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Tin- and Germanium-Substituted Enol Ethers from Fischer Carbene Complexes and Group 14 Vinyl Derivatives

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Summary: Trialkyltin- or trialkylgermanium-substituted enol ethers **5** *and 2-alkoxy-1,3-butadienes* **7** *have been prepared by the reaction of Fischer carbene complexes* **1**−**3** *and* **6** *with vinylstannanes and -germanes* **4**. *The opening of the metallacyclobutane intermediate by metalloid migration has been shown by using a 2,2-dideuteriated olefin.*

Fischer carbene complexes have attracted much attention as useful reagents in organic synthesis.[1] Among the great variety of reactions of group 6 metal carbene complexes, cyclopropanation of electron-deficient and electron-rich alkenes has been one of the most developed transformations.[2] However, only a few examples of intramolecular cyclopropanation of unactivated olefins have been reported.[3] In some cases, in addition to the expected cyclopropane, varying amounts of new products corresponding to C−H insertion into the starting alkene have been detected.[4] Moreover, the reaction of iron carbene complexes with functional olefins leads exclusively to C−H insertion products.[5] Here we report the preparation of tin- and germanium-substituted enol ethers and 2-alkoxy-1,3-butadienes from group 6 metal alkoxycarbene complexes and trialkylvinyltin and trialkylvinylgermanium compounds.

Scheme 1

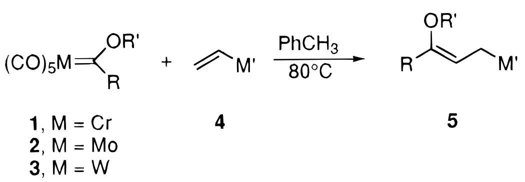
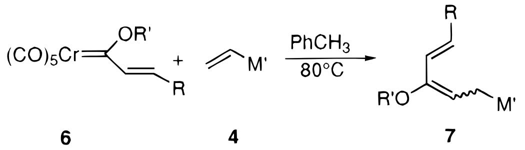


Table 1. Preparation of Products 5 and 7 from Carbene Complexes 1−3 and 6 and Vinylmetalloids 4

starting carbene	R	R′	vinyl-metalloid	M′	*t* (h)	pro-duct	*Z*/*E*	yield (%)[a]
1a	Ph	Me	**4a**	$SnBu_3$	1.5	**5aa**	*b*	62
2a	Ph	Me	**4a**	$SnBu_3$	0.25	**5aa**	*b*	60
3a	Ph	Me	**4a**	$SnBu_3$	3	**5aa**	*b*	27
1a	Ph	Me	**4b**	$GeEt_3$	1	**5ab**	*b*	72
1b	Me	Me	**4a**	$SnBu_3$	3	**5ba**	*b*	64
1b	Me	Me	**4b**	$GeEt_3$	3	**5bb**	*b*	69
6a	Ph	Me	**4a**	$SnBu_3$	0.5	**7aa**	1/3	60
6b	2-Fu[c]	Me	**4a**	$SnBu_3$	1	**7ba**	1/5	68
6b	2-Fu	Me	**4b**	$GeEt_3$	3	**7bb**	1/5	80
6c	Ph	(−)-menthyl	**4a**	$SnBu_3$	0.25	**7ca**	1/4	58
6d	2-Fu	2-Ph-c-C_6H_{11}	**4a**	$SnBu_3$	0.5	**7da**	1/5	65
6e	2-Fu	(−)-menthyl	**4b**	$GeEt_3$	3	**7eb**	1/5	76

[a] Isolated yield based on the starting carbene complex. [b] Only the *Z* isomer was detected. [c] Fu = furyl.

Scheme 2



The reaction of aliphatic and aromatic chromium carbene complexes **1** with tributylvinyltin (**4a**) in toluene at 80 °C gives rise to enol ethers **5** as a single diastereoisomer (Scheme 1 and Table 1). The *Z* configuration was established by NOE experiments. Molybdenum and tungsten complexes **2** and **3** also afford enol ethers **5** under the same reaction conditions. The relative reactivity of the three metal complexes is Mo > Cr > W. While complex **1a** (M = Cr) is consumed after 1.5 h when heated in the presence of **4a**, complex **3a** (M = W) requires a longer time (3 h) for the reaction to go to completion. The reaction of the molybdenum complex **2a** is the fastest (0.25 h). In order to study the scope of this reaction, we tested different metal-substituted olefins. When complexes **1** were heated in toluene in the presence of triethylvinylgermanium (**4b**), *(Z)*-germanium-substituted enol ethers **5** were isolated as the only product (Scheme 1 and Table 1). However, the formation of the corresponding enol ethers from trialkylvinylsilanes was not observed; instead, mixtures of unidentified compounds were obtained.

