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Highlight Review

Transition Metal-catalyzed Reactions Using Alkynes as Precursors of Carbene and Vinylidene Complexes

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Abstract

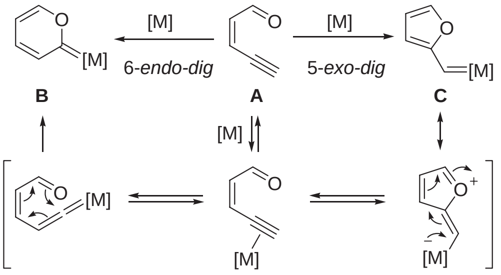
The transition metal-induced in situ generation of carbene complexes from alkynes having a carbonyl or imino group as a nucleophilic functionality has been investigated. These reactive carbenoid species are generated with high atom efficiency through a 6-*endo-dig* cyclization mode based on the electrocyclization 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.

◆ Introduction

Transition metal-catalyzed reactions involving carbenoid species, such as cyclopropanation, insertion, and metathesis reactions, are powerful and useful methods to construct structurally complex compounds and have been widely investigated in the past couple of decades.[1] Recently, much attention has been paid to the in situ generation of transition metal carbenoid species which have been applied to a wide range of carbene transfer reactions. One of the most versatile methods to generate these species is a decomposition reaction of diazoalkanes by transition metal complexes.[1b] The activation of alkynes with transition metal compounds to generate carbenoid species has also been investigated.[2,3] For example, metathesis reactions of alkynes,[4] cyclopropylcarbenoids in the cycloisomerization of α,ω-enynes,[5–8] dialkylidene ruthenium species from ω-diynes,[9] and vinylcarbenoids and/or metal-containing ylides from alkynes including nucleophilic functional groups,[10,11] have so far been recognized as new methods to generate metal carbenoids. This short account describes our recent progress in this field, focusing attention on the in situ generation of carbenoid species involving a nucleophilic attack of a carbonyl oxygen or an imino nitrogen on an alkyne moiety as well as the catalytic transfer of these intermediary carbenoid species to acceptors.

◆ General Concept

We developed a new catalytic cycloaromatization of acyclic enediynes involving vinylidene–metal intermediates in conjugated systems.[12] Recently, we have sought to develop new catalytic reactions of carbonyl-ene-yne compounds **A** and found several catalytic reactions involving the interesting formal 6-*endo-dig* cyclization mode based on the concept of electrocyclization of vinylidene complexes as well as in situ generation of carbene complexes through a 5-*exo-dig* cyclization mode (Scheme 1). The key step of these reactions is an intramolecular nucleophilic attack of carbonyl oxygen to the initially formed vinylidene complexes or π-alkyne complexes leading to six- or five-membered cyclic species, 2-pyranylidene complexes **B** and (2-furyl)carbene complexes **C**. The latter cyclization mode was also applied toward similar structures, propargylic carboxylates, to yield vinylcarbenoids, which undergo catalytic carbene transfer reactions.



Scheme 1.

◆ Cyclic Carbene Complexes from Conjugated Alkynes

We attempted the reaction of the carbonyl-ene-yne compound **1a** with an excess amount of a pre-activated tungsten pentacarbonyl complex, which is easily prepared by the irradiation of tungsten hexacarbonyl in tetrahydrofuran (THF) (Scheme 2).[13,14a] After column chromatography, the cyclic carbene complex, (2-pyranylidene)tungsten complex, **2a** was isolated in 63% yield. The reaction of the amide derivative **1b** also afforded the corresponding 2-pyranylidene complex **2b**. In the case of chromium complexes, the addition of triethylamine (Et_3N), which is well-known to promote the isomerization from π-alkyne complexes to vinylidene complexes,[12a] is essential to give the corresponding products **3a** and **3b**. Representative results of the synthesis of various 2-pyranylidene complexes are shown in Table 1. Carbonyl-ene-yne compounds containing unsaturated moieties as well as linear substrates would tolerate the conditions to give the corresponding complexes. When the reaction of a keto-ene-yne compound was examined, the 2-pyranylidene complex was obtained in only 8% yield together with many unidentified products. Reactions of keto-ene-yne compounds without Et_3N provided a deep-blue colored solution of (2-furyl)carbene complexes which were produced via 5-*exo-dig* cyclization (vide infra).[14a] Although the transformation of carbonyl-ene-yne com-

