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Catalytic Cyclopropanation of Alkenes via (2-Furyl)carbene Complexes from 1-Benzoyl-*cis*-1-buten-3-yne with Transition Metal Compounds

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The reaction of alkenes with conjugated ene-yne-ketones, such as 1-benzoyl-2-ethynylcycloalkenes, with a catalytic amount of $Cr(CO)_5(THF)$ gave 5-phenyl-2-furylcyclopropane derivatives in good yields. The key intermediate of this cyclopropanation is a (2-furyl)carbene complex generated by a nucleophilic attack of carbonyl oxygen to an internal alkyne carbon in π-alkyne complex or σ-vinyl cationic complex. A wide range of late transition metal compounds, such as $[RuCl_2(CO)_3]_2$, $[RhCl(cod)]_2$, $[Rh(OAc)_2]_2$, $PdCl_2$, and $PtCl_2$, also catalyzes the cyclopropanation of alkenes with ene-yne-ketones effectively. When the reactions were carried out with dienes as a carbene acceptor, the more substituted or more electron-rich alkene moiety was selectively cyclopropanated with the (2-furyl)carbenoid intermediate.

Introduction

Carbenoid species generated from diazoalkanes and transition metal complexes have been used for a wide range of carbene transfer reactions.[1] Diazo decomposition by transition metal complexes is often a useful but formidable task due to the explosive hazard and a number of unfavorable side reactions, such as diazo dimerization and azine formation. To circumvent such difficulties, safe alternatives to handling diazoalkanes or special techniques involving slow addition of them are required. Recently, much attention has been paid to activation of alkynes with transition metal compounds as a safe and facile alternative to diazo decomposition. Cyclopropylcarbenoid in skeletal reorganization of α,*ω*-enynes,[2,3] dialkylidene ruthenium species from *ω*-diynes,[4] transition metal-containing carbonyl ylides from *o*-ethynylphenylcarbonyl compounds,[5,6] copper-(isoindazolyl)-carbenoids from (2-ethynylphenyl)triazenes,[7] and vinylcarbenoids from propargylic carboxylates[8] have so far been recognized as new entries to metal carbenoids from alkynes. We have already reported electrocyclization of vinylidene intermediates generated from ene-yne-esters or -amides **1** (R = OR′ or R = NR″$_2$) with group 6 transition metal complexes leading to 2-pyranylidene complexes **2** (Scheme 1a)[9] and valence isomerization of 1-acyl-2-ethynylcyclopropanes **3** via [3,3]sigmatropy of acylcyclopropylvinylidene intermediates catalyzed by

(1) (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed.; University Science Books: Mill Valley, CA, 1999; p 143. (b) Doyle, M. P. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 421−468. (c) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (d) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223. (e) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091.

(2) Transition metal-catalyzed reorganization reaction of enynes. For example, [Pd] cat.: (a) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 1636. (b) Trost, B. M.; Trost, M. K. *Tetrahedron Lett.* **1991**, *32*, 3647. (c) Trost, B. M.; Trost, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 1850. [Ru] cat.: (d) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049. [Ru] or [Pt] cat.: (e) Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9140. (f) Chatani, N.; Inoue, H.; Ikeda, T.; Murai, S. *J. Org. Chem.* **2000**, *65*, 4913. [Pt] cat.: (g) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901. (h) Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704. [Ir] cat.: (i) Chatani, N.; Inoue, H.; Morimoto, T.; Muto, T.; Murai, S. *J. Org. Chem.* **2001**, *66*, 4433.

(3) The reactions of α,*ω*-enynes with dienes via cyclopropylcarbene complexes have been reported. See: (a) Trost, B. M.; Hashmi, A. S. K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1085. (b) Trost, B. M.; Hashmi, A. S. K. *J. Am. Chem. Soc.* **1994**, *116*, 2183. The reactions of α,*ω*-enynes with alcohols or alkynes with furans via cyclopropylcarbene complexes. See: (c) Méndez, M.; Muñoz, M. P.; Echavarren, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 11549. (d) Méndez, M.; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511. (e) Fernández-Rivas, C.; Méndez, M.; Nieto-Oberhuber, C.; Echavarren, A. M. *J. Org. Chem.* **2002**, *67*, 5197. (f) Martín-Matute, B.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757.

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(5) (a) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814. For an example of the azomethine ylide, see: (b) Kusama, H.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 11592.

(6) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650.

(7) (a) Kimball, D. B.; Herges, R.; Haley, M. M. *J. Am. Chem. Soc.* **2002**, *124*, 1572. (b) Kimball, D. B.; Weakley, T. J. R.; Herges, R.; Haley, M. M. *J. Org. Chem.* **2002**, *67*, 6395. (c) Kimball, D. B.; Weakley, T. J. R.; Herges, R.; Haley, M. M. *J. Am. Chem. Soc.* **2002**, *124*, 13463. (d) Kimball, D. B.; Haley, M. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3339.

(8) (a) Rautenstrauch, V. *Tetrahedron Lett.* **1984**, *25*, 3845. (b) Rautenstrauch, V. *J. Org. Chem.* **1984**, *49*, 950. (c) Mainett, E.; Mouriès, V.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2132. (d) Miki, K.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **2003**, *44*, 2019. (e) Miki, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 8505. Oxidative rearrangement of propargyl esters by palladium catalyst has been reported, see: (f) Kataoka, H.; Watanabe, K.; Goto, K. *Tetrahedron Lett.* **1990**, *31*, 4181.

(9) Ohe, K.; Miki, K.; Yokoi, T.; Nishino, F.; Uemura, S. *Organometallics* **2000**, *19*, 5525. For benzopyranylidene complexes, see: Iwasawa, N.; Shido, M.; Maeyama, K.; Kusama, H. *J. Am. Chem. Soc.* **2000**, *122*, 10226.

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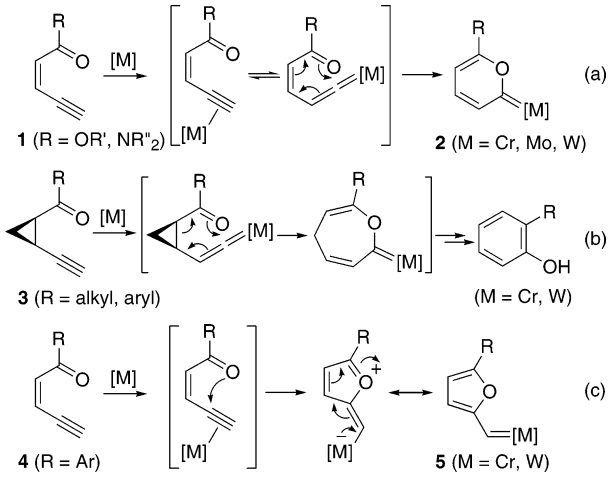
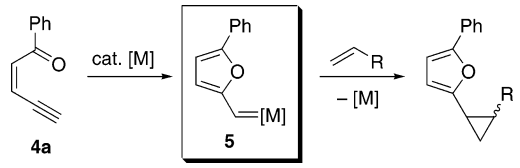
SCHEME 1



group 6 transition metal complexes (Scheme 1b).[10] We also demonstrated the formation of stable (2-furyl)-carbene−chromium or −tungsten complexes **5** from ene-yne-ketones **4** (R = Ar) (Scheme 1c).[11] The key of the third reaction is 5-*exo*-*dig* cyclization via nucleophilic attack of a carbonyl oxygen to an internal carbon of an alkyne moiety activated by transition metal complexes. Furylcarbene complexes **5** were somewhat more stable than the corresponding phenylcarbene complexes,[12] which could be stoichiometrically generated and used in cyclopropanation reactions.[13] Our continuous work mainly focusing on the catalytic activity of **5** led us to find new catalytic cyclopropanation via (2-furyl)carbene complexes without using the corresponding diazoalkane as a precursor.[14] Cyclopropanation with (2-furyl)diazomethane was scarcely investigated due to the instability of the (2-furyl)carbene intermediate.[15]

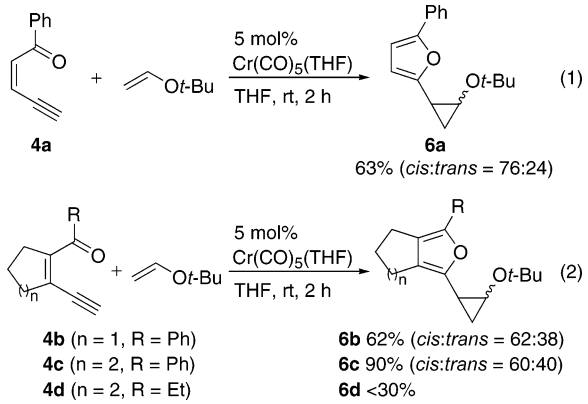
In this paper, we wish to report the details and the scope of the cyclopropanation reaction involving (2-furyl)-carbene complexes **5** directly generated from ene-yne-ketones **4** with a wide range of transition metal compounds (Scheme 2).

