

# Metal Vinylidenes in Catalysis

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## Introduction

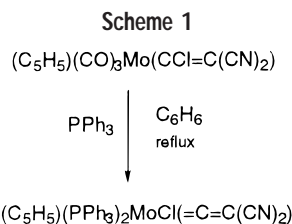
Modern chemistry aims at the discovery of selective combinations of simple, environmentally friendly substrates under mild conditions and with atom economy in order to create new efficient synthetic methods. The epic of vinylidenemetal complexes is an illustration of this type of research. An unforeseen reaction produced the first metal vinylidene moiety, and this novelty motivated chemists to discover more efficient stoichiometric ways to generate metal vinylidene intermediates or complexes and understand their reactivity. During the past decade, the direct simple formation of metal vinylidene intermediates from terminal alkynes has made possible the transfer from stoichiometric to catalytic reactions, and now organometallic vinylidenes are at the heart of selective transformations of terminal alkynes with atom economy. In this Account, after a brief presentation of some examples of the different routes to produce metal vinylidene species and their reactivity, we will focus on their implications in catalytic reactions according to the type of fundamental mechanism involved: (i) [2+2] cycloaddition, (ii) dimerization of alkynes, (iii) nucleophilic addition to alkynes, and (iv) radical cycloaromatization.

## Selected Synthesis and Reactivity of Metal Vinylidene Complexes

Stabilization of organic vinylidene species via coordination to a metal center is now a well-known feature which has

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Pierre H. Dixneuf studied in Rennes (Bretagne), obtained his Doctorate on Ferrocene Chemistry with Professor R. Dabard, and pursued postdoctoral work on carbene complexes with Professor M. F. Lappert in Brighton. Professor since 1978, he is now the head of the CNRS–University of Rennes research unit “Organometallics and Catalysis”. His interests at the boundary of metal complexes and catalysis include the design of carbon-rich organometallics and precatalysts, the activation of alkynes and polyynes via vinylidene, allenylidene, and cumulene intermediates, and the selective catalytic transformation of alkynes and alkenes, especially with ruthenium catalysts. He has received the A. von Humboldt Award for Science.



been encountered with many transition metals.<sup>1</sup> Whereas cationic vinylidene intermediates  $[\text{M}(\text{C}=\text{CHR})(\text{L}_n)]^+$  ( $\text{M} = \text{Fe}, \text{Pt}$ ), generated by protonation of alkynylmetal species, were initially suggested,<sup>2a,b</sup> the first reported and recognized mononuclear vinylidenemetal complexes ( $[\text{M}(\text{C}_5\text{H}_5)(\text{Cl})(\text{L})_2(\text{C}=\text{C}(\text{CN})_2)]$ ;  $\text{M} = \text{Mo}, \text{W}$ ) were prepared by migration of a chlorine atom from an  $\alpha$ -chloroalkenyl ligand with concomitant displacement of carbonyl ligands by a phosphine (Scheme 1).<sup>2c</sup>

The migration of a vinylic  $\alpha$ -hydrogen atom from an alkenyl ligand can also take place in the presence of a strong base.<sup>3</sup> Similarly, the treatment of carbonylmetal complexes with a 1-chloro-1-(trimethylsilyl)alkene under irradiation leads to oxidative addition of the C–Cl bond to the metal center followed by elimination of  $\text{Me}_3\text{SiCl}$  and formation of a vinylidene complex (Scheme 2).<sup>4</sup>

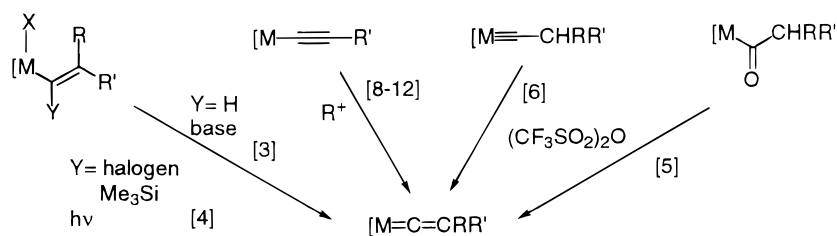
Vinylidenemetal complexes have also been prepared via deoxygenation of acylmetal derivatives by treatment with  $(\text{CF}_3\text{SO}_2)_2\text{O}$ ,<sup>5</sup> deprotonation of metal carbynes,<sup>6</sup> and rearrangement of alkylidene metallacyclobutane species.<sup>7</sup> Addition of a variety of electrophiles,<sup>8</sup> including alkyl groups,<sup>9</sup> diazonium salts,<sup>10</sup> and halogens,<sup>11</sup> to the  $\beta$ -carbon of an alkynyl ligand has been used to synthesize a variety of vinylidene complexes. The use of the proton as an electrophile provides a general access to monosubstituted vinylidenemetal complexes.<sup>12</sup>

The most straightforward route to vinylidenemetal complexes arises from the activation of a terminal alkyne to give an initial  $\eta^2$ -coordinated alkyne intermediate followed by either direct 1,2-hydrogen migration over the carbon–carbon triple bond<sup>13</sup> or oxidative addition of the C–H bond to the metal center and subsequent 1,3-shift of the hydride to the alkynyl ligand<sup>14</sup> (Scheme 3). The same type of rearrangement of an alkyne into a vinylidene ligand can take place from trialkylsilyl,<sup>15</sup> alkylthio,<sup>16a</sup> or iodoalkynes<sup>16b</sup> via the 1,2-migration of the labile silyl, thio, or iodo group.

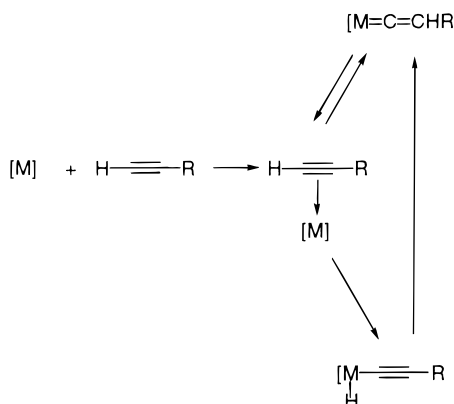
From ruthenium polyhydride complexes, the most favored pathway is the insertion of the triple bond into a Ru–H bond to form a vinylruthenium intermediate which undergoes  $\alpha$ -H migration to give the vinylidene complex.<sup>17</sup>

The reactivity of the metal vinylidene complexes largely depends on the nature of the metal. As carbenes, the vinylidene ligands linked to early transition metals are nucleophilic, whereas those linked to late transition metals act as electrophiles. Thus, the stoichiometric reaction with nucleophilic titanium vinylidene species constitutes an efficient synthetic method for the preparation of tetra-substituted allenes from ketones and 1,1-disubstituted allenes (Scheme 4),<sup>7</sup> but this process could not be made

Scheme 2



Scheme 3



catalytic because of the formation of stable titanium–oxygen bonds.

From electrophilic vinylidene complexes of group 6–10 metals, three types of properties can be underlined.

First, these vinylidenemetal species contain an electrophilic  $\alpha$ -carbon atom which readily reacts with nucleophiles when this site is not sterically hindered to stoichiometrically form functionalized metal carbene complexes.<sup>18</sup> Many catalytic reactions involve this electrophilic property of the  $\alpha$ -carbon atom of the vinylidene ligand  $[M=C^\alpha=CHR]$  favoring the addition of an external nucleophile (Scheme 5).