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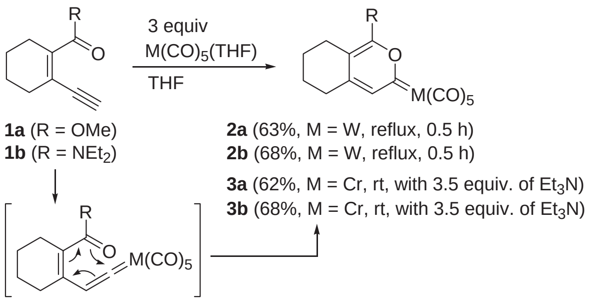
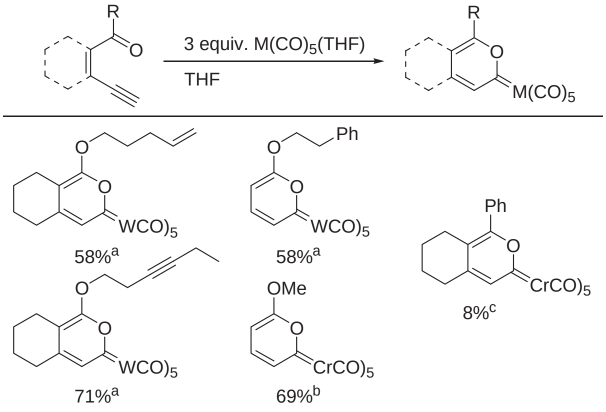


Scheme 2.

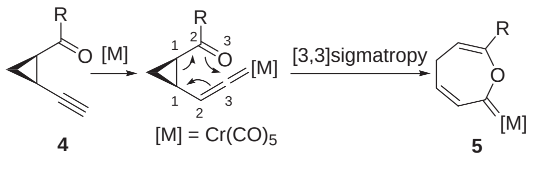
Table 1. Preparation of 2-pyranylidene complexes



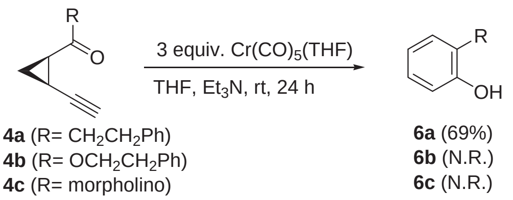
[a]At reflux temperature for 0.5 h. [b]With 3.5 equiv. of Et_3N at room temperature for 2 h. [c]With 1.2 equiv. of Et_3N at room temperature for 0.5 h.

pounds provides a facile method to prepare 2-pyranylidene complexes, these cyclic carbene complexes have not yet been applied to catalytic reactions.[13] By doing so, the concept of cyclic carbene complexes generated by pericyclic reactions could be extended to the catalytic isomerization of acylethynylcyclopropanes.

As shown in Scheme 3, [3,3]sigmatropy of an acylcyclopropylvinylidene intermediate from *cis*-1-acyl-2-ethynylcyclopropane **4** was envisioned to produce a seven-membered Fischer-type carbene complex **5**. However, an unanticipated product, phenol **6a** was isolated in 69% yield in the reaction of **4a** under conditions identical to that used for the synthesis of 2-pyranylidene-chromium complexes (Scheme 4).[15] A tungsten complex, $W(CO)_5(THF)$ showed similar reactivity in this isomerization reaction, while $Mo(CO)_5(THF)$ gave only **6a** in low yield. The addition of Et_3N was essential for this isomerization irrespective of group 6 metal carbonyls employed. Cyclopropanes such as an ester **4b** and an amide **4c** gave no isomerized products, and both substrates were recovered intact. The unreactive ester and amide derivatives are in sharp contrast with 2-pyranylidene-complex formation mentioned above. Although this interesting aspect has not been precisely accounted for, the proximity of the carbonyl oxygen to α-carbon of a vinylidene moiety and the stability of intermediates probably affect this isomerization reaction.

