Journal of Organometallic Chemistry, 394 (1990) 583–599
Elsevier Sequoia S.A., Lausanne
JOM 20907

Syntheses, structures, and reactions of alkenyl-dirhodium complexes: coupling μ-methylene and σ-vinyl to allyl; an entry to μ-ethylidene-μ-methylene dirhodium complexes. Crystal structures of $[\{(C_5Me_5Rh)(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$ and $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)Cl_2]$ *

Jesus Martinez, John B. Gill, Harry Adams, Neil A. Bailey, Isabel M. Saez, Glenn J. Sunley and Peter M. Maitlis *

Department of Chemistry, The University, Sheffield S3 7HF (U.K.)

(Received February 7th, 1990)

Abstract

Reaction of $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2Cl_2]$ with $R'CH{=}CHMgBr$ gave the dialkenyl-di-μ-methylenedirhodium complexes $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CHR')_2]$, (**4**, $R' = H$; **5**, $R' = Me$). Coupling of the μ-methylene and the σ-alkenyl occurs very easily: on heating (giving ca. 90% $R'C_3H_5$ olefins), and on reaction with $AgBF_4$ in MeCN (giving η^3-allylic complexes, $[C_5Me_5Rh(R'CHCHCH_2)(MeCN)]^+$; the *anti*-methylallyl isomer is the first product observed from reaction of **5** with $AgBF_4$, indicating that the coupling is stereospecific). The divinyl complex **4** also reacted with HCl in polar solvents to give the allyl, $[C_5Me_5Rh(\eta^3\text{-}C_3H_5)Cl]$ (**10**), and then $[(C_5Me_5RhCl_2)_2]$ and propene, and in non-polar solvents to yield the μ-methylene-μ-ethylidene complex $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)(Cl)_2]$ (**13a**) and propene. The reversible reaction of **4** with HCl/pentane gave an unstable complex, identified by ^1H NMR as *cis*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(CHClMe)_2]$ (**14**). The complexes have been identified spectroscopically and by X-ray crystal structure determinations on di-σ-vinyldi-μ-methylenebis(pentamethylcyclopentadienylrhodium) (**4**), and dichloro-μ-methylene-μ-ethylidenebis(pentamethylcyclopentadienylrhodium) (**13a**).

Introduction

The chemistry of various substituted di-μ-methylenedirhodium complexes $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(R)_2]$, (R = alkyl), $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CO)_2]^{2+}$, $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(R)L]^+$, (R = alkyl, L = MeCN, CO, etc), has been explored by our group

---

* Dedicated, with all best wishes, to Gordon Stone.

0022-328X/90/$03.50

[1]. The reactions of such complexes are of considerable interest since C–C and C–C–C couplings readily occur and, by suitable labelling, the decomposition paths can be elucidated [2]. Such reactions are shedding new light on, for example, the mechanism of Fischer–Tropsch polymerisation [3]. We here report the syntheses of the divinyldi-μ-methylene-dirhodium complex, $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CH_2)_2]$ (**4**), the related dipropenyl complex, $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CHMe)_2]$ (**5**), as well as mixed complexes, $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CH_2)Me]$ (**7**), and $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CHMe)Me]$ (**8**), and some of their reactions. Parts of this work have been communicated [4].

Results and discussion

Syntheses and structures of the σ-vinyl and σ-alkenyl complexes

$$[\{C_5Me_5RhCl_2\}_2] \xrightarrow{Al_2Me_6,\ Me_2CO} [(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(Me)_2]$$

(**1**) (**2**)

$$\mathbf{2} \xrightarrow{HCl} [(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(Cl)_2]$$

(**3**)

$$\mathbf{3} \xrightarrow{R'CH{=}CHMgBr} [(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CHR')_2]$$

(**4**, R′ = H; **5**, R′ = Me)

The divinyl complex **4** was prepared (75% yield) by reaction of the dichlorocomplex **3**, prepared as illustrated above from **1** and **2** [1b], with vinyl magnesium bromide. The complex was identified as the *trans*-isomer spectroscopically (Tables 1–3), which showed the presence of a terminal vinyl (IR, ν(C=C) 1559 cm^{-1}; ^{1}H NMR, δ 4.59 (dm), 5.21 (dm), and 5.97 (ddt); J(H–H) 8.5, 16.5 Hz; N(Rh–H) 1.5 Hz), and of a symmetrical μ-methylene (δ 8.09, t, J(Rh–H) 1 Hz).

The identity of the complex as **4** was confirmed by a single crystal X-ray determination (Fig. 1). This showed the expected centrosymmetric geometry with the two rhodiums directly linked (2.588(2) Å; Table 5), each bearing an η^5-C_5Me_5 and a σ-vinyl (Rh–C 2.001 (10) Å), and bridged by two μ-methylenes (Rh–C 1.982(9), 2.011(6) Å). The four atom bridge plane is located across a crystallographically imposed inversion centre. The η^5-C_5Me_5 rings are slightly asymmetrically bonded (RMS deviation of skeletal atoms from the mean plane, 0.012 Å) with the Rh 1.938 Å to one side of a ring and the methyls tilted away (by up to 0.19 Å) on the other. The Rh-σ-vinyl bond length is close to that expected for a Rh–C(sp^2) bond (cf. Rh–Me in *cis*-**2** is 2.102(16), 2.135(16) Å), but the vinylic bond is unexpectedly short (1.250(15) Å) for a C=C, and the angle Rh–C=C has been enlarged to 130.8(7)°. By comparison to the Rh–Rh bond length in **4** of 2.588(2) Å, those found in *cis*-**2** of 2.620(1) Å, and in *trans*-$[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CO)_2]^{2+}$ [1b], of 2.659(1) Å, are significantly longer. The difference lies in the short Rh–μ-CH_2 bonds present in **4** (1.982(9), 2.011(6) Å) compared to those in the dicarbonyl dication (2.060(7), 2.061(6) Å) rather than in the angles Rh–μ-C–Rh which are nearly the same (80.4, 80.8°).

Table 1

Microanalytical and infrared data

Complex	Microanalysis [a]			ν(C=C) [b] (cm^{-1})	M [c]
	C	H	X		
4	55.5	7.5		1559s	
	(55.9)	(7.2)			
5	56.9	7.8		1582m	586
	(57.3)	(7.6)			
7	54.9	7.3		1558s	
	(55.0)	(7.4)			
8	55.5	7.8		1586m	559 ($M-1$)
	(55.7)	(7.6)			
9a	43.7	5.7	3.7 N		320 (M^+)
	(44.3)	(5.7)	(3.4)		
9b	42.3	5.1		ν(CO), 2073s	307 (M^+)
	(42.7)	(5.1)			
9c	42.6	6.5			355 (M^+)
	(43.5)	(6.6)			
9d	48.3	5.6	3.0 N		358 (M^+)
	(48.6)	(5.7)	(3.2)		
10	49.3	6.7	11.5 Cl		314
	(49.6)	(6.4)	(11.3)		
13a	46.6	6.3	12.0 Cl		
	(46.9)	(6.2)	(12.0)		
13b	40.5	5.3	24.0 Br		
	(40.7)	(5.4)	(23.6)		
14	49.0	6.2	11.6 Cl		
	(49.5)	(6.7)	(11.2)		

[a] Analysis. Found (calcd.) (%). [b] Nujol mull. [c] Molecular peak from FAB mass spectrum.

