ORGANIC CHEMISTRY OF POLYNUCLEAR METAL CENTRES

S.A.R. Knox

Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

Abstract – Diruthenium complexes $[Ru_2(CO)_3(\mu-L)(\eta-C_5R_5)_2]$ (L = organic ligand, R = H or Me) have been synthesised and their reactions with unsaturated hydrocarbons investigated. A strong tendency towards carbon-carbon bond formation processes at a diruthenium centre is evident, exemplified by studies on the oligomerisation of alkynes and dimerisation of ethene. The discovery of the trihydride $[Ru_3H_3(CO)_3(\eta-C_5H_5)_3]$, and its high reactivity towards unsaturated hydrocarbons (alkenes, alkynes, allene) and other reagents (D_2, CO, H^+), allows access to the chemistry of the triruthenium centre. Comparison of the reactivities of the di- and tri-ruthenium centres in these complexes is drawn where appropriate and possible implications for metal surface processes are discussed.
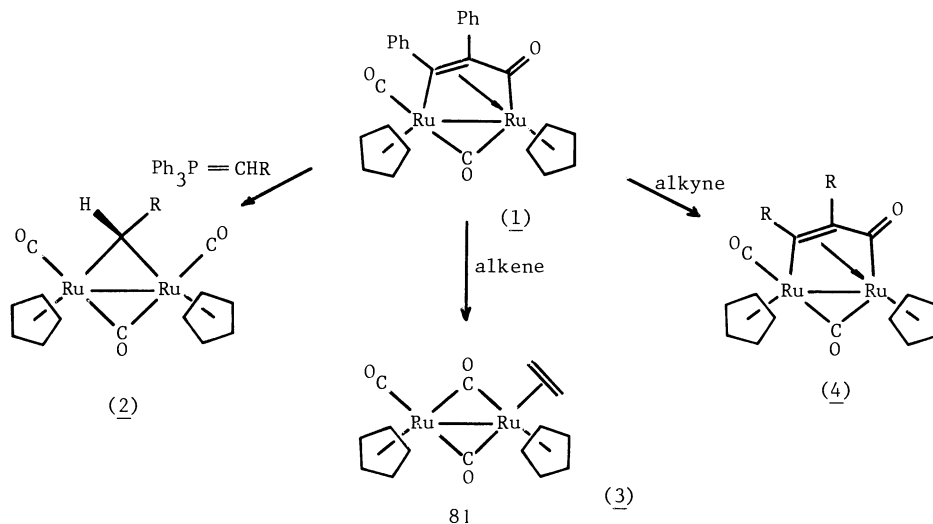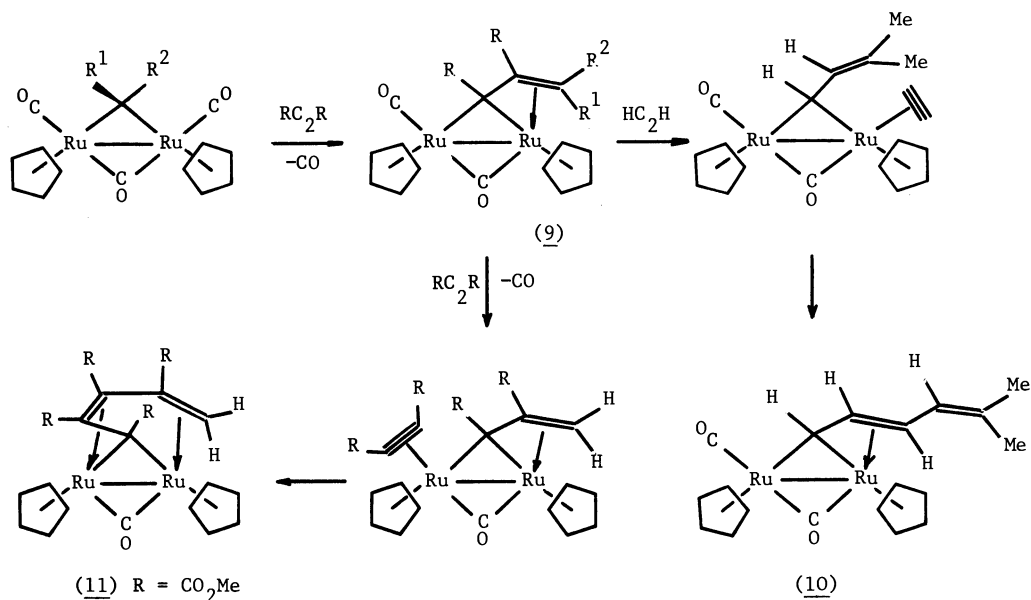
INTRODUCTION

