TUTORIAL REVIEW

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Non-stabilized transition metal carbenes as intermediates in intramolecular reactions of alkynes with alkenes

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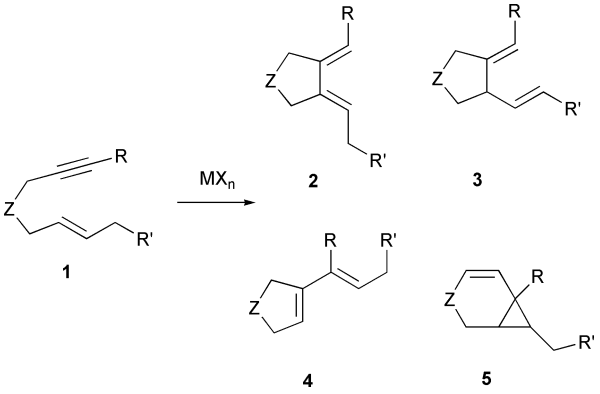
In this *tutorial review* we summarize the two major pathways followed in the reaction of alkenes with alkynes catalysed by electrophilic transition metals. If the metal coordinates simultaneously to the alkyne and the alkene, an oxidative cyclometallation can ensue to give a metallacyclopentene, which usually evolves by β-hydrogen elimination to give Alder-ene cycloisomerisation derivatives. On the other hand, coordination of the metal to the alkyne promotes the attack of the alkene to give metal cyclopropyl carbenes.

Introduction

Among the transformations of diynes, dienes, and enynes catalysed by transition metals, an important group includes the reactions of α,ω-enynes **1** catalysed by a wide variety of electrophilic transition metal complexes or halides MX_n to give carbo- or heterocycles **2–5** (Scheme 1).[1,2,3]

The first examples were reported by Trost using palladacyclopentadiene complexes, which usually favour formation of 1,4-dienes of type **3**.[4] More recently, cationic Ru(II) complexes such as $[CpRu(MeCN)_3]^+PF_6^-$ were found to catalyse the Alder-ene-type cycloisomerisation of enynes to selectively give dienes of type **3** under mild conditions.[5] Cationic Rh(I) complexes have also been shown to be excellent catalysts for the formation of cycloisomerisation products **3**.[6]

The skeletal rearrangement products **4** are also formed in reactions catalysed by Pd(II) complexes by an apparent metathesis reaction.[4,7] In addition, several electrophilic Ru(II) and Pt(II) complexes catalyse the formation of dienes of type **4** from enynes **1**.[8–11] Ir(I) complexes also catalyse the cycloisomerisation or rearrangement of enynes depending on the reaction conditions.[12,13] Yet another type of cyclisation has been observed for enynes tethered by heteroatoms (Z = O or NTs), which give cyclopropanes of type **5** with $PtCl_2$[9] or $PtCl_4$[14] as catalysts.



Scheme 1

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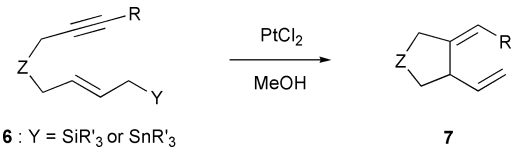
Transition metals catalyse the intramolecular reaction of alkynes with allyl silanes and allyl stannanes, thus allowing the transformation of substrates **6** into dienes **7** (Scheme 2).[15] This



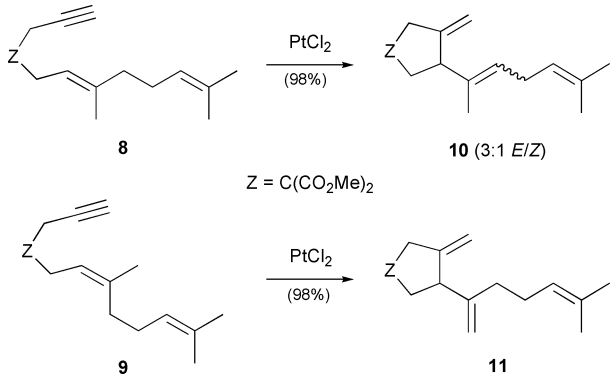
Scheme 2

reaction leads to five- and six-membered ring carbo- and heterocycles and is catalysed by several electrophilic metal halides, although more general results are usually obtained with $PtCl_2$ in MeOH. In this reaction, the transition metal probably coordinates to the alkyne to form an electrophilic (η^2-alkyne) metal complex, which is attacked intramolecularly by the allyl nucleophile in an *anti* manner. Although this cyclisation affords products that are similar to **3** obtained in the cycloisomerisation processes (Scheme 1), the configuration of the exocyclic alkene in **7** is the opposite.

