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Invited review

The lively chemistry of the di-μ-methylene-bis(pentamethylcyclopentadienyl-rhodium) complexes, analogues of surface reactions in heterogeneous catalysis

Peter M. Maitlis

Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, UK

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Abstract

The chemistry of the di-μ-methylene-bis(pentamethylcyclopentadienyl-rhodium) complexes is reviewed. The complex $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ (**1a**) reacted with MeLi to give, after oxidative work-up, blood-red *cis*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)_2]$, **2**. This has the two rhodiums in the +4 oxidation state (d^5), and linked by a metal–metal bond (2.620 Å). *Trans*-**2** was formed on isomerisation of *cis*-**2** in the presence of Lewis acids, or by direct reaction of **1a** with Al_2Me_6, followed by dehydrogenation with acetone. The Rh-methyls in $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)_2]$ were readily replaced under acidic conditions (HX) to give $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(X)_2]$ (X = Cl, Br or I); these latter complexes reacted with a variety of RMgX to give $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(R)_2]$ (R = alkyl, Ph, vinyl, etc.). *Trans*-**2** also reacted with HBF_4 in the presence of L to give first $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(L)]^+$ and then $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(L)_2]^{2+}$ (L = MeCN, CO, etc.). The $\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2$ core is rather kinetically inert and also forms a variety of complexes with oxy-ligands, both *cis*-, e.g. $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(\mu\text{-}OAc)]^+$ and *trans*-, such as $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(H_2O)_2]^{2+}$. The complexes $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(R)L]^+$ (R = Me or aryl) in the presence of CO, or $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(R)_2]$ (R = Me, Ph or CO_2Me) in the presence of mild oxidants, readily yield the C–C–C coupled products $RCH{=}CH_2$. The mechanisms of these couplings have been elucidated by detailed labelling studies: they are more complex than expected, but allow direct analogies to be drawn to C–C couplings that occur during Fischer–Tropsch reactions on rhodium surfaces.

Keywords: Rhodium; Methylene; C–C coupling; Heterogenous catalysis; Cyclopentadienyl; Pentamethyl; Fischer–Tropsch

1. The discovery of $[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(Me)_2]$

Jung Kang and I originally discovered the pentamethylcyclopentadienyl rhodium and iridium complexes, $[\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2]$ (**1a**, M = Rh; **1b**, M = Ir) in 1968 [1]. In the years since then, my group [2] and many other researchers around the world, have derived much pleasure and profit from the reactions of these sprightly molecules. Because of their unique combination of inert η^5-C_5Me_5-ring to metal bonds and labile anionic ligands, they undergo an enormous variety of reactions without loss of the ring, including nucleophilic substitution, C–H activation, hydrogen transfer, oxidation and reduction (both electrochemical and chemical), catalysis, as well as photochemical and bioinorganic transformations. Their low sensitivity to air and moisture, the ease with which they afford crystals, and their ability to promote enticing reactions and to stabilise unusual ligand systems, has made them great favourites with the organometallic community. The last time I counted, over 800 papers had been written on some aspect of their chemistry.

In 1980, Dr. Kiyoshi Isobe from Osaka in Japan joined my group as a postdoctoral fellow. We decided to see what would happen if he reacted the pentamethylcyclopentadienyl rhodium chloride complex with an organo-lithium or an organo-aluminium reagent. We knew that if we reacted $[(\eta^5\text{-}C_5Me_5)RhCl_2L]$ (where L is a neutral ligand, R_3P, for example) with a methyl Grignard or methyl-lithium reagent we would get $[(\eta^5\text{-}C_5Me_5)RhMe_2L]$; a straightforward six-coordinate Rh(III) complex, d^6, is quite stable of course. But what if there was no stabilising ligand L and we just reacted the chlorine bridged dimer, $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$, **1a** with an excess of the methylating agent? The initial

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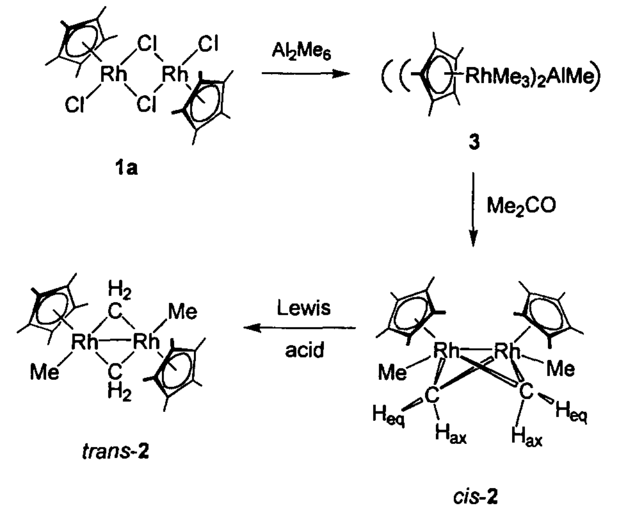
product might be expected to be the solvated [(η^5-C_5Me_5)Rh(Me)$_2$(solv)], but if the solvent was weakly bonded, that was unlikely to survive as such and should undergo further transformations. One of the great features of the (η^5-C_5Me_5)Rh system is that the stability of the ring–metal bond is so great that we felt confident we would get an isolable and stable product. But what would it be? It was this question which Kiyoshi and I then set out to answer.

In fact the reaction of **1a** with methyllithium in a hydrocarbon solvent produced a yellow solution which gave, after work-up, beautiful blood-red crystals, which turned out to be the *cis*-isomer of [{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(Me)$_2$] **2**. The *trans*-isomer was preferentially formed on reaction of **1a** with Al_2Me_6, and we later found that the *cis*-isomer readily isomerised to the *trans* in the presence of Lewis acids [3,4]. We also noticed that the characteristic red colour of the product **2** only developed after the yellow reacting solution had been exposed to air.

We deduced the structures of *cis* and *trans*-**2** from microanalysis, molecular weight measurements and, especially, their NMR spectra, which showed the presence of bridging methylenes at low field, both in the ^1H and the ^{13}C NMR spectra. The ^1H NMR spectrum of the *trans* (centrosymmetric) isomer showed the methylene hydrogens as a triplet (δ 8.03) with coupling to both rhodiums ($J = 1.8$ Hz; ^{103}Rh, 100%, $I = 1/2$). However in the lower symmetry *cis*-isomer the hydrogens on each μ-CH_2 are inequivalent, one being axial (and closer to the Rh-methyls), the other equatorial and closer to the η^5-C_5Me_5 rings (Scheme 1). Nuclear Overhauser enhancement experiments identified each and showed that only the equatorial hydrogens were coupled to both rhodiums, as well as to the axial hydrogens, overall showing a doublet of triplets (δ 8.10; $J = 1.8$ and 2.6 Hz). The axial hydrogens were only coupled to the equatorial giving a doublet (δ 6.96, $J = 1.8$ Hz). The structures thus deduced by sporting methods were then confirmed by X-ray crystal structure determinations.



