\text{-H}^2) \approx J(\text{Rh-H})$ 2.3 Hz, 1H, H), 1.89 (br.m, 1H, H), 1.46 (qm, $J(\text{CF}_3\text{-H}^4)$ 9.2 Hz, 1H, H⁴). ¹⁹F NMR spectrum (CDCl₃): δ 49.7 (q, $J(\text{F-F})$ 12.2 Hz, 3F, CF₃), 54.1 (m(A₃B₃X system), $J(\text{F-F})$ 12.2, $J(\text{H}^4\text{-F})$ 9.2 Hz, 3F, C=C(CF₃)H). Mass spectrum: 551 (7%, M), 550 (1%, M-H), 549 (12%, M-2H), 446 (10%, n.a.), 233 (100%, C₁₀H₁₀Rh⁺).

Repetition of the reaction with no irradiation from sunlight gave, as the major product, crimson crystals of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{H}_2\text{C}_2\text{HCN})(\text{CF}_3\text{C}_2\text{CF}_3)$ (40% yield after 24 h at 25°C) m.p. 235°C. (Found: C, 37.6; H, 2.3; F, 20.0; N, 2.5. $\text{C}_{18}\text{H}_{13}\text{F}_6\text{NORh}_2$ calcd.: C, 37.3; H, 2.3; F, 19.7; N, 2.4%). Infrared spectrum (CH_2Cl_2): $\nu(\text{C}\equiv\text{N})$ at 2220, $\nu(\text{CO})$ at 1855 cm^{-1} . ^1H NMR spectrum (CDCl_3): δ 5.61 (d, $J(\text{Rh}-\text{H})$ 1.0 Hz, 5H, C_5H_5), 5.59 (d, $J(\text{Rh}-\text{H})$, 1.0 Hz, 5H, C_5H_5), multiplets at 2.23, 2.18 and 1.85 (3H, $\text{CH}_2=\text{CHCN}$). ^{19}F NMR spectrum (CDCl_3): δ 50.8 (q, $J(\text{F}-\text{F})$ 12.2 Hz, 3F, CF_3), 59.4 (qd, $J(\text{F}-\text{F})$ 12.2 and $J(\text{F}-\text{H})$ 2.3 Hz, 3F, CF_3). Mass spectrum: 579 (4%, M), 551 (12%, $M - \text{CO}$), 550 (5%, $M - \text{CO} - \text{H}$), 549 (24%, $M - \text{CO} - 2\text{H}$), 524 (10%, $M - \text{CO} - \text{HCN}$), 233 (100%, $\text{C}_{10}\text{H}_{10}\text{Rh}^+$).

(ix) $\text{CH}_2=\text{CF}_2$. (mole ratio 20/1; irradiation time 60 min) gave unchanged $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ (10%), $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$ (48%), $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ (4%) and $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CHCF}_2)\{\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{H}\}$ (23%) m.p. 151–152°C. (Found: C, 34.6; H, 1.9; F, 27.0. $\text{C}_{16}\text{H}_{12}\text{F}_8\text{Rh}_2$ calcd.: C, 34.2; H, 2.2; F, 27.0%). ^1H NMR spectrum (CDCl_3): δ 8.02 (m, 1H, H^3), 5.57 (s, 5H, C_5H_5), 5.50 (s, 5H, C_5H_5), 3.63 (sext.m, $J(\text{F}-\text{H}^4)$ 9.2 Hz, H^4). ^{19}F NMR spectrum (CDCl_3): δ 38.2 (dm, $J(\text{F}^1-\text{F}^2)$ 106 Hz, 1F, $\text{F}^{1\text{ or }2}$), 49.8 (q, $J(\text{F}-\text{F})$ 12.2 Hz, 3F, CF_3), 54.2 (m, ($\text{A}_3\text{B}_3\text{X}$ system), $J(\text{F}-\text{F})$ 12.2, $J(\text{H}^4-\text{F})$ 9.2 Hz, 3F, $\text{C}=\text{C}(\text{CF}_3)\text{H}$), 106.4 (dm, $J(\text{F}^1-\text{F}^2)$ 106 Hz, 1F, $\text{F}^{1\text{ or }2}$). Mass spectrum: 562 (3%, M), 542 (8%, $M - \text{HF}$), 498 (5%, $M - \text{C}_2\text{H}_2\text{F}_2$), 233 (100%, $\text{C}_{10}\text{H}_{10}\text{Rh}^+$).