In the processes summarised in Scheme 1 and Scheme 2, the metal can selectively coordinate to the alkyne and then trigger the attack on the alkene or, alternatively, the metal can coordinate simultaneously to the alkyne and the alkene. In this review we present a unified mechanistic picture of the main processes that ensue from the different coordination modes of the metal fragment with enynes.

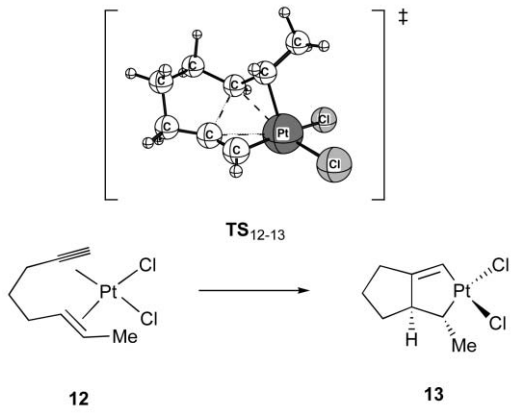
Alder-ene cycloisomerisation

Alder-ene cycloisomerisation of enynes is possible with $PtCl_2$ as the catalyst when the reaction is performed in acetone or 1,4-dioxane.[16] The process results in the formal migration of a hydrogen from the alkyl chain *trans* to the alkene. Thus, derivatives **8** and **9** give stereospecifically trienes **10** and **11**, respectively (Scheme 3). Similar cycloisomerisations also proceed with $RuCl_3$ or $Ru(L)_2Cl_2$ as the catalysts.[16]



Scheme 3

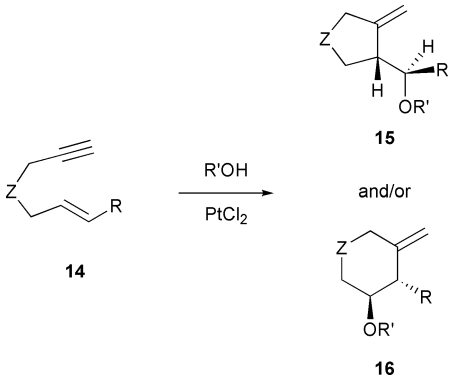
Deuteration studies demonstrate that the Alder-ene cycloisomerisation is an intramolecular process. According to DFT calculations performed on (*E*)-2-octen-1-yne complexed to $PtCl_2$ (**12**), the reaction gives platinacycle **13** by an oxidative cyclometalation (Scheme 4). This transformation is exothermic (25.7 kcal mol^{-1}), although it proceeds with a significant activation energy (E_a = 29.6 kcal mol^{-1}). Mechanistically related processes take place in other important organometallic transformations. Thus, oxidative cyclometallation is one of the key steps in the synthetically useful Pauson–Khand synthesis of cyclopentenones with $Co_2(CO)_8$[17] or other transition metals.[18]



Scheme 4

Alkoxycyclisation

The reaction of simple enynes **14** with $PtCl_2$ as catalyst in the presence of alcohols or water gives carbo- or heterocycles **15** and **16** by 5-*exo-trig* or 6-*endo-trig* cyclisations (Scheme 5).†[16]



