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25 Years with ruthenium

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As my contribution to this volume I have chosen to give a historical account of the development of my research. This is normally an approach reserved for those rather more advanced in their careers, but in my defence there is a special circumstance which makes it an appropriate approach on this occasion. As I write this there are two weeks remaining before Gordon Stone retires from the Professorship of Inorganic Chemistry at Bristol and moves to a Welch Chair at Baylor University in Texas. My career has been so strongly influenced by Gordon that I want to begin this account of my research in the very beginning, by returning to 1963 when we both arrived in Bristol for the first time within a few months of each other. In August the 38-year old Stone was installed as the first Professor of Inorganic Chemistry and in October the author, then 19, arrived with somewhat less ceremony as a new B. Sc. student. The dynamic young Professor made a great impression on me in lectures and when, two years later, students had to choose a supervisor for an undergraduate research project I opted for him, not without some trepidation. I have never regretted the choice. His enthusiasm is undiminished and infectious to this day and life at Bristol has never been dull.

In October 1965, therefore, I began project work on the then hot topic of covalent metal–metal bonds (subsequently I could never shake my father's belief that I was a metallurgist), co-supervised by an Australian postdoctoral worker John Cotton, now at the University of Queensland in Brisbane. We were then, and remain, dedicated cricket followers and our friendship has survived many condescending letters after England–Australia test matches over the past 20 years. I believe I may have received more than I have been able to send. In 1965–1966 we investigated together the reflux reaction of tributyltin chloride with iron pentacarbonyl in the absence of solvent. My recollection of the large quantities of the reagents employed and of my experimental inexperience is unnerving even now; I have vivid memories of some spectacular fires from pyrophoric iron residues. However, I survived to isolate several products from this fascinating reaction: Bu_2CO, $[Fe_2(\mu\text{-}SnBu_2)_2(CO)_8]$, $[Fe_4Sn(\mu\text{-}SnBu_2)_2(CO)_{16}]$ and $[Fe_4Sn(CO)_{16}]$ (**1**) [1,2]. The structure of the latter was determined by a fellow undergraduate Judith Duckworth (now Howard), who is a colleague at Bristol today. Many years later, Herrmann and others were to investigate such species as examples of complexes containing "naked" main group atoms.

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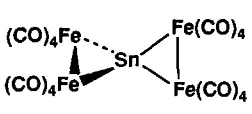
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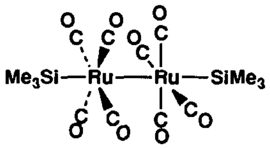
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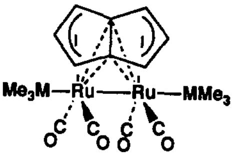
After this introduction to the hazards and excitements of research I was keen to carry on as a postgraduate student and, after a summer working on a farm, I returned in October 1966 to find metal–metal bonds still popular and the reactions of organotin halides and hydrides with $[Co(CO)_2(\eta\text{-}C_5H_5)]$ on the menu. This investigation was less than successful and did not even produce a decent fire, but I was rescued by Michael Bruce who had discovered an excellent synthesis of $[Ru_3(CO)_{12}]$ [3]. This began to come off the production line in 1967 and from the first experiments it proved to be very reactive and to give clean stable products. There is not much more a postgraduate student can reasonably ask for than a newly available metal carbonyl to explore and the next couple of years were a productive time. Reactions of $[Ru_3(CO)_{12}]$, and subsequently $[Os_3(CO)_{12}]$, with organo-silicon, -germanium and -tin hydrides gave numerous new species, the most interesting being $[Ru_2(SiMe_3)_2(CO)_8]$ (**2**) [4–6]. The realisation that this complex was structurally related to $[Mn_2(CO)_{10}]$ led to a comparative investigation of its chemistry, dominated by the formation of the anion $[Ru(SiMe_3)(CO)_4]^-$, analogous to $[Mn(CO)_5]^-$.

In 1970 the lure of California drew me to Herb Kaesz's laboratory at UCLA for postdoctoral work. Herb's enthusiasm, barrage of ideas and humour ensured that I spent a marvellous sixteen months studying polynuclear transition metal hydrides. Just before I arrived it had been discovered in the laboratory that when hydrogen is bubbled through a refluxing decalin solution of $[Re_2(CO)_{10}]$ the tetrahydride $[Re_4H_4(CO)_{12}]$ is formed. Rhenium was *the* metal of the Kaesz group at that time; my favourites were ruthenium and osmium and I had passed through U.S. customs with reasonable quantities of both $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ (sorry Gordon). It was not long, therefore, before Jeff Koepke, a graduate student, was being pressed to bubble hydrogen through a refluxing heptane solution of $[Ru_3(CO)_{12}]$. To our amazement $[Ru_4H_4(CO)_{12}]$ was formed quantitatively within the hour, leading to an intriguing situation. Two isomers of this species were reported [7,8] in the literature, named α and β, but our hydride had a more simple carbonyl IR spectrum than either. To cut a long story short, it turned out that there is only one $[Ru_4H_4(CO)_{12}]$ and that we had isolated it pure; the other syntheses in the literature invariably gave $[Ru_3(CO)_{12}]$ as a co-product and the two are effectively inseparable, confusing the situation. When I got around to bubbling hydrogen through an octane solution of $[Os_3(CO)_{12}]$ the results was even more impressive; after a couple of hours a beautiful purple solution of what turned out to be $[Os_3H_2(CO)_{10}]$ was formed. This unsaturated complex had been obtained previously [9,10] but in only 1–2% yields, and the discovery of this new high yield route was to quickly open up the now considerable organic chemistry of the triosmium unit, constructed by Shapley, Lewis and Johnson, Deeming and many others. Characteristically, Herb insisted we publish the synthesis immediately so that others might benefit from the discovery [11,12]. We contented ourselves with making trimethylphosphite derivatives of $[Ru_4H_4(CO)_{12}]$ and showing for the first time that the hydride ligands were in motion over all the edges of a metal cluster, via a study based on $^1H-^{31}P$ coupling [13]. This was followed by a similar study of $[Ru_4H_3(CO)_{12}]^-$, which *did* in fact have two isomers with the hydrides occupying different arrangements on the cluster [14].

There were two occasions on which Gordon Stone interrupted my Californian sojourn. Once he stayed in my apartment in Santa Monica on a conference trip and learned by phone while there that the Bristol department had suffered a major fire. His thermonuclear reaction to the news reminded me of what I was missing in Bristol and I responded positively when, some months later, I picked up the telephone in the laboratory at UCLA to hear Gordon ask whether I was interested in applying for a vacant lectureship. I got the job, freed by Eddie Abel's promotion to a Chair at Exeter, and returned to Bristol as a lecturer in January 1972.

