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Mini Review

Cyclopropenation of organometallic vinylidene complexes

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Abstract

The chemistry of metal cyclopropenyl complexes derived from deprotonation of cationic ruthenium vinylidene complexes is reviewed. Such a metal coordinated cyclopropenyl ligand can be used for the preparation of heterocyclic compounds. The chemical reactivity of cyclopropenyl complexes is influenced by the nature of substituents on the three-membered ring and by the nature of ancillary ligand around the metal centers. © 2001 Published by Elsevier Science B.V.

Keywords: Cyclopropenation; Organometallic vinyldiene complexes; Heterocyclic compounds

1. Introduction

Cyclopropene has been under intensive investigation [1] and has played a crucial role in the development of important concepts such as ring strain and aromaticity. The chemical reactivity of this molecule has also been studied in great detail [2]. Comparatively, little is known on metal coordinated cyclopropenes, either in σ- or π-coordination mode. The strain energy of cyclopropene is estimated to be more than 50 kcal mol^{-1} [3], which is expected to decrease via participation of a d-orbital by coordination to a transition metal. Three general methods are known for the synthesis of cyclopropenes [4]: addition of a carbene to an alkyne [5], ring closure of a vinylcarbene [6] and 1,2-elimination of a suitable precursor such as halocyclopropane [7]. Yet, a general synthetic method for metal-coordinated-cyclopropenes is still lacking. It has been suggested [1] that vinylidene (R_2C=C) is an intermediate in the thermal rearrangement of cyclopropene. When substituted cyclopropenes are heated or irradiated, complex mixtures of 1,3-dienes, allenes, and acetylenes are formed [8], strongly suggesting that the formation of acetylene involves vinylidene as an intermediate. Some theoretical results also suggest that acetylenic products are formed from vinylidene produced through bond breaking and hydrogen shift [9]. It thus appears that vinylidene is an important intermediate in the thermal rearrangement of cyclopropene to acetylene [10]. However, organic vinylidene is thermodynamically unstable and evidence for its existence are derived mostly from the reaction products. It has been shown that vinylidene can be stabilized by complex formation with transition metals affording stable organometallic compounds. Particularly the mononuclear ruthenium(II) moieties, $CpRu(PR_3)_2$ ($Cp = \eta^5$-C_5H_5), play an important role [11] in stabilizing [Ru]=C=CRR′ derivatives.

Metal vinylidene complexes offer the possibility of development of new types of organometallic intermediates that may have unusual reactivity. Reviews on this subject have appeared in the literature [11]. Recent advance in this field has made possible the transfer from stoichiometric to catalytic reactions [12]. The best entry [13] into transition metal vinylidene complexes is the addition of electrophiles to electron-rich carbon of metal alkynyl complexes. Theoretical studies of vinylidene complexes disclose localization of electron density at C_β (HOMO) or at the M=C double bond and electron deficiency at C_α [14]. Thus the M=C double bond and C_β are more susceptible to electrophilic attack, whereas the C_α atom is liable to nucleophilic

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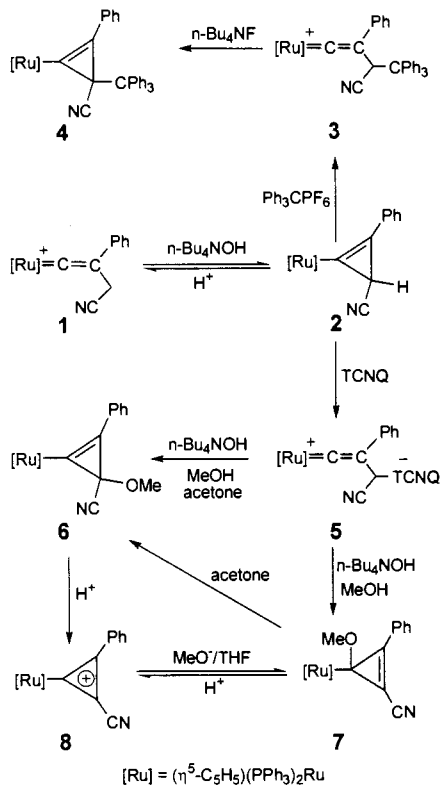
attack [15]. Hence, the reactions of such compounds containing electron-rich metals with electrophiles lead to the formation of carbene complexes [16]. On the other hand, their reactions with nucleophiles generally result in the formation of vinyl derivatives. With a more electron rich metal center, addition to the M=C bond yields an η^2-allene- or heteroketene-metal complexes [17]. A study [18] on the reaction of alcohols with Ru vinylidene complexes has shown that the electron-withdrawing groups on the acetylide unit or on the metal facilitate nucleophilic attack at C_α.