Second, stoichiometric carbon–carbon bond formation can take place via the intramolecular interaction of a vinylidene with an alkynyl ligand<sup>19</sup> and correspond to the insertion of a 2-electron ligand (similar to CO, CNR, carbene, ...) into a metal–carbon  $\sigma$  bond. This is the key step leading to dimerization of alkynes into enynes, butatrienes, or diynes according to the nature of the ancillary ligands (Scheme 6).

A third reaction pathway involves [2+2] interaction of the  $M=C$  bond with an unsaturated  $C=C$  bond or a triple

bond and provides the initiation step of polymerization via a metathesis mechanism (Scheme 7).<sup>20,21</sup>

The multistep preparations of metal vinylidene complexes described above using stoichiometric amounts of various reagents are not appropriate for the performance of catalytic reactions, and the most favorable conditions require a one-step formation of the reactive vinylidene species. Actually, catalytic reactions involving a vinylidene active species have been made possible by starting from terminal alkynes or silylated alkynes.

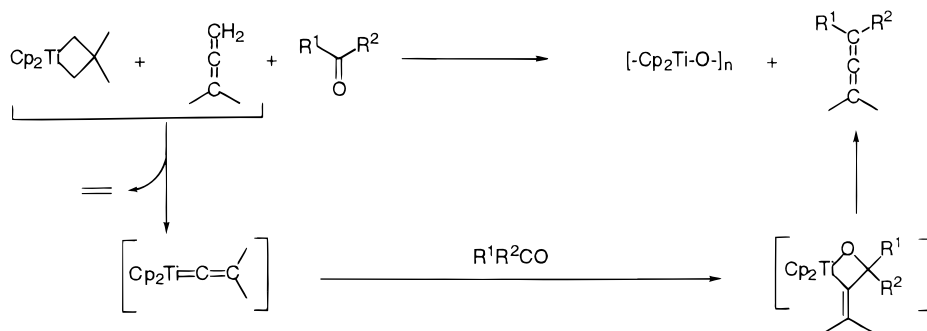
The stoichiometric formation and reactivity of vinylidene complexes reveal that the  $\eta^1$ -vinylidene ligand appears as an electron-deficient ligand with respect to the corresponding  $\eta^2$ -alkyne ligand.<sup>15b</sup> Thus, the vinylidene-metal complexes will be stabilized by electron-rich organometallic moieties. To perform catalytic reactions, a correct balance has to be found to obtain an organometallic active species not too electrophilic to allow transformation of the alkyne into vinylidene and not too electron-rich to avoid the stabilization of the vinylidene fragment.

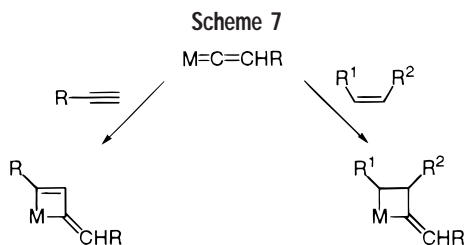
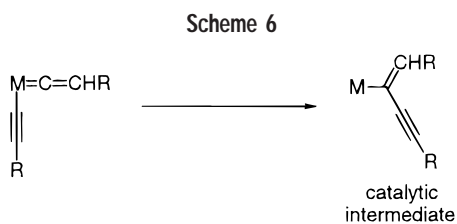
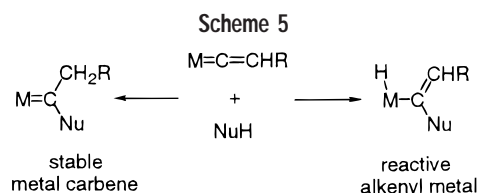
In this Account, we will report on metal vinylidene complexes as catalyst precursors and organometallic vinylidene species as postulated reactive intermediates in catalytic reactions.

## Vinylidenes in [2+2] Cycloaddition: Initiation of Polymerization

Actually, the first involvement of a vinylidenemetal species in catalysis, recognized as such, was reported in 1985 by Geoffroy for the polymerization of phenylacetylene (Scheme 8).<sup>20a</sup> Photolysis of  $\text{W}(\text{CO})_6$  at 366 nm in the presence of phenylacetylene generates the vinylidene complex  $[\text{W}(\text{CO})_5(=\text{C}=\text{CHPh})]$  which is an active precursor for polymerization of the alkyne. The evidence for the suggested mechanism is based on the catalytic activity of the

Scheme 4





analogous isolated  $[\text{W}(\text{CO})_5(=\text{C}=\text{C}(\text{Me})(\text{tBu}))]$  vinylidene complex, which generates the active species by photochemical displacement of one carbonyl ligand, and the absence of initiation by an internal alkyne such as but-2-yne. The polymerization of the latter was triggered by the addition of a trace of  $\text{PhC}\equiv\text{CH}$  generating the vinylidenetungsten precursor. Recently, polymerization of phenylacetylene via tungsten vinylidene intermediates was also performed by coupling electron transfer chain catalysis with organometallic catalysis.<sup>20c</sup>

$[\text{Ru}(\text{Cl})_2(\text{PR}_3)_2(=\text{C}=\text{CH}^t\text{Bu})]$  complexes polymerize functionalized norbornene derivatives containing oxygenated groups under mild conditions via ring-opening metathesis (Scheme 9).<sup>21</sup> The best representatives in the series correspond to  $\text{PR}_3 = \text{PCy}_3$  and  $\text{P}^i\text{Pr}_3$ , which allow a quantitative yield of poly(norbornene) from 1 mol of monomer at room temperature in 2 h, whereas the use of  $\text{PPh}_3$  requires heating at 40 °C for 1 day. It is noteworthy that the vinylidene complex  $[\text{Ru}(\text{Cl})_2(\text{PPh}_3)_2(=\text{C}=\text{CHSiMe}_3)]$  can be generated in situ from  $[\text{Ru}(\text{Cl})_2(\text{PPh}_3)_3]$  and  $\text{Me}_3\text{SiC}\equiv\text{CH}$  and is also an efficient strained cyclic olefin polymerization catalyst precursor.<sup>21</sup> This type of catalyst offers the possibility of modification of the vinylidene

ligand by simply varying the terminal alkyne and the other ancillary ligands. Thus, the isoelectronic pentamethylcyclopentadienyl (**A**<sub>1</sub>) and tris(pyrazolyl)borate (**A**<sub>2</sub>) ligands were found to give the neutral 18-electron  $[\text{Ru}(\text{A})(\text{PPh}_3)(\text{Cl})(=\text{C}=\text{CHPh})]$  complexes which catalyzed the polymerization of norbornene at 80 °C leading to 19% (24 h) and 99% (72 h) yields of polymer, respectively.<sup>22</sup> The unsubstituted vinylidene complex  $[\text{Ru}(\text{Cl})_2(\text{PCy}_3)_2(=\text{C}=\text{CH}_2)]$  generated from  $[\text{Ru}(\text{Cl})_2(\text{PCy}_3)_2(=\text{CHPh})]$  and allene was also active for the polymerization of norbornene.<sup>23</sup>

