Decomposition Reactions of Dimethyl-di-μ-methylene-bis(η-pentamethylcyclopentadienyl)dirhodium and their Relation to the Mechanism of the Fischer-Tropsch Reactions; the Formation of Propylene from Three C_1 Ligands

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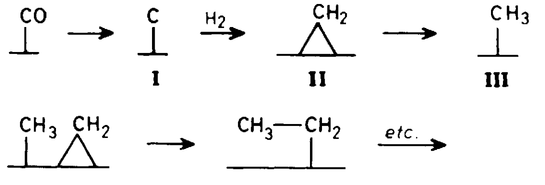
Thermal decomposition of $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$ (**1**) at temperatures from 275 to 375 °C yielded methane, propylene, ethylene, and some ethane. Using (**1**) selectively labelled with ^{13}C in the Rh–methylene and/or the Rh–methyl ligands showed that (*a*) the gases are formed in intramolecular decompositions not involving the $C_5(CH_3)_5$ rings, (*b*) the methane arises from both the rhodium–methyls and the rhodium–methylenes, and (*c*) the C_2 and C_3 gases arise predominantly from the coupling of a Rh–methyl and one or two Rh–methylenes; direct coupling of two methylenes or of two methyls is not a favourable process here. Very similar gas mixtures are formed (but at 20—50 °C) on reaction of complex (**1**) with excess $IrCl_6^{2-}$ (or other one-electron oxidisers and electrophiles). Carbon-13 and deuterium labelling studies show that these reactions are again intramolecular and do not involve the $C_5(CH_3)_5$ rings, or the coupling of two methyl or two methylene ligands. Methane arises mainly by combination of a Rh–CH_3 and a *methylene* hydrogen, probably after a two-electron oxidation, leaving a transient species (**A**) formulated as $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CH)(CH_3)]^{2+}$. The C_2 products must be formed from (**A**) by the coupling of the Rh–CH_3 with the methylene, to give an Rh–ethyl intermediate which β-eliminates to give ethylene (or acquires a hydrogen to give ethane). The labelling shows propylene to arise from the coupling of one methyl and two methylenes. It can be formed *via* migration of the methyl onto the μ-methyne in (**A**), giving a μ-methylene–μ-ethylidene species which couples to give propylene directly. Implicit in the route is the need for two metal centres to allow three C_1 fragments to couple together to form propylene. Labelling studies rule out appreciable ethylene formation from a Rh–ethylidene. Direct coupling of the methylenes does occur in the thermal decompositions of $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2X_2]$ (X = halide, SCN, or N_3), to give ethylene; the main product is again methane. The data are contrasted with results from the decomposition of the iridium analogue of (**1**) and of $[C_5(CH_3)_5Ir(CH_3)_4]$. The relationships of the mechanisms proposed to current models for the mechanism of the Fischer-Tropsch reaction on metal surfaces are discussed.

We have described the synthesis, characterisation and structure of the remarkable complex dimethyl-di-μ-methylene-bis(η^5-pentamethylcyclopentadienyl)dirhodium, (**1**).[1,2] Apart from the intrinsic chemical interest of (**1**) and its analogues and derivatives, the complex is also very relevant to the discussion about the mechanism of the formation of hydrocarbons in the Fischer-Tropsch reaction.

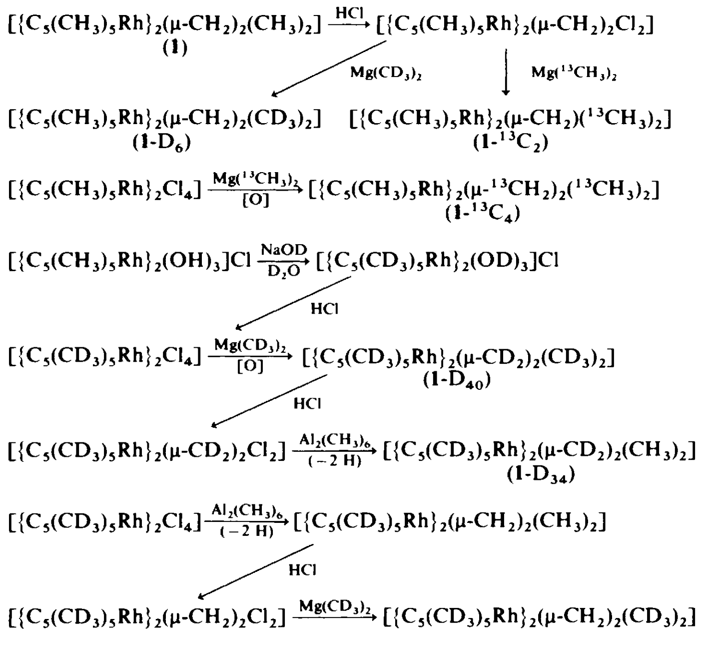
Thus, for example, Brady and Pettit[3] have drawn attention to the original Fischer-Tropsch hypothesis[4] and presented a version (Scheme 1; modified to take account of current ideas of bonding) to explain the results obtained when 'methylene' (derived from diazomethane) and hydrogen were passed over metal surfaces. This mechanism suggests that the production of, say, propylene from hydrogen and diazomethane over cobalt proceeds *via* an oligomerisation of surface-bound methylene groups (**II**, Scheme 1) initiated by a hydride, or by a methyl (**III**), which is equivalent to 'H + CH_2'. When CO is the source of the carbon, then a similar mechanism applies, with the surface-bound CO being converted into methylene *via* primary formation of a surface carbide species (**I**, Scheme 1). Both the methylenes and carbides are presumed to be bridging at least two metal atoms.



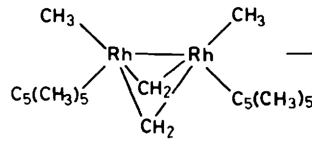
Scheme 1.

The postulated arrangement of methyl and methylene groups in such a metal surface closely resembles that which is actually found (from the *X*-ray crystal structure) in the *cis* isomer of (**1**). This molecule is thus potentially a very fine model for the propagation step of the Fischer-Tropsch reaction and allows some further tests of the mechanism to be carried out, for example, the mode by which formation of C_2—C_4 molecules occurs on decomposition.

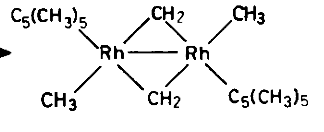
As well as giving details of the thermal decomposition reactions of (**1**), we also describe the products that are formed when (**1**) is reacted with electrophiles and one-electron oxidants. Preliminary results of work on these two topics have been



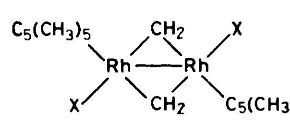
Scheme 2. Synthesis of labelled complexes



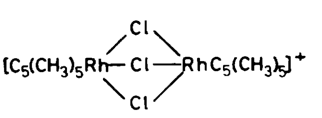
cis – (**1**)



trans – (**1**)



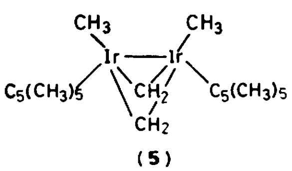
(**2a**), X = Cl
(**2b**), X = Br
(**2c**), X = I
(**2d**), X = N_3



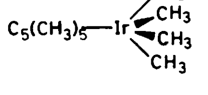
(**3**)

$[C_5(CH_3)_5Rh(CH_3CN)_3]^{2+}$

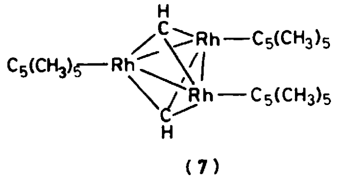
(**4**)



(**5**)



(**6**)



(**7**)

communicated.[1,5] To complement them, results of some studies are also reported on the decomposition reactions of the rhodium complexes $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2X_2]$ (**2a**, X = Cl; **2b**, X = Br; **2c**, X = I; **2d**, X = N_3)[6,7] and of some related iridium complexes.