On the basis of the aforementioned property of metal vinylidene complex it is anticipated that placing an electron-withdrawing functionality at C_γ could enhance the acidity of its neighboring proton thus enabling an intramolecular cycloaddition leading to the base-induced formation of a cyclopropenyl complex. We have investigated a number of ruthenium [19–23] and molybdenum [24] vinylidene complexes containing cyclopentadienyl, pentamethyl-cyclopentadienyl and tris(pyrazol-1-yl)borate ligand (Tp, $B(C_3H_3N_2)_3$) and demonstrated that deprotonation could indeed lead to preparation of cyclopropenyl complexes under mild conditions. This article summarizes mostly our recent work in this field.



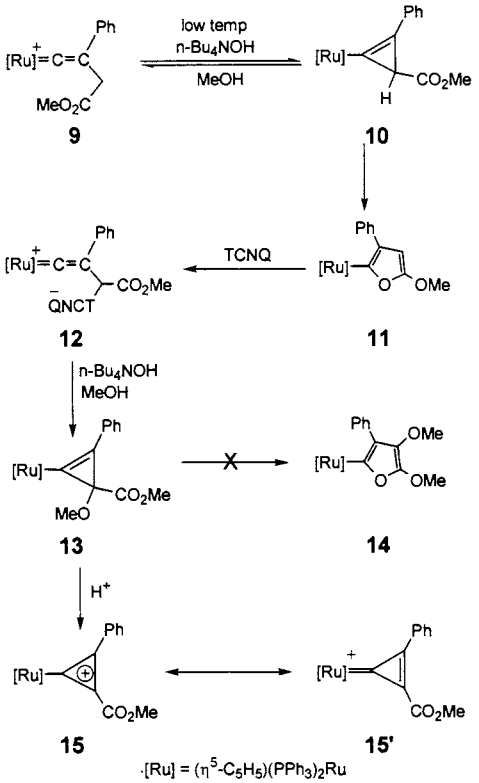
Scheme 1.

2. Cyclopropenation of metal vinylidene complexes

Of many chemical properties of metal vinylidene complexes, electrophilicity at the C_α is utilized in our strategy to design cyclopropenyl complexes. In addition, an electron-withdrawing group attached to C_γ of the vinylidene ligand is used to enhance the acidity of the proton on C_γ, allowing its removal by a base. Using various commercially available halides, a number of vinylidene complexes [M]=C=C(Ph)CH_2R^+ ([M] = (η^5-C_5H_5)$(PPh_3)_2$Ru, (η^5-C_5Me_5)$(Ph_2P(CH_2)_3PPh_2)$Ru, (Tp)$(PPh_3)_2$Ru, (η^5-C_5H_5)$(Ph_2P(CH_2)_2PPh_2)$Mo; R= CN, Ph, CH=CH_2, CH=CMe_2, $COOCH_3$, $COOC_2H_5$, OCH_3) have been prepared. The treatment of these vinylidene complexes with a base afforded cyclopropenyl complexes, a reaction much influenced by the nature of its solvent. The best yields were obtained in acetone. No cyclopropenation reaction was observed in CH_3CN or MeOH. For the preparation of **2** from **1** (Scheme 1), various bases such as *n*-Bu_4NF, *n*-Bu_4NOH, DBU (1,8-diazabicyclo[5.4.0]undecene), and KOH were used. For other vinylidene complexes, the use of *n*-Bu_4NOH as a proton abstractor gave better result and the reactions generally slower. A facile deprotonation is indicative of the acidic nature of the methylene proton next to the vinylidene ligand, which may be ascribed to a combined effect of the cationic character, the electron withdrawing substituent and the benzylic/allylic property of the vinylidene complexes. It also appears that the hybridization at C_δ should either be sp or sp^2 for the cyclopropenation to occur. For the cyclopropenyl complex, the cyclization reaction also results in the formation of a stereogenic carbon center in the three-membered ring, making this cyclization process potentially useful for organic synthesis. The ^{31}P-NMR spectrum of cyclopropenyl complex displays resonances with two doublets patterns arising from this stereogenic three-membered ring, in contrast to the singlet pattern generally observed for vinylidene complexes. Thus, the reaction can be readily monitored by NMR spectroscopy. The stability of cyclopropenyl complexes in solution follows the trend CN > Ph > CH=CH_2 > CH=CMe_2. Ancillary ligands on the metal and substituents on the cyclopropenyl ring govern the reactivity of metal complexes.

