Transition Metal-Catalyzed and -Promoted Reactions via Carbene
and Vinlylidene Complexes Generated from Alkynes†

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The transition metal-induced in situ generation of carbene complexes from alkynes having a carbonyl or imino group as a nucleophilic functionality has been investigated. These reactive carbenoid species are generated with high atom efficiency through a 6-endo-dig cyclization mode based on the electrocyclization of vinylidene complexes or a 5-exo-dig cyclization mode in π-alkyne complexes, and have been found to serve as versatile intermediates in catalytic carbene transfer reactions. Highlighted and reviewed in this account are the generation and preparation of pyranylidene, furylcarbene, pyrrolylcarbene, and vinylcarbene complexes and their application to [3,3]sigmatropic rearrangement of acyclocyclopropylvinylidene, catalytic cyclopropanation reactions, [2,3]sigmatropic rearrangement or condensation reactions via ylides, ring-opening and substitution reactions with heteroaromatic compounds, and catalytic isomerization of oligynes.

Key Words: Transition metals, Alkyne activation, Vinlylidene complexes, Carbene complexes, Catalytic reactions

Introduction

Transition metal-catalyzed and -promoted reactions involving carbene intermediates are powerful and useful methods for constructing important substructures of targeted molecules, and therefore they have been extensively studied for the past couple of decades.1 The in situ generation of metal carbene species is applicable to a wide range of carbene transfer reactions and has attracted recent attention in organic synthesis. One of the most common methods for in situ generation of metal carbene species is a decomposition reaction of diazoalkanes by transition metal compounds.1a,b The diazoalkane method is quite useful, but formidable because of its explosive hazard and a number of unfavorable side reactions. In this context, safe and sure alternatives for the diazoalkane method have been eagerly sought. The activation of alkynes with transition metal compounds has recently emerged as a new methodology to ensure the in situ generation of the metal carbene species.2,3 Vinlycarbene intermediates in enyne metathesis,4 cyclopropylcarbene species in the cycloisomerization of enynes,5,6 dialkylidene metal species via reductive cyclization of o-diyynes,7 and vinylcarbenes and/or metal-containing benzopyrylium from alkynes bearing nucleophilic functional groups8 have exemplified the rapidly emerging class of carbene species.

Recently, we have sought to develop new transition metal-catalyzed or -promoted reaction using carbonyl-ene-yynes A as precursors of metal carbene species, and found new types of reactions involving 5-exo-dig cyclization based on the coacrate reaction of π-alkyne complexes, as well as 6-endo-dig cyclization based on the electrocyclization of vinylidene complex intermediates, leading to six-membered 2-pyranylidene complexes B and five-membered (2-furyl)carbene complexes C (Scheme 1).2 We have also demonstrated that cyclization in the 5-exo-dig manner could be applied to similar structures, propargyl esters D, to yield vinylcarbene complexes E (Scheme 2).2

All of these reactions are promoted by a wide range of

† This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

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transition metal compounds. Moreover, these reactions are highly atom-economical and widely applicable to catalytic carbene transfer reactions. This account describes our recent progress in this field, particularly focusing attention not only on the in situ generation of metal carbene species from alkynes possessing a carbonyl, a thiocarbonyl, or an imine, but also on the application to catalytic carbene transfer reactions.

