Metal cyclopropyl carbenes in the reactions of alkynes with alkenes and furans*

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Abstract: Electrophilic transition-metal complexes catalyze the reaction of enynes in the presence of water or alcohols to give hydroxy- or alkoxycyclization derivatives. The reaction proceeds by the anti addition of the alkene and the metal to the alkyne. The key intermediates in this reaction are cyclopropyl metal carbenes, which are also probably involved in the metathesis-type rearrangement of enynes. A general scheme is proposed for the cyclization of enynes initiated by the coordination of the metal to the enyne by transition metals, which included 5-*exo*-dig and 6-*endo*-dig pathways. The intramolecular reaction of furans with alkynes also proceeds via cyclopropyl metal carbenes.

INTRODUCTION

Transition metals catalyze a variety of transformations of diynes, dienes, and enynes that lead to structurally complex products [1,2]. An important group of transformations comprise reactions of α,ω-enynes **1** catalyzed by electrophilic transition-metal complexes or halides MX_n to give carbo- or heterocycles **2–4** (Scheme 1) [3]. A remarkable aspect is the wide variety of transition metals MX_n that are able to promote these transformations, which suggests a rather nonspecific role for the metal in the process.

The first examples were reported by Trost using palladium(II) complexes $[Pd(L_2)X_2]$, which usually favor formation of 1,4-dienes of type **3** [3,4]. Cationic Ru(II) complexes such as $[CpRu(MeCN)_3]^+PF_6^-$ catalyze the cycloisomerization of enynes to give selectively dienes of type **3** under mild conditions [4,5].

Enynes with disubstituted *trans*-alkenes are also cycloisomerized by the early transition-metal complex $Cp_2Ti(CO)_2$ [6]. More recently, cationic Rh(I) complexes have been also shown to be excellent catalysts for the formation of cycloisomerization products **3** [9–11].

Metathesis-type products **4** are also formed in the reactions catalyzed by palladacyclopentadiene complexes [12]. In addition, several electrophilic Ru(II) and Pt(II) complexes catalyze the formation of dienes of type **4** from enynes **1** [12–15]. Complexes $[IrCl(CO)_3]_n$ also catalyze the cycloisomerization or rearrangement of enynes depending on the reaction conditions [16]. Yet another type of cyclization has been observed for enynes tethered by heteroatoms (Z = O or NTs), which give cyclopropanes of type **5** with $PtCl_2$ [14b,c] or $PtCl_4$ [17] as catalysts. This cyclization mode has also been observed in the reaction of an enyne promoted by $Co_2(CO)_8$ [18].
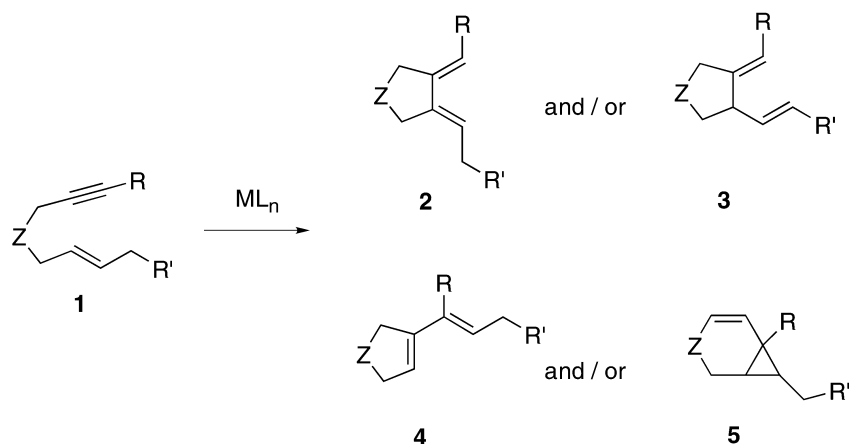
Scheme 1