There is a large and growing number of instances where the study of organic species co-ordinated at polynuclear metal centres in complexes has provided an insight into the behaviour of such species on a metal surface in heterogeneous catalysis. Perhaps the best example of this arises with the Fischer-Tropsch synthesis, whose essential features of $C \equiv O$ bond weakening and breaking, $C - H$ and $C - C$ bond formation, mobility of surface species, and release of products from the surface, are all modelled in organometallic complex chemistry (Refs. 1 and 2). This lecture describes studies designed to achieve a better understanding of the nature and reactivity of small organic species co-ordinated at dinuclear and trinuclear metal centres. The synthesis, structure, and reactivity of complexes of the form $[Ru_2(CO)_2(\mu-CO)(\mu-L)(\eta-C_5R_5)_2]$ (L = CH_2, CHMe, CCH_2, C_2H_4, CMe^+, etc) and $[Ru_3(\mu-CO)_3(\mu-L)(\eta-C_5R_5)_3]$ (L = $\mu-CHCH_2$, μ_3-CH, etc.; R = H or Me) will be described, revealing a strong tendency towards $C - C$ bond-forming reactions at a diruthenium centre and interesting differences between the di- and tri-ruthenium centres.
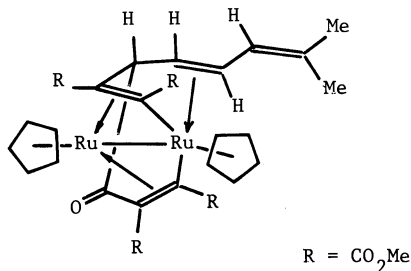
DIRUTHENIUM CHEMISTRY

Cyclopentadienyl Complexes

The complex $[Ru_2(CO)(\mu-CO)\{\mu-C(O)C_2Ph_2\}(\eta-C_5H_5)_2]$ (1) is readily obtained by the reaction of $[Ru_2(CO)_4(\eta-C_5H_5)_2]$ with diphenylacetylene under u.v. irradiation (Ref. 3), and acts as an excellent precursor of organo-diruthenium species (Ref. 4). In boiling toluene, conditions under which $[Ru_2(CO)_4(\eta-C_5H_5)_2]$ is unreactive, the molecule of diphenylacetylene is displaced rapidly by a wide variety of other reagents, some relevant examples of which are shown:

The μ-alkylidene complexes (2) may be obtained generally (R = H, Me, Et, Ph, etc), but the stability of the complexes (3) is very dependent on the nature of the alkene substituents and this restricts their availability. Thus, while the ethene complex is stable in boiling toluene the propene analogue decomposes at this temperature, and the but-2-ene complex does not survive at 25 °C for more than a few hours. Electronegative substituents increase stability substantially, presumably by increasing the π-acceptor capability of the alkene, and the complex of, for example, dimethyl fumarate is easily prepared.

The complexes (4) also serve as a useful source of μ-alkylidene complexes, exemplified in the sequence below (Ref. 5):

$$\text{(5)} \quad \xrightarrow{H^+} \quad \xrightarrow{H^-}$$

(5)   +

Hydride attack occurs predominantly on the β-carbon of the μ-vinyl ligand in the cation (5) to give the μ-CHMe complex, but attack at the α-carbon is also evident in the formation of the ethene complex. A situation will arise later in which the addition is exclusively at the α-carbon, directed by steric factors.

The μ-CHMe complex is best obtained by successive addition of methyllithium, tetrafluoroboric acid, and sodium borohydride to $[Ru_2(CO)_4(\eta-C_5H_5)_2]$; this sequence comprises the conversion of CO to μ-CMe$^+$ by the first two reagents and then hydride attack on this species. Recently, in extending this route, the preparation of $[Ru_2(CO)_2(\mu-CO)(\mu-CHPh)(\eta-C_5H_5)_2]$ was achieved from $[Ru_2(CO)_4(\eta-C_5H_5)_2]$ and phenyl lithium, HBF$_4$, and NaBH$_4$ in sequence. However, this synthesis also provided a low yield of $[Ru_2(CO)(\mu-CO)\{\mu-C(Ph)C(Ph)O\}(\eta-C_5H_5)_2]$ (6), identified by X-ray diffraction as containing a side-bound benzoyl group. The presence of two phenyl groups can be traced to nucleophilic attack by phenyl lithium on two carbonyl groups of $[Ru_2(CO)_4(\eta-C_5H_5)_2]$ to yield the dianion (7); protonation to afford (8), followed by carbon — carbon bond formation, accounts for (6):

$$\text{(7)} \quad \xrightarrow[-H_2O]{2H^+} \quad \text{(8)} \quad \longrightarrow \quad \text{(6)}$$

(7)   (8)   (6)

This tendency towards carbon — carbon bond formation processes is the most striking feature of organo-diruthenium chemistry. A prime example arises in the di-μ-alkylidene complex $[Ru_2(CO)_2(\mu-CHMe)(\mu-CMe_2)(\eta-C_5H_5)_2]$, which at 200 °C releases C$_5$ hydrocarbons (mainly Me$_2$C =CHMe) resulting from the coupling of the alkylidene ligands (Ref. 6). A more extensive area of study has evolved from the observation that μ-alkylidene complexes will initiate the oligomerisation of alkynes. The results of these studies (Ref. 7) are summarised on the next page.