Scheme 1.

The complex **2** was an alluring molecule with many possibilities; the only problem was that in order to explore the chemistry we needed a good high yield synthesis. Unfortunately, the original preparation gave a yield of only 15%–20% at best, and it had an unusual feature which made it impracticable to scale up substantially. If the first step was formation of a weakly solvated dimethylrhodium [(η^5-C_5Me_5)Rh(Me)$_2$(solv)] or a closely related molecule (see below), to get from there to **2**, one methyl needed C–H activation to lose one hydrogen, and the resultant "(η^5-C_5Me_5)Rh(CH_3)(CH_2)" had to dimerise. The need to lose hydrogen explained why oxygen was needed and why no colour was observed until it was admitted. In the first experiments we used air (inadvertently!) as oxidant, occasionally accompanied by spectacular fireworks(!); we then tried a variety of other oxidants and hydrogen transfer

Table 1
References to X-ray structures of di-μ-methylene-bis(pentamethylcyclopentadienyl rhodium) complexes, with Rh–Rh distances

Complex	Rh–Rh (Å)	Reference
cis-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(Me)$_2$], *cis*-**2**	2.620(1)	[3]
trans-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(Ph)(Br)], **6**	2.6410(10)	[15]
trans-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(Ph)$_2$], **7**	2.6218(11)	[15]
trans-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(σ-CH=CH_2)$_2$], **8a**	2.588(2)	[16]
trans-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(SCN)$_2$], **9**, X = SCN	2.657(2)	[17]
trans-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(N_3)$_2$], **9**, X = N_3	2.635(2)	[17]
trans-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(CO)$_2$]$^{2+}$, **12**, L = CO,	2.659(1)	[19]
cis-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(μ-O_2COH)]$^+$, **15b**	2.591(1)	[21]
trans-[{(η^5-C_5Me_5)Rh}$_2$(μ-CH_2)(μ-CHMe)(Cl)$_2$], **17**	2.678(3)	[16]
cis-,*cis*-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_4$(μ-CN)$_2$]$^{2+}$ **18**	2.676(3)	[22]
[(η^5-C_5Me_5)Rh(σ-CH_2Ph)(μ-CH_2)$_2$Rh(η^4-$C_5Me_5CH_2$Ph)], **20**	2.559(3)	[23]
cis-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(μ-SH)]BPh_4, **21**	2.554(1)	[24]
trans-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(SH)$_2$], **22**	2.6487(3)	[24]
cis-,*cis*-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_4$(μ_4-S)](CF_3SO_3)$_2$, **23**	2.5786(8)	[25]
cis-,*cis*-{{(η^5-C_5Me_5)Rh(μ-CH_2)}$_4$(μ-S_4)](BF_4)$_2$, **24**,	2.6618(4)	[26]

agents, without substantial improvement. The yield of the reaction remained obstinately low.

I asked a Spanish postdoctoral fellow, Amelio Vázquez de Miguel, who had come to our laboratory, to try if he could to improve the synthesis. He worked night and day for many weeks, trying every variation we could devise, but with little luck. One day he decided, for his *n*th attempt, to add acetone as a H-acceptor before work-up, using as model a H-transfer reaction we had been using in the laboratory at that time with ruthenium phosphine complexes [5]. He told me what he had done. I tried to be encouraging, but did not feel very hopeful. A couple of hours later Amelio came back to my office, very excited, "I've done it, the acetone worked" he said, "it gave a 90% yield!" [6].

With a good yield synthesis [7] under our belts, work on these di-μ-methylene complexes took off, and we were able to see what reactions these unusual molecules underwent.

One useful feature was that while the methyls were readily removed, for example, with acids, the methylene bridges were much more resistant. Thus we developed a chemistry of the di-μ-methylene dirhodium nucleus. This was exciting; such dirhodium species were unknown, in particular since in **2**, and the complexes derived from it, the rhodium was formally in the +4 oxidation state (d^5) and as the complexes were diamagnetic that predicated electron pairing via a Rh–Rh bond. Indeed the distance between the two metals was quite short (Table 1) in all these complexes, consistent with the presence of such a bond. Although the high (for rhodium) oxidation state did not manifest itself in oxidising reactions, the rhodiums were quite hard Lewis acid centres, and readily formed carbonates, nitrates and aquo-complexes.

That relative hardness of the metal centre may well be the reason for the rather different reactivity characteristics shown by these systems compared with those of the structurally related diruthenium systems studied by Knox and his coworkers [8]. The μ-methylenes in the Knox ruthenium complexes undergo even more extensive interconversions than those in our $Rh_2(\mu\text{-}CH_2)_2$ complexes, but the ligands normally remain complexed to the metal and are difficult to remove. The ease with which organic ligands can be coupled and then decomplexed under quite mild conditions in the dirhodium complexes (see below) may be a consequence of the presence of slightly harder metal centres.

Parenthetically, however, it should be noted that the formal oxidation state generally seems to have little effect on the electronic levels of the metal in these pentamethylcyclopentadienyl complexes. Photoelectron spectra show rather small and random differences in ionisation energies for iridium in the three complexes, $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$, $[(\eta^5\text{-}C_5Me_5)Ir(CH_3)_2(Me_2SO)]$, and $[(\eta^5\text{-}C_5Me_5)Ir(CH_3)_4]$, each of which has a very different formal oxidation state, Ir(I), Ir(III), and Ir(V) respectively [9].

Complexes such as **2** and the others featured in this review are by no means the only μ-methylene-dirhodium complexes, or even the first to be prepared. That distinction goes to those pioneered by Herrmann [10] and Shapley [11] and their coworkers. Thus, for example, Herrmann found that our $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)_2]$ [12] reacted readily with a variety of diazoalkanes to give mono-μ-alkylidene dirhodium complexes, such as $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)]$. That complex and its $\eta^5\text{-}C_5H_5$ analogue were much more labile than the $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(X)(Y)]$ systems; they underwent dynamic behaviour and were also easily protonated, with eventual loss of the C_1 ligand as methane.