We found that the intramolecular reaction of alkynes bearing allylsilanes and allylstannanes **6** in methanol affords dienes **7** (Scheme 2) [19]. This reaction allows for the synthesis of five- and six-membered ring carbo- and heterocycles and is catalyzed by a variety of electrophilic metal halides, although more general results are usually obtained with PtCl$_2$ in MeOH. Although this reaction affords products that are similar to **3** obtained in the cycloisomerization processes, the configuration of the exocyclic alkene of **7** is the opposite.
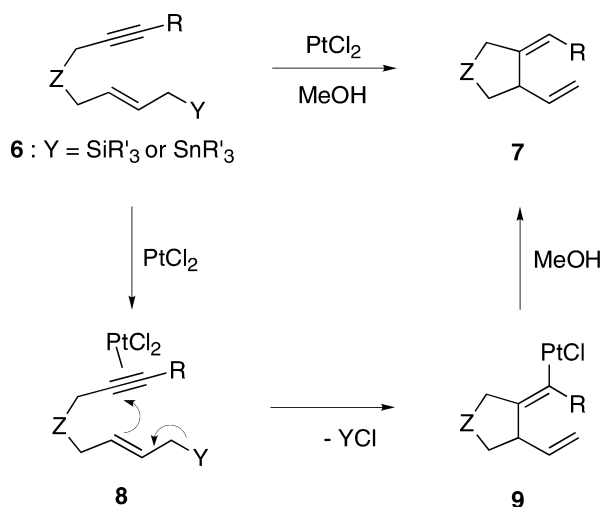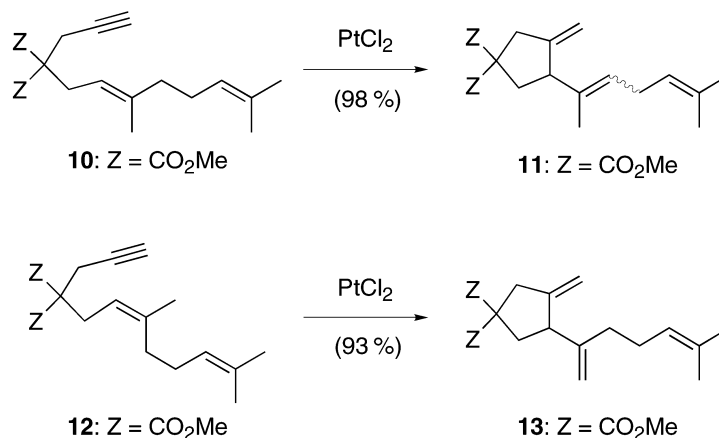

Scheme 2

In this reaction, the transition metal was proposed to coordinate the alkyne to form an electrophilic (η^2-alkyne)metal complex **8**, which could be attacked by the allyl nucleophile to give an alkenyl metal complex **9** in an anti manner. The final diene **7** could be formed by methanolysis of intermediate **9**, as demonstrated by deuteration experiments. In addition, intermediate **9** can be trapped with allyl halides to form an additional C–C bond [19].

The metal could also coordinate both the alkyne and the alkene, although this coordination results in cycloisomerization. Herein we present a unified mechanistic picture of the main reactions that follow the different coordination modes of the metal fragment with the enyne.

CYCLOISOMERIZATION

Cycloisomerization of enynes is also possible with $PtCl_2$ as the catalyst in acetone or 1,4-dioxane [20]. The process results in the formal migration of a hydrogen from the alkyl chain trans to the alkene. Thus, geranyl derivative **10** gives **11** as a 3:1 mixture of *E* and *Z* isomers (Scheme 3). On the other hand, neryl derivative **12** yields **13** as a result of hydrogen abstraction from the methyl group. The cycloisomerization also proceeded with $RuCl_3$ or $Ru(L)_2Cl_2$ as the catalysts.