For the first few years as a lecturer I co-supervised several of Gordon's research students while simultaneously building up my own group. Our collaborative research began with an investigation of the reactions of cyclic polyalkenes with the silyl and germyl derivatives of ruthenium and osmium carbonyls which I had prepared during my Ph. D. work. It was quickly shown that $[Ru_2(SiMe_3)_2(CO)_8]$ (**2**) reacted on heating with *cyclo*-octatetraene to give the μ-*cyclo*-octatetraene complex $[Ru_2(SiMe_3)_2(CO)_4(\mu\text{-}C_8H_8)]$, but that $[Ru(MMe_3)_2(CO)_4]$ (M = Si or Ge) reacted to give species $[Ru_2(MMe_3)_2(CO)_4(\mu\text{-}C_8H_6)]$ (**3**), which Judith Howard showed by an X-ray diffraction study to contain pentalene [15,16].



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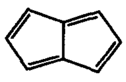
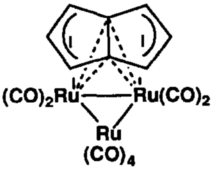


(4)

Pentalene (**4**) is a very unstable hydrocarbon, dimerising above −140 ° C, and the study of its complexation through dehydrogenative ring closure of *cyclo*-octatetraenes and *cyclo*-octatrienes was to command our attention for several very stimulating years [17]. In this period Victor Riera (now Professor at Oviedo, Spain) and Ron McKinney (now at Central Research, Du Pont) made considerable contributions. One of the highlights of this research was the synthesis of isomeric edge- and face-bridging triruthenium pentalene complexes of types **5a** and **5b**, respectively, notable for the observation that even a hydrocarbon as large as pentalene can migrate over all the edges and faces of the ruthenium triangle [18].



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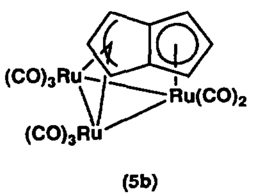
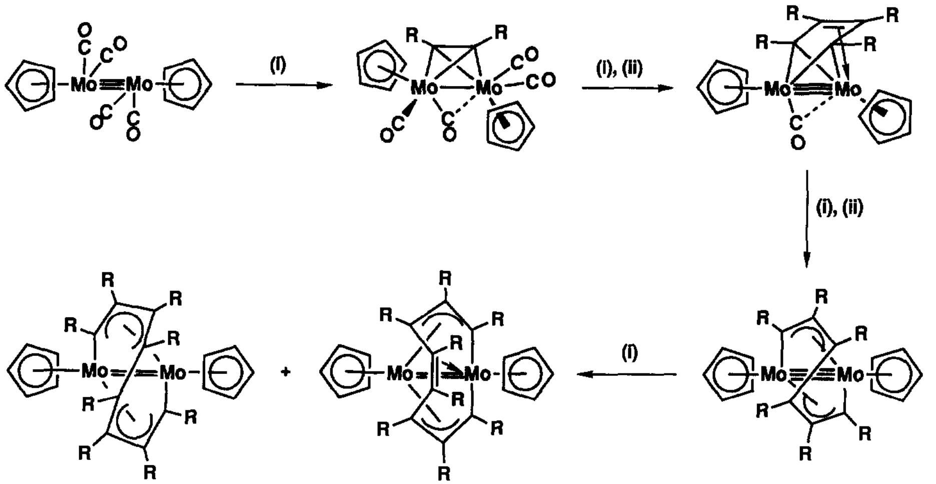


(5b)

An effort by Mark Winter to extend the pentalene story to molybdenum was unsuccessful, but the reaction of *cyclo*-octatetraene with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ did



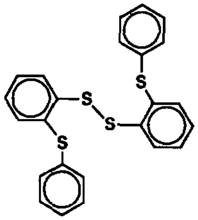
Scheme 1. Alkyne linking at a dimolybdenum centre: (i) +RC≡CR, (ii) −CO.

give a surprising product, $[Mo_2(CO)_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]$, containing the previously uncomplexed and thermally unstable hydrocarbon *cyclo*-octa-1,5-dien-3-yne [19]. This observation in turn led to a more general study of dimolybdenum μ-alkyne complexes $[Mo_2(\mu\text{-}C_2R_2)(CO)_4(\eta\text{-}C_5H_5)_2]$, which included the activation of μ-ethyne towards formal Diels–Alder addition of cyclic 1,3-dienes [20].

Complexes of the type $[Mo_2(\mu\text{-}C_2R_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ had first been reported by Nakamura, and subsequent work of Cotton and Chisholm led to a range of these species being available via the room temperature addition of an alkyne to the Mo≡Mo triply bonded complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$. We discovered that similar treatment of $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with an alkyne results in alkyne linking to give $[Cr_2(\mu\text{-}C_4R_4)(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ and in an effort to achieve the same linking at molybdenum we heated the monoalkyne complexes $[Mo_2(\mu\text{-}C_2R_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ with additional alkyne. We overachieved; the two-alkyne species reacted further with alkynes in this system to give complexes containing first three and then four linked alkynes, bound as "fly-over" ligands as seen in Scheme 1 [21]. The impressive ability of the dimetal unit to accommodate these substantial changes in organic ligand through variation of metal–metal bond order really excited my interest in this area. We suggested that this step-wise oligomerisation of four alkyne molecules at a dimetal centre could be providing an insight into the mechanism of the Reppe nickel-catalysed *cyclo*-tetramerisation of ethyne, but we were unable to complete the cyclisation of the C_8 chains in our dimolybdenum system to give *cyclo*-octatetraenes. This step was, however, observed by Wilke et al. who treated $[Cr_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]$, containing an open $(CH)_8$ chain, with CO and obtained *cyclo*-octatetraene [22].

