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Highly Chemo-, Regio-, and Stereoselective [3+2]-Cyclization of Activated and Deactivated Allenes with Alkenyl Fischer Carbene Complexes: A Straightforward Access to Alkylidenecyclopentanone Derivatives

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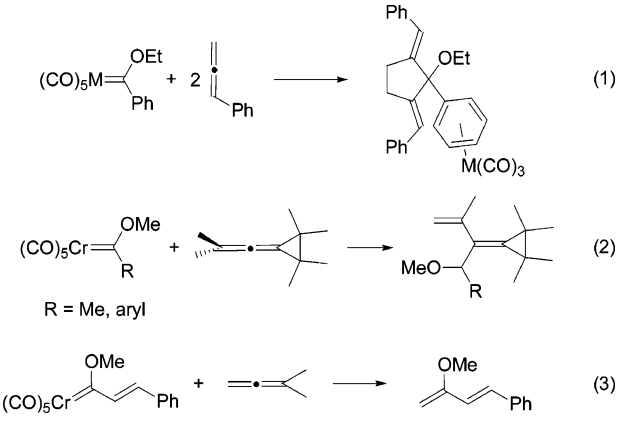
Abstract: A broad range of functionalized 5-alkylidenecyclopentene derivatives are synthesized by the rhodium(I)-catalyzed [3+2]-cyclization reaction of chromium alkenyl(methoxy)carbene complexes **1** and activated allenes. Thus, amidocyclopentenes **4a**−**n** are readily available from *N*-allenylamides **2a**−**c**, while phenoxyallene **2e** gives access to phenoxycyclopentenes **6**. In turn, the cyclization reaction with (alkoxycarbonyl)allenes **3** leads to (alkoxycarbonyl)methylidenecyclopentenes **7**−**10**. In terms of selectivity, most cyclization reactions take place with complete chemo-, regio-, and diastereoselectivity. Representative cycloadducts are efficiently hydrolyzed to the corresponding 2-alkylidenecyclopentanones **11a**−**e** without tautomerization or isomerization. Finally, a tentative reaction pathway is proposed that involves the rhodium(I) carbene complexes as the species responsible for the [3+2]-cyclization.

Introduction

Fischer carbene complexes have become valuable tools in stoichiometric transition metal-mediated organic synthesis.[1] Among other useful processes, the reaction of Fischer carbene complexes toward alkynes, the so-called benzannulation reaction, is by far one of the best studied and most exploited reactions of group 6 metal carbene complexes.[2] Unexpectedly, studies concerning the reactivity of these metal complexes with allenes are rather limited, although the latter have demonstrated great potential in the field of transition metal-catalyzed organic synthesis during the past years.[3] The isolated examples on this matter that have been reported are collected in Scheme 1. The first reaction was developed by Aumann in 1987, who found that pentacarbonyl[(methoxy)benzylidene]chromium(0) and phenylpropadiene lead to a dibenzylidenecyclopentane adduct via a metal trimethylenemetane complex intermediate (Scheme 1, eq 1).[4] Some years later, Hwu et al. described the formal ene reaction of vinylidenecyclopropanes and Fischer chromium carbene complexes to produce propenylidenecyclopropanes (Scheme 1, eq 2).[5] Recently, we observed that the thermal reaction of chromium alkenylcarbene complexes and 1,1-dimethylpropadiene results in the clean formation of the metathesis product (Scheme 1, eq 3).[6]

Scheme 1. Reported Reactions of Group 6 Fischer Carbene Complexes and Allenes



On the other hand, the transmetalation reaction of group 6 carbene complexes has become a unique tool to access transition metal carbenes of groups 9−11.[7] For instance, chromium−

(1) For recent reviews on Fischer carbene complexes, see: (a) Wulff, W. D. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12. (b) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (c) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257. (d) Barluenga, J.; Fañanás, F. J. *Tetrahedron* **2000**, *56*, 4597. (e) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (f) Aumann, R. *Eur. J. Org. Chem.* **2000**, 17. (g) de Meijere, A.; Schirmer, H.; Duestch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (h) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. *J. Organomet. Chem.* **2005**, *690*, 539.