Scheme 5

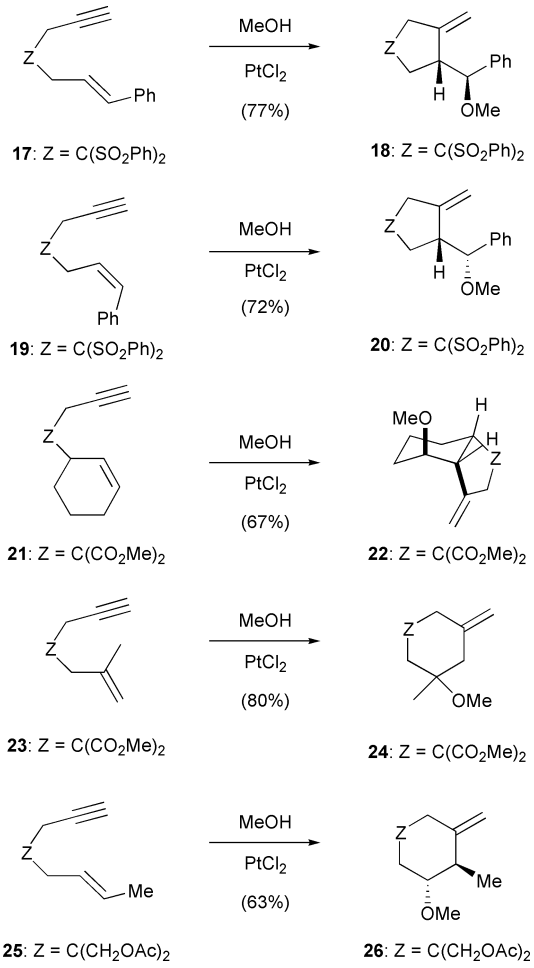
Although more limited in scope, the alkoxy- and hydroxycyclisation can also be promoted by Ru(II), Au(III)[16] and Pd(II) complexes.[19] The hydroxycyclisation reaction can also be catalysed by highly electrophilic $Hg(OTf)_2$.[20]

Representative cyclisation examples carried out in MeOH are shown in Scheme 6. The reaction is stereospecific, as shown in the transformation of *E*-enyne **17** to **18** and *Z*-enyne **19** to **20**. The reactions proceed, formally, by the *anti*-addition of the alkyne and ROH to the alkene, as demonstrated in the transformation of **21** into **22** (Scheme 6).

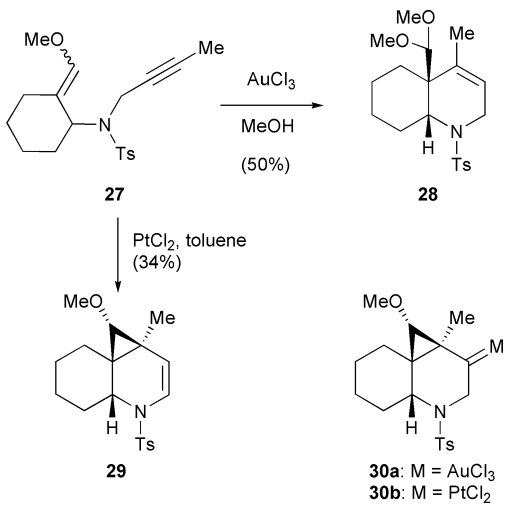
The 6-*endo-trig* pathway is favoured in the cyclisation of enyne **23**, a 2,2-disubstituted alkene, which gives the cyclohexane derivative **24**. Substrate **25**, a 1,2-disubstituted alkene, also reacts by a 6-*endo-trig* pathway to give **26** exclusively. Interestingly, a substrate similar to **25**, but with $C(CO_2Me)_2$ reacts to give a 1.5 : 1 mixture of 6-*endo-trig* and 5-*exo-trig* products, whereas the corresponding disulfone (Z = $C(SO_2Ph)_2$) cyclizes by the 5-*exo-trig* pathway.

The 6-*endo-dig* cyclisation is also possible.[21] Thus, enol ether **27** reacts in MeOH to give heterocycle **28** as the only isolated product (Scheme 7). In this case, the best results were obtained with $AuCl_3$ as the catalyst. When the reaction was carried out

† In this context, the terms 5-*exo-trig* and 6-*endo-trig* describe the overall cyclisation with regard to the C=C bond formation on the alkene. As discussed below, this is a stepwise process, where the formation of **15** or **16** depends on the regioselective cleavage of one of the cyclopropane bonds of the intermediate.



