

Metal-Controlled Selective [3+2] Cyclization Reactions of Alkenyl Fischer Carbene Complexes and Allenes

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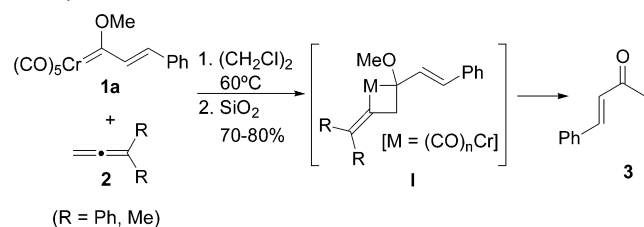
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Allenes are versatile building blocks with growing importance in organic synthesis and in transition metal-mediated carbon–carbon bond forming reactions.¹ The major synthetic limitation is concerned with the increasing selectivity problems derived of the presence of two reactive orthogonal double bonds, so that the control of the allene constitutional group selectivity represents currently an important challenge.² On the other hand, Fischer-type carbene complexes have become valuable tools in stoichiometric transition metal-mediated organic synthesis.³ Whereas the benzannulation reaction with alkynes represents probably the most relevant process of Fischer carbene complexes,⁴ studies of their reactivity toward allenes are restricted to the simplest systems.^{5,6} In 1987, Aumann found that pentacarbonyl[(methoxy)benzylidene]chromium(0) forms metal trimethylenemethane complexes with allenes,^{5a} while Hwu et al. described some years later the insertion reaction of pentacarbonyl[(methoxy)ethylidene]chromium(0) and -tungsten(0) into the C–H bond of vinylidene cyclopropanes.⁶ In both cases, the authors suggest the occurrence of an alkenylidenemetallacyclobutane intermediate which undergoes reductive demetalation or Cr–H β elimination/reductive demetalation, respectively. We report herein that pentacarbonyl[alkenyl(methoxy)carbene]chromium(0) complexes undergo selective [3+2] cycloaddition to allenes in the presence of nickel(0) or rhodium(I) species, the nature of the metal being responsible for the chemoselectivity.

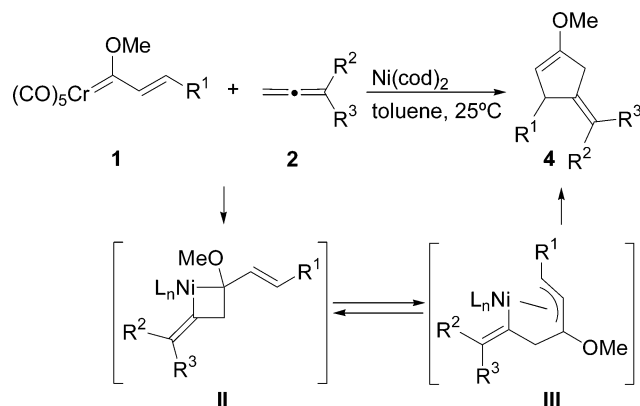
The thermal reaction (1,2-dichloroethane, 60 °C) of pentacarbonyl[*E*-styryl(methoxy)carbene]chromium(0) **1a** and 1,1-diphenyl- or 1,1-dimethyl allenes **2** leads, after silica gel treatment, to 4-phenyl-3-buten-2-one **3** in 70–80% yield. This metathesis reaction, a very unusual process for alkoxy carbenes of chromium,⁷ is in agreement with the participation of a metallacyclobutane species **I** that evolves via the retro [2+2] cycloaddition, rather than through reductive metal elimination, as found for simple carbenes (*vide supra*) (Scheme 1).

Scheme 1. Thermal Reaction of Alkenyl Carbene Complex **1a** and 1,1-Disubstituted Allenes **2**



Considering that Ni(0) is a well-known catalyst in carbon–carbon bond formation with allenes⁸ and our own experience on the change of reactivity of chromium carbene complexes toward alkynes when Ni(cod)₂ is present,⁹ the reaction of alkenyl carbenes **1** and allenes **2** (3 equiv) was carried out in the presence of 1 equiv of Ni(cod)₂ (toluene, 25 °C, 3–4 h). Exposure of the reaction crude to light,

Scheme 2. Ni(0)-Mediated [3+2] Cyclization of Chromium Alkenyl Carbene Complexes **1** with Allenes **2**



removal of the solvent, and column chromatography purification allowed one to isolate 4-alkylidenecyclopentenes **4** in 60–78% yield (Scheme 2, Table 1).^{10,11} This [3+2] cyclization is chemo- and regioselective, the unsubstituted allene C=C being solely involved. The formation of cycloadducts **4** can be explained by chromium–nickel exchange^{9,12} followed by [2+2] cycloaddition through the less substituted C=C to generate the intermediates **II** and **III**, and reductive elimination of Ni(0).