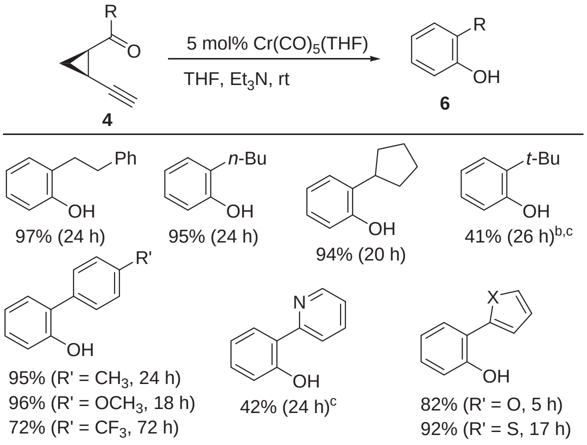


Scheme 3.



Scheme 4.

Table 2. Catalytic valence isomerization of **4** with $Cr(CO)_5(THF)$[a]



[a]Reactions were carried out at room temperature with **4** and Et_3N (3 equiv.) in the presence of $Cr(CO)_5(THF)$ prepared from the irradiation of a solution of $Cr(CO)_6$ (5 mol %) in THF. [b]Catalyst (30 mol %). [c]At reflux temperature.

Considering that no carbene complex was isolated, the valence isomerization of **4** could be expected to proceed in the presence of catalytic amount of group 6 metal carbonyls. As expected, the use of 5 mol % $Cr(CO)_5(THF)$ is sufficient to induce catalytic valence isomerization to give the corresponding product quantitatively (Table 2). Reactions of primary and secondary alkyl ketones gave phenols in nearly quantitative yields, respectively, while the reactivity of *tert*-butyl ketone was low because of its bulkiness. When the reactions of *p*-substituted phenyl ketone were examined, electron-withdrawing substituents on a phenyl group, e.g., CF_3, decelerated the reaction. These results suggest that the nucleophilicity of the carbonyl oxygen towards the α-carbon of a vinylidene moiety plays an important role in this reaction. Heterocycles such as 2-furyl and 2-thienyl group were tolerated in the reactions, but a 2-pyridyl substituent slightly retarded the isomerization probably due to stronger coordination of a nitrogen atom to group 6 metals.

A plausible mechanism of this isomerization can be explained by assuming a multistep-pathway as shown in Scheme 5. [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

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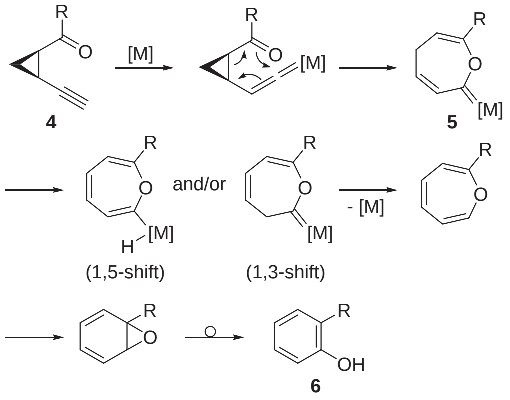


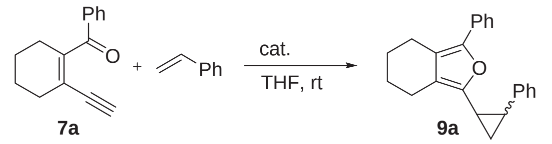
Scheme 5.