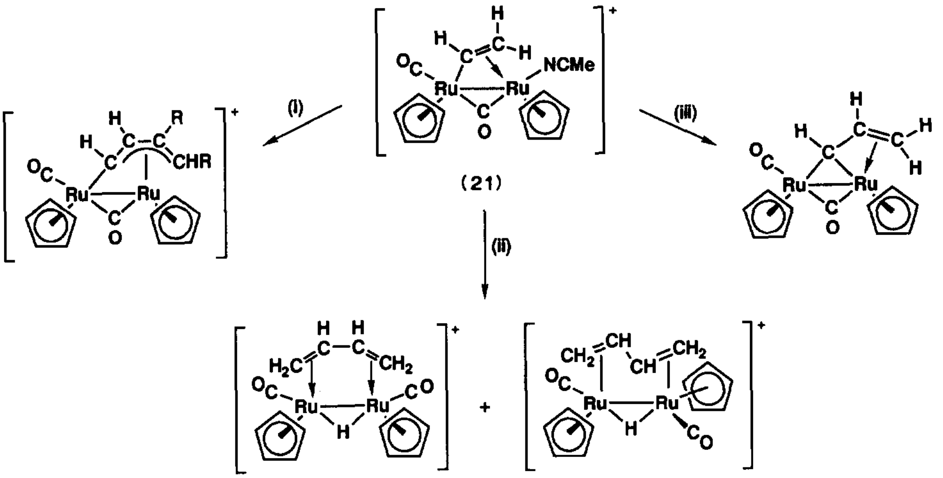
In the first October after returning from Los Angeles the construction of my own research group began when Gordon assigned me three undergraduate project students. Inadvertently, he was taking a hand in my personal life because one of these was Julie Edwards, later to become Julie Knox; on balance I have been grateful for the assignment. For tactical reasons Miss Edwards was subsequently transferred to work as a Ph. D. student for Gordon and disappears from this story, but her influence on my career has been considerable and generally beneficial.

For several years I devoted some independent research effort to a study of the sulphur inversion process in complexes. Energy barriers were determined in a variety of species but no simple understanding evolved and it became evident that the inversion is controlled by many factors. The synthetic side of the programme did, however, throw up many new and interesting observations, including (i) that metal carbonyl anions react with carbon disulphide and organic isothiocyanates to often incorporate sulphur, e.g. the formation of trithiocarbonates from CS_2 [23,24], and (ii) that the photolysis of diphenyl disulphide gives $S_2(C_6H_4\text{-}o\text{-}SC_6H_5)_2$ (6), a process in sulphur chemistry comparable with the benzidine rearrangement of nitrogen chemistry [25].



(6)

Throughout the period 1972–1978, however, my interest in the reactions of hydrocarbons with polynuclear metal complexes grew. My time at UCLA had pushed me in the direction of clusters and armed with the "hydrogen synthesis" I was ready to study reactions of $[Ru_4H_4(CO)_{12}]$ and $[Os_3H_2(CO)_{10}]$. Osmium chemistry was beyond the means of a young lecturer and so ruthenium it had to be. One of the first reactions tried was that of $[Ru_4H_4(CO)_{12}]$ with *cyclo*-octatetraene, which gave a new dimer of the hydrocarbon, formally derived by $(4+2)\pi$ cycloaddition [26,27]. This led to a more general study of *cyclo*-octatetraene dimerisation by iron, ruthenium and molybdenum carbonyls. The different dimers formed in each case were traced to the different co-ordination modes favoured by the metal carbonyl fragments, providing a nice illustration of the control of hydrocarbon reactivity by complexation [28,29]. Other studies of reactions with cyclic hydrocarbons generated several new ligands, e.g. η^2-*cyclo*-octatetraene [30], μ_3-η^7-*cyclo*-heptatrienyl [31], μ-η^7-*cyclo*-octatrienyl [32], μ-η^3,η^3-*cyclo*-octatetraene [33] and μ_3-*cyclo*-pentadienylidene [34]. During the course of this work, in 1973, Adrian Humphries discovered [35] that treatment of $[Ru_3(CO)_{12}]$ with cyclopentadiene in refluxing heptane provided a new and very convenient synthesis of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$; subsequently Michael Morris improved the synthesis, which now affords the complex routinely in 85% yield [36]. Although we could not know it at the time this observation was of great importance; we were later to show that this species supports a substantial and fascinating organic chemistry at the diruthenium centre and without the synthesis our progress would have been very slow. The breakthrough came six years later in 1978, when Andrew Dyke reacted $[(\eta\text{-}C_5H_5)(CO)_2RuMo(CO)_2(\eta\text{-}C_7H_7)]$ with diphenylacetylene under UV irradiation, hoping to obtain a μ-alkyne complex. A nice orange product was obtained in low yield and it certainly contained diphenylacetylene and ruthenium, but no molybdenum. The carbonyl IR showed bands for terminal and bridging carbonyls, and another unusual one at 1730 cm^{-1}. We were unable to assign a structure and so off it went to the diffractometer,



Scheme 2. (i) $RC{\equiv}CR$, (ii) $CH(CO_2Et)N_2$, (iii) $CH_2{=}C{=}CH_2$, (iv) $Ph_3P{=}CH_2$, (v) $CH_2{=}CH_2$.

which revealed the product to be $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)CPhCPh\}(\eta\text{-}C_5H_5)_2]$ (7), containing a dimetallacyclopentenone ring [37].

Complex 7 was to become one of the pillars of the development of organo-diruthenium chemistry in my laboratory over the twelve years up to the present. It was clear that it should be better made by photolysis of a mixture of diphenylacetylene and $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and this procedure duly gave the complex in 50% yield. It proved to be fluxional, undergoing a concerted ejection of CO from, and incorporation of the terminal CO into, the dimetallacycle on the NMR time scale. This striking indication of the ease of C–C bond cleavage and bond formation at a diruthenium centre was reinforced by the reactivity of the complex. Strangely, no other alkyne reacted cleanly with $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, but the analogues of 7 were readily obtained by heating the complex with another alkyne in toluene, when smooth exchange occurs [37]. This easy displacement of diphenylacetylene seemed to indicate that 7 could function as a source of "$[Ru_2(CO)_3(\eta\text{-}C_5H_5)_2]$" and this was amply confirmed when the complex was treated with a range of alkenes, alkynes, allenes, diazoalkanes, ylides, etc. as shown in Scheme 2 [38].

At this time there had been speculation that dinuclear metal complexes might be important in catalytic processes [39] and the influential reviews by Muetterties et al. on the cluster-surface analogy [40] and the Fischer–Tropsch synthesis [41] were appearing. It was clear that we had in our hands an excellent entry into a potentially substantial organic chemistry of the diruthenium centre and the opportunity to make a significant contribution to the development of the organic chemistry of polynuclear metal complexes, of possible relevance to surface chemistry. I therefore quickly changed the focus of the group's effort and threw nearly everybody into diruthenium chemistry, a strategic decision which has proved to be the best I ever made in research. I never expected that today this area would still be a major research area of mine, continuing to produce exciting results; it has truly been a gold mine, if one can say that of ruthenium!