Experimental

Preparation of Labelled (**1**).—The complexes $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(^{13}CH_3)_2]$ (**1**-$^{13}C_2$) and $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CD_3)_2]$ (**1**-D_6) were prepared in similar ways from the dichloro-complex $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2Cl_2]$ (**2a**)[7] by reaction with the appropriate dialkylmagnesium under nitrogen. Scheme 2 summarises the routes used to prepare all the labelled complexes. Thus a solution of $Mg(^{13}CH_3)I$ was prepared from magnesium turnings (0.17 g, 7 mmol) and $^{13}CH_3I$ (1.0 g, 7 mmol; 90% ^{13}C, Service des Molecules Marquees, France), in dry diethyl ether (10 cm^3) in a Schlenk tube under nitrogen. To this solution was added a solution of 1,4-dioxane (diox) (0.3 cm^3, 3.5 mmol) in diethyl ether (3.0 cm^3), with vigorous stirring. The thick creamy precipitate of MgI_2·diox was filtered off through a medium grade glass frit under nitrogen to give a clear solution of $Mg(^{13}CH_3)_2$. Part of this solution (4.5 cm^3, 0.19 mol dm^{-3}, 0.86 mmol) was then added (over 5 min) to a solution of (**2a**) (0.3 g, 0.51 mmol) in toluene (45 cm^3). The colour changed from the initial dark red to a clear light red as the reagent was added; after stirring (10 min) the reaction mixture was hydrolysed with aqueous acetone (4 cm^3), and worked-up in the conventional way by extraction with pentane to give (**1**-$^{13}C_2$) (245 mg, 88%). The identity of the complex was shown by its 400-MHz ^1H n.m.r. spectrum (in $CDCl_3$) which also indicated that it contained the *cis* and *trans* isomers in a 1:1 ratio [Rh–CH_3: *cis* isomer, δ −0.51, doublet of virtual triplets, J(C–H) 131 Hz; *trans* isomer, δ −0.95, doublet of virtual triplets, J(C–H) 130 Hz; remaining resonances as in ref. 2]. The presence of a small amount of the $^{12}CH_3$ isotopomer was shown by the weak virtual triplets at δ −0.51 (*cis*) and −0.95 (*trans*); integration established that 8% of the rhodium methyls contained ^{12}C, *i.e.* the species with one $^{12}CH_3$ and one $^{13}CH_3$.

The complex (**1**-D_6) containing two Rh–CD_3 groups was synthesised similarly (yield 65%), using CD_3I to make the Grignard. The ^1H n.m.r. spectrum showed the presence of *cis* and *trans* isomers in the ratio 2:1, and the absence of Rh–CH_3 groups; there was no significant deuteriation of the ring methyls.

A sample of $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}^{13}CH_2)_2(^{13}CH_3)_2]$ (**1**-$^{13}C_4$) was also prepared by reaction of $Mg(^{13}CH_3)_2$ [from $^{13}CH_3I$ (1.0 g) and magnesium in ether (10 cm^3) followed by addition of diox (0.3 cm^3) as above] with a suspension of $[\{C_5(CH_3)_5Rh\}_2Cl_4]$ (0.3 g, 0.51 mmol) in toluene (10 cm^3). The solid dissolved to give a dark green solution which slowly (15 h, 20 °C) turned yellow. When the reaction was complete, diox (3 cm^3) was added and stirring continued for 5 h; the solution was then exposed to air (18 h). The excess magnesium reagents were hydrolysed and the product worked up as usual to give complex (**1**-$^{13}C_4$) (44 mg, 17%), after crystallisation from methanol–pentane. The ^1H n.m.r. spectrum (Figure 1) showed the presence of both the *cis* and the *trans* isomer (ratio 1:1), and by integration it was also established that each isomer showed the same degree of labelling, namely that the rhodium-bound CH_2 and CH_3 each contained 92% ^{13}C and 8% ^{12}C, and that the $C_5(CH_3)_5$ methyls contained by contrast only the normal abundance of ^{13}C. The methyl resonances were as described above for (**1**-$^{13}C_2$); in addition the methylene resonances showed coupling J(C–H) 144 (*trans* isomer), 135.5 (*cis* isomer, equatorial H), and 150.6 Hz (*cis* isomer, axial H).

A sample of deuterium-labelled complex (**1**) (yield 10%) was made by reaction of $[\{C_5(CH_3)_5Rh\}_2Cl_4]$ with a solution of $Mg(CD_3)_2$; details were as for (**1**-$^{13}C_4$) above. However, n.m.r. analysis showed that the D-label was present in the $C_5(CH_3)_5$ as well as in the rhodium–methyl and methylene groups. Thus the ^2H spectrum showed deuteriums in the methyl, $C_5(CH_3)_5$, and methylene ligands in the ratio of approximately 3:6:0.1 in the *trans* isomer and 3:10:0.1 in the *cis* isomer; the corresponding ratios of hydrogens in the ^1H

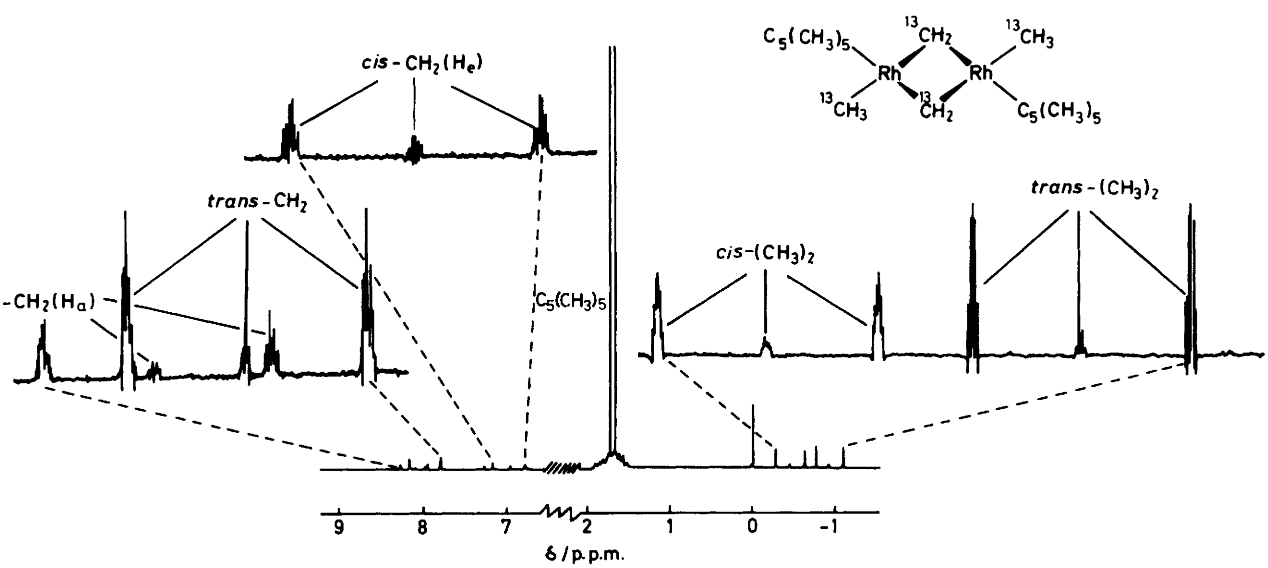


Figure 1. Hydrogen-1 n.m.r. spectrum of $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}^{13}CH_2)_2(^{13}CH_3)_2]$

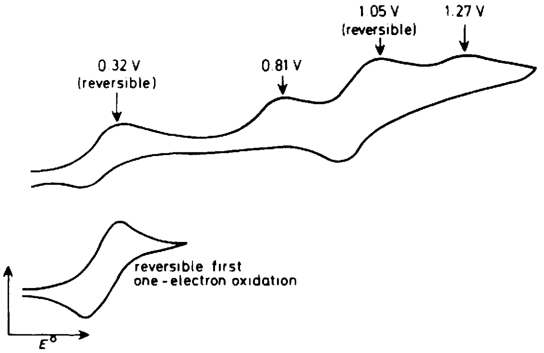


Figure 2. Cyclic voltammogram of $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$ (in CH_2Cl_2 + NBu_4PF_6)

spectrum was 3:48:11 (*trans*) and 3:48:8 (*cis*). Considerable hydride scrambling had therefore occurred during the synthesis, as had already been noted earlier,[2] and the material produced was of no use for the selective decomposition studies.

By contrast, when a sample of $[\{C_5(CD_3)_5Rh\}_2Cl_4]$[8] was reacted with $Mg(CD_3)_2$, prepared as above, the complex $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CD_2)_2(CD_3)_2]$ (**1**-D_{40}) was obtained (70 mg, 8% yield). Integration of the ^1H n.m.r. spectrum against a standard showed there to be 1.6 H (and 28.4 D) in the $C_5(CH_3)_5$, 0.2 H (3.8 D) in the μ-methylene, and 0.2 H (5.8 D) in the Rh–CH_3 position; the ^2H n.m.r. spectrum confirmed the deuterium in each case.

When (**1**-D_{40}) was reacted with HCl and the resultant $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CD_2)_2Cl_2]$ was treated with $Al_2(CH_3)_6$, the complex $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CD_2)_2(CH_3)_2]$ (**1**-D_{34}) was obtained (60% yield). Integration of the ^1H n.m.r. spectrum against a standard and the ^2H spectrum showed there to be 6 H (100%) in the Rh–CH_3, 0.8 H (3.2 D) in the methylenes, and 2.3 H (27.7 D) in the $C_5(CH_3)_5$.