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 *cis*-1-ethynyl-2-vinylcyclopropane as a carbon analogue of **4a** under the isomerization conditions strongly supports the intermediary seven-membered oxacarbene complexes **5**.[15]

◆ (2-Furyl)carbene Complexes from Conjugated Alkynes

In the course of the investigation of 2-pyranylidene complexes we have found a new carbenoid generation mode from carbonyl-ene-yne compounds **7** through 5-*exo-dig* cyclization leading to (2-furyl)carbene complexes **8** (Scheme 6).[14a] These complexes **8** are less stable than 2-pyranylidene complexes and they gradually decompose to give dimerized products, 1,2-difurylethene derivatives, in high yield after 4 d.[16b] In the presence of carbene acceptors, such as alkenes and allyl sulfides, the carbene transfer reactions proceeded smoothly even when a catalytic amount of the metal complex was used. Catalytic (2-furyl)carbene transfer reactions using keto-ene-yne compounds as carbenoid precursors were explored as described below.

Table 3. Catalytic cyclopropanation of **7a**[a]

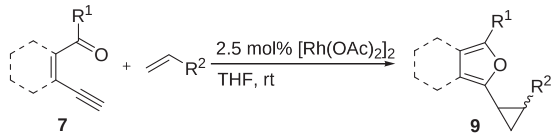


7a **9a**

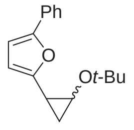
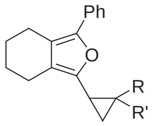
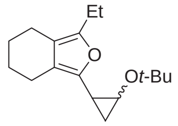
Cat.	Time/h	Yield (*cis:trans*)
$Cr(CO)_5(THF)$	14	85% (76:24)
$[RuCl_2(p\text{-cymene})]_2$[b]	2	85% (33:67)
$[RuCl_2(CO)_3]_2$[b]	24	42% (12:88)
$[Rh(OAc)_2]_2$[b]	1	93% (8:92)
$[IrCl(cod)]_2$[b]	2	92% (57:43)
$PdCl_2$	2	79% (21:79)
$PtCl_2$	1	81% (23:77)

[a]Reactions were carried out at room temperature with **7a**, styrene (20 equiv.), and a catalyst (5 mol %) in THF unless otherwise noted. [b]Styrene (2 equiv.) with a catalyst (2.5 mol %).

Table 4. Rh-catalyzed cyclopropanation of **7**[a]

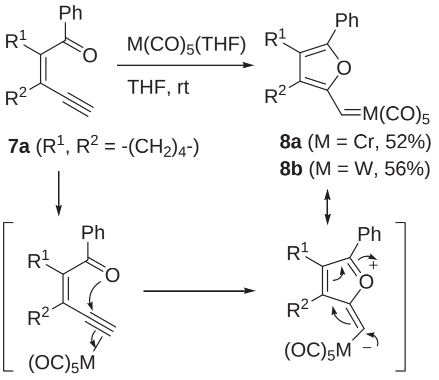


7 **9**

 99% (85:15)[b]	 99% (90:10,[b] R = O*t*-Bu, R' = H) 99% (R, R' = OEt)	 80% (91:9)[b,c]

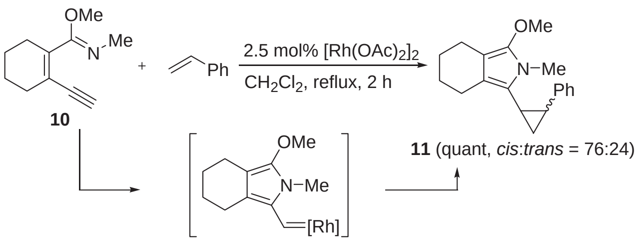
[a]Reactions were carried out at room temperature with **7**, alkene (2 equiv.), and $[Rh(OAc)_2]_2$ (2.5 mol %) in THF for 1 h unless otherwise noted. [b]The ratio of *cis:trans*. [c]In dichloromethane.

