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Some complexes of all-carbon ligands and related chemistry

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Contents

Abstract

Recent developments in the chemistry of all-carbon ligands and related molecules include the synthesis and reactions of mono-, bi- and poly-nuclear complexes containing C_2, C_4 and C_8 ligands, as well as of substituted derivatives of allenylidene ($:C{=}C{=}CH_2$) and butatrienylidene ($:C{=}C{=}C{=}CH_2$) ligands. The work of the Adelaide group on the pentanuclear ruthe-

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nium cluster carbonyl containing a reactive C_2 ligand and on the synthesis, chemistry and electrochemistry of a variety of complexes containing C_4 and C_8 ligands, is described.

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1. Introduction

Of the three familiar forms of carbon, namely diamond (sp^3), graphite (sp^2) and the fullerenes (sp^2), only the latter (in the forms of C_{60}, C_{70}, C_{84}) are known for their ability for multiple addition of transition metal fragments. In C_{60}, this occurs at the C=C double bonds which are found at the junctions of the six-membered rings. Examples of these fullerene–metal complexes include $C_{60}\{M(PEt_3)_2\}_6$ (M=Ni, Pd or Pt) [1] and $C_{70}\{Pt(PPh_3)_2\}_4$ [2].

There are also many other, more reactive, forms of carbon which have been studied [3]. The simplest carbon molecule, C_2, is found in carbon-rich stars, in comets and in the oxidising flames of hydrocarbons (Bunsen burners). Spectroscopists have long studied this molecule, which has become known for the many different electronic states which are available. However, it is also extremely reactive, and reactions employing it have been being limited to the generation of C_2 (and other C_n molecules) in a carbon arc and condensing the vapours at liquid nitrogen temperatures [4].

There is much current interest in long unsaturated carbon chains in view of their supposed potential in the manufacture of electronic devices (nano technology, molecular engineering and non-linear optics) [5]. One method of stabilising C_n chains has been to cap the ends with silyl groups or transition metals, when more or less stable compounds can be isolated. The commonly available routes of chain lengthening by coupling (Cadiot–Chodkiewicz, Eglinton–Glaser or Hay reactions) have been used to good effect by Gladysz and coworkers [6], who have succeeded in isolating complexes containing chains of up to 20 carbon atoms capped by $Re(NO)(PPh_3)Cp^*$ groups at each end.

2. C_2 complexes

Our interest in these molecules was sparked by our earlier studies of metal acetylide complexes. In these, the HOMO extends to C_β making it susceptible to attack by electrophiles, particularly the proton, to form vinylidenes, the simplest unsaturated carbene [7]. The question arises: what is the effect on their chemistry of having a second transition metal on the C_2 fragment? The presence of two metal units separated only by a C≡C triple bond might be expected to confer unique properties on the resulting complexes, some resulting from the formation of a strongly bonded MC_2M system of which the HOMOs show strong M–C bonding and some C–C antibonding character [8].

This is not the place to give a comprehensive survey of the chemistry of complexes of the type $L_nM{-}C{\equiv}C{-}M'L'_n$. Suffice it to say, however, that very few studies of the reactivity of such species have been reported. Of considerable interest in this regard is the selective double insertion of isocyanides into the Pd–C bonds of complexes containing the Pd–C$\equiv$C–Pd unit and the successive multiple insertions (living polymerisation) found with the corresponding heteronuclear Pd–C$\equiv$C–Pt systems [9]. Others have used these complexes as building blocks for metal cluster synthesis [10], and Akita's group has pioneered a detailed study of the chemistry of manganese, iron, and ruthenium derivatives [11].

A second feature of interest is the varying nature of the C_2 bridge as a function of the metal–ligand caps. Examples of the three forms **A**, **B** and **C** have been isolated and crystallographically characterised:

$$\begin{array}{ccc} M-C\equiv C-M & M=C=C=M & M\equiv C-C\equiv M \\ \mathbf{A} & \mathbf{B} & \mathbf{C} \end{array}$$

This series represents a sequential oxidation of the M_2C_2 system. System **A** is represented by the complexes $\{MX(PR_3)_2\}_2(\mu\text{-}C_2)$ (M=Pd or Pt; X=Cl or I; R=Me, Et or Bu) [12]. System **B** is found in $(Bu^t_3SiO)_3Ta=C=C=Ta(OSiBu^t_3)_3$ [13], while the first example of system **C** was the complex $(Bu^tO)_3W\equiv C-C\equiv W(OBu^t)_3$ [14].

One of our approaches to the synthesis of complexes containing the C_2 ligand took advantage of the facile cleavage reactions undergone by tertiary phosphines when attached to metal carbonyl clusters, particularly those of the group 8 metals. Many studies [15] have shown that the ease of cleavage of the P–C bonds in these ligands when attached to ruthenium cluster carbonyls increases in the order:

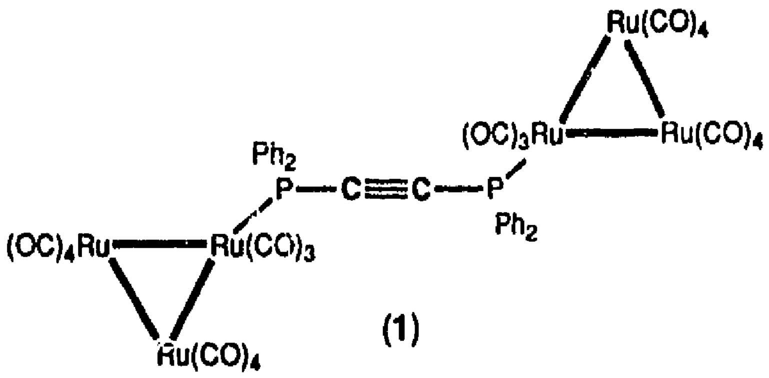
$$P-C(sp) > P-C(sp^2) > P-C(sp^3)$$

We reasoned that such reactions applied to complexes of the commercially available ligand $Ph_2P-C\equiv C-PPh_2$ (dppa) might afford complexes of C_2 by cleavage of the P–C(sp) bonds. As the P–C–C–P chain is linear, this ligand cannot form chelate complexes (as can dppe or *cis*-dppee). However, in the case of the tungsten thiocarbamate complex $W(CO)(S_2CNEt_2)_2\{\eta^2\text{-}C_2(PPh_2)_2\}$ (L), where coordination of the C$\equiv$C triple bond before the PPh_2 groups occurred, the usual bending at the carbon atoms resulted in a conformation whereby the two P atoms could chelate a second metal–ligand fragment, as found in $M(CO)_4(L)$ (M=Cr, Mo or W) or bridge a Co–Co bond, in $Co_2(\mu\text{-}L)(CO)_6$ [16]. Only two cases are known where the dppa ligand itself bridges metal–metal bonds, with third row transition metal atoms in $Re_3(\mu\text{-}H)_3(\mu\text{-}dppa)(CO)_{10}$ [17] and $Ir_3W(\mu\text{-}dppa)(\mu\text{-}CO)_3(CO)_6Cp$ [18].

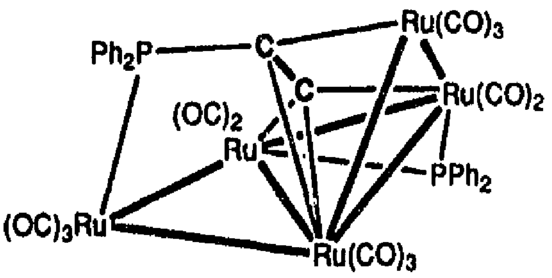
With cluster carbonyls such as $Ru_3(CO)_{12}$, the expected behaviour would be to form novel complexes containing one cluster moiety attached to each P atom. If cleavage of a P–C(sp) bond occurred, then the resulting ligands might react further via the C$\equiv$C triple bond to give cluster build-up.

This expectation was fulfilled in practice and the sodium benzophenone ketyl-catalysed reaction [19] between the two reactants afforded the dppa-bridged dicluster complex **1** in high yield. Simple pyrolysis then gave the black pentanuclear cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**2**); the sixth ruthenium was recovered as

$Ru_3(CO)_{12}$ [20]. Only one of the P–C(sp) bonds in the original dppa ligand has been cleaved and much effort and time was spent trying to discover conditions under which the second such bond would be broken. Much of the rich chemistry of **2** that resulted has already been described in an earlier account [21].



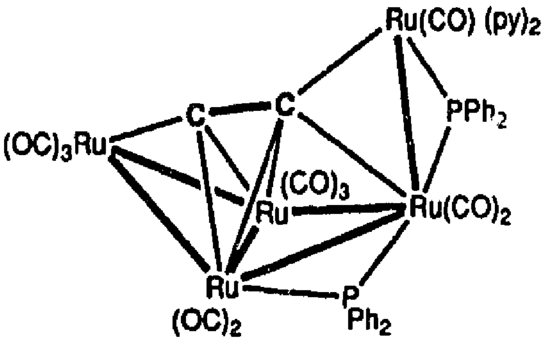
(1)



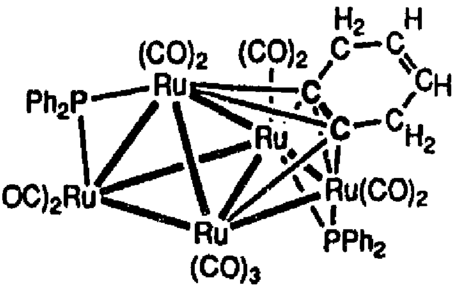
(2)

Some of these results, for example, the reaction with pyridine, which afforded **3** [22], or with buta-1,3-diene, which gave **4** [23], indicated that several complexes which either contained the C_2 ligand, or were formed via putative C_2 complexes, could indeed be obtained. Unfortunately, none was isolated in yields high enough to make further investigation of their chemistry worthwhile.

The solution to this problem was found in the reaction of **2** with dimethyl disulfide,

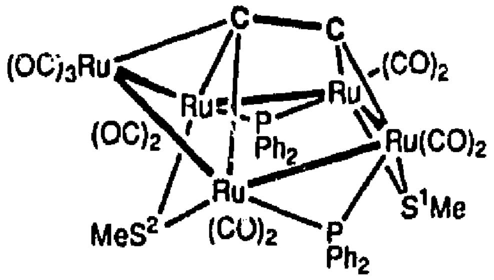


(3)



(4)

a reaction which is remarkably complex while at the same time being unusually clean. During the reaction, **2** is converted via a series of intermediate complexes to the unprecedented cyclic cluster **5**, which contains the C_2 ligand sitting on top of the bent pentagonal array of five metal atoms [24]. Several complexes are formed sequentially in the conversion; opening of the Ru_5 core of **2** occurs before cleavage of the $P–C_2$ bond. Fortunately for further studies, **5** can be obtained in an overall yield of about 80% from **2**, thus enabling gram quantities to be obtained from $Ru_3(CO)_{12}$ over a period of three days. Furthermore, as shown by the crystal structure determination, the sterically demanding PPh_2 and SMe ligands have their substituents directed to the other side of the metal array, thus allowing unhindered approach of other reagents to the C_2 fragment, which is the centre of reaction in this molecule. Related compounds have been obtained from a similar sequence of reactions using $C_2(PBu_2)_2$; although enabling an easier study of the ^{13}C NMR parameters of the C_2 ligands, none have given crystals suitable for X-ray structural studies [25].



