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Vinylidene complexes in organic synthesis*

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Abstract

Application of vinylidene complexes in organic synthesis is discussed. Mechanism of formation from η^2 alkyne complexes of transition metals, preparation from η^2 alkyne, acetylide, carbene, carbyne or acyl complexes as well as the structure of the vinylidene complexes are outlined. Reactions of vinylidene complexes with electrophiles and nucleophiles are also detailed. In addition, catalytic reactions involving transition metal complexes for the synthesis of a variety of organic compounds and polymers from acetylenic compounds which invoke an *in situ* formation of vinylidene intermediates are discussed in detail.

Key words: η^2-alkyne–vinylidene rearrangement, vinylidene complexes.

1. Introduction

The term vinylidene describes the first member of the homologous series of unsaturated carbenic species of the generic formula C_nH_2. The parent vinylidene, C_2H_2, has never been isolated as it undergoes an extremely rapid 1,2-hydrogen shift to give acetylene (eqn 1).

(1)

However, it has been shown that it is possible to stabilise vinylidene as ligands in transition metal complexes. Some chemical transformations which relate vinylidene to other monohapto ligands are shown in Scheme 1[1].

Stepwise reduction of an ethynyl iron complex to a neopentylidene unit has been reported and here it was concluded by ^{1}H-NMR studies that a vinylidene complex is an intermediate (Scheme 2)[2]. A series of cationic vinylidene complexes have been isolated containing the 'CpFeL$_2$' fragment (Fig. 1)[1]. A few examples of mono, bi, tri and tetra nuclear metal complexes[3–7] are shown in Fig. 2 and review articles are available in literature detailing their synthesis and structure[8–10].

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* Dedicated to Prof. C. N. R. Rao on the occasion of his sixtieth birthday.

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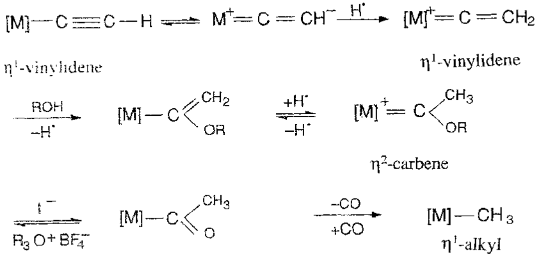
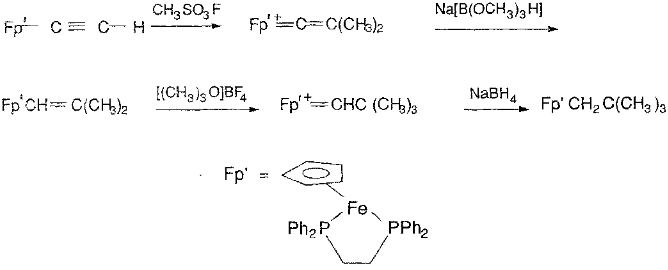


SCHEME 1. Placing vinylidene ligand with other monohapto-carbonic ligands.

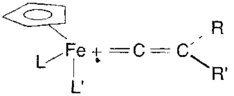


SCHEME 2. Conversion of ethynyl iron to a neopentylidene iron complex *via* a vinylidene complex.

Several reactions of organometallic reagents may also contain intermediacy of vinylidene complexes. Such reactions have proved to be highly useful in the synthesis of organic compounds which otherwise require many cumbersome steps, as shall be shown later. In this paper, the mechanism of vinylidene rearrangement, a few preparative methods, the structure and several reactions of the vinylidene complexes will be discussed. For the sake of brevity, we restrict ourselves to the chemistry of mononuclear M–C vinylidene complexes, as comprehensive literature is available for heterovinylidenes[11].

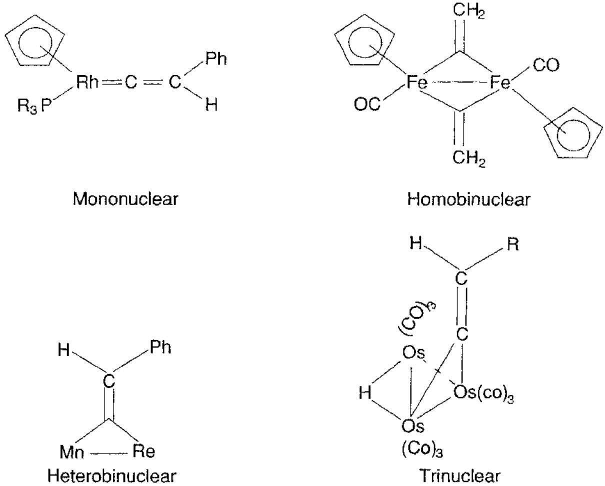
2. Isomerisation of 1-alkynes to vinylidenes on metal templates