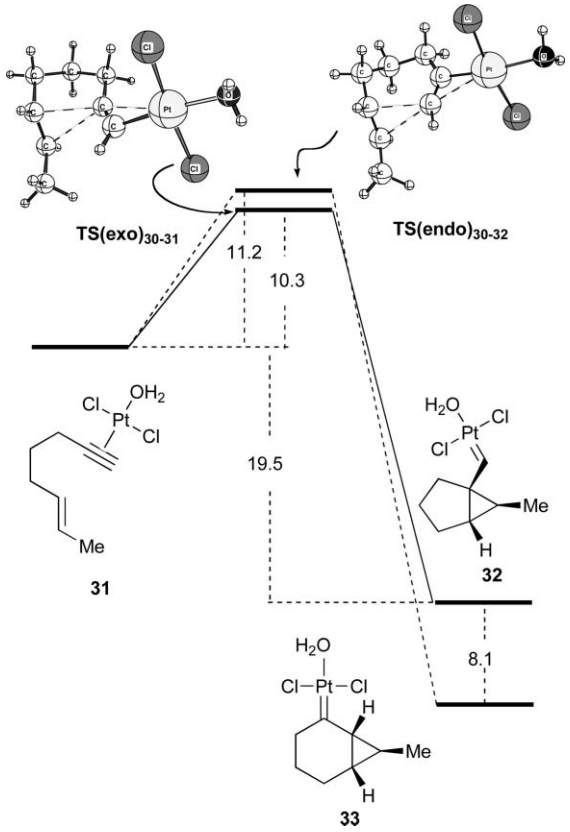
Scheme 6



Scheme 7

in a non-nucleophilic solvent, cyclopropane **29** was obtained. Formation of **28** and **29** can be rationalized by the evolution of intermediates **30a** or **30b** by nucleophilic attack by MeOH or β-hydrogen elimination, respectively.

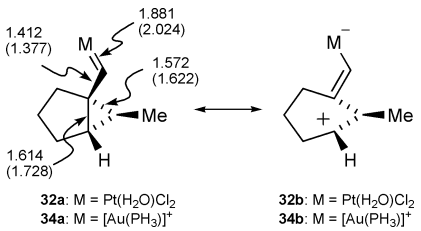
To analyze the competitive 5-*exo-dig* and 6-*endo-dig* cyclisation modes, DFT calculations were performed on (*E*)-6-octen-1-yne complexed to $PtCl_2(H_2O)$ (**31**) (Scheme 8).[21] Evolution of **31** was found to provide bicyclic complexes **32** and **33**, which can be described as Pt cyclopropyl carbenes or cyclopropyl methyl cations[22] stabilized by $PtCl_2(H_2O)$. Both reactions are



Scheme 8

exothermic (−19.5 and −27.6 kcal mol^{-1}), the six-membered product **33** being more stable. For related cases, but with an oxygen at the tether, the 6-*endo-dig* pathway was found to be both kinetically and thermodynamically the most favoured process. Similar results were obtained for analogous $AuCl_3$ complexes.[21]

Calculations from (*E*)-6-octen-1-yne complexed to $[Au(PH_3)]^+$ indicate that a highly polarized complex similar to **31** is formed, which shows substantial electron-deficiency at C-2.[23] This complex reacts by *exo* cyclisation with a very small activation energy (E_a = 0.1 kcal mol^{-1}) to give intermediate **34** (Scheme 9).



Scheme 9 Bond distances (Å) for the calculated (DFT) structures of the *exo-dig* intermediates. Values in parentheses correspond to the Au(I) intermediate **34**.

Complex **34** shows a very distorted cyclopropyl structure in which the cyclopropane C=C bonds conjugated with the carbene are particularly long. The structure of this intermediate resembles the canonical form of **34b**, which can be envisioned as a Au(I)-stabilized homoallylic carbocation. The activation energy for the 6-*endo-dig* process to give a carbene similar to **33** is 6.1 kcal mol^{-1}, which indicates that the *exo* cyclisation is favoured with Au(I) catalysts, at least for substrates related to (*E*)-6-octen-1-yne.