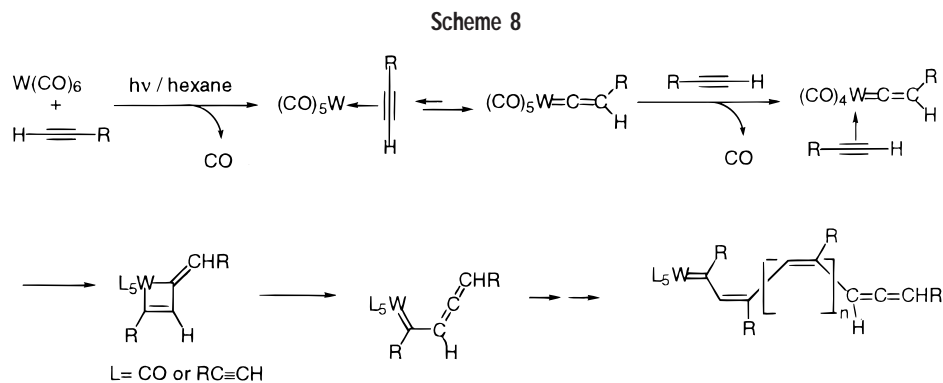
A mechanism involving insertion of a triple bond into a vinylidene  $\text{Ru}=\text{C}$  double bond has been postulated for the catalytic cyclocarbonylation of 1,1'-bis((trimethylsilyl)ethynyl)ferrocene according to Scheme 10.<sup>24</sup> The catalytic cycle involves the 1,2-migration of a silyl group on reaction with  $\text{Ru}_3(\text{CO})_{12}$  to form a vinylidene intermediate which interacts with the triple bond to produce a ruthenacyclobutene. A double insertion of carbon monoxide followed by reductive elimination gives the new ferrocene derivative.

## Dimerization of Terminal Alkynes

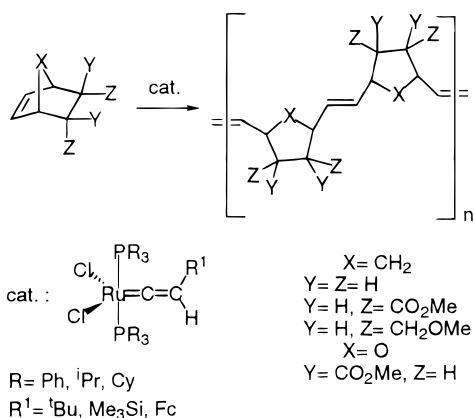
Ruthenium complexes containing a very bulky electron-donating polydentate nitrogen ligand, such as tris(pyrazolyl)borate (**Tp**), a poly podal phosphorus ligand like  $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  (**PP**<sub>3</sub>), or a pentamethylcyclopentadienyl ligand, are efficient catalysts for the dimerization of terminal alkynes into enynes **I–III** (Scheme 11).

In the presence of phenylacetylene,  $[\text{Ru}(\text{Cl})(\text{PPh}_3)_2(\text{Tp})]$  (**1a**) and  $[\text{Ru}(\text{Cl})(\text{PPh}_3)(\text{pyridine})(\text{Tp})]$  (**1b**) are precursors of the neutral vinylidene complex  $[\text{Ru}(\text{Cl})(\text{PPh}_3)(\text{Tp})(=\text{C}=\text{CHPh})]$  (**1c**),<sup>25</sup> which participates in the dimerization process according to the general pathway depicted in Scheme 12.<sup>18</sup> In the presence of  $[\text{Ru}(\text{Cl})(\text{PPh}_3)_2(\text{Tp})]$  (**1a**), phenylacetylene is transformed into the (*E*)-1,4-diphenylbut-1-en-3-yne **II**, whereas the more bulky (trimethylsilyl)acetylene and *tert*-butylacetylene afford the *Z* isomer **I** with a low conversion of the latter (10%).

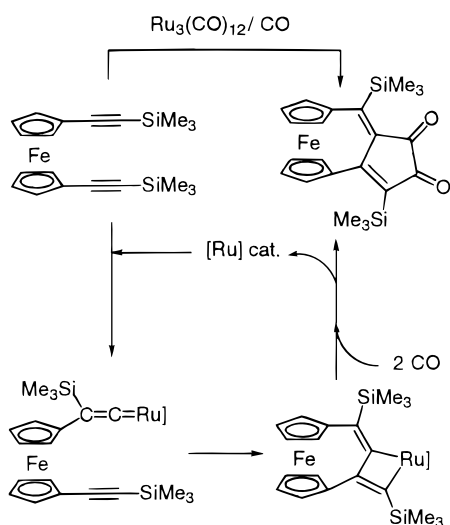
From the catalyst precursors **2a–d** containing a  $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  (**PP**<sub>3</sub>) ligand coordinated to a Ru(II) center, a vinylidene is postulated as the reactive intermediate resulting from protonation by the free terminal alkyne of a preformed (**2b**) or in situ generated alkynyl ligand.<sup>26</sup> Migration of the other alkynyl ligand onto the  $\text{Ru}=\text{C}$  carbon atom of the vinylidene ligand generates an enynyl



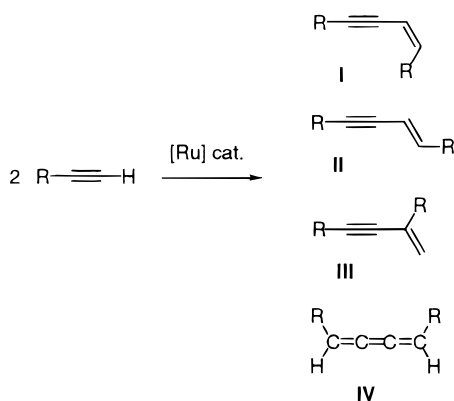
Scheme 9



Scheme 10



Scheme 11



ligand which is removed by protonolysis to selectively afford the (*Z*)-enynes **I** as the major dimer. The stereochemistry is suggested to result from the  $\text{PP}_3$  ligand, in which the repulsive interaction between the six phenyl rings on the phosphine ligand and the substituents on the vinylic moiety forces the coordinated 1,4-substituted butenylnyl ligand to adopt an *E* configuration. In the case of (trimethylsilyl)acetylene, a ruthenium complex containing an  $\eta^3$ -butenylnyl ligand, expected to result from migration of an alkynyl to a vinylidene ligand, was isolated.<sup>27</sup>

Ruthenium hydride complexes **3** containing the  $\text{C}_5\text{Me}_5$  ligand also dimerize terminal alkynes.<sup>28a</sup> Depending on the nature of the catalyst and the alkyne, the main products are the (*Z*)- and (*E*)-enynes **I** and **II** or the enyne **III** corresponding to head-to-tail coupling. The same authors recently showed that  $[\text{Ru}(\text{Cl})(\text{C}_5\text{Me}_5)(\text{PPh}_3)(=\text{C}=\text{CHPh})]$  was an efficient catalyst precursor for the coupling reaction of terminal alkynes with internal alkynes to produce enynes.<sup>28b</sup>