Terminal alkynes isomerise to the corresponding vinylidene *via* two possible mechanistic pathways. In the first case, a stepwise process, 1-alkyne undergoes an oxidative addition at the metal centre (before or after π-coordination) to give a hydrido-alkynyl complex. This can



a: L,L' = dppe; R,R'=CH_3, X=SO_3F
b: L,L' = dppe; R=CH_3, R'=H; X=PF_6
c: L,L' = dppe; R,R'=H, X=PF_6

FIG. 1 Some cationic $CpFeL_2$ (vinylidene) complexes.



Mononuclear

Homobinuclear

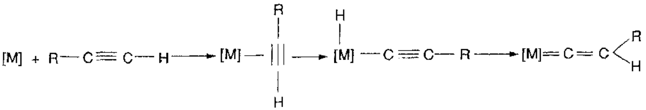
Heterobinuclear

Trinuclear

[Mn] = Mn $(CO)_2$ (η^5-C_5H_5)
[Re] = Re $(CO)_2$ (η^5-C_5H_5)s

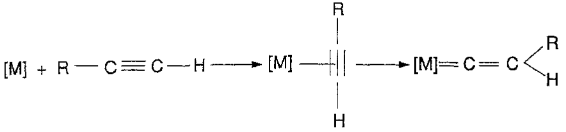
FIG 2. Some examples of mono to multi nuclear complexes with vinylidene ligands.

further rearrange to the vinylidene *via* a 1,3 hydrogen shift from the metal to C_β (eqn 2).



$$[M] + R{-}C{\equiv}C{-}H \longrightarrow [M]{-}\overset{R}{\underset{H}{|||}} \longrightarrow \overset{H}{[M]}{-}C{\equiv}C{-}R \longrightarrow [M]{=}C{=}C\begin{smallmatrix}R\\H\end{smallmatrix} \qquad (2)$$

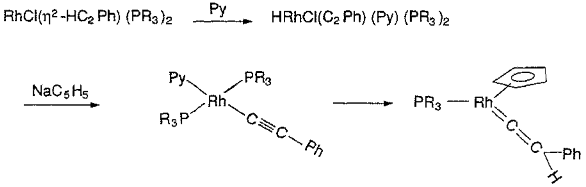
Alternatively, a concerted shift of hydrogen atom from C_α to C_β as the metal approaches C_α can also be envisaged (eqn 3).



$$[M] + R-C\equiv C-H \longrightarrow [M]-\underset{\displaystyle H}{\overset{\displaystyle R}{\Vert}} \longrightarrow [M]=C=C\langle^{R}_{H} \qquad (3)$$

Both these mechanisms may be valid but which one predominates may depend on the nature of the metal-containing species. Also as a rule of thumb, η^2-alkyne complexes of d^4 and d^2 metal centres do not isomerise to the vinylidene analog, while the rearrangement is highly favoured in d^6 complexes, possibly due to the unfavourable 4e-2-centre d–π interaction[12,13].

Evidence for acetylene–hydride intermediate can be found in the reaction of the rhodium complex, $RhCl(\eta^2\text{-}HC_2Ph)(PR_3)_2$. On treatment with pyridine, the η^2-alkyne complex is converted to the hydrido–acetylide, a species that rearranges to the vinylidene on addition of cyclopentadienide anion. The intermediate $Rh(C_2Ph)(Py)(PR_3)_2$ can be isolated if the reaction is carried out at 0°C (Scheme 3)[14].



SCHEME 3. Vinylidene formation *via* a metal-hydrido-acetylide complex.

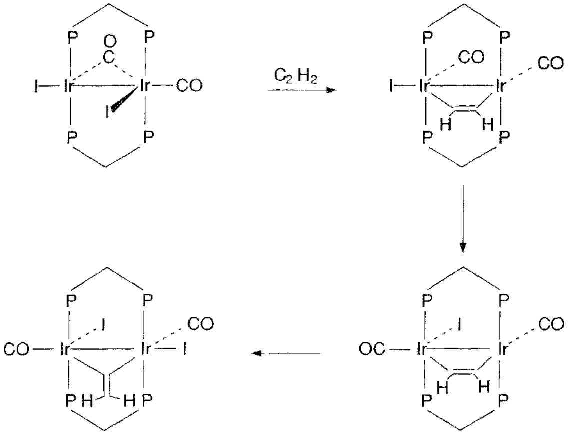
On the other hand, in the acetylene–vinylidene transformation in the diiridium complex, the first such example involving a dimetallic complex, the sequence of steps envisaged by the authors could be suggestive of a concerted pathway for the rearrangement (Scheme 4)[15].