There are two different pathways for oligomerisation, one leading to a complex of type (10) with a trans carbon chain, and one to a complex of type (11) with a cis carbon chain. The choice of path appears to be controlled by the nature of the μ-alkylidene substituents. X-Ray diffraction studies establish that the R^1 site in (9) is very crowded. Consequently, when R^1 ≠ H there is a steric inducement for the olefinic unit in (9) to dissociate, providing a co-ordination site for a second molecule of alkyne. Subsequent carbon — carbon bond formation will be constrained to generate a complex {e.g. (10)} in which the extended carbon chain is trans and avoids the R^1 site. Conversely, when in (9) R^1 is hydrogen there is no steric inducement for the olefinic unit to dissociate and oligomerisation can proceed via CO dissociation, with carbon — carbon bond formation now controlled to provide a cis carbon chain, as in (11), which is capable of 'wrapping around' the diruthenium centre. The complex (10) can be viewed as a complex of type (9) with R^1 = H and R^2 = CH =CMe$_2$ and should therefore react further with a third molecule of alkyne to create an extended carbon

(9)

(11) R = CO$_2$Me

(10)

chain with a cis configuration at the new point of linking. This is indeed the case, but X-ray diffraction also reveals that a fourth alkyne also enters, joins with a CO, and then links to the new carbon chain. The unusual product is

R = CO$_2$Me

Support for the idea that crowding in the R^1 site of a complex (9) controls the oligomerisation pathway, and therefore the stereochemistry of carbon — carbon bond formation, comes from a surprising source. Earlier we had shown that the μ-ethylidyne cation [Ru$_2$(CO)$_2$(μ-CO)-(μ-CMe)(η-C$_5$H$_5$)$_2$]$^+$ (12) reacts with ethene under u.v. irradiation to produce the complex [Ru$_2$(CO)(μ-CO){μ-C(Me)CHCH$_2$}(η-C$_5$H$_5$)$_2$], an analogue of (9), in another carbon — carbon bond forming process (Ref. 8). In an extension of this study (12) and the "alkene" [Ru$_2$(CO)$_2$(μ-CO)(μ-C=CH$_2$)(η-C$_5$H$_5$)$_2$] (13), in reality a μ-vinylidene complex, were brought together. Again the two organic fragments link, followed by a hydrogen shift, to yield the exotically-substituted μ-vinyl cation (14) which has been the subject of an X-ray diffraction study(see diagrams next page).

Treatment of (14) with sodium borohydride was expected, in the light of the work on μ-vinyl cations described, to effect hydride addition to the β-carbon of the vinyl and give a μ-alkylidene complex. In the event the product isolated was the complex (16), which derives from hydride addition to the α-carbon of the vinyl. We presume this is a consequence of the β-carbon being inaccessible because of the large diruthenium substituent associated with it. The α-addition would initially provide an alkene complex (15) of low stability (see earlier), from which the observed product is released. The significance of complex (16) lies in the position of the methyl group. Normally such a complex would readily suffer CO loss and co-ordination of the vinyl substituent upon photolysis, to give a complex of type (9). In this case such a product would have a methyl substituent occupying the R^1 site. However, the previous discussion of alkyne oligomerisation rested on the crowded nature of this site, and the photolysis of (16) bears this out. The observed product is (17), with a methyl group occupying the uncrowded R^2 site. It is evident that the crowding of the R^1 site is severe enough to induce a transformation which brings a hydrogen to this position. The similar transformation of (18) to (19) reveals that the process is not a simple one.

Me

(12)   (13)   (14)

H⁻

(16)   -Ru₂   (15)