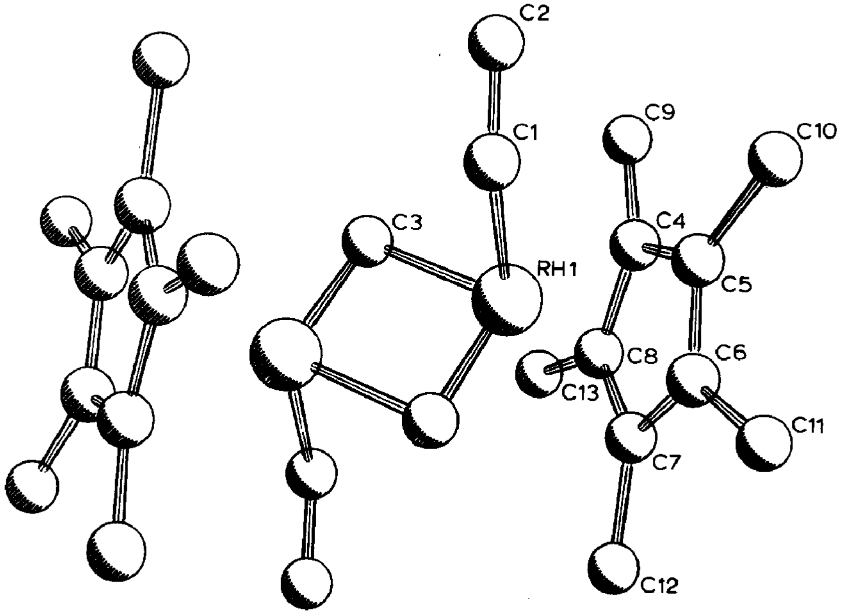


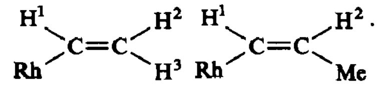
Fig. 1. The molecular structure of complex **4** with atom labelling.

Table 2a

^1H NMR spectra (δ (ppm)) in $CDCl_3$ [a]

Complex	C_5Me_5	μ-CH_2	μ-CHMe	vinyl [b]			Me
				H^1	H^2	H^3 (Me)	
4	1.63	8.09t [1]		5.97ddt (tr, 16.5) (*Z*, 8.5) [1.5]	5.21dm	4.59dm	
5	1.65	8.37br		5.32dm (*Z*, 8.5)	5.60m	1.70dd (H^2Me, 6.5) (H^1Me, 1)	
7	1.61d [1]	7.86ddd (3) [3] [1]		5.97ddd (tr, 16.5) (*Z*, 8.5) [2]	5.20ddd (*gem*, 1) [3]	4.55ddd [1]	−0.93d [2.5]
	1.67d [1]	8.06dd (3) [3]					
8	1.61d [1]	7.97br		5.28dm (*Z*, 9) (H^1Me, 1.5) [1.5]	5.60dqd (H^2Me, 6.5) [3]	1.70dd	−0.95d [3]
	1.69	8.26br					
13a	1.56	10.16ddd (4) [2] [2]	CH, 11.46qdd (7) [2.5] [2.5] Me, 2.85ddd (7) [1] [1]				
	1.59	10.58ddd (4) [2] [2]					
13b	1.64	10.35ddd (4) [2] [2]	CH, 11.74qdd (7) [2.5] [2.5] Me, 2.96ddd (7) [1] [1]				
	1.65	10.76ddd (4) [2] [2]					

[a] *J*(H–H) (Hz) values are in parentheses and *J*(Rh–H) (Hz) in square brackets.

[b] 

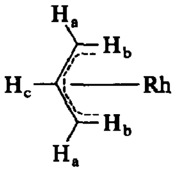
The di-σ-propenyl complex **5** was prepared similarly by reaction of the dichloro-complex **3** with propenyl magnesium bromide (mainly *Z*-isomer). The NMR spectrum of **5** was consistent with the propenyls (and the C_5Me_5 rings) being mutually *trans*- (e.g. only one μ-CH_2 resonance), while the geometry about the propenyl double bond was *Z*-(*cis*-). This last point was shown by the magnitude of the vicinal propenyl *J*(H–H) of 8.5 Hz, indicating a *cis*-disposition of hydrogens. By comparison, the divinyl **4** showed two vicinal H–H couplings, one of 8.5 Hz (*Z*), the other of 16.5 Hz (*E*)

Table 2b

^1H NMR spectra (δ(ppm)) in $CDCl_3$ [a]

Complex	C_5Me_5	allyl [b]			Other
		H_a	H_b	H_c	
9a	1.84	3.60d	2.68d	4.21m	MeCN, 2.42
9b	2.13	3.60d	2.99d	4.66m	
9c	1.92d [c]	3.01dm	2.02ddm [d]	3.98m [e]	Me_3P, 1.47dd [f]
9d	1.71	3.91d	2.31d	4.41m	py, 7.55m, 7.92m, 8.54m
10	1.72	3.40d	2.83d	4.05d	

[a] J(H–H) (Hz) values are in parentheses and J(Rh–H) (Hz) in square brackets.

[b] 
$J(H_a-H_c)$ 7, $J(H_b-H_c)$ 11, $J(Rh-H_c)$ 2 Hz.

[c] J(P–H) 3 Hz. [d] $J(P-H_b)$ 14 Hz. [e] $J(P-H_c)$ 1 Hz. [f] J(P–H) 10, J(Rh–H) 1 Hz.

Table 3a

$^{13}C\{^1H\}$ NMR spectra (δ/ppm) in $CDCl_3$ [a]

Complex	$C_5\mathit{Me}_5$	C_5Me_5	μ-CH_2	vinyl [b]			Me
				C^1	C^2	Me	
4	10.0	101.1	167.1t [29]	157.8dd [43] [4]	117.6		
5	9.9	101.4	166.1br	146.4dd [44] [4]	126.9	19.8	
7	9.6	100.4d [3]	163.9t [29]	157.7d [38]	116.8d [2]		−2.4d [33]
	10.1	100.9d [3]					
8	9.4	100.6d [3]	163.5t [29]	146.1d [40]	126.2	19.5	−3.0d [33]
	10.3	101.1d [3]					
13a	9.4	102.1d [5]	CH_2, 186.1t [26] CH, 207.3t [25] Me, 34.7				
	9.7	103.2d [5]					
13b	10.0	102.4d	182.4t [26]				
		103.5					

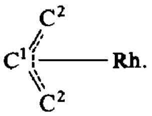
[a] J(Rh–C) (Hz) values are in square brackets. [b] $Rh-C^1{=}C^2$.