3. Preparation of vinylidene complexes

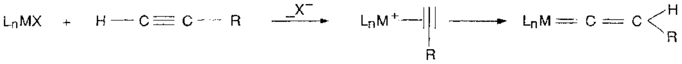
Mononuclear vinylidene complexes can be obtained by any one of the four methods, *viz.*, from (i) η^2-bound terminal alkynes, (ii) carbene or carbyne complexes, (iii) metal-acetylides, or (iv) by dehydration of metal-acyl complexes.

3.1. *From terminal alkynes*

A 1,2-hydrogen shift on the acetylenes attached to a metal centre results in the formation of a vinylidene. As the rearrangement is very facile, detection of η^2 alkyne complex is generally elusive, while in the case of a non-terminal alkyne like 2-butyne, the η^2-bound complex has been isolated (eqn 4)[50].



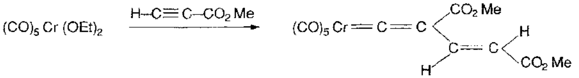
SCHEME 4. Vinylidene formation by a concerted mechanism in a bisiridium complex.



$$L_nMX + H{-}C{\equiv}C{-}R \xrightarrow{X^-} L_nM^+{-}\|| \longrightarrow L_nM{=}C{=}C\begin{smallmatrix}H\\R\end{smallmatrix}$$

(4)

As a prelude to polymerisation reactions involving vinylidene intermediates, like metathetical polymerisations, more than one alkyne can get incorporated into the vinylidene ligand. One such example is given in eqn 5[50].



(5)

Cationic vinylidene complexes are immune to ligand exchange reactions; however, mixed ligand vinylidene complexes can be obtained by performing the exchange reactions on the corresponding acetylides followed by protonation[16]. Chiral vinylidene complexes of the formula, $[\eta^5\text{-}C_5H_5]$ Re (NO) (PPh_3) $(=C=CRR')$ $^+X^-$ where R, R'=H, CH_3 C_6H_5 have also been synthesised. Geometrical isomerism has been observed in these complexes and various reactions have also been performed on them[17,18].

Anionic vinylidene complexes have been observed to be formed by the reaction of molybdenum and tungsten alkylidene complexes with a base[19].

3.2. *From carbyne or carbene complexes*

Vinylidene derivatives can be obtained readily from metal–carbyne complexes possessing β-hydrogens when treated with strong bases like η-butyllithium (eqn 6)[19].

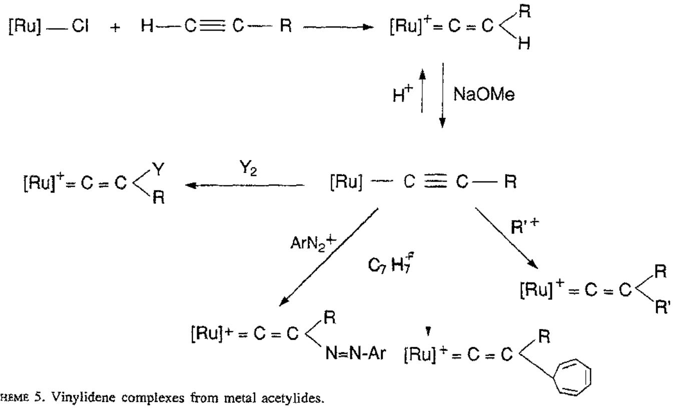
(6)

Chlorocarbene complexes of Iron(II) porphyrins[20] (on reaction with DDT) undergo elimination of HCl to give the diarylvinylidene complexes (eqn 7)[20, 21].

$$\text{(Por) Fe [CClCH(C}_6\text{H}_4\text{Cl)}_2] \xrightarrow{-\text{HCl}} \text{(Por) Fe = C = C (C}_6\text{H}_4\text{Cl)}_2 \qquad (7)$$

3.3. *From metal acetylides*

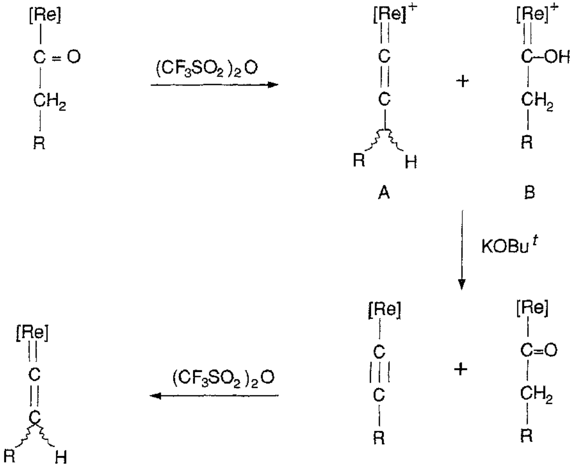
An efficient way to obtain disubstituted vinylidene complexes is by the addition of electrophiles to metal acetylides, accessed by reacting acetylides with the metal halide (Scheme 5)[22].