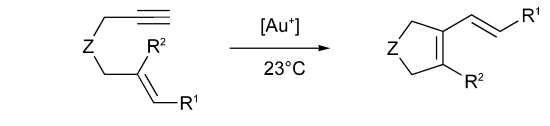
Accordingly, cationic Au(I) catalysts formed by the

activation of [Au(PPh$_3$)Me] with protic acids catalyse the methoxycyclisation of enynes (**14** → **15**) under much milder conditions than those required when using $PtCl_2$ or any other metal catalyst.[23] With this cationic Au(I) catalyst, most enynes are efficiently cyclised at room temperature, whereas reactions catalysed by Pt(II) require longer times and higher temperatures (60–65 °C).

Skeletal rearrangement

Skeletal rearrangement products **4** (Scheme 1) are also obtained by metathesis reactions of **1** catalysed by Grubbs Ru(II) carbenes.[24] However, the reactions of **1** catalysed by electrophilic metal complexes MX_n are mechanistically different, proceeding intramolecularly.

One of the most active catalysts for these transformations are Au(I) complexes formed *in situ* from [Au(PPh$_3$)Cl]–AgX (X = BF_4 or SbF_6).[23] With these catalysts, the rearrangements of α,ω-enynes **35–38** are completed in less than 15 min at room temperature to give products **39–42** in good to excellent yields (Scheme 10).

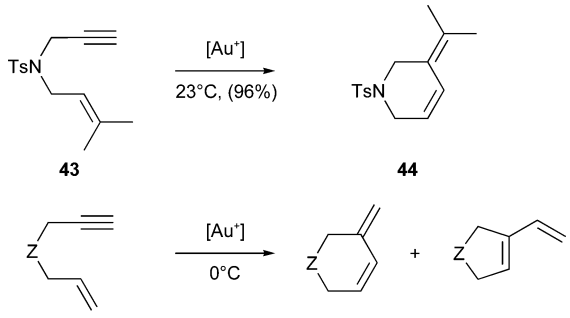


35: Z = C(SO$_2$Ph)$_2$, R^1 = R^2 = H — **39** (100%)
36: Z = C(CO$_2$Me)$_2$, R^1 = Me, R^2 = H — **40** (96%)
37: Z = C(SO$_2$Ph)$_2$, R^1 = Me, R^2 = H — **41** (100%)
38: Z = C(CO$_2$Me)$_2$, R^1 = H, R^2 =Me — **42** (76%)

[Au$^+$] = [Au(PPh$_3$)Cl] / AgSbF$_6$

Scheme 10

Significantly, skeletal rearrangement by an *endo-dig* pathway was observed for the first time with Au(I) catalysts.[23] Thus, enyne **43** gives heterocycle **44**, while enyne **45** affords a 7 : 1 mixture of *endo* (**46**) and *exo* (**47**) rearrangement products (Scheme 11).



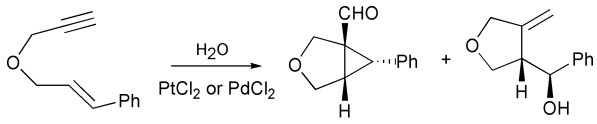
45: Z = C(CO$_2$Me)$_2$ — **46** (67%) — **47** (10%)