(16) R = H   u.v.   (17) R = H
(18) R = Me   -CO   (19) R = Me
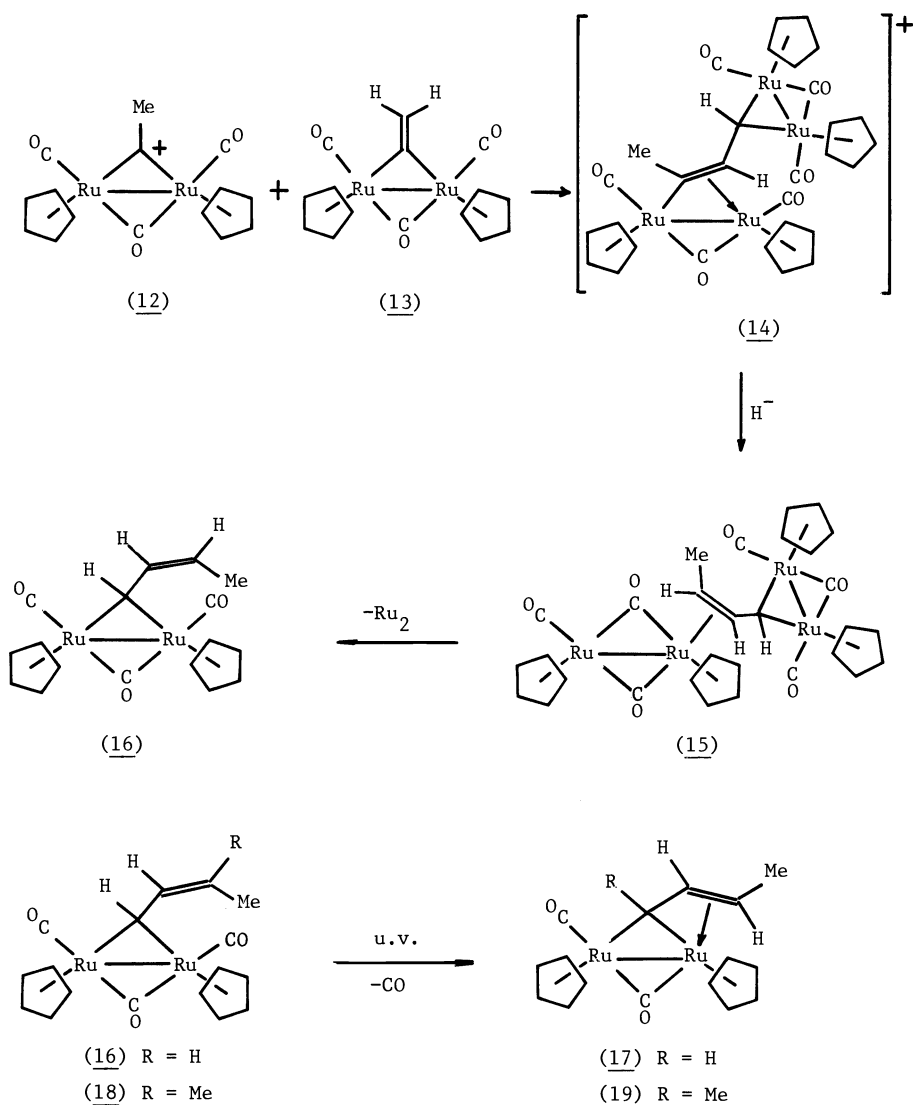
Pentamethylcyclopentadienyl Complexes

We have recently begun to explore the chemistry of diruthenium complexes analogous to those above, but employing η-C₅Me₅ as a ligand in place of η-C₅H₅. The influence of the substantially different electronic and, especially in view of the above discussion, steric properties of η-C₅Me₅ was of interest. The starting point of these studies is [Ru₂(CO)₄-(η-C₅Me₅)₂] (20), obtained in high yield from [Ru₃(CO)₁₂] and pentamethylcyclopentadiene. As with [Ru₂(CO)₄(η-C₅H₅)₂], a carbon monoxide ligand is converted to μ-CHMe by addition of methyl lithium, HBF₄, and NaBH₄ in sequence, to give complex (21). The size of the η-C₅Me₅ ligand is reflected immediately in the adoption of trans geometries by (20) and (21). However, it is their reactivity towards ethene, in contrast to the unreactivity of the η-C₅H₅ analogues, which is of more significance. The reaction of ethene with (20) yields, as illustrated on the next page, the complexes (21) and (22), each containing a C₂ fragment, and the complex [Ru₂(CO)(μ-CO){μ-C(Me)CHCH₂}(η-C₅Me₅)₂] (23) which contains a C₄ unit. The latter is clearly the result of ethene dimerisation, and further experiments have revealed that this follows the pathway (22) → (21) → (23). Thus, photolysis of (22) induces a rearrangement of co-ordinated ethene to μ-CHMe in forming complex (21), which upon further photolysis in the presence of ethene (1 atm) yields (23). The transformation of ethene to μ-CHMe is the first observation in a complex of what is probably common behaviour on a metal surface (see later). Its promotion by the η-C₅Me₅ ligand may be due to the steric pressure for ethene to adopt a bridging site, i.e. form a dimetallacyclobutane ring, which will allow a hydrogen shift via β-elimination. A related transformation of μ-CF₂CF₂ to μ-C(F)CF₃ has been reported (Ref. 9). The greater electron-donating ability of η-C₅Me₅ c.f. η-C₅H₅ would also be expected to stabilise Ru — C σ-bonds and therefore favour such dimetallacycle formation. This may also be the key to the linking of μ-CHMe and ethene in the conversion of (21) to (23), which is likely to proceed via the formation of a dimetallacyclopentane ring. An overall view of these experiments with ethene suggests a mechanism for its dimerisation on a metal surface, and there are also implications for carbon chain
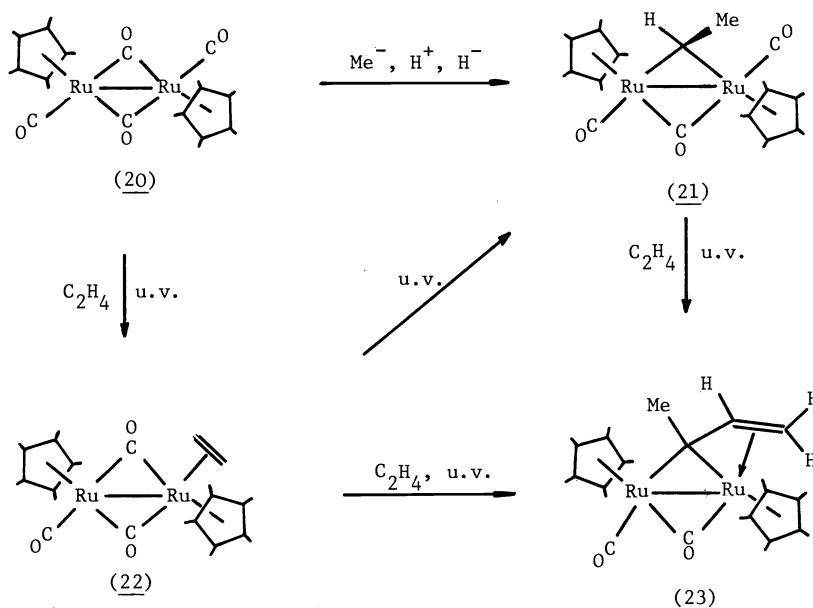
growth in the Fischer–Tropsch synthesis.