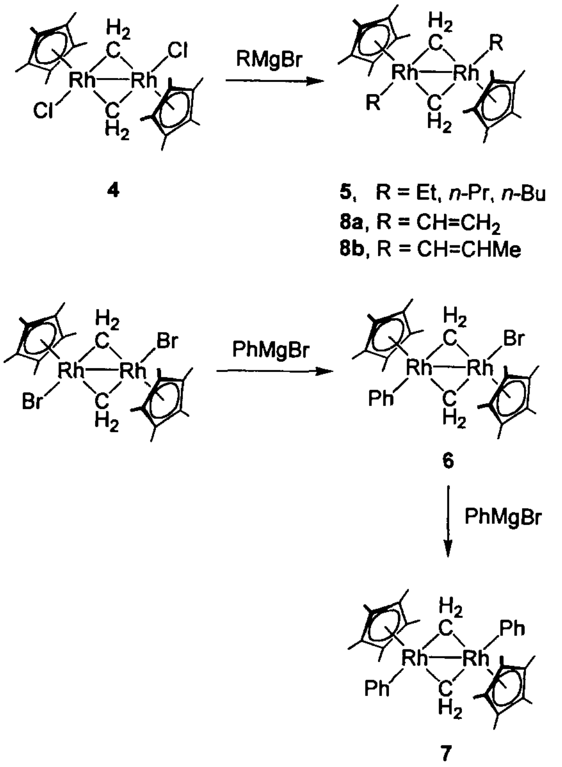
2. The formation of $[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(Me)_2]$ 2 and homologues thereof

The reaction of the dichloro-rhodium(III) complex **1a** with Al_2Me_6 at low temperature was monitored by ^{13}C NMR spectroscopy [6,13]. Only one rhodium-containing product **3** (Scheme 1) was detected at −90°C in toluene-d_8; this had a single $\eta^5\text{-}C_5Me_5$ and two different methyls (in the ratio 2 : 1) both showing coupling to a single ^{103}Rh. In addition, there were resonances due to Al_2Me_6 (present in excess), $Al_2Cl_2Me_4$, as well as a single methyl belonging to another aluminium species. Careful integrations showed that the reaction of **1a** and Al_2Me_6 proceeded along the path indicated by Eq. (1).

$$2\left[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2\right] + 5Al_2Me_6 \rightarrow 2\underset{\mathbf{3}}{\left[\{(\eta^5\text{-}C_5Me_5)RhMe_3\}_2AlMe\right]} + 4Al_2Cl_2Me_4 \quad (1)$$

$$\left[\{(\eta^5\text{-}C_5Me_5)RhMe_3\}_2AlMe\right] + 2Me_2SO \rightarrow 2\left[(\eta^5\text{-}C_5Me_5)RhMe_2(Me_2SO)\right] + 2AlMe_3(Me_2SO) \quad (2)$$

If the reaction was quenched with dimethyl sulphoxide at this point, the six-coordinate Rh(III) complex $[(\eta^5\text{-}C_5Me_5)Rh(Me)_2(Me_2SO)]$ was isolated in good yield. It was not possible to investigate the subsequent reaction of **3** with acetone as H-acceptor to give **2** plus isopropanol since that was too fast, however it was clear that the aluminium was also involved since there was no reaction between $[(\eta^5\text{-}C_5Me_5)Rh(Me)_2(Me_2SO)]$ and acetone by themselves. The iridium-complex $[\{(\eta^5\text{-}C_5Me_5)IrCl_2\}_2]$ formed a similar species, $[\{(\eta^5\text{-}C_5Me_5)IrMe_3\}_2AlMe]$ with Al_2Me_6 at low temperature,



Scheme 2.

but this did not readily give the iridium analogue of complex **2** [14].

The higher aluminium alkyls did not react with **1a** in the same way, and thus the homologues of **2** need to be made by indirect routes from **2**. For example, reaction of the dimethyl complex **2** with Al_2Et_6 or reaction of the dichloro-complex $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Cl)_2]$ **4**, X = Cl, with a Grignard (EtMgBr, Pr^nMgBr, or Bu^nMgBr) gave the dialkyls $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(R)_2]$ **5**, R = Et, Pr^n, and Bu^n (Scheme 2). A similar route has recently been developed to make the monophenyl **6** and the diphenyl complexes **7**; however, those preparations are very sensitive to the halide and only work well if the bromides **4**, X = Br, are used [15].

One further useful set of derivatives of **2**, the divinyl and dipropenyl complexes (**8a**, R = H and **8b**, R = Me, respectively), have also been made by related routes [16].

3. Reaction of $[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(Me)_2]$ with acids; the loss of one and two methyls

Some of the simplest reactions of **2**, and the first to be carried out, were those with acids, where first one rhodium methyl and then the other was replaced, and methane was liberated. When a pentane solution of complex **2** was treated with hydrogen chloride brown crystals of *trans*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Cl)_2]$ precipitated from the solution. The highly coloured *trans*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(X)_2]$ (**9** X = Br (purple), I (blue–purple), SCN (pink), N_3 (pale red), CN or NCO) could be obtained from this by metathesis (Scheme 3) [17].

The dimethyl complex **2** also reacts directly with two equivalents of halogen (Br_2 or I_2) to give the dihalo-complex and the alkyl halide (Eq. (3))

$$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me_2)_2] + X_2 \rightarrow [\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(X)_2] + 2MeX \tag{3}$$

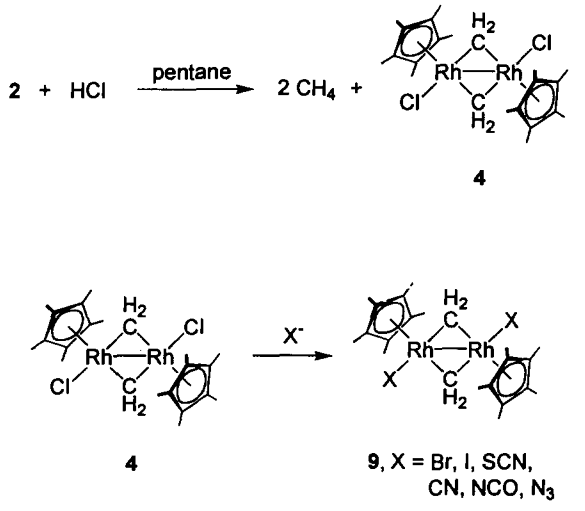
with an excess of the halogen further reaction occurs, leading to the formation of the pentamethylcyclopentadienyl rhodium(III) dihalide and ethene (Eq. (4))

$$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(X)_2] + X_2 \rightarrow [\{(\eta^5\text{-}C_5Me_5)RhX_2\}_2] + C_2H_4 \tag{4}$$