[Au$^+$] = [Au(PPh$_3$)Cl] / AgSbF$_6$

Scheme 11

Cyclopropyl carbenes as intermediates

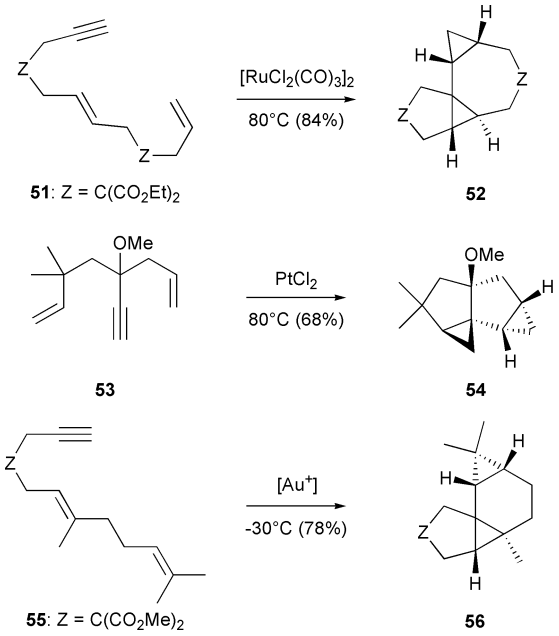
Products of intramolecular cyclopropanation (**5**, Scheme 1) are obtained for enynes where Z = O or NTs.[9,14] An example of cyclopropanation catalysed by $PtCl_2$ is shown in Scheme 7 (**27** → **29**). Cyclopropyl derivatives were occasionally obtained as secondary products in the hydroxycyclisation reactions of enynes. Thus, reaction of substrate **48**, using $PtCl_2$ or $PdCl_2$ as catalysts, leads to cyclopropane **49**, in addition to the expected alcohol **50** (Scheme 12).[16,19]



48 — **49** (10-12%) — **50** (12-40%)

Scheme 12

These results support the involvement of **32–34** as the actual intermediates in the intramolecular reactions of alkenes with alkynes catalysed by electrophilic MX_n. Additional support was obtained by Murai *et al.* in the cyclisation of **51** to give tetracycle **52**, in which a Ru(II) carbene is intramolecularly trapped by the terminal alkene[25] (Scheme 13). Related

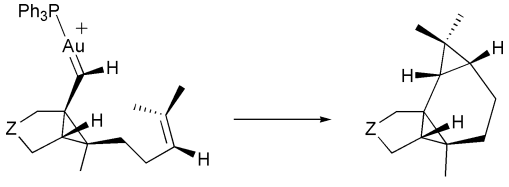


51: Z = C(CO$_2$Et)$_2$ — **52**
53 — **54**
55: Z = C(CO$_2$Me)$_2$ — **56**

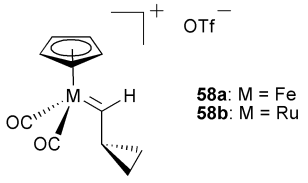
Scheme 13

cyclisations of substrates **53** and **55** are catalysed by Pt(II)[26] and Au(I)[23] complexes, respectively.[27] Other Rh(I) carbenes, formed by intramolecular reactions of carbonyl compounds or imines with alkynes, have been trapped intermolecularly with alkenes.[28]

The polycyclisations shown in Scheme 13 provide tetracycles **52**, **54** and **56** stereoselectively. The stereochemistry of the second cyclopropanation can be rationalised by assuming an antiperiplanar arrangement of the cyclopropane and the metal carbene (*i.e.* **57**, Scheme 14), which is in full agreement with the