10: Z = CO$_2$Me   **11**: Z = CO$_2$Me

**12**: Z = CO$_2$Me   **13**: Z = CO$_2$Me

Scheme 3

Deuteration studies demonstrate that the cycloisomerization is a fully intramolecular process. According to DFT calculations performed on (*E*)-2-octen-1-yne complexed to $PtCl_2$ (**14**), oxidative cyclometallation gives platinacycle **15** (Scheme 4). This transformation proceeds with a significant activation energy (E_a = 29.6 kcal·mol^{-1}), although it might be lowered by interaction with coordinating solvents. The optimized structure for Pt(IV) complex **15** shows an octahedral arrangement of the ligands around the d^6 metal center, with two vacant coordination sites. However, in the presence of coordinating solvents, such as acetone or 1,4-dioxane, the coordination sphere might be completed by two additional ligands. Reaction from **14** to **15** is significantly exothermic (25.7 kcal·mol^{-1}), even in the absence of other ligands.

TS$_{14\text{-}15}$

14   **15**
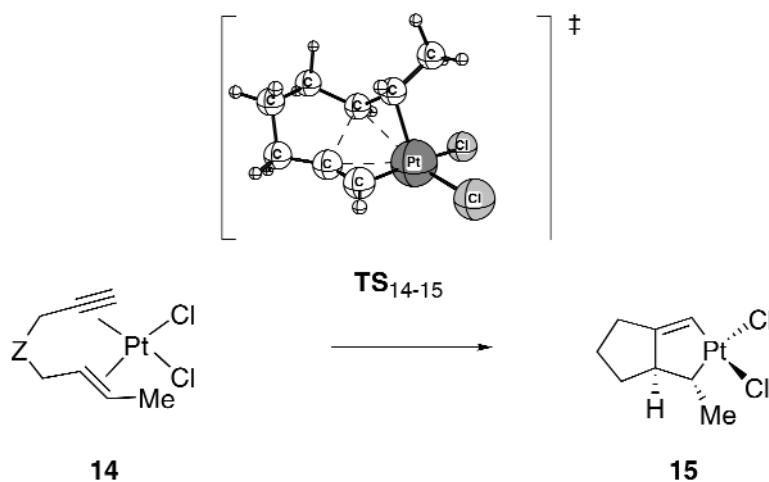
Scheme 4

ALKOXY- AND HYDROXYCYCLIZATION

The reaction of simple enynes **16** with PtCl$_2$ as catalyst in the presence of alcohols or water gives carbo- or heterocycles **17** and **18** (Scheme 5) [20]. In most cases, this reaction takes place preferentially to the Pt(II)-catalyzed addition of ROH to the alkyne to form acetals or ketones [21,22].
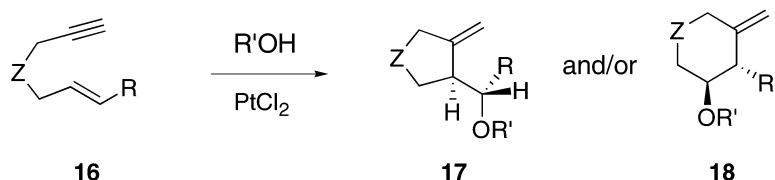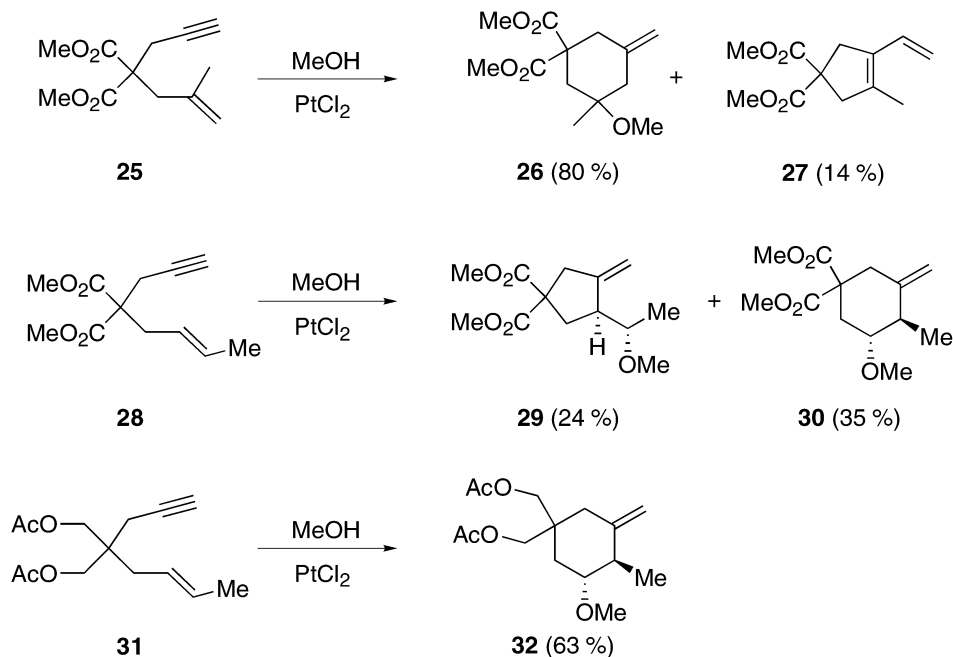