Table 3b

$^{13}C\{^1H\}$ NMR spectra (δ (ppm)) in $CDCl_3$ [a]

Complex	$C_5\mathit{Me}_5$	C_5Me_5	allyl [b]		Other
			C^1	C^2	
9a [c]	9.4	100.9d [6]	97.4d [6]	60.6d [9]	MeCN, 3.4, 126.1
9b	9.8	106.2d [5]	94.6d [5]	56.8d [9]	CO, 186.7d [77]
9c [d]	9.7d [1]	101.5dd [5] (2)	88.6dd [5] (2)	51.3dd [11] (3)	PMe_3, 16.1dd [1] (33)
9d	9.0	99.4d [6]	96.8d [6]	61.9d [10]	py, 127.2, 139.2, 155.4
10	9.4	97.9d [7]	94.5d [6]	60.0d [10]	

[a] J(Rh–C) (Hz) values are in square brackets. [b] Rh–C^1 = C^2.

[b]


[c] In $(CD_3)_2CO$. [d] J(P–C) (Hz) are in parentheses.

In addition to these symmetrical di-alkenyl complexes, we have also made the methyl-vinyl and the methyl-propenyl complexes, **7** and **8**, by reaction of **6** with the appropriate alkenyl Grignard,

$$\underset{(\mathbf{2})}{\left[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(Me)_2\right]} \xrightarrow{H^+/MeCN;\ Cl^-} \underset{(\mathbf{6})}{\left[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(Cl)Me\right]}$$

$$\mathbf{6} \xrightarrow{R'CH{=}CHMgBr} [(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CHR')Me]$$

$$(\mathbf{7},\ R' = H;\ \mathbf{8},\ R' = Me)$$

The NMR spectra of **7** and **8** are again consistent with *trans*-C_5Me_5 rings, using the rule of thumb previously adumbrated [1c] that in such geometries the difference in chemical shift of the two methylene ^1H resonances is less than ca. 0.5 ppm. Once again, the propenyl in **8** also has the *Z*-configuration, $J(H\text{-}H_{vic})$ 9 Hz.

The ^{13}C NMR spectra also confirm the structures proposed for the complexes **4**, **5**, **7** and **8**. Thus, for example, both **7** and **8** showed two signals for both the C_5 and the Me_5 of the two different η^5 rings, while **4** and **5** showed only one set. The μ-methylene carbons were triplets, with couplings of ca. 30 Hz, implying that they were equivalently bonded to both rhodiums. For the symmetric complexes **4** and **5** the α-carbons of the vinyls were observed as double doublets, J(Rh–C) 44 and 4 Hz respectively, indicating strong coupling to one Rh, and weak coupling to the other. The α-vinyl carbons of the asymmetric complexes **7** and **8** were doublets, J(Rh–C) ca. 39 Hz, and the methyls were also simple doublets, J(Rh–C) 33 Hz. Thus the spectra confirmed the structures and indicated no significant mobility at these temperatures.

Table 4

Atom coordinates ($\times 10^4$) and temperature factors (Å$^2 \times 10^3$) for $[\{(C_5Me_5Rh)(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$

Atom	x	y	z	U_{eq} [a]
Rh(1)	100(1)	523(1)	1024(1)	37(1)
C(1)	625(15)	1503(5)	−96(10)	94(5)
C(2)	1956(14)	1947(5)	81(10)	87(4)
C(3)	1884(9)	−220(6)	653(7)	69(3)
C(4)	1342(9)	814(5)	3254(6)	55(2)
C(5)	104(9)	1458(4)	2699(6)	53(2)
C(6)	−1472(8)	1050(5)	2288(6)	55(3)
C(7)	−1288(11)	156(5)	2616(7)	66(3)
C(8)	457(14)	−3(5)	3238(7)	75(4)
C(9)	3214(10)	980(9)	3903(9)	111(5)
C(10)	443(14)	2441(5)	2691(9)	93(4)
C(11)	−3183(11)	1541(8)	1672(10)	116(5)
C(12)	−2664(18)	−511(7)	2453(13)	149(8)
C(13)	1253(19)	−867(7)	3833(9)	138(7)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Reactions of the divinyl complex 4

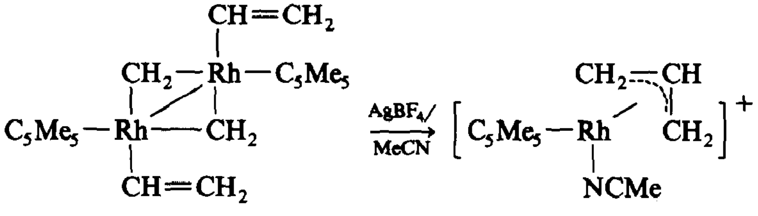
(i) Reactions with oxidants (Ag^+); the coupling of μ-methylene and σ-vinyl to η^3-allyl. Reaction of the divinyl complex **4** with silver tetrafluoroborate (molar ratio 1/2) in acetonitrile/THF (1/1, to improve solubility), gave a deposit of silver metal and the ionic η^3-allyl complex **9a** in 85% yield. On reaction with the

Table 5

Bond lengths (Å) and angles (°) with estimated standard deviations for $[\{(C_5Me_5Rh)(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$ (4)

Rh(1)–Rh(1a)	2.588(2)	Rh(1)–C(1)	2.001(10)
Rh(1)–C(3)	1.982(9)	Rh(1)–C(3a)	2.011(6)
Rh(1)–C(4)	2.230(6)	Rh(1)–C(5)	2.220(7)
Rh(1)–C(6)	2.254(8)	Rh(1)–C(7)	2.344(10)
Rh(1)–C(8)	2.333(7)	C(1)–C(2)	1.250(15)
C(4)–C(5)	1.392(10)	C(4)–C(8)	1.429(12)
C(5)–C(6)	1.378(10)	C(6)–C(7)	1.385(11)
C(7)–C(8)	1.397(13)	C(4)–C(9)	1.496(10)
C(5)–C(10)	1.506(11)	C(6)–C(11)	1.539(12)
C(7)–C(12)	1.484(16)	C(8)–C(13)	1.496(13)
C(1)–Rh(1)–C(3)	89.7(4)	C(1)–Rh(1)–C(3a)	86.8(4)
C(3)–Rh(1)–C(3a)	99.2(3)	Rh(1)–C(1)–C(2)	130.8(7)
Rh(1)–C(3)–Rh(1a)	80.8(3)	C(5)–C(4)–C(8)	106.8(7)
C(5)–C(4)–C(9)	125.8(8)	C(8)–C(4)–C(9)	127.0(8)
C(4)–C(5)–C(6)	108.2(6)	C(4)–C(5)–C(10)	125.0(7)
C(6)–C(5)–C(10)	126.5(7)	C(5)–C(6)–C(7)	109.9(6)
C(5)–C(6)–C(11)	124.4(7)	C(7)–C(6)–C(11)	125.5(7)
C(6)–C(7)–C(8)	107.1(7)	C(6)–C(7)–C(12)	127.6(8)
C(8)–C(7)–C(12)	125.2(8)	C(4)–C(8)–C(7)	107.9(7)
C(4)–C(8)–C(13)	126.0(9)	C(7)–C(8)–C(13)	126.1(9)

appropriate ligands, this was converted into (again in high yields) the chloride **10**, and the ionic complexes (9b-d).