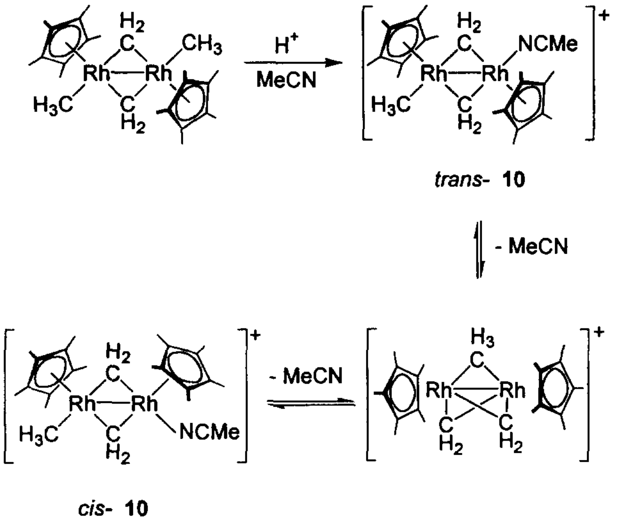
Parenthetically it may be noted that in this last reaction a rhodium(IV) complex reacts with halogen to yield a rhodium(III) complex and the olefin; one's normal concepts of oxidisers and reducers need modification here!

Dr. Seichi Okeya, also from Japan, and Neil Meanwell, showed that **2** reacted with acids of nonnucleophilic anions (e.g. HBF_4) in the presence of acetonitrile, to give methane and initially, the monocation $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]^+$ **10** [18]. The acetonitrile could be replaced by other ligands to give $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(L)]^+$ **10** (L = py, 2-methylpyridine, RCN, CO, etc) (Eq. (5));

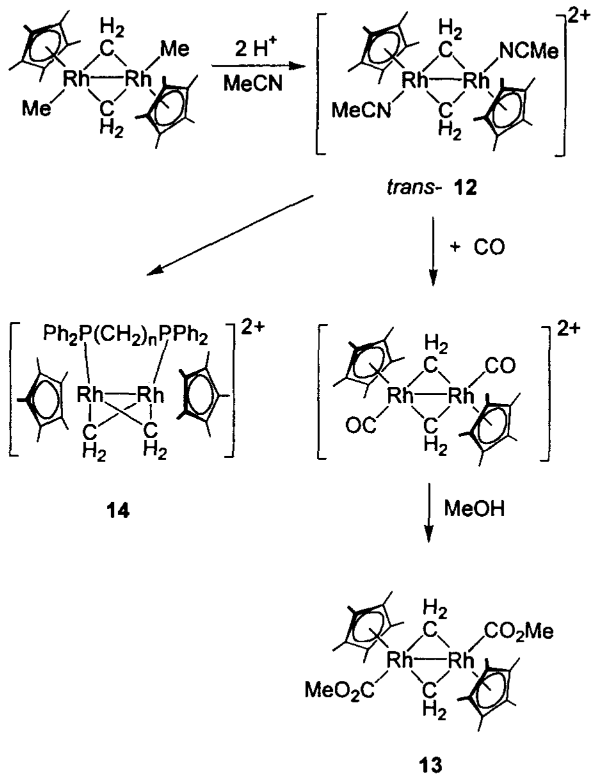
$$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]^+ + L \rightarrow [\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(L)]^+ \tag{5}$$



Scheme 3.



Scheme 4.



Scheme 5.

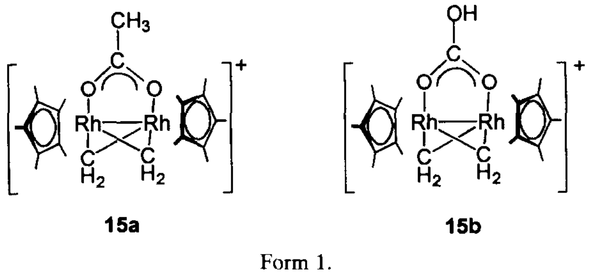
The higher dialkyls **5** gave a range of monoalkyl complexes $[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(R)L]^+$, **11**, similarly.

The pyridine complexes $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(R)(py)]^+$ were reasonably stable, but the acetonitrile complexes $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(R)(MeCN)]^+$ showed dynamic behaviour on the NMR timescale. The observations were consistent with the acetonitrile moving between sites so that *cis* and *trans* as well as the two rhodiums, are all equilibrated via a transition state with a bridging alkyl (or aryl), $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(\mu\text{-}R)]^+$ (Scheme 4). Thus, for example, at −80°C the ^1H NMR spectrum of $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]^+$ shows the rhodium methyl as two doublets (J(Rh–H) 2.3, 2.5 Hz), due to the *cis*- **1** and *trans*-**10** isomers; as the temperature is raised these broaden and coalesce and then sharpen up again until at +20°C the methyl is seen as a triplet with coupling to both rhodiums of about half the magnitude of that to one rhodium in the low temperature spectrum. Thus, on the NMR timescale the migrating methyl appears to be equally coupled to both rhodiums.

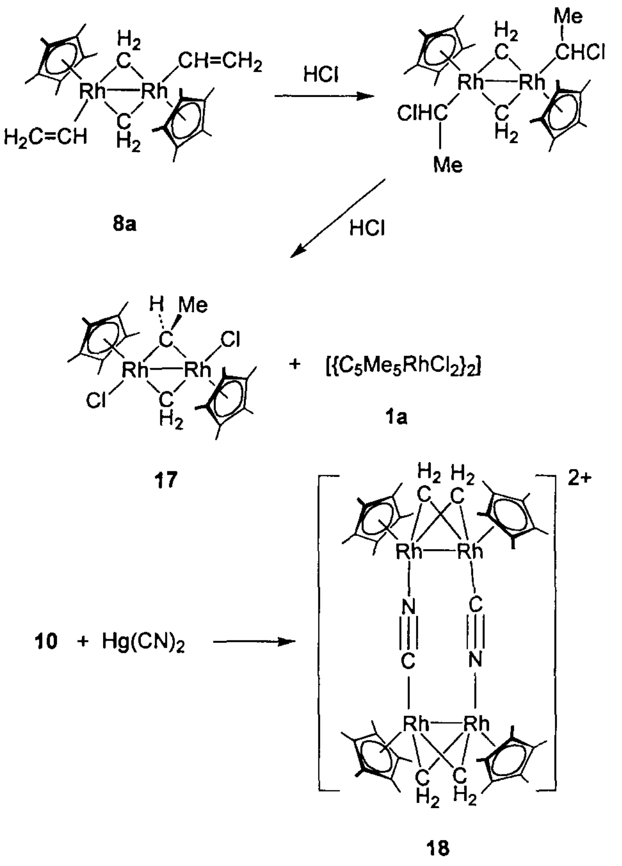
The pyridine complex was much more inert and showed the presence of two non-interconverting isomers at ambient temperatures; only on heating was there evidence for dynamic behaviour. Interestingly, the carbonyl complex $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(CO)]^+$ showed spectra characteristic of the presence of both *cis* and *trans* forms at +22°C. This suggests that the Rh–CO bond must be rather inert towards substitution, a conclusion reinforced by the ν(CO)s of the two isomers (2042 and 2059 cm^{-1}) which suggest substantial back-bonding from the metal, even though it is formally in the +IV oxidation state.