The complex (23) is also formed when the μ-vinylidene complex $[Ru_2(CO)_2(\mu-CO)(\mu-C=CH_2)-(\eta-C_5Me_5)_2]$ (24) and ethene react under u.v. irradiation; once again the intermediacy of a dimetallacyclopentane ring is likely but now no loss of hydrogen is necessary in the subsequent rearrangement. A minor and surprising product of this reaction is $[Ru_2(CO)_2(\mu-CO)-(\mu-CH_2)(\eta-C_5Me_5)_2]$ (25), which has been shown to evolve directly from the photolysis of (24) in ca. 15 % yield. This unprecendented pathway to a μ-CH₂ ligand appears to involve cleavage of the vinylidene carbon — carbon double bond and then hydrogen abstraction from solvent; photolysis of $[Ru_2(CO)_2(\mu-CO)(\mu-C=CD_2)(\eta-C_5Me_5)_2]$ yields $[Ru_2(CO)_2(\mu-CO)(\mu-CH_2)-(\eta-C_5Me_5)_2]$.
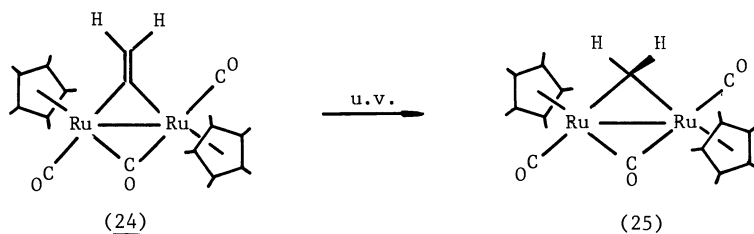
TRIRUTHENIUM CHEMISTRY

Cyclopentadienyl Complexes

The μ-alkylidene complexes $[Ru_2(CO)_2(\mu-CO)(\mu-CHR)(\eta-C_5H_5)_2]$ (R = H, Me, Et, etc) (26) have proved useful precursors of triruthenium complexes through their thermolysis, and their photolysis in the presence of hydrogen. Heating at ca. 250 °C results in a rearrangement to give $[Ru_3(\mu-CO)_3(\mu_3-CR)(\eta-C_5H_5)_3]$ (27) in moderate yield, the spare ruthenium appearing as
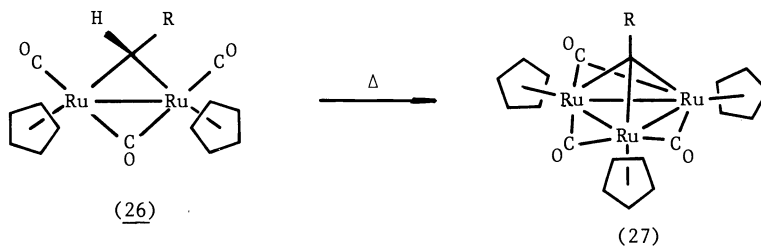
$[Ru_2(CO)_4(\eta-C_5H_5)_2]$ and $[Ru_4(CO)_4(\eta-C_5H_5)_4]$. Some μ-alkylidene ligand is lost as hydrocarbons, but always with C — C bond retention; e.g. μ-CHEt appears as propene (mainly) and propane. In contrast, the thermally very stable μ-alkylidyne complexes (27) decompose at 550 – 600 °C to evolve methane almost exclusively, independent of whether R = H, Me, or Et. This predominant C — C cleavage at a triruthenium centre may be relevant to recent studies of C — C cleavage on a Pt(111) surface, which is suggested to occur via μ₃-alkylidyne species

(Ref. 10).   The μ_3-alkylidyne complexes (27) are unreactive towards unsaturated hydrocarbons, and the organic chemistry of the triruthenium centre is better approached via the complex [Ru$_3$H$_3$(μ-CO)$_3$(η-C$_5$H$_5$)$_3$] (28), prepared by the photolysis of the μ-alkylidene complexes (26) under 1 atm of hydrogen (Ref. 11).   Blue crystalline (28) is shown by X-ray diffraction to have mirror symmetry in the solid state (i.e. two cyclopentadienyls to one side of the Ru$_3$ plane and one on the other) and n.m.r. spectra indicate that this is also the case in solution at room temperature.   However, at higher temperatures a fluxional process occurs to render the three cyclopentadienyls and three μ-H ligands each equivalent.   This may or may not involve hydride mobility but certainly the η-C$_5$H$_5$ groups must 'rotate' from one side of the Ru$_3$ plane to the other.