(5)

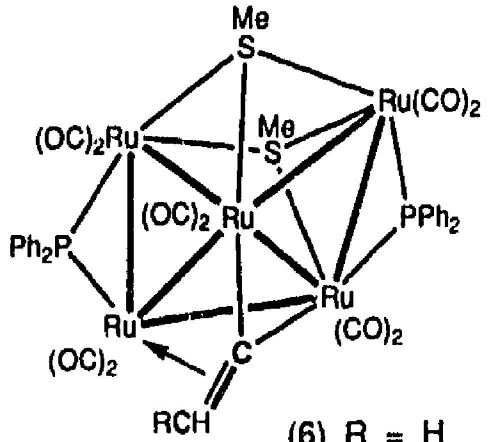
Cluster **5** is small enough to be studied by extended Hückel MO methods: initial calculations were carried out on the simplified system containing PH_2 and SH ligands [26], but recently more sophisticated studies of the real molecule have been carried out [27]. Both approaches give essentially the same result and show that the two carbon atoms carry substantial negative charges and so should enter into reactions as nucleophiles. At the same time, there is also significant electron density on the bridging S^2Me group and it would be expected that conversion to a μ_3 bridging mode would occur. The chemistry of **5** has amply confirmed these expectations.

3. Some reactions of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (5)

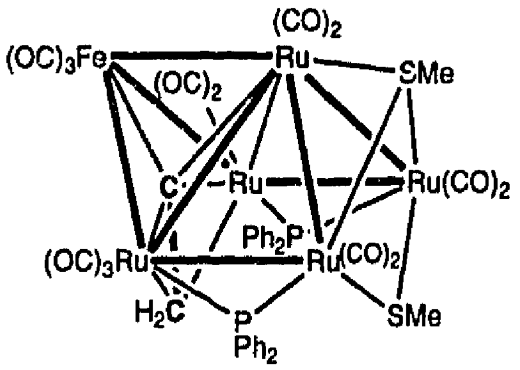
3.1. Dihydrogen

Reactions of **5** with dihydrogen result in insertion of one of the carbons into the H–H bond to give the vinylidene complex **6** [26]. In this complex closure of the Ru_5 ring to a skeleton with three fused Ru_3 triangles has occurred to regenerate the cluster core found in the precursor **2**, while the SMe groups have adopted the μ_3 bridging mode.

Further reaction of **6** with $Fe_2(CO)_9$ afforded the heterometallic complex **7**, which at the time of its discovery, contained the first example of a $\mu_4\text{-}CCH_2$ ligand [28].



(6) R = H
(8) R = $CH=CH_2$



3.2. *Olefins and dienes*

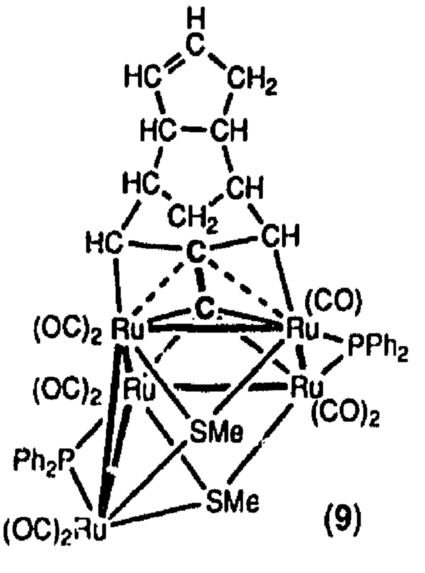
In reactions between **5** and terminal olefins, insertion of one of the carbon atoms into the terminal C–H bonds gives the vinylvinylidene derivatives **8** shown, whose structures are closely related to that of **6** [26,29]. Note that this reaction occurs even with ethene. The complexes show an interesting fluxionality by which the vinylidene ligand moves from one Ru_3 face to the opposite one, with concomitant changes in the remainder of the molecule.

With cyclopenta-1,3-diene, the unusual product **9** was obtained [30]. Its formation is rationalised on the basis of addition of one carbon to a C=C double bond, followed by ring-opening. It is not clear at what stage the second molecule of cyclopentadiene adds on, i.e. whether **1** catalyses the usual dimerisation of cyclopentadiene, which then adds to the C_2 ligand, or whether a second molecule of cyclopentadiene reacts with an intermediate formed from **5** and cyclopentadiene itself.

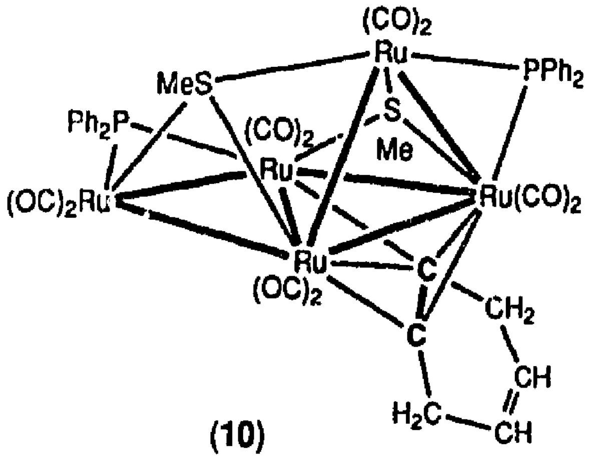
With buta-1,3-diene, cycloaddition to the C_2 ligand in **5** gives an unusual isomer of benzene, namely cyclohex-1-en-4-yne, which is stabilised by interaction with the cluster in **10** in the same way as alkynes do with other polynuclear systems [31]. Complex **4** obtained from **1** and buta-1,3-diene also contains this ligand.

3.3. *Alkynes*

In reactions with 1-alkynes, carbon–carbon bond formation is preferred over insertion into the C–H bond. Consequently, both terminal and non-terminal alkynes

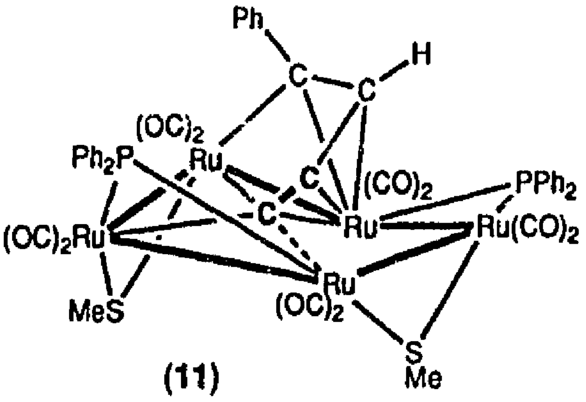


(9)



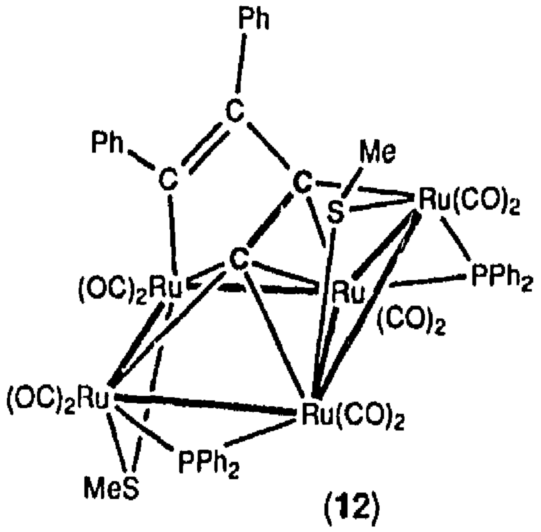
(10)

give similar complexes, although the structure of the final product is determined by the steric bulk of the substituents on the acetylenic carbons. Thus, HC≡CPh gave **11**, in which a double bond of the resulting C_4 ligand is coordinated to one of the Ru atoms, the cluster retaining the open pentagonal geometry of **5**. In contrast, a similar reaction with C_2Ph_2 gave **12**, in which the double bond does not coordinate and an extra Ru-Ru bond is formed in electronic compensation [32]. Complexes of these structural types are formed from a range of alkynes [31].



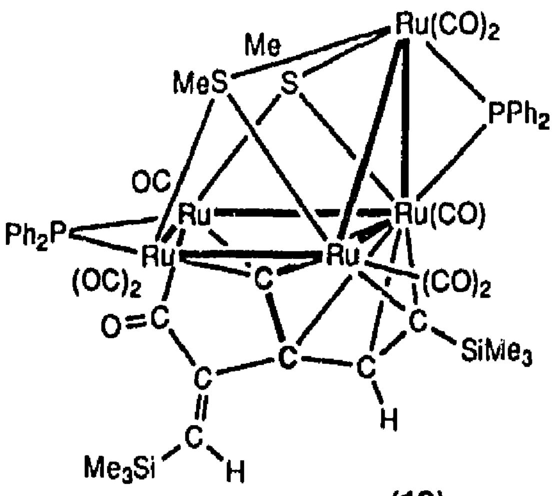
(11)

Other minor products have been isolated from these reactions or by subsequent carbonylation or thermal degradation [[illegible]]. Notable among these are **13**, in which CO has inserted into an Ru-C bond derived from the alkyne, **14**, in which an SMe group has migrated to the alkyne, and **15**, where both reactions have occurred. In several products, the presence of μ_3-SMe groups is in accord with the theoretical

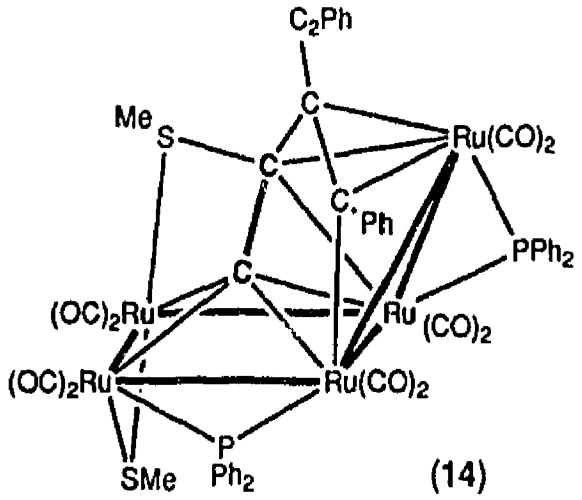


(12)

expectations outlined above: it seems that the μ_2 to μ_3 transformations may be reversible and thus generate "vacant" coordination sites for further reactions.

