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Chromium- and Tungsten-Triggered Valence Isomerism of *cis*-1-Acyl-2-ethynylcyclopropanes via [3,3]Sigmatropy of (2-Acylcyclopropyl)vinylidene−Metal Intermediates

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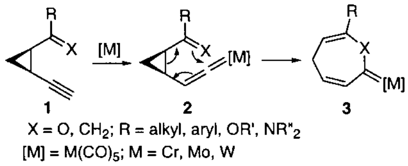
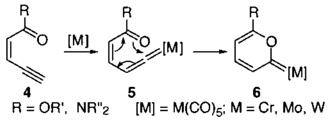
We report herein the novel group 6 metal-triggered [3,3]-sigmatropy of cis vicinal acyl- or vinyl-ethynylcyclopropanes **1** (X = O, CH_2) via cyclopropylvinylidene complexes **2**, as shown in Scheme 1. Vinylidene complexes which can be generated directly from terminal alkynes and a variety of transition metals have been identified as particularly versatile synthetic intermediates during the past decade.[1] We recently reported that group 6 transition metals undergo pericyclic or pseudopericyclic reaction of (*Z*)-*β*-ethynyl α,*β*-unsaturated carbonyl compounds **4** via ene−carbonyl−vinylidene complexes **5** to produce 2-pyranylidene complexes **6** (Scheme 2).[2] We then decided to extend this pericyclic mode to a cyclopropane system having both a vinylidene−metal moiety and an unsaturated side chain, which could exemplify [3,3]sigmatropy represented with a [σ2s+π2s+π2s] process. As shown in Scheme 3, [3,3]sigmatropy of cyclopropanes bearing a variety of unsaturated substituents, such as vinyl,[3] iminyl,[3] carbonyl,[3] heterocumulenyl,[3,4] and metal−carbene,[5] heretofore has been well investigated,[6] whereas there has been no report on [3,3]sigmatropy of cyclopropanes involving a vinylidene−metal moiety (Y = C=[M]) as a vinylogous function. We therefore set out to prepare the vicinal carbonyl- or vinyl-substituted ethynylcyclopropanes.[10]

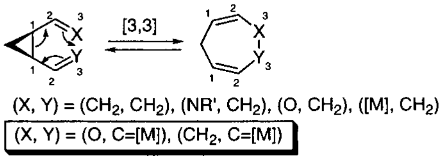
Scheme 1



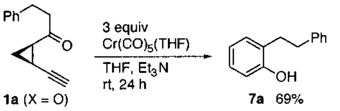
Scheme 2



Scheme 3



When we carried out the reaction of cis vicinal acylethynylcyclopropane **1a** (0.2 mmol) under the identical conditions for the synthesis of 2-pyranylidene−chromium complexes **6** employing 3 equiv of $Cr(CO)_5(THF)$[11] in THF (20 mL) in the presence of Et_3N at room temperature, we obtained not a seven-membered Fischer-type carbene complex **3a**, but an unanticipated product, phenol **7a**, in 69% isolated yield (eq 1). This result shows that valence isomerization of **1a** was promoted by chromium. We next examined the reaction using other group 6 metal carbonyls and other cyclopropanes having an alkoxycarbonyl or a carbamoyl group (Table 1). The reaction of **1a** with 3 equiv of $W(CO)_5(THF)$ also gave **7a** in 72% yield (entry 3), while $Mo(CO)_5(THF)$ was almost ineffective in the reaction (entry 5). Reactions required the addition of Et_3N and no reactions occurred in the absence of it (entries 2 and 4). Triethylamine seems to facilitate the formation of a vinylidene complex.[12] When reactions of other cyclopropanes such as an ester **1b** and an amide **1c** were carried out with 3 equiv of $Cr(CO)_5(THF)$ in the presence of Et_3N, no reactions took place and **1b** and **1c** were recovered intact (entries 6 and 7). The lack of reaction of an ester and an amide is in sharp contrast with pyranylidene-complex formation.