(c) Reactions of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ with cyclic alkenes

(i) Cyclooctene. C_8H_{14} (mole ratio 10/1; irradiation time 60 min) gave $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$ (50%), $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ (1%) and $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{C}_8\text{H}_{13})\{\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{H}\}$ (34%) m.p. 194°C (dec.). (Found: C, 43.7; H, 4.1; F, 18.9. $\text{C}_{22}\text{H}_{24}\text{F}_6\text{Rh}_2$ calcd.: C, 43.4; H, 4.0; F, 18.7%). ^1H NMR spectrum (CDCl_3): δ 5.45 (s, 5H, C_5H_5), 5.23 (s, 5H, C_5H_5), 3.0–0.9 (overlapping multiplets, 14H, $\text{C}_8\text{H}_{13} + \text{C}=\text{C}(\text{CF}_3)\text{H}$). ^{19}F NMR spectrum (CDCl_3): δ 48.4 (q, $J(\text{F}-\text{F})$ 12.2 Hz, 3F, CF_3), 53.4 (m, ($\text{A}_3\text{B}_3\text{X}$ system), $J(\text{F}-\text{F})$ 12.2, $J(\text{H}-\text{F}) \approx 9$ Hz, 3F, $\text{C}(\text{CF}_3)\text{H}$). Mass spectrum: 608 (4%, M), 607 (2%, $M - \text{H}$), 606 (6%, $M - 2\text{H}$), 498 (5%, $M - \text{C}_8\text{H}_{14}$), 442 (85%, $M - \text{C}_4\text{H}_4\text{F}_6$), 233 (100%, $\text{C}_{10}\text{H}_{10}\text{Rh}^+$).

(ii) Norbornene. C_7H_{10} (mole ratio 10/1; irradiation time 45 min) gave $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$ (43%) and $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{C}_7\text{H}_9)\{\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{H}\}$ (47%) m.p. 174°C. (Found: C, 42.9; H, 3.4; F, 19.2. $\text{C}_{21}\text{H}_{20}\text{F}_6\text{Rh}_2$ calcd.: C, 42.6; H, 3.4; F, 19.3%). ^1H NMR spectrum (CDCl_3): δ 5.49 (s, 5H, C_5H_5), 5.30 (s, 5H, C_5H_5), multiplets at 3.15 (1H), 2.44 (2H) and 1.6–0.9 (7H) ($\text{C}_7\text{H}_9 + \text{C}(\text{CF}_3)\text{H}$). ^{19}F NMR spectrum (CDCl_3): δ 49.4 (q, $J(\text{F}-\text{F})$ 12.2 Hz, 3F, CF_3), 53.4 (m, ($\text{A}_3\text{B}_3\text{X}$ system), $J(\text{F}-\text{F})$ 12.2, $J(\text{H}-\text{F}) \approx 9$ Hz, 3F, $\text{C}(\text{CF}_3)\text{H}$). Mass spectrum: 592 (2%, M), 591 (2%, $M - \text{H}$), 590 (8%, $M - 2\text{H}$), 233 (100%, $\text{C}_{10}\text{H}_{10}\text{Rh}^+$).

Acknowledgements

This work was supported by grants from the Australian Research Grants Scheme. One of us (S.M.J.) thanks the Government for a Commonwealth Postgraduate Research Award. We are grateful to Johnson–Matthey for the loan of rhodium trichloride.