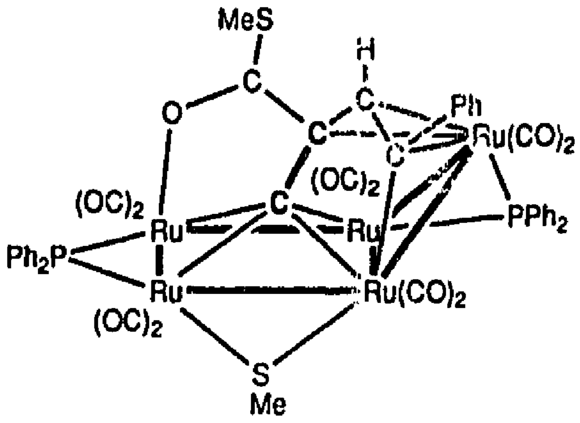


(13)

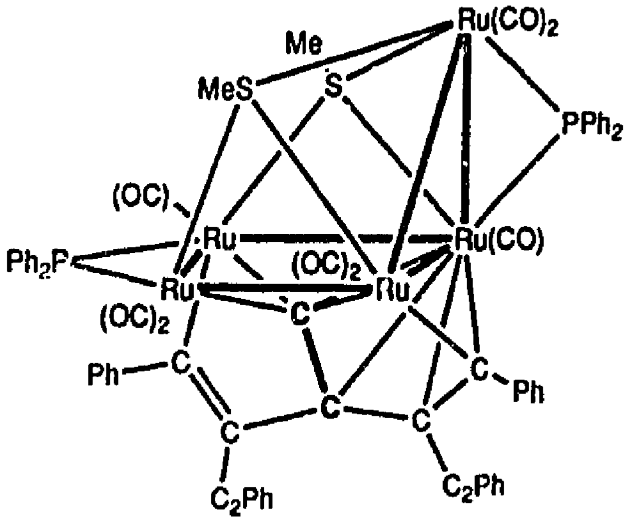


(14)

The question of multiple addition to one carbon of the C_2 fragment to give branched chain derivatives is of relevance to the postulated intermediacy of C_2 fragments in the chain lengthening process which must occur in Fischer–Tropsch chemistry. In the case of 1,4-diphenylbuta-1,3-diyne, the first-formed product has the structural type anticipated from the results described above. Addition of a second molecule of the diyne to the same carbon affords **16**, containing an unusual ten-carbon branched chain [31].



(15) $R^1 = H, R^2 = Ph$ or $SiMe_3$



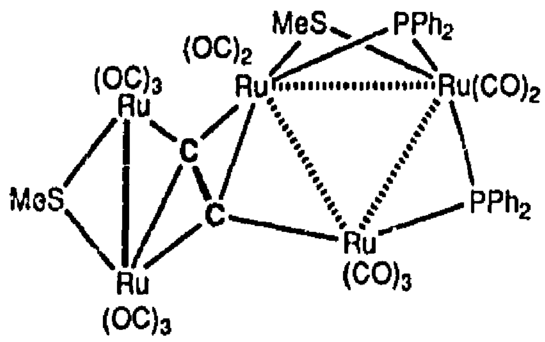
(16)

A notable structural feature of many of the products mentioned above is the close association of one of the carbons of the C_2 ligand with four of the five Ru atoms, resembling the square base of cluster carbides such as $Ru_5C(CO)_{15}$. The second carbon atom is the one which enters into the reactions with the various substrates to give ligands which others have considered to be alkylated alkylidynes [33].

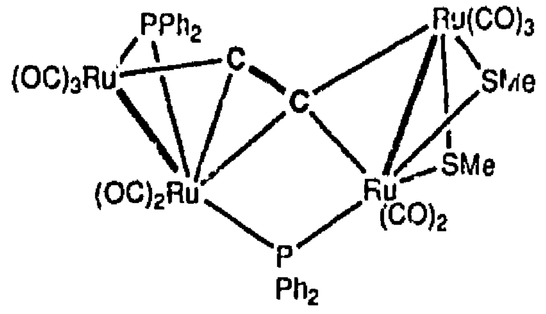
3.4. Reactions with CO and related ligands

The reaction between **5** and CO results in both addition to give another Ru_5 cluster (**17**) and excision of an $Ru(CO)_3$ fragment to give the Ru_4 derivative **18** [34]. In the former, fragmentation of the cluster gives Ru_2 and Ru_3 cores linked by the C_2 unit. The latter is electron-rich (50e) as often found with PPh_2-bridged systems [35,36] and this is manifested by elongation of the Ru–Ru bonds to ca. 3.1 Å. In the Ru_4 complex, only two Ru–Ru bonds are formally present; three tautomeric forms can be written and theoretical calculations suggest that it is the C_2 fragment which plays the predominant important role in holding the molecule together [34].

With $CNBu^t$, addition to the cluster results in expansion of the metal framework, which has the effect of pulling one of the carbon atoms down into the pentagon [37]. The resulting geometry (**19**) is of a planar tetraco-ordinate carbon atom, although the weak interaction with one of the Ru atoms suggests an alternative

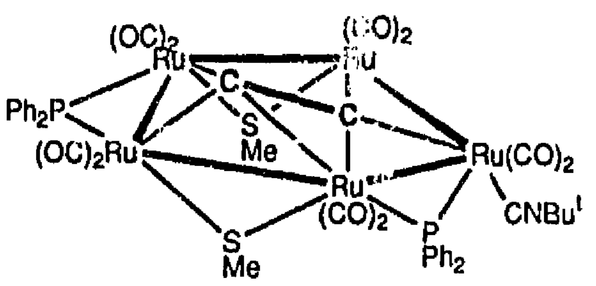


(17)



(18)

structure in which the C_2 unit behaves as a 4e donor. On heating, **19** loses CO to give a Bu^tNC derivative of **5**.

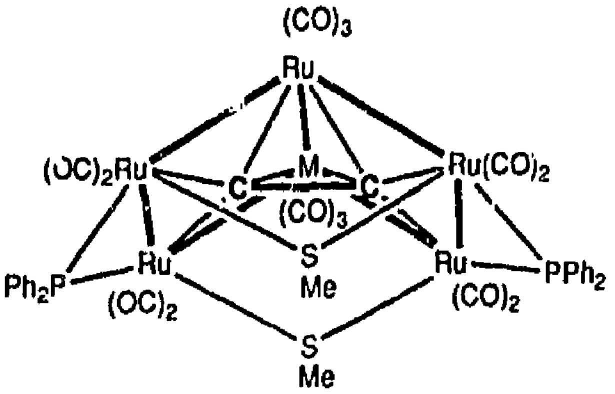


(19)

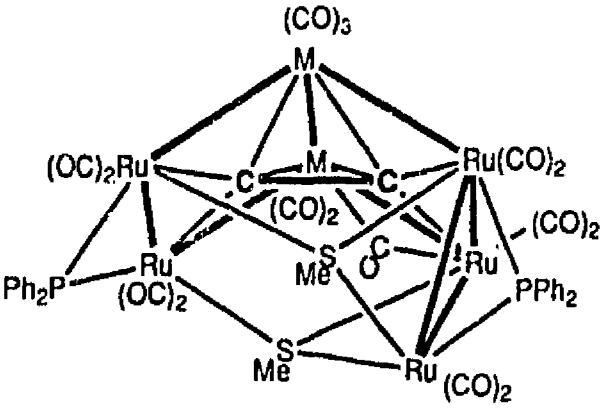
4. Higher nuclearity clusters from $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$

The chemistry of **5** is not limited to reactions with organic substrates. With metal carbonyls and related complexes, the formation of higher nuclearity clusters with novel geometries is found. Thus, with $Ru_3(CO)_{12}$, the hexa- and hepta-nuclear clusters **20** and **21** are formed. With $Fe_2(CO)_9$, the heterometallic clusters **22** and **23** with similar geometries are formed, although there is disorder in two of the metal atoms in **22** [31,38]. The latter reactions show that the extra metal atoms are incorporated into the original cluster, rather than being involved in simple bridging or capping reactions.

With $Co_2(CO)_8$, two complexes are obtained containing either two (**24**) or four Co atoms (**25**); in the latter, it can be seen that the carbon atoms can interact with a total of eight metal atoms, the resulting metal cores being related to the well-known metal carbido complexes typified by $Fe_5C(CO)_{15}$, but containing a further interaction between the two carbon atoms [31,38]. It is interesting that many

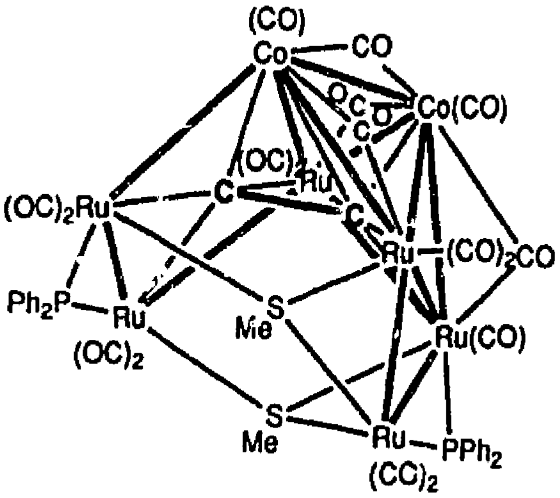


M = Ru (20), Fe (22)



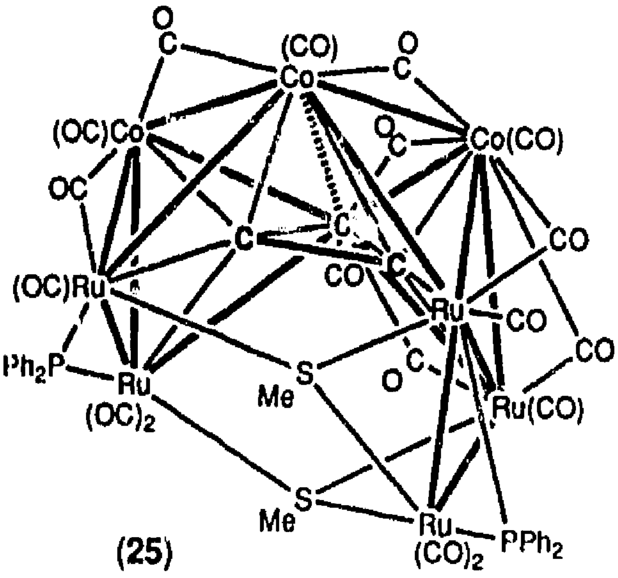
M = Ru (21), Fe (23)

attempts to induce the cluster carbides to enter into carbon–element bond forming reactions have been unsuccessful, although there seems to be no reason why the resulting complexes would not be stable.



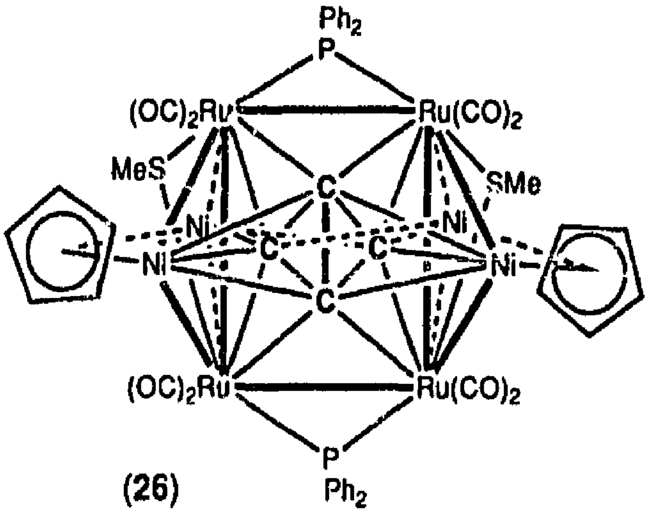
(24)

An unusual feature of one of the products (**26**) obtained from **5** and $NiCp_2$ is the disorder found in the positions of the Ni and C atoms only [31]. One interpretation is that the bonding arrays in the two isomers can be represented as shown in **26a** and **26b**. These isomers are related to the μ-η^1:η^1- and μ-η^2-bonding of alkynes found in binuclear metal complexes, the two forms reflecting differences between open (square: electron rich) and closed (tetrahedral: electron precise) C_2M_2 clusters.