57: Z = C(CO$_2$Me)$_2$ — **56**

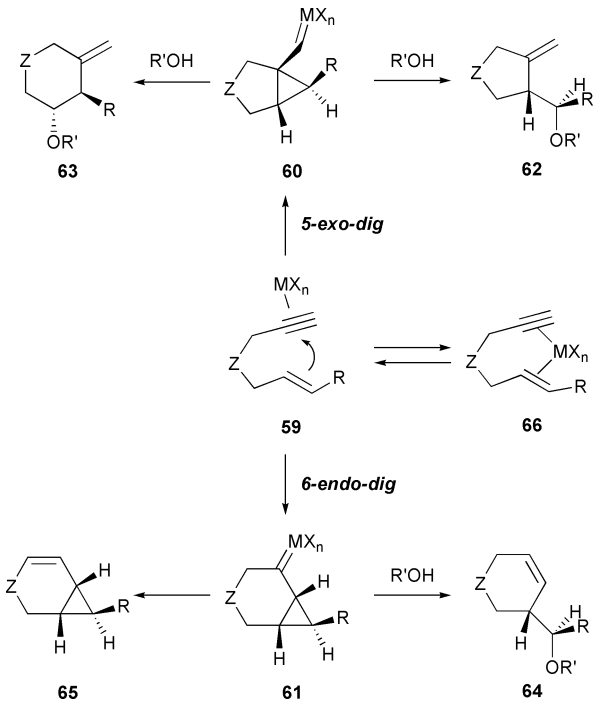


58a: M = Fe
58b: M = Ru

Scheme 14

results of the calculations.[16,21,23] This arrangement is also in accord with the results of Brookhart *et al.*,[29] which show a preferred s-*trans*-anticlinal (antiperiplanar) conformation for iron cyclopropyl carbene (**58a**) and ruthenium (**58b**) complexes.

Calculations and experimental results from the alkoxy- and hydroxycyclisations are in accord with the general mechanistic interpretation summarized in Scheme 15. Thus, coordination

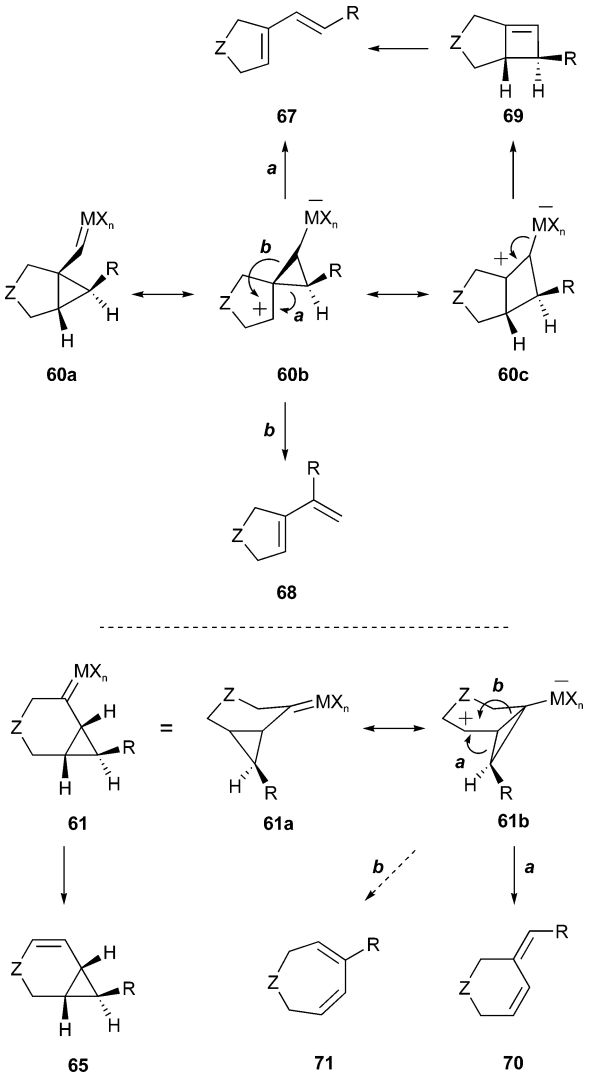


Scheme 15

of MX_n to the alkyne forms an (η^2-alkyne) metal complex **59**. In addition to the 5-*exo-dig* cyclisation to form complex **60**, a 6-*endo-dig* process gives complexes like **61**. Attack of R′OH at the electrophilic cyclopropyl carbons of **60** leads to **62** or **63**. On the other hand, intermediate **61** could suffer nucleophilic attack to give **64** or undergo β-hydrogen elimination to give **65** in the case of Z = O or NTs. The alternative nucleophilic attack at the other electrophilic cyclopropyl centre of **61** would give seven-membered ring compounds, although this process has not yet been observed. The regioselectivity of the nucleophilic attack is controlled by the substitution pattern of the alkene and the electronegativity of the substituent Z. Accordingly, attack at the more substituted site of the alkene is usually observed. Strong electron-withdrawing substituents at the tether Z favour the formation of five-membered ring derivatives **62**, while less electron-withdrawing substituents at the tether favour formation of six-membered ring derivatives **63**.