(2) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. For recent applications of the Dötz reaction, see: (b) Minatti, A.; Dötz, K. H. *J. Org. Chem.* **2005**, *70*, 3745. (c) Jiang, M. X.-W.; Rawat, M.; Wulff, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 5970. (d) Gopalsamuthiram, V.; Wulff, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 13936.

(3) For recent reviews, see: (a) *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley: Weinheim, 2004. (b) Ma, S. *Chem. Rev.* **2005**, *105*, 2829. For a microreview on the allenic Pauson−Khand reaction, see: Alcaide, B.; Almendros, P. *Eur. J. Org. Chem.* **2004**, 3377.

(4) (a) Aumann, R.; Uphoff, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 357. (b) Aumann, R.; Melchers, H.-D. *J. Organomet. Chem.* **1988**, *355*, 351. (c) Aumann, R.; Trentmann, B. *Chem. Ber.* **1989**, *122*, 1977.

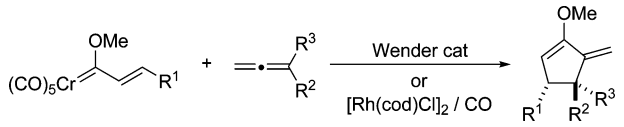
(5) Hwu, C.-C.; Wang, F. C.; Yeh, M.-C. P.; Sheu, J.-H. *J. Organomet. Chem.* **1994**, *474*, 123.

(6) Barluenga, J.; Vicente, R.; Barrio, P.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2004**, *126*, 5974.

(7) For a recent and excellent review on group 6 metal exchange: Sierra, M. A.; Mancheño, M. J.; Gómez-Gallego, M. *Acc. Chem. Res.* **2005**, *37*, 44.

10.1021/ja0586788 CCC: $33.50

Scheme 2. Rh(I)-Catalyzed [3+2]-Cyclization Reaction of Chromium Alkenyl Carbene Complexes and Unactivated Allenes



rhodium exchange resulted in the formation of Fischer-type rhodium(I) carbene complex, whose structure was established by X-ray analysis.[8] This structure represents a novel sort of rhodium carbenes that are worth further investigation, particularly if one realizes the impressive chemistry that has been achieved, mainly by M. P. Doyle[9] and H. M. L. Davies,[10] with rhodium(II) alkoxycarbonyl-substituted carbenes. Where the electronic demand of the carbene ligand is concerned, both types of carbene complexes are expected to be complementary, or at least not to overlap. Moreover, it is rather surprising that no cyclization reactions of rhodium carbenes and allenes have been reported.[11]

In relation to this specific field, it was certainly delightful to find that the reaction of chromium carbene complexes with allenes can be drastically modified if the reaction is carried out in the presence of several rhodium(I) catalysts (Scheme 2). Thus, the reaction of chromium alkenylcarbene complexes with unactivated allenes (R^2, R^3 = alkyl, aryl, hydrogen) catalyzed by the Wender catalyst [Rh(naphthalene)(cod)][SbF_6] produces cyclopentene derivatives resulting from a [3+2]-cyclization reaction. The same products are obtainable by using the neutral catalyst [Rh(cod)Cl]$_2$ provided that the reaction is run under a CO atmosphere.[6]

Herein, we report the rhodium(I)-catalyzed reaction of electron-rich and electron-poor allenes with chromium carbene complexes. The process results in a facile and selective access to functionalized alkylidenecyclopentanones. This study was carried out using the carbene complexes **1a**−**h**, and electron-donating and -withdrawing substituted allenes **2** and **3** (Figure 1).

Results and Discussion

Rhodium(I)-Catalyzed Reactions of Chromium Alkenyl Carbene Complexes and Electron-Rich Allenes. We initiated this investigation by studying the rhodium(I)-catalyzed reaction of chromium alkenyl Fischer carbene complexes **1** and electron-rich allenes **2**. We chose first *N*-allenylamide **2a** and *N*-allenyltosylamines **2b**,**c** because they are easily available and possess a right balance between stability and reactivity.[12] The treatment of the chromium alkenyl carbene complex **1a** with excess of allenamide **2a** in the presence of 10 mol % of [Rh(cod)Cl]$_2$ resulted in complete disappearance of the carbene complex after stirring in CH_2Cl_2 at room temperature for 2 h. However, removal of volatiles and filtration of the residue through a pad of Celite afforded a complex mixture from which the cycloadduct **4a** could be isolated by column chromatography in very low yield (Table 1). Fortunately, it was found that running the reaction in the presence of carbon monoxide was essential. Accordingly, carbene complexes **1**, allenamides **2a**−**c** (1.2−2 equiv), and catalyst [Rh(cod)Cl]$_2$ (10 mol %) were stirred (CH_2Cl_2, 25 °C, 0.5−18 h) under a CO atmosphere (1 bar) to furnish methylenecyclopentenes **4a**−**n** in good yields after column chromatography (47−99%).