**Cyclic Carbene Complexes from Conjugated Alkynes**

In 1996, we developed rhodium-catalyzed cycloaromatization of conjugated acyclic enediyne involving vinylidene-metal and radical intermediates (Scheme 3). Our continuing investigation has led to new findings involving the interesting 6-endo-dig cyclization based on the concept of electrocyclization of vinylidene complexes. When we carried out the reaction of the carbonyl-ene-yne compound 1a with a tungsten pentacarbonyl THF complex, the cyclic carbene complex, (2-pyranylidene)tungsten complex 2a, was isolated in 63% yield (Scheme 4). The reaction of the amide derivative 1b also yielded the corresponding 2-pyranylidene complex 2b. With chromium complexes, the addition of triethylamine (Et$_3$N), which is well known to promote the isomerization from ω-alkyne complexes to vinylidene complexes, is essential to produce the corresponding products 3a and 3b. Representative results of the synthesis of various 2-pyranylidene complexes are summarized in Table 1. Irrespective of the cyclic or acyclic carbonyl-ene-yne compound used, 2-pyranylidene complexes were obtained in good yields. Alkynyl and alkynyl moieties were tolerated under the reaction conditions, leading to 2-pyranylidene complexes. However, in the reaction of a keto-ene-yne compound the 2-pyranylidene complex was obtained in only 8% yield together with many unidentified products. Surprisingly, reactions of keto-ene-yne compounds without Et$_3$N yielded deep-blue (2-furyl)carbene complexes, which were produced via 5-exo-dig cyclization (vide infra). Since we found that the six-membered Fischer-type carbene complexes could be generated by electrocyclization (pericyclic reaction) of vinylidene intermediates, we extended the concept for cyclopropane analogues.

As shown in Scheme 5, [3,3]sigmatropy of an acyclocyclopropylvinylidene intermediate from cis-1-acyl-2-ethynylcyclopropane 4 was envisioned to produce a seven-membered Fischer-type carbene complex 5. However, in the reaction of 4a, phenol 6a as an unanticipated isomerized product was isolated in 69% yield under reaction conditions identical to those used for the synthesis of 2-pyranylidene-chromium complexes (eq. 1). A tungsten complex, W(CO)$_5$(THF) showed similar reactivity to give 6a in 72% yield, while Mo(CO)$_5$(THF) gave 6a in low yield. The addition of Et$_3$N was essential for this isomerization, irrespective of the group.
6 metal carboxyls employed. Ester 4b and amide 4c gave no isomerized products, and both substrates were recovered intact. The lack of reactivity of ester and amide derivatives is in sharp contrast with 2-pyranylidene-complex formation (	extit{vide supra}). Although this interesting reactivity has not been precisely accounted for, the proximity of the carbonyl oxygen to the $\alpha$-carbon of a vinylidene moiety and the stability of intermediates probably affect the isomerization reaction.

Considering that no carbene complex was isolated, the isomerization of 4 could be expected to proceed in the presence of catalytic amounts of group 6 metal carboxyls. As expected, the use of 5 mol\% Cr(CO)$_5$(THF) is sufficient to induce the catalytic valence isomerization to give the corresponding product quantitatively (Table 2). Reactions of primary and secondary alkyl ketones gave phenols in nearly quantitative yields, while the reactivity of tert-butyl ketone was low because of its bulkiness. When the reactions of $p$-substituted phenyl ketones were examined, electron-withdrawing substituents on a phenyl group, e.g., CF$_3$, decelerated the reaction. These results suggest that the nucleophility of the carbonyl oxygen towards the $\alpha$-carbon of a vinylidene moiety plays a critical role in this reaction. Heterocyclic substituents such as the 2-furyl and 2-thienyl groups were tolerated in the reactions, but a 2-pyridyl substituent slightly retarded the isomerization, probably due to the stronger coordination of a nitrogen atom to group 6 metals.

A plausible mechanism for this isomerization can be explained by assuming a multistep pathway as shown in Scheme 6. The [3,3]-sigmatropic reaction of an acylcyclopropylvinylidene complex produces 1-oxa-3,6-cycloheptadien-2-ylidene complex 5. A [1,5]-H shift and/or [1,3]-H shift from CH$_2$ in the seven-membered ring of 5, followed by reductive elimination of M(CO)$_5$ (M = Cr, Mo, W) results in a formation of an oxepin as a primary product. The oxepin, which is in equilibrium with the arene oxide, is converted into a phenol with the assistance of M(CO)$_5$ as a Lewis acid under the reaction conditions. The formation of a mixture of cycloheptatrienes from \textit{cis}-1-ethyl-2-vinylcyclop propane as a carbon analogue of 4a under the isomerization conditions strongly supports the intermediary seven-membered oxacarbene complexes 5 (Scheme 7).\textsuperscript{13}