(25)

The second product (27) has a structure related to those of the other complexes mentioned above.



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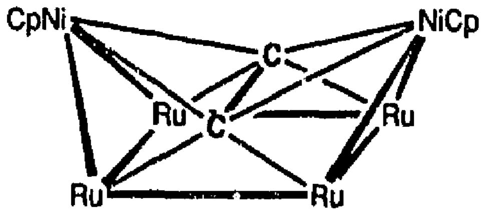
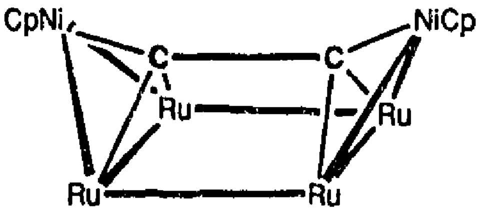
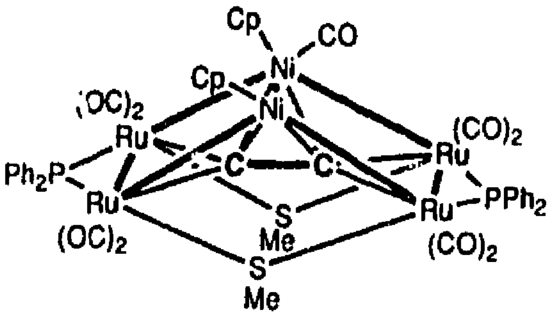


(26a)



(26b)

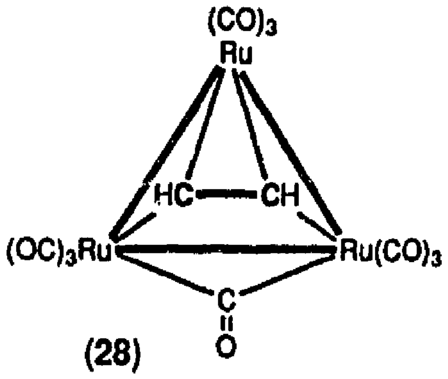
These complexes are formed by using the C_2 ligand to facilitate the build-up of the heterometallic cluster: some of the geometries are reminiscent of structures used to construct roofs of buildings. If this analogy is pursued, the C_2 unit can be seen to act as the "collar" of the resulting structure.



(27)

5. Complexes from ethyne

Another approach to complexes containing two-carbon fragments is from ethyne. We have studied the reactions of ethyne with activated ruthenium cluster carbonyls and in addition to novel trimers stabilised by the cluster framework, we have characterised a number of complexes of varying nuclearity which contain $C{\equiv}CH$, $HC{\equiv}CH$ or $:C{=}CH_2$ ligands [39]. In addition to the simple alkyne and hydrido-ethynyl complexes previously described by Italian workers [40], namely $Ru_3(\mu_3\text{-}C_2H_2)(\mu\text{-}CO)(CO)_9$ (**28**) and $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2H)(CO)_9$ (**29**), the reaction with $Ru_3(CO)_{10}(NCMe)_2$ affords the tetranuclear cluster $Ru_4(\mu_4\text{-}C_2H_2)(CO)_{12}$ (**30**), the pentanuclear vinylidene cluster $Ru_5(\mu_4\text{-}C{=}CH_2)(CO)_{15}$ (**31**) and the hexanuclear bis-vinylidene cluster $Ru_6(\mu_4\text{-}CCH_2)_2(CO)_{18}$ (**32**). Theoretical calculations have shown that the ready conversion of the alkyne to the hydrido-alkynyl (**28**→**29**) is facilitated by an orbital that allows easy migration of the H atom from carbon to the cluster at the same time as a CO ligand is lost.



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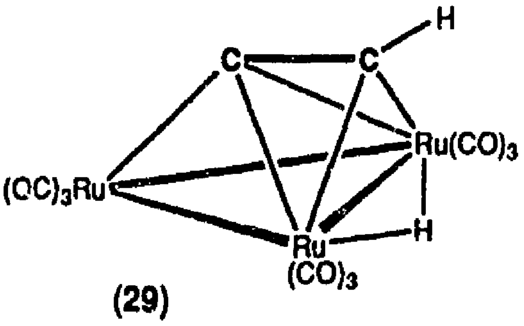
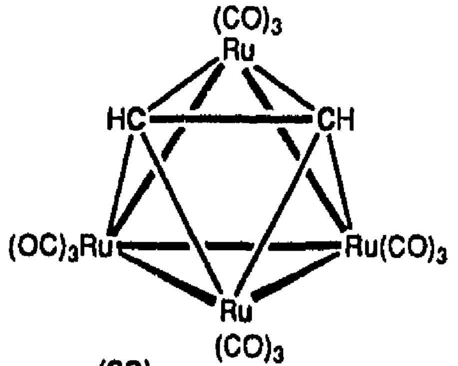


(29)

We were interested to examine the deprotonation of these systems. However, although loss of the cluster-bound proton is readily achieved by treatment with base, giving the anion $[Ru_3(\mu_3\text{-}C_2H)(CO)_9]^-$, we find that reaction with K-Selectride ($K[BHBu^s_3]$), which we have previously used as an efficient generator of anionic



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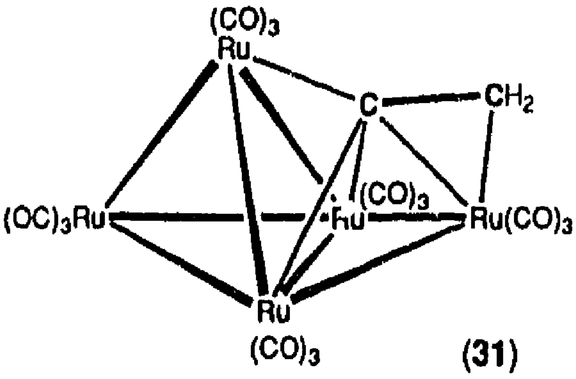

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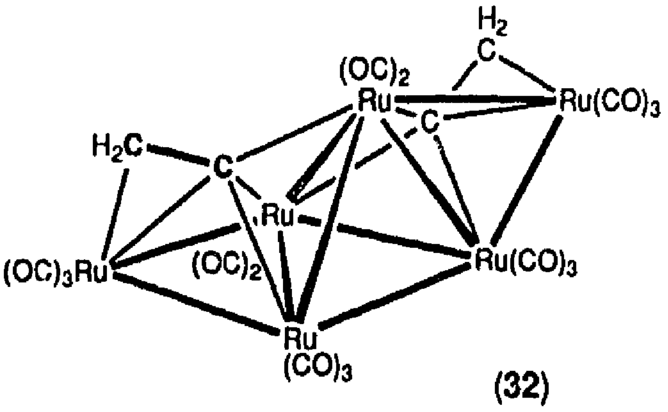


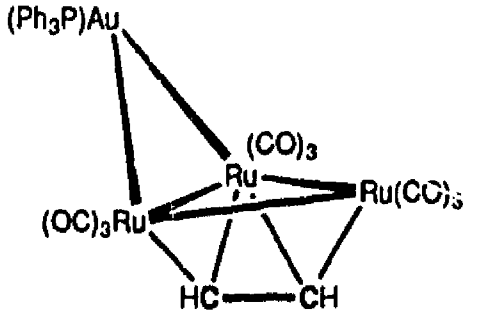
(32)

species from cluster hydrides, instead results in addition of hydride to the C_2 ligand to regenerate ethyne in the anion $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2H_2)(CO)_9]^-$. Derivatisation of this anion is achieved by treatment with $AuCl(PPh_3)$, which afforded $AuRu_3(\mu\text{-}H)(\mu_3\text{-}C_2H_2)(CO)_9$ (**33**), together with the digold vinylidene cluster $Au_2Ru_3(\mu_3\text{-}CCH_2)(CO)_9$ (**34**). Unusually, the former complex gives two types of crystals, one red, the other yellow. Structural studies show that the differences arise from different $AuRu_3$ cluster cores, either butterfly (in yellow **33a**) or tetrahedral (in red **33b**) [39]. These changes may be considered as a change in attachment of the $Au(PPh_3)$ group from μ_2 to μ_3, and are similar to the isomers of $AuRu_5C(CO)_{13}(NO)(PEt_3)$ [41].

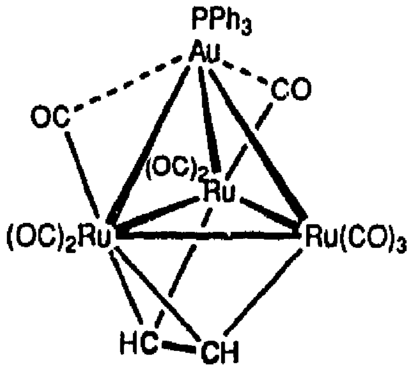
6. Complexes containing C_4 ligands

6.1. C_4 complexes from $PPh_2C{\equiv}CC{\equiv}CPPh_2$

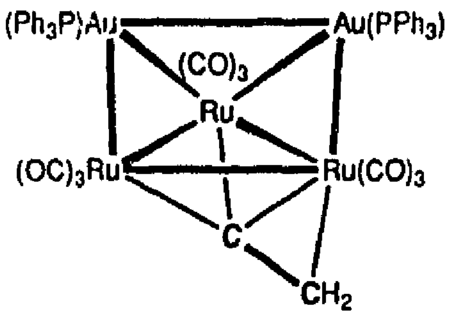
Extension of the approach used to generate **5** to complexes containing the ligand $Ph_2PC{\equiv}CC{\equiv}CPPh_2$ resulted in much more facile cleavage of both P–C(sp) bonds,



(33a) yellow



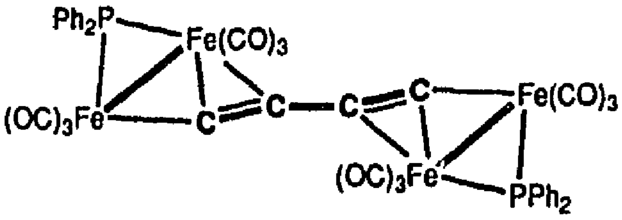
(33b) red



(34)

simple heating in an inert solvent being sufficient to afford complexes containing C_4 ligands. In this way the iron (**35**) and ruthenium complexes (**36**) were obtained [42]. The chemistry of these seems to be that of two acetylide complexes joined by a shortened C–C single bond [1.371(8) Å (Fe), 1.417(8) Å (Ru)], each unit apparently acting independently and there being no cooperative bonding or tendency to engage all four carbon atoms in bonding to a suitably sized cluster. A related system is found in the anion $[\{Fe_3(CO)_9\}_2(\mu_3,\mu_3\text{-}C_4)]^{2-}$, which was obtained from $[Fe_3(\mu_3\text{-}CCO)(CO)_9]^-$ and triflic anhydride [43].

