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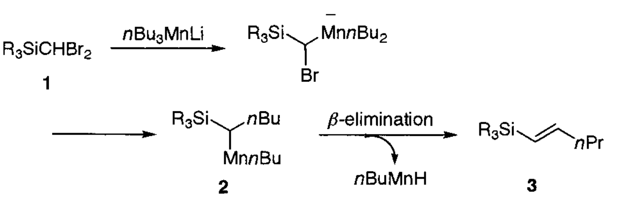
Alkylative Preparation of α-Silylalkylmagnesium from $R_3SiCHBr_2$ Using a Magnesate Reagent[**]

Junichi Kondo, Atsushi Inoue, Hiroshi Shinokubo, and Koichiro Oshima*

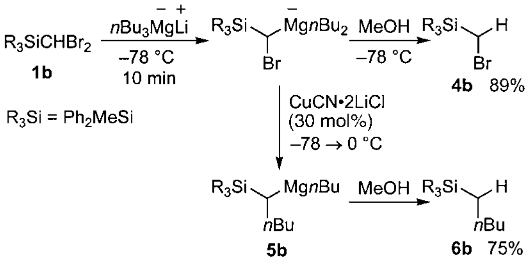
The Peterson olefination reaction utilizing α-silylalkylmetals has been established as a highly stereoselective method to prepare alkenes.[1] Therefore, α-silylalkylmetal species have gained importance as reagents for organic synthesis.[2] Methods for the preparation of α-silylalkylmetals are usually based on 1) deprotonation,[3] 2) halogen–metal exchange with metals (Li or Mg) or organometallic compounds (BuLi or RMgX),[4] or 3) addition of an organometallic species to vinylsilanes.[5] Deprotonation methods require strong bases (typically *t*BuLi) and are not effective for the deprotonation of alkylsilanes which lack an activating group (such as a carbonyl group). The requisite α-haloalkylsilanes for halogen–metal exchange reactions are not readily available; the most efficient method for their preparation is the addition of an organometallic species to a vinylsilane.

Metal carbenoid species are well-known to undergo alkylation by the action of alkylmetals.[6] Therefore, the alkylation of silyl-substituted carbenoids could be an attractive route to α-silylalkylmetals. We have previously reported the synthesis of 1-alkenylsilanes **3** from dibromomethylsilanes **1**[7] via manganese carbenoids (Scheme 1).[8] The α-silylalkylmanganese **2** formed in this reaction cannot be trapped with electrophiles because of its rapid conversion into alkenylsilane **3** by β-hydride elimination. We then investigated alternative methods to generate α-silylalkylmetallic compounds. Herein we report a copper-catalyzed alkylative preparation of α-silylalkylmagnesium compounds via trialkylmagnesium ate complexes and its application to the synthesis of α-silyl ketones.

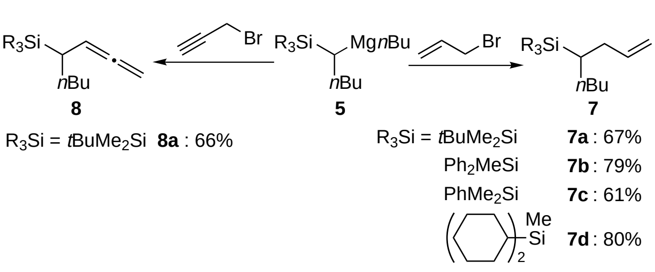


Scheme 1. Reaction of dibromomethylsilanes **1** with tributylmanganate.