(4) (9a)

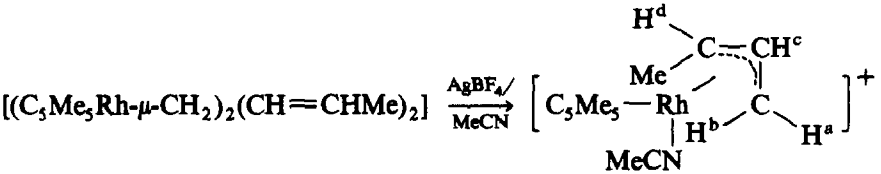
$$[C_5Me_5Rh(\eta^3\text{-}C_3H_5)(MeCN)]BF_4 + Cl^- \longrightarrow [C_5Me_5Rh(\eta^3\text{-}C_3H_5)(Cl)]$$

(9a) **(10)**

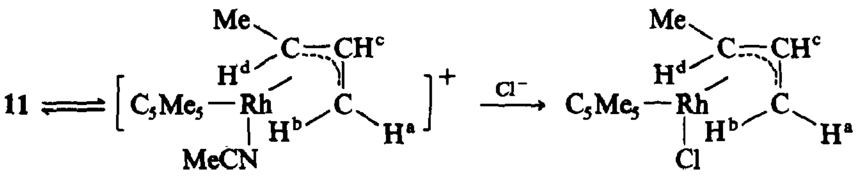
$$\mathbf{9a} + L \longrightarrow [C_5Me_5Rh(\eta^3\text{-}C_3H_5)(L)]BF_4$$

(**9b**, L = CO; **9c**, L = PMe$_3$; **9d**, L = py)

The dipropenyl complex **5** also reacted with AgBF$_4$ in acetonitrile/THF, to give the 1-methylallyl cation, [C$_5$Me$_5$Rh(η^3-MeC$_3$H$_4$)(MeCN)]BF$_4$ (**11**). The ^{1}H NMR spectrum of the freshly prepared solution showed that the *anti*-methyl isomer was formed (CD$_3$CN, δ 1.00 (d, Me); 1.73 (C$_5$Me$_5$), 2.91 (d, H^b), 3.64 (d, H^a), 4.10 (m, H^d), 4.32 (m, H^c); J(Me-H^d) 6, J(H^c-H^a) 7, J(H^c-H^b) 11 Hz). On standing in solution, signals due to the *syn*-methyl isomer appeared, and on addition of tetraphenylarsonium chloride, the known [5] *syn*-methylallyl chloride complex **12** was formed (^{1}H NMR (CDCl$_3$): δ 1.61 (d, Me), 1.72 (C$_5$Me$_5$), 2.88 (d, H^b), 3.28 (d, H^a), 3.50 (m, H^d), and 3.92 (m, H^c); J(Me-H^d) 6, J(H^b-H^c) 11, J(H^a-H^c) 6.5, J(H^c-H^d) 11, J(H^c-Rh) 2.5 Hz). Isomerisation of methylallylrhodium complexes has been well-documented; the fact that the initial product has the *anti*-Me geometry is completely consistent with a stereospecific coupling of the Z-propenyl and the μ-methylene, showing no rotation about the propenyl bond has occurred during that step.



(11)



(12)

(ii) Products from pyrolyses. C–C coupling also occurred when the complexes were pyrolysed; the major products were olefins resulting from the combination of a μ-methylene with an alkenyl. Thus, the divinyl complex **4** at 330 °C gave a mixture of gases containing propene (88%) and methane (8%), together with traces of other hydrocarbons. The dipropenyl complex (**5**) at 340 °C gave 90% butenes (mixed 1- and 2-isomers, ratio 25/65), as well as methane (6%) and propene (3%).

The products from the methyl-alkenyl complexes were more complicated, but again a major reaction pathway was the methylene plus alkenyl coupling. Thus, for example, the methyl vinyl complex **7** gave largely propene (63%), some ethene (14%), methane (12%), and butenes (9%). The methylpropenyl complex **8** gave largely butenes (77%), some methane (12%), propene (7%), and ethene (4%).

(iii) Reactions with hydrogen halides. The most unexpected reactions of the divinyl complex **4** were with HCl. The precise products depended greatly on the exact conditions. Thus, with HCl/$CDCl_3$ the main product was the allyl complex **10**, especially at low conversion, together with propene and the dimer **1**, $[(C_5Me_5RhCl_2)_2]$. It was shown separately that the η^3-allyl complex **10** reacted readily with HCl to give the chloride **1** and propene.

$$\underset{\textbf{(4)}}{[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CH_2)_2]} \xrightarrow{HCl} \underset{\textbf{(10)}}{\left[(C_5Me_5Rh\left(\eta^3\text{-}C_3H_5\right)Cl\right]} +$$

$$\underset{\textbf{(1)}}{\left[(C_5Me_5RhCl_2)_2\right]} + CH_2{=}CHCH_3 + \underset{\textbf{(13a)}}{\left[(C_5Me_5Rh)_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)(Cl)_2\right]}$$

$$2\underset{\textbf{(10)}}{\left[C_5Me_5Rh\left(\eta^3\text{-}C_3H_5\right)Cl\right]} + 2HCl \longrightarrow \underset{\textbf{(1)}}{\left[(C_5Me_5RhCl_2)_2\right]} + 2\,CH_2{=}CHCH_3$$

In addition, a new complex **13a** was formed in the presence of an excess of HCl; the relative yields of **1** and **13a** depended on solvent, more of the allyl complex (and

Table 6

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)Cl_2]$

Atom	x	y	z	U_{eq} [a]
Rh(1)	701(1)	137(1)	295(1)	43(1)
Cl(1)	996(2)	200(6)	−2241(4)	120(3)
C(1)	991(8)	586(13)	2500(15)	61(6)
C(2)	1186(8)	−376(15)	2354(18)	75(7)
C(3)	1710(7)	−446(11)	1298(17)	62(6)
C(4)	1858(7)	515(12)	817(15)	61(5)
C(5)	1413(7)	1110(11)	1583(14)	48(5)
C(6)	494(8)	955(15)	3713(16)	94(8)
C(7)	917(11)	−1106(16)	3351(21)	120(10)
C(8)	2121(10)	−1300(16)	839(27)	132(12)
C(9)	2426(8)	778(14)	−293(19)	93(8)
C(10)	1415(8)	2136(13)	1556(22)	98(9)
C(11)	−107(9)	1044(11)	−68(23)	83(7)
C(12)	−286	1759	580	123(16) [b]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. [b] Atom C(12) has 50% occupancy.