The  $[\text{Ru}^0(\text{cod})(\text{cot})]$  complex had little activity toward dimerization of terminal alkynes, but the addition of a tertiary phosphine had a drastic effect and led to the selective catalytic formation of (*Z*)-butatrienes **IV** (Scheme 11), corresponding to the formal head-to-head coupling of two vinylidene ligands. However, the best catalytic precursor for the selective formation of (*Z*)-1,4-di-*tert*-butylbutatriene **IV** from *tert*-butylacetylene in benzene at 100 °C was  $[\text{Ru}(\text{CO})(\text{PPh}_3)_3(\text{H}_2)]$  (**4**) in association with  $\text{P}^i\text{Pr}_3$ , which easily provided a ruthenium vinylidene intermediate (Scheme 13).<sup>29</sup> It is noteworthy that another example of butatriene has been selectively obtained from  $\text{PhCH}_2\text{C}\equiv\text{CH}$  in THF at 80 °C in the presence of  $[\text{Ru}(\text{H})_3(\text{C}_5\text{Me}_5)(\text{PCy}_3)]$  (**3b**) as the catalyst precursor.<sup>28a</sup> In both mechanism leading to either an enyne or a butatriene, an intermediate enynyl ligand is suggested. The equilibrium depicted in Scheme 14 is strongly influenced by the bulkiness of both the starting alkyne and the ancillary ligands linked to the metal center.

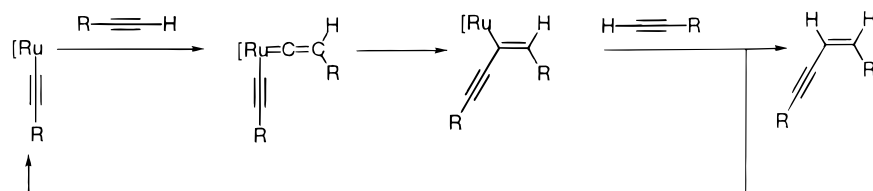
A dinuclear bis(pentamethylcyclopentadienyl)ruthenium complex containing bridging sulfur ligands has shown a very good efficiency to form the head-to-head *Z* dimer together with the *Z,Z* trimer from ethynylferrocene.<sup>30</sup> The mechanism proposed for this catalytic reaction involves the alkynylvinylidene and butenylnyl ligands coordinated to two metal centers instead of only one, as corroborated by the isolation of the active dinuclear cationic butenylnyl complex **5** (Scheme 15).<sup>30</sup>

The formation of conjugated diynes from bis(alkynyl)-metal derivatives with a ruthenium catalyst involves elemental steps similar to those encountered in dimerization of terminal alkynes. This is illustrated by the catalytic demercuration of bis(alkynyl)mercury derivatives, which gives  $\text{Hg}^0$  and buta-1,3-diynes in the presence of  $[\text{M}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$  ( $\text{M} = \text{Ru}, \text{Os}$ ) catalysts.<sup>31</sup> The first step is the transfer of the two alkynyl ligands of  $[\text{Hg}(\text{C}\equiv\text{C}-\text{R})_2]$  onto a hydridoruthenium species to give an alkynyl ligand and the free alkyne. Then, the migration of the alkynyl to the  $\text{C}^\alpha$  of the vinylidene species formed via coordination of the free alkyne takes place. The enynyl ligand is removed from the metal center via  $\beta$ -elimination to give the butadiyne and regenerate a  $\text{Ru}-\text{H}$  catalytic species (Scheme 16).

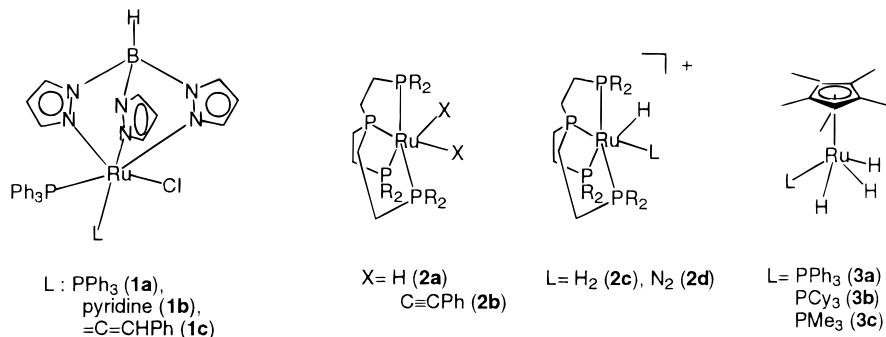
## Addition of Nucleophiles to Terminal Alkynes

**a. C–O Bond Formation: Selective Synthesis of Vinyl Carbamates and Ureas.** Ruthenium(II) complexes are usually able to promote the electrophilic activation of alkynes to give classical Markovnikov addition reactions.

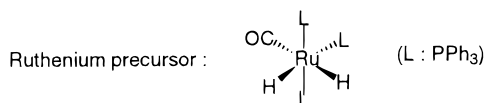
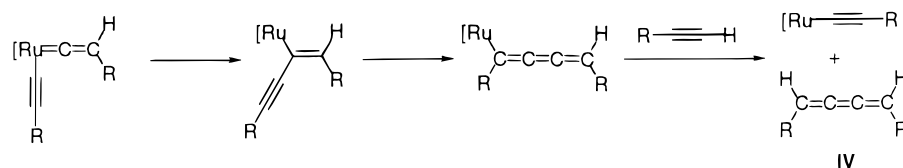
Scheme 12



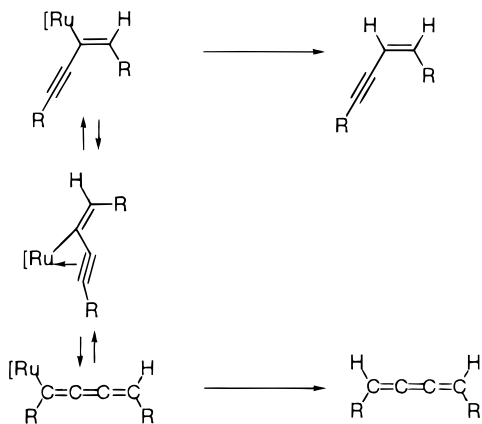
Ruthenium precursors :



Scheme 13



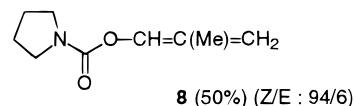
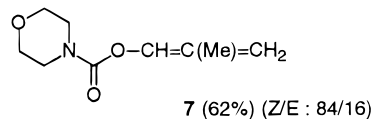
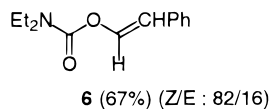
Scheme 14



However, some ligand modulated ruthenium(II) complexes have been shown to favor *anti*-Markovnikov addition of weak nucleophiles to alkynes. In all cases, the formation of a ruthenium vinylidene is suggested as the active species. Indeed, the activation of terminal alkynes by a transition metal via formation of a vinylidene moiety affords an intermediate species bearing an electrophilic carbon atom linked to the metal. The involvement of this reactive center in catalytic reactions with nucleophiles implies formation of functional alkenes corresponding to *anti*-Markovnikov addition to the triple bond. The first