The trihydride (28) reacts readily in boiling toluene with a wide variety of unsaturated hydrocarbons; some examples are shown:

(28)
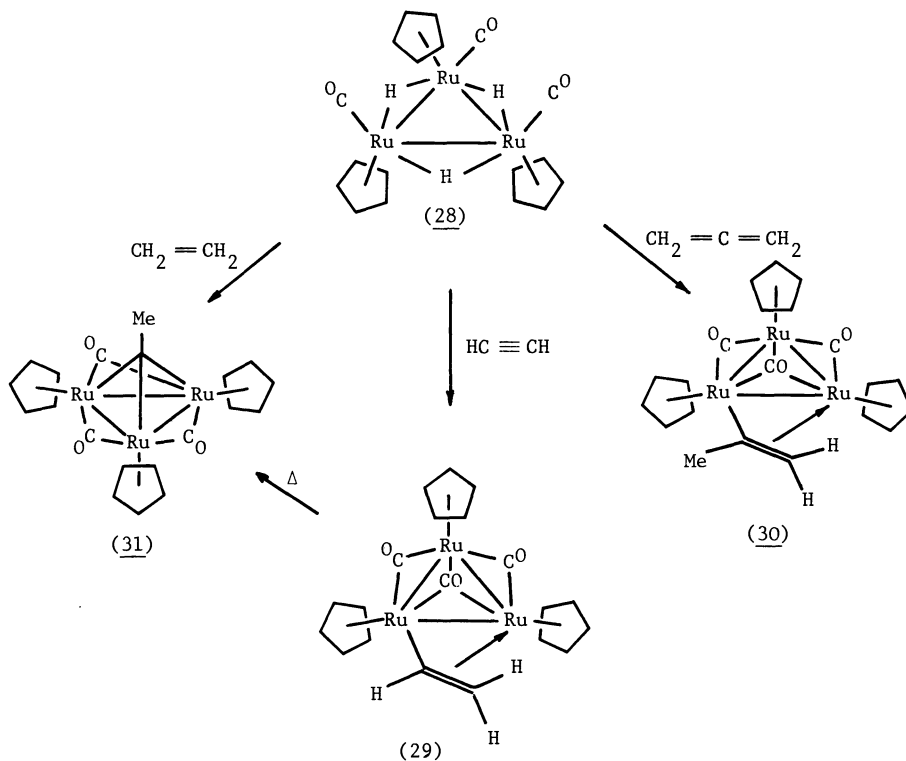
μ-Vinyl complexes (29) and (30) of the same type are derived from ethyne and allene, respectively, each the result of 'insertion' of the hydrocarbon into an Ru$_2$(μ-H) bond.   Further, heating (29) induces a hydrogen shift, yielding the μ-ethylidyne complex (31).   This is also formed directly when the trihydride (28) is heated with ethene (1 atm), but (29) is not an intermediate in this reaction, since its relatively long lifetime would have enabled it to have been detected if present.   In view of the observed ability of ethene to rearrange to μ-CHMe at a diruthenium centre, and the rearrangement of μ-CHMe to μ_3-CMe discussed earlier in this section, it is attractive to consider that this train of events is followed in the reaction of ethene with [Ru$_3$H$_3$(μ-CO)$_3$(η-C$_5$H$_5$)$_3$].

The formation of the μ_3-CMe complex from either ethyne or ethene reveals a striking capacity of (28) to effect hydrogenation or dehydrogenation of a hydrocarbon in order to bring it into co-ordination at the triruthenium centre.   It is noteworthy in this regard that ethene or ethyne chemisorbed on a Pt(111) surface are both transformed at 300 - 350 K to the μ_3-ethylidyne species (Ref. 12).   These observations give strong encouragement to the belief that studies of the Ru$_3$ centre in these complexes will be relevant to the M$_3$ site in catalysis.

The trihydride (28) also reacts with propene and styrene in boiling toluene, but slowly, to give a low yield of the appropriate μ_3-CCH$_2$R (R = Me or Ph) complex analogous to (31).   High yields of μ-vinyl complexes like (29) are, however, obtained from a variety of alkynes RC$_2$R (R = Me, Ph, or CO$_2$Me) and RC$_2$H (R = Me, Et, or Ph) in reactions with (28).   All but two of these are fluxional, undergoing the oscillatory σ-π rearrangement typical of a vinyl ligand; the exceptions are the μ-C(R) = C(R)H (R = Ph or CO$_2$Me) species.   In these latter the high electronegativity of R must make the vinyl group a sufficiently strong π-acceptor that its co-ordination is not easily transferred from one ruthenium to the other.