Reaction of $[\{C_5(CD_3)_5Rh\}_2Cl_4]$ with $Al_2(CH_3)_6$ gave, after conventional work-up, $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$ (ring methyls contain 2 H and 28 D); this was converted, *via* the chloride and $Mg(CD_3)_2$, into $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CD_3)_2]$ (84%). N.m.r. analysis showed 1.8 H (28.2 D) in the ring methyls, zero H (6 D) in the rhodium–methyls, and 3.8 H (0.2 D) in the μ-methylenes.

Reaction of Complex (**1**) *with Iodine.*—Portions of iodine (14 mg, 0.055 mmol) were added to a solution of complex (**1**) (30 mg, 0.56 mmol) in $CDCl_3$ (0.5 cm^3) and the ^1H n.m.r. spectra run after each addition. The spectrum characteristic of (**1**) was replaced by new peaks at δ 1.81 and 10.51, due to complex (**2c**),[7] and at 2.10, due to MeI; this reaction was complete after the addition of two portions of iodine when the three peaks which had appeared had intensity ratios 30:4:7, very close to the expected, 30:4:6. Addition of a third portion of iodine changed the spectrum completely; the bands due to (**2c**) were replaced by one at δ 1.98, due to $[\{C_5(CH_3)_5Rh\}_2I_4]$, and the methyl iodide peak did not grow further. Instead, a small peak, shown to be due to dissolved ethylene, appeared at δ 5.37. Repetition of the experiment in a sealed tube such that the volatiles could be examined by g.c. showed the production of *ca.* 0.04 equivalents of methane, 0.66 of ethylene, and 1.75 of methyl iodide per molecule of complex (**1**).

Rather similar results were obtained on reaction of complex (**1**) with bromine under the same conditions; in this case however, analysis of the gas phase showed the presence of some propylene as well as methane and ethylene.

Electrochemical Investigation of Complex (**1**).—Cyclic voltammograms were recorded using a PAR 175 Universal Programmer connected to a PAR 173 potentiostat/galvanostat; current–voltage curves were recorded on a PAR model RE0074 *X–Y* recorder. The system was equipped with a Pt wire working electrode, an Ag/AgCl reference electrode with a saturated ethanolic LiCl salt bridge, and a Pt gauze counter electrode. Purified dichloromethane, containing tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) as supporting electrolyte, was the solvent (E^0 for ferrocene oxidation was found to be 0.49 V under these conditions). Under these conditions complex (**1**) showed four oxidation waves (Figure 2; range 0—1.5 V, scan rate 200 mV s^{-1}), at 0.32 (reversible), 0.81 (irreversible), 1.05 (reversible), and 1.27 V (irreversible); the positions of the waves were unchanged in the presence of acetonitrile.

Gas Analysis from Decomposition Reactions.—Two basic methods were used to decompose the complexes. The sample was either injected into the preheater of a gas chromatograph as a solid and the gaseous products analysed directly, or the sample was reacted in a sealed flask with a reagent in solution and the gases were then sampled and analysed.

(*a*) A solids injector, comprising a syringe with a retractable knurled needle, was used. The needle was coated with a known amount of solution of complex (**1**) (*e.g.*, 10 μl of solution containing 2.0 mg in 280 μl benzene), the solvent was dried off, and the syringe plunged into the inlet septum of the preheater of a Carlo Erba 4100 or a Pye-Unicam 104 gas chromatograph, at the desired temperature (usually 350 °C). The needle was then pushed out into the preheater and left there for 5 s; it was found that essentially all the complex had decomposed under these conditions. Tests showed that the amounts of gases formed and their nature were not dependent on the conditions of the pyrolysis other than the temperature. Thus, for example, the decomposed metal which gradually built up on the column inlet of the g.c. had no effect. However, as a precaution and to ensure clean conditions, the column was purged every two runs by heating to 200 °C for 15 min, and a replaceable short glass inlet tube (in which the decomposition occurred) was fastened to the top of the chromatography column in order to minimise contamination of the packing. A glass column (2 m × 4 mm) packed with Poropak Q was used for analysis. This was operated isothermally at 100 °C at a flow rate of *ca.* 15 cm^3 min^{-1}. Under these conditions typical retention times were as follows: methane, 32; ethylene, 64; ethane, 78; and propylene, 192 s. The peak areas were integrated and the integrals and retention times compared with those of known amounts of authentic samples; this allowed the estimation of the absolute amounts of the gases formed during the decomposition. In order to check for other volatiles, a temperature program was used and the column was heated (70 °C for 2 min and then at 5 °C min^{-1} to 140 °C); solvent acetonitrile was found to come off at 100 °C, and the separation between ethylene and ethane was improved, using these conditions. The identity of the gases was also checked by g.c.–m.s. using a Kratos MS-25S mass spectrometer, the samples being introduced through a Carlo-Erba gas chromatograph operating under the same conditions as above.

(*b*) For reactions in solution the typical procedure was as follows. The solid sample of complex (**1**) (0.01 g) was placed in a small flask of accurately known volume (4.0 cm^3); this was fitted with a Suba-seal tightly wired on. The air in the flask was removed by application of a vacuum *via* a syringe needle and was replaced with nitrogen; this was repeated several times. The reagent $Na_2[IrCl_6]\cdot 6H_2O$ (53 mg, 112 μmol) dissolved in acetonitrile (0.5 cm^3) was added and the contents of the flask shaken to ensure dissolution of the sample. Reaction was indicated by an immediate change in colour and/or deposition of metal; the reaction was then completed by heating to 50 °C for 2 h. The flask was cooled to room temperature and a sample (50 μl) of the gas inside was removed with a gas syringe through the rubber septum. The gas was then introduced into the gas chromatograph and analysed as indicated above. The solution was also analysed for dissolved gases and other products.

Complex $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$ (**1**) (100 mg, 0.19 mmol) in acetonitrile (10 cm^3) was oxidised with sodium hexachloroiridate (475 mg, 0.85 mmol) (18 h 60 °C). After addition of KPF_6 and a conventional work-up the known complex $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}Cl)_3]PF_6$[8] (**3**) was isolated (72 mg, 53%). It was characterised by microanalysis, n.m.r. and i.r. spectra. This complex is quite labile and in some cases, when the decomposition was carried out under slightly different conditions, the tris(acetonitrile) complex, $[C_5(CH_3)_5Rh(CH_3CN)_3][PF_6]_2$ (**4**) was isolated instead; it was also characterised by microanalysis, i.r. and n.m.r. spectra.[9]

Analysis of Isotopomers.—The proportions of isotopomers present in the gases from labelled samples of (**1**) were estimated by mass spectrometry (Kratos MS-25S) of the appropriate eluates from the g.c. column. The mass spectra on each fraction were averaged and were run under conditions such that saturation of the peaks did not occur. The measured intensities of the four or five highest peaks of the mass spectra of the various ^{12}C gases under the same conditions were used as databases; these were methane, *m/e* 16 (100%), 15 (82), 14 (15), 13 (2); ethylene, *m/e* 28 (100), 27 (69), 26 (68), 25 (8); ethane, *m/e* 30 (23), 29 (22), 28 (100), 27 (33); and propylene, *m/e* 42 (72), 41 (100), 40 (36), 39 (76). For evaluating the proportions of the various ^{13}C isotopomers present, it was assumed that the isotope effect would be minimal, and the expected patterns were based on those determined above by the addition of +1, +2, or +3, as appropriate, to the values of *m/e* for the all-^{12}C gases.

A problem sometimes arose in analysis at *m/e* 44, corresponding to both $^{12}C^{13}C_2H_6$ and carbon dioxide. Although most of the carbon dioxide was removed in the g.c. separation and any trace residue was compensated for electronically, the relatively small amount of propylene eluting from the g.c. into the mass spectrometer could complicate the analysis here. Similar difficulties were occasionally encountered with analysis at *m/e* 32 (C_2H_6, coincident with O_2), and at 28 (C_2H_4, coincident with N_2). (*N.B.* It may be noted that *no* carbon dioxide was detected in the products of hexachloroiridate oxidation.)

Analysis of deuterium-containing gases from deuterium-labelled complex (**1**) were carried out similarly. In this case however, the isotope effects could not be ignored and the data-bases used were either from our own measurements (*e.g.*, for CD_4), or literature values.[10]

Results

Thermal Decomposition Reactions of the Dimethyl Complex (**1**).—(*a*) *Unlabelled* (**1**). The results presented in Table 1 show that complex (**1**) decomposed thermally to give a mixture of methane, ethylene, ethane and propylene. No higher hydrocarbons were detected, though pentamethylcyclopentadiene and tetramethylfulvene were found when the g.c. was run for long retention times, indicating that some breaking of the Rh–$C_5(CH_3)_5$ bonds did occur. Although *cis*-(**1**) decomposed more easily than *trans*-(**1**), the gas compositions were similar, the predominant products being methane and propylene, with smaller amounts of ethylene (10—20%) and ethane (1—3%).