Chromium alkenylcarbene complexes **6** also react with trialkylvinyltin or -germanium compounds, affording 2-alkoxy-1,3-butadienes **7** as a mixture of *Z*/*E*

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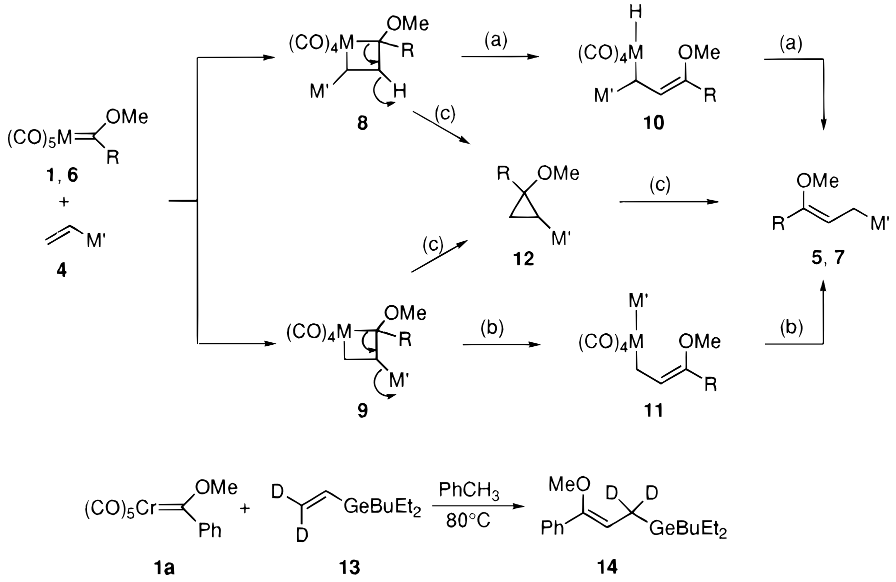
Scheme 3



diastereoisomers (Scheme 2 and Table 1). In all cases, the *E* isomer is the major one, as shown by NOE experiments. The reactions of chiral complexes **6c**–**e** are especially interesting, since they lead to chiral 2-alkoxy-1,3-butadienes **7ca**, **7da**, and **7eb**.

The possible mechanisms for the formation of compounds **5** and **7** are depicted in Scheme 3. Two regioisomeric metallacyclobutanes **8** and **9** could be obtained in the first step. Enol ethers **5** and **7** could be formed from metallacyclobutane **8** by β-hydride elimination to afford **10** followed by reductive elimination (pathway a).[5] On the other hand, pathway b would involve the opening of metallacyclobutane **9** by group 14 metal (Sn, Ge) migration to the electrophilic center[6] (M) and subsequent reductive elimination from intermediate **11**. Finally, there is a third possibility from both metallacyclobutanes via reductive elimination to give cyclopropane **12** (pathway c).[4a] Ring opening of this intermediate would lead to the final products.

In order to study the mechanism of this transformation, chromium carbene complex **1a** was treated with 2,2-dideuteriated vinylgermanium derivative **13,** giving rise exclusively to compound **14** in 68% yield (Scheme 3). This result rules out pathways a and c, since they would afford an enol ether bearing the deuterium atoms at different positions. However, formation of **14** is in agreement with pathway b.[7] Therefore, we can conclude that the reaction of group 6 metal carbene complexes and tin- or germanium-substituted alkenes involves the migration of the trialkyltin or -germanium moieties. The diastereoselectivity of the process can be explained by assuming *trans* positions of the R group and the group 14 metal in the metallacyclobutane **9**, which would lead to *Z* enol ethers. However, in the case of α,β-unsaturated carbenes, the interaction of the double bond with the empty d orbitals of the tin or germanium atoms would favor *cis* positions of both groups, affording the *E* isomers as major compounds.

In conclusion, we have described the reaction of Fischer carbene complexes and tin- and germanium-substituted olefins, leading to enol ethers and 2-alkoxy-1,3-butadienes bearing a trialkyltin or -germanium moiety, in a process involving a tin or germanium migration. We are currently investigating the synthetic applications of the reaction products, in particular, of the tin-substituted derivatives which can be further derivatized by tin-lithium transmetalation followed by treatment with electrophiles.[8] The study of their behavior as allylic tin reagents in addition reactions with carbonyl compounds[9] and as dienes[10] in [4 + 2] cycloadditions also is underway.

In a typical procedure tributylvinyltin **4a** (1.2 mmol, 0.35 mL) was added to a solution of chromium carbene complex **1a** (1 mmol, 0.31 g) in anhydrous toluene (10 mL) under nitrogen. The reaction mixture was heated at 80 °C for 1.5 h, cooled, and then filtered through Celite. The solvent was removed under vacuum, and the product was purified by column chromatography on silica gel using hexane as eluent. Yield: 0.27 g (62%).

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Supporting Information Available: Listings of spectral data and figures giving ^{13}C NMR spectra for **5**, **7**, and **14** (15 pages). Ordering information is given on any current masthead page.

OM9703999

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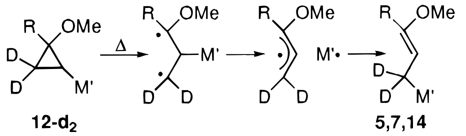
[7] One of the reviewers has suggested an alternative mechanism involving cleavage of the cyclopropane to give a biradical intermediate. However, this opening usually occurs at higher temperatures. For a review, see: Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165.



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