3. Ruthenium complex with a CN group on the cyclopropenyl ligand

The electron-withdrawing CN substituent in the vinylidene ligand of **1** (Scheme 1) not only imposes high acidity to the neighboring methylene group thus giving rise to high yield of **2**; it also stabilizes the cyclopropenyl ligand after deprotonation [19]. Reactions of this complex are summarized in Scheme 1. The crystal



Scheme 2.

structure of **2** indicates that two C–C single bonds of the three-membered ring are significantly different. The two C–C bond lengths are 1.58(1) and 1.45(1) Å. Many cyclopropenyl complexes possess this feature, namely, the C–C bond near the metal center being significantly longer. C–C Cleavage was observed only for the longer bond. However, such a cleavage is not depending on the bond length. Indeed, the presence of a methoxy group on the three-membered cyclopropenyl ring led to a change of such a property. While there remain significant differences between the bond lengths of two C–C single bonds, the three-membered ring is more stable toward electrophilic addition. In the absence of a methoxy group on the ring, electrophiles readily add to the sp^3 carbon of the three-membered ring to cause ring opening forming the vinylidene ligand. An attempt to prepare the cyclopropenylium complex **8** by treating **2** with Ph_3CPF_6 caused addition of the trityl group to the three-membered ring resulting in the formation of **3**, which could be further deprotonated to give **4**, with Ph_3C^+ serving as an electrophile.

Complex **8** was prepared via an indirect route shown in Scheme 1. TCNQ was first used as an electrophile, which adds to the methyne carbon resulting in a weak C–C bond formation (1.60(1) Å from X-ray diffraction analysis) and an opening of the three-membered ring affording the zwitterionic vinylidene complex **5**. Chemical shifts of ^{31}P-NMR resonances of **5** fall in the same region as that of other cationic complexes indicating the cationic nature of the Ru center and the localization of the negative charge at TCNQ. The reaction of **5** with MeOH in the presence of Bu_4NOH resulted in the formation of a mixture of **6** and **7**. In the absence of n-Bu_4NOH, no reaction occurred. Replacing MeOH with EtOH yielded an ethoxy product analogous to **6**. In acetone **7** converted into **6**. The protonation of **6** or **7** led to the loss of MeOH yielding the cyclopropenylium complex **8**. Such a reactivity is different from the opening of the three-membered ring of **2**, and yet similar to the reactivity of organic cyclopropenes possessing a methoxy substituent [25]. The reaction of MeONa with **8** in THF gave **7** which is stable in THF and converts to **6** in acetone. This result reveals the influence of a methoxy group present in the three-membered ring, which effectively maintains the three-membered ring through protonation reaction. The fact that the reaction requires a base may be indicative that the deprotonation step may still be the first one in the formation of **6**. Cleavage of the weak C_γ–C(TCNQ) bond accompanying the addition of the MeO group initially at C_α, followed by a shift to C_γ satisfactorily accounts for the formation of **6**. The crystal structure of **6** reveals that the C–C bond near the Ru center (1.541(4) Å) is significantly longer than the other one (1.447(5) Å). However, in the deprotonation process, the presence of a stronger nucleophile prohibits formation of the MeO-substituted complex **6**. For example, the reaction of **5** with n-Bu_4NCN in the presence of MeOH does not yield **6** but brings about addition of a CN group along with the removal of TCNQ, giving [Ru]–C=C(Ph)C$(CN)_2$. The protonation of this cyclopropenyl complex containing no MeO substituent produces the vinylidene complex $[Ru{=}C{=}C(Ph)CH(CN)_2^+$.