Reaction of the dimethyl complex **2** with two equivalents of acid in the presence of a ligand gave the dication *trans*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(L)_2]^{2+}$ **12** (L = CO, py, MeCN, etc.) [19]. The orange–yellow dicarbonyl reacted in methanol (and other alcohols) to give the bis-carboalkoxy complexes, for example, the brown *trans*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(CO_2Me)_2]$, **13**.

In addition to these *trans*-complexes bidentate ligands react with **12** to form bridged *cis*-complexes; thus the neutral diphosphines form $[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]^{2+}$ **14**, [20] while chelating uni- and di-negative ligands form *cis*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(Y)]^+$ (**15a**, Y = acetate, **15b**, Y = bicarbonate [21]) or *cis*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(Z)]$, **16** (Z = carbonate) respectively (Scheme 5). Thus, the carbonate **16** (Z = carbonate) was formed on reaction of the dichloride **4** with sodium carbonate in methanol; it was water-soluble and on addition of HBF_4 the bicarbonate, identified by an X-ray crystal structure determination, was precipitated as orange crystals. On



Form 1.



Scheme 6.

addition of more acid to the bicarbonate **15b**, CO_2 was given off. However, the μ-CH_2 bridges were stable in water even at pH 1 and the di-aquo dication *trans*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(H_2O)_2]^{2+}$ could be isolated as the tetrafluoroborate salt.

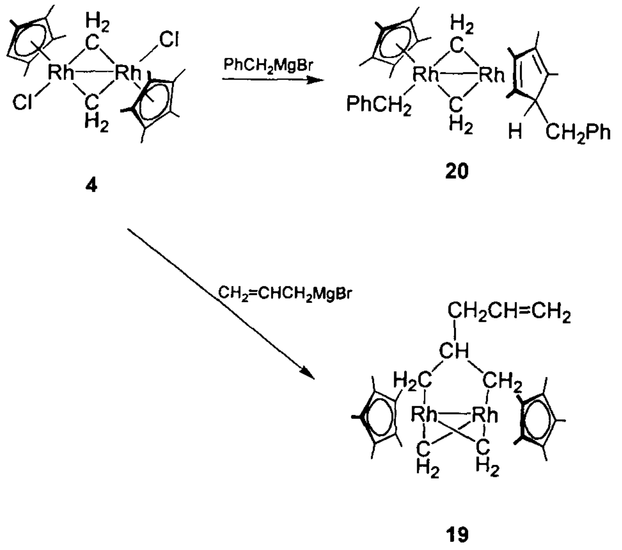
By contrast with the reactions of the mono- and di-alkyl complexes, where only cleavage of the alkyl was found, Dr. Jesus Martinez showed that the divinyl complex $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(CH{=}CH_2)_2]$ **8a** reacted reversibly with hydrogen chloride in pentane to give an unstable and only sparingly soluble complex identified on the basis of spectroscopy and microanalysis as $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(CHMeCl)_2]$. On standing in benzene with more HCl, this was converted into **1a** plus *trans*-$[\{(\eta^5\text{-}C_5Me_5)Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)(Cl)_2]$ **17** which was identified by an X-ray structure determination (Scheme 6) [16]. This reaction now allows entry into μ-ethylidene chemistry, a subject actively under investigation at present.

Another unexpected product, the tetranuclear *cis-cis*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_4(CN)_2]^{2+}$ **18**, was obtained when $[\{(\eta^5\text{-}C_5Me_5)Rh(\text{-}\mu\text{-}CH_2)\}_2(Me)(MeCN)]^+$ reacted with $Hg(CN)_2$ in methanol; complex **18** was again characterised by an X-ray structure determination [22].

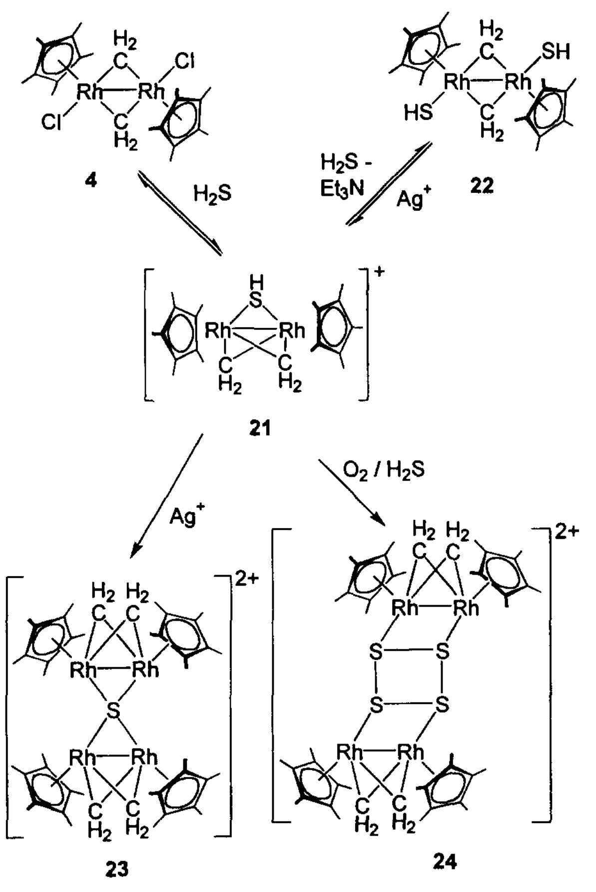
While the dichloride **4** reacted with a wide variety of Grignard reagents to give the expected products such as **5–8**, the reactions with allylic and benzylic Grignards proceeded quite differently. In the first case the product was a neutral organo-rhodium complex **19** which had three ligands bridging the rhodiums, two μ-CH_2 and one μ-$CH_2CR(CH_2CR{=}CH_2)CH_2$ made up from two allyls. Intermediate complexes with only one allyl have not yet been isolated [20].