SCHEME 5. Vinylidene complexes from metal acetylides.

3.4. *From acyl complexes by dehydration reaction*

The acetyl complex of rhenium, $Re(NO)(PPh_3)$ η^5-C_5H_5 $(COCH_2R)$ on treatment with triflic anhyride resulted in the protonation of the acyl group to yield a mixture of stable hydroxycarbene and a vinylidene from dehydration of an oxycarbene. Deprotonation of the vinylidene/hydroxycarbene mixture so obtained by potassium tertiary butoxide base led to a 1:1 acetylide/acyl complex mixture which on further reaction with triflic anhydride resulted in protonation of the acetylide to give the vinylidene (Scheme 6)[17,18].

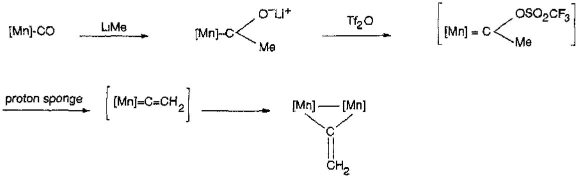


[Re] = Re (NO) (PPh$_3$) (η-C$_5$H$_5$)

R = H, Me, Ph, 1-C$_{10}$H$_7$

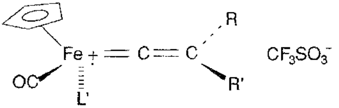
Scheme 6. Vinylidene complex from acyl–metal complex.

Similarly, the acylate anion from Mn(CO)$_3$ (η^5-C$_5$H$_5$,)with MeLi, on reaction with a proton sponge like, 1,8-bis(dimethylamino) naphthalene, gives the vinylidene complex as an intermediate but it is the binuclear complex that is isolated finally (eqn 8)[23].



(8)

The pseudo-tetrahedral complexes of (η^5-Cp) (acyl) (CO) (PR_3) Fe complexes also react rapidly with triflic anhydride to afford a variety of cationic complexes *via* the intermediacy of cationic carbene complexes (Fig. 3)[24].

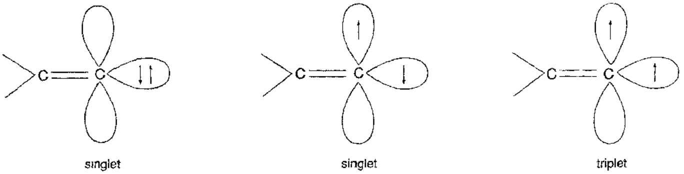


R = Me; L = PPh_3
R = H; L = PPh_3
R = H; L = PMe_2Ph

FIG. 3. Some of the vinylidene complexes obtained from (η^5–Cp) (acyl) (CO) (PR_3) Fe complex.

4. Structure of the vinylidene complexes

Free vinylidenes, if they exist, can be either in the singlet or triplet state and may be represented as follows:



In the metal complexes, either of the species is bonded to the metal atom *via* a ligand to metal σ-donor bond and a metal to ligand π–acceptor bond. Back donation of the electron density to the π* orbitals of the C–C multiple bond systems can thus take place. The M=C=C group is almost linear. The angle at C_α is between 1.25 and 1.41 Å which corresponds to a bond order between two and three. The M–C bond length is consistent with a bond order of around two[25–27].

The IR spectra of all these complexes invariably show a characteristic $\gamma_{C=C}$ between 1620 and 1680 cm^{-1}. The ^{1}H-NMR spectrum does not give any information on the vinylidene as such. However, ^{13}C-NMR spectral data generally show a highly deshielded carbon at 320–380 ppm (*i.e.*, the C_α) and C_β between 90 and 140 ppm. Mass spectral data for some of the complexes are also available[28]. UV visible spectroscopic studies and electrochemical studies on such vinylidene complexes have been carried out and are well documented[29]. Structural parameters of several complexes are available and a typical crystal structure of vinylidene complex is shown in Fig. 4[30].