The variation of gas formed during decomposition was also investigated over the temperature range 275—375 °C. Thus at 275 °C, 4.7 × 10^{-8} mol of *cis*-(**1**) gave a total amount of gas corresponding to 10.2 × 10^{-8} mol C_1. This calculation is based on the fact that one mole of methane contains one mole of C_1, but one mole of ethylene or ethane contains two, and one mol of propylene contains three. Since on this basis each mol of complex (**1**) contains 4 mol of 'available' C_1, the total amount of gases formed at 275 °C corresponds to 54% of that possible. The pyrolysis at 375 °C gave a total of 17.4 × 10^{-8} mol of gases, *i.e.*, 93% of available C_1. While the amounts of all the gases formed increased with temperature, that of propylene (which represented 24% of the total C_1) at 275 °C, increased more than the others, to 36% at 375 °C; in fact there was 2.5 times as much propylene formed in the higher temperature reaction as in the lower, while the amount of methane increased by 26%. The pyrolysis of the pure *trans*-(**1**) followed a similar pattern, except that smaller amounts of gases (20% decomposition at 300 °C) were formed at lower temperatures than at higher ones (79% decomposition at 375 °C); again the amount of propylene increased much more sharply than the amount of methane.

In fact, much of the work discussed here was undertaken with the *trans* isomer or with *cis/trans* mixtures since these were more

Table 1. Gases formed on decomposition of complex (**1**)[a]

Compound	θ/°C	Decomposition (%)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
			10^{-8} mol				
cis-(**1**)[b]	275	54	6.6	0.4	0.1	0.8	
			[65]	[8]	[3]	[24]	
	300	65	6.9	0.6	0.2	1.1	0.1
			[57]	[10]	[3]	[27]	[2]
	325	73	7.0	0.7	0.2	1.5	0.1
			[51]	[10]	[3]	[34]	[2]
	350	80	7.4	0.8	0.2	1.7	0.1
			[50]	[11]	[3]	[34]	[2]
	375	93	8.3	0.9	0.3	2.1	0.1
			[49]	[10]	[3]	[36]	[2]
trans-(**1**)[b]	300	20	1.8	0.4		0.4	
			[49]	[22]		[30]	
	325	35	3.3	0.9		0.5	
			[50]	[27]		[23]	
	350	60	4.9	1.2	0.1	1.3	
			[44]	[21]	[1]	[34]	
	375	79	5.5	1.2	0.1	2.0	0.2
			[37]	[16]	[1]	[41]	[4]

Compounds	Decomposition (%)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
		10^{-6} mol				
cis-(**1**) + *trans*-(**1**)[c]						
$+1\ IrCl_6^{2-}$	67	22.0	5.1	1.5	5.1	0
		[44]	[20]	[6]	[30]	
$+4\ IrCl_6^{2-}$	77	15.8	3.3	1.9	10.6	trace
		[27]	[11]	[7]	[55]	
$+6\ IrCl_6^{2-}$	77	14.7	2.8	1.3	11.4	trace
		[26]	[10]	[5]	[60]	

[a] Numbers in square brackets are normalised percentages, see text. [b] 4.7×10^{-8} mol. [c] Total 18×10^{-6} mol; 20—50 °C.

Table 2. Gases formed on decomposition of other rhodium complexes *trans*-$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2X_2]$*

X	θ/°C	Decomposition (%)	CH_4	C_2H_4	C_2H_6	C_3H_6
Cl	375	39	[34]	[55]	[11]	0
Br	375	88	[28]	[62]	[5]	[4]
I	375	73	[30]	[55]	[2]	[13]
N_3	375	60	[22]	[70]	0	[8]
SCN	375	74	[28]	[65]	0	[6]

* Numbers in square brackets are normalised percentages.

accessible than the pure *cis* isomer, which can only be made free from the *trans* with some difficulty. In order to understand the intimate details of the subsequently described decomposition reactions a total of *eight* isotopomers of (**1**) were prepared in which the ring methyls, the rhodium methyls and/or the methylenes were labelled, with either deuterium or ^{13}C. The routes to the various isotopomers are illustrated in Scheme 2 and details are given in the Experimental section.

(*b*) (**1**-$^{13}C_4$). The complex $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}^{13}CH_2)_2(^{13}CH_3)_2]$ (**1**-$^{13}C_4$) was also decomposed thermally. The gases (methane, ethane, ethylene, and propylene) all showed the presence of ^{12}C and ^{13}C labels very close to those expected for decomposition of rhodium–methyl and–methylene groups each containing 92% ^{13}C and 8% ^{12}C [found (expected): methane, 93% $^{13}CH_4$ (92%); ethylene, 88% $^{13}C_2H_4$ (85%); ethane, 88% $^{13}C_2H_6$ (85%); propylene, 76% $^{13}C_3H_6$ and 24% $^{13}C_2{}^{12}CH_6$ (78 and 22%)]. There was no evidence at all for the incorporation of (unlabelled) carbons from the $C_5(CH_3)_5$ rings. This shows that the reactions observed are only those arising from combination of the rhodium–methylene and the rhodium–methyl groups.

A 1:1 mixture of unlabelled complex (**1**) and (**1**-$^{13}C_4$) was also pyrolysed (at 360 °C). G.c.–m.s. analysis of the gases showed the presence of only those isotopomers expected from each of the components separately; thus the proportions of $^{13}C^{12}CH_4$, of $^{13}C^{12}CH_6$, and of $^{13}C^{12}C_2H_6$ in the ethylene, the ethane, and the propylene were found to be approximately 4%, 4%, and 0% respectively. This agrees well with those expected (5%, 5%, and 0.5%) for a reaction without crossover where the only mixed species arise from the small (8%) residual ^{12}C in (**1**-$^{13}C_4$). If there had been complete crossover between (**1**) and (**1**-$^{13}C_4$), the expected proportions of these isotopomers would have been 33%, 33%, and 26%. This indicates that even in the solid state there can be little reaction involving, say, one molecule of (**1**) and one of (**1**-$^{13}C_4$) in the formation of the gases and we may therefore conclude that the observed decomposition reactions are indeed largely intramolecular and involve only the two methyl and the two methylene ligands bound to rhodium in the one molecule.

(*c*) (**1**-$^{13}C_2$). When (**1**) (*cis*:*trans* = 1:1) labelled with 92% Rh–$^{13}CH_3$ was decomposed, the C_2 and C_3 gases formed contained *one* ^{13}C each. Both the ethylene and the ethane contained at least 90% $^{13}C^{12}C$; no appreciable amounts of $^{12}C_2$ or $^{13}C_2$ gases were found. Accurate analysis of the propylene formed was a little more difficult (see Experimental section), however, we can say with confidence that *at least* 70% of the propylene has *m*/*e* 43, corresponding to $^{13}C^{12}C_2H_6$. A smaller amount, possibly up to 30%, was $^{13}C_2{}^{12}CH_6$. The methane was also made up of a 1:1 mixture of $^{13}CH_4$ and $^{12}CH_4$. There was no significant change in isotope composition of any of the gases when the decompositions were carried out at 250 °C.

These results show that neither the coupling of two Rh–CH_3 (to give ethane) nor the coupling of two methylenes (to give ethylene) is a significant process in the thermal decomposition of complex (**1**).

(*d*) *Deuterium-labelled* (**1**). Analysis of the isotope ratios of the gases formed by thermal decomposition of (**1**-D_6) (containing two Rh–CD_3 ligands), was complicated owing to the extensive H/D scrambling reactions which occurred on heating. This was shown, for example, by the presence in the methane of 5% CD_4, 39% CH_3D, 24% CH_2D_2 and 45% of the expected CHD_3. Similarly, the ethylene contained approximately 68% D_0, 17% D_1, 9% D_2, and 3% of each of D_3 and D_4, while the propylene contained approximately 31% D_0, 36% D_1, 23% D_2, and 10% D_3. Nevertheless, the data broadly confirm the studies involving ^{13}C labelled complexes. Similar scrambling was observed when the other deuteriated complexes (**1**) were decomposed thermally.

(*e*) *Decomposition of other complexes*. The pyrolyses of the complexes $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2X_2]$ (**2a**)—(**2d**)[7] all gave largely ethylene and methane, together with small amounts of propylene and ethane (Table 2).