(1)

Table 1. Valence Isomerization of **1** (X = O) with $M(CO)_5(THF)^a$

entry	R in **1**	M	additive[b]	time (h)	product	yield[c] (%)
1	CH_2CH_2Ph (**1a**)	Cr	Et_3N	24	**7a**	69
2	CH_2CH_2Ph (**1a**)	Cr	−	72	nr[d]	
3	CH_2CH_2Ph (**1a**)	W	Et_3N	24	**7a**	72
4	CH_2CH_2Ph (**1a**)	W	−	72	nr[d]	
5	CH_2CH_2Ph (**1a**)	Mo	Et_3N	72	**7a**	4
6	OCH_2CH_2Ph (**1b**)	Cr	Et_3N	72	nr[d]	
7	morpholino (**1c**)	Cr	Et_3N	72	nr[d]	

[a] Reactions were carried out at room temperature with **1** (0.2 mmol) and $M(CO)_5(THF)$ prepared by irradiating a solution of $M(CO)_6$ (0.6 mmol) in THF (20 mL). [b] 0.6 mmol. [c] Isolated yield. [d] **1** was completely recovered.

As it was found that the group 6 metals induce valence isomerization of *cis*-1-acyl-2-ethynylcyclopropanes **1** leading to phenols **7**, catalytic reactions of **1** were next examined. Selected results on catalytic reactions are shown in Table 2. Both chromium and tungsten showed the catalytic activity to a similar extent (entries 1 and 2). The use of 5 mol % $Cr(CO)_5(THF)$ is enough to induce catalytic valence isomerization of **1a** to give **7a** quantitatively (entry 3). Reactions of butyl and *p*-tolyl ketones gave **7d** and **7e** in almost quantitative yields, respectively (entries 4 and 5). While the reaction of 1-naphthyl ketone **1f** gave **7f** with much lower yield probably due to the steric hindrance,[13] the reaction of 2-naphthyl ketone **1g** gave the corresponding product **7g** in 92% yield (entries 6 and 7). Heterocycles such as 2-furyl or 2-thienyl were tolerated in the reactions (entries 8 and 9), but 2-pyridyl substituent slightly precluded the product formation (entry 10).

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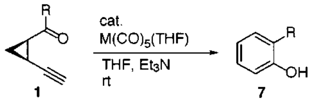
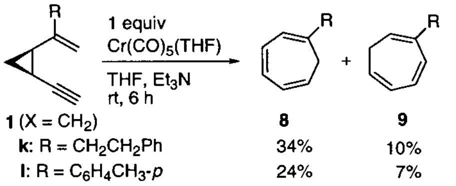
Table 2. Catalytic Valence Isomerization of **1** (X = O) with $M(CO)_5(THF)$[a]



entry	R in **1**	M	mol %[b]	time (h)	product	yield[c] (%)
1	CH_2CH_2Ph (**1a**)	Cr	20	20	**7a**	92
2	CH_2CH_2Ph (**1a**)	W	20	24	**7a**	99
3	CH_2CH_2Ph (**1a**)	Cr	5	24	**7a**	97
4	*n*-Bu (**1d**)	Cr	5	24	**7d**	95
5	$C_6H_4CH_3$-*p* (**1e**)	Cr	5	24	**7e**	95
6[d]	1-naphthyl (**1f**)	Cr	5	24	**7f**	trace
7	2-naphthyl (**1g**)	Cr	5	6	**7g**	92
8	2-furyl (**1h**)	Cr	5	5	**7h**	82
9	2-thienyl (**1i**)	Cr	20	17	**7i**	92
10[d]	2-pyridyl (**1j**)	Cr	30	24	**7j**	42

[a] **1** (0.5 mmol), Et_3N (1.5 mmol), and THF (5 mL) at room temperature. [b] Based on the amount of $M(CO)_6$ loaded. [c] Isolated yield. [d] At reflux temperature.