In addition to the inherent synthetic interest of the present reaction, wherein polyfunctionalized cyclopentane derivatives containing a nitrogen functionality are accessed, several intriguing features deserve comment. First, the reaction exhibits complete chemoselectivity, being the more substituted C=C bond of the allene solely involved. Moreover, assembly of the C_3 carbene ligand and the C_2 allene units occurs with complete regioselectivity. Finally, the reaction proved to be totally stereoselective because only the *trans*-configurated products were obtained.[13]

We found that removal of the *N*-sulfonyl group in compounds **4** can be readily undertaken with lithium/naphthalene.[14] For instance, compound **4j** was desulfonylated to the secondary amine derivative **5** in 57% yield (Scheme 3). In this sense, allenamide **2b** can be considered as a stable synthetic equivalent of the hypothetic *N*-phenylallenamine.

To expand the reaction scope, we turned our attention into allenes bearing another common activating substituent, like the alkoxy group. First, the reaction of methoxyallene **2d** and various carbene complexes **1**, under the above reaction conditions, did not lead to any defined reaction product, but rather complex mixtures resulted in all cases. This failure led us to take into consideration more stable oxygen-based allenes, and actually phenoxyallene was found to be a much more promising substrate. When alkenyl carbene complexes **1** were reacted with phenoxyallene **2e** (2 equiv) and [Rh(CO)$_2$Cl]$_2$ (10 mol %) under a CO atmosphere (1 bar) (CH_2Cl_2, room temperature, 6−18 h), phenoxycyclopentene derivatives **6** were isolated in moderate yields after column chromatography purification (Table 2). As in the case of the reaction with allenamides, the formation of compounds **6** takes place with total chemo-, regio-, and stereoselectivity.[13]

Rhodium(I)-Catalyzed Reactions of Chromium Alkenyl Carbene Complexes and Electron-Poor Allenes. Next, we decided to check the reactivity of chromium alkenyl Fischer carbene complexes **1** toward allenes **3** bearing an electron-withdrawing group. A number of exploratory experiments using complex **1a** and allene **3a** allowed us to set up the best reaction conditions: [Rh(naphthalene)(cod)][SbF_6] (10 mol %), CO (1 bar), CH_2Cl_2, room temperature. We were delighted to find that the reaction of carbene complexes **1** and monosubstituted allenes **3a**−**d** under such reaction conditions afforded exclusively the cyclopentene derivatives **7a**−**i** in 48−72% yield after column chromatography purification (Table 3).[15] This new Rh(I)-catalyzed [3+2]-cycloaddition of chromium carbene complexes and electron-poor allenes takes place with complete chemo- and regioselectivity. In this case, the chemoselectivity is opposed to that attained with neutral and electron-rich allenes as only the unactivated C=C bond of the allene is involved. Moreover,

(8) Barluenga, J.; Vicente, R.; López, L. A.; Rubio, E.; Tomás, M.; Alvarez-Rúa, C. *J. Am. Chem. Soc.* **2004**, *126*, 470.
(9) See, for example: Doyle, M. P.; Yan, M.; Hu, W.; Gronenberg, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 4692.
(10) (a) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861. (b) Davies, H. M. L.; Loe, O. *Synthesis* **2004**, 2595.
(11) For an isolated [3+2] heterocyclization involving an α-carbonyl rhodium-(II) carbene and methoxyallene, see: Pirrung, M. C.; Zhang, J.; Morehead, A. T., Jr. *Tetrahedron Lett.* **1994**, *35*, 6229.
(12) For a review on the applications of allenamides in organic synthesis, see: Wei, L.-L.; Xiong, H.; Hsung, R. P. *Acc. Chem. Res.* **2003**, *36*, 773.
(13) The chemo-, regio-, and stereochemistry of compounds **3**, **4**, and **5** were ascertained by NMR experiments.
(14) Alonso, E.; Ramón, D. J.; Yus, M. *Tetrahedron* **1997**, *53*, 14355.
(15) Other rhodium(I) cationic systems such as [Rh(cod)$_2$][OTf] or [Rh(cod)Cl]$_2$/$AgSbF_6$ also catalyze efficiently the reaction to give compounds **7**.