The immediate aims of the research were to develop routes for the synthesis of simple, fundamental hydrocarbon species co-ordinated at the diruthenium centre, to characterise these spectroscopically and structurally and then to investigate their reactivity patterns. Syntheses of μ-alkylidene (CH_2 [42], CHMe [43,44], CMe_2 [45], etc.), μ-alkylidyne (CMe^+ [43]), μ-vinylidene ($C{=}CH_2$ [43], C=CHMe [43]), μ-vinyl ($CH{=}CH_2$ [44], CH=CHMe [44], $CMe{=}CH_2$ [45], etc.), alkene ($CH_2{=}CH_2$ [38], $CH_2{=}CHCH{=}CH_2$ [46], etc.) and related diruthenium complexes were devised relatively quickly. These included some unprecedented transformations, such as the sequential addition of H^+ and H^- to alkynes to give μ-vinyl cations and then μ-alkylidenes [44], and to allene to give μ-CMe_2 [45]. Complex 7 was important in many of these but we were also able to enter organo-diruthenium chemistry directly from $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ by applying Rosenblum's technique [47], i.e. by attacking a CO of the complex with methyl lithium, followed by acid to give μ-CMe^+, then hydride to give μ-CHMe or water to give μ-$C{=}CH_2$ [43]. Later Bercaw and Berry showed that treatment of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with "Super Hydride", $LiBHEt_3$, followed by water will convert μ-CO to μ-CH_2 and this has been a valuable addition to our synthetic armoury [48].

In the $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L)(\eta\text{-}C_5H_5)_2]$ system both *cis* and *trans* isomers are possible and usually present, and we showed early that these interconvert. For $L = \mu\text{-}CMe_2$ this occurs on the NMR time scale and variable temperature studies revealed the involvement of bridge-terminal alkylidene site exchange [45]. A similar study of the μ-methyl cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_3)(\eta\text{-}C_5H_5)_2]^+$ confirmed that methyl behaved likewise [49], but an unexpected result during this work led us to an extensive exploration of the activation of hydrocarbon ligands through the oxidation of di- and tri-ruthenium complexes. An X-ray diffraction study of what was believed to be $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_3)(\eta\text{-}C_5H_5)_2][BF_4]$, derived by protonation of $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$, proved in reality to have been undertaken on a crystal of the μ-methyne complex $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH)(\eta\text{-}C_5H_5)_2][BF_4]$ [49]. The bulk sample certainly was $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_3)(\eta\text{-}C_5H_5)_2][BF_4]$ and the question was, therefore, where had the methyne complex come from? Electrochemical studies in association with my colleague Neil Connelly were to provide the answer. Cyclic voltammetry (see Fig. 1) showed that the μ-CH_2 complex $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ was readily oxidised in two one-electron steps, the first reversible and the second irreversible, and that the chemical transformation of the di-cation appeared to involve spontaneous ejection of a proton to give $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH)(\eta\text{-}C_5H_5)_2][BF_4]$, which was observed as a product in the CV through its own oxidation wave at ca. 1.2 V. This was confirmed by chemical oxidation of $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ with two equivalents of $[Fe(\eta\text{-}C_5H_5)_2]^+$, in the presence of 2,6-dimethylpyridine as a proton scavenger, when the methyne cation was obtained quantitatively [50].

By a fortuitous coincidence we showed at almost the same time that oxidation of a triruthenium centre could also effect C–H activation in a coordinated hydrocarbon. Nigel Forrow, investigating pentamethylcyclopentadienyl-ruthenium chemistry [51], attempted to protonate $[Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}CMe)(\eta\text{-}C_5Me_5)_3]$ and instead produced the radical cation $[Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}CMe)(\eta\text{-}C_5Me_5)_3]^+$. Cyclic voltammetry revealed a very low oxidation potential of 0.17 V for the neutral μ_3-CMe species, low enough that the proton was a sufficiently strong oxidant to generate the mono-cation. CV also indicated, however, a second oxidation wave at 0.86 V and

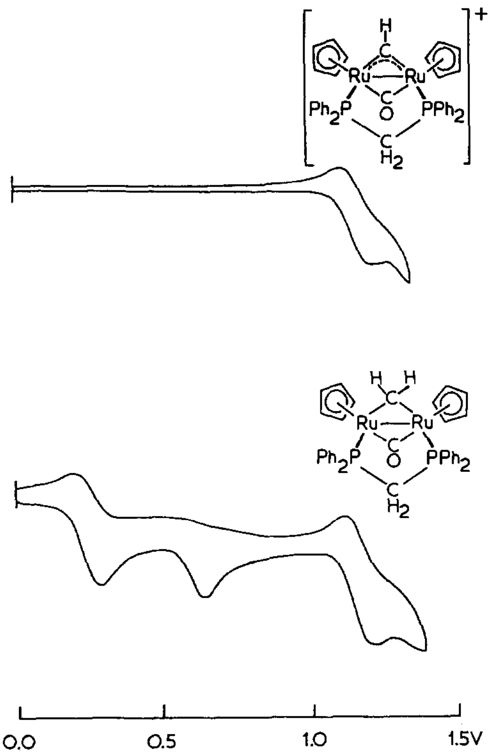
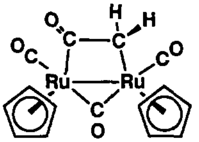


Fig. 1. Cyclic voltammograms of diruthenium μ-CH_2 and μ-CH^+ complexes.

treatment of the mono-cation with Ag^+ accordingly gave the dication $[Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}CMe)(\eta\text{-}C_5Me_5)_3]^{2+}$. This proved to be surprisingly stable but did slowly deprotonate to form the corresponding μ_3-vinylidene complex $[Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}C{=}CH_2)(\eta\text{-}C_5Me_5)_3]^+$ [52].

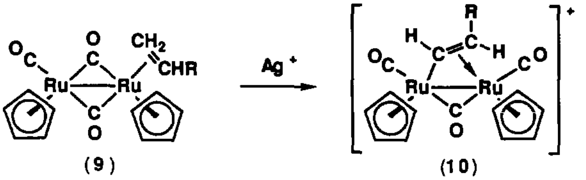
This fascinating C–H activation, driven by the desire of the polynuclear metal centre to release a proton in order to recoup the two electrons lost on oxidation, clearly required extension to other hydrocarbons. It was evident that the method could prove synthetically very valuable in that the products, being cations, would be susceptible to nucleophilic attack, allowing the derivatisation of the original hydrocarbon. The first complexes we investigated contained μ-alkylidenes and it was soon shown by CV that $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5Me_5)_2]$ had similar oxidation behaviour to the previous species [50]. Chemical oxidation with Ag^+ then resulted in specific β-proton loss to give the μ-vinyl cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5Me_5)_2]^+$. Subsequent treatment of the latter with Me^- gave $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHEt)(\eta\text{-}C_5Me_5)_2]$, which on oxidation gave $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CHMe)(\eta\text{-}C_5Me_5)_2]^+$, which with Me^- gave $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH^iPr)(\eta\text{-}C_5Me_5)_2]$, which in turn was readily oxidised to $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CMe_2)(\eta\text{-}C_5Me_5)_2]^+$. Unfortunately, this amusing vinyl homologation sequence was broken when upon treatment of the latter with Me^- μ-$C(H)CMe_3$ was not formed; instead proton abstraction occurred in preference to give the complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CMe_2)(\eta\text{-}C_5Me_5)_2]$ and $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CHC(Me){=}CH_2\}(\eta\text{-}C_5Me_5)_2]$ [53].