Scheme 5

Representative examples are shown in Scheme 6. Importantly, the reaction is stereospecific, as shown in the transformation of *E*-enyne **19** to **20** and *Z*-enyne **21** to **22**. The reactions proceed, formally, by the *anti*-addition of the alkyne and ROH to the alkene, as demonstrated in the transformation of **27** into **28** (Scheme 6). The alkoxy- and hydroxycyclization can also be promoted by using Ru(II), Au(III), and Pd(II) complexes [23] as catalysts. Recently, the hydroxycyclization reaction can also be catalyzed by Hg(OTf)$_2$ [24].
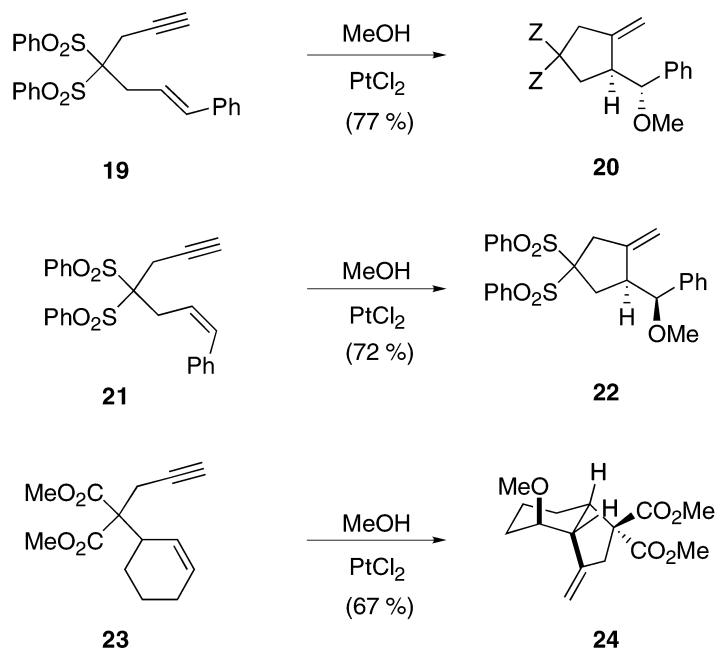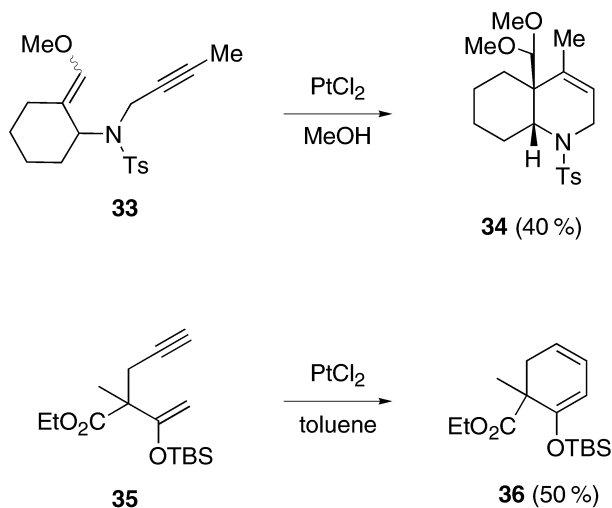