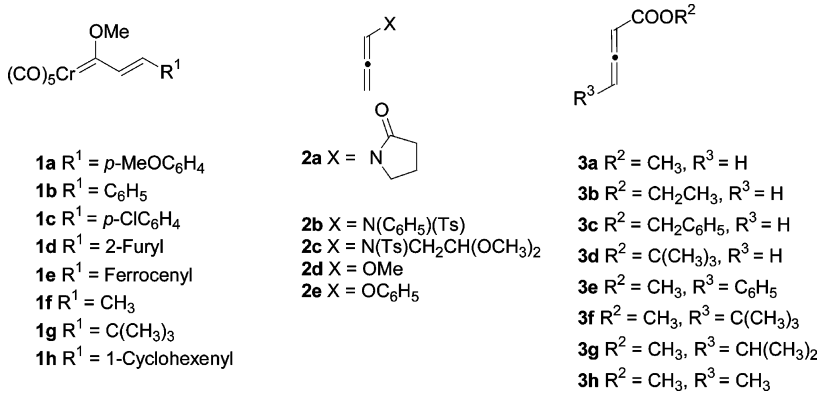
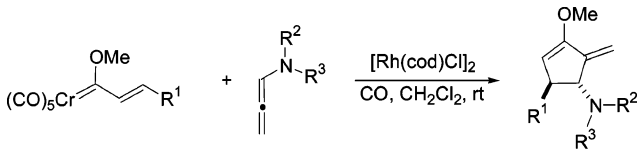


Figure 1. Fischer carbene complexes **1** and allenes **2** and **3** used in this work.

Table 1. Synthesis of Cyclopentene Derivatives **4** from Carbene Complexes **1** and Allenamides **2**

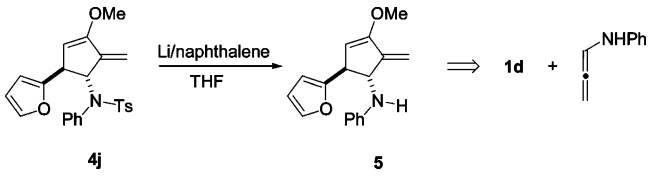


1 **2a-c** **4**

entry	R^1	R^2	R^3	**4** (%)[a]
1	*p*-$MeOC_6H_4$	$-(CH_2)_3CO-$		**4a** (76)
2	C_6H_5	$-(CH_2)_3CO-$		**4b** (78)
3	*p*-ClC_6H_4	$-(CH_2)_3CO-$		**4c** (83)
4	2-furyl	$-(CH_2)_3CO-$		**4d** (80)
5	$C(CH_3)_3$	$-(CH_2)_3CO-$		**4e** (63)
6	1-cyclohexenyl	$-(CH_2)_3CO-$		**4f** (78)
7	*p*-$MeOC_6H_4$	C_6H_5	Ts	**4g** (98)
8	C_6H_5	C_6H_5	Ts	**4h** (88)
9	ferrocenyl	C_6H_5	Ts	**4i** (99)
10	2-furyl	C_6H_5	Ts	**4j** (88)
11	$C(CH_3)_3$	C_6H_5	Ts	**4k** (60)
12	1-cyclohexenyl	C_6H_5	Ts	**4l** (78)
13	Me	C_6H_5	Ts	**4m** (47)
14	*p*-$MeOC_6H_4$	$CH_2CH(OMe)_2$	Ts	**4n** (98)

[a] Yields of isolated products.