However, reaction of **36** with H_2 has afforded an Ru_5 derivative (**37**), while



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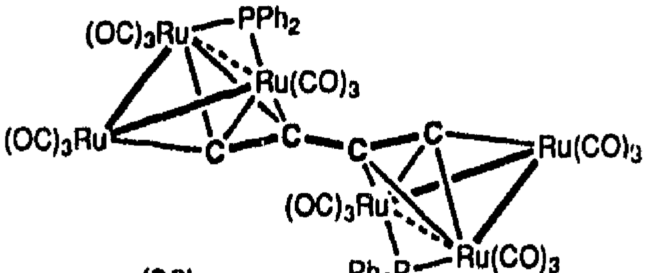
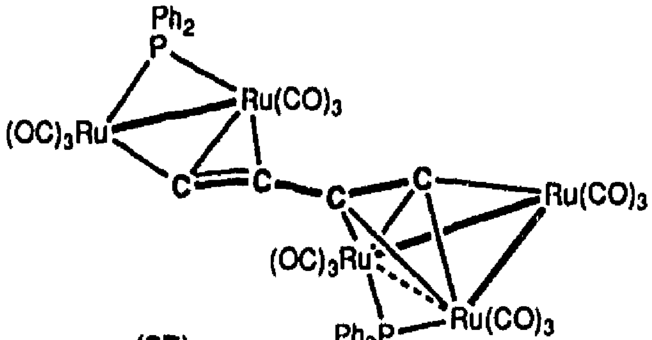


(36)

sequential treatment with H^-/H^+ (electronically equivalent to the addition of H_2) afforded a novel example of the bis-vinylidene ligand :C=CHCH=C: in **38** [31]. These products are different from those expected on the basis of chemistry directly related to that of a simple μ_3-alkynyl derivative, but resolution of this anomaly awaits further study.



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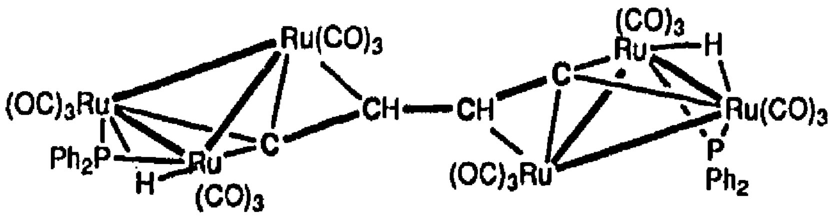


(38)

6.2. Diynyl and diyndiyl complexes from buta-1,3-diyne

The first complex containing a bridging C_4 ligand was described back in 1957 [44], while more detailed studies were reported by Hagihara and coworkers in the 1970s [45]. Since that time, sporadic investigations have been reported by several groups, usually as a result of extension of alkyne reactions to diynes. This chemistry is the subject of a review [46] and will not be considered further here.

Recently, we have found that reactions of buta-1,3-diyne with transition metal halides in the presence of a tertiary amine affords good yields of the diynyl complexes **39** [47]. These reactions can be extended to cover metals of groups 6–10 and the complexes are generally obtained in good to excellent yields. The acetylenic proton can be readily replaced by a variety of other groups. In the context of this account, we note that a second application of this synthetic route to complexes **39** allows the syntheses of complexes **40** containing the same or different metal–ligand combinations linked by the C_4 unit.

Further reactions of these and related complexes enable the complexation of the

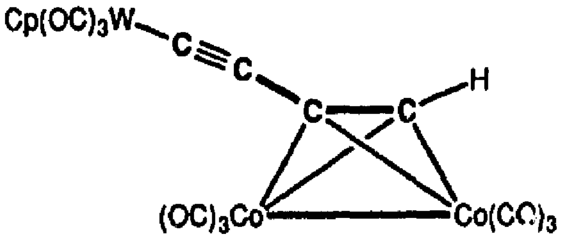
$Cp(CO)_nM{-}C{\equiv}C{-}C{\equiv}C{-}H$

(**39**) M = Mo, W, n = 3; M = Fe, n = 2

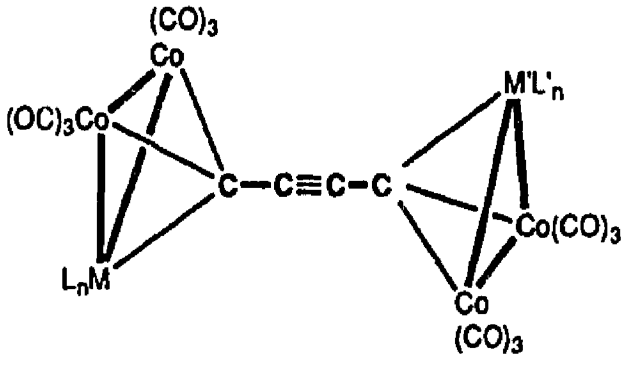
$Cp(CO)_3W{-}C{\equiv}C{-}C{\equiv}C{-}M(CO)_nCp$

(**40**) M = Mo, W, n = 3; M = Fe, n = 2

C≡C triple bond to ynophilic fragments such as $Co_2(CO)_6$ or $\{Mo(CO)_2Cp\}_2$ [see **41**]. Where there is a choice, the Co_2 fragment is found attached to the least sterically hindered C≡C triple bond [48]. When the Mo_2, W_2 or MoW complexes are used, incorporation of the terminal C atoms into a trimetal cluster occurs with concomitant electronic rearrangement along the C_4 chain [see **42a–c**]. No doubt this is the result of the extra bulk of the $M(CO)_3Cp$ groups [48]. An example of the latter arrangement was previously described in the complex $\{Co_3(CO)_9(\mu_3\text{-}C)\}_2(C{\equiv}C)$ (**43**) [49] and the replacement of $Co(CO)_3$ units by isolobal metal–ligand fragments, such as $M(CO)_3Cp$, is also known [50].



(**41**)



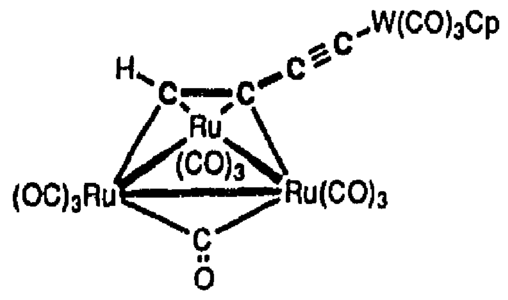
(**42a**) $ML_n = M'L'_n = Mo(CO)_3Cp$

(**42b**) $ML_n = M'L'_n = W(CO)_3Cp$

(**42c**) $ML_n = Mo(CO)_3Cp$, $M'L'_n = W(CO)_3Cp$

(**43**) $ML_n = M'L'_n = Co(CO)_3$

The 1-alkyne character of **39-W** is also reflected in its reactions with ruthenium carbonyl clusters. Under mild conditions, reaction of $Ru_3(CO)_{10}(NCMe)_2$ gave the μ_3-alkyne complex **44**, which on gentle heating is smoothly converted to **45** by migration of the H atom from the acetylenic carbon to the Ru_3 cluster [39]. This can be considered to be another example of a C_4 complex in which the all-carbon ligand is σ-bonded to the W atom and σ, π-bonded to the cluster. A similar product (**46**) was obtained from $Ru_3(\mu\text{-dppm})(CO)_{10}$; this cluster is unusual in existing as isomers (shown) which differ in respect of the relative orientations of the μ-dppm and C_4W ligands.



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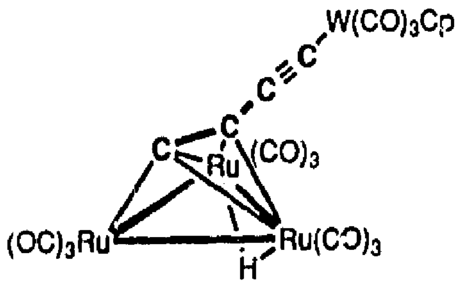

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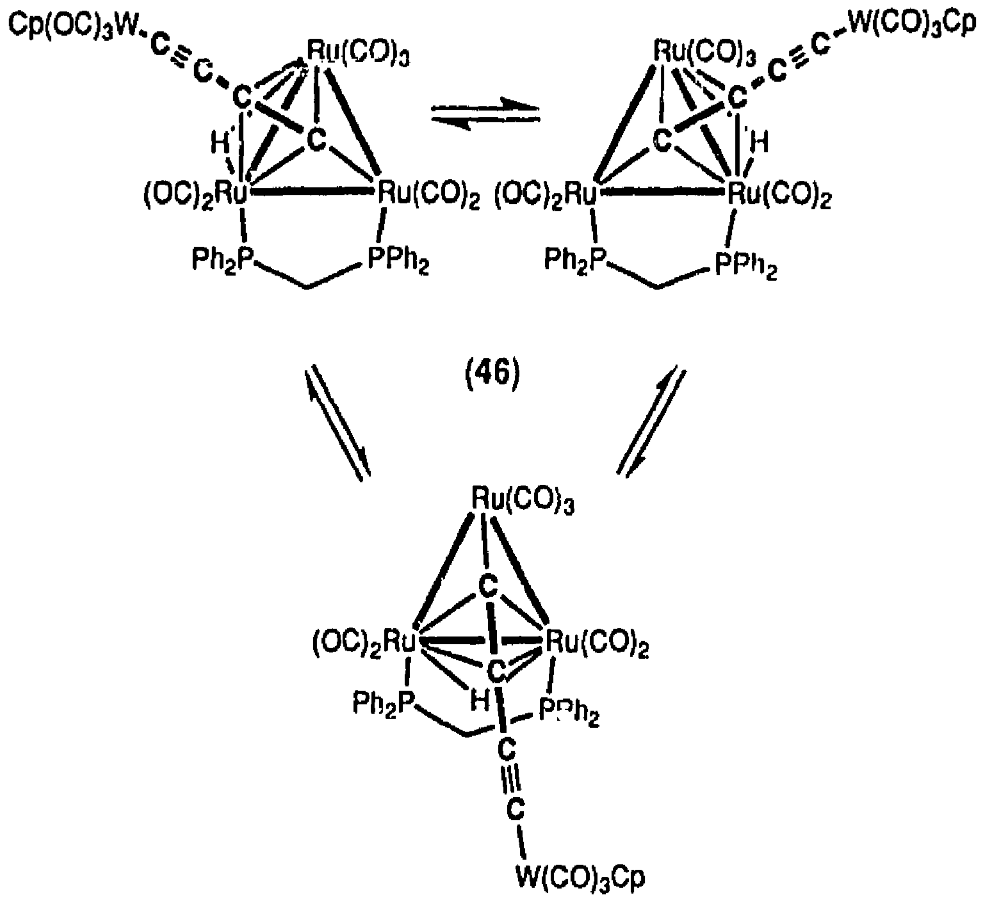
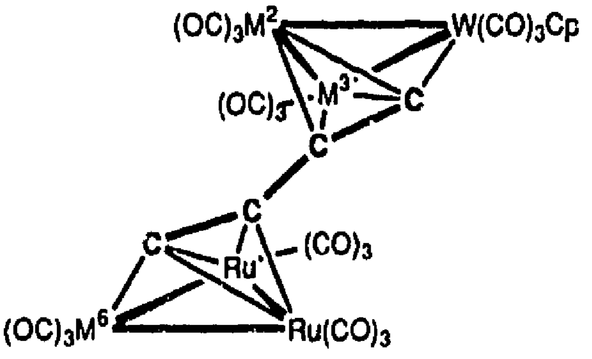


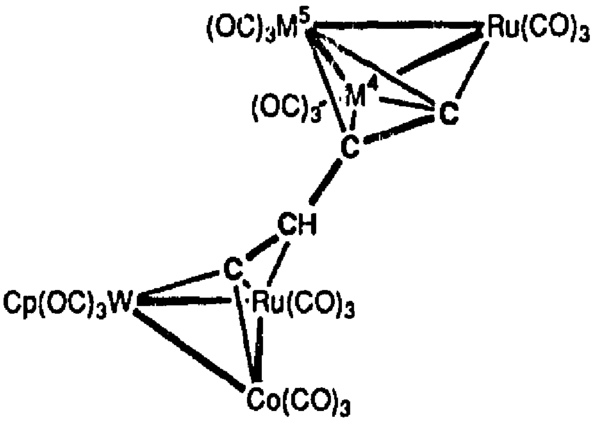
(46)

Complex **44** reacts with ynophilic reagents to form novel heterometallic clusters incorporating the entering metal atom(s) in the two M_3 clusters which are coordinated to the C_4 ligand. Thus, with $Fe_2(CO)_9$, addition of one iron atom (found disordered over three sites) gives **47**; while reaction with $Ru_3(CO)_{12}$ gives the analogous Ru_5W complex **48**. With $Co_2(CO)_8$, two Co atoms are similarly incorporated in **49**, but in this case, the cluster-bound H atom migrates to the C_4 chain to give a μ_3,μ_3-(:C=CHC≡C) ligand [39].