### Table 2. Catalytic Valence Isomerization of 4 with Cr(CO)$_5$(THF)$^a$

<table>
<thead>
<tr>
<th>R</th>
<th>5 mol% Cr(CO)$_5$(THF)</th>
<th>THF, Et$_3$N, rt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>97% (24 h)</td>
<td></td>
</tr>
<tr>
<td>$n$-Bu</td>
<td>95% (24 h)</td>
<td></td>
</tr>
<tr>
<td>$t$-Bu</td>
<td>94% (20 h)</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>41% (26 h)$^{b,c}$</td>
<td></td>
</tr>
<tr>
<td>$R'$</td>
<td>95% (R = CH$_2$, 24 h)</td>
<td></td>
</tr>
<tr>
<td>$96%$ (R = OCH$_3$, 18 h)</td>
<td>42% (24 h)$^{b,f}$</td>
<td></td>
</tr>
<tr>
<td>$X$</td>
<td>82% (R = O, 5 h)</td>
<td></td>
</tr>
<tr>
<td>$X$</td>
<td>92% (R = S, 17 h)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reactions were carried out at room temperature with 4, Et$_3$N (3 equiv) in the presence of M(CO)$_6$(THF) prepared from the irradiation of a solution of MCO$_6$ (5 mol\%) in THF. $^b$Catalyst (30 mol\%). $^c$At reflux temperature.
These complexes $8a$ and $8b$ are less stable than 2-pyran-ylidene complexes and they gradually decompose to give dimerized products, 1,2-difurylethene derivatives, in high yield after 4 days.\(^{14b}\) We further examined catalytic (2-furyl)carbene transfer reactions using keto-ene-yne compounds as carbene precursors in the presence of carbene acceptors, such as alkenes and allyl sulfides.

The reaction of carbonyl-ene-yne $7a$ with styrene in the presence of a catalytic amount of Cr(CO)$_5$(THF) afforded (2-furyl)cyclopropane $9a$ in 85% yield (eq. 2).\(^{14}\) Interestingly, complexes of late transition metals, such as Ru, Rh, Ir, Pd, and Pt, also catalyze cyclopropanation involving (2-furyl)carbene intermediates (Table 3). The complex [Rh(OAc)$_2$]$_2$ showed the highest catalytic activity in the cyclopropanation reaction. The selected results from cyclopropanation reactions of several alkenes using [Rh(OAc)$_2$]$_2$ as a catalyst are shown in Table 4. Electron-rich alkenes such as tert-butyl vinyl ether and ketene diethyl acetal served as good acceptors of carbene intermediates to give the cyclopropanated products in excellent yields. The complex [Rh(OAc)$_2$]$_2$ can act as an effective catalyst in the cyclopropanation with an alkyl ketone, which led to lower yield of cyclopropanated product in other transition metal catalysis.

We next attempted to study the reactivity of the nitrogen analogue of 7. As shown in Scheme 9, imino ether 10 reacted with styrene to give (2-pyrrolyl)cyclopropane 11 in quantitative yield. The pyrrolylcyclopropanes can be easily converted to 2-pyrrolinones in good yields under mild hydrolysis conditions.\(^{15}\)

To extend the scope of the in situ generation of metal carbene in organic synthesis, we examined the reaction with other carbene acceptors, such as allyl sulfides or phosphines.
which are well known as effective carbene acceptors in catalytic carbene transfer reactions using diazoalkanes. We undertook the rhodium (II)-catalyzed Doyle-Kirmse type reaction using carbonyl-ene-yne compound 12a as an alternative source of diazoalkanes (Scheme 10). The resulting sulfurylde produced by 2-furylcarbene transfer, efficiently undergoes [2,3]sigmatropic rearrangement to give furan-containing sulfide 13a. Using a diallyl sulfide instead of the monoallyl sulfide, a reaction cascade of [2,3]sigmatropy followed by an intramolecular furan Diels-Alder reaction allows the one-pot synthesis of polycyclic heterocycles (Scheme 11).