Table 3. Gases formed on decomposition of iridium complexes[a]

Complex	θ/°C	Decomposition (%)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
			10^{-8} mol				
$[\{C_5(CH_3)_5Ir\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$[b]							
	350	22	4.7	0.6	0.1	1.0	
			[53]	[13]	[3]	[32]	
	375	36	8.1	0.9	0.2	1.4	
			[55]	[13]	[2]	[29]	
	400	62	12.7	1.4	0.5	2.3	0.5
			[52]	[11]	[4]	[27]	[6]
$[C_5(CH_3)_5Ir(CH_3)_4]$[c]							
	300	43	20.6	0.2	0.5	0.05	
			[93]	[2]	[5]		
	350	48	22.4	0.4	0.7	0.1	
			[90]	[3]	[6]	[1]	

Compounds	Decomposition (%)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
		10^{-6} mol				
$[C_5(CH_3)_5Ir(CH_3)_4]$[d]						
$+1\ IrCl_6^{2-}$	17	11.8	1.9	1.1	0	0
		[66]	[21]	[12]		
$+2\ IrCl_6^{2-}$	30	26.1	1.2	1.1	0	0
		[85]	[8]	[4]		
$+4\ IrCl_6^{2-}$	46	40.9	1.6	1.5	0	0
		[87]	[7]	[6]		
$+5\ IrCl_6^{2-}$	49	44.8	1.6	1.5	0	0
		[88]	[6]	[6]		

[a] Numbers in square brackets are normalised percentages. [b] 1.0×10^{-7} mol. [c] 1.3×10^{-7} mol. [d] 258×10^{-7} mol; 20—50 °C.

Some experiments were also carried out with the di-iridium complex $[\{C_5(CH_3)_5Ir\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$[11] (**5**) corresponding to *cis*-(**1**) (Table 3). Very similar results to those for the rhodium complex were obtained, except that *cis*-(**5**) was more difficult to decompose (only 11% decomposition at 325 °C, but 62% at 400 °C). In contrast to (**1**), however, the relative amounts of the four gases were rather similar throughout the temperature range investigated. Rather more propylene was found than in the corresponding decomposition of *cis*-(**1**), a little more ethylene, and less methane. On oxidative decomposition with hexachloroiridate, (**5**) gave the same gases; however, significantly less propylene was obtained than from (**1**).

A comparison with the thermal decomposition of the Ir^V complex $[C_5(CH_3)_5Ir(CH_3)_4]$[11] (**6**) under similar conditions was also interesting. Thus, the pyrolysis of 13×10^{-8} mol of (**6**) at 350 °C gave 22.4×10^{-8} mol of methane, but only 0.7×10^{-8} mol of ethane, 0.4×10^{-8} mol of ethylene, and 0.1×10^{-8} mol of propylene (Table 3). At lower temperatures comparable amounts of methane were obtained but even less of the C_2 and C_3 products.

Decompositions induced by Reactions with Oxidising Agents and other Electrophiles.—The (relatively simple) reactions of complex (**1**) with iodine in chloroform proceeded in two discrete steps. The first, essentially quantitative, reaction was the cleavage of the two rhodium-bound methyls to give the known *trans*-$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2I_2]$ (**2c**) and methyl iodide, equation (1). Both *cis*- and *trans*-(**1**) yielded this product with equal facility. The second step of the reaction gave largely ethylene (together with a little methane), and the anticipated and known complex $[\{C_5(CH_3)_5Rh\}_2I_4]$, equation (2).

$$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2] + 2\,I_2 = 2\,MeI + \underset{(\mathbf{2c})}{[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2I_2]} \quad (1)$$

$$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2I_2] + 2\,I_2 = C_2H_4 + [\{C_5(CH_3)_5Rh\}_2I_4] \quad (2)$$

Ethylene was also a main product of thermal decomposition of (**2a**)—(**2d**) (see above).

Different and more interesting decompositions of (**1**) were those induced by electrophiles and especially by addition of stoicheiometric amounts of one-electron oxidisers.

Hydrogen chloride cleaved both Rh–CH_3 groups to give (**2a**) and methane. One equivalent of a protonic acid with a non-co-ordinating anion (*e.g.*, HBF_4), in the presence of a good co-ordinating solvent such as acetonitrile, gave the monomethyl cation, $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)(CH_3CN)]^+$, cleanly together with methane.[6] The use of excess HBF_4 again gave largely methane; however, some ethylene, ethane, and propylene were also formed.

A large number of oxidisers and other electrophiles were tried in reactions with (**1**); most (*e.g.*, $KMnO_4$, OsO_4, tetracyanoethylene, and various peroxides) were slow or gave little coupling product. Ce^{IV} and Ag^+ (as ceric ammonium sulphate and silver tetrafluoroborate respectively) reacted faster and gave ethylene, ethane, and propylene as well as methane,[5] but the most useful reactions were those induced by $IrCl_6^{2-}$ (Table 1). The reactions discussed below, with a four- to six-fold excess of $IrCl_6^{2-}$, were complete within *ca.* 1 h at temperatures of less than 50 °C.

Reaction of Unlabelled (**1**) *with Hexachloroiridate*(IV).—Reaction of hexachloroiridate(IV) with (**1**) in acetonitrile solvent caused decomposition with the formation of methane, ethylene, ethane, and propylene in ratios very close to those found for the thermal reactions (Table 1); small amounts of methyl chloride were also found. The organometallic compound isolated from these reactions was a Rh^{III} complex, either $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}Cl)_3]^+$ (**3**) or $[C_5(CH_3)_5Rh(CH_3CN)_3]^{2+}$ (**4**), depending on the exact reaction conditions.

Reaction of ^{13}C-*Labelled* (**1**) *with Hexachloroiridate*(IV).—Decomposition of complex (**1**-$^{13}C_4$) with hexachloroiridate in acetonitrile gave methane, ethylene, ethane, and propylene, each gas showing the amount of ^{12}C anticipated from the residual ^{12}C methyls and methylenes in the complex. Thus, the methane contained 7%, the ethylene 12%, and the propylene 20% of $^{12}C_1$, compared to the expected values of 8, 15, and 22% respectively.

As in the pyrolyses, reaction of an equimolar mixture of unlabelled (**1**) and (**1**-$^{13}C_4$) showed no crossover. The amounts of $^{12}C^{13}CH_4$, $^{12}C^{13}CH_6$, and $^{12}C_2{}^{13}CH_6$ found were 6, 0, and 0% respectively, compared to the expected of 5, 5, and 0.5% for no crossover and 33, 33, and 26% for complete scrambling.

Thus, in the reaction with hexachloroiridate(IV), as in the thermal decomposition, there is no evidence in the products for the participation either of two molecules of (**1**) or of the $C_5(CH_3)_5$ rings, and we conclude that the products arise only from the combination of methyls and methylenes in one molecule of (**1**).

The gases from the reaction of (**1**-$^{13}C_2$) with hexachloroiridate *each contained just one* ^{13}C *label.* Thus the mass spectra showed the presence of 91% $^{13}CH_4$ in the methane (expected 92%), 92% $^{12}C^{13}CH_4$ in the ethylene (expected 92%), and 89% $^{12}C_2{}^{13}CH_6$ in the propylene (expected 92%); the ethane appeared to be entirely $^{12}C^{13}CH_6$.

Reaction of Deuterium-labelled (**1**) *with Hexachloroiridate*(IV).—The products from complex (**1-D**$_6$), containing two Rh–CD_3 groups, were similarly clean. Thus the methane was 90% CD_3H (and 5% each CD_2H_2 and CD_4), the ethylene 91% $C_2D_2H_2$ (and 7% C_2HD_3), and the propylene 93% $C_3D_3H_3$ (and 3% C_3H_6, 4% C_3H_5D).

The fact that the methane from complexes containing labelled rhodium methyls was virtually all CD_3H (or $^{13}CH_4$) incorporation in the methane, but the amount was quite small (typically *ca.* 5% CDH_3 and 95% CH_4). Similarly, while decomposition of $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$ in cated that when the decomposition of all-protio (**1**) was undertaken in CD_3CN using excess sodium hexachloroiridate(IV) hydrate recrystallised from D_2O, there was some deuterium incorporation in the methane, but the amount was quite small (typically *ca.* 5% CDH_3 and 95% CH_4). Similarly, while decomposition of $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$ in CH_3CN–H_2O gave 99% CH_4 and 1% CH_3D, the same complex decomposed in CD_3CN–D_2O gave 94% CH_4 and 6% CH_3D. Thus we conclude that, while they both can occur, neither solvent cleavage of the rhodium methyl nor hydrogen abstraction from a ring methyl represent the major reaction pathways.

The complex $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CD_3)_2]$ decomposed in CH_3CN–H_2O gave 97% CD_3H and 3% CD_4, while in CD_3CN–D_2O, the ratios were 90:10. This confirms that the extra H (or D) to make the methane does not, in the main, come from either the C_5 ring or from the other rhodium methyl. The only remaining place for it to arise therefore is from one of the bridging methylenes.

That this was indeed the case was shown by decomposition of $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CD_2)_2(CH_3)_2]$, which gave CH_3D (55%) and CH_4 (45%), and that of $[\{C_5(CD_3)_5Rh\}_2(\mu\text{-}CD_2)_2(CD_3)_2]$, which gave CD_4 (40%) as well as CD_3H (60%). The formation of the isotopomer containing more deuterium shows that attack on the deuterium of a methylene does occur. The formation of the isotopomer containing more hydrogen is also expected since neither of these samples contained 100% D (see Experimental section); however the magnitude is higher than might be anticipated and this must be due to the operation of a large deuterium isotope effect influencing the relative rates of cleavage of the methylene C–H and C–D bonds.