The reactions of [Ru$_3$H$_3$(μ-CO)$_3$(η-C$_5$H$_5$)$_3$] with carbon monoxide and deuterium promise a significant extension of triruthenium chemistry.   Bubbling CO through a boiling toluene solution

of (28) displaces two μ-H ligands and gives purple [Ru$_3$H(CO)$_3$(μ-CO)(η-C$_5$H$_5$)$_3$] (32) quantita-
tively.   The process is reversed when (32) is subjected to 1 atm of hydrogen, a feature

(28)   (32)
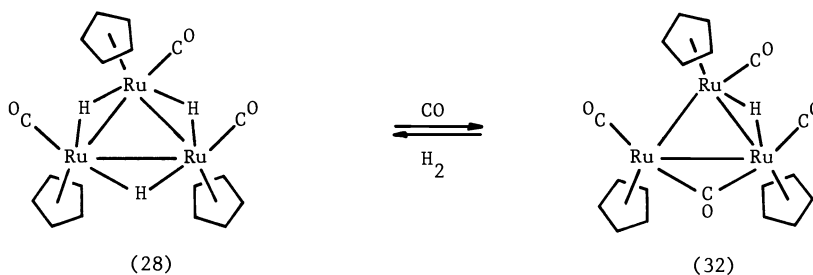
which provokes interest in the possibility of developing a catalytic cycle based on (28) and
(32).   The reactions of (32) with unsaturated hydrocarbons are under investigation.
Heating (28) in toluene at 100 °C under 1 atm of deuterium effects rapid exchange of μ-H for
D; the product [Ru$_3$D$_3$(μ-CO)$_3$(η-C$_5$H$_5$)$_3$] is seen as an important precursor in establishing
the role of metal-bound H(D) in organic ligand rearrangements.

Both (28) and (32) are protonated by HBF$_4$ to yield the cations [Ru$_3$(μ-H)$_3$(μ$_3$-H)(CO)$_3$-
(η-C$_5$H$_5$)$_3$]$^+$ (33) and [Ru$_3$(μ-H)$_2$(CO)$_4$(η-C$_5$H$_5$)$_3$]$^+$ (34), respectively, but these are not
related through a CO/H$_2$·exchange process in the way that (28) and (32) are.   The dihydride
(34) is stable only when held under an atmosphere of carbon monoxide.   Interestingly,

(33)   (34)
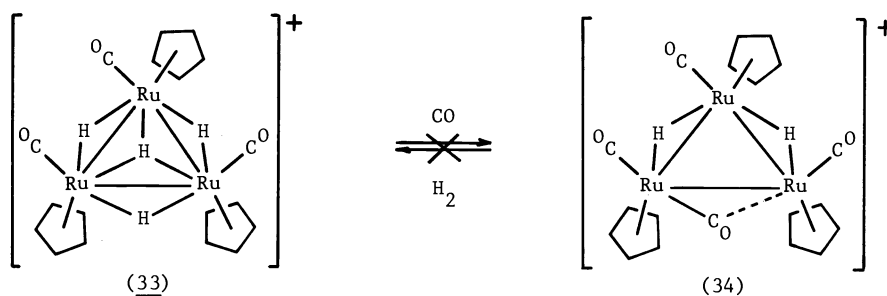
whereas the hydrides in (34) are equivalent in the n.m.r. spectrum even at -90 °C, as a
result of fluxional exchange, the doubly- and triply-bridging hydrides in (33) do not
exchange their environments up to 100 °C.

Pentamethylcyclopentadienyl Complexes.
Earlier the rearrangement of ethene to μ-CHMe was described in the conversion of (22) to
(21).   A further modification to the organic ligand is achieved when (21) is heated at

(22)   (21)   (35)
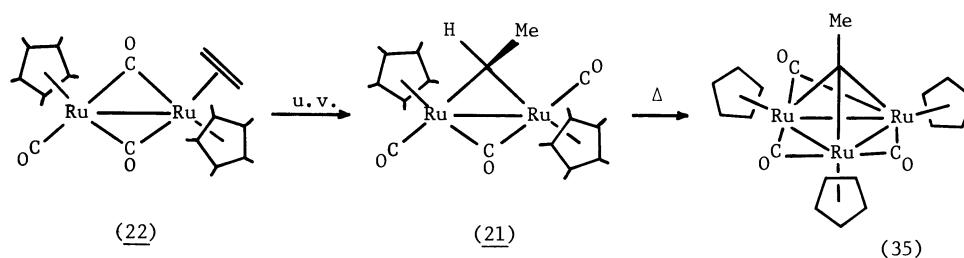
200 °C; the product is the μ$_3$-ethylidyne complex (35).   This sequence may provide an
insight into the path followed by ethene in its transformation to ethylidyne bound at an M$_3$
site on the Pt(111) surface (Ref. 12).   Heating [Ru$_2$(CO)$_2$(μ-CO)(μ-CH$_2$)(η-C$_5$Me$_5$)$_2$] at 200 °C
gives [Ru$_3$(μ-CO)$_3$(μ$_3$-CH)(η-C$_5$Me$_5$)$_3$] similarly.   Preliminary results of studies with these
μ$_3$-CH and μ$_3$-CMe species reveal a much higher reactivity than that exhibited by their
analogues with η-C$_5$H$_5$ ligands, especially towards alkynes and protonation.