In a similar manner to sulfurylde formation, carbene transfer to phosphines, which sequentially undergo a Wittig-type condensation with formyl groups, could produce phosphorus ylides. The catalytic reaction of carbonyl-ene-yne monomer 14 having a formyl group could be applied to the polycondensation reaction leading to \( \pi \)-conjugated polymers 15 with low polydispersity (PDI = 1.1) (Scheme 12). The low polydispersity is probably due not only to the low concentration of ylides but also to the selective reaction between the resulting oligomeric ylides and the monomer substrate 14 (carbonyl-ene-yne) involving a highly electrophilic formyl group para to a ketone moiety.

Vinylcarbene Complexes from Propargyl Esters and Related Compounds

We have described that (2-furyl)carbene complexes C could be generated from carbonyl-ene-yne compounds A with a wide range of transition metal complexes and could be applied to catalytic carbene transfer reactions (vide supra). This protocol was envisioned to extend to the system of propargyl esters in almost similar manner. We successfully explored a novel method for generation of vinylcarbenoid intermediate E from propargyl esters D (Scheme 13).

In 1984, Rautenstauch reported that a palladium catalyst undergoes 1,2-migration of an acetate group in 1-ethynyl-2-propenyl acetates to give cyclopentenones. However, facile isomerization of propargyl esters into allenyl esters catalyzed by transition metal compounds has precluded the further progress of this unique and potentially useful reaction.

In 2002, it was reported that intermediate vinylcarbenoids were effectively trapped intramolecularly by an alkenyl moiety in the PtCl\(_2\)-catalyzed cycloisomerization of dienynes. Our continuing investigation of the generation of carbene species by transition metal-promoted alkyne activation led us to develop efficient catalytic carbene transfer reactions, such as cyclopropanation, annulation, ring-opening and substitution reactions, and other miscellaneous reactions using propargyl esters and related compounds as precursors of vinylcarbene complexes.

Cyclopropanation of styrene with 2-methyl-3-butyn-2-yl acetate (16a) in the presence of transition metal catalysts that had been effective for catalytic cyclopropanation via (2-furyl)carbene complexes was examined (eq. 3). Representative results of catalyst screening and optimization are given in Table 5. The reaction of 16a with styrene in the presence of a catalytic amount of PtCl\(_2\) in toluene at 60 °C for 1 h
afforded the cyclopropanated product 17a in 93% yield, along with 7% of allenyl acetate 18 as the isomerization product of 16a. On the other hand, the use of 1,2-dichloroethane (DCE) as solvent in platinum catalysis decreased both yield and selectivity. The complex, [RuCl₂(CO)₃]₂ was found to be a most effective catalyst with excellent yield in the cyclopropanation reaction with 16a in DCE at 50 °C. In contrast, [Rh(OCOCF₃)₂]₂ catalyzed isomerization of 16a into allenyl acetate 18 with high selectivity. AuCl₃ also catalyzed the cyclopropanation, but 18 was produced to some extent.

Under optimized conditions (2.5 mol% [RuCl₂(CO)₃]₂, DCE, 50 °C), the reactions of several types of propargyl esters with alkenes were carried out (Table 6). The reactions of propargyl benzoate and esters of an ethynylcycloalkanol with styrene gave the cyclopropanated products in excellent yields. The reaction with secondary propargyl acetate substituted with phenyl proceeded smoothly to give cis-alkenylcyclopropane in 77% yield. However, a secondary propargyl ester having an alkyl group at the propargylic position was less reactive than those having an aryl group, affording a cyclopropane in low yield (< 30%). Primary propargyl esters and propargyl esters having a substituent on an alkyne terminus were much less reactive and cyclopropane formation scarcely occurred. The reaction of α-methylstyrene with 16a proceeded smoothly to give cyclopropane in good yield. 2-Ethylbut-1-ene and allyltrimethylsilane slowly reacted with 16a to give the corresponding products in good yields, although the use of excess alkenes was required. On the other hand, cyclopropanation of tert-butyl vinyl ether with 16a resulted in lower yield. Electron-deficient alkenes such as methyl acrylate did not work at all in the present cyclopropanation.