Scheme 6

The 6-*endo*-trig cyclization mode is favored in the cyclization of enyne **25**, with a 2,2-disubstituted alkene. In this reaction, in addition to the cyclohexane derivative **26**, a rearrangement (metathesis-type) product was also obtained as a secondary product (Scheme 7). Interestingly, the 5-*exo*-trig vs. 6-*endo*-trig cyclization selectivity also depends on the nature of the tether of the enyne. Thus, **27** gives a 1:1.5 mixture of 5-*exo*-trig and 6-*endo*-trig products **28** and **30**, whereas **31** gives exclusively 6-*endo*-trig product **32**.
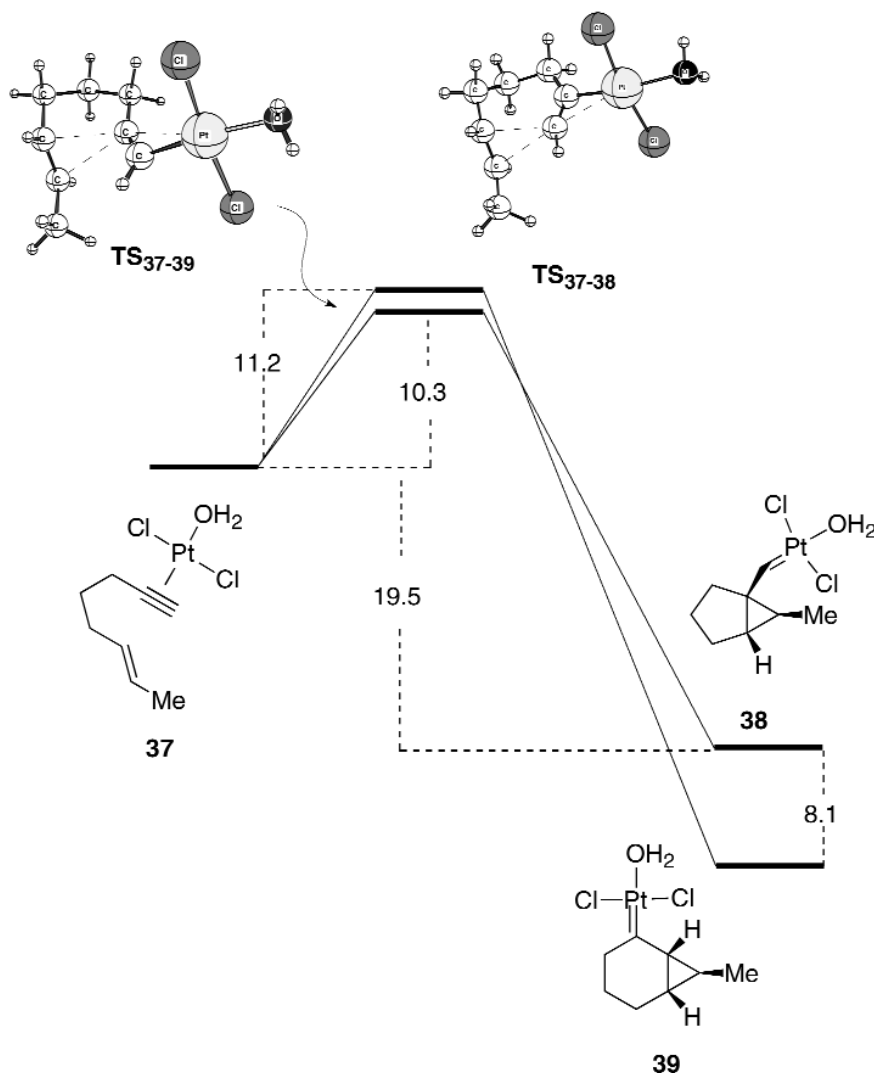
Scheme 7