A quite different reaction occurred when the dichloride **4** was reacted with a benzyl Grignard reagent. In this case the product, characterised by an X-ray determination [23] was a different type of dinuclear complex $[(\eta^5\text{-}C_5Me_5)Rh(CH_2Ph)(\mu\text{-}CH_2)_2Rh(\eta^4-C_5Me_5\text{-}CH_2Ph)]$ **20**. Here one rhodium is bonded to a $\eta^5-C_5Me_5$, and also bears a σ-benzyl and two μ-CH_2 groups linked to the second rhodium. However, the second rhodium is bound not to a η^5-C_5Me_5 ring but to a η^4-pentamethylcyclopentadiene which has an *exo*-benzyl substituent. The formation of this curious complex has been rationalised.

Isobe and Vâzquez de Miguel have recently made μ-methylene complexes with sulphur ligands. They found that the dichloride **4** reacted with H_2S in methanol to give the μ-SH cation, $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]Y$, **21**, Y = Cl [24]. On removal of the solvent, H_2S was also lost, and the formation reaction was reversed; the cation of **21** was however stabilised in the presence of nonnucleophilic anions such as BPh_4^-. The NMR spectrum of complex **21** $Y = BPh_4$, showed fluxional behaviour, which has been interpreted as arising from inversion at the bridging SH. On reaction of **21**, Y = Cl, with more H_2S in the presence of Et_3N, the bis-hydrosulphide $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(SH)_2]$ **22** was ob-



Form 2.



Scheme 7.

tained (Scheme 7). This was a *trans cis* mixture at −20°C but only the trans-isomer (confirmed by an X-ray structure determination) was present at 25°C.

The μ-SH cation **21** was also accessible from **22** on reaction with $AgSO_3CF_3$ (Eq. (6)); further reaction (Eq. (7)) gave the tetranuclear complex, *cis-,cis*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_4(\mu_4\text{-}S)]^{2+}$, **23**, with a tetrahedral μ_4-S ligand bridging all four rhodiums [25]. These two reactions also give Ag_2S and some H_2S, according to

$$\begin{aligned}&2[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(SH)_2] + 2Ag^+\\&\quad\rightarrow 2[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]^+\\&\quad + Ag_2S + H_2S\end{aligned}\tag{6}$$

$$\begin{aligned}&2[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]^+ + 2Ag^+\\&\quad\rightarrow [\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_4(\mu_4\text{-}S)]^{2+}\\&\quad + Ag_2S + H^+\end{aligned}\tag{7}$$

When either complex **21** or **23** was reacted with silver acetate, the product was the μ-acetate cation, **15a**. Another novel complex, the tetra-rhodium-tetra-sulphur dication, $[\{(\eta^5 - C_5Me_5)Rh(\mu\text{-}CH_2)\}_4(\mu\text{-}S_4)]^{2+}$, **24**, was obtained by reaction of the μ-hydrosulphide cation **21**, with oxygen in the presence of H_2S, according to Eq. (8):

$$\begin{aligned}&2[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]^+\\&\quad + 2H_2S + 3/2O_2\\&\quad\rightarrow [\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_4(\mu\text{-}S_4)]^{2+}\\&\quad + 3H_2O\end{aligned}\tag{8}$$

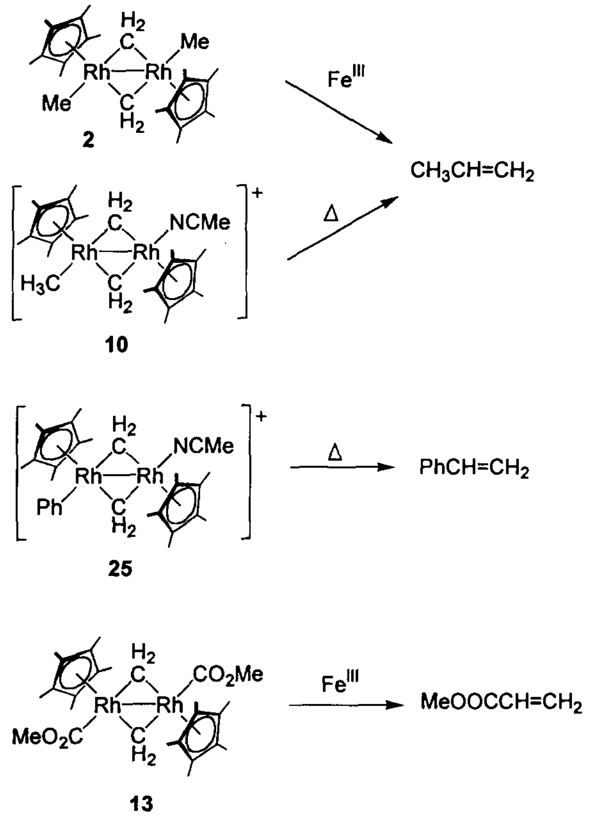
Complexes **21**, Y = BPh_4, and **23**, Y = CF_3SO_3, were shown to have the expected structures by X-ray determinations; an unusual feature was the very acute Rh–S–Rh angle in both (64.3(1) and 65.85(2)°, respectively). The X-ray structure of **24**, shows the four sulphurs to form a square linking the two pairs of rhodiums in a shallow step arrangement (∠Rh–S–S 112°) [26]; this structure forms an interesting contrast to that of the tetranuclear *cis-,cis*-$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_4(CN)_2]^{2+}$ **18** where the four rhodiums and the two bridging cyanides are coplanar.

4. Decomposition reactions of the methyl-di-μ-methylene-dirhodium complexes

Some of the most interesting reactions of these di-μ-methylenedirhodium complexes are those which lead to decomposition and the coupling of the bridging and terminal C_1 units. A variety of such reactions have been carried out; in general only three of the four C_1 units (or their equivalents, i.e. the phenyl in $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Ph)(MeCN)]^+$, and the methoxycarbonyl in **13**) are found in the organic products. The neutral complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(R)_2]$ (R = Me, Ph and CO_2Me) need to lose one R (as RH) before they decompose to give the C–C–C coupled organic. Thus, for example, complex **2** was extremely inert and stable to ca. 300°C; however in the presence of one-electron oxidants (Ag^+, Fe^{3+}, $IrCl_6^{2-}$, etc.) the decomposition was enormously accelerated and occurred rapidly just above room temperature. One methyl was lost (as methane) and then the major product was propene, derived from a coupling of the remaining CH_3, CH_2 and CH ligands (Eq. (9)) [27]

$$\begin{aligned}&\underset{\mathbf{2}}{[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)_2]} + 6MeCN - 4e^-\\&\quad\rightarrow CH_4 + CH_2{=}CHMe\\&\quad + 2[\{(\eta^5\text{-}C_5Me_5)Rh(MeCN)_3]^{2+}\end{aligned}\tag{9}$$

Interestingly, the dicarbonyl **12**, L = CO, in methanol gave the dicarbomethoxy complex **13**, which decomposed similarly in methanol in the presence of Fe(III) to give methyl acrylate [28]. Thus, the C–C–C carbon-



Scheme 8.

coupling reaction occurs with a wide range of substituents on the rhodium (Scheme 8).