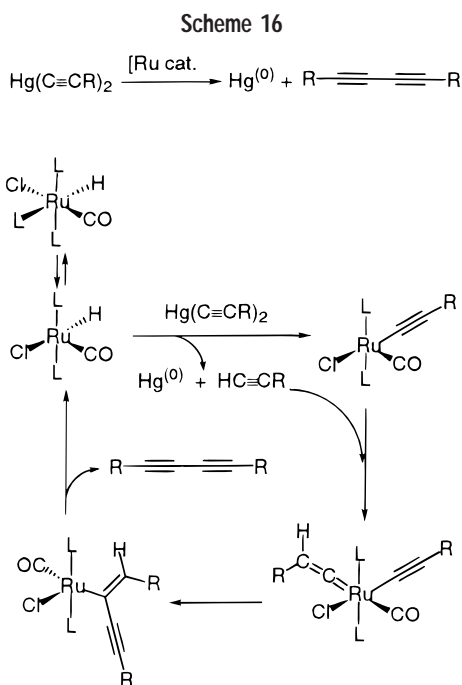
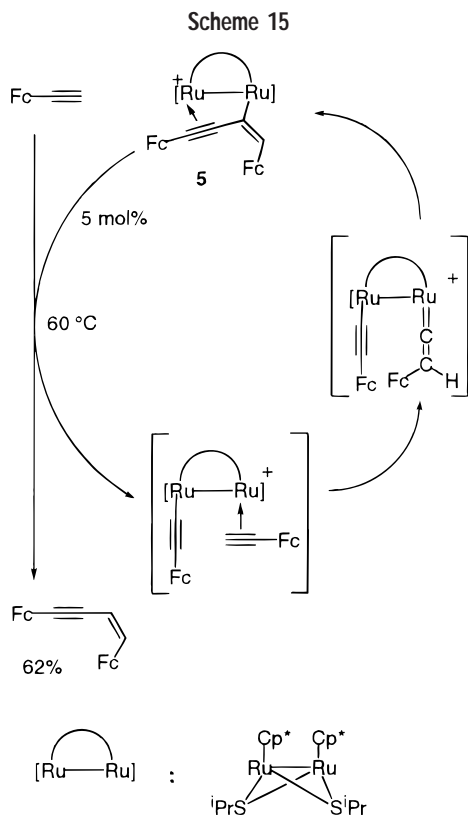
example reported in the literature was the catalytic addition to terminal alkynes of ammonium carbamates generated in situ from secondary amines and CO<sub>2</sub>, which selectively led to vinylic carbamates in the presence of a ruthenium catalyst (Scheme 17).<sup>32a</sup>

The reaction is restricted to terminal alkynes, those able to lead to a vinylidenemetal intermediate.<sup>32</sup> This one-pot reaction allows the direct formation of functional olefins from CO<sub>2</sub> without using phosgene derivatives. It can be applied to a variety of secondary amines and alkynes in the presence of ruthenium complexes as exemplified by compounds **6–8** with the *Z* isomer as major product. The



most suitable catalysts are ruthenium(II) precursors in the



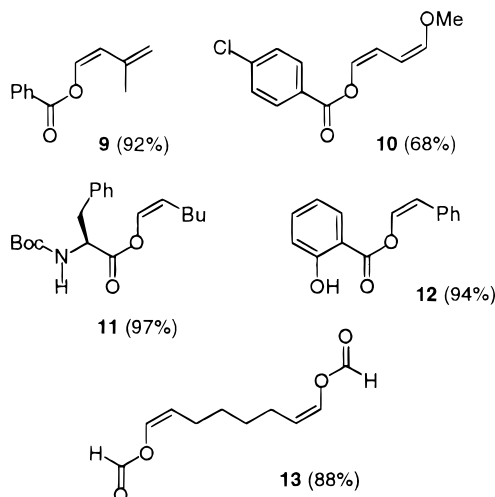


series  $[Ru(Cl)_2(arene)(PR_3)]$ , which are known to interact with terminal alkynes to give vinylidene intermediates.<sup>1c,18b</sup>

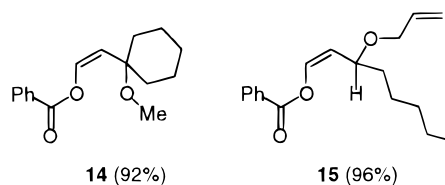
The reaction with primary amines which directly leads to symmetrical ureas under similar conditions is also thought to proceed via a vinylideneruthenium intermediate by reaction of an amine with a carbamatoalkenyl-ruthenium intermediate (Scheme 18).<sup>33</sup>

**b. C–O Bond Formation: Selective Synthesis of (Z)-Alk-1-en-1-yl Esters.** A second class of nucleophiles which selectively add to the terminal carbon atom of alkynes are

carboxylates. Whereas the classical activation of terminal alkynes toward the addition of carboxylates by simple Lewis acids such as mercury<sup>34</sup> or ruthenium complexes such as  $Ru_3(CO)_{12}$ ,<sup>35</sup>  $[Ru(cod)(cot)]/PR_3$ ,<sup>36</sup>  $[Ru(Cl)_2(arene)-(PR_3)]$ ,<sup>37</sup> or  $[Ru(PPh_3)(CO)_2(HCO_2)]_2$ <sup>38</sup> selectively leads to alk-1-en-2-yl esters via addition to the internal carbon atom of the triple bond (Scheme 19), we have found a new class of ruthenium complexes able to reverse the regioselectivity of the addition and afford (Z)-alk-1-en-1-yl esters, stereoselectively (Scheme 20).<sup>39</sup>

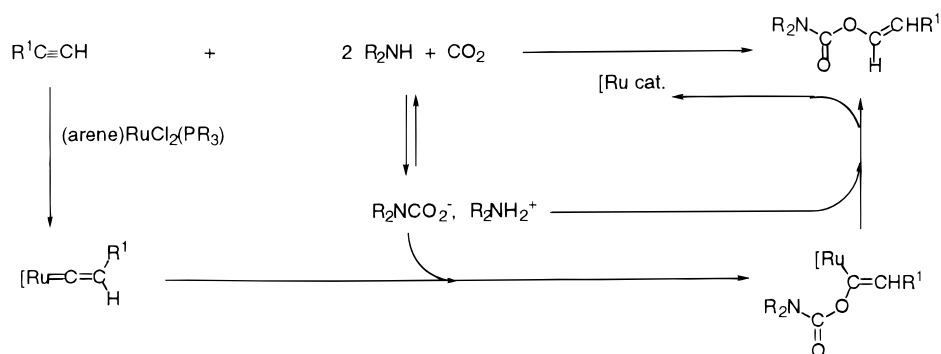


Thus, selected  $[Ru(\text{diphosphine})(2\text{-methylpropenyl})_2]$  complexes<sup>39c</sup> react with carboxylic acids to generate active  $[Ru(\text{diphosphine})(\text{carboxylate})_2]$  catalysts. The choice of the diphosphine and the reaction conditions drastically depends on the nature of the reactants. Thus, the less sterically hindered alkynes  $R-C\equiv CH$  and  $H_2C=C(Me)C\equiv CH$  require the utilization of 1,4-bis(diphenylphosphino)butane (dppb) as a bidentate ligand and a low reaction temperature. For the transformation of bulky alkynes such as  $Me_3SiC\equiv CH$  or  $HC\equiv CCR_2OMe$ , this diphosphine is not adapted and leads to catalysts of low activity.<sup>39d</sup> For anti-Markovnikov addition of these bulky alkynes, the use of 1,2-bis(diphenylphosphino)ethane (dppe) as a bidentate ligand affords the most efficient catalytic system in terms of rate of reaction and selectivity.