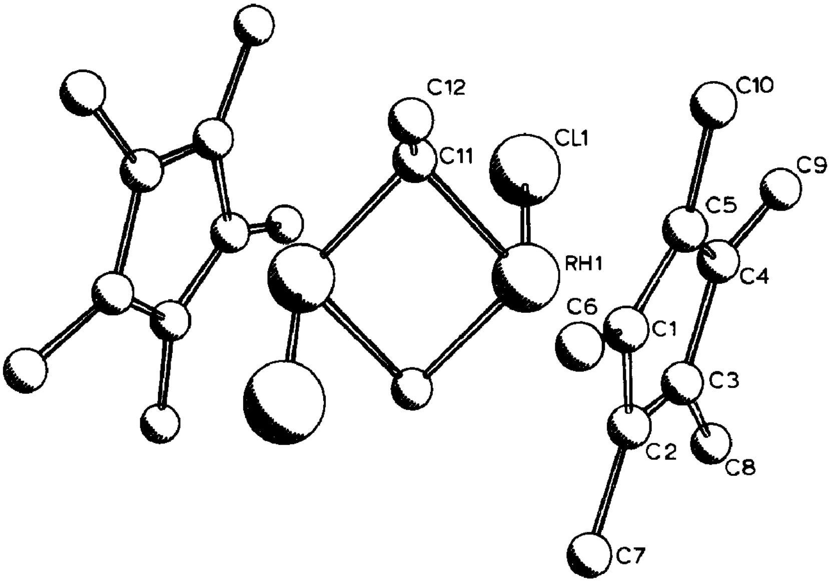


Fig. 2. The molecular structure of complex **13a** with atom labelling (the bridging ligands are disordered across the centre of the molecule).

hence of **1**) being formed in the more polar solvents. For example, only **1** was formed in THF or nitromethane; the yield of **13a** was 20% in acetone, 25% in chloroform, but 50% in toluene at ambient temperatures. The best yield of **13a** was

Table 7

Bond lengths (Å) and angles (°) with estimated standard deviations for $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)Cl_2]$

Rh(1)–Cl(1)	2.406(5)	Rh(1)–C(1)	2.203(15)
Rh(1)–C(2)	2.228(17)	Rh(1)–C(3)	2.244(15)
Rh(1)–C(4)	2.259(14)	Rh(1)–C(5)	2.258(14)
Rh(1)–C(11)	2.010(17)	Rh(1)–Rh(1) [a]	2.678(3)
Rh(1)–C(11) [a]	2.031(16)	C(1)–C(2)	1.434(28)
C(1)–C(5)	1.374(21)	C(1)–C(6)	1.543(22)
C(2)–C(3)	1.378(22)	C(2)–C(7)	1.482(28)
C(3)–C(4)	1.475(23)	C(3)–C(8)	1.503(27)
C(4)–C(5)	1.380(20)	C(4)–C(9)	1.515(21)
C(5)–C(10)	1.474(24)	C(11)–C(12)	1.233(18)
Cl(1)–Rh(1)–C(11)	89.0(6)	Cl(1)–Rh(1)–C(11) [a]	93.1(6)
C(11)–Rh(1)–C(11) [a]	97.0(6)	C(2)–C(1)–C(5)	109.0(13)
C(2)–C(1)–C(6)	123.3(15)	C(5)–C(1)–C(6)	126.7(17)
C(1)–C(2)–C(3)	108.3(16)	C(1)–C(2)–C(7)	122.6(15)
C(3)–C(2)–C(7)	128.6(18)	C(2)–C(3)–C(4)	106.0(15)
C(2)–C(3)–C(8)	127.8(17)	C(4)–C(3)–C(8)	125.8(14)
C(3)–C(4)–C(5)	108.3(12)	C(3)–C(4)–C(9)	124.4(14)
C(5)–C(4)–C(9)	127.3(15)	C(1)–C(5)–C(4)	108.4(14)
C(1)–C(5)–C(10)	124.0(14)	C(4)–C(5)–C(10)	127.4(13)
Rh(1)–C(11)–C(12)	131.2(13)	Rh(1)–C(11)–Rh(1) [a]	83.0(6)
C(12)–C(11)–Rh(1) [a]	126.9(12)		

[a] Symmetry operation is $[-x, -y, -z]$.

in toluene at −78° when a yield of 67% was obtained. Very similar results were obtained when **4** was reacted with HBr; in this case the dibromo analogue **13b** was formed, but in lower yield (optimal 50% in pentane), together with $[(C_5Me_5RhBr_2)_2]$. In both reactions the organic product was shown to be propene.

The new complex **13a** was identified as the *trans*-dichloro-μ-ethylidene-μ-methylene complex by a single crystal X-ray structure determination (Fig. 2), and by NMR spectroscopy. The molecule of complex **13a** comprises two rhodium atoms, each bearing an η^5-C_5Me_5 ring and a Cl, and bridged by one μ-CH_2 and one μ-CHMe; the C_5Me_5 ligands are *trans* to each other, as are the chlorides. The Rh–Rh distance, 2.678(3) Å (Table 7), is a little greater than in other complexes of this series, (cf. 2.659 Å in $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CO)_2]^{2+}$, 2.620(1) Å in *cis*-**2**, and 2.588 Å in $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(CH{=}CH_2)_2]$), but is still well within bonding range, as required for a diamagnetic complex of Rh^{IV}. The C_5Me_5 ligands are symmetrically η^5-bonded with the ring atoms close to the mean plane (rms deviation 0.009 Å); the rhodium is 1.890 Å from this plane on one side and the methyls are displaced (0.05–0.22 Å) away from it on the other. The bridging ligands are disordered across a crystallographic inversion centre, and thus no detailed comparison can be made between their bridging geometries, but they appear very similar to those in the di-μ-methylene complexes. The ^1H NMR spectrum confirms the X-ray, and the absence of a centre of symmetry in the molecule is shown in particular by two different signals for the two μ-CH_2 hydrogens (Table 2).

A sparingly soluble orange solid (**14**) with analysis corresponding to $[\{C_5Me_5Rh(\mu\text{-}CH_2)(CHClMe)\}_2]$, was obtained from reaction of **4** with HCl gas in pentane. The reaction to give **14** was reversible; thus, on standing, the orange solid slowly lost HCl to regenerate the divinyl complex **4**. Unfortunately the material was also too unstable to be crystallised; no X-ray structure determination was therefore possible and only rather limited ^1H NMR spectra could be obtained. In C_6D_6, the ^1H NMR of **4** showed four equal intensity triplets (*J* 1–2 Hz) in the methylene region, two C_5Me_5, and two doublets in the methyl region (1.68, 1.71 (overlapping a C_5Me_5), *J* 7 Hz), coupled to a multiplet at δ 3.44. This spectrum is consistent with a bis-σ-(1-chloroethyl) complex having a *cis*-geometry, and the presence of a

$$[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CH_2)_2] \xrightarrow{HCl}$$

(4)

$$[(C_5Me_5)Rh(H)(CH{=}CH_2)(\mu\text{-}CH_2)_2Rh(Cl)(CH{=}CH_2)(C_5Me_5)] \longrightarrow$$

$$[(C_5Me_5)(H)(CH_2CH{=}CH_2)Rh(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(CH{=}CH_2)(C_5Me_5)] \longrightarrow$$

$$CH_2{=}CHCH_3 + [(C_5Me_5)Rh(\mu^{?}\text{-}CH_2)(\mu\text{-}Cl)(\mu^{?}\text{-}CH{=}CH_2)Rh(C_5Me_5)] \xrightarrow{HCl}$$

(I)

$$[(C_5Me_5)Rh(Cl)(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(H)(CH{=}CH_2)(C_5Me_5)] \longrightarrow$$