SCHEME 2



Results and Discussion

Chromium-Catalyzed Cyclopropanation of Alkenes. At first, the reaction of **4a** with 2 equiv of *tert*-butyl vinyl ether was carried out in the presence of 5 mol % of $Cr(CO)_5(THF)$ at room temperature (eq 1). The color of the reaction mixture gradually changed from deep blue to yellow as the reaction proceeded.[16] After 2 h, 1-*tert*-butoxy-2-[(5-phenyl)fur-2-yl]cyclopropane (**6a**) was isolated in 63% yield as a mixture of cis and trans isomers (cis:trans = 76:24). As shown in eq 2, similar eneyne-ketones **4b** and **4c** also afforded the corresponding cyclopropanated products **6b** (62% yield, cis:trans = 62:38) and **6c** (90% yield, cis:trans = 60:40), respectively.[17]



The reaction of ethyl ketone **4d** with *tert*-butyl vinyl ether was quite complex and many unidentified products formed, reducing the yield of cyclopropanated product **6d** to 20−30%. To our knowledge, examples of chromium-catalyzed cyclopropanation have been thus far limited to reports by Dötz et al.[18] Since the chromium-catalyzed cyclopropanation with ene-yne-ketones as carbenoid precursors was efficiently delineated, cyclopropanations of several alkenes with **4a** and **4c** were next examined. Typical results are given in Table 1. Reactions of **4a** and **4c** with ketene diethyl acetal proceeded quite smoothly to give furylcyclopropanes **7a** (82%) and **7c** (99%), respectively (entries 1 and 2). Ene-yne-ketone **4c** also reacted with enol silyl ether to give **8c** in 83% yield with a 66:34 diastereomeric ratio (entry 3). Interestingly, the reaction of **4c** with 3,4-dihydro-2*H*-pyran as a cyclic vinyl ether exclusively gave *endo* cyclopropanated product **9c**

(10) Ohe, K.; Yokoi, T.; Miki, K.; Nishino, F.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 526.

(11) Miki, K.; Yokoi, T.; Nishino, F.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **2002**, *645*, 228. For 6-*endo*-*dig* cyclization of 2-acylethynylbenzene with $W(CO)_5(THF)$ complex, see: Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814.

(12) (a) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097. (b) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (c) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282. (d) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802. (e) Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53. (f) Fischer, H.; Zeuner, S.; Ackermann, K. *J. Chem. Soc., Chem. Commun.* **1984**, 684. (g) Fischer, H.; Hofmann, J. *Chem. Ber.* **1991**, *124*, 981. (h) Casey, C. P.; Vosejpka, L. J. S *Organometallics* **1992**, *11*, 738. (i) Fischer, H.; Mauz, E.; Jaeger, M. *J. Organomet. Chem.* **1992**, *427*, 63. (j) Jaeger, M.; Prosenc, M.-H.; Sontag, C.; Fischer, H. *New J. Chem.* **1995**, *19*, 911.

(13) (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) Helquist, P. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, UK, 1991; Vol. 2, pp 143−194. (c) Doyle, M. P. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, UK, 1995; Vol. 12, pp 387−420.

(14) Preliminary communication of catalytic cyclopropanation with ene-yne-carbonyl compounds. See: Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260.

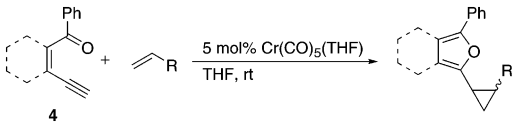
(15) (a) Hoffman, R. V.; Shechter, H. *J. Am. Chem. Soc.* **1971**, *93*, 5940. (b) Hoffman, R. V.; Orphanides, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7927. (c) Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **2000**, *122*, 8585.

(16) The blue color indicates the generation of a (2-furyl)carbene chromium complex. Thus, consumption of the starting material **4** could be visibly monitored.

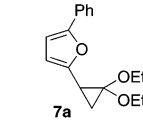
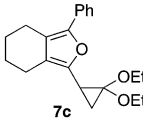
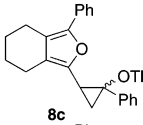
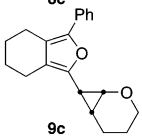
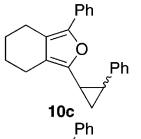
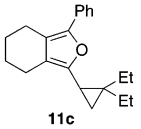
(17) When the reaction with a catalytic amount of $Cr(CO)_6$ instead of $Cr(CO)_5(THF)$ was conducted under thermal (reflux in THF for 24 h) or photoirradiation (in toluene for 2 h) conditions, the yield of **6c** was lower than that obtained by use of $Cr(CO)_5(THF)$, being in 10% and 32% yields, respectively, with a similar diastereoselectivity.

(18) Catalytic approach for a 9-(9*H*-fluorenylidene)chromium complex, see: (a) Pfeiffer, J.; Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2828. (b) Pfeiffer, J.; Nieger, M.; Dötz, K. H. *Eur. J. Org. Chem.* **1998**, 1011.

TABLE 1. Chromium-Catalyzed Cyclopropanation of Alkenes with 4[a]



4

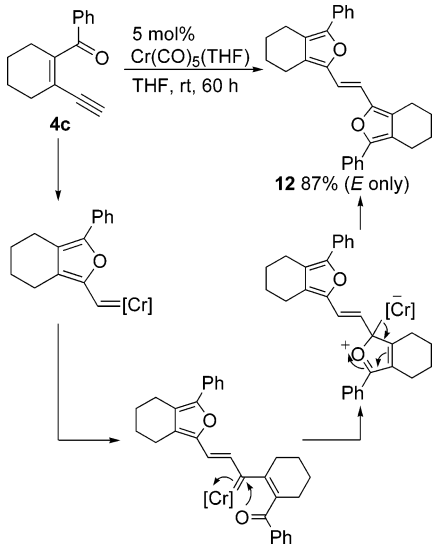
entry	4	alkene	time (h)	product	isolated yield	*cis:trans*[b]
1	**a**		1.5	 **7a**	82%	N.A.[c]
2	**c**		2	 **7c**	99%	N.A.[c]
3	**c**		4	 **8c**	83%	66:34[d]
4	**c**		22	 **9c**	90%	endo only
5[e]	**c**		14	 **10c**	85%	74:26
6[f]	**c**		96	 **11c**	52%	N.A.[c]

[a] Reactions were carried out at room temperature with **4** (0.5 mmol), alkene (1.0 mmol), and $Cr(CO)_5(THF)$ prepared in situ by irradiating a solution of $Cr(CO)_6$ (0.025 mmol) in THF (2 mL) unless otherwise noted. [b] Determined by ^1H NMR. [c] N.A. = not applicable. [d] Configuration is not yet clear. [e] Alkene (10 mmol). [f] 2-Ethylbut-1-ene (7.5 mmol).