We examined the reaction of dibromomethylsilane **1** with trialkylmagnesate (Scheme 2).[9, 10] Tributylmagnesate (nBu$_3$MgLi) was easily prepared by mixing butyllithium (2.0 equiv) and butylmagnesium bromide (1.0 equiv) in THF at 0 °C. Treatment of dibromomethylsilane **1** with a magnesium ate complex induced clean bromine–magnesium exchange to provide bromomethylsilane **4** upon quenching with methanol at -78 °C.[11] Warming the reaction mixture to room temperature before quenching resulted in the migration of the butyl group to yield α-silylpentylmagnesium **5**.[12, 13] This migration was facilitated by a copper salt.[14] The addition of CuCN · 2LiCl (30 mol %) to the reaction mixture induced smooth migration of the butyl group at lower temperatures (-30 °C for **1a** and 0 °C for **1b**) to afford **5** in good yield. The use of butyllithium or nBuMgBr instead of tributylmagnesate also induced the metalation and the subsequent butylation. Under these conditions, however, the yields of the desired products were quite low. The α-silylpentylmagnesium **5** could be trapped with allyl bromide to give **7** in good yield (Scheme 3). The reaction with propargyl bromide furnished exclusively the allenylated product **8**.



Scheme 2. Bromine–magnesium exchange and the subsequent migration of an alkyl group.



Scheme 3. Reaction of α-silylalkylmagnesium compounds **5** with allyl or propargyl bromide.

α-Silyl ketones are quite useful intermediates in organic synthesis.[15] Therefore, we undertook the preparation of α-silyl ketones using this new methodology.[16] The reaction of α-silylalkylmagnesiums **5** with various acyl chlorides was

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[*] Prof. Dr. K. Oshima, J. Kondo, A. Inoue, Dr. H. Shinokubo
Department of Material Chemistry
Graduate School of Engineering
Kyoto University, Kyoto 606-8501 (Japan)
Fax: (+81) 75-753-4863
E-mail: oshima@fm1.kuic.kyoto-u.ac.jp

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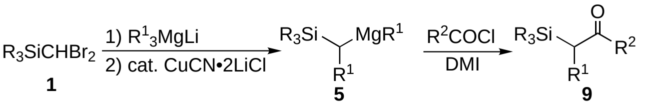
examined (Table 1).[17] The addition of acyl chlorides to the resulting solution of **5** furnished the corresponding α-silyl ketones **9** in good yields. 1,3-Dimethyl-2-imidazolidinone (DMI) proved to be an effective additive for the formation of α-silyl ketones. The yield of the product decreased when DMI was not used (entry 7).

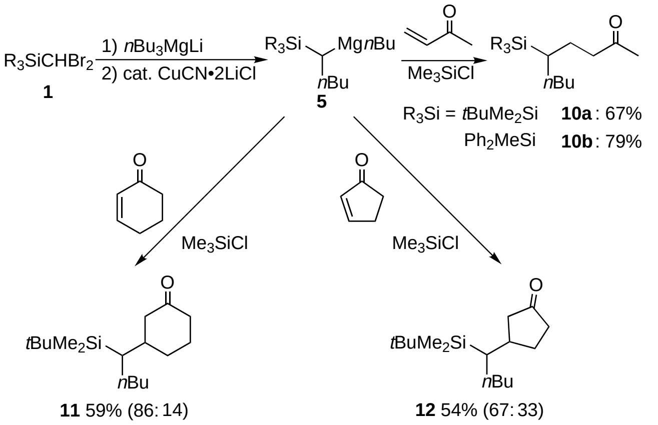
Table 1. Synthesis of α-silyl ketones from dibromomethylsilanes.[a]



Entry	Substrate	R_3Si	R^1	R^2	Product	Yield [%]
1	**1a**	tBuMe$_2$Si	nBu	CH_3	**9a**	60
2				cPr	**9b**	56
3				Ph	**9c**	66
4				(E)-CH_3CH=CH–	**9d**	53
5				(E)-PhCH=CH–	**9e**	51
6	**1b**	Ph$_2$MeSi	nBu	CH_3	**9f**	63
7				nPr	**9g**	49
8[b]				nPr	**9g**	74
9[b]				iPr	**9h**	63
10[b]				cPr	**9i**	69
11[b]				Ph	**9j**	77
12[b,c]			nC$_6$H$_{13}$	nPr	**9k**	85
13[c]				Ph	**9l**	70