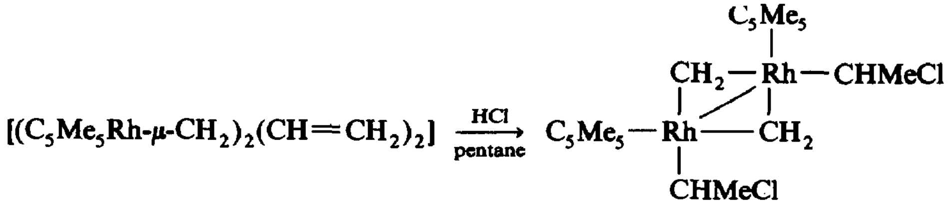
$$[(C_5Me_5)Rh(Cl)(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(CHCH_3)(C_5Me_5)] \longrightarrow$$

$$[C_5Me_5Rh)_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)(Cl)_2]$$

(13a)

Scheme 1

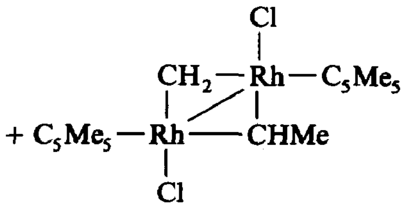
mixture of equal parts of the *meso*- and the *d*- + *l*- (racemic) isomers, arising from the chirality of the two CHClMe ligands. Consistent with this formulation of **14** as *cis*-$[\{C_5Me_5Rh(\mu\text{-}CH_2)(CHClMe)\}_2]$, arising from addition of HCl to the double bonds of **4**, the vinylic $\nu(C{=}C)$ at 1559 cm^{-1} in the IR spectrum of **4**, is not present in **14**. Compound **14** was converted into a 1/1 mixture of **13a** and **1**, together with propene, on reaction with HCl in C_6D_6 at 20 °C.



(14)

$$14 + HCl \longrightarrow [(C_5Me_5RhCl_2)_2] + CH_3CH{=}CH_2$$

(1)



(13a)

Further investigations of the reactions of **4** with acids are in progress, but it is clear that the medium plays a vital role. The allyl **10** is the preferred product in more polar solvents, the μ-ethylidene-μ-methylene **13a** is formed most readily in less polar solvents, especially in toluene at low temperature, and the adduct **14** precipitates from pentane. Since **14** requires more HCl to yield **13a** and propene, it may not be a direct intermediate. We may speculate that the transformation **4** to **13** takes place via two successive oxidative additions of HCl to the two-metal centre (Scheme 1). The first one leads, via coupling of the vinyl and the methylene, followed by reductive elimination, to propene. The remaining fragment I, formally a Rh^{III}-Rh^{III} species, possibly stabilised by a bridging chloride or vinyl, undergoes a second oxidative addition, followed by a rearrangement, leading to **13a**.

While reactions of a number of cationic η^1,η^2 (ie, bridging) vinyl complexes with hydride to yield μ-ethylidene complexes are known [6], and there has been a recent account of the transformation of a μ-vinylidene into a μ-ethylidene on protonation [7], this work appears to be the first example of the transformation of a terminal vinyl by protonation, into a μ-ethylidene.

Conclusion

The facile coupling of μ-methylene and σ-alkenyl in these dirhodium species is clearly demonstrated by the high yield reactions of the divinyl **4** (and the dipropenyl, **5**) complexes with silver ion (one electron oxidation) to give η^3-allyls, and by the pyrolyses to give propene (from **4** and butenes from **5**). Even acid can convert **4** into the η^3-allyl and/or to propene.

It is also possible that part of the driving force for the conversion of the divinyl complex **4** into the μ-methylene-μ-ethylidene dihalides **13** may be the formation of propene from just such a coupling.

There is considerable interest in the mechanism of C–C bond formation on di- and poly-nuclear complexes as possible models for coupling/polymerisation reactions on metal surfaces such as the Fischer–Tropsch reaction. Several possibilities have been considered for that, including the direct combination of μ-methylenes [9], the coupling of hydroxymethyl ligands [10], CO insertion into metal alkyl bonds, followed by reduction [11], and the reactions of methylene with olefins [12]. The first of these is very popular and is widely quoted; however the comparative stability of many complexes with two μ-alkylidene ligands suggests that considerable activation may be needed for coupling. It is very likely that the CO insertion mechanism is operative in some cases, especially in the formation of oxygenates (aldehydes, alcohols). There has been considerable interest too in the possibility of reaction of μ-methylenes with coordinated olefins; however, a molecular orbital theoretical analysis of one such system has suggested that to be a high energy process and a direct insertion of (uncoordinated) olefin into the CH_2–metal bond was proposed instead [13].

We have proposed a new mechanism for the Fischer–Tropsch polymerisation [4], based partly on the data presented here, in which a key step is the μ-methylene plus σ-alkenyl coupling. While this has yet to be verified for metal surface reactions, the organometallic reaction does seem to have wider potential than just for dirhodium systems. Thus, Doherty et al. [8] have recently reported a related reaction in which $[(CpRu(CO))_2(\mu\text{-}CH_2)(\eta^1\eta^2\text{-}CH{=}CH_2)]^+$ is converted by BH_4^- into $[(CpRu(CO))_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)]$ which, on pyrolysis, yields propene. Thus σ-vinyl and μ-methylene also come together on ruthenium, albeit seemingly via a μ-methylene-μ-ethylidene. Bercaw has also noted a facile vinyl plus methylene coupling on tantalum [14].

Experimental

All reactions were carried out under nitrogen by normal Schlenk techniques. Microanalyses were determined out by the University of Sheffield Microanalysis Service; IR spectra were measured on PE-1710 FTIR, mass spectra on Kratos MS-80 (FAB mode), and NMR spectra on Bruker AM-250, WH-80, and PE-220 spectrometers. Typical preparations are described below; microanalyses, FAB mass spectra and IR spectra are collected in Table 1, ^1H NMR spectra in Table 2, and ^{13}C NMR spectra in Table 3.

Preparation of trans-$[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CH_2)_2]$ *(4) and related complexes*

Freshly distilled toluene (150 cm^3) was transferred by cannula, with stirring to a flask containing $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2Cl_2]$ (**3**) [1c] (1 g, 1.74 mmol). Vinylmagnesium bromide in THF (Aldrich, 1.0 *M*; 8 cm^3) was added by syringe and a colour change from dark wine red to orange red occurred. The solution was stirred (30 min), acetone/water (1/1; 3 cm^3) added to destroy the excess of Grignard reagent, and filtered. The filtrate was evaporated to dryness, and the resulting red solid was extracted with light petroleum (b.p. 40–60 °C; 3 × 50 cm^3) and the extract filtered and evaporated. The compound was further purified by column chromatography on wet neutral alumina (some decomposition occurred on dry alumina) with light petroleum (b.p. 40–60 °C) as eluent. The collected fraction was evaporated and the solid triturated with methanol to yield complex **4**, 0.73 g (75%).

The complex *trans*-$[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2Me(CH{=}CH_2)]$ (**7**) was synthesised and purified (80% yield) in identical fashion to **4** by adding vinylmagnesium bromide to $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2MeCl]$ (**6**).