By this time the oxidative activation process seemed predictable and Melanie Fildes and I were therefore confident that oxidation of the μ-vinylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)(\eta\text{-}C_5Me_5)_2]$ would produce the μ-ethynyl cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{\equiv}CH)(\eta\text{-}C_5Me_5)_2]^+$. The CV was as required, showing two oxidation waves, the first reversible and the second irreversible, consistent with proton ejection from a di-cation. However, chemical oxidation with Ag^+ resulted in the surprising formation of a *ketene* complex $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(O)CH_2\}(\eta\text{-}C_5Me_5)_2]$ (**8**) in good yield. Normality was restored when it turned out that the μ-C≡CH cation had in fact been formed and that the ketene derived from hydroxide attack (from alumina) on the α-carbon of the ethynyl ligand followed by a hydrogen shift to the β-carbon, i.e. keto–enol tautomerisation. The ketene ligand displayed some unusual reactivity, including decarbonylation to $\mu\text{-}CH_2$ and isomerisation to μ-C(H)C(H)O [54].



(8)

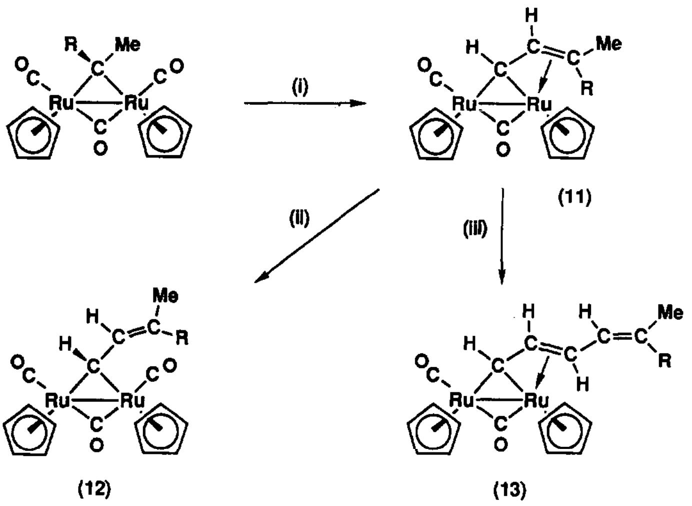
When we turned our attention to the oxidation of diruthenium alkene complexes, Dr. Nancy Doherty (now a faculty member at Irvine) found the CV data to be unpromising. Unlike all previous complexes the ethene species $[Ru_2(CO)(C_2H_4)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$ (**9**, R = H) displayed only a single irreversible oxidation wave at 0.66 V (scan rate 100 mV s^{-1}), but addition of one equivalent of Ag^+ still gave the μ-vinyl cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]^+$(**10**, R = H) [55]:



(9) (10)

Apparently C–H activation occurs at the radical mono-cation stage in this system, via hydrogen radical loss. The behaviour of the propene analogue $[Ru_2(CO)(CH_2{=}CHMe)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (**9**, R = Me) was similar, with selective loss of a methylenic hydrogen occurring to afford $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CHMe)(\eta\text{-}C_5H_5)_2]^+$ (**10**, R = Me). Interestingly, the treatment of these μ-vinyl cations with hydride yields μ-CHMe and μ-CHEt respectively, completing the isomerisation of alkene to alkylidene. Maitlis et al. have suggested [56] that vinyl groups may be important surface species in the Fischer–Tropsch synthesis and it is not inconceivable that they could be derived from alkenes or alkylidenes by processes related to those described in these preceding paragraphs.

Although the oxidative activation of co-ordinated hydrocarbons was an interesting and satisfying study because of the interplay between synthetic and electrochemistry, it is carbon-carbon bond formation which has dominated the investigation of

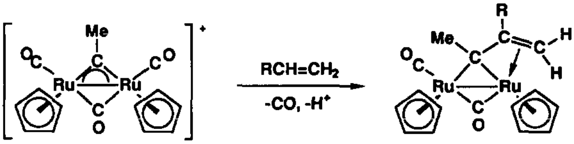


Scheme 3. (i) HC≡CH, −CO, (ii) CO, (iii) HC≡CH.

the organic chemistry of the diruthenium centre. Thus, one of the first reactions we studied was that of ethyne with the μ-ethylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$. Under UV irradiation this gave, via CO loss, the μ-allylidene complex $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CHMe)(\eta\text{-}C_5H_5)_2]$ (**11**, R = H), involving in principle an ethyne insertion into an Ru–alkylidene bond (see Scheme 3) [57].

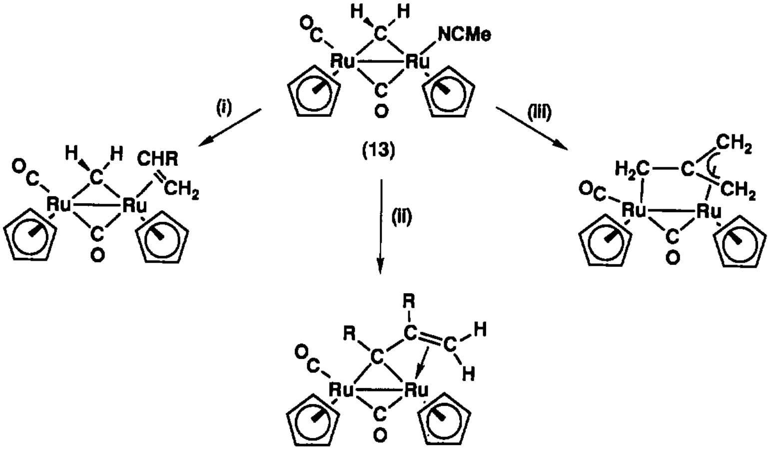
The structure of **11** can be represented in several ways, but the one shown suggested to us that it might be possible to "lift off" the double bond from its coordination with ruthenium and thus bring other species to occupy the vacant site so-created. We soon showed that under CO pressure this could be done, the product $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}\eta^1\text{-}CHCH{=}CHMe)(\eta\text{-}C_5H_5)_2]$ (**12**, R = H) being formed quantitatively. More importantly, this observation led us to suggest a mechanism for alkyne polymerisation at a dinuclear metal centre, based on alkynes repeatedly occupying this site and extending the carbon chain in step-wise fashion [58]. The reaction of the μ-CMe_2 complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ with ethyne subsequently gave a nice confirmation of this possibility, in that the mono-alkyne product $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CHCH{=}CMe_2)(\eta\text{-}C_5H_5)_2]$ (**11**, R = Me) was not isolated and the reaction proceeded quickly to the di-alkyne insertion species $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CHCH{=}CHCH{=}CMe_2)(\eta\text{-}C_5H_5)_2]$ (**13**, R = Me). Extensive study of the alkyne–alkylidene system later showed that the nature of the substituents on the alkylidene were instrumental, through a steric effect, in controlling the extent and nature of alkyne oligomerisation, with up to four molecules of alkyne being eventually linked [59,60].