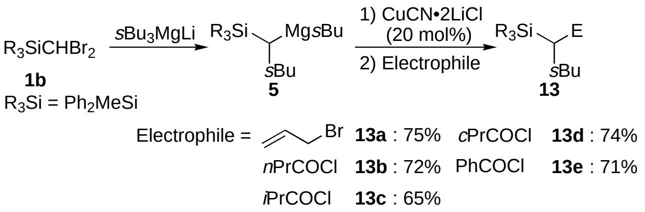
[a] Reaction conditions: Magnesate was prepared from butyllithium (1.0 mmol) and butylmagnesium bromide (2.0 mmol) in THF (5 mL) at 0 °C. Solutions of the dibromomethylsilanes (1.0 mmol) in THF (2 mL) were introduced at -78 °C. CuCN · 2LiCl (0.3 mL, 1.0 M solution in THF, 0.3 mmol) was added. [b] DMI (2.0 mmol) was added before introduction of the acyl chlorides. [c] Magnesate was prepared from hexyllithium (3.0 mmol) and $MgBr_2$ (1.0 mmol) in THF (5 mL) at 0 °C.

We also explored the conjugate addition of **5** to α,β-unsaturated ketones (Scheme 4). The addition of methyl vinyl ketone to the solution of **5** containing Me_3SiCl provided 5-silyl-2-nonanones **10a** and **10b** in good yields.[18] The addition of **5** to cyclohexenone or cyclopentenone also furnished the desired silyl ketones.



Scheme 4. 1,4-Addition of α-silylalkylmagnesium compounds **5** to enones.

In the case of tri(s-butyl)magnesate, which was prepared from sBuLi (3.0 equiv) and $MgBr_2$ (1.0 equiv), migration of the secondary butyl group afforded the corresponding α-silylalkylmagnesium **5** smoothly without the assistance of a copper catalyst (Scheme 5). However, the addition of CuCN · 2LiCl was beneficial for producing the coupling products **13** in good yields from the acylation or allylation step.



Scheme 5. Reaction of dibromomethylsilanes **1** with sBu$_3$MgLi.

Experimental Section

9g: nBuLi (1.2 mL, 1.6 M solution in hexane, 2.0 mmol) was added to a solution of nBuMgBr (1.0 mL, 1.0 M solution in THF, 1.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to -78 °C and a solution of $Ph_2MeSiCHBr_2$ (**1b**, 370 mg, 1.0 mmol) in THF (2 mL) was added. After stirring the mixture for 10 min, CuCN · 2LiCl (0.3 mmol) was added and the mixture was allowed to warm to 0 °C before adding DMI (2.0 mmol) and butyryl chloride (2.5 mmol) successively. After stirring the mixture for 1 h at 0 °C, the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with ethyl acetate (10 mL × 3), and the organic layers were dried over anhydrous Na_2SO_4 and concentrated. Purification by column chromatography on silica gel yielded 5-(methyldiphenylsilyl)-4-nonanone (**9g**) in 74 % yield.

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Fluorinated Bis(enyl) Ligands by Metal-Induced Dimerization of Fluorinated Allenes**