The 6-*endo*-dig cyclization mode is also possible [25]. Thus, enol ether **33** reacts in methanol to give heterocycle **34** as the only isolated product (Scheme 8). The cyclization of **35** to give **36** illustrates a rare example of a formal 6-*endo*-dig/*endo*-trig process. Related cyclization of silyl enol ethers with alkynes catalyzed by W(CO)$_5$·L (L = THF, amine) proceeds with *exo*-dig or *endo*-dig selectivity depending on the reaction conditions [26]. In this case, tungsten vinylidenes have been proposed to be key intermediates in the formation of the *endo*-dig products. However, the reactions catalyzed by Pt(II), Pd(II), Au(III), and related electrophilic transition-metal complexes, do not proceed through vinylidene complexes as intermediates [27].
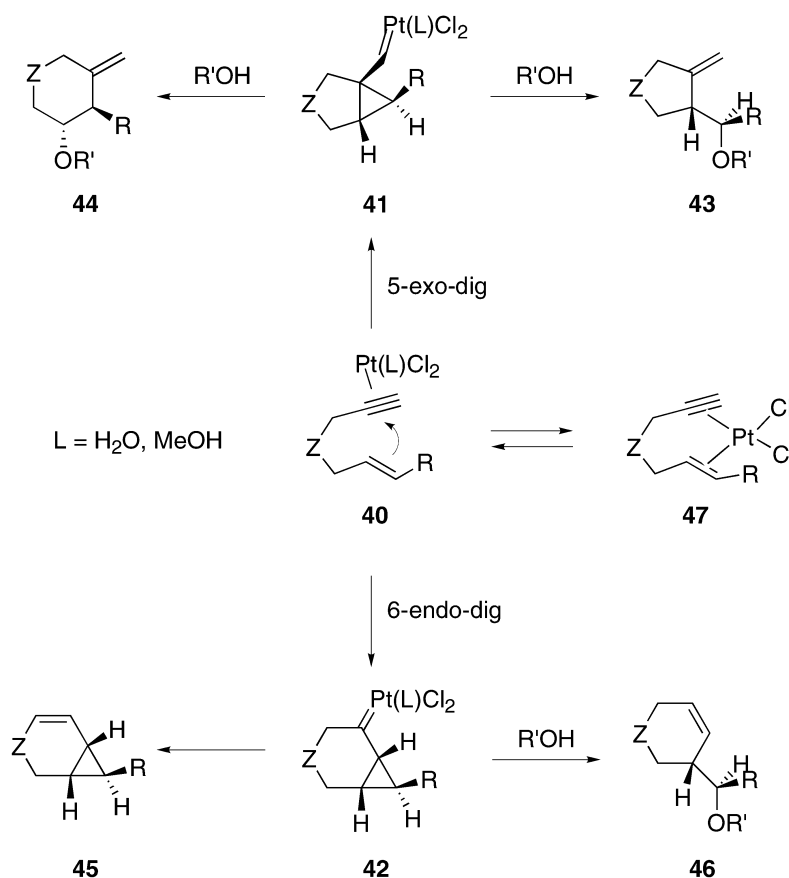

Scheme 8

To analyze the competitive 5-*exo*-dig and 6-*endo*-dig cyclization modes, DFT calculations were performed on 6-octen-1-yne complexed to PtCl$_2$ (**37**) (Scheme 8) [25]. Starting from **37**, we located bicyclic complexes **38** and **39** (Scheme 9), which can be described as platinum cyclopropyl carbenes or methylcyclopropane cations stabilized by PtCl$_2$(H$_2$O). Both reactions are exothermic (–19.5 and –27.6 kcal mol^{-1}), the six-member-ring product **39** being more stable. For related cases, but with an oxygen instead of the methylene at C-4, the 6-*endo*-dig was found to be both kinetically and thermodynamically the most favored process. Similar results were obtained for the analogous AuCl$_3$ complexes.