The next species we investigated was the μ-ethylidyne cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2]^+$ (**14**). To our surprise this did not give products with alkynes, but this was compensated for when ethene, under UV irradiation, gave a complex analogous to those obtained from ethyne–ethylidene linking, i.e. $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)CH{=}CH_2\}(\eta\text{-}C_5H_5)_2]$ (**15**, R = H), via proton loss [61]. With propene regiospecific linking occurred at the substituted carbon of the alkene to give $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)CMe{=}CH_2\}(\eta\text{-}C_5H_5)_2]$ (**15**, R = Me), suggesting that the branched chain hydrocarbons of the Fischer–Tropsch synthesis could be formed by such alkene–alkylidyne linking on a metal surface. This behaviour of the μ-ethylidyne cation contrasts sharply with that of the di-iron μ-methyne cation $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)(\eta\text{-}C_5H_5)_2]^+$, which Casey has shown to undergo the "hydrocarbation" reaction with ethene to give $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CEt)(\eta\text{-}C_5H_5)_2]^+$ [62]. Our μ-methyne cation $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH)(\eta\text{-}C_5H_5)_2]^+$ did not react with ethene, probably due to a combination of the μ-CH being sterically well protected and by its reduced electrophilicity due to the presence of dppm.



(14) (15)

Following these indications of the ease of carbon–carbon bond formation at a diruthenium centre I was very keen to explore the prospect of alkene–alkylidene linking. Such linking at a mono-metal centre is generally recognised to be the basis of alkene metathesis and there were reports [63,64] that the carbon chain growth of the Fischer–Tropsch synthesis occurs by alkene–methylene combination, rather than the currently popular alkyl–methylene combination suggested by Pettit [65]. Ethene–methylene linking had been observed in other dinuclear systems [66–68], but no complex containing the two hydrocarbons as ligands was known. However, in the diruthenium system we had obtained a stable ethene complex and a stable μ-methylene complex, so why shouldn't one containing both simultaneously be possible? It did not seem to me we could lose. Either such a complex would undergo easy C–C linking or it would not, in each case telling us something about ethene–methylene linking. The initial attempts to induce alkene–alkylidene linking by photolysing μ-alkylidene complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CR_2)(\eta\text{-}C_5H_5)_2]$ in the presence of alkenes were unsuccessful. We suspected that products were being formed but were not surviving the UV irradiation employed to eject a CO in the first stage of the process. We therefore sought some other means of ejecting CO to provide a site for the incoming alkene and Michael Yates found that treatment of organo-diruthenium complexes with Me_3NO in MeCN worked well, as it does in several carbonyl systems. This was to prove an important discovery, as the rest of this review will reveal. Addition of Me_3NO to $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ in MeCN smoothly removed one CO as CO_2 and formed $[Ru_2(CO)(MeCN)(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ (**16**), which reacted well in situ with ethene (1 atm, 25 °C) to afford $[Ru_2(CO)(C_2H_4)(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$, as shown in Scheme 4 [55]. The very existence of the complex indicated that ethene–methylene linking was by no means a low energy process at a diruthenium centre in this system. Linking could be induced, but only by heating the complex to destruction at 250 °C, when propene comprised about 30% of the evolved gases. From this we then went on to show that propene was evolved more efficiently (90% of evolved gases) when the di-μ-alkylidene complex $[Ru_2(CO)_2(\mu\text{-}CHMe)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ was heated at 250 °C, leading us to suggest that alkene–methylene combination on a metal surface might occur best via an initial isomerisation of the alkene to an alkylidene [55]. We had

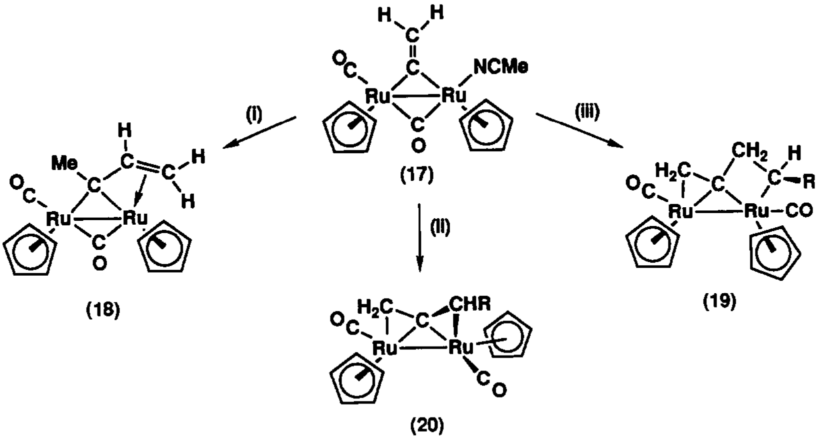


Scheme 4. (i) $CH_2{=}CH_2$, (ii) $RC{\equiv}CR$, (iii) $CH_2{=}C{=}CH_2$.

observed earlier that, although orbitally "forbidden", intramolecular linking of two μ-alkylidene ligands took place when $[Ru_2(CO)_2(\mu\text{-}CHMe)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ was heated at 250 °C to form a variety of C_5 alkenes, primarly $Me_2C{=}CHMe$ [69]. Related studies on the thermolysis of $[Ru_2(CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Ph)C(Ph){=}CH_2\}(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ were to reveal the importance of least motion effects in determining the course of C–C bond formation at a diruthenium centre [70].