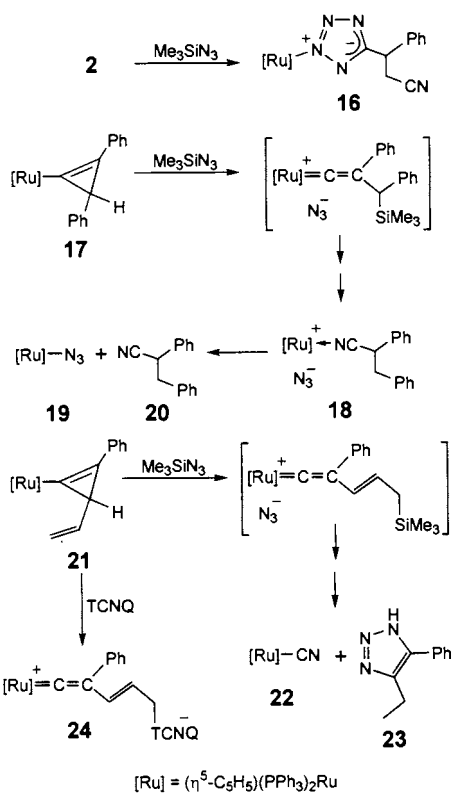
4. Chemistry of a ruthenium cyclopropenyl complex bearing an ester substituent

When the CN group was replaced by an ester group, the three-membered cyclopropenyl ligand was unstable and converted to a less-strained furanyl ligand [20]. As shown in Scheme 2, the cyclopropenyl complex **10** can be prepared from the reaction of **9** with a base only at low temperature. The more stable furanyl complex **11** was obtained as a thermodynamic product. The protonation of **10** occurred in MeOH giving back **9**. From an X-ray diffraction study, the C–O bond length of 1.442(8) Å near the Ru center in the five-membered ring was again longer than the other of 1.347(8) Å. Opening of the five-membered ring by TCNQ also gave the zwitterionic vinylidene complex **12** and the deprotonation reaction in the presence of MeOH gave the methoxy-substituted cyclopropenyl complex **13**. Interestingly, unlike **10** which is a kinetic product, the

cyclopropenyl complex **13** with a methoxy substituent and an ester group was stable even under thermolytic condition. The transformation of **13** into **14** was not observed. The presence of a methoxy substituent influences reactivity of these complexes, namely, protonation yields the cyclopropenylium complex **15**, which has a resonance form **15′**. The cyclopropenyl ligand with one vinyl and one MeO group cannot be obtained via electrophilic addition of TCNQ, since the addition of TCNQ takes place at the terminal vinyl group of **21**, Scheme 3, whereas TCNQ can no longer be removed in its subsequent reaction with a base. The effect of MeO group in stabilizing the cyclopropenyl ring is consistent with what has been observed in many analogous organic compounds [26]. With the TCNQ group present at a distant carbon atom, complex **24** (Scheme 3) is inert in n-Bu_4NOH–MeOH. Interestingly, an ester containing cyclopropenyl ligand bonded to the (C_5Me_5)(Dppp)Ru moiety is also found to be stable with respect to the expansion to a five-membered ring [23]. This could possibly due to steric effects of ancillary C_5Me_5 and dppp ligands.

5. Reaction of cyclopropenyl complexes with $TMSN_3$

The cyclopropenyl ligand of these complexes was used for the organic synthesis. A clean reaction [21] was observed in its reaction with $TMSN_3$ as shown in Scheme 3. The substituents on the three-membered ring again have noticeable effects on the reactivity of these complexes. For the reaction of the CN substituted cyclopropenyl complex **2** with $TMSN_3$, the formation of the tetrazolate complex **16** was observed. Complex **17** with a phenyl group in the cyclopropenyl ring reacted with $TMSN_3$ to give **18** containing a coordinated nitrile ligand. Then substitution by the counter anion occurred to give **19** and an organic nitrile **20**. Formation of **16** and **18** can be accounted for by electrophilic addition of Me_3Si to the sp^3 carbon of the three-membered ring, causing ring opening to give a vinylidene intermediate. Hydrolysis of the TMS group and nucleophilic addition of azide at C_α of the resulting vinylidene portion gave a new N–C bond. Formation of the nitrile complex **18** can then be explained by loss of N_2. The formation of **16** could be the result of a further [2 + 3] cycloaddition of the nitrile ligand with an excess Me_3SiN_3 accompanied with a metal migration to a nitrogen atom of the resulting tetrazolate ligand.