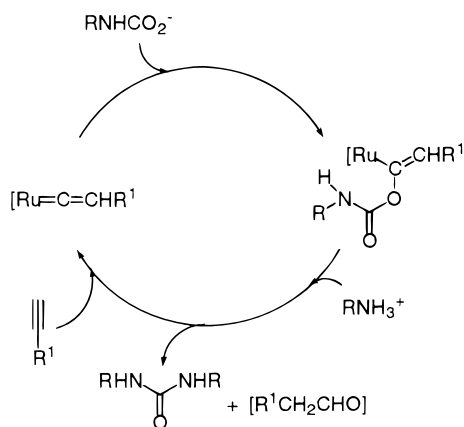


In all cases, the reaction was found to be stereoselective as the Z isomer was always formed as the major compound in more than 95% stereoselectivity. Ruthenium catalysis provides the first very efficient route to this type of alkenyl ester by formal trans-addition of carboxylic acids to terminal alkynes. We have shown that they were good starting materials for the synthesis of (E)-enamines **16** upon treatment with secondary amines<sup>40</sup> and for the preparation of  $\alpha$ -cyanoesters **17** upon reaction with potassium cyanide in the presence of silane (Scheme 21).

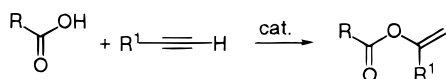
Scheme 17



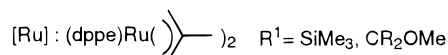
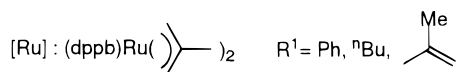
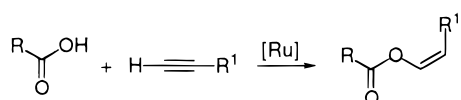
Scheme 18



Scheme 19



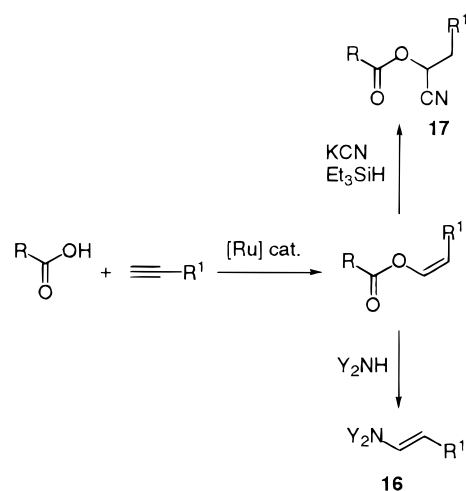
Scheme 20



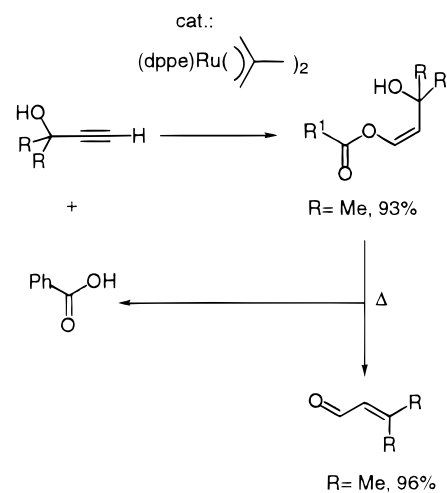
The addition of benzoic acid to propargylic alcohols in the presence of  $[Ru(dppe)(CH_2CMeCH_2)_2]$  at 65 °C leads to hydroxylated alk-1-en-1-yl esters via anti-Markovnikov addition. These esters are not thermally stable and are easily transformed into aldehydes upon heating at 100 °C.<sup>41</sup> Thus, the one-pot experiment based on first ruthenium-catalyzed addition of benzoic acid to propargylic alcohol at 65 °C, followed by heating of the reaction mixture at 100 °C, constitutes a new simple way to formally isomerize propargylic alcohols into enals (Scheme 22).

Although not shown experimentally, a general mechanism involving a vinylideneruthenium intermediate has

Scheme 21

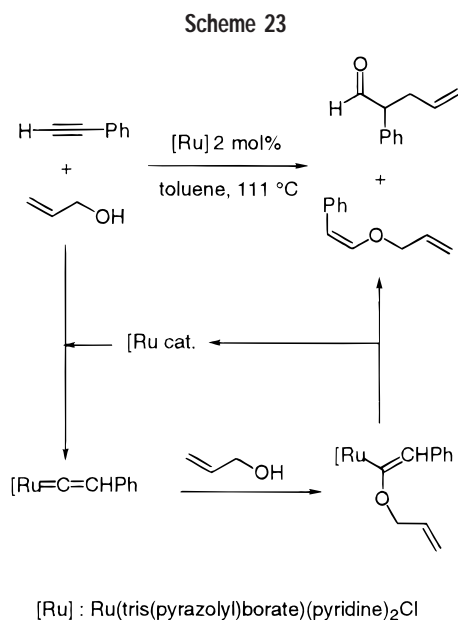


Scheme 22



been postulated for all these reactions leading to the regioselective formation of *Z* enol esters,<sup>39b</sup> analogous to that of the formation of vinyl carbamates (Scheme 17). The anti-Markovnikov addition of benzoic acid to phenylacetylene has also been performed in the presence of neutral ruthenium complexes containing the tris(pyrazolyl)borate (Tp) ligand in good yields but with a low stereoselectivity in favor of the *E* isomer  $\text{PhCO}_2\text{CH}=\text{CHPh}$  ( $1.22 < E/Z < 1.63$ ).<sup>42</sup>

**c. C–O Bond Formation: Synthesis of Alk-1-en-1-yl Ethers and Furans.** The direct selective addition of



aliphatic alcohols to unactivated alkynes to produce enol ethers still remains a challenge. However, some ruthenium catalysts make possible the addition of allylic alcohols to alkynes and lead to rearranged addition compounds.

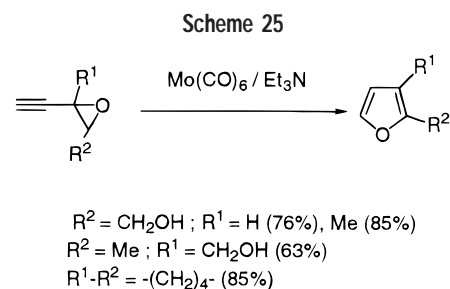
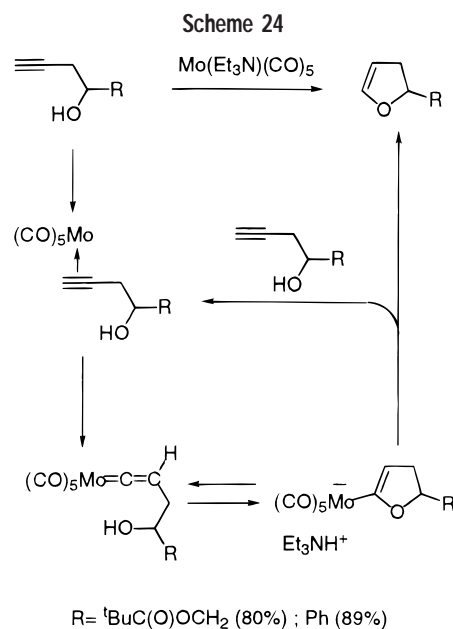
Thus, allyl alcohol adds to phenylacetylene in refluxing toluene in the presence of 2 mol % of [Ru(Cl)(Tp)(py)<sub>2</sub>] to afford a 1:1 mixture of allyl  $\beta$ -styryl ether and 2-phenylpent-4-en-1-al in 72% overall yield (Scheme 23).<sup>42</sup>

The formation of the ether derivative is explained by a mechanism involving the selective addition of the OH functionality to a neutral vinylideneruthenium moiety generated via interaction of the terminal alkyne with the ruthenium complex (Scheme 23). The nonconjugated unsaturated aldehyde results from a thermal Claisen rearrangement of the initially formed mixed allyl vinyl ether.