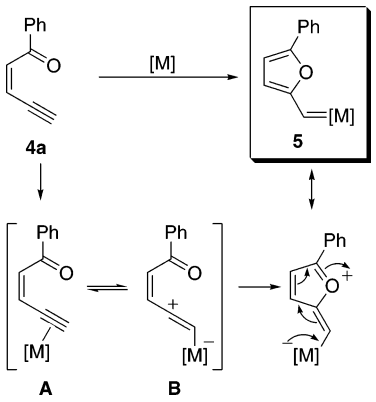
in 90% yield (entry 4).[19] Styrene reacted slowly with **4c** to give **10c** (85%, cis:trans = 74:26), although the reaction required 20 equiv of styrene (entry 5). In the cyclopropanation of 2-ethylbut-1-ene with **4c**, both prolonged reaction time (96 h) and excess use of alkenes (12.5 eqiuv to **4c**) were requisite, the product **11c** being produced in 52% yield (entry 6). On the other hand, cyclopropanation of vinyl acetate and 1-octene with **4c** was sluggish, the yields of the corresponding cyclopropanated products being 22% (6 days) and 19% (10 days), respectively. Here, the complete consumption of the starting ene-yne-ketone **4c** was observed, indicating that other reactions catalyzed by chromium compete with the cyclopropanation reaction. In fact, treatment of **4c** in THF without an alkene in the presence of a catalytic amount of $Cr(CO)_5$-(THF) yielded 1,2-difurylethene **12** in 87% yield with high trans stereoselectivity for 60 h. The plausible mechanism giving **12** is considered to be similar to the one proposed by Herndon et al. (Scheme 3).[20] Since the side reaction occurs more slowly compared with the desired cyclopropanation, the slow addition of **4** is not always required in the present cyclopropanation reaction.

(19) The structure was unambiguously determined by X-ray diffraction analysis of **9c**. See the Supporting Information.

SCHEME 3



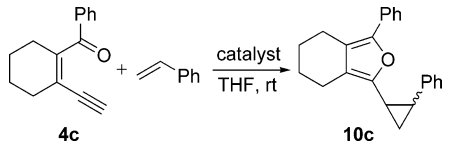
SCHEME 4



Other Transition Metal-Catalyzed Cyclopropanation of Alkenes. As shown in Scheme 4, 5-*exo*-*dig* cyclization of ene-yne-ketone **4**[10] via nucleophilic attack of a carbonyl oxygen to an internal carbon of an alkyne in π-alkyne complex **A** might be the most plausible pathway for generation of (2-furyl)carbene−chromium complex **5** (M = $Cr(CO)_5$). A slipped and polarized η^1-complex **B** from complex **A** would be an alternatively possible intermediate. It is well-known that **A** is prone to isomerize to **B**, which has been widely accepted for an intermediate for cyclization and skeletal reorganization of 1,6-enynes with a diversity of metal complexes.[2,3] Considering the possibility of the intervention of **B**, we examined cyclopropanation of styrene with **4c** in the presence of other transition metal compounds as catalysts (Table 2). Other group 6 metal complexes such as Mo-$(CO)_5(THF)$ and $W(CO)_5(THF)$ were found to catalyze the cyclopropanation to give **10c** in 23% and 54% yields with 54:46 and 70:30 cis and trans ratios, respectively (entries 1 and 2). $Mn(CO)_5Br$ of the group 7 triad was marginally effective in the cyclopropanation reaction (entry 3). Of

(20) Furan ring construction from enyne-aldehyde derivatives with a stoichiometric amount of Fischer carbene complexes has been demonstrated. See: (a) Herndon, J. W.; Wang, H. *J. Org. Chem.* **1998**, *63*, 4564. (b) Zhang, Y.; Herndon, J. W. *J. Org. Chem.* **2002**, *67*, 4177.

TABLE 2. Catalytic Cyclopropanation of Styrene with 1c[a]



entry	catalyst	time, h	yield,[b] %	cis/trans[c]
1	$Mo(CO)_5(THF)$[d]	2	23	54:46
2	$W(CO)_5(THF)$[d]	2	54	70:30
3	$Mn(CO)_5Br$	24	21	9:91
4	$[(p\text{-cymene})RuCl_2]_2$[e]	2	85	33:67
5	$[RuCl_2(CO)_3]_2$[e]	24	42	12:88
6	$[Rh(OAc)_2]_2$[e,f]	1	93	8:92
7	$[RhCl(cod)]_2$[a]	2	69	56:44
8	$[IrCl(cod)]_2$[e]	2	92	57:43
9	$PdCl_2$	2	79	21:79
10	$PtCl_2$	1	81	23:77

[a] Reactions were carried out at room temperature with **4c** (0.20 mmol), styrene (4.0 mmol), and a catalyst (0.010 mmol) in THF (2 mL) unless otherwise noted. [b] Isolated yield. [c] Determined by ^1H NMR. [d] Prepared in situ by irradiating a solution of $M(CO)_6$ in THF. [e] 0.005 mmol. [f] Styrene (0.40 mmol).

group 8 triad metals, ruthenium complexes such as $[(p\text{-cymene})RuCl_2]_2$ and $[RuCl_2(CO)_3]_2$ were effective to give **10c** in 85% (cis:trans = 33:67) and 42% (cis:trans = 12:88) yields, respectively (entries 4 and 5).[21] Rhodium and iridium complexes of the group 9 triad exhibited high catalytic efficiency in the present reaction (entries 6−8). In particular, $[Rh(OAc)_2]_2$ catalyzed the cyclopropanation of 2 equiv of styrene with **4c** to give **10c** for 1 h with exquisite efficiency (93% yield) and selectivity (cis:trans = 8:92) (entry 6). $PdCl_2$ and $PtCl_2$ of the group 10 triad effectively catalyzed the cyclopropanation of styrene to give **10c** in 79% (21:79 ratio) and 81% yields (23:77 ratio), respectively (entries 9 and 10). Other metal compounds such as Cp_2Ti(isobutylene), $Mn(acac)_2$, $NiCl_2$, CuOTf-$(^1/_2C_6H_6)$, $Cu(OTf)_2$, and $AuCl_3$ were not effective as catalysts in the present cyclopropanation. Variable stereoselectivity obtained in these reactions indicates that cyclopropanation proceeds in a different manner depending on each catalyst. The stereochemistry of the present cyclopropanation reaction will be argued in the last section (vide infra).

To compare the chromium catalysis with other transition metal catalysts, we next examined cyclopropanation of several alkenes with ene-yne-ketones **4a**−**c** in the presence of $[Rh(OAc)_2]_2$ and $PtCl_2$ as selected catalysts. These results are summarized in Table 3. The reactions of **4a**−**c** with *tert*-butyl vinyl ether, ketene diethyl acetal, cyclic vinyl ether, and styrene proceeded quite smoothly to give the cyclopropanated products **6a**−**c**, **7c**, **9c**, and **10c** in good yields, respectively (entries 1−11). In the presence of $[Rh(OAc)_2]_2$ as a catalyst, the cyclopropanation of 2-ethylbut-1-ene with **4c** gave **11c** in 67% yield (entry 12), while a similar reaction with $PtCl_2$ catalyst gave **11c** in only 18% yield together with other unidentified products (entry 13). $[Rh(OAc)_2]_2$ can act as an

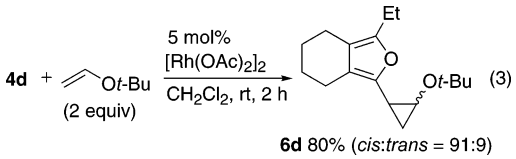
(21) In the case of $[(p\text{-cymene})RuCl_2]_2$, a remarkable solvent effect was observed. Thus, the use of $ClCH_2CH_2Cl$ in place of THF as solvent led to the rapid formation of the cyclopropanated product **10c** in 96% yield in the reaction of styrene with **4c** at room temperature for 1 h with a high trans selectivity (cis:trans = 11:89).