References

- 1 J.P. Collman and L.S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, California, 1980.
- 2 G.W. Parshall, *Homogeneous Catalysis*, Wiley-Interscience, New York, 1980.
- 3 J. Halpern, *Inorg. Chim. Acta*, 100 (1985) 41.
- 4 R.H. Crabtree and C.P. Parnell, *Organometallics*, 4 (1985) 519.
- 5 R.S. Dickson, A.P. Oppenheim and G.N. Pain, *J. Organomet. Chem.*, 224 (1982) 377.
- 6 R.S. Dickson, G.D. Fallon, R.J. Nesbit and G.N. Pain, *Organometallics*, 4 (1985) 355.
- 7 R.S. Dickson, R.J. Nesbit, H. Pateras, C.W. Baimbridge, J.M. Patrick and A.H. White, *Organometallics*, 4 (1985) 2128.
- 8 See, for example, references 12–19.
- 9 Assignments and measurements of coupling constants assisted by decoupling experiments.
- 10 R.R. Burch, A.J. Shusterman, E.L. Muetterties, R.G. Teller and J.M. Williams, *J. Am. Chem. Soc.*, 105 (1983) 3546; see also, references 15, 19.
- 11 R.S. Dickson, C. Mok and G.N. Pain, *J. Organomet. Chem.*, 166 (1979) 385.
- 12 Z. Dawoodi and M.J. Mays, *J. Chem. Soc., Dalton Trans.*, (1984) 1931.
- 13 M.R. Awang, J.C. Jeffery and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1983) 1426.
- 14 R.E. Colborn, A.F. Dyke, S.A.R. Knox, K.A. Mead and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1983) 2099.
- 15 M.D. Fryzuk, T. Jones and F.W.B. Einstein, *Organometallics*, 3 (1984) 185.
- 16 J.B. Keister and J.R. Shapley, *J. Organomet. Chem.*, 85 (1975) C29.
- 17 S. Bhaduri, B.F.G. Johnson, J.W. Kelland, J. Lewis, P.R. Raithby, S. Rehani, G.M. Sheldrick, K. Wong and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1979) 562.
- 18 P.O. Nubel and T.L. Brown, *J. Am. Chem. Soc.*, 106 (1984) 644 and 3474.
- 19 K-H. Franzreb and C.G. Kreiter, *J. Organomet. Chem.*, 246 (1983) 189.
- 20 A.J. Canty, A.J.P. Domingos, B.F.G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1973) 2056.
- 21 A.J. Deeming, S. Hasso, M. Underhill, A.J. Canty, B.F.G. Johnson, W.G. Jackson, J. Lewis and T.W. Matheson, *J. Chem. Soc., Chem. Commun.*, (1974) 807.
- 22 A.J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, (1974) 1415.
- 23 R.H. Crabtree and C.P. Parnell, *Organometallics*, 4 (1985) 519; and references therein.
- 24 J.J. Bonnet, R. Mathieu, R. Poilblanc and J.A. Ibers, *J. Am. Chem. Soc.*, 101 (1979) 7487.
- 25 Z. Dawoodi, M.J. Mays, P.R. Raithby, K. Henrick, W. Clegg and G. Weber, *J. Organomet. Chem.*, 249 (1983) 149; and references therein.
- 26 M.E. Howden, R.D.W. Kemmitt and M.D. Schilling, *J. Chem. Soc., Dalton Trans.*, (1983) 2459.
- 27 R.S. Dickson, *Organometallic Chemistry of Rhodium and Iridium*, Chapter VI, Academic Press, London, 1983.
- 28 C.W. Baimbridge, R.S. Dickson, G.D. Fallon, I. Grayson, R.J. Nesbit and J. Weigold, *Aust. J. Chem.*, in press.
- 29 R.S. Dickson and R.J. Nesbit, unpublished results.
- 30 M.E. Howden, R.D.W. Kemmitt and M.D. Schilling, *J. Chem. Soc., Dalton Trans.*, (1983) 2459.
- 31 A.J. Canty, N. Chiachit and B.M. Gatehouse, *Acta Crystallogr.*, B, 36 (1980) 786.
- 32 J.A. Ibers and W.C. Hamilton (Eds.), *International Tables for X-Ray Crystallography Vol. 4* Kynoch Press; Birmingham. 1974.
- 33 G.M. Sheldrick, *SHELX-76 Program for Crystal Structure Determination* Cambridge; England, 1975.
- 34 J.M. Stewart and S.R. Hall (Eds.), *The XTAL System of Crystallographic Programs: User's Manual*, Technical Report TR-901, Computer Science Centre, University of Maryland, U.S.A., 1983.
- 35 F.C. Mijlhoff, G.H. Renes, K. Kohata, K. Oyanagi and K. Kuchitsu, *J. Mol. Struct.*, 39 (1977) 241.
- 36 P. Caddy, M. Green, L.E. Smart and N. White, *J. Chem. Soc., Chem. Commun.*, (1978) 839.
- 37 J.J. Guy, B.E. Reichert and G.M. Sheldrick, *Acta Crystallogr.*, B, 32 (1976) 3319.
- 38 A.G. Orpen, A.V. Rivera, E.G. Bryan, D. Pippard and G.M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, (1978) 723.
- 39 A.D. Claus, M. Tachikawa, J.R. Shapley and C.G. Pierpont, *Inorg. Chem.*, 20 (1981) 1528.
- 40 S. Bhaduri, B.F.G. Johnson, J.W. Kelland, J. Lewis, P.R. Raithby, S. Rehani, G.M. Sheldrick, K. Wong and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1979) 562.
- 41 R.S. Dickson, C. Mok and G.N. Pain, *J. Organomet. Chem.*, 166 (1979) 385.