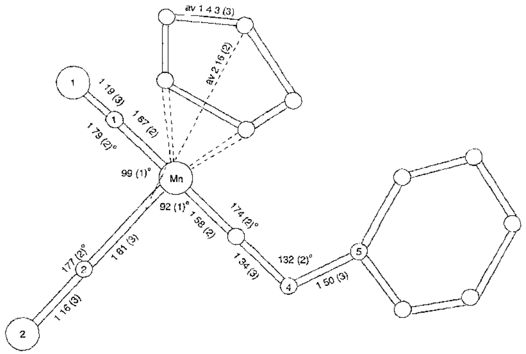
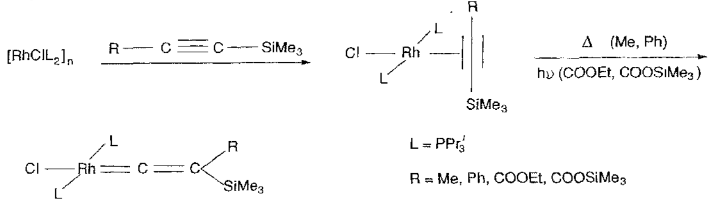


FIG. 4. ORTEP diagram of a vinylidene complex showing the linear arrangement of the metal–carbon–carbon bonds.

Compounds having vinylidene ligands which have groups like Ph_3Ge or Ph_3Sn instead of hydrogen atom have been synthesised from the manganese complex, CpMn(CO)(THF). Various acetylenes like H–C≡C–Ph, Ph_3Si–C≡C–Ph, and Ph_3Sn–C≡C–Ph form the vinylidene complex readily from the corresponding η^2-alkyne complexes (Scheme 7)[5]. This type of rearrangement is observed in the coordination sphere of rhodium with various trimethylsilyl acetylenes[31].



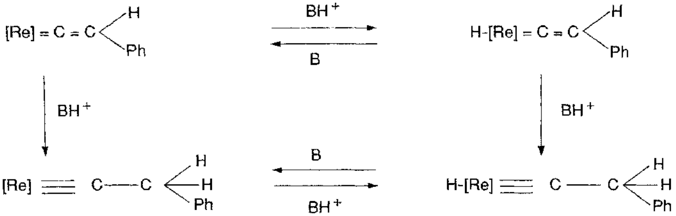
SCHEME 7. η^2-alkyne to vinylidene rearrangement with trialkylsilyl groups.

5. Reactions of vinylidene complexes

It has been shown by theoretical calculations that the electron deficiency at C_α renders it susceptible to nucleophilic attack and the localization of electron density in the metal–carbon double bond and on C_β causes the chemical reactivity to be oriented towards electrophiles[32]. This prediction is very well borne by experimental results and it may also be conveniently said that barring addition reactions of vinylidenes with olefins or alkynes, their chemistry is dominated by nucleophilic attack on C_α carbon, be it inter- or intra-molecular reactions with the intermediacy of vinylidene complex implied or confirmed.

5.1. Electrophilic addition to β-carbon

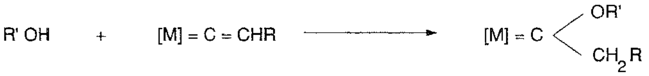
Vinylidenes react with electrophiles at the β-carbon leading to the formation of the carbyne complex. The formation of the carbyne complex could follow any of the steps outlined in Scheme 8[33].



SCHEME 8. Reaction of vinylidene complex with electrophiles; possible modes of formation of the metal carbyne complex.

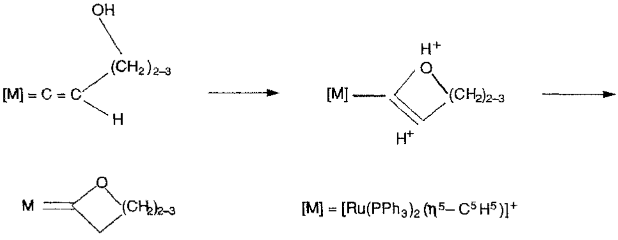
5.2. Nucleophilic addition to the α-carbon

One of the most common reactions of the vinylidene is its ability to convert readily to the metalla–carbene complex upon treatment with alcohols (eqn 9)[34].