TABLE 3. Rh- or Pt-Catalyzed Cyclopropanation of Alkenes with 4[a]

entry	4	alkene	cat.[b]	product	yield[c]	cis:trans[d]
1	**a**		[Rh]	**6a**	99%	85:15
2	**a**		[Pt]	**6a**	89%	32:68
3	**b**		[Rh]	**6b**	92%	85:15
4	**c**		[Rh]	**6c**	99%	90:10
5	**c**		[Pt]	**6c**	68%	27:73
6	**c**		[Rh]	**7c**	96%	N.A.[e]
7	**c**		[Pt]	**7c**	56%	N.A.[e]
8	**c**		[Rh]	**9c**	75%	endo only
9	**c**		[Pt]	**9c**	60%	endo only
10	**c**		[Rh]	**10c**	93%	8:92
11[f]	**c**		[Pt]	**10c**	81%	23:77
12	**c**		[Rh]	**11c**	67%	N.A.[e]
13[g]	**c**		[Pt]	**11c**	18%	N.A.[e]

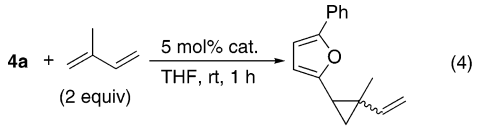
[a] Reactions were carried out at room temperature with **4** (0.2 mmol), alkene (0.4 mmol), and $[Rh(OAc)_2]_2$ (0.005 mmol) or $PtCl_2$ (0.01 mmol) in THF (2 mL) for 1 h unless otherwise noted. [b] [Rh] = $[Rh(OAc)_2]_2$, [Pt] = $PtCl_2$. [c] Isolated yield. [d] Determined by ^1H NMR. [e] N.A. = not applicable. [f] Styrene (4.0 mmol). [g] 3 h.

effective catalyst in cyclopropanation of *tert*-butyl vinyl ether with ethyl ketone **4d** (eq 3), which led to a lower yield of cyclopropanated product in chromium catalysis (<30% yield, see eq 2).



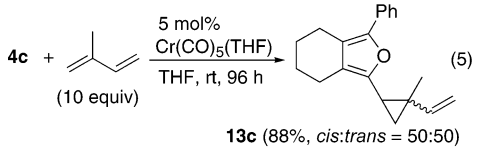
Regioselectivity and Chemoselectivity in Catalytic Cyclopropanation. The pronounced preference for the cyclopropanation reaction to take place at electron-rich C=C bonds was verified by the chromium-, rhodium-, and platinum-catalyzed reaction of **4** with isoprene and 2-vinyloxyethyl acrylate as shown in eqs 4−6. In each reaction of isoprene with **4a** and **4c**, a more substituted double bond was selectively cyclopropanated to give **13a** and **13c** in good yields with nondiastereoselective manner, respectively (eqs 4 and 5). As shown in eq 6, a more electron-rich C=C double bond of 2-vinyloxyethyl acrylate was selectively cyclopropanated to give **14c** (73% with [Cr], 92% with [Rh], and 46% with [Pt]) as a mixture of diastereoisomers (67:33 to 90:10), respectively. A higher reactivity of electron-rich alkenes and preferential formation of *cis*-cyclopropanes in this reaction indicate that the cyclopropanation proceeds through the formation of an electrophilic (2-furyl)carbenoid intermediate like phenylcarbene−tungsten and −iron complexes.[12,13]

Plausible Reaction Pathway. To elucidate the reaction pathway, cyclopropanation of stereodefined *cis*- and *trans*-but-2-ene was examined. In the presence of $Cr(CO)_5(THF)$ and $PtCl_2$ as selected catalysts, the cyclopropanation reaction of *cis*- and *trans*-but-2-ene with an



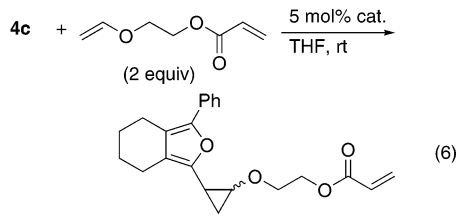
(4)

$[Rh(OAc)_2]_2$ **13a** (78%, *cis*:*trans* = 43:57)
$PtCl_2$ **13a** (66%, *cis*:*trans* = 45:55)



(5)

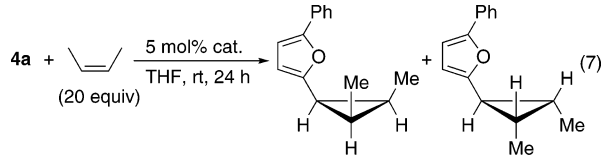
13c (88%, *cis*:*trans* = 50:50)



(6)

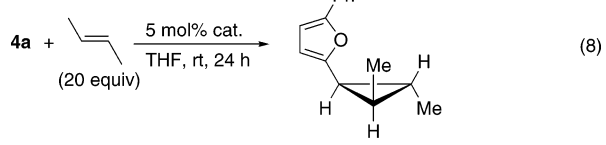
$Cr(CO)_5(THF)$ [24 h] **14c** (73%, *cis*:*trans* = 89:11)
$[Rh(OAc)_2]_2$ [0.5 h] **14c** (92%, *cis*:*trans* = 90:10)
$PtCl_2$ [3 h] **14c** (46%, *cis*:*trans* = 67:33)

ene-yne-ketone **4a** proceeded stereospecifically to give only the cyclopropanated products with retention of configuration of alkenes, **15a** (14%, syn:anti = 91:9 with [Cr]; 26%, syn:anti = 75:25 with [Pt]) and **16a** (7% with [Cr]; 23% with [Pt]), respectively (eqs 7 and 8).[22]



(7)

$Cr(CO)_5(THF)$ **15a** (14%, *syn*:*anti* = 91:9)
$PtCl_2$ **15a** (26%, *syn*:*anti* = 75:25)

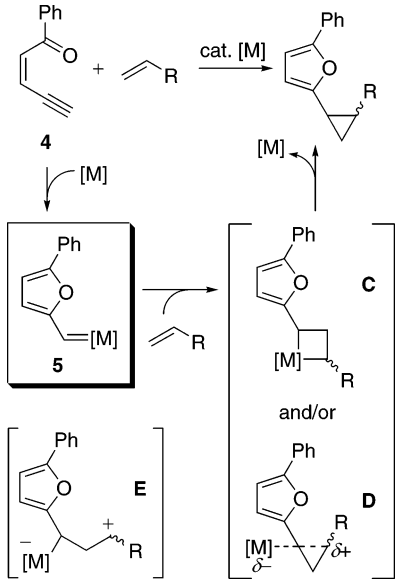


(8)

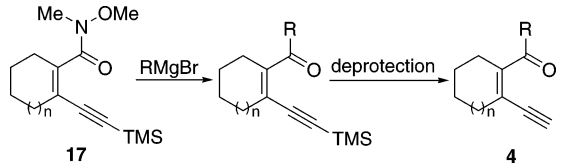
$Cr(CO)_5(THF)$ **16a** (7%)
$PtCl_2$ **16a** (23%)

The outcomes of the stereochemistry show that the most plausible reaction pathway for cyclopropanation of an alkene with an ene-yne-ketone **4** is illustrated as Scheme 5. The ene-yne-ketone **4** reacts with a transition metal complex to give a (2-furyl)carbene complex **5** as shown in Scheme 4. Subsequently, the complex **5** reacts with an alkene to give the cyclopropanated product through a metallacyclobutane **C** or a charge-developed intermediate **D**.[12a,c,h,j,13] The preference for the *cis*-cyclopropane isomer is a characteristic feature of the electrophilic metal-carbenoid having the same or similar steric environment ($Cr(CO)_5$ or $[Rh(OAc)_2]_2$ in octahedral geometry) except for the styrene case with $[Rh(OAc)_2]_2$.[23] In the case of the late transition metals having the square-planar geometry, the diastereoselectivity depends considerably on the structure of alkenes and the stability of metallacycles. The logical contention about the relationship between plausible intermediates and stereoselectivity of cyclopropanation still remains, but at least a carbocationic intermediate **E** can be presumably excluded in the present reaction.