The most convenient entry into Ru$_3$(η-C$_5$H$_5$)$_3$ chemistry was provided by the complex [Ru$_3$H$_3$-
(μ-CO)$_3$(η-C$_5$H$_5$)$_3$] (28), formed by photolysis of [Ru$_2$(CO)$_2$(μ-CO)(μ-CHMe)(η-C$_5$H$_5$)$_2$] in the
presence of hydrogen.   Under the same conditions [Ru$_2$(CO)$_2$(μ-CO)(μ-CHMe)(η-C$_5$Me$_5$)$_2$] (21)
generates the multiply Ru—Ru bonded species [Ru$_2$H$_2$(CO)$_2$(η-C$_5$Me$_5$)$_2$] (36) and
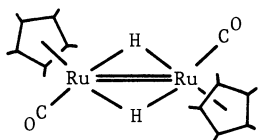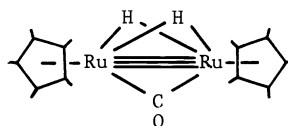
(36)   (37)

$[Ru_2H_2(\mu-CO)(\eta-C_5Me_5)_2]$.   Whereas (28) is a trimer of the $RuH(CO)(\eta-C_5R_5)$ unit, (36) is interesting in being a dimer, perhaps for steric reasons.   Both (36) and (37) are likely to be very reactive towards hydrocarbons, but their formation in low yields will restrict their utility in the exploration of organo-diruthenium chemistry.   The osmium analogues of (36) and (37) have been described, formed in the photochemical reaction of $[OsH(CO)_2(\eta-C_5Me_5)]$ with hydrogen (Ref. 13).

The dihydrides (36) and (37) are also products, again in low yield, when $[Ru_2(CO)_4(\eta-C_5Me_5)_2]$ is treated with hydrogen (1 atm) under u.v. irradiation.   However, photolysis of $[Ru_2(CO)_4-(\eta-C_5H_5)_2]$ proceeds differently, independent of the presence of hydrogen, to produce in good yield a tetraruthenium complex (38), identified by X-ray diffraction.   The $\mu_3-C_5H_4$ ligand, previously seen bridging $AlTi_2$ (Ref. 14) and $FeAu_2$ (Ref. 15) units, is converted to μ_2-bridging in (39) when (38) is treated with iodine:

(38)   (39)
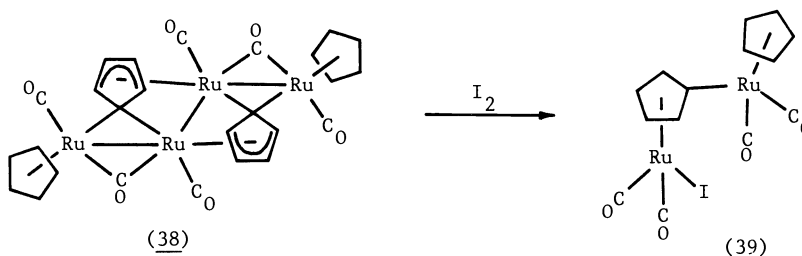
CONCLUSIONS AND NEW APPROACHES

The di- and tri-ruthenium complexes described in this lecture are a rich source of information on the behaviour of organic species at metal centres.   When co-ordinated at a diruthenium centre such species are reactive and readily participate in a variety of carbon — carbon bond formation processes, the oligomerisation of alkenes and alkynes being of special interest. There is evidence that steric factors have a strong influence.   The chemistry of the tri-ruthenium centre, accessed via $[Ru_3H_3(CO)_3(\eta-C_5H_5)_3]$, is marked by a tendency for hydro-carbons to rearrange, aided by the presence of metal-bound hydrogen, to very stable μ_3-alkylidyne species.   Studies with pentamethylcyclopentadienyl complexes are at an early stage but it is already emerging that substantial differences exist compared with cyclopenta-dienyl analogues.   This is encouraging the exploration of further modifications to the system, by employing the complexes $[FeRu(CO)_4(\eta-C_5H_5)_2]$ (40) and $[Ru_2(CO)_4(\eta-C_5H_4CH_2C_5H_4)]$ (41) as precursors of organo-dimetal chemistry.   Both are proving adept in this respect.
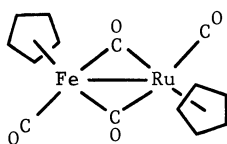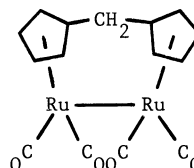
(40)   (41)

With (40) the influence which the heteronuclear nature of the dimetal centre exerts upon the chemistry of co-ordinated organic species is of interest.   The linked cyclopentadienyl rings in (41) constrain complexes derived from this to have a cis configuration, but of more significance is likely to be the effect of the different bonding characteristics of this new diruthenium unit.   These are indicated by the strong preference for the terminal mode of carbonyl bonding in (41) compared with unlinked $[Ru_2(CO)_4(\eta-C_5H_5)_2]$, a normal consequence of a longer metal — metal bond.

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