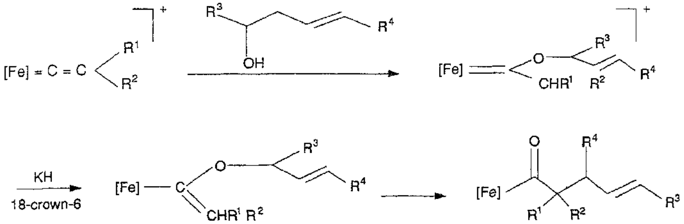
$$R'OH + [M]=C=CHR \longrightarrow [M]=C\begin{cases}OR'\\CH_2R\end{cases} \qquad (9)$$

In some cases, a cyclic carbene complex was isolated when the substrates like HC≡C $(CH_2)_nOH$ react with metal halide complexes. This could occur by a rapid intermolecular addition of the alcohol function to a short-lived vinylidene complex (eqn 10)[35]. (See later part for more examples with implied vinylidene complex formation.)



(10)

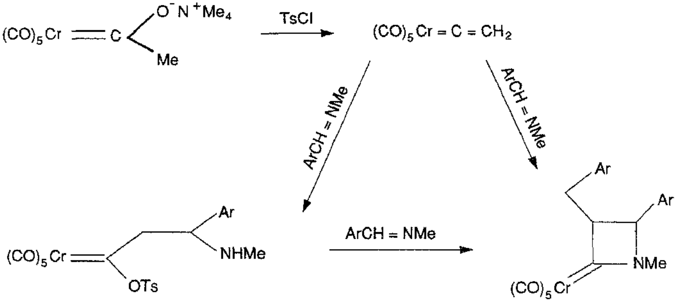
Another interesting reaction of the vinylidene complexes is the formation of a Claisen system from $R^1R^2C=C=Fe(CO)(PR_3)(\eta^5\text{-}C_5H_5)^+$ and the allyl alcohol, $R^3(OH)CHCH=CH(R^4)$ to give the indicated product (eqn 11)[36]. This concept was utilised more effectively in an Ru-mediated coupling of acetylenes and allyl alcohol and will be dealt with shortly.



[Fe] = Fe (CO) (PR'$_3$) (η-C$_5$H$_5$)

(11)

β-lactam synthesis has been carried out exploiting the formation of the vinylidene intermediate from $[NMe_4][CrC(O)Me(CO_5)]$ and the end product was isolated in 87–100% yield (eqn 12)[37].



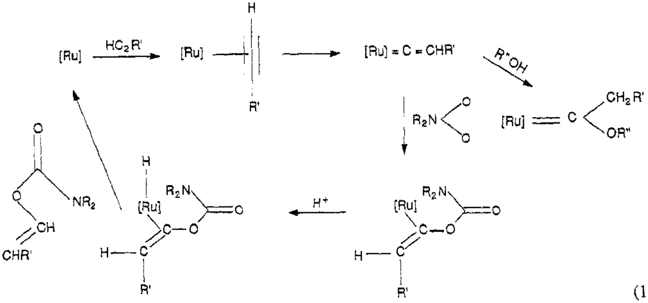
(12)

6. Reactions thought to proceed *via* vinylidenes

With the existence of vinylidene complexes established and their modes of generation characterized, postulating them as intermediates in reactions involving both a transition metal complex and a terminal alkyne have become acceptable. Thus the following catalytic reactions all have in common the suggestion of a vinylidene intermediate, although their occurrence in the catalytic cycle is only a matter of inference.

6.1. *Vinylcarbamates*

Vinylcarbamates can be synthesised from carbamates and terminal alkynes and the coupling reaction is catalysed by $RuCl_2(PR_3)$ $(\eta^6\text{-}C_6Me_6)$ (eqn 13)[38].

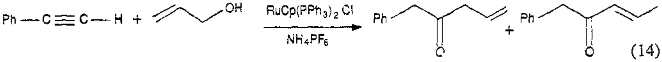


(13)

[Ru] = RuCl $(PMe_3)_2$ $(\eta\text{-}C_6H_6)$

6.2. α , β *and/or* β , γ- *Unsaturated ketones*

A general synthetic procedure for obtaining unsaturated ketones was reported recently by Trost where a ruthenium catalyst mediates coupling of terminal alkynes and allyl alcohols in good yields (eqn 14)[39].