SCHEME 5



SCHEME 6



Conclusion

We have demonstrated new catalytic cyclopropanation of alkenes based on the generation of (2-furyl)carbene complexes from conjugated ene-yne-ketones. This catalytic system has wide applicability to a diversity of transition metal complexes as well as a variety of ene-yne-ketones, and indeed finds some applications in other catalytic 2-furfurylidene transfer reactions such as the Doyle−Kirmse reaction.[24] This reaction represents a new protocol to generate carbenoid species via activation of alkynes with transition metal complexes.

Experimental Section

Synthesis of Substrates. Substrates **4a**[14] and **4c**[11] were prepared by our reported procedures. Substrates **4b** and **4d** were prepared from ene-yne-carbonyl compound **17**[11] by the following procedures (Scheme 6).

1-Ethynyl-2-benzoylcyclopent-1-ene (4b). To a solution of **17** (1.2 g, 4.4 mmol, *n* = 1) in THF (10 mL) was added PhMgBr (9 mL, 9.0 mmol, 1.0 M in THF) at 0 °C. The mixture

(22) Lower yields of cyclopropanated products were due to the formation of either 1,2-difurylethene **12** in the Cr-catalyzed reaction or many unidentified products in the Pt-catalyzed reaction.

(23) Cis preference was observed in the cyclopropanation of styrene with $PhCHN_2$ as a carbenoid precursor, the ratio of cis:trans being 77:23. See ref 12e.

(24) Kato, Y.; Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *Org. Lett.* **2003**, *5*, 2619.

was stirred at room temperature for 30 min. The mixture was washed with saturated NH_4Cl solution (10 mL) and the aqueous phase was extracted with AcOEt (3 × 10 mL). The combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v 10/1) as an eluent to afford the crude ene-yne-carbonyl compound (0.56 mg, 2.4 mmol, 54%) as a pale yellow oil. To a solution of this crude ene-yne-carbonyl compound in MeOH (20 mL) was added K_2CO_3 (0.66 g, 4.8 mmol) at room temperature. After being stirred for 30 min, the suspension was poured into a mixture of saturated aqueous NH_4Cl solution (30 mL) and Et_2O (30 mL), and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v 15/1) as an eluent to afford ene-yne-carbonyl compound **4b** (0.35 g, 2.2 mmol, 64% yield for 2 steps) as a pale yellow oil; IR (neat) 1639 (C═O), 2087 (C≡C), 3242 (≡C−H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.03 (quint, J = 7.6 Hz, 2H), 2.74 (tt, J = 2.0, 7.6 Hz, 2H), 2.87 (tt, J = 2.0, 7.6 Hz, 2H), 3.03 (s, 1H), 7.43 (dd, J = 7.6, 7.6 Hz, 2H), 7.54 (dd, J = 7.6, 7.6 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 22.5, 35.4, 39.2, 79.0, 86.4, 128.1, 129.3, 129.5, 132.7, 137.3, 148.4, 194.9. Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.38; H, 6.04.

1-Ethynyl-2-propionylcyclohex-1-ene (4d). Substrate **4d** was prepared from **17** (1.3 g, 5.0 mmol, n = 2) by a similar procedure for **4b**. A colorless oil (0.37 g, 0.24 mmol, 47% yield for 2 steps); IR (neat) 1662 (C═O), 2088 (C≡C), 3256 (≡C−H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.10 (t, J = 7.2 Hz, 3H), 1.58−1.72 (m, 4H), 2.26−2.40 (m, 4H), 2.87 (q, J = 7.2 Hz, 2H), 3.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.1, 21.6, 21.8, 26.1, 31.7, 34.9, 84.0, 100.5, 122.5, 145.7, 205.3. HRMS (FAB) calcd for $C_{11}H_{15}O$ (M + H^+) 163.1123, found 163.1120.

Typical Procedure for Chromium-Catalyzed Cyclopropanation Reactions. The complex $Cr(CO)_6$ (5.5 mg, 0.025 mmol) was placed in the flame-dried Schlenk flask and dissolved in dry and deoxygenated THF (2.0 mL) at room temperature under N_2. This solution was irradiated with a high-pressure Hg lamp for 2 h at room temperature. Then, N_2 gas was bubbled into the yellow solution for 5 min. To this yellow solution were added a solution of **4** (0.5 mmol) and an alkene in THF (2 mL). After the reaction was complete (the color of the solution changed from blue to yellow), the organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt as an eluent to afford cyclopropanes.

Typical Procedure for Other Transition Metal-Catalyzed Cyclopropanation Reactions of Styrene with 4b. To a solution of **4** (0.20 mmol) and alkene (0.4−4.0 mmol) in THF (2 mL) was added a transition metal complex (0.010 mmol) at room temperature under N_2. After the reaction was complete, the reaction mixture was filtered through Florisil. The organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt as an eluent to afford the corresponding cyclopropanes.

Cyclopropane 6a (by [Rh] Catalyst). A pale yellow oil (51 mg, 0.20 mmol, 99% yield, cis/trans = 85/15); IR (neat) 692, 758, 784, 885, 972, 1014, 1025, 1190, 1365, 1390, 1487, 1549, 1595, 2975 cm^{-1}; ^1H NMR (300 MHz, d_8-THF, 25 °C) cis isomer, δ 0.95 (ddd, J = 4.0, 6.4, 6.8 Hz, 1H), 1.09 (s, 9H), 1.13 (ddd, J = 6.4, 6.8, 9.6 Hz, 1H), 1.95 (ddd, J = 6.4, 6.4, 9.6 Hz, 1H), 3.51 (ddd, J = 4.0, 6.4, 6.4 Hz, 1H), 6.04 (d, J = 3.6 Hz, 1H), 6.62 (d, J = 3.6 Hz, 1H), 7.15 (dd, J = 7.6, 7.6 Hz, 1H), 7.30 (dd, J = 7.6, 7.6 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H); ^1H NMR (300 MHz, d_8-THF, 25 °C) trans isomer, δ 1.07−1.13 (m, 2H), 1.25 (s, 9H), 1.94−1.99 (m, 1H), 3.36 (ddd, J = 2.8, 2.8, 8.0 Hz, 1H), 6.01 (d, J = 3.6 Hz, 1H), 6.60 (d, J = 3.6 Hz, 1H), 7.14 (dd, J = 7.6, 7.6 Hz, 1H), 7.30 (dd, J = 7.6, 7.6 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) cis isomer, δ 12.9, 17.3, 28.2, 52.4, 75.0, 106.6, 107.7, 123.7, 127.0, 129.2, 132.3, 152.5, 154.6; ^{13}C NMR (100 MHz, d_8-THF, 25 °C) trans isomer, δ 14.1, 19.1, 28.6, 54.2, 75.4, 106.5, 106.6, 123.8, 127.3, 129.2, 132.1, 152.8, 155.9. HRMS (FAB) calcd for $C_{17}H_{20}O_2$ (a mixture of cis and trans isomers) (M^+) 256.1463, found 256.1463. Anal. Calcd for $C_{17}H_{20}O_2$ (a mixture of cis and trans isomers): C, 79.65; H, 7.86. Found: C, 79.75; H, 8.01.

Cyclopropane 6b (by [Rh] Catalyst). A colorless oil (55 mg, 0.18 mmol, 92%, cis/trans = 85/15); IR (neat) 692, 761, 894, 922, 1010, 1024, 1190, 1363, 1389, 1494, 1604, 2973 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) cis isomer, δ 0.96−1.10 (m, 2H), 1.08 (s, 9H), 1.89 (ddd, J = 6.4, 6.4, 10.0 Hz, 1H), 2.30−2.40 (m, 2H), 2.51−2.67 (m, 2H), 2.75−2.79 (m, 2H), 3.48 (ddd, J = 4.4, 6.4, 6.4 Hz, 1H), 7.07 (dd, J = 7.6, 7.6 Hz, 1H), 7.28 (dd, J = 7.6, 7.6 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) cis isomer, δ 10.6, 16.5, 24.1, 25.0, 27.4, 32.1, 51.6, 74.0, 122.8, 125.0, 128.2, 129.3, 130.2, 132.2, 141.2, 142.4. HRMS (FAB) calcd for $C_{20}H_{24}O_2$ (a mixture of cis and trans isomers) (M^+) 296.1776, found 296.1782. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.95; H, 8.27.