The most facile decomposition was undergone by the cationic mono-methyl complexes, such as **10**, which decomposed spontaneously on gentle warming [29]. In the presence of a mild oxidant, a clean reaction resulted giving propene and $[(C_5Me_5)Rh(solv)_3]^{2+}$, according to Eq. (10):

$$\underset{\mathbf{10}}{[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]^+} + MeCN - 3e^- \rightarrow CH_2{=}CHMe + 2[\{(\eta^5\text{-}C_5Me_5)Rh(MeCN)_3]^{2+} \quad (10)$$

The mono-phenyl complex **25**, derived from the bromide **6**, reacted similarly to give styrene (Eq. (11)) [30];

$$\underset{\mathbf{25}}{[\{(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}CH_2)\}_2(Ph)(MeCN)]^+} + MeCN - 3e^- \rightarrow CH_2{=}CHPh + 2[\{(\eta^5\text{-}C_5Me_5)Rh(MeCN)_3]^{2+} \quad (11)$$

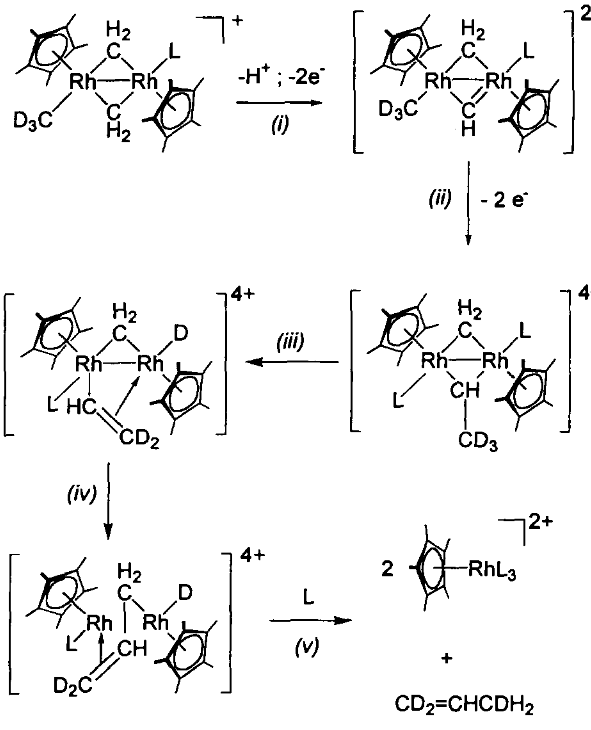
The decomposition of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Ph)(MeCN)]^+$ also occurs easily in the presence of one atmosphere of CO. Again, the major organic product is styrene, and the organometallic product is the rhodium(I) dicarbonyl complex, which form via the phenyl-monocarbonyl (Eq. (12)),

$$[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Ph)(CO)]^+ + 3CO \rightarrow CH_2{=}CHPh + 2[\{(\eta^5\text{-}C_5Me_5)Rh(CO)_2] + H^+ \quad (12)$$

A similar reaction occurs with the methyl complex **10** but there the major product is the ketone $(CH_3COCH_2CH_3)$ and less of the C–C–C coupled product, propene is found [31].

Two other very talented collaborators, Isabel Saez, another postdoctoral follow from Spain, and Glenn Sunley, one of our own students, were brought together by their work on these complexes, and became dinuclear (and more recently trinuclear) themselves too. Isabel did a remarkable series of very careful labelling experiments on the reactions of the methyl complexes **2** and **10** and showed that neither the hydrogens nor the carbons of the η^5-C_5Me_5 rings were involved, and that the products were derived only from the C_1 ligands and their hydrogens. Thus, **2** and its analogues can be considered as excellent models for the polymerisation step of the Fischer–Tropsch reaction on metal surfaces, since that reaction has been postulated to proceed by a series of methylene coupling steps.

Isabel's labelling studies of the products from $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(CD_3)(MeCN)]^+$ showed that the expected $CD_3CH{=}CH_2$ was only a minor component; the major isotopomer (ca. 80%) was $CD_2{=}CHCDH_2$, identified by ^2H NMR spectroscopy. This result showed that the coupling of the three C_1 ligands was not a straightforward C + C + C coupling. Scheme 9, comprising five steps, has been put forward to explain the formation of $CD_2{=}CHCDH_2$ [32]. Step (i) is the loss of H^+ from a μ-CH_2 to give a μ-CH, accompanied by



Scheme 9.

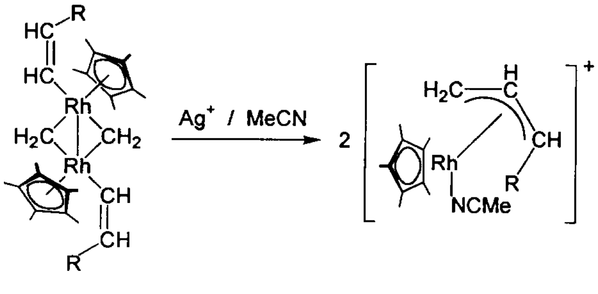
two one-electron oxidations; this μ-methyne then couples with the CD_3 in step (ii) under the influence of further oxidation to give a μ-$CHCD_3$, which then β-eliminates (step (iii)) to give a σ-vinyl ($-CH{=}CD_2$) deuteride. We suggest that in the next step (iv) the μ-CH_2 couples with the $-CH{=}CD_2$ giving a σ-allyl which then adds the D to release the products $CD_2{=}CHCDH_2$ and $[(\eta^5\text{-}C_5Me_5)Rh(L)_3]^{2+}$ in the final step (v). Although complicated, this appears to represent a lower energy path than a direct C + C + C coupling.

Similarly, we find that loss of H^+ is the first step in the decomposition of the mono-phenyl complex **25** and we suggest that subsequent steps include the coupling of the μ-CH to the μ-CH_2 giving a σ-vinyl which then couples with the phenyl to give styrene [30].

These results also indicate that a coupling involving a σ-vinyl is a low energy process. Several other workers have noted that the coupling of a metal-bonded alkenyl sp^2 carbon to a metal-bonded alkyl sp^3 carbon is generally preferred to the coupling between two metal-bonded alkyl sp^3 carbons [33]. This can be understood because, while the latter is a direct reductive elimination, the former can occur as a migration process (followed by decomplexation) with a lower activation energy. Calhorda et al. have provided theoretical explanations for such concepts in coupling reactions on palladium and nickel complexes in solution [34].