Scheme 3



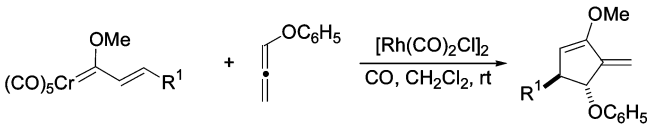
4j **5**

the reaction proved to be totally stereoselective becayse only the *E*-configurated isomer was obtained.[16]

Furthermore, the influence of a substituent at the Cγ of the buta-2,3-dienoate framework on the cyclization reaction was evaluated (Table 4). Thus, the reaction of representative allenes **3e**−**h** with carbene complexes **1** under the above reaction conditions (Wender catalyst 10 mol %, room temperature, CH_2Cl_2, 2−16 h) resulted in the exclusive formation of the 5-methoxycarbonylmethylidenecyclopentene ring (compounds **8**−**10**). This means that neither the chemoselectivity nor the regioselectivity are affected by the presence of a substituent, even as large as the *tert*-buytl group, at the γ-position of the

(16) The chemo-, regio-, and stereochemistry of compounds **7** were ascertained by NMR experiments. Moreover, an X-ray analysis was performed on compound **7a**.

Table 2. Synthesis of Cyclopentene Derivatives **6** from Carbene Complexes **1** and Phenoxyallene **2e**

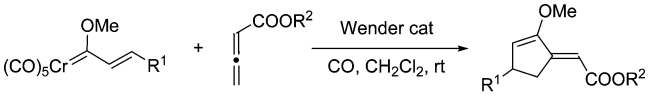


1 **2e** **6**

entry	R^1	**6** (%)[a]
1	*p*-$MeOC_6H_4$	**6a** (63)
2	C_6H_5	**6b** (59)
3	*p*-ClC_6H_4	**6c** (53)
4	2-furyl	**6d** (60)
5	ferrocenyl	**6e** (68)

[a] Yields of isolated products.

Table 3. Synthesis of Cyclopentene Derivatives **7a**−**i** from Alkenyl Carbene Complexes **1** and Allenes **3a**−**d**



1 **3a-c** **7**

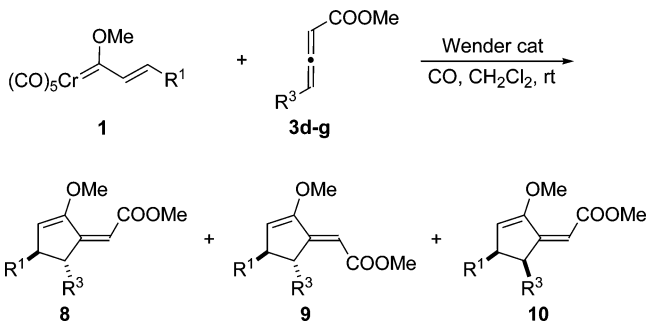
entry	R^1	R^2	**7** (%)[a]
1	*p*-$MeOC_6H_4$	CH_3	**7a** (72)
2	C_6H_5	CH_3	**7b** (66)
3	*p*-ClC_6H_4	CH_3	**7c** (62)
4	ferrocenyl	CH_3	**7d** (48)
5	2-furyl	CH_3	**7e** (59)
6	*p*-$MeOC_6H_4$	CH_2CH_3	**7f** (52)
7	*p*-$MeOC_6H_4$	$CH_2C_6H_5$	**7g** (56)
8	2-furyl	$CH_2C_6H_5$	**7h** (54)
9	*p*-$MeOC_6H_4$	$C(CH_3)_3$	**7l** (51)

[a] Yields of isolated products.

allene. On the other hand, the steroselectivity was found to depend on the nature and bulkiness of the R^3 substituent. Thus, the (*Z*),*trans*-isomer **8** (entries 1−5) was solely formed from phenyl- and ^{t}butyl-substituted allenes [R^3 = C_6H_5, $C(CH_3)_3$], while a mixture consisting of the (*E*),*trans*- and (*Z*),*cis*-isomers **9** and **10** (entry 7) resulted from methyl penta-2,3-dienoate (R^3 = Me). Finally, the (*Z*),*trans*-isomer **8**, accompanied by minor amounts of the (*E*),*trans*- and (*Z*),*cis*-isomers **9** and **10**, raised from an allene with a medium-sized R^3 group (entry 6; R^3 = ^{i}Pr).