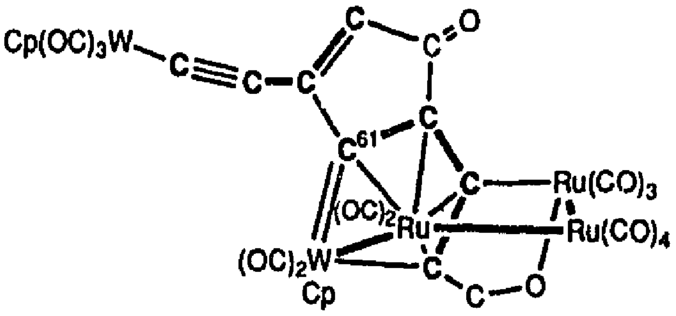
(47) M^2 Fe/Ru = 0.52/0.48
M^3 0.14/0.86
M^6 0.31/0.69

(48) $M^2 = M^3 = M^6 =$ Ru



(49) M^4 Co/Ru = 0.86/0.14
M^5 0.14/0.86

Further reactions of **44** with an excess of **39-W** gives the unusual complex **50** [51]. This contains an open Ru_3W array which supports an organometallic ligand formed by addition of the second molecule of **39-W** and concomitant incorporation of two CO molecules. Detailed investigation of the structure shows that the W–C(61) separation is rather short and consistent with a carbenic interaction, as also suggested by the electron count. Compared with other ruthenium cluster complexes containing alkynes, this reaction is also unusual in that it is the non-complexed C≡C triple bond which is involved in the ligand-forming reaction.



(50)

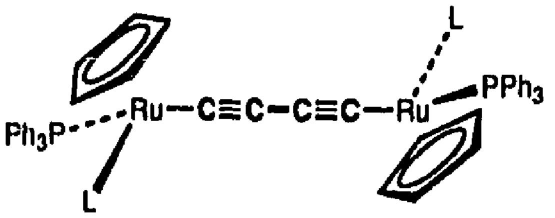
6.3. Electrochemistry of the M_2C_4 system

The electronic properties of the C_4 chain are interesting. Formally, at least, three arrangements can be envisaged:

$$\underset{\mathbf{D}}{M{-}C{\equiv}C{-}C{\equiv}C{-}M} \qquad \underset{\mathbf{E}}{M{=}C{=}C{=}C{=}C{=}M} \qquad \underset{\mathbf{F}}{M{\equiv}C{-}C{\equiv}C{-}C{\equiv}M}$$

which represent a progressive oxidation of the M_2C_4 chain. These systems have obvious similarities to those found for M_2C_2 units (**A**, **B** and **C**, above). Indeed, both Gladysz [52] and Lapinte [53] have described the one- and two-electron oxidations of C_4-linked metal ligand systems which have been explained in terms of oxidations of **D** to **E** via a radical intermediate. In the case of the iron complex, the Mössbauer data are not in agreement with this interpretation but favour oxidation of the metal centres. In contrast, the bis-rhenium complexes are converted into a cumulenic system on oxidation, as shown by an X-ray structural determination.

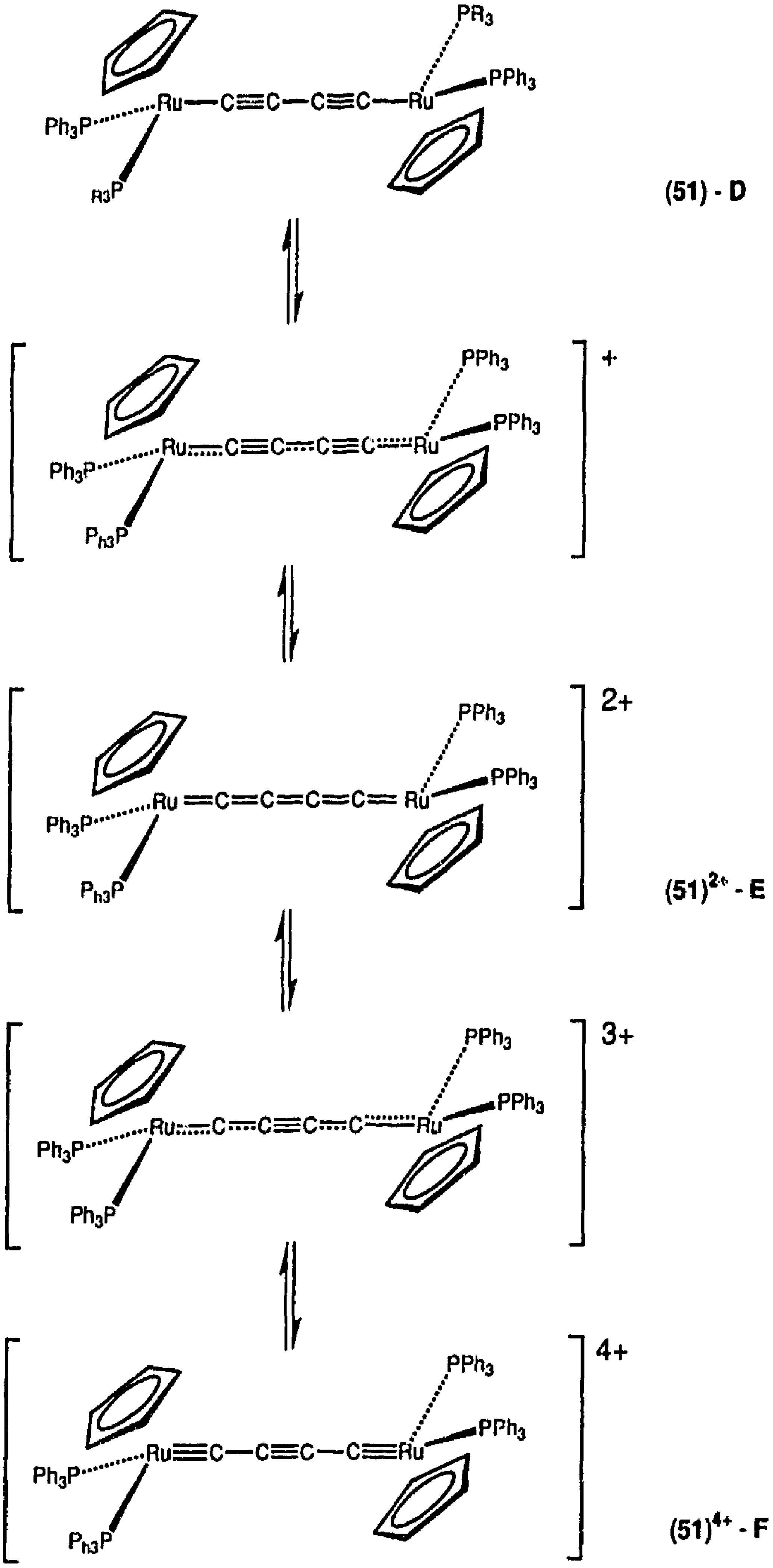
The complex $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_4)$ (**51**) was first reported as a product of reactions between $[Ru(NCMe)(PPh_3)_2Cp]^+$ and Li_2C_4 [54]. This complex is remarkable in that X-ray structure determinations revealed that the compound crystallises in at least two rotameric forms. While in solution, only one form (cisoid) appears to be present, heating of a solution in tetrahydrofuran and rapid crystallisation gives the transoid isomer [55].



L = PPh_3 (**51**); PMe_3 (**52**)

More importantly, we considered that the relative ease of oxidation of organoruthenium systems to the +4 oxidation state might provide the opportunity to obtain more highly oxidised forms of **51**, although we also favoured the electronic structure involving not only the two metal atoms, but also the unsaturated carbon chain. Electrochemical studies revealed that reversible oxidation to the +3 state occurred, which was followed by a partially irreversible oxidation to the +4 cation [56]. This has been interpreted as showing a series of oxidations of the RuC_4Ru chain from neutral **D** through dicationic **E** to tetracationic **F**, with odd-electron intermediates whose valence bond representations necessarily involve several tautomeric forms (Scheme 1). Theoretical calculations show that the two HOMOs are considerably separated from lower energy orbitals and that they involve the six atoms Ru_2C_4; oxidation involves loss of electrons from these orbitals, i.e. the cations are not metal-centred. Differences from the related iron system are at present unexplained. Not surprisingly, the mixed complex **52**, in which one of the PPh_3 ligands has been replaced by PMe_3, behaves similarly, although it is oxidised more easily.

Spectroelectrochemical studies (with Stephen Best in Melbourne and Graham


PR3
PPh3
Ph3P
Ru
C≡C—C≡C
Ru
R3P
(51) - D
PPh3
PPh3
Ph3P
Ph3P
+
2+
(51)2+ - E
3+
4+
(51)4+ - F

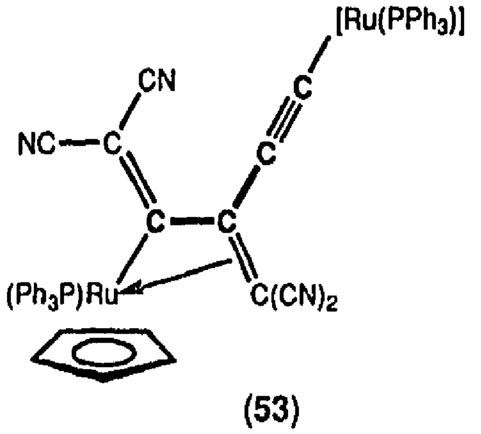
Scheme 1.

Heath in Canberra) have given useful structural information, supporting the assignment of structures to the C_4 chain as indicated in structures **D**, **E** and **F** [57].

While the electrochemistry revealed the accessibilty of an unprecedented five oxidation states for this system, the synthesis and isolation of each of these presents a challenge which has only been met so far in the cases of the neutral complex and the +1 and +2 cations. The latter are obtained by Ag^+ oxidation of the neutral complex (orange), which gives the green monocation and deep blue dication. The trications can be generated electrolytically at −50 °C, at which temperature they are stable for several hours. Unfortunately, no crystals suitable for a structural investigation of the MC_4M systems in these cations have yet been obtained [58].