Cyclopropane 6c (by [Rh] Catalyst). A pale yellow oil (61 mg, 0.20 mmol, 99% yield, cis/trans = 90/10); IR (neat) 693, 762, 1048, 1153, 1191, 1364, 1440, 1493, 1600, 2931, 2974 cm^{-1}; ^1H NMR (300 MHz, d_8-THF, 25 °C) cis isomer, δ 1.01−1.09 (m, 1H), 1.08 (s, 9H), 1.26−1.31 (m, 1H), 1.66−1.73 (m, 4H), 1.84 (ddd, J = 6.3, 6.3, 9.9 Hz, 1H), 2.44−2.64 (m, 2H), 2.73−2.78 (m, 2H), 3.49 (ddd, J = 4.2, 6.3, 6.3 Hz, 1H), 7.08 (dd, J = 7.8, 7.8 Hz, 1H), 7.29 (dd, J = 7.8, 7.8 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H); ^1H NMR (300 MHz, d_8-THF, 25 °C) trans isomer, δ 1.04−1.11 (m, 1H), 1.19 (ddd, J = 6.3, 6.3, 6.3 Hz, 1H), 1.26 (s, 9H), 1.68−1.76 (m, 4H), 1.90 (ddd, J = 3.0, 6.3, 9.6 Hz, 1H), 2.52−2.67 (m, 2H), 2.70−2.76 (m, 2H), 3.48 (ddd, J = 3.0, 6.3, 6.3 Hz, 1H), 7.10 (dd, J = 7.8, 7.8 Hz, 1H), 7.30 (dd, J = 7.8, 7.8 Hz, 2H), 7.49 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, d_8-THF, 25 °C) cis isomer, δ 11.0, 16.7, 22.0, 24.0, 24.1, 24.5, 28.2, 52.3, 74.8, 119.8, 120.1, 124.4, 125.9, 129.1, 133.6, 144.9, 146.6; ^3C NMR (75 MHz, d_8-THF, 25 °C) trans isomer, δ 13.9, 18.0, 21.4, 23.9, 23.9, 24.4, 28.5, 53.4, 75.2, 118.7, 120.1, 124.4, 126.2, 129.1, 133.3, 144.8, 147.9. HRMS (FAB) calcd for $C_{21}H_{26}O_2$ (a mixture of cis and trans isomers) (M^+) 310.1933, found 310.1935. Anal. Calcd for $C_{21}H_{26}O_2$ (a mixture of cis and trans isomers): C, 81.25; H, 8.44. Found: C, 80.97; H, 8.52.

Cyclopropane 6d (by [Rh] Catalyst). A pale yellow oil (42 mg, 0.16 mmol, 80% yield, cis/trans = 91/9); IR (neat) 893, 1000, 1039, 1062, 1150, 1192, 1238, 1259, 1364, 1388, 1444, 1593, 2855, 2932, 2973 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) cis isomer, δ 1.03 (ddd, J = 5.6, 6.8, 10.0 Hz, 1H), 1.01 (s, 9H), 1.06 (t, J = 7.6 Hz, 3H), 1.07 (ddd, J = 4.0, 5.6, 7.2 Hz, 1H), 1.52−1.61 (m, 4H), 1.66 (ddd, J = 6.0, 7.2, 10.0 Hz, 1H), 2.30−2.51 (m, 4H), 2.41 (q, J = 7.6 Hz, 2H), 3.33 (ddd, J = 4.0, 6.0, 6.8 Hz, 1H); ^{13}C NMR (75 MHz, d_8-THF, 25 °C) cis isomer, δ 9.4, 12.6, 15.9, 19.6, 20.6, 21.2, 23.8, 23.8, 27.4, 51.0, 73.7, 115.2, 116.5, 143.1, 147.1. HRMS (FAB) calcd for $C_{17}H_{27}O_2$ (a mixture of cis and trans isomers) (M + H^+) 263.2011, found 263.2006.

Cyclopropane 7a (by [Cr] Catalyst). A pale yellow oil (45 mg, 0.16 mmol, 82% yield); IR (neat) 691, 759, 1023, 1056, 1117, 1212, 1285, 1443, 1487, 1548, 1595, 2884, 2929, 2975 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) δ 0.99 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H), 1.31 (dd, J = 6.0, 6.8 Hz, 1H), 1.41 (dd, J = 6.0, 10.4 Hz, 1H), 2.37 (dd, J = 6.8, 10.4 Hz, 1H), 3.38−3.51 (m, 1H), 3.58−3.75 (m, 3H), 6.09 (d, J = 3.6 Hz, 1H), 6.62 (d, J = 3.6 Hz, 1H), 7.15 (dd, J = 7.6, 7.6 Hz, 1H), 7.30 (dd, J = 7.6, 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) δ 15.6, 15.8, 19.2, 24.5, 62.3, 62.8, 92.3, 106.7, 108.1, 123.9, 127.3, 129.2, 132.1, 153.0, 153.4. HRMS (FAB) calcd for $C_{17}H_{20}O_3$ (M^+) 272.1412, found

272.1407. Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.90; H, 7.37.

Cyclopropane 7c (by [Cr] Catalyst). A pale yellow oil (65 mg, 0.20 mmol, 99% yield); IR (neat) 693, 762, 983, 1054, 1070, 1118, 1201, 1269, 1441, 1493, 1561, 1601, 2929, 2974 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) δ 0.99 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 1.35 (dd, J = 5.2, 10.4 Hz, 1H), 1.57 (dd, J = 5.2, 6.8 Hz, 1H), 1.65−1.78 (m, 4H), 2.26 (dd, J = 6.8, 10.4 Hz, 1H), 2.50−2.58 (m, 2H), 2.71−2.78 (m, 2H), 3.42−3.50 (m, 1H), 3.57−3.73 (m, 3H), 7.09 (dd, J = 7.6, 7.6 Hz, 1H), 7.29 (dd, J = 7.6, 7.6 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) δ 15.8, 15.8, 17.8, 21.8, 23.7, 24.0, 24.0, 24.5, 62.2, 62.8, 92.3, 120.0, 120.2, 124.4, 126.1, 129.0, 133.3, 144.9, 145.1. HRMS (FAB) calcd for $C_{21}H_{26}O_3$ (M^+) 326.1882, found 326.1884.

Cyclopropane 8c (by [Cr] Catalyst). A colorless oil (67 mg, 0.17 mmol, 83% yield, as a mixture of cis and trans isomers); IR (neat) 695, 760, 843, 1203, 1250, 1447, 1494, 1601, 2933 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) δ −0.18 (s, 9H), −0.01 (s, 9H), 1.54−1.66 (m, 4H), 1.62 (dd, J = 6.0, 10.0 Hz, 1H), 1.66−1.80 (m, 4H), 1.74 (dd, J = 6.4, 10.0 Hz, 1H), 1.96 (dd, J = 6.4, 7.2 Hz, 1H), 2.00 (dd, J = 6.0, 7.2 Hz, 1H), 2.16 (dd, J = 7.2, 10.0 Hz, 1H), 2.38−2.42 (m, 2H), 2.47−2.66 (m, 4H), 2.49 (dd, J = 7.2, 10.0 Hz, 1H), 2.71−2.75 (m, 2H), 7.02−7.36 (m, 16H), 7.40 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) δ −0.4, −0.4, 17.5, 18.1, 20.0, 20.3, 22.1, 22.3, 22.4, 22.4, 22.8, 23.0, 24.3, 24.6, 61.7, 62.8, 118.0, 118.6, 119.2, 119.9, 122.9, 122.9, 124.4, 124.5, 124.8, 124.8, 125.7, 126.1, 126.6, 127.2, 127.3, 127.4, 131.5, 131.8, 139.4, 139.4, 143.4, 143.4, 143.7, 143.8. HRMS (FAB) calcd for $C_{26}H_{30}O_2Si$ (a mixture of cis and trans isomers) (M^+) 402.2015, found 402.2018. Anal. Calcd for $C_{26}H_{30}O_2Si$ (a mixture of cis and trans isomers): C, 77.57; H, 7.51. Found: C, 77.28; H, 7.43.