Scheme 9

The experimental and theoretical results are in accord with the general mechanistic interpretation summarized in Scheme 10. Thus, coordination of PtCl$_2$ to the alkyne forms a (η^2-alkyne)metal complexes **40**. In addition to the 5-*exo*-dig cyclization via complex **41**, a 6-*endo*-dig process gives complexes like **42**. Attack at R′OH at the electrophilic cyclopropane carbons of **41** gives **43** or **44**. On the other hand, intermediate **42** could evolve to give **45** by β-hydrogen elimination or suffer nucleophilic
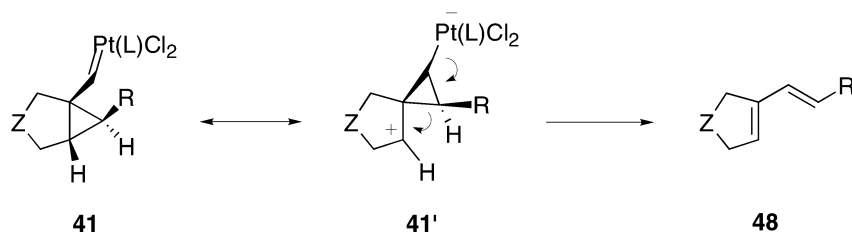
Scheme 10

attack to give **46**. The alternative nucleophilic attack at the other electrophilic cyclopropane center would give seven-membered ring compounds, although this process has not yet been observed.

The regioselectivity in 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, which is in accord with the building up of substantial positive charge in the transition state of the nucleophilic opening of intermediate **41**. Strong electron-withdrawing disulfone substituents favored the formation of five-membered ring derivatives **43** (Scheme 10), while less electron-withdrawing substituents at Z favors six-membered ring derivatives **44**.

The mechanistic proposal outlined in Scheme 10 is fully supported by deuteration experiments on the hydroxy- and methoxycyclizations [20]. In addition, the involvement of intermediates like **41** explains the formation of products with cyclopropane structure that have been isolated in some reactions of enynes [13,20,23,27]. On the other hand, platinum cyclopropyl carbenes can also be viewed as methylcyclopropane cations stabilized by $PtCl_2(H_2O)$, which can evolve by rearrangement pathways reminiscent of those of the cyclopropylmethyl carbocation. Indeed, the formation of metathesis-like products **4** (Scheme 1) can be explained by rearrangement of intermediates like **41↔41′** to form dienes **48** (Scheme 11) [28].
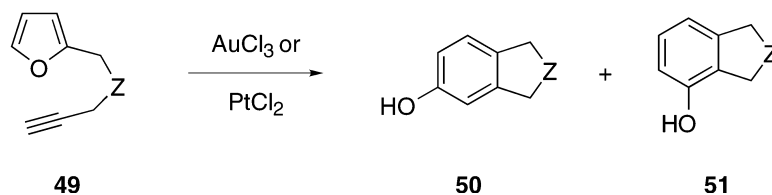
Scheme 11

Although the cycloisomerization and alkoxy- and hydroxycyclization processes are mechanistically distinct, they are related by an equilibrium between species in which the metal coordinates the alkyne **40** and species with the enyne coordinates to the metal through both the alkyne and the alkene **47**. Calculations carried out on a model system indicated that displacement of the alkene ligand of complex **14** (see Scheme 4) by H_2O to give complexes of type **40** (Scheme 10) is an exothermic process.

## FURANS AS ALKENES IN THE CYCLIZATION WITH ALKYNES

The reaction of 5-(2-furyl)-1-alkynes **49** affords phenols **50** and **51** by using $AuCl_3$ as the catalyst (Scheme 12) [29]. The cyclization of substrates like **49** substituted at C-5 of the furan led to phenols of type **51**. This reaction was proposed to proceed by an intramolecular [4+2] cycloaddition promoted by the η^2-coordination of $AuCl_3$ to the alkyne.

Scheme 12

We have found that substrates **52** also give bicyclic phenols **53** and **54** in the presence of Pt(II) catalysts [30]. The scope of the Pt(II)-catalyzed reactions is broad and allows for the ready preparation of functionalized phenols.