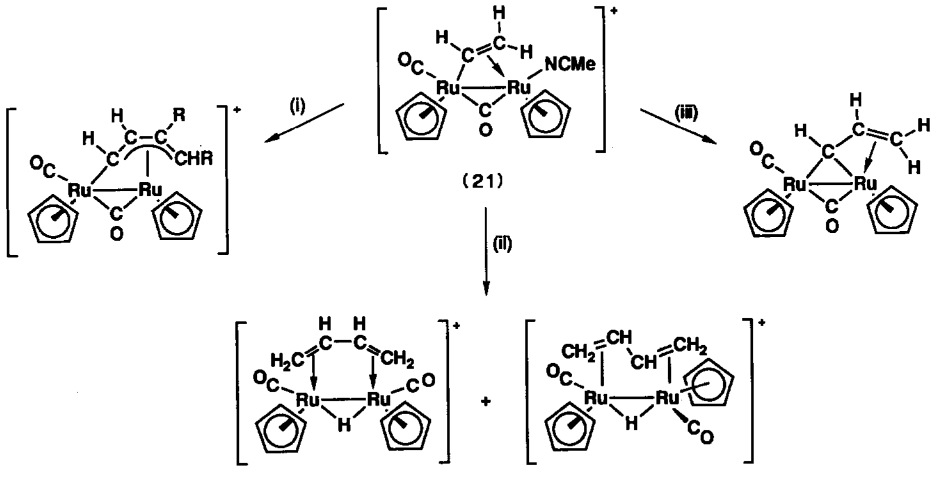
The reluctance of ethene to link with μ-methylene was subsequently shown to be unusual, as alkynes $RC{\equiv}CR$ and allene each underwent rapid C–C bond formation at or below room temperature with $[Ru_2(CO)(MeCN)(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ (**16**) to give μ-$CRCR{=}CH_2$ and μ-trimethylenemethane [71] respectively (see Scheme 4). From this we were able to conclude that C–C bond formation in this system, a reductive-elimination process which creates an unsaturated 32-electron centre, will occur readily when the centre can easily regain two electrons to give the saturated 34-electron configuration. For both alkynes and allene the π-systems of the hydrocarbons can provide such electrons, while coordinated ethene has none available.

The existence of a source of additional electrons in promoting C–C bond formation was again apparent recently when the μ-vinylidene/MeCN complex $[Ru_2(CO)(MeCN)(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)(\eta\text{-}C_5H_5)_2]$ (**17**) was treated with alkenes at room temperature by Helen Dickson (see Scheme 5). Unlike the corresponding μ-CH_2 species, hydrocarbon coupling occurred rapidly, a difference attributable to the involvement of the vinylidene π-electrons in compensating for those "lost" by the dimetal centre in the C–C bond formation step. With ethene the product was $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Me)CH{=}CH_2\}(\eta\text{-}C_5H_5)_2]$ (**18**), shown by a ^{13}C-labelling study to involve linking of ethene with the α-carbon of the μ-vinylidene. The probable nature of the precursor of **18** was suggested by the reactions of acrylonitrile or methyl acrylate $CH_2{=}CHR$ ($R = CN$ or CO_2Me) with **17**; these gave stable complexes $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CH_2CCH_2CHR)(\eta\text{-}C_5H_5)_2]$ (**19**) in which the alkene spanned the α-carbon and the metal. Treatment of **17** with diazoalkanes provides μ-allene complexes **20** in good yield following rapid linking of an alkylidene with the α-carbon of vinylidene [72].



Scheme 5. (i) $CH_2=CH_2$, (ii) $CHRN_2$, (iii) $CH_2=CHR$.

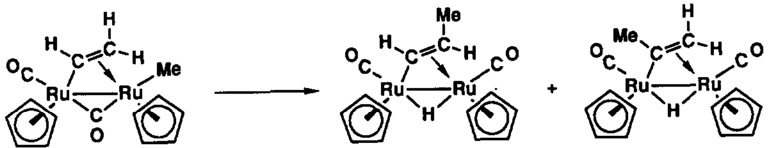
In 1989 Dr. Gregg Bruce arrived from Steve Stobart's group in Canada. He was surprised that in view of the above we had not yet explored the C–C bond-forming chemistry of the μ-vinyl ligand and soon synthesised the μ-vinyl cation $[Ru_2(CO)(MeCN)(\mu\text{-}CO)(\mu\text{-}CH=CH_2)(\eta\text{-}C_5H_5)_2]^+$ (**21**). The reactivity of this species towards hydrocarbons was the most impressive yet observed, so impressive that I immediately brought Andrew Phillips, a postgraduate student, into the project. We thus rapidly established the ability of the μ-vinyl group to enter C–C bond-forming reactions at room temperature with alkenes, alkynes, and alkylidenes as shown in Scheme 6. The combination with methylene is significant in view of the suggestion [56] that such linking is involved in the Fischer–Tropsch synthesis. The formation of μ-butadiene/μ-hydride complexes by vinyl-ethene linking is particularly striking and adds another factor to the emerging picture of C–C bond formation at a dinuclear metal centre, namely that β-hydrogen elimination will also



Scheme 6. (i) $RC\equiv CR$, (ii) $CH_2=CH_2$, (iii) CH_2N_2, $-H^+$.

allow the centre to readily regain two electrons to replace those now in the new C–C bond [73].

The prodigious ability of alkyl groups to migrate in organo-transition metal chemistry encouraged us to prepare the σ-methyl complex $[Ru_2Me(CO)(\mu\text{-}CH{=}CH_2)(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ (**22**) via sequential treatment of **21** with LiCl then $LiCuMe_2$, in the hope that methyl–vinyl linking would occur. This was realised; the complex was stable at −15 °C but at room temperature it rearranged smoothly to give the isomeric μ-propenyl complexes **23** and **24**, apparently via methyl migration followed by β-hydrogen elimination [74]. Vinyl homologation of this type could again provide a pathway for carbon chain growth on metal surfaces, and it is also interesting to note that methyl migration to μ-vinyl has features in common with the migration of alkyl to alkene generally accepted as the basis of Ziegler–Natta alkene polymerisation.



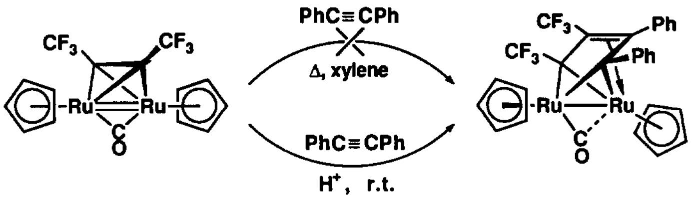
(22) (23) (24)

^{13}C-Labelling studies have recently revealed an interesting situation, namely that $\mu\text{-}CH{=}CH_2$ links through its α-carbon with ethene and methyl, and through the β-carbon with ethyne and methylene. In order to probe this, studies are in progress with a range of hydrocarbons and μ-vinyl ligands, and promise to greatly extend the knowledge of C–C bond formation at dinuclear metal centres.