6.4. Reaction of tetracyanoethene with $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_4)$ *(51)*

The reactivity of **51** has been little explored: approach to the bridging carbon atoms is hindered by the PPh_3 groups. However, the reaction of tetracyanoethene with **51** affords red **53**, a reaction rationalised by initial [2+2]-cycloaddition of the electron-deficient olefin to one of the C≡C triple bonds. The resulting cyclobutenyl underwent ring-opening followed by intramolecular displacement of a PPh_3 ligand to give the enyl complex. Similar chemistry has been described earlier for monoacetylide complexes [59]. In solution, **53** exists in equilibrium with the unusual yellow tetranuclear complex **54**, in which a CN group from one molecule of **53** displaces the coordinated C=C double bond in a second molecule, forming the ten-membered cyclic system shown [55].



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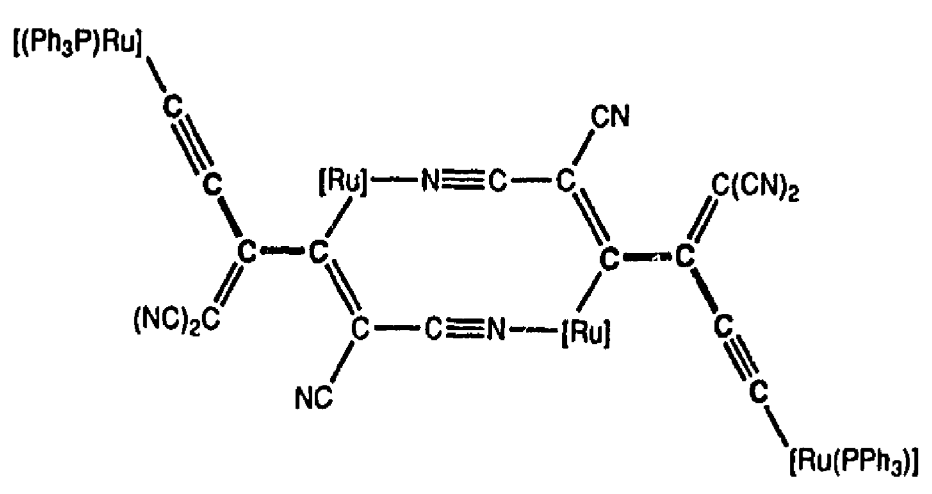


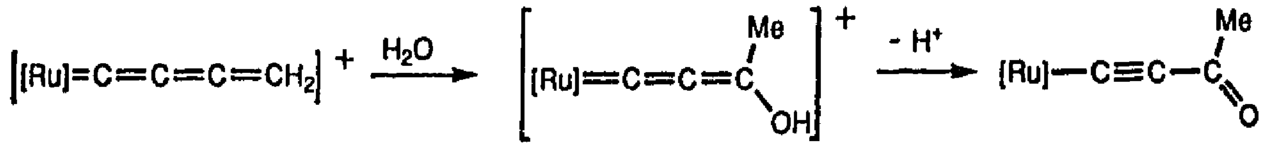
(54) [Ru] = Ru(PPh$_3$)Cp

7. Butatrienylidenes

7.1. Mononuclear complexes

By analogy with 1-alkynes, coordination of buta-1,3-diyne to a transition metal centre would be expected to result in a 1,2-H shift to give the ethynylvinylidene ligand, :C=CHC≡CH. However, a 1,4-H shift is also possible, to give the butatrienylidene ligand, :C=C=C=CH_2. Both molecules have almost the same stability, by ab initio calculations [60]. Direct reactions between $[Ru(thf)(PPh_3)_2Cp]^+$ and buta-1,3-diyne have given a cationic species, which from its reactions is thought to be the butatrienylidene cation **55** [61].

Deprotonation of the cation results in formation of a diynyl complex, whose extreme reactivity contrasts with that found for the complexes described above. In air, almost immediate conversion to the acetylethynyl complex **56** is found, although this probably proceeds by reaction with traces of water [54].



(55) (56)

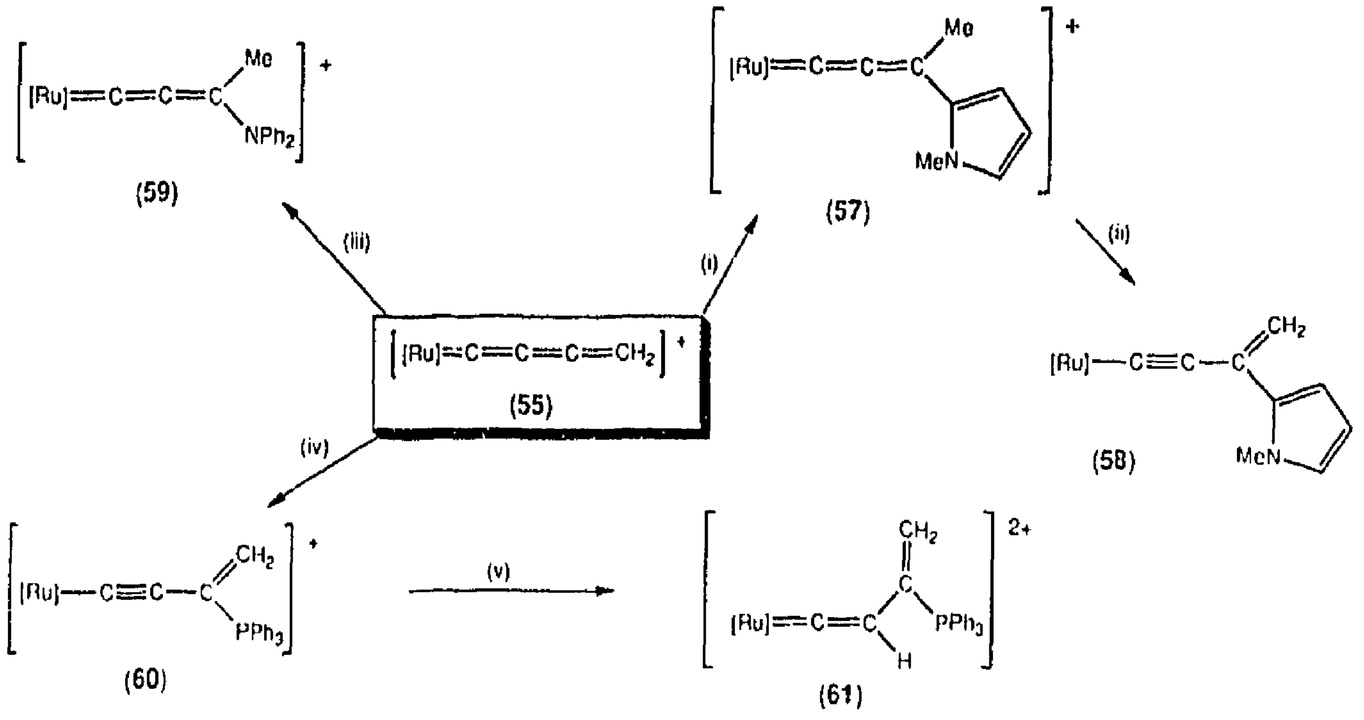
[Ru] = $Ru(PPh_3)_2Cp$

Addition of other nucleophiles to **55** has given a variety of products (Scheme 2) involving formation of new C-element bonds. Thus, the reaction of *N*-methylpyrrole gives **57**, formed by attack on the heterocyclic nucleus, with migration of the proton to the CH_2 group. In turn, deprotonation of **57** with butyllithium gave **58**. Similar behaviour is found with other nucleophiles containing reactive H atoms, such as $NHPh_2$, which gives **59**. Aprotic nucleophiles, such as PPh_3, also add to C_γ to give **60**, which can be further protonated to the dication **61**.

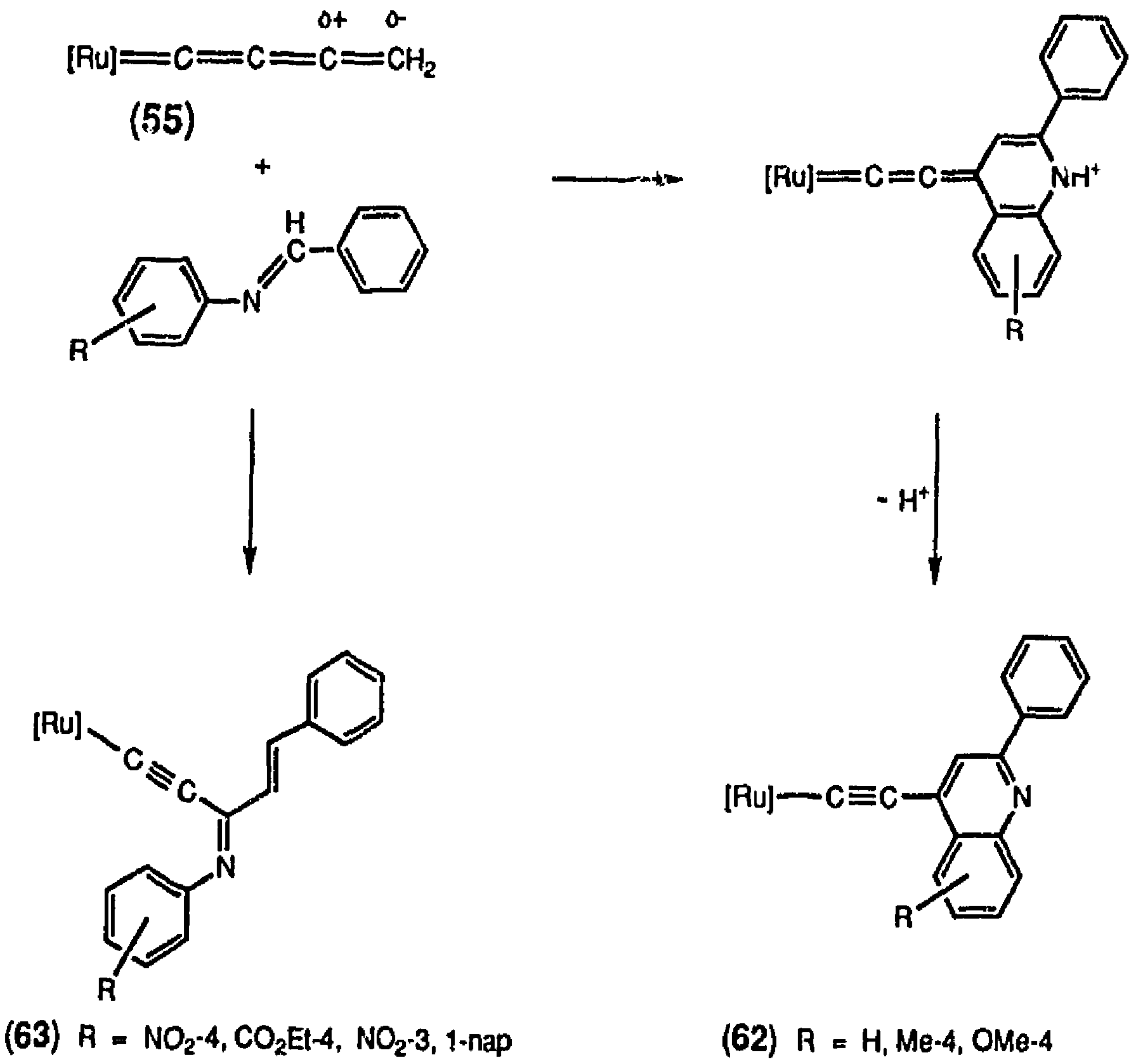
This behaviour bears out theoretical studies of the reactivity of the carbons in this and related unsaturated carbenes, which are expected to be alternately electron-poor and electron-rich as one moves out from the metal centre. In the case of acetylides, this has been amply demonstrated by the highly nucleophilic nature of C_β, which is readily attacked by electrophiles such as H^+, R^+, ArN_2^+ etc. [7].