Cyclopropane 9c (by [Cr] Catalyst). A pale yellow solid (53 mg, 0.18 mmol, 90% yield); mp 87.0−88.8 °C; IR (KBr) 698, 766, 1041, 1105, 1142, 1236, 1245, 1438, 1447, 1599, 2854, 2929, 2939, 2953 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) δ 0.64−0.76 (m, 1H), 1.07−1.20 (m, 1H), 1.33 (ddd, J = 6.8, 6.8, 6.8 Hz, 1H), 1.64−1.77 (m, 5H), 1.93 (dddd, J = 6.8, 6.8, 12.0, 14.0 Hz, 1H), 2.25 (dd, J = 4.2, 14.0 Hz, 1H), 2.43−2.51 (m, 1H), 2.69−2.78 (m, 3H), 3.16−3.23 (m, 1H), 3.35−3.40 (m, 1H), 3.78 (dd, J = 6.8, 6.8 Hz, 1H), 7.12 (dd, J = 7.2, 7.2 Hz, 1H), 7.32 (dd, J = 7.2, 7.2 Hz, 2H), 7.57 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) δ 14.9, 17.1, 19.0, 21.8, 23.4, 24.0, 24.0, 24.6, 54.9, 64.8, 119.9, 122.3, 124.5, 126.1, 129.1, 133.5, 145.8, 145.8. HRMS (FAB) calcd for $C_{20}H_{22}O_2$ (M^+) 294.1620, found 294.1619.

Cyclopropane 10c (by [Rh] Catalyst). A colorless oil (58 mg, 0.19 mmol, 93% yield, cis/trans = 8/92); IR (neat) 693, 762, 906, 1029, 1072, 1439, 1494, 1560, 1601, 2855, 2929 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) cis isomer, δ 1.45 (ddd, J = 5.2, 8.8, 8.8 Hz, 1H), 1.53−1.70 (m, 4H), 1.61 (ddd, J = 5.2, 6.4, 6.4 Hz, 1H), 2.19−2.45 (m, 2H), 2.30 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.42 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.58−2.68 (m, 2H), 7.02−7.16 (m, 6H), 7.24−7.37 (m, 4H); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) trans isomer, δ 1.39 (ddd, J = 4.8, 6.0, 8.8 Hz, 1H), 1.65 (ddd, J = 4.8, 6.0, 8.8 Hz, 1H), 1.66−1.76 (m, 4H), 2.09 (ddd, J = 4.8, 6.0, 8.8 Hz, 1H), 2.44 (ddd, J = 4.8, 6.0, 8.8 Hz, 1H), 2.54 (t, J = 6.0 Hz, 2H), 2.76 (t, J = 6.0 Hz, 2H), 7.12−7.21 (m, 4H), 7.29 (dd, J = 7.8, 7.8 Hz, 2H), 7.35 (dd, J = 7.8, 7.8 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) cis isomer, δ 10.7, 16.7, 20.7, 22.8, 22.9, 23.4, 23.6, 119.2, 121.1, 125.4, 125.4, 125.8, 127.6, 128.1, 128.4, 132.3, 138.9, 144.3, 145.2; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) trans isomer, δ 15.8, 20.3, 20.7, 23.0, 23.1, 23.5, 24.8, 118.5, 119.6, 123.8, 125.6, 125.7, 125.8, 128.3, 128.4, 132.1, 142.0, 143.9, 147.3. HRMS (FAB) calcd for $C_{23}H_{22}O$ (a mixture of cis and trans isomers) (M^+) 314.1671, found 314.1671. Anal. Calcd for $C_{23}H_{22}O$ (a mixture of cis and trans isomers): C, 87.86; H, 7.05. Found: C, 87.99; H, 7.20.

Cyclopropane 11c (by [Rh] Catalyst). A colorless oil (39 mg, 0.13 mmol, 67% yield); IR (neat) 691, 760, 1034, 1441, 1458, 1493, 1560, 1601, 2932, 2961 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.80 (dd, J = 4.4, 8.8 Hz, 1H), 0.84 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H), 1.02 (dd, J = 4.4, 5.2 Hz, 1H), 1.13 (qd, J = 7.2, 14.4 Hz, 1H), 1.27 (qd, J = 7.2, 14.4 Hz, 1H), 1.35 (qd, J = 7.2, 14.4 Hz, 1H), 1.50 (qd, J = 7.2, 14.4 Hz, 1H), 1.64 (dd, J = 5.2, 8.8 Hz, 1H), 1.67−1.79 (m, 4H), 2.45−2.53 (m, 2H), 2.72−2.79 (m, 2H), 7.14 (dd, J = 7.6, 7.6 Hz, 1H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 10.7, 10.8, 17.4, 20.8, 21.2, 23.1, 23.2, 23.3, 23.6, 28.8, 29.6, 119.5, 119.8, 123.7, 125.3, 128.3, 132.4, 143.7, 147.3. HRMS (FAB) calcd for $C_{21}H_{26}O$ (M^+) 294.1984, found 294.1976. Anal. Calcd for $C_{21}H_{26}O$: C, 85.67; H, 8.90. Found: C, 85.42; H, 9.16.

Cyclopropane 13a (by [Rh] Catalyst). A colorless oil (35 mg, 0.16 mmol, 78% yield, cis/trans = 43/57); IR (neat) 691, 758, 786, 898, 1019, 1487, 1548, 1595, 1636, 2929, 2956, 3002 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.10 (s, 3H), 1.15−1.22 (m, 4H), 1.32 (s, 3H), 2.08 (dd, J = 6.4, 8.8 Hz, 1H), 2.12 (dd, J = 6.4, 8.8 Hz, 1H), 4.94 (dd, J = 1.2, 10.4 Hz, 1H), 4.98 (dd, J = 0.8, 10.8 Hz, 1H), 5.04 (dd, J = 0.8, 17.2 Hz, 1H), 5.05 (dd, J = 1.2, 17.6 Hz, 1H), 5.54 (dd, J = 10.8, 17.2 Hz, 1H), 5.56 (dd, J = 10.4, 17.6 Hz, 1H), 6.07 (d, J = 3.2 Hz, 1H), 6.09 (d, J = 3.2 Hz, 1H), 6.54 (d, J = 3.2 Hz, 1H), 6.56 (d, J = 3.2 Hz, 1H), 7.20 (dd, J = 7.6, 7.6 Hz, 1H), 7.20 (dd, J = 7.6, 7.6 Hz, 1H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 15.8, 19.6, 20.2, 21.8, 24.1, 25.1, 26.1, 26.2, 105.7, 105.7, 108.3, 108.7, 110.6, 112.4, 123.3, 123.3, 126.7, 126.7, 128.5, 128.5, 131.0, 131.0, 140.9, 145.1, 152.2, 152.4, 153.6, 153.9. HRMS (FAB) calcd for $C_{16}H_{16}O$ (a mixture of cis and trans isomers) (M^+) 224.1201, found 224.1202. Anal. Calcd for $C_{16}H_{16}O$ (a mixture of cis and trans isomers): C, 85.68; H, 7.19. Found: C, 85.66; H, 7.36.