Complex *trans*-$[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(Z\text{-}CH{=}CHMe)_2]$ (**5**) was synthesised by a similar route. MeCH=CHMgBr was prepared in THF: 1-bromobut-1-ene (Aldrich, $Z/E = 3/1$, 8 cm^3, 93.4 mmol) dissolved in THF (100 cm^3) was added to Grignard grade magnesium turnings (3.0 g, 123.4 mmol, previously dried in vacuo, 4 h/110 °C) and THF (30 cm^3). When addition was complete, the brown solution was refluxed (3 h) and filtered. A measured excess of hydrochloric acid (0.1 *M*) was added to a 1 cm^3 portion of the solution; this was then back-titrated with standard NaOH (0.1 *M*) (phenolphthalein indicator), showing the concentration of the Grignard to be 0.56 *M*.

The solution of MeCH=CHMgBr in THF (14 cm^3, 0.56 *M*, 7.84 mmol) was added by syringe to a solution of $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2Cl_2]$ (**3**) (1 g, 1.74 mmol) in dry toluene (100 cm^3); a colour change from dark wine red to orange red was noted. After stirring (1 h) acetone/water 1/1 (4 cm^3) was added to destroy any residual Grignard reagent and the product was isolated as described for **4**: yield 0.785 g (77%). *trans*-$[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(Z\text{-}CH{=}CHMe)Me]$ (**8**) was similarly obtained from **6** in 69% yield.

Note: when the propenyl Grignard was made from the commercial 3/1 mixture of *Z*- and *E*-1-bromobut-1-ene, the product was almost entirely the *Z*-propenyl isomer. When a sample was used which had a lower *Z*/*E*-ratio, complex mixtures were obtained, which contained *E*-propenyl isomers.

Preparation of $[Rh(C_5Me_5)(C_3H_5)(MeCN)]BF_4$ *(9a)*

$[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(CH{=}CH_2)_2]$ (**4**) (0.37 g, 0.66 mmol) was added to a solution of $AgBF_4$ (0.26 g, 1.34 mmol) in THF/CH_3CN 1/1 (20 cm^3) and the mixture stirred (20 °C, 3 h). The starting material slowly dissolved and an orange-yellow solution was formed together with a black precipitate; this was filtered off and the solution evaporated to dryness. Addition of CH_3CN (10 cm^3) followed by filtration led to a clear solution, which gave a furry yellow precipitate of $[Rh(C_5Me_5)(C_3H_5)MeCN]BF_4$ on addition of diethyl ether (130 cm^3) (0.46 g, 85%; ν(CN) 2289, 2230 cm^{-1}).

$[Rh(C_5Me_5)(C_3H_5)(CO)]BF_4$ *(9b)*

Carbon monoxide was bubbled slowly (20 °C, 1 atm, 15 min) into a solution of $[Rh(C_5Me_5)(C_3H_5)(MeCN)]BF_4$ (**9a**) (0.122 g, 0.26 mmol) in CH_2Cl_2 (25 cm^3). The solvent was removed and the carbonylation repeated. The solvent was then evaporated off and the residue crystallised from CH_2Cl_2/diethyl ether to give **9b** as a yellow powder (0.072, 70%). The complexes $[Rh(C_5Me_5)(C_3H_5)L]BF_4$ (**9c**, L = PMe_3, **9d**, L = py) were prepared (75% yield) by addition of two equivalents of L to a solution of $[Rh(C_5Me_5)(C_3H_5)(MeCN)]BF_4$ in CH_2Cl_2, followed by a conventional work-up.

[Rh(C_5Me_5)(C_3H_5)Cl] (10)

A solution of tetraphenylarsonium chloride (0.309 g, 0.74 mmol) in CH_3CN (10 cm^3) was added to a vigorously stirred solution of complex [Rh(C_5Me_5)(C_3H_5)-MeCN]BF_4 (**9a**) (0.30 g, 0.74 mmol) in acetonitrile (5 cm^3). The solution deposited a pale yellow solid; the solvent was then removed in vacuo and the residue extracted with toluene and crystallised by addition of hexane to give pale yellow **10**, 75% yield.

Preparation of [($C_5Me_5Rh)_2$(μ-CH_2)(μ-CHMe)Cl_2] (13a)

Hydrogen chloride gas was bubbled slowly (2 min) through a cooled solution (−78 °C) solution of [{C_5Me_5Rh(μ-CH_2)(CH=CH_2)}$_2$] (4) (480 mg) in toluene (200 cm^3). A colour change from wine red to dark red occurred; the solution was stirred (15 min) at this temperature, and was then allowed to warm up to ambient. The solvent was removed in vacuo, leaving a brown-red residue, which was dissolved in chloroform (10 cm^3). A large excess of petroleum ether (40–60 °C; 100 cm^3) was added, and the orange red complex **1** (30%) which separated filtered off, to give a purple filtrate which yielded purple-black crystals of **13a** (from dichloromethane/hexane), yield 340 mg (67%).

Preparation of [($C_5Me_5Rh)_2$(μ-CH_2)(μ-CHMe)Br_2] (13b)

[{C_5Me_5Rh(μ-CH_2)(CH=CH_2)}$_2$] (4) (735 mg) was dissolved in petroleum ether (150 cm^3) with warming. Hydrogen bromide gas was bubbled through slowly (4 min), the solution turning dark red. After removal of the solvents the solid was dissolved in the minimum of chloroform (10 cm^3), petroleum ether (100 cm^3) was added, and the solution shaken. The orange precipitate of [{$C_5Me_5RhBr_2$}$_2$] which formed was filtered off to leave a purple filtrate. Solvent was removed from the filtrate, the residue was taken up in the minimum of dichloromethane, and petroleum ether added to give purple crystals of **13b**, yield 458 mg, 52%.

Preparation of [{C_5Me_5Rh(μ-CH_2)(CHClCH_3)}$_2$] (14)

Hydrogen chloride gas was bubbled (1 min) through a solution of [{C_5Me_5Rh(μ-CH_2)(CH=CH_2)}$_2$] (4) (500 mg) in pentane (100 cm^3). The orange solid which separated was filtered off and washed with pentane, to give [{C_5Me_5Rh(μ-CH_2)(CHClCH_3)}$_2$] (**14**) 456 mg (81%). ^{1}H NMR spectrum (C_6D_6): δ 8.04, 8.77, 9.19, 9.91 (μ-CH_2, all t or dd, J(Rh–H) ≈ J(H–H) 1–2 Hz), 3.44 (m, C*H*ClMe), 1.66, 1.67 (2 × C_5Me_5); assignments are somewhat tentative since the complex was poorly soluble and decomposed slowly in the spectrometer.

Thermal decomposition reactions

These were carried out as described previously [2], using a solids injector, comprising a syringe with a retractable knurled needle, which was coated with the complex. The syringe was plunged into the inlet septum of the preheater of a Carlo–Erba gas-chromatograph and left for 5 s. The gases produced were analysed by GC (Poropak Q, 2m; 100 °/5 min; 10 °C/min to 220 °C) and by GC-MS (Kratos MS25).