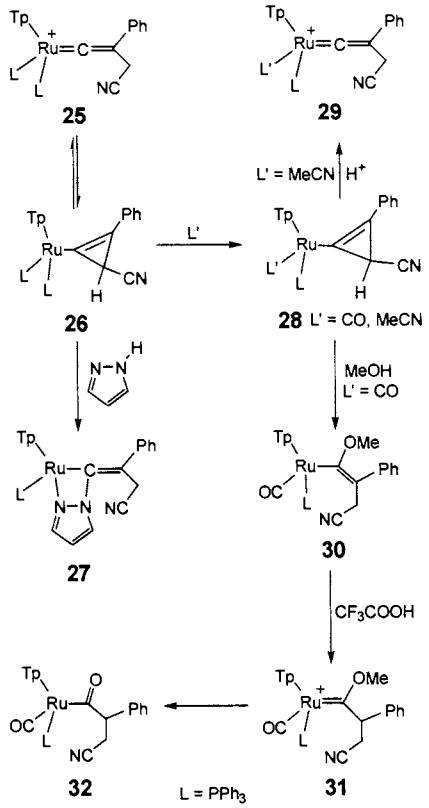


Scheme 3.

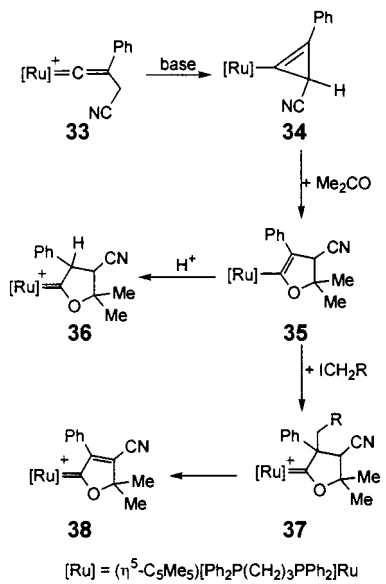
The vinyl group in **21** induces a significantly different reactivity in its reaction with $TMSN_3$, which gave **22** and an organic triazolate product **23**. The net effect of this series of reactions from a metal acetylide to **22** is the cleavage of the triple bond of acetylene to form a cynide ligand. The transformation of the vinyl group to an ethyl group indicated that the reaction possibly sets out at the terminal vinyl group. This is similar to what was observed in the reaction of TCNQ with **21** where electrophilic addition takes place at the terminal carbon atom of the vinyl substituent but not at the three-membered ring. The reaction of TCNQ with **21** yields the zwitterionic vinylidene complex **24** with TCNQ attached to the terminal carbon atom of the allylic unit. The relatively more electron-rich vinyl group of **21** serves as a better nucleophilic center than the sp^3 carbon of the three-membered ring.

6. Facile displacement of a phosphine ligand of Tp ruthenium cyclopropenyl complexes

Ancillary ligands around the metal center modify the chemical reactivity of cyclopropenyl complexes. The Cp ruthenium cyclopropenyl complexes **2**, **17**, and **21** are stable with respect to ligand substitution reactions i.e. two phosphine ligands are strongly bound to the ruthenium center, making the coordination site unavailable for an incoming substrate. Replacement of Cp with a Tp (tris(pyrazol-1-yl)borate) [27] ligand in cyclopropenyl complexes brings about lability to one of the phosphine ligand [22]. Deprotonation of the vinylidene complex **25** containing a Tp ligand also resulted in the formation of the cyclopropenyl complex **26**. The chemistry of this complex is shown in Scheme 4. The phos-



Scheme 4.