Discussion

Mode of Formation of the C_1—C_3 *Gases.*—The decompositions of (**1**), giving as major products methane and propylene, together with some ethylene and a little ethane, either thermally or by oxidation with one-electron oxidants such as hexachloroiridate(IV) must be related processes. The lack of crossover when equimolar (**1**) and (**1-**^{13}**C**$_4$) were reacted indicated that in each case the major reactions occurred within one molecule of (**1**). However, as the oxidative reactions are cleaner, with less scrambling (of deuterium, probably since they take place at 20—50 °C rather than 275—375 °C), they will be considered first.

(*a*) *In the hexachloroiridate oxidations.* The labelling experiments show that the methane is derived primarily from the rhodium methyls in the hexachloroiridate oxidations. Our preliminary cyclic voltammetry studies indicate that the first step in oxidation is a reversible one-electron oxidation, followed by an irreversible further one-electron process (which is in turn followed by one other reversible and one other irreversible steps). We interpret this to mean that decomposition with release of methane only occurs after the second electron is removed, presumably from a transient Rh^V–Rh^V species, equation (3).

$$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2] + 2\,IrCl_6{}^{2-} = [\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]^{2+} + 2\,IrCl_6{}^{3-} \quad (3)$$

There is no evidence that this species gives a methyl radical, since that would be expected to abstract hydrogen from the solvent (or a ring methyl) to form methane. The deuterium labelling studies show that at high hexachloroiridate ratios, such paths only account for perhaps 10% of the overall reaction; the major reaction path involves an intramolecular abstraction of hydrogen from a methylene bridge, to yield a further intermediate methyl–μ-methylene–μ-methyne dicationic species (**A**): equation (4).

$$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]^{2+} = \underset{\textbf{(A)}}{[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CH)(CH_3)]^{2+}} + CH_4 \quad (4)$$

We further suggest that (**A**) is the source of the C_2 and the C_3 gases after further oxidation. The fact that the oxidation of (**1**) has effectively gone to completion after the addition of four equivalents of hexachloroiridate is consistent with the cyclic voltammogram which suggests that four electrons can be removed from (**1**).

Although there seems to be no direct previous analogy for the process leading to (**A**), we note that the complex $[(C_5H_5Ru)_2(\mu\text{-dppm})(\mu\text{-}CH_2)(\mu\text{-}CO)]$ [dppm = bis(diphenylphosphino)methane], containing a μ-methylene group, undergoes a two-electron oxidation, the product of which, after loss of a proton, is the cationic μ-methyne complex, $[(C_5H_5Ru)_2(\mu\text{-dppm})(\mu\text{-}CH)(\mu\text{-}CO)]^+$.[12]

Attempts to trap (**A**) have so far not been successful. However, support for the idea that methane is formed in the first step has been obtained. We find that methane (together with *ethane*, but no ethylene or propylene) is the main product when (**1**) is gently oxidised at low temperatures with ferrocenium ion.

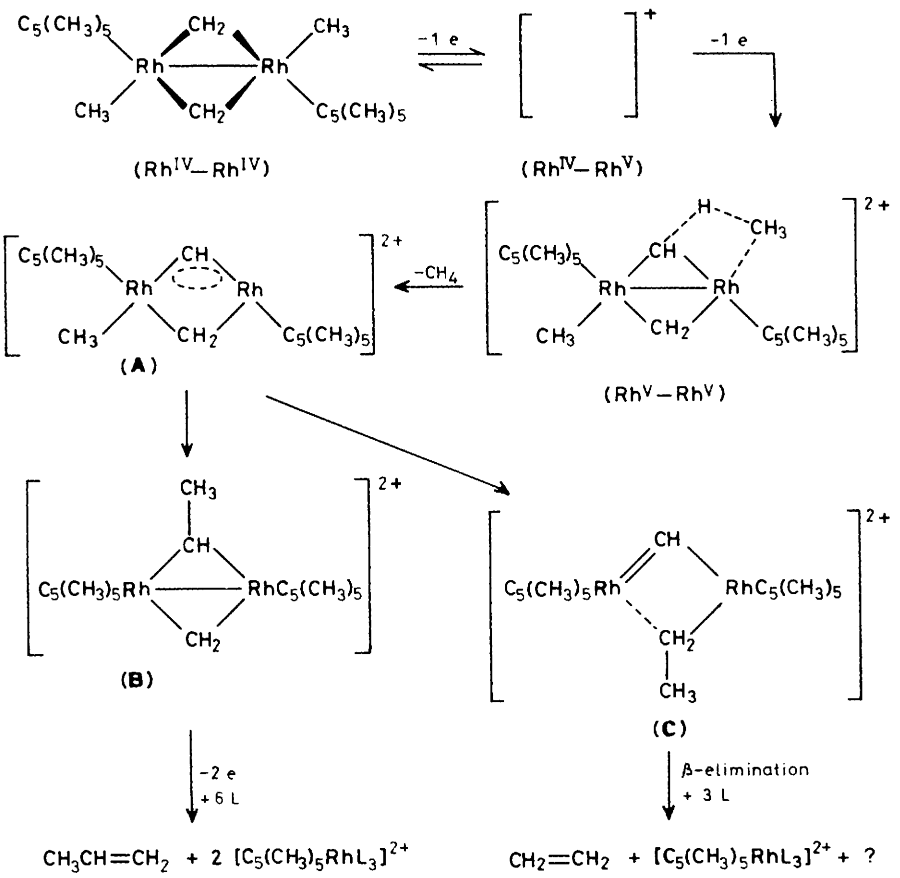
Intermediate (**A**) can, in principle, decompose by migration of the methyl onto either the μ-methyne or onto the μ-methylene carbon. Either path may be ligand assisted, as for example, when the reaction is carried out in acetonitrile solution (L = CH_3CN).

Possible paths are illustrated in Scheme 3 (all the species are expected to be solvated by L but these have not been specifically included). In the first case, the product of migration of the methyl onto the methyne would be the dicationic μ-methylene–μ-ethylidene intermediate (**B**), equation (5). Further oxidation, in the presence of a ligand L, could then lead from (**B**) to propylene by coupling of the μ-methylene–μ-ethylidene bridges, and to the final product, $[C_5(CH_3)_5RhL_3]^{2+}$ (**4**, L = MeCN), in the presence of L, equation (6).

$$\underset{\textbf{(A)}}{[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CH)(CH_3)]^{2+}} + 2\,L = \underset{\textbf{(B)}}{[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CHCH_3)L_2]^{2+}} \quad (5)$$

$$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CHCH_3)L_2]^{2+} + 4\,L - 2\,e = 2\,[C_5(CH_3)_5RhL_3]^{2+} + CH_3CH{=}CH_2 \quad (6)$$

Cationic μ-methyne complexes have been shown to electrophilically attack olefins,[13] and to react with $LiCH_3$ giving an



Scheme 3. 'Heterolytic' decomposition paths

ethylidene.[12] It is therefore quite plausible that, in the presence of an internal substrate, in the form of a rhodium–methyl, migration [(**A**) to (**B**)] should occur.

Such a route *via* (**A**) and (**B**) agrees with the labelling pattern of the propylene obtained from labelled precursors. Thus, the hexachloroiridate decomposition of the Rh–CD$_3$ labelled complex showed that most of the propylene (93%) was $C_3H_3D_3$.

The formation of olefins from the coupling of di-μ-methylene complexes has been well documented; in particular Knox and co-workers[14] found that $[(C_5H_5Ru)_2(CO)_2\{C(CH_3)_2\}(CHCH_3)]$, which contains two rutheniums bridged by a μ-$C(CH_3)_2$ and a μ-$CHCH_3$ ligand, gave $CH_3CH{=}C(CH_3)_2$ (and C_5 isomers) but no C_4 or C_6 hydrocarbons on pyrolysis. This indicated that the reactions there were also intramolecular and implied that the C_5 olefins were formed by coupling of the μ-alkylidenes. Similar results have been described for a dicobalt system,[15] and such a step is invoked in the above mechanism in order to explain the labelling we see of the propylene.

The labellings seen in the ethylene derived from decompositions of (**1**-$^{13}C_2$) and of (**1**-D_6) also give valuable mechanistic information. They indicate first that the formation of ethylene from (**1**) does *not* take place by coupling of two methylenes, since it contains one carbon derived from a methyl and one from a methylene. The deuterium labelling of the ethylene (91% $C_2D_2H_2$ and only 7% C_2HD_3), formed on oxidation of the Rh–CD$_3$ complex implies that the methyl which has become one carbon of the ethylene has lost one of its original hydrogens. This is *not* consistent with the ethylene arising by rearrangement and release of the bridging ethylidene in the intermediate (**B**), $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CHCH_3)L_2]^{2+}$, since that would be expected to yield only C_2D_3H.