Further evidence that this also applies here comes from the ease of coupling of a vinyl and a μ-CH_2. Thus, the divinyl complex **8a** reacts readily with Ag^+ in acetonitrile to give the allyl cation **26a**. Even more persuasive is the fact that the Z-propenyl complex **8b** undergoes the same reaction stereospecifically to give the *anti*-1-methylallyl complex **26b** [16].

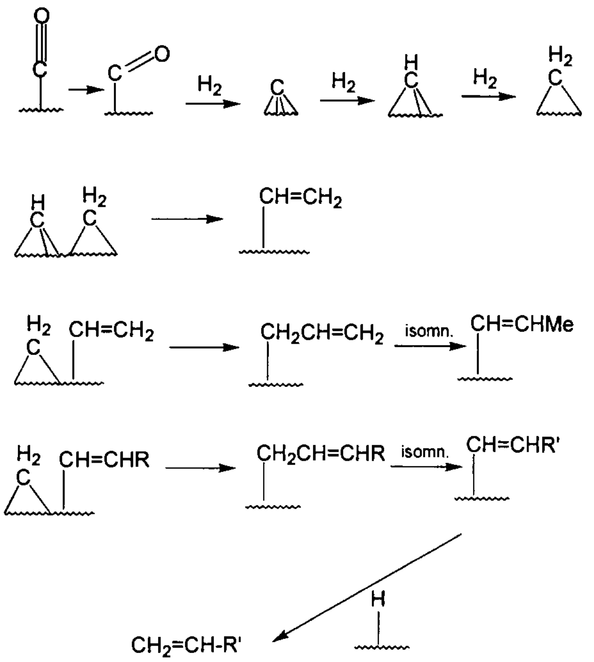
The point should perhaps be made that $sp^3 + sp^3$ couplings can occur, however they are not necessarily the lowest energy route to the formation of a C–C bond. Thus, for example, with excess halogen (X_2) the dihalo complexes $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(X)_2]$, **4** (X = Br or I) give ethene and $[\{(\eta^5\text{-}C_5Me_5)RhX_2\}_2$ (Eq. (3)).



8, a, R = H; b, R = Me

26, a, R = H; b, R = Me

Form 3.



Scheme 10.

The mechanism of this reaction is not clear, but it may be a direct coupling induced by oxidation.

5. Mechanistic conclusions: the value of the di-μ-methylene-bis(pentamethylcyclopentadienyl-rhodium) complexes in understanding catalysed reactions

The concept that if a mechanistic pathway involving a $sp^2 + sp^3$ migratory decomplexation can occur, it will have lower activation barriers than $sp^3 + sp^3$ reductive elimination has also been applied to the Fischer–Tropsch reaction. There it suggests that alternative routes for the surface methylene couplings may have lower activation energies than the straightforward μ-CH_2 + μ-CH_2 pathway; thus, other methylene oligomerisation routes are possible. In work, first with Futai Ma, and more recently with Peter Byers and Mike Turner, we have tested this idea and have shown that in the hydrogenation of carbon monoxide over rhodium catalysts to give alkenes (Fischer–Tropsch reaction) the CH_2 oligomerisation can be initiated by a vinyl and carried by alkenyl chains in the surface, thus making each step of the coupling process a $sp^2 + sp^3$ migratory decomplexation. This result is shown by the ease with which vinyl (but not ethyl) initiates the oligomerisation and is incorporated in the oligomers. An outline of the proposed mechanism is shown in Scheme 10 [32,35].

6. Summary

We have shown that reaction of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ with methylating agents yields $[\{(\eta^5\text{-}$

C_5Me_5)Rh(μ-CH_2)}$_2$(Me)$_2$] **2**; the rhodium-methyls are removed with acid and can be replaced by a wide variety of ligands to give complexes of the type [{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(X)(Y)] (where X,Y can be anionic: alkyls, aryls, alkenyls, halides, carboxylate, nitrate, etc.) or [{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(L^1)(L^2)]$^{2+}$ (where L^1 and L^2 are neutral: CO, pyridine, MeCN, etc.) All of these are diamagnetic complexes of Rh(IV), d^5, in which the odd electrons are paired in metal–metal bonds. The two μ-CH_2 bridges are remarkably stable and are retained throughout the interconversions, except in the presence of oxidising agents.

Information about the complexes which have had their structures determined by X-ray methods is collected in Table 1, together with the Rh–Rh distances, which range from 2.554(1) Å in *cis*-[{(η^5-C_5Me_5)Rh-(μ-CH_2)}$_2$(μ-SH)]BPh_4 **21** to 2.676(3) in *cis-,cis*-[{(η^5-C_5Me_5)Rh(μ-CH_2)}$_4$(μ-CN)$_2$]$^{2+}$ **18**. There is no immediately obvious correlation of bond length with the nature or size of the substituent on the rhodium, and thus it is likely that the precise distance apart is determined by steric factors, this is supported by the long Rh–Rh distance found in *trans*-[{(η^5-C_5Me_5)Rh}$_2$(μ-CH_2)(μ-CHMe)(Cl)$_2$], **17**, with the more sterically demanding μ-CHMe ligand.

The most intriguing feature of the chemistry of these complexes is the ease with which they undergo C–C coupling. This is especially so for the complexes [{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(R)(L)]$^+$ (R = alkyl or aryl) which give $RCH{=}CH_2$ at ambient temperature under either mildly oxidising conditions or under CO; the complexes [{(η^5-C_5Me_5)Rh(μ-CH_2)}$_2$(R)$_2$] (R = Me, Ph, COOMe) also give $RCH{=}CH_2$, but rather more vigorous conditions are needed to break up the molecules. Detailed examination using isotope labelling showed that both the carbons and hydrogens of the $RCH{=}CH_2$ were only derived from the R and μ-CH_2 ligands and that the complex underwent intramolecular coupling. However, analysis of the data for R = CH_3 showed that the process by which $CH_3CH{=}CH_2$ was formed was considerably more complex than a simple C + C + C coupling. This led to the concept that the reactions were initiated by loss of H from a μ-CH_2, giving a reactive μ-CH centre which then initiated the C + C coupling reactions. These ideas in turn allowed the postulation of a new mechanism for the formation of alkenes from the hydrogenation of CO under Fischer–Tropsch conditions in which the key step is the oligomerisation of methylenes, initiated by a vinylic surface species.

Thus, not only has the study of the di-μ-methylene-bis(pentamethylcyclopentadienyl-rhodium) complexes been rewarding in its own right in leading to fascinating and novel organometallic chemistry, but it has also been able to illuminate further details of an important and useful heterogeneous process.

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