Although the Alder-ene cycloisomerisation and alkoxy- and hydroxycyclisation processes are mechanistically different, they are related by an equilibrium between species in which the metal coordinates to the alkyne **59** and species **66** where the enyne coordinates to the metal through both the alkyne and the alkene. Calculations show that the equilibrium is shifted towards **59** for $MX_n = PtCl_2$ by the addition of H_2O, which is a better ligand for Pt(II) than the alkene.[16]

Cyclopropyl metal complexes can also be viewed as analogues of the cyclopropyl carbinyl cation.[22] Indeed, skeletal rearrangement of α,ω-enynes **1** is best envisioned *via* the canonical form of **60b** (Scheme 16). Thus, cleavage of bond ***a*** of **60b** would form conjugated dienes **67**, while cleavage of bond ***b*** would furnish dienes **68**.[11] Cyclobutenes **69**, observed in some reactions of α,ω-enynes **1** catalysed by Pd(II),[4,30] Pt(II)[9], Ir(I),[12]



Scheme 16

and $GaCl_3$,[13] could be formed from intermediate **60** (canonical form **60c**). Cyclobutenes **69** can form dienes by a thermally allowed conrotatory opening.[2,4,7]

The *endo* carbenes **61** may evolve by β-hydrogen elimination to give **65** (Scheme 16) (or compounds **5**, Scheme 1). On the other hand, the skeletal rearrangements by a 6-*endo-dig* process (Scheme 11) could be explained by cleavage of bond ***a*** from canonical form **61b** (Scheme 16). The alternative cleavage of bond ***b*** to give seven-membered ring compounds **71** has not been documented until now.

Summary and outlook

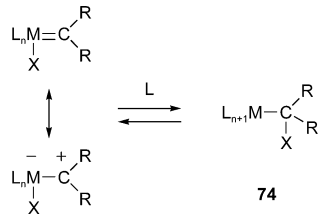
Following the pioneering work of Trost *et al.*[4,5] and Murai *et al.*,[8,12] more recent work has allowed us to establish a clearer picture of the mechanisms followed in the intramolecular reactions of alkynes with alkenes catalysed by late-transition metal complexes. The similarities between this chemistry and the carbocationic rearrangements of the cyclopropylmethyl–cyclobutyl manifold, first pointed out by Fürstner,[9] is remarkable. However, differences undoubtedly exist due to the metal stabilization of the reactive species. Significant progress has been made in broadening the scope of these synthetically useful transformations. At present, cationic Pt(II)[11] and Au(I)[23] complexes are the most reactive (alkynophilic) catalysts for the activation of α,ω-enynes **1** *via* complexes of type **59** (Scheme 15).

The work summarised in this review shows that alkenes react with (η^2-alkyne) metal complexes to form metal cyclopropyl carbenes **72** (Scheme 17) as intermediates. This reaction mode corresponds to an electrophilic addition to an alkene, in which the electrophile is an (η^2-alkyne) metal complex.

72

Scheme 17

Although all experimental and theoretical studies point to metal cyclopropyl carbenes as the likely intermediates in these transformations, it should be stressed that no such carbene has been isolated in any reaction from an enyne and MX_n.[31] Possible alternatives to metal carbenes **73** (Fischer-type) are metal carbenoids[32] **74** (Scheme 18), which could be in equilibrium with the carbene species.



73 **74**

Scheme 18

Other aspects also require further clarification. Thus, the factors that control the *exo*/*endo*-*dig* selectivity in the attack of the alkene on the alkyne as well as the regioselectivity of the skeletal rearrangements (**67** *vs.* **68**, Scheme 16) are not completely understood. In addition, it is not clear if two alternative pathways exist for the formation of dienes **67**, or if these products are formed in all cases by conrotatory ring opening of cyclobutenes **69**. Additional mechanistic work is required to clarify the mechanism of these rearrangements.

Furans have also been shown to react like alkenes (similar to enol ethers)[21] in intramolecular reactions with alkynes catalysed by Pt(II).[33] Whether or not similar pathways are followed in the Friedel–Crafts-type reactions of arenes with alkynes catalysed by electrophilic MX_n complexes[34] remains to be established.

Acknowledgements

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