The reaction of carbonyl-ene-yne compound **7a** with styrene in the presence of a catalytic amount of $Cr(CO)_5(THF)$ formed (2-furyl)cyclopropane **9a** in 85% yield (Table 3).[16] Late transition metal complexes, such as Ru, Rh, Ir, Pd, and Pt, could also be applied to this catalytic cyclopropanation involving (2-furyl)carbene intermediates. In Table 4, the selected results using $[Rh(OAc)_2]_2$ as an effective catalyst for this cyclopropanation reaction are shown. 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, respectively. The complex $[Rh(OAc)_2]_2$ can act as an effective catalyst in the cyclopropanation of an alkyl ketone, which led to lower yield of cyclopropanated product in other transition metal catalysis.

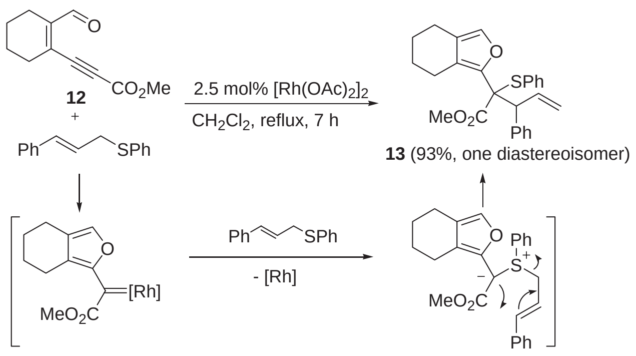


Scheme 6.

We next attempted to study the reactivity of nitrogen analogue of **7**. As shown in Scheme 7, imino ether **10** showed a similar reactivity with styrene to afford 2-pyrrolylcyclopropane derivative **11** in quantitative yield.[17] The pyrrolylcyclopropanes could be converted to 2-pyrrolinones in good yields by using mild protic conditions.

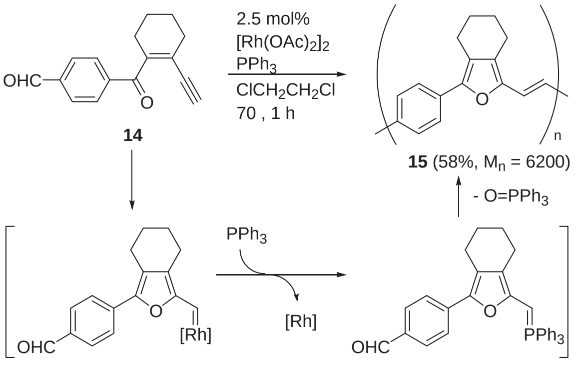


Scheme 7.



Scheme 8.

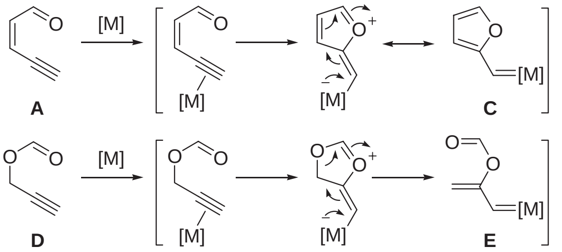
To extend the scope of this in situ carbenoid generation in organic synthesis, we examined the reaction using other carbene acceptors, such as allyl sulfides or phosphine compounds, which are well-known as effective carbene acceptors in catalytic carbene transfer reactions with diazoalkanes. We undertook the rhodium(II)-catalyzed Doyle–Kirmse type reaction using carbonyl-ene-yne compound **12** as an alternative source of diazoalkanes (Scheme 8).[18] The resulting sulfur ylide produced by 2-furylcarbene transfer efficiently undergoes [2,3]sigmatropic rearrangement to give furan-containing sulfide **13**. Using a diallyl sulfide instead of the monoallyl sulfide, a reaction cascade of [2,3]sigmatropy followed by an intramolecular Diels–Alder reaction between the furan and the allyl group allows the one-pot synthesis of polycyclic heterocycles.[18] In a similar manner to sulfur ylide formation, phosphorus ylides could be produced by carbene transfer to phosphines, which sequentially underwent a Wittig-type condensation with formyl groups.[19] The catalytic reaction of carbonyl-ene-yne monomer **14** having a formyl group could be applied to poly condensation reaction leading to π-conjugated polymers **15** with low polydispersity (PDI = 1.1) (Scheme 9).[19a]



Scheme 9.