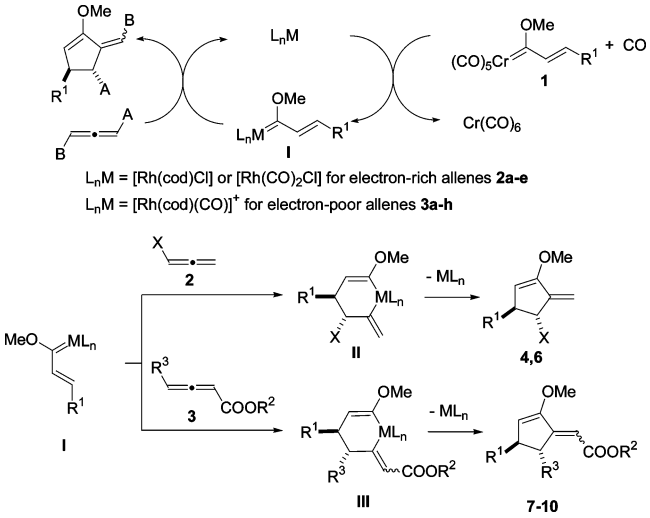
Proposed Mechanism. A tentative reaction pathway is outlined in Scheme 4. In the top is shown the overall catalytic process that is initiated by the chromium(0)−rhodium(I) ex-

Table 4. Synthesis of Cyclopentene Derivatives **8**−**10** from Alkenyl Carbene Complexes **1** and Allenes **3e**−**h**



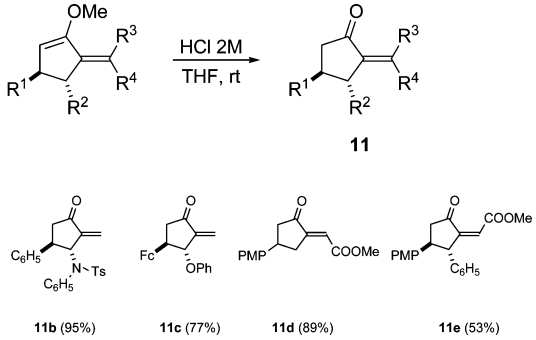
entry	R^1	R^3	**8** (%)	**9** (%)	**10** (%)
1	*p*-$MeOC_6H_4$	C_6H_5	**8a** (70)		
2	C_6H_5	C_6H_5	**8b** (66)		
3	2-furyl	C_6H_5	**8c** (65)		
4	*p*-$MeOC_6H_4$	$C(CH_3)_3$	**8d** (66)		
5	ferrocenyl	$C(CH_3)_3$	**8e** (62)		
6	*p*-$MeOC_6H_4$	$CH(CH_3)_2$	**8f** (68)	**9f** (5)	**10f** (5)
7	C_6H_5	CH_3		**9g** (50)	**10g** (10)

Scheme 4. Proposed Mechanism for the [3+2]-Cyclization Reaction of Chromium Alkenyl Carbene Complexes **1** and Allenes **2** and **3**



change[17] to produce the active rhodium carbene complex **I** and $Cr(CO)_6$. It is noteworthy the two-fold role of CO, which not only improves the efficiency of the catalytic reaction, probably by favoring the transmetalation step, but also allows one to recover almost quantitatively the chromium material. In the case of the cationic rhodium catalyst, at least, the likely active catalytic species L_nM is thought to be $[Rh(cod)(CO)]^+$, on the basis of control experiments which reveal that (i) the rhodium carbene complex **I** (R^1 = ferrocenyl) is formed from chromium complex **1e** and $[Rh(cod)(naphthalene)]^+$, either in the presence or in the absence[8] of CO (1 bar), (ii) the carbene complex **I** itself does not undergo cod/CO ligand exchange under the reactions conditions, and (iii) the reaction of **1e** and methyl buta-2,3-dienoate in the presence of 10% mol of **I** (Ln = (cod)(CO); M = Rh^+; R^1 = ferrocenyl) leads to the cycloadduct **7d** (48% yield).[18] Next, the rhodium species **I** undergoes the [3+2]-carbocyclization toward the allene substrate to yield the corresponding cyclopentenes and regenerating the catalyst. The cyclization process might proceed through the [4+2]-cycloaddition between the metaladiene **I** and the allenes **2**,**3** (Scheme 4, bottom).[19] In the case of electron-rich allenes **2a**−**c** and **2e**, the cycloaddition would take place through the activated carbon−carbon double bond to produce the intermediate **II**, which would gives rise to cyclopentenes **4** and **6** by reductive metal elimination. In turn, in the case of electron-poor allenes, the productive cycloaddition would involve the nonactivated carbon−carbon double bond yielding the metalacyclohexene species **III**, precursor of the cyclopentenes **7**−**10**.