Mechanistically, the reaction is quite remarkable since it is initiated by the nucleophilic attack of the furan on a (η^2-alkyne)platinum(II) complex **52** (Scheme 13) to form a platinum cyclopropyl carbene **53**. This reaction is more favorable than the alternative intramolecular [4+2] cycloaddition. This first step is followed by cleavage of a C–C and a C–O bond of the tricyclic intermediate to form a carbonyl compound **54**, which cyclizes to give **55**. Elimination of Pt(L)Cl$_2$ forms oxepin **56**, which is in equilibrium with arene oxide **57**. Finally, opening of the epoxide gives substituted phenol **58**. Therefore, furans behave as reactive alkenes (similar to enol ethers) and react with alkynes by a process that is mechanistically related to that of enynes in polar solvents with $PtCl_2$ as the catalyst.
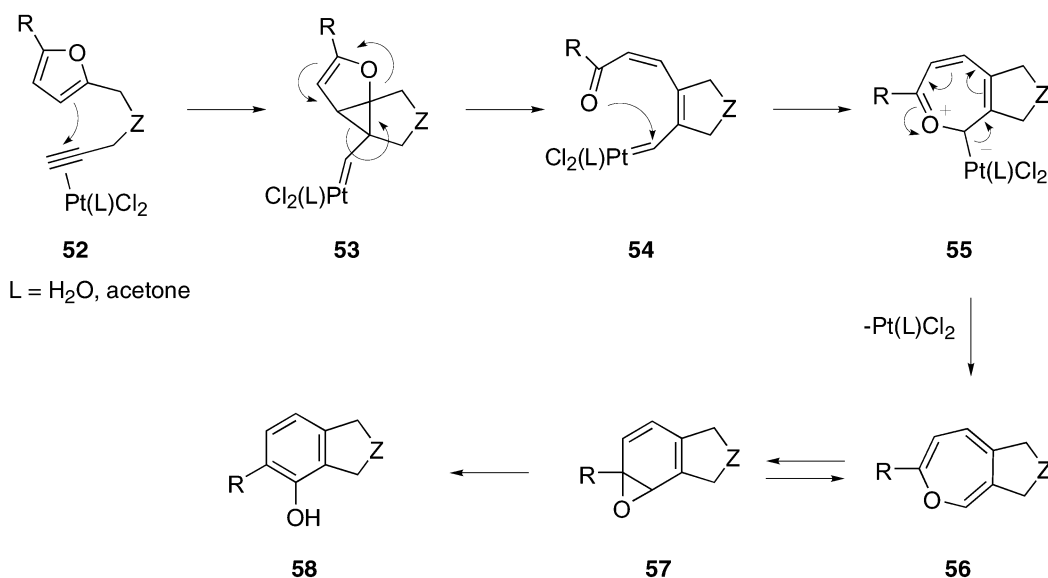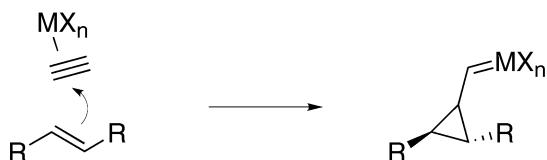
Scheme 13

SUMMARY AND OUTLOOK

Our work had shed light on the involvement of metal carbenes as the key intermediates in the transition metal-catalyzed reactions of alkynes with alkenes or furans. These conclusions support the initial suggestions by Trost [12a,12f] and Murai [13c] on the involvement of this type of intermediate in the cyclizations of enynes.

From a fundamental point of view, our work shows that an alkyne reacts with a (η^2-alkyne)metal complex to form platinum cyclopropyl metal carbenes (Scheme 14) as the reactive intermediates. This reaction mode corresponds to an electrophilic addition to an alkene, in which the electrophile is a (η^2-alkyne)metal complex.

Scheme 14

Although the main pathways in these transition metal-catalyzed processes are now reasonably understood, a number of aspects require additional clarification. Thus, it is not clear why metathesis is preferred over cycloisomerization in the absence of coordination solvents. In addition, the factors that control the *exo/endo* selectivity on the attack to the alkyne are not clearly understood.

Finally, electron-rich arenes also react intramolecularly with alkynes in the presence of transition metals as catalysts [31–33] to give products of apparent Friedel–Crafts-type reactions. However, these, and related reactions of heteroaromatic compounds with alkynes, might also be explained by mechanisms involving the formation of platinum cyclopropyl carbenes. Additional mechanistic work (theoretical and experimental) is clearly needed in other to fully comprehend these processes.

ACKNOWLEDGMENTS

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