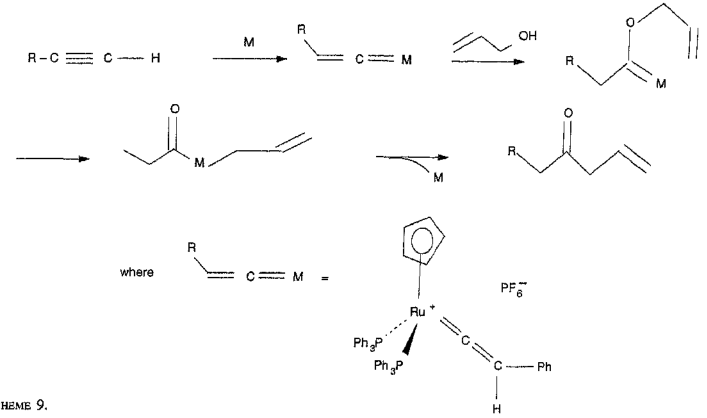


(14)

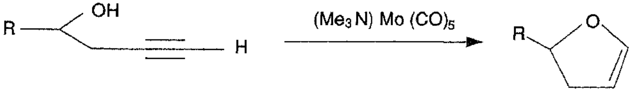
A variety of acetylenic compounds have been coupled with a series of allyl alcohols and a sample list is given in Table I. The catalytic cycle proposed by the authors involves the formation of a vinylidene intermediate arising out of the interaction between the alkyne and the metal catalyst as the key step. The vinylidene, presumably then reacts with the alcohol to give a 'Claisen'-type intermediate (vide eqn 11) which by reductive elimination gives the product ketone and the metal catalyst, thus regenerating the catalytic cycle (Scheme 9) [40,41].

6.3. *Dihydrofurans*

Conventional synthesis of dihydrofurans (cyclic enol ethers) normally call for a multi-step procedure[42-45]. Singly decarbonylated (by trimethylamine-N-oxide) $Mo(CO)_6$ induces cyclization of 1-alkyn-4-ols to 2,3-dihydrofurans in a single step process with *en route* formation of a vinylidene intermediate. The carbonyls of chromium and tungsten, however, give rise to the corresponding metallacarbenes (eqn 15)[46].



SCHEME 9.



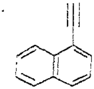
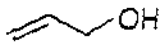
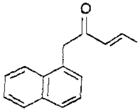
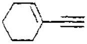
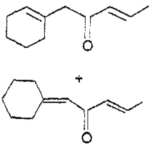
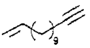
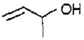
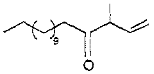
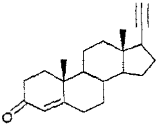
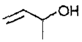
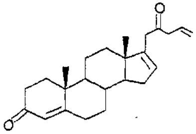
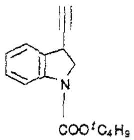
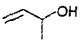
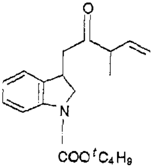
(15)

The authors suggest that the cyclo-isomerisation proceeds the following way. An η^2-alkyne complex formed initially isomerises to the vinylidene which cyclises intra-molecularly to give an η^1-bound cyclic enol ether. This complex can yield the dihydrofuran by protonation or can isomerise to the corresponding oxycarbene. In the case of chromium and tungsten, according to the authors, the activation barrier is high compared to molybdenum for protonation[47] and so the formation of dihydrofuran is difficult (*vide* Scheme 10).

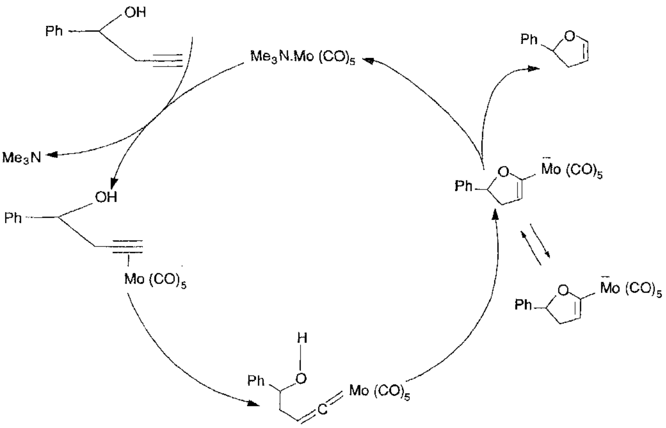
6.4. Polymerisation of alkynes and cyclic olefins

It was demonstrated by Katz not long ago that metal carbenes catalyse polymerisation of alkynes and strained cyclic olefins[48]. As vinylidene complexes are also structurally, in part, metallacarbenes, they should be able to initiate such polymerisation reactions. It should also be noted that stable vinylidene complexes may not be good catalysts. For instance, the cationic complex containing the phenyl vinylidene ligand, *viz*., {*trans*-$[FeCl(C_2HPh)(depe)_2]$ PF_6, depe =1,2-bis (diethyl phosphino)ethane} is very stable and shows no tendency to react with alcohols to form alkoxy carbenes[49]. Thus, vinylidene complexes of metal carbonyls containing no other stabilising ligand could very well be good catalysts for polymerisation of alkynes and cyclic olefins. This was demonstrated by Geoffroy who showed that presence of preformed metal carbene is unnecessary for initiating such reactions[50] and can be accomplished by photolysis of metal carbonyls in the presence of a terminal alkyne, the key step suggested