In an extension of the work on μ-vinyl the bis(acetonitrile) derivative $[Ru_2(MeCN)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]^+$ has recently been prepared by Gregg Bruce and the reactions of the ligand with two incoming hydrocarbons are therefore within reach. Early results indicate that some fascinating new chemistry is in prospect; thus, treatment of this species with ethyne results in double C–C bond formation to give a $\mu\text{-}CHCHCHCHCHCH_2$ ligand, while ethene reacts to afford μ-CHMe and $\mu\text{-}C(Me)CH{=}CH_2$ simultaneously bridging the dimetal centre [75].

This research on the reactivity of the simple, fundamental hydrocarbon species at a dinuclear metal centre shows that most combine readily with one another at room temperature if a pathway for bringing them into simultaneous coordination is available. A startling example of this was observed recently when Sara Nicholls showed that the μ-alkyne complex $[Ru_2(\mu\text{-}CO)(\mu\text{-}CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)_2]$ (**25**) reacts with dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$, to give the "ruthenole" $[Ru_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)C(CO_2Me)C(CO_2Me)\}(\eta\text{-}C_5H_5)_2]$ either *at 150 °C* in refluxing xylene or *at room temperature* when acid is present. More striking still, **25** does not react at all with diphenylacetylene at 150 °C but does so readily *at room temperature* when acid is present to give $[Ru_2(CO)\{\mu\text{-}C(CF_3)C(CF_3)CPhCPh\}(\eta\text{-}C_5H_5)_2]$ (**26**) [76].

We have shown that this acid catalysis involves the protonation of the μ-alkyne in **25** to give a 30-electron Ru≡Ru triple-bonded μ-vinyl cation $[Ru_2(CO)\{\mu\text{-}C(CF_3){=}CH(CF_3)\}(\eta\text{-}C_5H_5)_2]^+$, by trapping this species with CO as stable $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CF_3){=}CH(CF_3)\}(\eta\text{-}C_5H_5)_2]^+$. Coordination of the second alkyne to this very electrophilic 30-electron cation now occurs readily, followed by vinyl–alkyne linking in a reductive-elimination step, then β-hydrogen

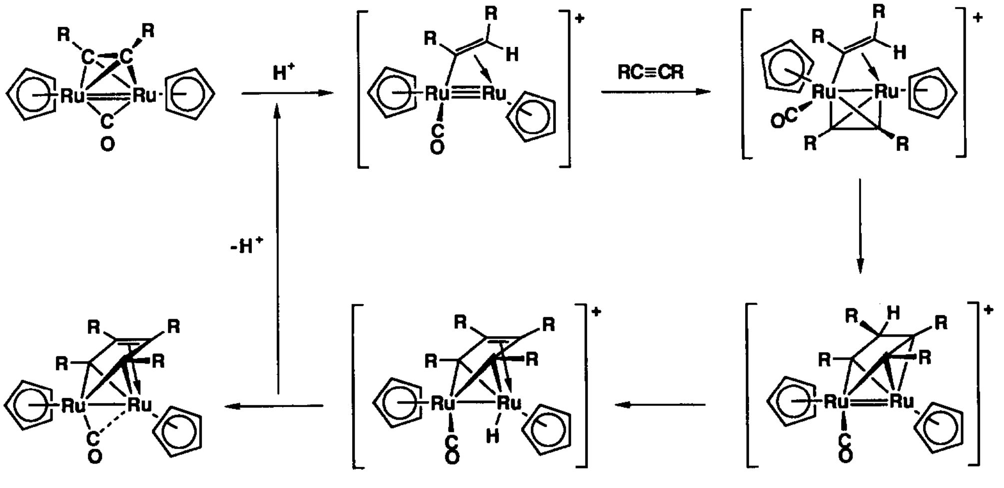


(25) (26)

elimination/H^+ loss, to give the ruthenole, as laid out in Scheme 7. The C–C bond-forming capacity of the μ-vinyl ligand is again evident in this chemistry.

The $[Ru_2(\mu\text{-}CO)(\mu\text{-}CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)_2]/H^+$ system is also capable of activating ethene, which yields $[Ru_2(CO)(\mu\text{-}CH{=}CH_2)\{\mu\text{-}C(CF_3){=}CH(CF_3)\}(\eta\text{-}C_5H_5)_2]$ at 25 °C and 1 atm. Complexation of ethene to the 30-electron μ-vinyl cation has been shown to be followed by isomerisation to μ-CHMe, through the trapping of the intermediate $[Ru_2(CO)(\mu\text{-}CHMe)\{\mu\text{-}C(CF_3){=}CH(CF_3)\}(\eta\text{-}C_5H_5)_2]^+$ as an MeCN complex. The μ-CHMe species is observed to undergo β-hydrogen elimination and H^+ ejection to give the 34-electron di-μ-vinyl product.

We are now up to date in this brief and selective story of the historical development of organo-diruthenium chemistry in my Laboratory. It is clear that the system does not want to let go of me; every time I think the results are becoming routine and shift students to other areas some surprising observation draws them back. I find the chemistry so interesting that I return to it happily. I should just briefly indicate, however, that other chemistry of polynuclear metal centres has and is being investigated in the laboratory! This involves (i) organic chemistry of the dimolybdenum centre, highlighted by the first discoveries of the "side-bound" μ-η^2-vinylidene [77] ligand and the planar μ_3-nitrido ligand [78,79], (ii) organic chemistry of the diphosphine-stabilised di-iron centre, highlighted by the elucidation of the pathway for tropone synthesis from ethyne and CO [80], (iii) C–P bond cleavage at di- and tri-metal centres [78–80], (iv) chemistry of tetra- and penta-



Scheme 7. Acid-catalysed alkyne linking at a diruthenium centre.

ruthenium benzyne complexes which mimic dissociative benzene chemisorption [84,85] and (v) the organic chemistry of the triruthenium centre [86,87].

Acknowledgements

I am grateful to a succession of talented research students and postdoctoral assistants whose efforts have put me in a position to write this review; their names are to be found in the text and in the references. The support of the S.E.R.C., The Petroleum Research Fund, administered by the American Chemical Society, and of Johnson Matthey plc has been invaluable. The enthusiastic collaboration of my colleagues Neil Connelly, Judith Howard, Guy Orpen and Peter Woodward has been essential and stimulating. I dedicate this review to Gordon Stone C.B.E., F.R.S.; it is hard to imagine Bristol without him.

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