The formation of vinylidene species from terminal acetylenic alcohols with group 6 carbonylmetals makes possible the preparation of cyclic metal oxacarbenes via intramolecular addition of the hydroxy group to the activated terminal carbon atom of the C $\equiv$ C triple bond.

In the presence of [Mo(Et<sub>3</sub>N)(CO)<sub>5</sub>], this process can be made catalytic and produces dihydrofurans (Scheme 24).<sup>43,44</sup> This reaction has been extended to acetylenic amines to afford pyrrole derivatives in the presence of a tungsten mediator.<sup>45</sup> Furans have also been prepared with the same type of molybdenum catalyst precursor starting from acetylenic alcohols containing a suitable functionalization at the propargylic position,<sup>43,44</sup> or acetylenic epoxides (Scheme 25).<sup>46</sup>

**d. C–C Bond Formation: Direct Access to Unsaturated Ketones via Selective Coupling of Alkynes with Allylic Alcohols.** With [Ru(Cl)(cyclopentadienyl)(PPh<sub>3</sub>)<sub>2</sub>]/NH<sub>4</sub>PF<sub>6</sub> as the catalyst precursor, the addition of allylic alcohols to terminal alkynes takes another route and affords unsaturated ketones.<sup>47</sup> The mechanism of this reaction has been studied in detail, especially on the basis of labeled experiments, and it has been shown that the



key step is the nucleophilic addition of allylic alcohols to a vinylidene complex which is facilitated by the precoordination of the allylic double bond and the liberation of a phosphine ligand (Scheme 26).<sup>47b</sup> The catalytic cycle involves the participation of an allylic intermediate and the reductive elimination with the acyl group. A migration of the terminal double bond can take place depending on the substitution pattern of the starting allylic alcohol.

This catalytic reaction has been applied for the modification of a side chain of steroids and the development of a new preparation of rosefuran from acetylenes and allylic alcohols (Scheme 27).<sup>48</sup>

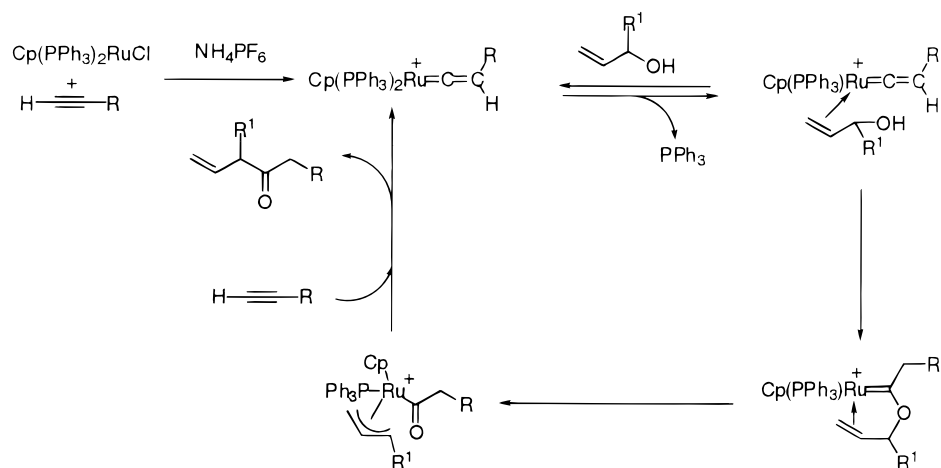
Recently, the use of an optically pure ruthenium vinylidene complex containing a cyclopentadienyl-ferrocenyldiphenylphosphine bidentate ligand has made possible the obtention of a chiral  $\beta,\gamma$ -unsaturated ketone with an enantiomeric excess of 25% under catalytic conditions.<sup>49</sup>

A more sophisticated version of this reaction is exemplified by the ruthenium-catalyzed tandem cyclization-reconstitutive addition of propargylic alcohols containing another hydroxy group with allylic alcohols.<sup>50</sup>

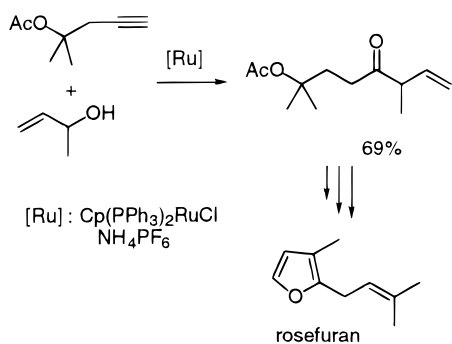
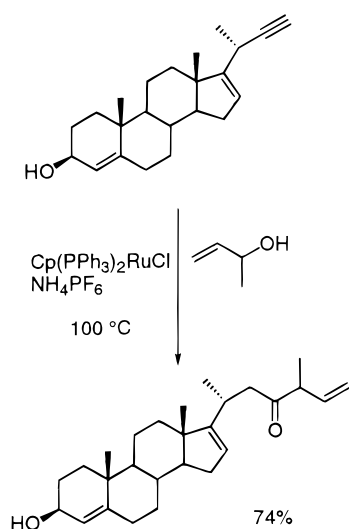
The first step of this reaction involves the initial formation of an allenylideneruthenium intermediate from propargylic alcohol<sup>51</sup> and the intramolecular addition of the other OH group to the electrophilic C $\gamma$  of the unsaturated C<sub>3</sub> ligand (Scheme 28). This reaction generates a