Table I
Some of the acetylenes and allyl alcohols coupled by Ru complex (*vide* Scheme 9) to yield unsaturated ketones (taken from ref. 39)

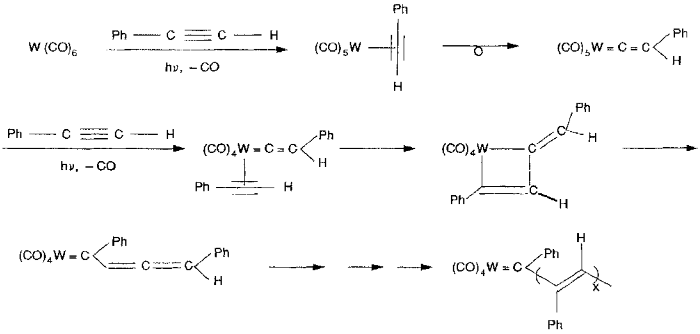
Acetylene	*Alcohol*	*Product*	*Time*	*Yield*
			11 h	45%
			19 h	74%
			1 h	63%
			13 h	62%
			13 h	44%

herein being the rearrangement of η^2-alkyne to vinylidene preceded by photochemically aided loss of carbon monoxide ligand. In the presence of excess alkyne and extended irradiation addition of alkyne molecule to the vinylidene and propagation of polymerisation



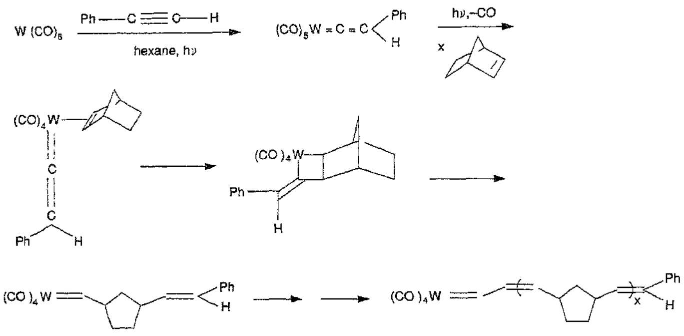
SCHEME 10. Proposed mechanism for the cyclo-isomerisation of 1-alkyn-4-ols to 2,3-dihydrofurans by Mo $(CO)_3$ (NMe_3).

reaction becomes straightforward (see Scheme 11). It is of pedantic interest to note here that acetylene requires irradiation only for initiation of polymerisation while phenylacetylene when used as the monomer calls for continuous irradiation through the course of the reaction.



SCHEME 11. Mechanism of polymerisation of terminal alkynes by $W(CO)_6$ under photolytic conditions.

The need for a vinylidene intermediate for initiating metathetical polymerisation is supported by the observation that internal alkynes and strained cyclic olefins which could be polymerised readily by, say, metallacarbenes, do not react under these conditions to give polymers. However, addition of a small amount of an initiator like phenylacetylene triggers the ring-opening-polymerisation reaction of norbornene, possibly *via* the initial generation of the vinylidene (Scheme 12)[51].



SCHEME 12. Polynorbornene from $W(CO)_6$ hν system with phenylacetylene as initiator.

7. Conclusion

From a pristine organometallic reation η^2-alkyne to vinylidene rearrangement has grown into a synthetically useful tool. Many reactions need to be unfolded that utilise such vinylidene species because of their simplicity in generation; one needs just a transition metal complex with a vacant coordination site and a terminal alkyne, and its high utility, as a variety of electrophiles and nucleophiles can add on to the vinylidene as have been shown earlier. Since many such reactions involving vinylidenes are catalytic in nature and as the products obtained are novel and difficult to obtain otherwise, the importance of this rearrangement has been recognised in the recent literature[52]. It is only hoped that many such useful reactions can be uncovered, like, for instance, application of chiral vinylidenes for synthesis of chiral compounds.

Acknowledgement

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52. Seebach, D. *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 1320–1367. In this context, it is apt to recall a rather provocative comment made by Prof. Dieter Seebach in this article: 'The discovery of truly *new* reactions is likely to be limited to the realm of transition–metal organic chemistry, which will almost certainly provide us with additional 'miracle reagents' in the years to come'.