Cyclopropane 13c (by [Cr] Catalyst). A colorless oil (49 mg, 0.18 mmol, 88% yield, cis/trans = 50/50); IR (neat) 692, 760, 896, 995, 1030, 1071, 1441, 1493, 1558, 1601, 1633, 2857, 2930 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.12 (s, 3H), 1.17 (dd, J = 4.4, 8.8 Hz, 1H), 1.20 (dd, J = 4.8, 9.2 Hz, 1H), 1.33 (s, 3H), 1.35 (dd, J = 4.8, 6.4 Hz, 1H), 1.46 (dd, J = 4.8, 6.4 Hz, 1H), 1.64−1.80 (m, 8H), 1.95 (dd, J = 6.4, 9.2 Hz, 1H), 2.00 (dd, J = 6.4, 8.8 Hz, 1H), 2.45−2.55 (m, 4H), 2.70−2.80 (m, 4H), 4.92 (dd, J = 1.2, 10.8 Hz, 1H), 4.96 (dd, J = 1.2, 10.8 Hz, 1H), 5.02 (dd, J = 1.2, 17.6 Hz, 1H), 5.04 (dd, J = 1.2, 17.6 Hz, 1H), 5.58 (dd, J = 10.8, 17.6 Hz, 1H), 5.58 (dd, J = 10.8, 17.6 Hz, 1H), 7.13 (dd, J = 7.6, 7.6 Hz, 1H), 7.15 (dd, J = 7.6, 7.6 Hz, 1H), 7.35 (dd, J = 7.6, 7.6 Hz, 2H), 7.35 (dd, J = 7.6, 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 16.2, 19.3, 20.2, 20.9, 21.0, 21.7, 23.0, 23.0, 23.1, 23.1, 23.1, 23.5, 23.5, 24.1, 25.7, 25.9, 108.3, 110.1, 111.8, 119.5, 120.3, 120.7, 120.7, 123.8, 123.8, 125.5, 125.5, 128.4, 132.2, 132.2, 141.7, 144.2, 144.3, 145.5, 145.7, 146.1. HRMS (FAB) calcd for $C_{20}H_{22}O$ (a mixture of cis and trans isomers) (M^+) 278.1671, found 278.1668. Anal. Calcd for $C_{20}H_{22}O$ (a mixture of cis and trans isomers): C, 86.29; H, 7.97. Found: C, 86.38; H, 8.17.

Cyclopropane 14c (by [Rh] Catalyst). A pale yellow oil (65 mg, 0.18 mmol, 92% yield, cis/trans = 90/10); IR (neat) 694, 764, 810, 986, 1071, 1098, 1192, 1271, 1296, 1406, 1440, 1493, 1600, 1725 (C=O), 2858, 2931 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) cis isomer, δ 1.03 (ddd, J = 6.4, 6.4, 9.6 Hz, 1H), 1.33−1.37 (m, 1H), 1.62−1.73 (m, 4H), 1.85 (ddd, J = 6.4, 6.4, 9.6 Hz, 1H), 2.48−2.51 (m, 2H), 2.67−2.70 (m, 2H), 3.47−3.53 (m, 2H), 3.57−3.62 (m, 1H), 3.99−4.03 (m, 2H), 5.59 (d, J = 10.0 Hz, 1H), 5.88 (dd, J = 10.0, 16.4 Hz, 1H), 6.16 (d, J = 16.4 Hz, 1H), 7.05 (dd, J = 7.6, 7.6 Hz, 1H), 7.25 (dd, J = 7.6, 7.6 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) cis isomer, δ 14.9, 21.0, 23.1, 24.1, 24.3, 24.7, 57.7, 63.1, 68.4, 119.1, 119.8, 123.6, 125.2, 128.1, 128.4, 129.4, 132.4, 144.3, 144.3, 164.9. HRMS (FAB) calcd for $C_{22}H_{24}O_4$ (a mixture of cis and trans isomers) (M^+) 352.1675, found

352.1674. Anal. Calcd for $C_{22}H_{24}O_4$ (a mixture of cis and trans isomers): C, 74.98; H, 6.86. Found: C, 74.60; H, 6.83.

Cyclopropane 15a (by [Pt] Catalyst). A colorless oil (11 mg, 0.05 mmol, 26% yield, syn/anti = 75/25); IR (neat) 691, 758, 786, 1020, 1070, 1385, 1449, 1487, 1548, 1594, 2875, 2953, 3008 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) syn isomer, δ 1.07 (s, 3H), 1.09 (s, 3H), 1.24−1.31 (m, 2H), 1.94 (t, J = 8.7 Hz, 1H), 6.11 (d, J = 3.3 Hz, 1H), 6.56 (d, J = 3.3 Hz, 1H), 7.20 (dd, J = 7.5, 7.5 Hz, 1H), 7.35 (dd, J = 7.5, 7.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H); ^1H NMR (300 MHz, $CDCl_3$, 25 °C) anti isomer, 1.15 (s, 3H), 1.17 (s, 3H), 1.24−1.31 (m, 2H), 1.91−1.97 (m, 1H), 5.95 (d, J = 3.3 Hz, 1H), 6.51 (d, J = 3.3 Hz, 1H), 7.15−7.20 (m, 1H), 7.30−7.36 (m, 2H), 7.58 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) syn isomer, δ 8.9, 12.2, 15.3, 16.9, 20.0, 105.6, 109.5, 123.3, 126.6, 128.6, 131.2, 152.2, 153.5; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) anti isomer, δ 8.9, 12.2, 15.2, 19.9, 24.9, 104.6, 105.9, 123.1, 126.5, 128.5, 131.2, 151.3, 157.5. HRMS (FAB) calcd for $C_{15}H_{16}O$ (a mixture of cis and trans isomers) (M^+) 212.1201, found 212.1209.

Cyclopropane 16a (by [Pt] Catalyst). A colorless oil (10 mg, 0.05 mmol, 23% yield); IR (neat) 691, 758, 783, 1020, 1062, 1383, 1449, 1487, 1548, 1595, 2867, 2953, 3004 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.90−0.96 (m, 1H), 1.00 (d, J = 5.6 Hz, 3H), 1.00−1.07 (m, 1H), 1.19 (d, J = 5.6 Hz, 3H), 1.70 (dd, J = 4.8, 8.4 Hz, 1H), 6.03 (d, J = 3.6 Hz, 1H), 6.55 (d, J = 3.6 Hz, 1H), 7.19 (dd, J = 7.6, 7.6 Hz, 1H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.3, 18.5, 20.6, 22.3, 22.7, 105.7, 108.0, 123.2, 126.5, 128.5, 131.2, 151.8, 154.9. HRMS (FAB) calcd for $C_{15}H_{16}O$ (a mixture of cis and trans isomers) (M^+) 212.1201, found 212.1207.

Chromium-Catalyzed Synthesis of Bisfurfurylidene 12. Bisfurfurylidene **12** was obtained by chromium-catalyzed reaction of **4c** (42 mg, 0.20 mmol) without alkenes.

A yellow solid (37 mg, 0.09 mmol, 87% yield); mp 213.5−216.4 °C; IR (KBr) 692, 761, 944, 1033, 1246, 1352, 1437, 1491, 1596, 2858, 2938 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) δ 1.72−1.80 (m, 8H), 2.59−2.65 (m, 4H), 2.72−2.78 (m, 4H), 6.75 (s, 2H, vinyl), 7.13 (dd, J = 7.6, 7.6 Hz, 2H), 7.32 (dd, J = 7.6, 7.6 Hz, 4H), 7.63 (d, J = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) δ 21.0, 22.7, 22.9, 23.4, 111.2, 120.7, 122.8, 124.1, 126.1, 128.3, 131.8, 146.0, 146.8. HRMS (FAB) calcd for $C_{30}H_{28}O_2$ (trans isomer) (M^+) 420.2089, found 420.2080.

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Supporting Information Available: The X-ray diffraction analysis of **9c** and **12** and ^1H and ^{13}C NMR spectra of compounds **4d**, **6d**, **7c**, **8c**, **9c**, **12**, **13c**, **14c**, **15a**, and **16a**, including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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