◆ *Vinylcarbene Complexes from Propargylic Carboxylates*

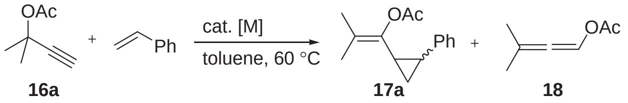
We described that (2-furyl)carbene complexes **C** could be generated from carbonyl-ene-yne compounds **A** with a wide range of transition metal complexes and could be applied to catalytic carbene transfer reactions (Scheme 10). The key to the reaction is a 5-*exo-dig* cyclization through a nucleophilic attack of the carbonyl oxygen to an internal carbon of the alkyne activated by transition metal compounds. This leads to a stable furan structure with aromatic stabilization. This stimulated us to develop a new method for the preparation of vinylcarbenoid intermediate **E** from propargylic carboxylates **D**. In this transformation, we envisioned that the nucleophilic attack of the carbonyl oxygen was followed by bond cleavage at the propargyl position as a neighboring group rearrangement. This concept was not realized in most cases due to facile isomerization of propargylic carboxylates into allenyl carboxylates catalyzed by transition metal compounds, such as Ag and Cu compounds.[20] Rautenstrauch first demonstrated the validity of the protocol for a vinylcarbenoid intermediate **E** in palladium-catalyzed inter-and intramolecular carbene transfer reactions using propargylic acetate.[21] Most recently, it was shown that intermediary vinylcarbenoids were effectively trapped by an alkenyl moiety in the molecule to give carbocyclic compounds in the $PtCl_2$-catalyzed cyclization of dienynes.[22] Our continuous investigation of the generation of carbene species from functionalized alkynes led us to develop an efficient ruthenium-catalyzed intermolecular cyclopropanation of alkenes using propargylic carboxylates as precursors of vinylcarbene complexes.[23]



Scheme 10.

Cyclopropanation of styrene with 2-methyl-3-butyn-2-yl acetate (**16a**) in the presence of transition metal catalysts which had been effective for catalytic cyclopropanation via (2-furyl)-carbene complexes was examined. 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 $PtCl_2$, which acts as a good catalyst for intramolecular cyclopropanation, in toluene at 60 °C for 1 h afforded the cyclopropanated product **17a** in 93% yield, along with 7% of allenyl acetate **18**, the isomerization product of **16a**. Although $[RuCl_2(CO)_3]_2$ is less effective under the same conditions, it was found that the cyclopropanation took place with excellent yield and high diastereoselectivity by heating a solution of **16a** and styrene in dichloroethane (DCE) at 50 °C. The reaction using $PtCl_2$ in

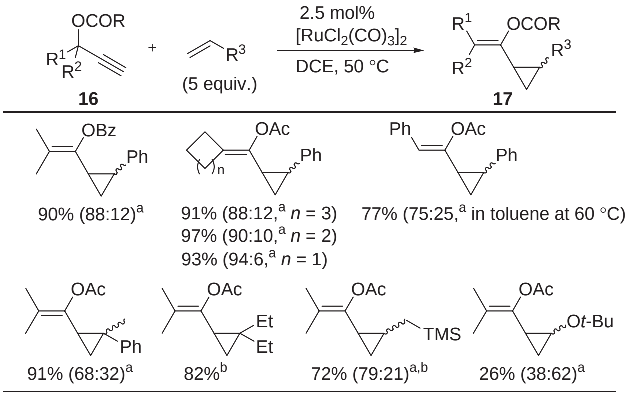
Table 5. Transition metal-catalyzed cyclopropanation of **16a**[a]