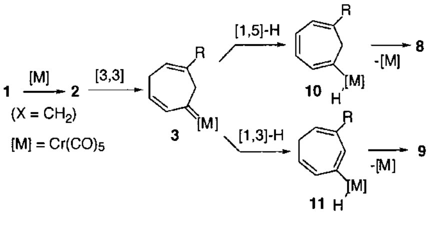
To gain further insight into a mechanism for the group 6 metal triggering valence isomerism of **1**, we next carried out two sets of experiments. Thus, we undertook the reaction of *cis*-1-ethynyl-2-vinylcyclopropane as a carbon analogue, in which a carbonyl oxygen of **1** was replaced with CH_2. The reaction of **1k** (0.3 mmol) with 1 equiv of $Cr(CO)_5(THF)$ in THF (10 mL) in the presence of Et_3N at room temperature for 6 h gave a mixture of 1- and 2-substituted 1,3,5-cycloheptatrienes **8k** and **9k** in 34 and 10% yields, respectively (eq 2).[14] Reaction of vinylcyclopropane **1l** also



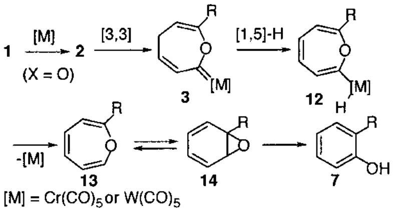
(2)

gave a mixture of cycloheptatrienes **8l** (24%) and **9l** (7%). The formation of cycloheptatrienes indicates that [3,3]sigmatropy of a vinylcyclopropylvinylidene intermediate **2** (X = CH_2) proceeds to give a seven-membered carbene complex **3** (X = CH_2) as shown in Scheme 1. Formation of two isomeric 1,3,5-cycloheptatrienes **8** and **9** can be explained by assuming the subsequent [1,5]- and [1,3]-hydrogen shifts in the complex **3** (X = CH_2) followed by reductive elimination of pentacarbonylchromium, $Cr(CO)_5$, from hydride complexes **10** and **11**, respectively (Scheme 4). Accordingly, isomerism of *cis*-1-acyl-2-ethynylcyclopropane **1** (X = O) also can be explained by assuming a multistep pathway as shown in Scheme 5. Thus, [1,5]-H shift from CH_2 in a seven-membered ring of 1-oxa-2,5-cycloheptadien-7-ylidene complex **3** (X = O) to a metal and the subsequent reductive elimination of $M(CO)_5$ from **12** give rise to the formation of an oxepin **13** as a primary product. The oxepin **13**, which is in equilibrium with the arene oxide **14**,[15] cannot be isolated, but it is converted into phenol **7** under the present reaction conditions.[16] It has been reported that an equilibrium mixture of an oxepin and a benzene oxide reacted with $Fe(CO)_5$ under irradiation to give benzene and phenol together with an (η^4-oxepin)-$Fe(CO)_3$ complex as a minor product.[17]

Scheme 4



Scheme 5



In conclusion, we demonstrated the group 6 metal-triggered valence isomerization of cis vicinal acyl- or vinyl-ethynylcyclopropanes in stoichiometric and catalytic processes. This represents the first example of [3,3]sigmatropy in which a vinylidene-metal works as a function of a two-π-electron moiety like a ketene.

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Supporting Information Available: Experimental procedures and analytical and spectral data for all new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) It has been reported that thermal [3,3]sigmatropic rearrangements of 1,2-diethynylcyclopropanes,[7] 1-ethynyl-2-vinylcyclopropane,[8] and 1-ethynyl-2-iminyl- or 1-ethynyl-2-formylcyclopropane[9] gave rise to seven-membered diallenic and allenic intermediates. For brevity, limited references are shown below.

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(10) All new cyclopropanes prepared gave satisfactory spectral and combustion analytical data. See Supporting Information.

(11) The solution of $Cr(CO)_5(THF)$ (*n* equiv) used was prepared by irradiating a solution of a THF solution of $Cr(CO)_6$ (*n* equiv) at room temperature for 4 h with a high-pressure Hg lamp.

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(13) Isomerization of **1f** to *trans*-1-ethynyl-2-(1-naphthoyl)cyclopropane (20%) was observed in this reaction.

(14) Structures of **8** and **9** were confirmed by comparing their NMR spectra in two regions of δ 1.0−2.5 and 5.0−7.0 ppm with those of 1- and 2-methyl-1,3,5-cycloheptatrienes reported, see: Egger, K. W.; Moser, W. R. *J. Phys. Chem.* **1967**, *71*, 3699. See Supporting Information.

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