In the case of the butatrienylidene, we were intrigued to find that cycloaddition occurred to suitable 1,3-dipolar molecules with the formation of cyclic systems. Thus, in the reaction with aryl imines, initial electrophilic attack on C_δ (by the =CHAr group) is followed by C–C bond formation between C_γ and the N-bonded aromatic ring, to give a novel synthesis of substituted quinolines **62** (Scheme 3) [62]. The two H atoms required to be lost for aromatisation to occur are taken up by a second molecule of the imine to give an equivalent of the corresponding benzylamine.

Exploring the scope of this reaction further, we found that the presence of electron-withdrawing substituents on the *N*-aryl group resulted in the reaction taking a different course, namely a formal [2+2]-cycloaddition of the imine to the C_γ=C_δ double bond, followed by ring-opening, to give the enamine complexes **63** [62].



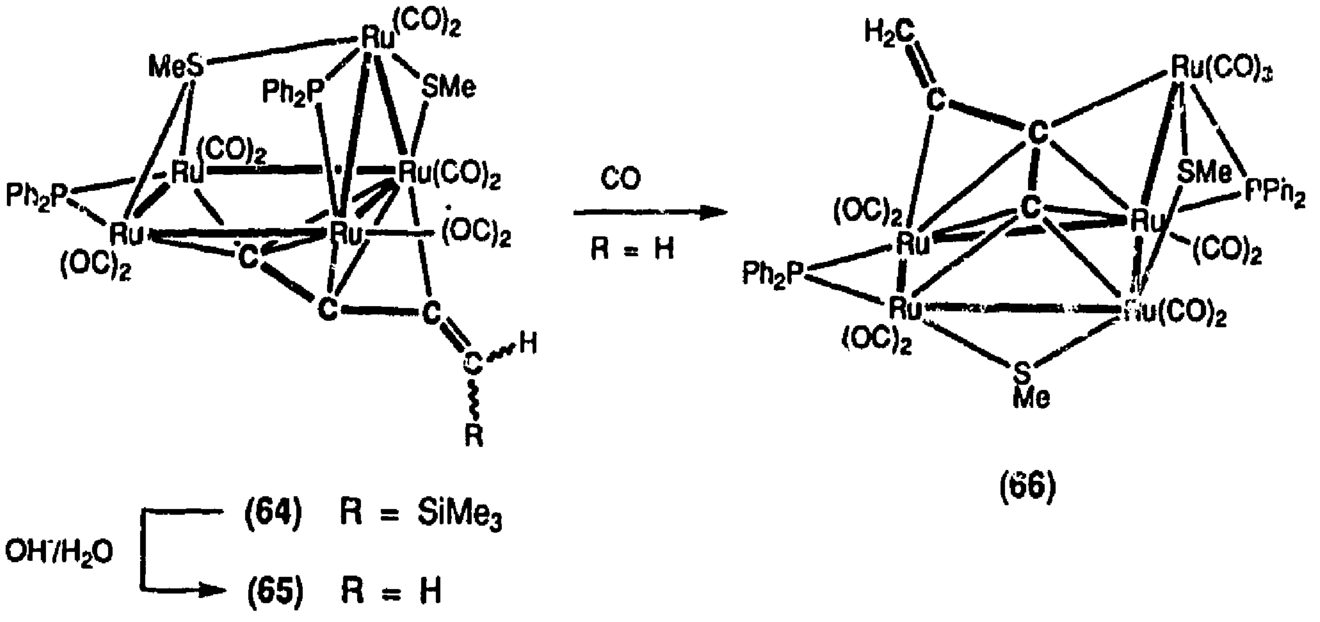
Scheme 2. [Ru] = Ru(PPh$_3$)$_2$Cp. *Reagents*: (i) N-mthylpyrrole; (ii) LiBu; (iii) NHPh$_2$; (iv) PPh$_3$; (v) H$^+$.



Scheme 3.

7.2. *A cluster-bound butatrienylidene*

We have also been able to make the first structurally characterised complexes containing butatrienylidene. These were formed from cluster **5** and $C_2(SiMe_3)_2$, via a desilylation which occurred during the reaction. The resulting complex **64** is obtained as two geometrical isomers, which have similar IR ν(CO) spectra to that of the crystallographically characterised parent compound (**65**) obtained by a further, designed (rather than fortuitous!) desilylation. Carbonylation results in a rearrangement to give a spiked-rectangular cluster (**66**) now containing two μ-SMe groups with the butatrienylidene interacting with all five Ru atoms [63]. We surmise that formation of the trienylidene ligand occurs by coupling of the C_2 ligand in **5** with the partially desilylated vinylidene [:C=CH(SiMe$_3$)] formed during the reaction.



8. C_8 complexes

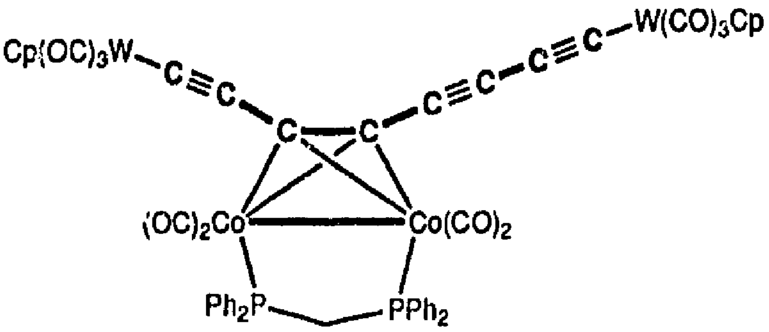
As found for the rhenium complexes of Gladysz [52] and the iron systems of Lapinte [64], oxidative coupling of the diyne in **39-Mo** or **39-W** affords good yields of the stable C_8 complexes **67-Mo$_2$** and **67-W$_2$**, respectively [56]. Interestingly, oxidation of a stoichiometric mixture of **39-Mo** and **39-W** affords the mixed complex **67-MoW** in over 80% yield, neither of the homonuclear complexes being detected. These compounds have been characterised by appropriate ^{13}C resonances for the carbons of the C_8 chain, which are found between δ 30–115. The C≡C groups are reactive towards $Co_2(CO)_6$(μ-dppm), complexation occurring at the least hindered C≡C triple bond, i.e. the second one out from the metal, to give **68**.

9. Prognosis

It is evident from these few results that all-carbon molecules complexed to metal–ligand fragments have an extensive and exciting chemistry. Much more work needs

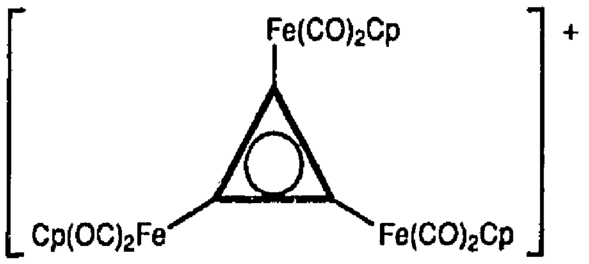
$Cp(OC)_3M—C{\equiv}C—C{\equiv}C—C{\equiv}C—C{\equiv}C—M'(CO)_3Cp$

(67) M = M' = Mo, W; M = Mo, M = W



(68)

to be done, for we have only just scratched the surface of this area. In future work, we shall be trying to obtain complexes containing these ligands in further differing modes of attachment, for these in turn will exhibit differing modes of reactivity. A persistent challenge is the synthesis of odd-carbon ligands, which while available in principle by established reactions, remain elusive. That success can be achieved is shown by the dirhenium complex $\{Re(NO)(PPh_3)Cp^*\}_2(\mu\text{-}C_3)$ of Gladysz, which readily takes up a third metal atom [65], and the molybdenum and tungsten complexes of Templeton [66]; success depends on a suitable choice of supporting ligands. An alternative approach to a cyclic C_3 complex is that of Selegue, who has made the tri-iron complex **69** by displacement of chloride from the trichlorocyclopropenium cation [67]. A cumulenic five-carbon chain is found in $[\{Mn(CO)_2(\eta\text{-}C_5Cl_5)\}(\mu\text{-}C{=}C{=}C{=}C{=}C)\{Re(NO)(PPh_3)Cp^*\}][BF_4]$ [68].

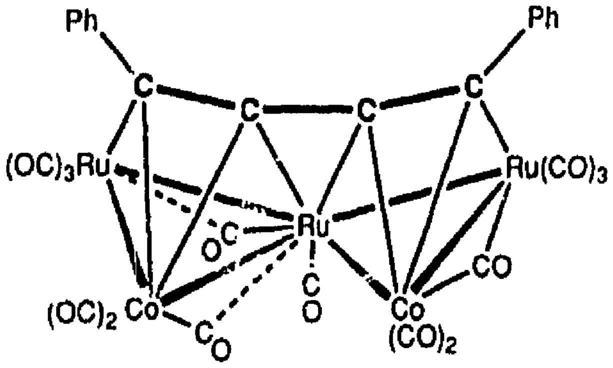


(69)

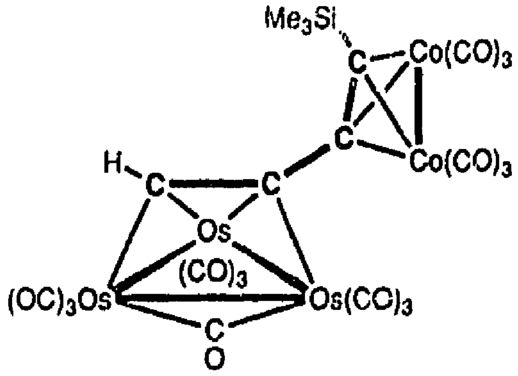
We note that at least four metal atoms seem to be necessary to fully coordinate a C_4 chain. The five-atom cluster **70** has been obtained from the reaction of $Co_2(CO)_8$ with $Ru_3(\mu_3\text{-}PhC_2C{\equiv}CPh)(CO)_{10}$ [69]; it is interesting that a related Os_3 cluster forms only the complex **71**, the third-row metal framework resisting the incorporation of the Co atoms [70].

Acknowledgements

The results summarised in this article were obtained over the last five years or so, largely from the fine and devoted work of Drs. Chris Adams and Natasha Zaitseva, and of Paul Low for his doctoral thesis. The structural work, without which signifi-



(70)



(71)

cant progress in this area is impossible, was carried out by Allan White and Brian Skelton in Perth. More recently, theoretical calculations on some of these complexes have been carried out by Jean-Francois Halet and Gilles Frapper in Rennes, France. The work has been supported by the Australian Research Council and a generous loan of platinum metal compounds from Johnson Matthey Technology plc.

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