Furthermore, this catalytic system could be applied to the reaction with conjugated dienes as carbene acceptors. The 6π-electrocyclization of a ruthenatriene intermediate was proposed as the most likely mechanism for the indene formation. This is also considered as a formal insertion of the carbene center into a C-H bond of a phenyl ring. Most recently, we have found that the similar pentannulation of 1-aryl-2-propynyl esters is catalyzed by PtCl₂ efficiently. The diazoalkane-free in situ generation of metal-vinylcarbene intermediates from propargyl esters can be applied

Table 5. Transition Metal-Catalyzed Cyclopropanation of 16a with Styrene

<table>
<thead>
<tr>
<th>Entry</th>
<th>[M]</th>
<th>Time</th>
<th>17a (%)</th>
<th>cis:trans 18 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PtCl₂</td>
<td>1 h</td>
<td>93</td>
<td>78:22</td>
</tr>
<tr>
<td>2</td>
<td>PtCl₂</td>
<td>10 h</td>
<td>74</td>
<td>80:20 2.3</td>
</tr>
<tr>
<td>3</td>
<td>[RuCl₂(CO)₃]₂</td>
<td>18 h</td>
<td>86</td>
<td>80:20 5</td>
</tr>
<tr>
<td>4</td>
<td>[RuCl₂(CO)₃]₂</td>
<td>18 h</td>
<td>99</td>
<td>87:13 0</td>
</tr>
<tr>
<td>5</td>
<td>[Rh(OCOCF₃)₂]₂</td>
<td>30 min</td>
<td>trace</td>
<td>- 99</td>
</tr>
<tr>
<td>6</td>
<td>AuCl₃</td>
<td>10 min</td>
<td>63</td>
<td>79:21 26</td>
</tr>
</tbody>
</table>

*a Reaction conditions: 16a, styrene (5 equiv), catalyst (2.5 mol%), toluene, 60 °C. In DCE (1,2-dichloroethane) at 50 °C. At 25 °C.

Table 6. Ru-Catalyzed Cyclopropanation

<table>
<thead>
<tr>
<th>R²</th>
<th>R³</th>
<th>2.5 mol% [RuCl₂(CO)₃]₂</th>
<th>DCE, 50 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bz</td>
<td>Ph</td>
<td>90% (88:12)</td>
<td></td>
</tr>
<tr>
<td>n = 3</td>
<td>91% (88:12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n = 2</td>
<td>97% (90:10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n = 1</td>
<td>93% (94:6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ac</td>
<td>Et</td>
<td>91% (88:32)</td>
<td></td>
</tr>
<tr>
<td>82%</td>
<td>72% (79:21)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26%</td>
<td>38:62)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The ratio of cis:trans in parentheses. *In toluene at 60 °C. †Alkene (20 equiv).
to ring-opening and substitution reactions of heteroaromatic compounds. The reaction of 2-methyl-3-butyne-2-yl acetate (16a) with furan in the presence of a catalytic amount of [RuCl₂(CO)₃]₂ affords triene (2E,4E)-21 in 62% yield (Scheme 16). Trienes obtained are in general a mixture of stereoisomers, which are prone to isomerize to the most thermally stable (2E,4E)-isomer. Ruthenium-vinylcarbene formation followed by electrophilic attack to a furan gives a charge-separated intermediate, which undergoes the ring-opening of the furan structure to produce the triene. The ruthenium-catalyzed reaction of 16a with 2,5-dimethylfuran gives 3-substituted 2,5-dimethylfuran 22 in 50% yield instead of ring-opened products (Scheme 17). The charge-separated intermediate, which is formed by electrophilic attack of a ruthenium-vinylcarbene at the 3-position of 2,5-dimethylfuran, probably because of the steric preference, allows hydride shift exclusively to give 3-substituted products.