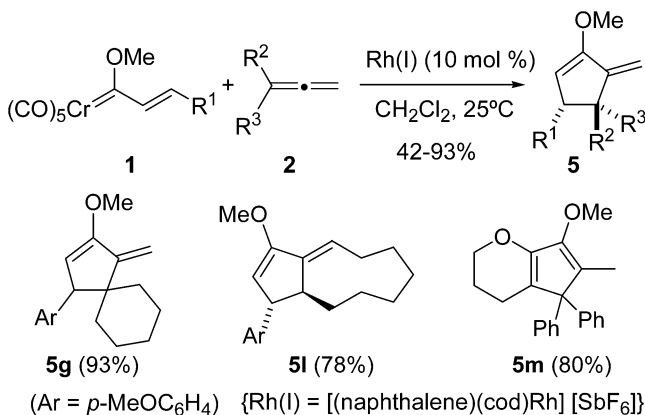
The particular nature of rhodium carbene complexes¹³ prompted us at this point to examine whether a new reaction course might operate. Gratifyingly, when carbene complexes **1** were mixed with 1,1-disubstituted allenes **2** (1.5–3 equiv) (CH₂Cl₂, 25 °C, 18–36 h) in the presence of 10 mol % of [(naphthalene)(cod)Rh][SbF₆], cyclopentene derivatives **5a–h** were obtained in good yields, after column chromatography (Scheme 3, Table 1). The reaction of carbene complexes **1** with monosubstituted allenes under the same reaction conditions afforded exclusively the *trans*-configured

Table 1. Cyclization of Carbene Complexes **1** and Allenes **2** to Cyclopentenes **4** and **5** in the Presence of Ni(0) and Rh(I)

entry	R ¹	R ²	R ³	4 (%) ^a	5 (%) ^a
1	<i>p</i> -MeOC ₆ H ₄	Ph	Ph	4a (70)	5a (75)
2	Ph	Ph	Ph		5b (84)
3	2-furyl	Ph	Ph		5c (92)
4	Ph	Me	Me	4b (78)	
5	<i>p</i> -MeOC ₆ H ₄	Me	Me	4c (68)	5d (82)
6	2-furyl	Me	Me	4d (69)	
7	ferrocenyl	Me	Me		5e (65)
8	1-cyclohexenyl	Me	Me		5f (42)
9	<i>p</i> -MeOC ₆ H ₄	–(CH ₂) ₅ –			5g (93)
10	2-furyl	–(CH ₂) ₅ –		4e (72)	
11	<i>p</i> -MeOC ₆ H ₄	Ph	Me		5h (68) ^b
12	2-furyl	Ph	H		5i (78)
13	<i>p</i> -MeOC ₆ H ₄	Ph	H		5j (81)
14	<i>p</i> -MeOC ₆ H ₄	CH ₂ CH ₂ OH	H		5k (77)

^a Yields of isolated products. ^b Isolated as a 1.5:1 *trans*/*cis* mixture.

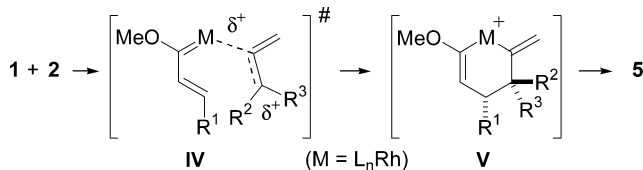
Scheme 3. Rh(I)-Catalyzed [3+2] Cyclization of Chromium Alkenyl Carbene Complexes **1** with Allenes **2**



cyclopentene derivatives **5i–k**. Different types of bicyclic structures, like **5g** (from vinylidenecyclohexane), **5i** (from 1,2-nonadiene), and **5m** (from pentacarbonyl [methoxy(4*H*-5,6-dihydropyran-2-yl)-carbene]chromium), are readily accessible. This unprecedented rhodium-catalyzed [3+2] cycloaddition reaction of chromium alkenyl Fischer carbene complexes and allenes takes place with complete chemo-, regio-, and stereoselectivity.^{10,11} Interestingly, only the more substituted C=C of the allene is now involved.¹⁴

The mechanistic proposal (Scheme 4) is based on our previous report and takes into consideration the less carbene character of the rhodium carbene.¹³ The process would be initiated by chromium–rhodium exchange, followed by a nonconcerted metalla-[4+2] cycloaddition to form **V** and reductive metal elimination. Thus, the observed chemo- and regioselectivity would be rationalized by assuming a charge-developing transition state of type **IV**. The *exo*-approach (*trans*-cycloadducts **5i–k**, **5i**) would be conceivable in terms of minimizing steric interactions.

Scheme 4. Proposed Mechanism for the Rh(I)-Catalyzed [3+2] Cyclization of Chromium Alkenyl Carbene Complexes **1** with Allenes **2**



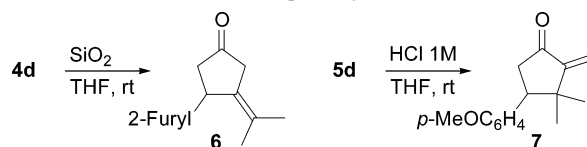
In conclusion, we have discovered a new [3+2] carbocyclization of alkenyl carbene complexes toward neutral allenes which shows that expanding the synthetic potential of Fischer carbene complexes is feasible. While chromium carbenes simply undergo thermal metathesis through the terminal C=C bond,¹⁵ nickel and rhodium carbenes cleanly cycloadd to monosubstituted, 1,1-disubstituted, and 1,3-disubstituted allenes with complete and complementary chemo- and regioselectivity. This may be regarded as an unusual way for selectivity tuning of allenes. From a synthetic point of view, it can be envisioned that either 2-alkylidene and particularly 3-alkylidene cyclopentanone derivatives can be readily synthesized starting from a single series of alkenylcarbene complexes. Although no mechanistic studies have been performed as yet, the specific behavior of either metal carbene stimulates us to pursue further studies in this field.

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Supporting Information Available: Experimental procedures and spectral and analytical data for all products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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