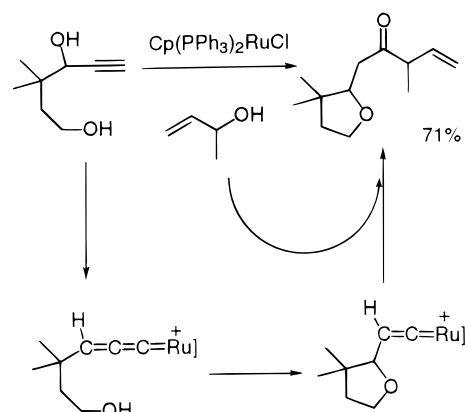
Scheme 26



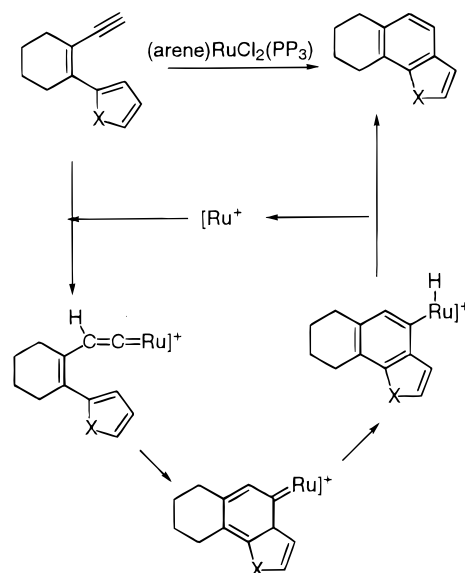
Scheme 27



Scheme 28



Scheme 29

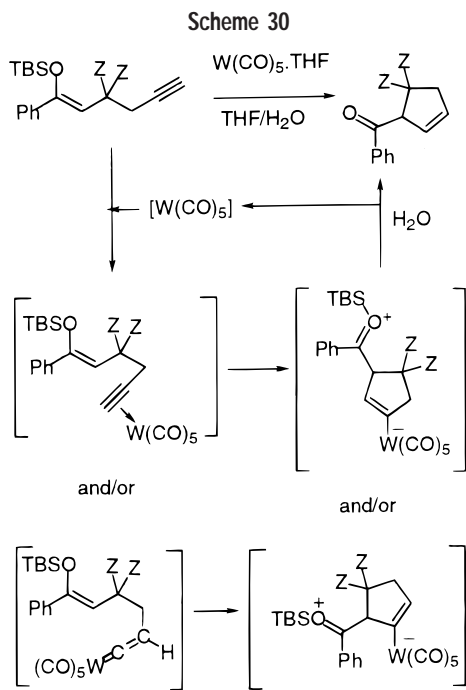


vinylideneruthenium moiety which reacts with allylic alcohol according to the previous mechanism (Scheme 26).

**e. C–C Bond Formation: Intramolecular Addition of Carbonucleophiles.** A recent example of cycloaromatization, starting from conjugated dienylalkynes, has been described (Scheme 29). The most efficient catalytic system is based on  $[\text{Ru}(\text{Cl})_2(\text{PPh}_3)](p\text{-cymene})/\text{NH}_4\text{PF}_6$  and makes possible the formation of benzofurans, pyrroles and

thiophenes in good yields.<sup>52</sup> This cyclization reaction is based on the nucleophilic attack of an electron-rich carbon center on the electrophilic vinylidene moiety and represents a rare example where the nucleophilic center is not a heteroatom.

The catalytic cyclization of  $\omega$ -acetylenic silyl enol ethers at room temperature in the presence of  $[\text{W}(\text{CO})_5\cdot\text{THF}]$



represents another recent example of intramolecular addition of a carbonucleophile to a vinylidenemetal species generated from a terminal alkyne and tungsten. In less-donating solvents, the endo-cyclization compounds are selectively formed according to Scheme 30, leading to unsaturated rings.<sup>53</sup>

### Cycloaromatization of Conjugated Enediynes and Dienynes

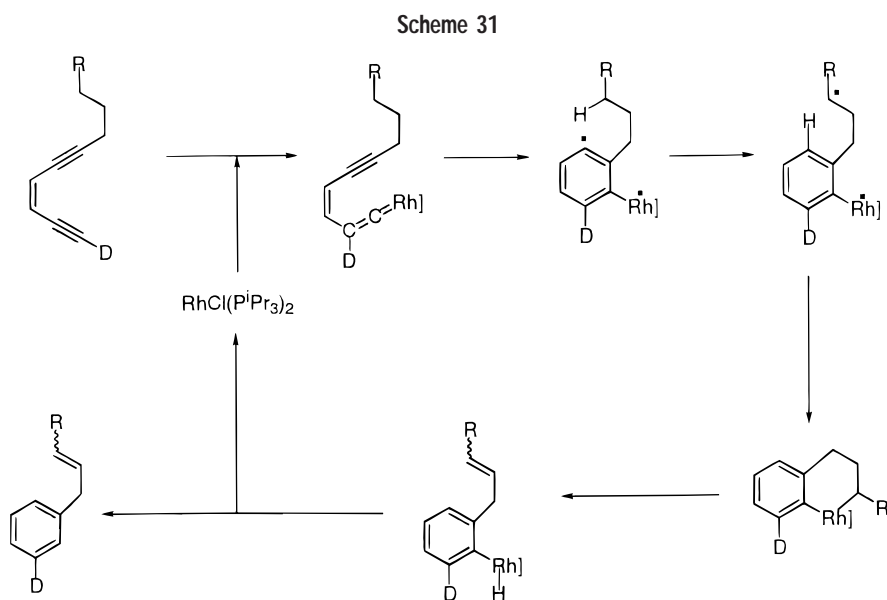
The chemistry of enediynes is rapidly developing because of the recent discovery of the anticancer antibiotic activity of polycyclic compounds containing both double and triple carbon-carbon bonds.<sup>54</sup>

Both ruthenium and rhodium derivatives have been used to cyclize enediynes containing a terminal triple

bond into aromatic derivatives via radical processes involving a vinylidene intermediate. The proposed mechanism suggests the formation of a biradical system where one electron is located on the metal center and the other one is located on the ligand. The latter electron migrates along the organic fragment to generate a new biradical system which forms a metallacycle and  $\beta$ -eliminates as shown in Scheme 31. A stoichiometric reaction from enediynes with  $[\text{Ru}(\text{Cl})(\text{PMe}_3)_2(\text{cyclopentadienyl})]/\text{NH}_4\text{PF}_6$  in methanol at room temperature leading to aromatic compounds had first been reported.<sup>55</sup> The utilization of the rhodium complex  $[\text{Rh}(\text{Cl})(\text{P}^i\text{Pr}_3)_2]$  has made possible the catalytic reaction (Scheme 31).<sup>56</sup>

### Conclusion

The evidence that vinylidenemetal intermediates were easily formed from terminal alkynes and transition metals, especially from ruthenium(II) complexes, and the understanding of their stoichiometric reactivity motivated chemists to search for catalytic reactions involving vinylidenes from alkynes. Most of the examples of the transformations of terminal alkynes via vinylidenes are chemo- and regioselective and take place under mild conditions with atom economy, thus meeting the criteria of modern chemistry. There is no doubt that new reactions will appear and will be developed soon. The successful strategies elaborated to transform the chemical process  $\text{M} + \text{HC}\equiv\text{CR} \rightarrow \text{M}(\text{=C}=\text{CHR})$  into useful synthetic catalytic reactions should now rapidly be transferred to the next member of the metallacumulene series. Indeed, the metal allenylidene  $[\text{M}(\text{=C}=\text{C}=\text{CR}_2)]$  intermediates are readily produced by activation of propynols according to the reaction  $\text{M} + \text{HC}\equiv\text{CCR}_2(\text{OH}) \rightarrow \text{M}(\text{=C}=\text{C}=\text{CR}_2)$ <sup>51</sup> and one can predict that they should become key intermediates in the catalytic transformation of propargylic alcohol derivatives.<sup>50,57</sup>



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