Scheme 5. Synthesis of 2-Alkylidenecyclopentanone Derivatives **11** (PMP = *p*-$MeOC_6H_4$; Fc = Ferrocenyl)



Access to Substituted 2-Methylenecyclopentanones. Finally, we thought it interesting to elaborate the methoxycyclopentene adducts into the useful methylene cyclopentanone framework. Despite the thermodynamic instability of the exocyclic double bond, this transformation can be achieved by a simple acid hydrolysis without isomerization. Representative examples are displayed in Scheme 5. Thus, nitrogen- and oxygen-derived cycloadducts **4b**,**h** and **6e** afforded diastereochemically pure cyclopentanones **11a**−**c** on treatment with 2 M HCl in THF at room temperature. In the same way, the cycloadducts **7a** and **8a**, derived from electron-poor allenes, underwent hydrolysis into the expected cyclopentanone derivatives **11d** and **11e** without affecting the *Z*/*E*-stereochemistry of the exocyclic carbon−carbon double bond.

In conclusion, we have demonstrated that the rhodium(I)-catalyzed [3+2]-carbocyclization of neutral allenes and Fischer alkenyl carbene complexes, previously developed in our laboratory,[6] can be efficiently extended to a diverse array of activated allenes. The chemospecificity of the process is noteworthy. While electron-rich allenes undergo the [3+2]-cyclization through the heteroatom-substituted C=C bond of the allene (the more activated site), the [3+2]-cyclization of activated allenes bearing an alkoxycarbonyl group takes place at the C=C bond that is orthogonally placed with respect to the electron-withdrawing group (the less activated site). This fact along with the regio- and diastereoselectivity of the cyclization and the ease of the hydrolysis of the resulting cycloadducts make this process

(17) For Cr/Rh exchange, see: (a) Aumann, R.; Göttker-Schnetmann, I.; Fröhlich, R.; Meyer, O. *Eur. J. Org. Chem.* **1999**, 2545. (b) Göttker-Schnetmann, I.; Aumann, R. *Organometallics* **2001**, *20*, 346. (c) Göttker-Schnetmann, I.; Aumann, R. *Organometallics* **2001**, *20*, 3574. See also refs 7 and 8.

(18) It cannot be ruled out that the cod/CO ligand exchange would take place on the metalacyclohexene intermediate **III**. On the other hand, some attempts directed to form the neutral rhodium carbene complexes **I** from chromium carbenes **1** and $[Rh(cod)Cl]_2$ or $[Rh(CO)_2Cl]_2$ were unsuccessful.

(19) (a) This mechanistic proposal was proposed in the case of rhodium carbenes and neutral allenes; see ref 6. (b) The [4+2]-cycloaddition has been recognized by H. M. L. Davies as a valid mechanism in the [3+2]-cyclization of rhodium(II) carbenes and methoxyalkenes; see: Davies, H. M. L.; Xiang, B.; Kong, N.; Stafford, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 7461.

a simple and efficient way to access functionalized 3,4-disubstituted 2-alkylidenecyclopentanones. This report clearly confirms that synthetic advantages can be accomplished when the chemistry of well-developed group 6 Fischer carbene complexes and the transmetalation reaction with late transition metals are combined. Continuing in this way, further efforts are in progress in our laboratory toward the applicability of enantiopure (diene)rhodium complexes in the asymmetric synthesis of cyclopentanoids.[20]

(20) For examples of catalytic asymmetric synthesis with Rh−diene complexes, see: (a) Shintani, R.; Tsurusaki, A.; Okamoto, K.; Hayashi, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3909. (b) Paquin, J.-F.; Defieber, C.; Stephenson, C. R. J.; Carreira, E. M. *J. Am. Chem. Soc.* **2005**, *127*, 10850.

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Supporting Information Available: Full experimental details 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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