X-ray structure determinations

Complex $[\{(C_5Me_5Rh)(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$ (4). A crystal of $[\{(C_5Me_5Rh)(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$ (**4**) crystallised from dichloromethane as red bricks, was selected; dimensions, 0.40 × 0.25 × 0.20 mm. Crystal data: $C_{26}H_{40}Rh_2$, $M = 558.41$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, C_{2h}^5, No. 14), a 8.261(5), b 15.055(14), c 10.257(9) Å, β 108.72(6)°, U 1208.1(17) Å^3, D_c 1.535 g cm^{-3}, $Z = 2$, Mo-K_α radiation ($\bar{\lambda}$ 0.71069 Å; μ(Mo-K_α) 13.54 cm^{-1}), $F(000) = 571.94$. Three dimensional room temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3m four-circle diffractometer by the omega scan method. The 1801 independent reflections for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 7 azimuthal scans. The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods. Hydrogen atoms were included in predicted positions with isotropic thermal parameters related to those of the supporting atom. Refinement converged at a final R 0.0447, with allowance for the thermal anisotropy of all non-hydrogen atoms. Complex scattering factors were taken from reference [15] and from the program package SHELXTL programs as implemented on the Data General Nova 3 computer. A weighting scheme with $\omega^{-1} = [\sigma^2(F) + g(F)^2]$ and $g = 0.00198$ was used in the later stages of the refinement. The atomic coordinates are in Table 4, and selected bond lengths and angles are in Table 5.

Complex $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)Cl_2]$ (13a). A crystal of $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)Cl_2]$ (**13a**) crystallised from pentane as deep red prisms, was selected; dimensions, 0.30 × 0.25 × 0.175 mm. Crystal data: $C_{23}H_{36}Cl_2Rh_2$, $M = 589.25$, orthorhombic, space group $Pccn$ (D_{2h}^{10}, No. 56), a 18.485(19), b 14.357(17), c 9.233(6) Å, U 2451(4) Å^3, D_c 1.597 g cm^{-3}, $Z = 4$, Mo-K_α radiation ($\bar{\lambda}$ 0.71069 Å; μ 15.53 cm^{-1}), $F(000) = 1191.90$. Three dimensional room temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3m four-circle diffractometer by the omega scan method. The 1571 independent reflections for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of azimuthal scans. The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods. The two bridging ligands are disordered between their centrosymmetrically related sites, thus the composite model was refined with constrained geometry with C(11) common to the two ligands. Hydrogen atoms were placed in predicted positions with isotropic thermal parameters related to those of the supporting atom. Refinement converged at a final R 0.0750, with allowance for the thermal anisotropy of all non-hydrogen atoms, with the exception of the half-occupancy C(12). Complex scattering factors were taken from reference [15] and from the program package SHELXTL programs as implemented on the Data General Nova 3 computer. Unit weights were used throughout. The atomic coordinates are in Table 6, and selected bond lengths and angles are in Table 7.

Acknowledgements

We thank the SERC for support, Johnson Matthey for the loan of rhodium salts, Dr. B.F. Taylor for NMR spectra, Mr. D.G. Andrews, Mr. P.R. Ashton, and Mr. I.R. Johnstone for GC and GC-MS measurements, and Dr. S.A.R. Knox and Professor J. Bercaw for sending us information prior to publication.

References

1 (a) K. Isobe, A. Vazquez de Miguel, P.M. Bailey, S. Okeya, and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1983) 1441; (b) K. Isobe, S. Okeya, N.J. Meanwell, A.J. Smith, H. Adams, and P.M. Maitlis, ibid., (1984) 1215; (c) S. Okeya, N.J. Meanwell, B.F. Taylor, K. Isobe, A. Vazquez de Miguel, and P.M. Maitlis, ibid., (1984) 1453.

2 I.M. Saez, N.J. Meanwell, A. Nutton, K. Isobe, A. Vazquez de Miguel, D.W. Bruce, S. Okeya, D.G. Andrews, P.R. Ashton, I.R. Johnstone, and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1986) 1565; I.M. Saez, N.J. Meanwell, B.F. Taylor, B.E. Mann, and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1987) 361.

3 I.M. Saez, D.G. Andrews, and P.M. Maitlis, Polyhedron, 7 (1988) 827; P.M. Maitlis, I.M. Saez, N.J. Meanwell, K. Isobe, A. Nutton, A. Vazquez de Miguel, D.W. Bruce, S. Okeya, P.M. Bailey, D.G. Andrews, P.R. Ashton, and I.R. Johnstone, New J. Chem., 13 (1989) 419; P.M. Maitlis, Pure Appl. Chem., 61 (1989) 1747.

4 J. Martinez, H. Adams, N.A. Bailey, and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1989) 286; J. Martinez, J.B. Gill, H. Adams, N.A. Bailey, I.M. Saez, and P.M. Maitlis, Can. J. Chem., 67 (1989) 1698.

5 K. Moseley, J.W. Kang, and P.M. Maitlis, J. Chem. Soc., (A), (1970) 2875; H.B. Lee and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1975) 2316.

6 A.F. Dyke, S.A.R. Knox, P.J. Naish, and A.G. Orpen, J. Chem. Soc., Chem. Commun., (1980) 440; A.F. Dyke, S.A.R. Knox, M.J. Morris, and P.J. Naish, J. Chem. Soc., Dalton Trans., (1983) 1417; D.L. Davies, S.A.R. Knox, K.A. Mead, M.J. Morris, and P. Woodward, ibid., (1984) 2293; see also A.F. Dyke, S.A.R. Knox, and P.J. Naish, J. Organomet. Chem., 199 (1980) C47; R.E. Colborn, A.F. Dyke, S.A.R. Knox, K.A. Mead, and P. Woodward, J. Chem. Soc., Dalton Trans., (1983) 2099.

7 D.B. Jacobson, J. Am. Chem. Soc., 111 (1989) 1626.

8 N.M. Doherty, J.A.K. Howard, S.A.R. Knox, N.J. Terrill, and M.I. Yates, J. Chem. Soc., Chem. Commun., (1989) 638.

9 F. Fischer and H. Tropsch, Brennst. Chem., 7 (1926) 97; R.C. Brady and R. Pettit, J. Am. Chem. Soc., 102 (1980) 6182; 103 (1981) 1287; P. Biloen, Recl. Trav. Chim. Pays-Bas, 99 (1980) 33; P. Biloen and W.M.H. Sachtler, Adv. Catal., 30 (1981) 165.

10 H.H. Storch, N. Golombic, and R.B. Anderson, The Fischer–Tropsch and Related Syntheses, Wiley, New York, 1951; J.F. Kummer and P.H. Emmett, J. Am. Chem. Soc., 75 (1953) 5177.

11 H. Pichler and H. Schultz, Chem. Ing. Tech., 12 (1970) 1160; see also M. Akita, O. Mitani, and Y. Moro-Oka, J. Chem. Soc., Chem. Commun., (1989) 527.

12 C.E. Summer, P.E. Riley, R.E. Davis, and R. Pettit, J. Am. Chem. Soc., 102 (1980) 1752; K.M. Motyl, J.R. Norton, C.K. Schauer, and O.P. Anderson, ibid., 104 (1982) 7325; M. Leconte, A. Theollier, D. Rojas, and J.M. Basset, Nou. J. Chim., 8 (1984) 69; R.A. Strelow and E.C. Douglas, J. Chem. Soc., Chem. Commun., (1983) 259.

13 B. Bigot and F. Delbecq, Organometallics, 6 (1987) 172.

14 J. Bercaw, personal communication.

15 International Tables for Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.