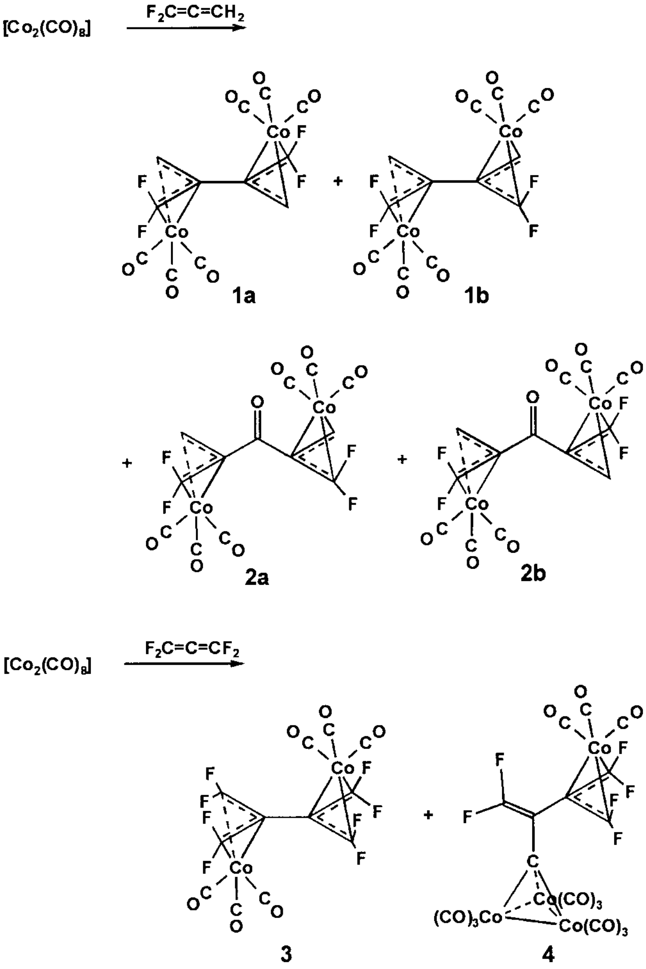
Dieter Lentz* and Stefan Willemsen

It is often extremely difficult to synthesize fluorinated analogues of ligands frequently used in organometallic chemistry,[1] such as cyclopentadienyl and propenyl (allyl) ligands. After many unsuccessful attempts pentafluorocyclopentadiene was synthesized and deprotonated;[2] however, no C_5F_5 complex could be prepared thereof. The synthesis of pentamethylcyclopentadienyl(pentafluorocyclopentadienyl)-ruthenium by vacuum pyrolysis of pentamethylcyclopentadienyl(pentafluorophenoxy)ruthenium with elimination of carbon monoxide at 750 °C demonstrates that fluorinated enyl complexes are not generally unstable,[3] but suitable synthetic methods are often missing. As the C–F bond is the strongest element–carbon bond (D(C–F) = 109–130 kcal mol^{-1}) and C–F activation is gaining increasing importance,[4] we are looking for methods to construct more complex ligands directly at metal complexes from simple, readily available fluoroorganic starting materials.

We started our investigations by studying the ligand properties of fluorinated allenes, which turned out to be very strong π-acceptor ligands; thus, stressing the importance of π backbonding as shown also by theoretical calculations.[6]

We expected to be able to construct new ligands by metal-induced dimerization of 1,1-difluoroallene and tetrafluoroallene on manganese and cobalt complex fragments, as reactions of allenes with decacarbonyldimanganese[7] and octacarbonyldicobalt[8] resulted in new ligand systems through C–C coupling. Furthermore the dimerization is the first step of a polymerization reaction which is not a metal-catalyzed process in the case of fluorinated alkenes. The polymerization of fluorinated alkenes to technically important products, such as polytetrafluoroethene (PTFE) and fluorinated ethylene propylene copolymer (FEP), is generally acheived by free radical polymerization.[9] In the presence of radical trapping agents, such as terpenes, fluorinated alkenes yield [2+2] cycloaddition products.[10] Tetrafluoroallene polymerizes to give a not fully characterized polymer and dimerizes in the presence of α-terpinene to give perfluoro-1,2-methylenecyclobutane.[11]

Reaction of 1,1-difluoroallene and tetrafluoroallene with octacarbonyldicobalt yielded the dinuclear cobalt complexes **1** and **3**, respectively (Scheme 1). The reaction with 1,1-



Scheme 1. Reactions of octacarbonyldicobalt with 1,1-difluoroallene and with tetrafluoroallene.

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[*] Priv.-Doz. Dr. D. Lentz, Dr. S. Willemsen
Fachbereich Biologie, Chemie, Pharmazie
Institut für Chemie
Anorganische und Analytische Chemie
Freie Universität Berlin
Fabeckstrasse 34–36, 14195 Berlin (Germany)
Fax: (+49) 30-8385-2424
E-mail: lentz@chemie.fu-berlin.de

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