The labelling observed in the ethylene would however be quite consistent with a β-elimination from a rhodium ethyl, *e.g.* equation (7). This can only arise from (**A**) if migration occurs

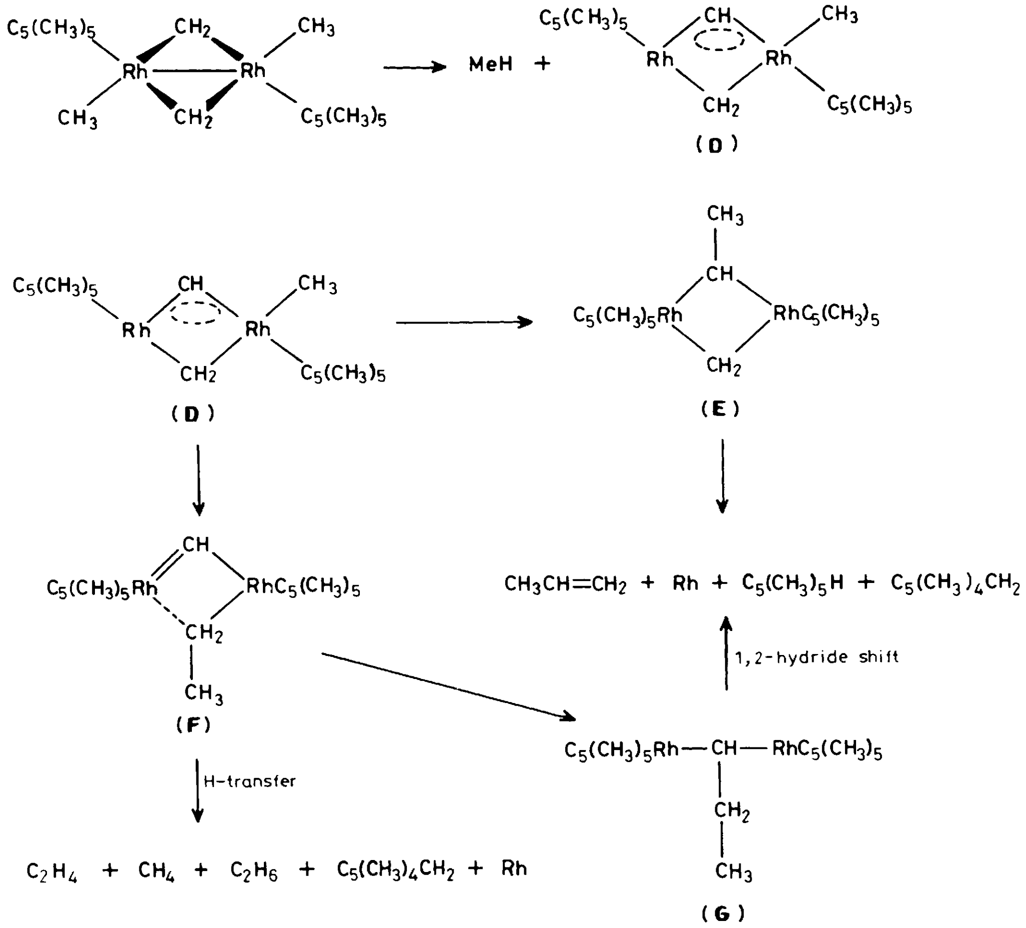
$$RhCH_2CD_3 = RhD + CH_2{=}CD_2 \qquad (7)$$

of a methyl onto a *methylene*. We therefore suggest that the methyl in the intermediate (**A**), $[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CH)(CH_3)]^{2+}$ is able to migrate onto the methylene carbon giving the intermediate (**C**). In that case, the reaction path in equation (8) is established. β-Elimination from the μ-ethyl

$$\begin{aligned}&[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CH)(CH_3)]^{2+} + nL = \\ &\qquad [\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2CH_3)(\mu\text{-}CH)L_n]^{2+} \qquad (8)\\ &\qquad\qquad\qquad\qquad (\mathbf{C})\end{aligned}$$

(which may exist in equilibrium with a terminal ethyl) would then give ethylene with the correct deuterium labelling. The ethylene from (**1**-$^{13}C_2$) would also be expected to have one ^{12}C and one ^{13}C, as found.

There is ample precedent for the formation of ethylene by migration of methyl onto a methylene, and this type of reaction has been investigated by several workers,[16,17] especially for $[(C_5H_5)_2W(R)(CH_3)]$ complexes where the migration of methyl, ethyl, and phenyl onto methylene has been described.[16] It has been noted that such migrations are facilitated when the complex has a formal positive charge, *i.e.* when the CH_2 may be presumed electrophilic.



Scheme 4. 'Homolytic' decomposition paths

The data (Table 1) show that on oxidation with excess hexachloroiridate, one methane arises from each molecule of (**1**) and that the amounts of C_2 plus C_3 products are about the same. If both migration paths (onto a μ-methylene and onto a μ-methyne) occur, this would imply that there is approximately three times the probability of the methyl migrating onto the μ-methyne [to give (**B**)] as on to the μ-methylene [to give (**C**)].

However, these processes must be very susceptible to the precise reaction conditions. Thus for example, there is more ethylene formed with lower amounts of oxidant (and also in the thermal decomposition, at lower temperature). Propylene begins to be a more dominant product at higher amounts of oxidant (or thermally, at higher temperatures).

A major reaction path of the hexachloroiridate oxidation of (**1**) may therefore be represented by equation (9). Although the

$$[\{C_5(CH_3)_5Rh\}_2(CH_2)_2(CH_3)_2] + 4\,IrCl_6^{2-} + 6\,CH_3CN = 2\,\underset{\textbf{(4)}}{[\{C_5(CH_3)_5Rh\}(CH_3CN)_3]^{2+}} + CH_4 + CH_3CH{=}CH_2 + 4\,IrCl_6^{3-} \quad (9)$$

tris(acetonitrile) complex dication (**4**) could be isolated when such a reaction was run on a larger scale, the more usual product was the tri-μ-chloro cation (**3**), since chloride (from the hexachloroiridate) readily displaced the acetonitrile. The overall reaction leading to propylene (and methane) is thus more correctly given as in equation (10).

$$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2] + 4\,IrCl_6^{2-} + 3\,CH_3CN = \underset{\textbf{(3)}}{[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}Cl)_3]^{+}} + 3\,[IrCl_5(CH_3CN)]^{2-} + IrCl_6^{3-} + CH_4 + CH_3CH{=}CH_2 \quad (10)$$

The labelling results effectively exclude a mechanism in which propylene is formed by the coupling of a CH_2 with ethylene (or a $M{-}CH_2{-}CH_2{-}M$ bridge), *via* a dimetallacyclopentane, $\overline{M{-}M{-}CH_2{-}CH_2{-}CH_2}$, as has been shown to occur in other systems.[18–20] If this were an important mechanism of the reaction then the predominant product from (**1**-D_6) would not be expected to be $C_3H_3D_3$.

We can also make some observations on the minor reactions which occur. Methane can be formed by protolysis [equation (11)] (especially at low $IrCl_6^{2-}$ concentrations, but also in small amount at high $IrCl_6^{2-}$ levels).

$$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2] + 2\,H^+ + 2\,CH_3CN = [\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3CN)_2]^{2+} + 2\,CH_4 \quad (11)$$

Decomposition of such dicationic species leads to ethylene [see equations (1), (2), and below]. Hydrogen abstraction by a rhodium propyl from a ring methyl can yield propane, traces of which are occasionally observed.

Ethane is a very minor product both from the thermal and the oxidative decomposition of (**1**). The ^{13}C labelling experiments indicate that it is formed chiefly in a reaction parallel to that forming the ethylene, and we suggest that a rhodium–ethyl intermediate acquires a hydrogen, either from solvent or from another part of the molecule, for example a ring methyl, to form the ethane. However, this process is very much less favoured than the β-elimination. There is no evidence that ethane is formed by combination of two rhodium–methyls; this agrees with the theoretical analysis by Trinquier and Hoffmann[21] that a concerted reductive elimination of R_2 from a dinuclear system R–M–M–R (R = alkyl) is a very unfavourable process.