Scheme 5.

phine ligand in the precursor vinylidene complex **25** is not activated toward substitution, but the phosphine ligand in **26** becomes labile and substitution readily occurs. Substitution can take place for two-electron-donor ligands, such as CO, CNR, MeCN, and nitrogen donor ligands. The reaction of **26** with CNR, MeCN gave **28** (L′ = CNR and MeCN). However, the reaction of **26** with pyrazole did not yield the expected neutral substituted cyclopropenyl complex giving instead, the metallacyclic complex **27**. The reaction proceeds via substitution of a phosphine ligand by a pyrazole molecule. Subsequent protonation by NH on the coordinated pyrazole opens the three-membered ring. Then, nucleophilic addition of this pyrazolic nitrogen atom to C_α gives **27**. Similar metallacyclic structures with a five-membered-ring were reported [28]. The cyclopropenyl ligand is also susceptible to electrophilic attack in Tp complexes. The reactions of CF_3COOH with **26** and **28** yield **25** and **29**, respectively, indicate the basic character of the methyne carbon of the three-membered ring.

The reaction of **28** with CO in the presence of MeOH gives the vinyl ether complex **30**. The formation of **30** can be rationalized in terms of the following mechanism. The reaction of **28** with CO in the presence of MeOH causes substitution of a phosphine ligand by a CO group. This is followed by protonation of the three-membered ring by MeOH, possibly giving a vinylidene intermediate, yielding **30** after subsequent addition of MeO^-. In the absence of MeOH, the reaction gives an unstable complex, possibly a simple substitution product. The reaction of **30** with CF_3COOH ultimately leads to the formation of the acylruthenium complex **32**. When the reaction was followed by ^{1}H-NMR spectroscopy, the initial formation of the cationic alkoxycarbene complex **31** was apparent, followed by a slow reaction giving **32**.

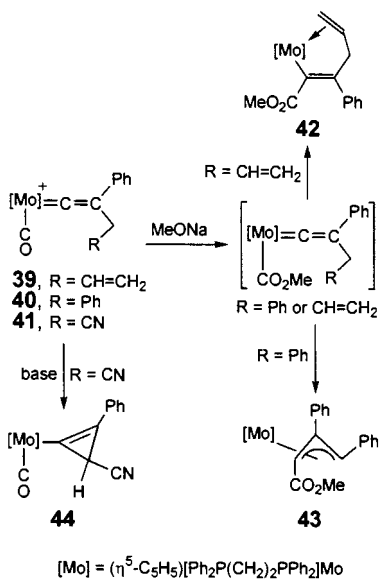
7. Insertion of a carbonyl group into the cyclopropenyl C–C bond

When the Cp ligand is replaced by a pentamethylcyclopentadienyl ligand and two triphenylphosphines by a dppp (diphenylphosphinylpropane) ligand, complex **34** can also be prepared from deprotonation of **33** [23]. A novel insertion reaction of the carbonyl group of acetone into one of C–C single bonds of the three-membered ring of **34** led to the dihydrofuranyl complex **35** (Scheme 5). This reaction, unique to the combination of these two ligand, can be reasonably explained by the enhanced nucleophilic nature of the sp^3 carbon of the three-membered ring by pentamethylcyclopentadienyl and dppp ligands. The double bond in the five-membered dihydrofuranyl ligand plays an essential role for subsequent reactions. Electrophilic additions take place at the remote sp^2 carbon atom, giving carbene complexes **36** and **37**. For **37**, elimination of small organic molecules from the five-membered ring readily occurs to yield **38**. In addition, in this system, the cyclopropenyl complex bearing an ester substituent could be stabilized probably by the bulkier pentamethylcyclopentadienyl ligand.

8. Chemistry of molybdenum vinylidene complexes

To study cyclopropenyl complexes of other metals, we selected a Mo system [24]. It is known that the presence of a donor ligand assists preparation of cationic metal vinylidene complexes [11]. Indeed the presence of a CO ligand could be utilized to study carbon–carbon bond formation. Therefore, we chose a molybdenum vinylidene system containing a $Cp(Ph_2PCH_2CH_2PPh_2)(CO)Mo$ group [29]. Preparation of vinylidene complexes **39**–**41** can be achieved by using synthetic method in ruthenium system. Treatment of these vinylidene complexes containing a terminal CO ligand with sodium methoxide afforded products via a coupling of a methoxycarbonyl group with the C_α of the vinylidene ligand (Scheme 6) [30]. Coupling reactions involving C_α of a vinylidene ligand on the metal complex are limited in the literature. The site preference for this coupling reaction is possibly due to the relatively strong Ru=C bond and proximity of the two groups on the ruthenium metal center.