Entry	[M]	Time	**17a**/%	*cis*:*trans*	**18**/%
1	$PtCl_2$	1 h	93	78:22	7
2	$[RuCl_2(CO)_3]_2$	18 h	86	80:20	5
3	$[RuCl_2(CO)_3]_2$[b]	18 h	99	87:13	0
4	$[Rh(OCOCF_3)_2]_2$	30 min	trace	—	99

[a]Reaction conditions: **16a**, styrene (5 equiv.), catalyst (2.5 mol %), toluene, 60 °C. [b]In DCE (dichloroethane) at 50 °C.

Table 6. Ru-catalyzed cyclopropanation



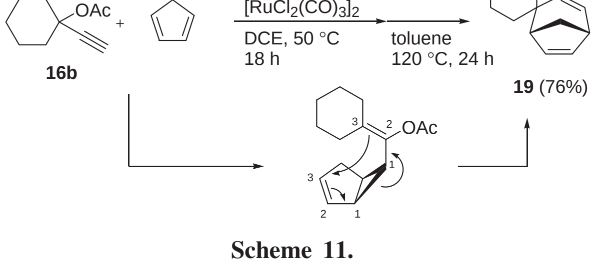
^{a}The ratio of *cis:trans*. ^{b}Alkene (20 equiv.) was used.

DCE at 50 °C afforded the corresponding product in 74% yield with 23% yield of allenyl acetate. In contrast, $[Rh(OCOCF_3)_2]_2$ selectively catalyzed isomerization of **16a** into allenyl acetate **18**.

Under the optimized conditions (2.5 mol % $[RuCl_2(CO)_3]_2$, DCE, 50 °C), the reactions of several types of propargylic carboxylates with alkenes were carried out (Table 6). The reactions of propargyl benzoate and cyclic acetates with styrene gave the cyclopropanated products in excellent yields, respectively. The reaction with secondary propargylic acetate substituted with phenyl proceeded smoothly to give *cis*-alkenylcyclopropane in 77% yield. However, a secondary propargylic carboxylate having an alkyl group at the propargyl position was less reactive than those having an aryl group, affording a cyclopropane in low yield (<30%). Primary propargylic carboxylates and internal propargylic carboxylates 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 carbenoid acceptors.[23b] In this case, the seven-membered ring could be constructed from the cyclopropanation followed by [3,3]sigmatropic rearrangement of *vic*-divinylcyclopropane intermediate. The ruthenium-catalyzed reactions using cyclopentadiene produced a bicyclo[3.2.1]octadiene skeleton (Scheme 11). Efficient [3,3]sigmatropic isomerization of initially formed *syn*-divinylcyclopropane led to the rearranged product **19** by heating the solution at 120 °C after ruthenium-catalyzed cyclopropanation. The present vinylcarbenoid transfer reaction is chemically equivalent to the reaction using a combination of α-diazoketone and transition metal compounds. This provides another method for generating carbenoid species from readily available alkynes.



Scheme 11.

♦ Conclusion

We have developed a new route to carbene complexes, 2-pyranylidene, (2-furyl)carbene, (2-pyrrolyl)carbene, and vinylcarbene complexes, from alkynes possessing nucleophilic auxiliaries and demonstrated several efficient catalytic reactions involving in situ generation of such carbene species. The latent nature of alkynes as carbene precursors $(-C{\equiv}C- \leftrightarrow -\ddot{C}-\ddot{C}-)$ 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]sigmatropy to create cyclic oxacarbene 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 π-alkyne complexes. The present study based on the in situ generation of carbenoid 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 carbenoid species contributes to the development of organic synthesis as well as organometallic chemistry. Further advances in this area await discovery.

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