(*b*) *Thermal decomposition reactions*. The labelling studies using (**1**-$^{13}C_4$) alone and in admixture with unlabelled (**1**) showed that the thermal decompositions were also intramolecular and did not involve carbons from the $C_5(CH_3)_5$ rings. This fact is supported by other evidence showing that C–C cleavage of the pentamethylcyclopentadienyl rings does not occur under such pyrolysis conditions. Thus, for example, the di-μ_3-methyne-trirhodium complex (**7**)[22] and $[C_5(CH_3)_5Rh(cod)]$ (cod = cyclo-octa-1,5-diene) gave only trace amounts of methane (< 1%) and other gases under conditions where (**1**) and its analogues gave substantial quantities. The absence of fragmentation for those molecules under conditions where (**1**) breaks down easily [equation (12)] also implies that the

$$[\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2] = [\{C_5(CH_3)_5Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CH)(CH_3)] + CH_4 \quad (12)$$

$C_5(CH_3)_5$ ring cannot be the source of these gases.

Unfortunately, the pyrolyses of the deuterium-labelled complexes generated no useful information owing to the extensive scrambling which interchanged not only rhodium methyl and methylene hydrogens but also those on the ring methyls.

The methane from (**1**-$^{13}C_2$), where both rhodium methyls are labelled, was composed equally of $^{12}CH_4$ and $^{13}CH_4$. Clearly, half of the methane must then originate from a methyl and half from a methylene. The origin of the first is straightforward and, in the absence of other, contrary data, we may assume a mechanism not too dissimilar from that described for the hexachloroiridate oxidation. Scheme 4 depicts related reaction sequences, similar to those for the oxidative reaction except that much more energy is needed to break the appropriate bonds (homolytically) in the absence of a stabilising solvent (ligands) and the oxidant.

The ^{12}C-methane may then arise as a by-product of the ethylene/ethane formation, where a bridging CH, not required to build up the C_2 hydrocarbon is free to acquire hydrogens to give methane. Alternatively, it is possible that, at the high temperatures involved in the thermal decompositions, methyl/methylene exchange may take place, perhaps *via* terminal Rh(=CH_2)(–CH_3). (The ability of μ-methylenes to equilibrate into terminal positions has been described for other, related systems by a number of authors.[23]) The reaction may then be completed by the transfer of hydrogen, probably from a $C_5(CH_3)_5$ ring; support of this is lent by our observation that one product from the pyrolysis is tetramethylfulvene.

The ethylene and the ethane formed from (**1**-$^{13}C_2$) did not show such extensive scrambling and the data allow useful conclusions to be drawn. Thus since both the ethylene and the ethane contained at least 90% $^{12}C^{13}C$ (and negligible amounts of $^{12}C_2$ or $^{13}C_2$), neither arises by direct coupling (of two methylenes or of two methyls).

We can also rule out a complete scrambling of *all* the C_1 ligands prior to coupling, since on that basis a statistical distribution of $^{12}C_2$, $^{12}C^{13}C$, and $^{13}C_2$ would be expected. Further, if there were complete scrambling, the propylene from this reaction should contain 50% $^{12}C_2{}^{13}CH_6$ and 50% $^{12}C^{13}C_2H_6$, which is not the case. Thus, we may conclude that the formation of ethylene, ethane, and propylene in the pyrolyses is quite separate and distinct from any interchange which equilibrates the methyl and methylenes. This suggests a decomposition path very similar to that described above in the hexachloroiridate decompositions, the H/D exchange acting as a further perturbation on top of that.

Although more homolytic pathways such as are shown in Scheme 4 may operate, we cannot rule out the possibility that the transient intermediates are also ions similar to those shown in Scheme 3, the high decomposition temperatures being needed to form ions in the absence of solvent and oxidant.

Other Complexes.—By contrast to those reactions discussed above, both thermal and oxidative decomposition of the di-iodo complex (**2c**) gave much ethylene, which, it is reasonable to expect, comes from a coupling of the two methylene bridges. The mechanisms of the reaction of (**2c**) with iodine giving ethylene, and of the closely similar thermal breakdown of (**2a**), (**2b**), and (**2d**) are not known, but one possibility is that they both involve X–CH_2–Rh and X–CH_2–CH_2–Rh intermediates (X = halide, *etc*.), the last of which undergoes β-elimination of ethylene to leave Rh–X.

Grubbs and co-workers[24] found that while the di-μ-methylene-dititanium complex $[(C_5H_5)_2Ti(\mu\text{-}CH_2)_2Ti(C_5H_5)_2]$ underwent thermal breakdown to give largely (92%) methane, a little ethane (7%) and only a trace of ethylene, with iodine it gave largely ethylene (78%) and only a little methane (22%). These reactions may be related to the decompositions we find for (**2**).

However, Hoffmann *et al.*[25] predicted that the conversion of a bis(carbene) complex into an olefin complex would be allowed for d^4, d^6, and some d^8 electron counts and could be facilitated by making the metal more electronegative. It is therefore possible that the observed formation of ethylene from decomposition of (**2**) is a concerted coupling of two carbenes, by analogy to what appear to be direct coupling reactions in the pyrolyses of the d^6 ruthenium complex $[(C_5H_5Ru)_2(CO)_2\{\mu\text{-}C(CH_3)_2\}(\mu\text{-}CHCH_3)]$[14] and of the d^8 cobalt complex $[(dppm)Co_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}CHR)]$ (R = alkyl).[15]

The thermal decompositions of (**5**), the iridium analogue of (**1**), show that a series of very similar processes to those described for (**1**) take place. The chief differences observed were (*i*) *cis*-(**5**) was more thermally stable and more difficult to decompose than (**1**), (*ii*) the relative amounts of the gases obtained were similar throughout the temperature range investigated, and (*iii*) less methane but more propylene and more ethylene were formed from (**5**) than (**1**). These data are consistent with the intermediates to propylene and ethylene being more stable for the iridium than for the rhodium and are entirely consistent with the usually observed greater kinetic inertness of iridium compared to rhodium complexes.

This quality may also be responsible for the iridium complex (**5**) giving less propylene (and proportionately more methane) than does (**1**) on oxidation with hexachloroiridate. This could be the case if the species remaining after loss of methane from (**5**) were more stable than (**A**) and therefore rearranged in other ways. We have not as yet examined this reaction fully.

The fact that, by comparison to (**5**), the iridium(v) tetramethyl complex (**6**) gave only traces at most of propylene on thermal decomposition, and no detectable amount of propylene on oxidative decomposition, emphasises the very unique nature of (**1**), (**5**), and their analogues. This is presumably due to their being dinuclear and indicates the need for two metal centres in the three-carbon coupling reaction.

Conclusions

This work has shown that propylene is formed by the specific coupling of three C_1 fragments in two steps from one methyl and two methylenes, that ethylene (and ethane) arise from the coupling of one methylene and one methyl, and that both are formed by similar paths in both pyrolytic and oxidative decompositions.

The first stage in the oxidative decomposition is promoted by initial formation of a methyne in a dicationic centre, which arises by loss of hydrogen from a methylene to a methyl, giving methane. Although we prefer a path to propylene *via* migration of methyl onto methyne and a coupling of the resultant ethylidene with a further methylene, alternatives are possible.* The ethylene formed arises neither from an ethylidene, nor from direct coupling of two methylenes, but from a rhodium–ethyl.

The path proposed here for the formation of propylene is also different from the one postulated to occur through the intermediacy of a dimetallacyclopentane, formed by insertion of ethylene into a $M-CH_2-M$ bridge.[18—20,26]

Perhaps the most intriguing result from this work, however, is the discovery that the thermal decomposition and the ensuing coupling reactions are most dramatically accelerated by electrophiles, and especially by one-electron oxidants. This may well be because the alkyl migrations are facilitated by a positive charge.

This result is complementary to but quite different from the work of Kochi[27] and others[28] who have shown that one-electron oxidisers very significantly promote direct coupling reactions, such as $L_nMR_2 \longrightarrow R_2$, by what is most probably a one-electron oxidation of the metal centre.

There may also be a parallel activation to the one we see in the true catalytic Fischer-Tropsch reaction. Thus several authors have recently noted that, in the hydrogenation of carbon monoxide on rhodium metal, the amounts of products and the proportion of hydrocarbons higher than methane increased very dramatically when the rhodium was supported on an oxidising substrate, for example, TiO_2,[29,30] or when a (partly) oxidised rhodium catalyst was employed.[31,32] It is not inconceivable that the oxidiser is playing a role similar to that of the hexachloroiridate in the decomposition of (**1**), in other words that it creates positively charged hydrocarbyl species on the metal surface to which migration is greatly facilitated, thus increasing the rates and the chain lengths of the products formed.

If this is the case, then we may conclude that there is a further variant on the Brady-Pettit version[3] of the Fischer-Tropsch mechanism, namely a path that in outline goes most easily, equation (13), where M_n bears positive charge.

$$M_n(CH)(CH_2)R \longrightarrow M_n(CH)CH_2R \longrightarrow M_nCHCH_2R \longrightarrow M_n + RCH{=}CH_2 \quad (13)$$

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* *Note added in proof*: further studies, currently in progress, are expected to show more fine detail of the process.