Treatment of **39** with MeONa caused nucleophilic attack to occur at the terminal CO ligand. This was followed by a coupling reaction of the resulting methoxycarbonyl group with C_α of the vinylidene ligand and accompanied with coordination of the terminal olefin to afford **42**. The terminal olefin group, acting as a two-electron donor, fills into the vacant site generated by the coupling reaction. Moreover, from X-ray diffraction analysis of **42**, the terminal olefin appeared to be oriented such that the C=C bond was contained in a symmetry plane defined by the metal and the center of the Cp ring. Similar coupling was observed when **40** was treated with MeONa, but the reaction afforded the neutral allylic complex **43**. Due to the lack of a terminal olefin donor group, the vinylidene ligand in **40** transforms to an η^3-allylic ligand of **43**, possibly by coupling followed by a 1,3-hydrogen shift. Treatment of **39** or **40** with n-Bu_4NOH, DBU and n-Bu_4NF gave no reaction.



Scheme 6.

Treatment of **41** with MeONa in MeOH gave an unstable green complex. The FAB mass spectrum of this complex displays peaks that could be attributed to the cyclopropenyl complex **44**. In the IR spectrum of **44** the absorption at 1846 cm^{-1} is assigned to the vibrational stretching of the terminal CO ligand indicating that there is no nucleophilic addition. In addition, in the ^{31}P-NMR spectrum, chemical shifts of two singlet resonances differ significantly from the range observed for **42** and **43**. Only spectroscopic data of **44** are obtained and there is no established data for a molybdenum cyclopropenyl complex for comparison. The unstable nature of **44** is somewhat surprising since in the ruthenium system, the presence of an electron-withdrawing CN substituent stabilizes a number of cyclopropenyl complexes. In this Mo vinylidene system with a terminal CO ligand, the CN group provides no similar effect. In our attempts to carry out addition reactions of **41** using nucleophilic reagents other than MeO^-, we did not observe any coupling products as in the reactions of **42** and **43**.

In the literature there are other types of metal cyclopropenyl derivatives. When the metal is bound to the sp^3 carbon of the cyclopropene ring the three-membered ring can be viewed as an antiaromatic cyclopropenide ion [31]. A few different transition metal cyclopropenylidene complexes, mostly prepared from dichlorocyclopropene [32] and a number of π-cyclopropene complexes [33], are also known.

9. Concluding remark

Previously, relatively little is known on cyclopropenyl complexes with an M–C(sp^2) bond. We have demonstrated that this kind of cyclopropenyl ligand is readily obtainable via deprotonation of a methylene group bound to a vinylidene ligand at the γ carbon substituted by an attracting group. The concept can be applied to the synthesis of a wide range of cyclopropenyl complexes containing different substituents or with various ancillary ligands on the metal. These complexes display a rich chemical reactivity. By comparing the protonation reactions of our neutral cyclopropenyl complexes, leading to cationic vinylidene complexes, with the same type of reaction of similar complexes reported in the literature [25], it was noted that the cyclopropenyl complex containing a methoxy substituent, which leads to cyclopropenylium complex upon protonation, behaves differently from those without such a group. It is thus clear that the sp^3 carbon center of the cyclopropenyl complexes **3** without an alkoxy group is an electron-rich center. Thus, it is inapplicable to use simple nucleophilic substitution reaction for direct ad-

dition of groups such as CN or OMe to the three-membered ring. However, when TCNQ was employed for this purpose, the addition reaction could be modified, leading eventually to the formation of the cyclopropenyl complex with a methoxy substituent, which displays higher stability of the three-membered ring. Thus in the ruthenium system, use of TCNQ appears to serve as an entry to the cyclopropenylium complex. For the aforementioned Mo system, the three-membered ring can not be readily acquired. Although ruthenium is known to stabilize a large variety of vinylidene ligands, there are other metal systems that could make organometallic vinylidenes stable as well. Such a deprotonation-induced-cyclization process can thus be widely applied to discover new reactivity patterns of vinylidene ligands in various metal systems. The idea to make nucleophilic addition by taking advantage of electrophilic C_α has been applied to prepare cyclic ligands with five- or six-membered or even larger ring systems. We believe that such a property in transition metal complexes can be manipulated exquisitely to devise new ligand for the synthesis of useful complexes.

Acknowledgements

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