Although 1,1-dialkyl- or 1,1-diarylated-2-propynyl esters and 1-aryl-2-propynyl esters can act as vinylcarbene precursors, no vinylcarbene complex formation from 1-alkyl-2-propynyl and simple propargyl esters was observed. The reaction of acetate 16d (X = O, Y = Me) with 2-methoxyfuran did not take place, 16d being recovered intact (eq. 4). We have found that O-propargyl thiocarbamate 16e (X = S, Y = NMe₂) works as vinylcarbene precursors and could be used for transition metal-catalyzed vinylcarbene transfer reactions. However, the similar reaction of 3-butyne-2-yl N,N-dimethylcarbamate 16f (X = O, Y = NMe₂) afforded ring-opened products in lower yields. These results indicate that the higher nucleophilicity of the sulfur atom and the mesomeric effect of the N,N-dimethylamino moiety synergistically promote the efficient generation of a metal-vinylcarbene intermediate. The extended reactivity of propargyl substrates as vinylcarbene precursors might find application in the construction of important substructures of desired molecules.

The [1,3]shift of the carbene center to the remote alkynyl carbon in free alkynyl carbaines (a) and alkynyl carbene complexes (b) have been recognized as an intriguing dynamic process (Scheme 18). Recently, the in situ generation of carbene complexes from oligoynes has been applied to study the dynamic behavior of an intermediary carbene complex in catalytic reactions. When we examined the generation of ruthenium-carbene complexes from conjugated oligoynes possessing propargyl acetate moieties as a carbene donor, we found the metallotropism in intermediates from oligoynes leading to the catalytic isomerization.

The reaction of 1,6-diacetoxy-1,6-diphenylhexa-2,4-diyne (24a) bearing the secondary propargyl acetate moiety in DCE in the presence of [RuCl₂(CO)₃]₂ gave (1Z,5E)-2,5-diacetoxy-1,6-diphenylhexa-1,5-diene-3-yne (25a) as an isomerized product (Scheme 19). Since we know that the...
secondary propargyl acetate gives Z-vinylcarbene complex (See Table 6). The Z-stereochemistry of 25a strongly supports the generation of the vinylcarbene complex. We have proposed that the most plausible mechanism involves the generation of a vinylcarbene complex and subsequent [1,3] shift of the carbene center to the remote alkynyl carbon followed by stereoselective migration of vicinal acetate.

Reactions of symmetrical diyne 24b and triyne 24c gave 3,6-diacetoxy-2,7-dimethyl-octa-2,6-diene-4-yne (25b) and 3,8-diacetoxy-2,9-dimethyl-deca-2,8-diene-4,6-diene (25c) (Scheme 20). The results suggest the ruthenium-catalyzed isomerization of diynes and triynes by using in situ generation of transition metal-carbene complexes from propargyl esters, followed by [1,1]-metallicopic carbene shift (n - 3, 5) (carbene walk) of initially generated alkynyl carbene complexes.

Conclusion

We have developed a new route to carbene complexes, 2-pyrynilidene, (2-furyl)carbene, (2-pyrrolyl)carbene, and vinylcarbene complexes, from alkynes possessing nucleophilic auxiliaries, and have demonstrated several efficient catalytic reactions involving the in situ generation of such carbene species. The latent nature of alkynes as carbene precursors (-C≡C- ↔ -C=C- - ) is brought out by the perturbation of π-electrons in alkynes coordinated with transition metals. Vinylidene complexes generated in situ from terminal alkynes serve as a 2π-unit for a 6-endo-dig cyclization mode in electrocyclization and [3,3] sigmatropic to create cyclic oxoacarbene complexes. Vinylidene formation is not a prerequisite for producing (2-furyl)carbene, (2-pyrrolyl)carbene, and vinylcarbene complexes, formation of which are driven by 5-exo-dig cyclization with a carbonyl or imino group as nucleophiles to an internal carbon in alkynyl complexes. The present study, based on the in situ generation of carbeneoid species from alkynes coordinated with transition metals, provides a variety of efficient carbene transfer reactions with high atom efficiency. We believe that this new accessibility to carbeneoid species contributes to the development of organic synthesis as well as organometallic chemistry. Further advances in this area await discovery.

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References


Transition Metal-Catalyzed and -Promoted Reactions via Carbenes


